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An overview of corrosion of additively manufactured alloys

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Additive manufacturing (AM), often termed 3D printing, has rapidly become a means of producing metallic components from a variety of metallic alloys. The numerous benefits of AM include net shape manufacturing, efficient use of material, rapid production of low volume or custom product, and the ability to explore alloy compositions not previously accessible to conventional casting. The process of AM, which is nominally performed using laser (or electron) based local melting, has a definitive role in the resultant alloy microstructure. This has an associated impact on the corrosion of alloys prepared by AM which are described and discussed. Such features include unique porosity, grain structures, dislocation networks, residual stress, solute segregation, and surface roughness. Correlations between reported results and deficiencies in present understanding are highlighted. A number of examples are given – with some attention to lessons from corrosion of AM prepared alloys that advance our understanding of corrosion science.

Towards a Virtual Corrosion Lab: a new generation of mechanistic, multi-physics models for pitting and stress corrosion cracking

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Corrosion has long been considered too complex to be predicted with computer models. However, increasing computer power and new multi-physics, phase field-based corrosion models enable the development of electro-chemo-mechanical phase field models that explicitly resolve the meso-scale phenomena involved and can therefore deliver predictions based on physical parameters and with minimal assumptions [1]. Phase field modelling has revolutionised the modelling of many interfacial problems, from solidification to fracture mechanics, and this paradigm can also be used to predict the evolution of the corrosion front (electrolyte-metal interface) [2]. Recent developments in this emerging field of phase field corrosion have shown that this new class of models can capture key phenomena such as film rupture and repassivation, the transition from activation- to diffusion-controlled corrosion, interactions with mechanical fields, microstructural and electrochemical effects, intergranular corrosion, material biodegradation, and the interplay with other environmentally-assisted damage phenomena such as hydrogen embrittlement [3-5]. A very good agreement with experiments is observed.

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“Corrosion and Passivation of Multi-Principal Element Alloys in Aqueous Solutions”

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There are many degrees of freedom associated with multi-principal element alloys (MPEAs). This is enabled by the wide variety of alloying elements and atomic structures available to produce a large number of single-phase, solid solution, or multi-phase alloys. Consequently, there is the possibility of producing a wide range of material properties, often unique. However, a structure, composition, and processing paradigm governing the corrosion properties of MPEAs has not yet emerged. Corrosion properties depend on many factors and resultant properties are difficult to predict in such complex systems. The quest for superior corrosion properties requires an understanding of the fate of each element during corrosion, the functions of elements whether in the alloy, substrate or both, and the ability to harness interactive effects. One example of the latter is the beneficial “3rd element effect” which can improve passivity and oxidation behavior even at low passivator alloying contents. Large gaps in knowledge still exist regarding the (a) specific functions of each element, (b) effects of elements in unusual combinations, and (c) possible formation of complex protective oxides that regulate corrosion and breakdown. Several strategies to address these concerns are underway. These include but are not limited to high throughput experimental testing, use of CALPHAD and other thermodynamic tools as well as artificial intelligence. Guiding principles relevant to specific alloy families are beginning to emerge such as the identification of certain specific elemental roles, functions, and types of nearest neighbor atomic interactions which may be beneficial. These issues are discussed with the goal of accelerating the understanding of the corrosion behavior in this class of materials.

Corrosion big data for the design of application of low-alloy steels

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In order to establish the correlation between long-term corrosion mechanism and the corresponding influence factors, the concept of "corrosion big data" was developed including high-throughput corrosion data collection, multi-source database, mining, modeling and application. Based on "corrosion big data" theory, a multi-scale data miming mode was built between microalloying elements, microstructure, environmental factors and corrosion rate, which is a data-driven approach for the design of high-quality corrosion resistant steels. Moreover, corrosion initiation and evolution of low-alloy steels induced by inclusions, microstructures and internal acidification of surface micro-defects were also comprehensively revealed, which was used to propose corrosion control strategies, such as inclusion modification, microstructure optimization and oxide film stabilization. On the basis of achievements above, new corrosion-resistance low-alloy steel series were developed.

Keywords: Corrosion big date; Low-alloy steels; Miming mode; Corrosion mechanism, Steel design.

Machine learning assisted performance optimization of corrosion inhibitors and active protective coatings

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Substituting chromates in structural coating systems within various industries with non-toxic and environmentally friendly alternatives remains a persistent challenge. Numerous hexavalent-chromium-free organic compounds have been studied experimentally for many different metallic substrates focusing on their intrinsic protective performance but the underlying set of molecular descriptors determining their effectiveness mostly remains yet to be elucidated which hampers efficient inhibitor optimization.

The generation of molecular descriptors that are used as input features, either derived directly from the molecular structure or atomistic simulations, represent a key step in the development of predictive inhibitor performance models. Quantitative structure-activity relationship models offer the possibility to preselect a short list of promising candidates for experimental testing without deep knowledge of the underlying chemical mechanisms, provided a sufficiently large and chemically versatile training dataset is available. The molecular descriptors augmented with experimental input features can then be analysed for their relevance to the corrosion inhibition efficiencies using different feature selection techniques. In this way several machine learning models can be built with such molecular and experimental descriptor set and their performance can be evaluated by predicting the behaviour of compounds that were not used for training the models.

Furthermore, while many different inhibitor chemistries are reported and predicted to have high intrinsic corrosion protection efficiency over the last decades, straightforward incorporation of these inhibitors in active protective coatings and implementation in practice is not apt. Several challenges in active protective coating design may arise such as, but not limited to, unwanted inhibitor-polymer matrix interaction or unfavourable intrinsic dissolution kinetics hindering bespoke in-coating mobility and release characteristics and hence their long term protective performance. While effective, comprehensive and rapid experimental screening and optimization of novel protective coating chemistries in an industrial context remains an utopia at present, recent machine learning framework developments have led to enhanced and efficient optimizing strategies for self-healing composite coatings. In such machine learning frameworks, active learning and Bayesian optimization are used to model and maximize common electrochemical protection indicators for various scratched self-healing coatings to improve their active protective performance.

All in all, this presentation will focus on promising pathways, challenges and opportunities of machine learning assisted performance optimization of corrosion inhibitors and active protective coatings.

The influence of “non-innocent” metal ions in silica scale formation

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The interest in the utilization of geothermal energy has increased exponentially in the past few decades, and researchers internationally are currently focusing on improving harvesting methods and promoting it due to its numerous benefits compared to traditional energy sources. Corrosion and scaling are two of the significant problems in modern geothermal industry that occur during the harvesting of geothermal energy. Scaling occurs due to the variety of anions and cations that the majority of geothermal reservoir waters contain. Dramatic changes in temperature and pressure causes failures in several parts of the plant forming the elusive “iron silicate”, whose identity, as it is formed in geothermal waters, differs from its geological counterparts. In this presentation we present how several factors influence the chemistry of amorphous silica formation. These include: (a) pH, (b) temperature, (c) presence of certain metal ions (eg. Mg^{2+}, Al^{3+}, Fe^{2+}, Fe^{3+}), (d) supersaturation, etc. We also present mitigation strategies based on carefully-designed chemical additives and we attempt to delineate possible control mechanisms that could be applied in practical applications in the field.

Model development and simultaneous optimization of chemical dosages to minimize the corrosion rate in a cooling water circuit

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Monitoring the corrosion rate of a cooling cycle in a chemical plant is imperative, owing to the constant evaporation of water via cooling towers. Previous studies reported on predicting the corrosion rate using neural networks are based on experimental data either in a controlled environment or using small amounts of data (e.g. < 100 data points). Optimization studies with regard to the chemical dosage of a single corrosion inhibitor were reported both via experiments as well as predictive models. Currently available commercial software enables optimizing the dosages of several inhibitors. However, the chemicals are optimized one after the other. Therefore, only a handful of chemicals can be optimized at a time.

The current study develops an Artificial Neural Network (ANN) model based on three years of daily real-time data obtained from a chemical plant, including the addition of a multitude of added chemicals and ions. Next, the model is tested by predicting the corrosion rate for an independent 5-month period. The model was able to predict the corrosion rate with prediction accuracies of R values of 0.99 (training), 0.92 (validation) and 0.80 (testing). Applying an input variable selection method provides user control over the variables included in the model is important given the optimization objective. Hence, dosages of chemicals need to be included to enable their optimization in view of minimizing the corrosion rate.

Building on the developed model, we propose a methodology that can optimize dosages of multiple chemicals simultaneously with less effort. The objective function allows the user to customize the weighted impact of reducing dosages of some chemicals over others as well as that of reducing either the corrosion rate or the amount of chemicals added. We demonstrate the impact of optimization on corrosion rate (weight 43%) and dosages of benzotriazole (weight 29%, for environmental reasons), orthophosphate (weight 14%, due to biological fouling), zinc (weight 14%) and inhibitor A – proprietary compound (weight 0%) in Figure 1. The average chemical usage has been minimized through optimization. This methodology can be used for optimizing chemical dosages for an anticipated set of water qualities within the scope of the training data set.

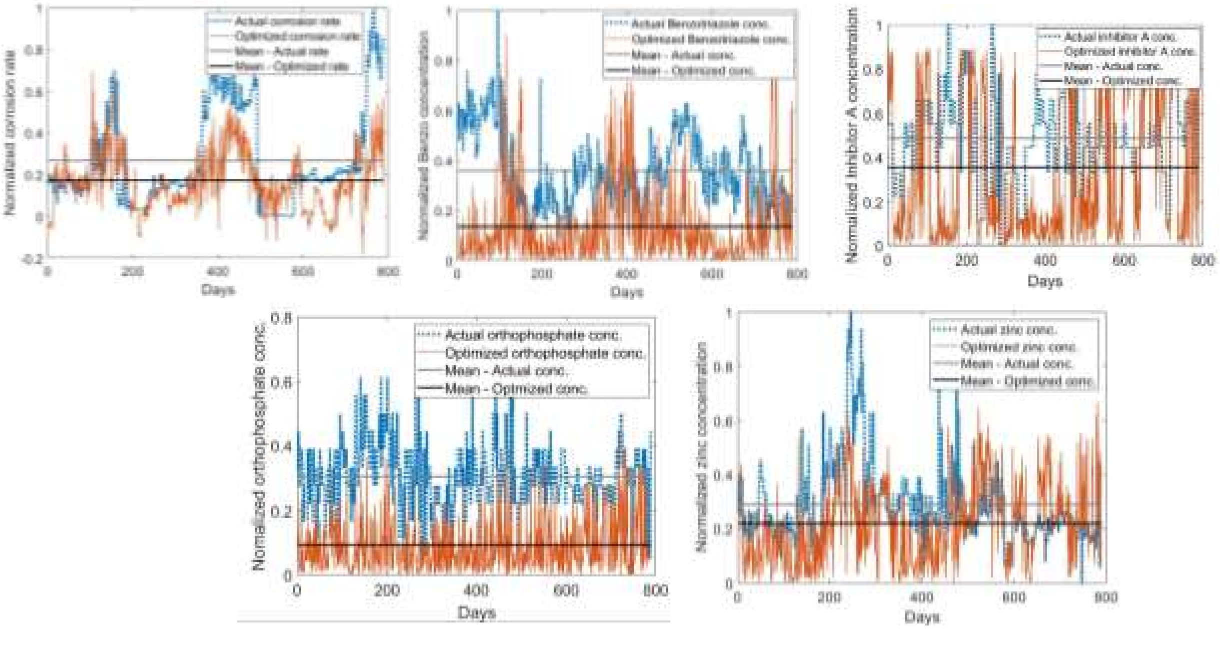

Figure 1 - Optimized chemical dosages and corrosion rate.

Challenges in non-ferrous metal corrosion protection

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Triazoles with a wide variety of substitution patterns have long been known to provide excellent corrosion protection for metals, especially copper, but also brass, solder and aluminum.

The corrosion protection is realized via firmly adherent thin surface layer, which is very stabil, so that the triazoles (TA) have a wide range of applications. These include open and closed cooling circuits. But also in the area of surface preservation of museum art objects. TA in a glycol matrix, together with other corrosion inhibitors, can be used just as advantageously in the field of engine cooling coolants. Triazoles are also used over a very wide temperature range depending on the respective application

Starting with regulatory restrictions on the use of heat transfer fluids in the geothermal energy sector, we launched our project last year. In the geothermal energy sector, any use of raw materials with WGK 2 and WGK 3 is prohibited, even if, according to the AWSV, the use of WGK 2 materials would result in a WGK 1 for the mixture in purely mathematical terms.

In addition, the biodegradability of TA is very poor and benzotriazole, for example, is listed as a vM substance in more recent regulations. In the future, this could mean that TA will become Annex XIV substances with application-specific authorizations. In the context of the regulatory aspects, a need for action arose for us.

In our search for alternatives to the effective TA, we did not look for a general over-all-solution for all temperature and application areas. In a step-by-step process, we tested organic molecules in neutralized form.

In different matrices, aqueous and/or glycolic, we have tested the effectiveness of a new inhibitor package for selected metals and at different concentrations. The aim was to develop an application-adapted product. In a kind of modular system, we want to extend the positive results so far to other applications. We are very pleased to be able to present our results to you today.

Protection of galvanic corrosion by Polyphosphate corrosion inhibitor in cooling water systems of oil and gas industry

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The use of corrosion inhibitors in cooling systems in the oil and gas industry are classified depending on the type of the cooling system and the metals of their construction. Due to the presence of more than one metal (mild steel and copper) in a cooling system galvanic corrosion is possible. The inhibitors that are used in a cooling system should be effective on both metals.

This research is aimed to study the efficiency of polyphosphate on galvanic coupling in cooling systems. The corrosion inhibition was studied on mild steel and copper individually and coupled. Test carried out using the electrochemical potentiodynamic polarisation technique while the inhibition effect on the separate parts of a galvanic couple was studied by the measurment the currents individually flowing to the metals during polarization using individual zero resistance ammeters (ZRAs). It is a method that is rarely used but has great benefit especially since the corrosion rate can be directly determined by the intersection of two partial curves and Tafel estimation is unnecessary. Polyphosphate was found to perform as a good corrosion inhibitor for mild steel giving a low corrosion current density values thus low corrosion rate. On the other hand, not for copper since the inhibition effect was relatively low. However, when the two metals (mild steel and copper) were coupled there was a reverse change in the potential where the copper became an anode and mild steel a cathode, this was related to the inhibition of the mild steel and not the copper.

Keywords: Galvanic coupling, Corrosion inhibitor, Potentiodynamic polarisation

Mechanistic studies of protection of carbon steel against corrosion with molecular inhibitors using couplings of Atomic Force Microscopy with ElectroChemistry and Quartz Crystal Microbalance

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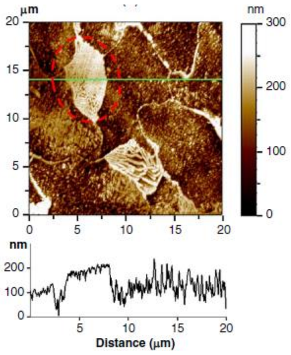
Carbon steel is commonly used in industry as a consequence of its well adapted mechanical properties, easy machining and low cost. In particular, it is widely used for the construction of pipelines and tanks aimed at the transportation and storage of crude oil and petroleum products. On the other hand, its most severe drawback is its vulnerability to corrosion. Nevertheless, a good protection of carbon steel against corrosion can be achieved by using ionic surfactant type molecular corrosion inhibitors. Even if their adsorption on the carbon steel surface is obviously known to lead to the formation of a molecular layer acting as a barrier against dissolved corrosive species, it is still quite difficult nowadays i) to correlate the performance of such inhibitors with their molecular structure, and ii) to explain why some of them perform better than others. In this contribution, AFM studies focusing on model corrosion inhibitors and performed in-situ in chloride containing aqueous solutions on carbon steel samples in the presence of CO_2 are reported [1,2]. It will be shown that, beyond various working modes of AFM, couplings of AFM with electrochemistry and quartz crystal microbalance (QCM) offer relevant and powerful tools to provide information on the morphology and the mechanical properties of adsorbed inhibitor layers, as well as on the adsorption kinetics and the anti-corrosion protection mechanism of molecular corrosion inhibitors.



EC-AFM monitoring of carbon steel topography in a CO_2 saturated 1 wt% NaCl aqueous electrolyte after 1 h.

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Synergistic effect of Fe_3C on Corrosion Inhibition efficiency of a QAC: Galvanic Corrosion interaction and adsorption behavior

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The presence and formation of corrosion products (i.e. Fe_3C, $FeCO_3$, and FeS) on carbon steel exposed to Oil and Gas environments can lead to severe corrosion problems due to inappropriate adsorption of corrosion inhibitors (CI). The interaction of pre-corroded layers with the CI along with the pipe flow results in corrosion product dissolution which might lead to galvanic corrosion. As parts of the corrosion product layer is removed local galvanic cells arise, accelerating the corrosion process on the exposed steel. Specifically, for Fe_3C layer, it is well known that there exists a direct effect on decreasing the inhibition adsorption and efficiency of commonly used CI compounds such as imidazolines and quaternary ammonium compounds. However, little research has been performed on the protectiveness of such CIs on a galvanic corrosion system between the pre-corroded surface (Fe_3C in this study) and fresh surface metal. A quaternary ammonium based Benzyldimethylhexadecylammonium chloride (BAC-C_{16}) was used as a corrosion inhibitor for X65 carbon steel in CO_2-saturated 10% NaCl brine at 50^oC and 500RPM in this study. The inhibitive effects and preferential adsorption behavior were investigated for the X65/Fe_3C system. Electrochemical tests were performed using a double RCE system at high salinity simulating the harsh environment at Qatar's fields. Samples were pre-corroded for 48h to allow homogenous Fe_3C films to be formed on the X65 steel surface. ZRA tests were performed under blank and inhibited conditions. Surface characterization was done prior and post galvanic corrosion tests by means of, step-profilometer, SEM/EDS, XRD, FTIR and XPS. Even though the presence of BAC-C16 reduced the galvanic corrosion rate from 1.2mm/y to 0.1 mm/y such inhibition only occurs after 5 hours from CI injection. Preferential inhibitor adsorption on the fresh steel surface was observed through FTIR and XPS analysis. Localized corrosion inhibition on the Fe_3C surface was observed which can be related to low coverage of the CI on the pre-corroded surface.

An effective inhibitor for Q235 Steel Protection In 15% HCl Under Hydrodynamic Condition: Combination Of Experimental, Surface And Computational Approach

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ABSTRACT

This study describes the environmentally friendly manufacture and inhibitory activity of the pyrimidine derivative 4-(3-Methoxy-4-hydroxyphenyl)-2-phenyl-1,4-dihydro-benzo[4,5]I midazo [1,2-a] pyrimidine-3-carboxylicacid ethyl ester (PD) over Q235 steel in 15% HCl under dynamic conditions. The effect of KI addition on the inhibitive performance (%) is also investigated. The outcome of EIS indicates that Rct will increase when PD increases. The mixed character of PD inhibitive effect is revealed by the PDP outcome. At 400 mg/L, the solo PD performance value is 93%. However, the performance value increases to 97% when KI (0.5 mM) + PD (400 mg/L) are added. The best adsorption of PD is supported by the Freundlich isotherm.

Key words: Corrosion, inhibitor, impedance, polarization, isotherm, computational chemistry

Novelty and Developments in Compatibility Evaluation of the Oil Field Chemicals

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Abstract

Oil Field Chemicals (OFC) are injected downhole, at the wellhead or between the wellhead and the oil/water separation facilities. The injected fluid is a complex mixture of chemicals designed to impart several functions including inhibition of scale deposition, gas hydrates, corrosion, and scavenging of Oxygen. An important element that is often overlooked during chemical qualification and application is the compatibility between oilfield chemicals (OFCs), which can critically impact the ability of the chemicals to meet their desired function in the field. In the area of corrosion control, one important example of this is the interference of oilfield chemicals on corrosion inhibitor effectiveness. In this study, compatibility evaluation of the oil field chemicals was conducted at best practical approach based on experimental results. Several laboratory corrosion experiments were conducted in a simulated field environment to quantitatively evaluate the impact of different OFCs on corrosion inhibitors performance. Negative effects that downgrade the inhibition performance such as chemical incompatibility and formation of emulsion are also investigated.

Corrosion inhibition of biowaste derived carbon dots for mild steel in 15% HCl solution

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Abstract

Traditional corrosion inhibitors often rely on toxic chemicals, raising environmental and health concerns. In response, there is a growing interest in developing green corrosion inhibition strategies that are both effective and environmentally friendly. Carbon quantum dots (CDs) primarily composed of carbon atoms represent a novel category of zero-dimensional carbon nanoparticles, typically smaller than 10 nm. In response to the increasing emphasis on environmental sustainability, researchers have turned to utilizing waste materials for CD synthesis, not only for cost reduction but also to mitigate environmental pollution. In this study, CDs were synthesized via a hydrothermal method using biowaste, specifically banana peel, as the carbon source. The corrosion inhibition performance of the resulting BP-CDs on mild steel in a 15% HCl solution was assessed through gravimetric measurement, electrochemical impedance spectroscopy, potentiodynamic polarization curve analysis, and surface analysis. The findings revealed that BP-CDs exhibited a remarkable 95.69% inhibition efficiency at a concentration of 400 mg/L. Furthermore, BP-CDs effectively acted as a mixed type inhibitor. Additionally, XPS analysis was employed to elucidate the adsorption mechanism of BP-CDs, providing insights into their corrosion inhibition mechanism.

Acknowledgments

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Experimental and computational investigations of corrosion protection by *Callistemon viminalis* for mild steel in 1 M HCl

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This study investigates the corrosion protection properties of leaves and flower extract of *Callistemon viminalis* as natural inhibitors for mild steel in 1 M HCl. The primary objectives are to assess the inhibition efficiencies and elucidate adsorption mechanisms of the plant extracts. Experimental analyses, including electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (PDP) and linear polarization resistance (LPR) revealed a substantial reduction in mild steel corrosion rate with increasing extract concentration. The inhibition efficiencies reach a maximum of over 90% at higher concentrations, highlighting the inhibition properties of the extracts in mitigating corrosion. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDS) visually established the formation of a protective layer on the steel surface, providing a physical barrier against corrosive ions. The adsorption of *Callistemon viminalis* extracts on mild steel obeyed the Langmuir adsorption isotherm. Furthermore, density functional theory (DFT) and molecular dynamics simulations (MDS) were employed to gain molecular-level insights into the interaction between Callistemon viminalis extract components and the mild steel surface. The simulations corroborate experimental outcomes, emphasizing robust extract adsorption onto the steel surface. The computational approach offers valuable mechanistic understanding, supporting and complementing the experimental findings. In conclusion, *Callistemon viminalis* extracts prove to be effective and environmentally friendly corrosion inhibitors for mild steel in acidic conditions. The study underscores the synergistic potential of combining experimental and computational approaches. The findings bear importance for corrosion control in industrial applications, advocating for the transformative use of natural extracts in developing sustainable and eco-friendly corrosion inhibitors.

Evaluation of Black Tea Extract as a Green Corrosion Inhibitor for mild Steel in CO_2 Corrosive Environments

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Abstract

The use of corrosion inhibitors is one of the generally used approaches to mitigate corrosion damage and protect the metal, particularly in aqueous environments containing CO_2. However, these inhibitors cause environmental hazards. Consequently, researchers have turned their attention to plant extracts due to their appealing attributes including naturally sourced, non- or low-toxic, biodegradability, cost effective.

In this study the corrosion inhibition properties of black tea extract (BTE) in CO_2 corrosive environment on L80-1Cr (API 5CT) steel at 40 °C were tested using a combination of chemical analysis, molecular modelling, and electrochemical techniques.

Overall, BTE was found to have significantly better corrosion inhibition properties than uninhibited sample as reflected by a higher polarization resistance, inhibition efficiency and stronger adsorption energy. Moreover, SEM and TEM results showed that BTE influenced the corrosion film morphology and chemical composition as an organic layer and thinner corrosion scale were observed in the inhibited samples. The inhibitory mechanisms of Black Tea Extract (BTE) could be attributed to a combination of adsorption and chelation processes.

Key Words

Black tea, CO_2 corrosion, mild steel, SEM, TEM, inhibitor

Novel Method to Quantify the Corrosion Inhibitors Concentration Injected in Produced Water

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Abstract

Numerous laboratory methods have been developed to evaluate the concentration of various corrosion inhibitors in produced water systems. The laboratory evaluation, often referred to as residual analysis, provides quick monitoring of the adequacy of treatment levels of corrosion inhibitors in different applications, time of dispersion or travel through fluids as well as efficiency of the inhibitor. This paper discusses some methods such as the organic extraction method and the residual methods. It is highlighted the need for methods to monitor the concentration of production chemicals in produced water in order to optimize their process efficiency and for environmental reasons. The study includes analysis of the industry needs and challenges facing the researchers developing new procedures.

Inhibitive effect of phosphates on corrosion of gray cast iron in automotive braking systems

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Brake pads-rotor adhesion, commonly known as stiction phenomenon, as a consequence of the exposure of the disc-brake assembly system to aggressive environments, such as, wet conditions in the presence of pollutants or exposure to chlorides during winter drive, is a critical aspect for the braking systems of vehicles. This phenomenon is strongly connected to the corrosion of the gray cast iron disc, followed by the formation of corrosion products capable to penetrate between the porosity of the friction material when static brake is applied. The development of friction materials with low susceptibility to stiction, targeting an accurate selection of the constituents, including corrosion inhibitors, is then an important approach in order to control the local conditions at the pads–disc interface. This work explores the use of phosphates as low environmental impact corrosion inhibitors in friction material. In order to study the possible inhibition mechanism, corrosion of gray cast iron rotor is studied by several electrochemical and complementary techniques in different electrolytes simulating the condition that may be present at the interface between the disc and the pad, in the presence of phosphates. A particular form of pitting corrosion of passivated gray cast iron disc, in mild basic conditions, in the presence of phosphate, is also discussed.

Comparative review of geochemical and exploitation data from fifteen geothermal operations in the Paris area for deep understanding and solving corrosion and scaling troubles

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Abstract

More than 50 geothermal operations (GOs) in France are exploiting low-enthalpy geothermal fluids (GF) of the Dogger aquifer in the Paris Basin. The GOs are generally made up of two wells (production-injection, both are about 1,800 m deep), and of surface installations. The GFs flow assisted by an immersed pump through the carbon steel (CS) casings to the surface without releasing their gases, and, after flowing through heat-exchangers, are re-injected into the same aquifer. GOs experience has shown that, in well casings, there are several CS corrosion and deposits of iron sulfides, when a high sulfide content was present initially in the GFs or acquired later by bacterial sulfate-reduction (BSR). Since 1990, progressively, the doublets were treated, using a well-bottom treatment tube, with various organic corrosion inhibitors (OCI), which have enabled GOs to eliminate most of their corrosion/scaling problems. However, new problems are now arising on some sites. In order to understand and control them, we present a comparative review of all the data obtained during several years from 15th GOs, from various anoxic and acidic GFs with varying degrees of mineralization and gases and different exploitation conditions. All GFs are treated by different OCI under different dosages. The corrosion rates (CR) were measured by both mass losses of CS samples exposed to the GF and electrochemical instantaneous methods. GF flowrate (m^3/h) are correlated to sulfide, inhibitor and suspended matter contents and to CR. Solid matter gone up under different conditions, characterized mainly by XRD and SEM/XPS, gives aquifer particles (mainly pyrite, silica) and neo-formed minerals (mackinawite, pyrrhotite). Based on compositions of the GFs sampled at the surface, saturation indices (SI) for the relevant minerals are calculated by Phreeqc geochemical code. The simulations predict a constant super-saturation of all GFs with respect to pyrite. Mackinawite and pyrrhotite are, for most of GFs, undersaturated or very close to thermodynamic equilibrium, except for a few GFs, which show positive SI for these two minerals, indicating potential precipitation. Only few of treated GFs present problems, because of their varying exploitation conditions.

A new generation of Vapor phase Corrosion Inhibiting (VpCI) films with recycled content

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Abstract: Legislative and regulatory efforts addressing recycling have increased significantly at an international level. The EU Packaging and Packaging Waste Directive (Directive 94/62/EC) promotes the reuse, recycling and other forms of recovering of packaging waste, instead of its final disposal, thus contributing to the transition towards a circular economy.

A new generation of Vapor phase Corrosion Inhibiting (VpCI) films has been developed to address sustainability concerns by using post-consumer recycled content and post-industrial recycled content in the VpCI film extrusion process. This paper investigates the corrosion inhibiting performance of VpCI films with 30 percent post-consumer recycled content or with 20 percent post-industrial content. In order to evaluate corrosion inhibiting performance, both films were tested in accordance with NACE Standard TM0208 for Vapor-Inhibiting Ability (VIA). Following mechanical properties of both products were tested: percent elongation, tensile strenght, impact resistance, and tear strength in accordance with ASTM D882-02, ASTM 1709-04 Test Method A, ASTM D1922-06a, respectively.

Corrosion inhibiting and mechanical properties testing demonstrated that these new films provide excellent corrosion protection, with no or minimal compromises in mechanical properties.

Keywords: recycling, post-consumer content, post-industrial content, VpCI films, corrosion protection, mechanical properties

CORROSION MITIGATION STRATEGIES FOR EVAPORATOR'S ALUMINIUM BRASS TUBES IN MULTI-EFFECT DESALINATION PLANT

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Abstract

Seawater corrosion (vapor phase CO2 corrosion in presence of dissolved oxygen) to the In-Service Aluminum Brass tubes is investigated based on quality of seawater (dissolved oxygen, CO2, free residual chlorine, chloride contents), fluid velocity, chemicals injection rate and concurrent galvanic effect on Aluminum Brass tubes lie adjacent to the Titanium tubes & lean duplex stainless steel supporting structures. For which, operational data is collected from two separate facilities (same year of commissioning) having different design configuration and different chemical injection rate with respect to the same source (quality) of seawater used. This operational data is corelated with the results of metallographic analysis of corroded tubes and Energy Diffraction Spectroscopy (EDS) analysis of their corrosion deposits. In view of the operating history of both facilities (dissolved chlorides, free residual chlorine & fluid velocities remained same) and same material of construction, the facility which is exposed to higher dissolved oxygen (based on chemicals injection rate, and equipment design configuration) revealed severe carbonic acid corrosion due to the combined effect of dissolved oxygen and CO2 contents. The dissolved oxygen is the main trigger which changes the nature of protective passive oxide-film on the Aluminum Brass tubes. Hence, the chemicals injection rates corresponding to the seawater quality and original design configuration of the desalination plant are the keys to prevent corrosion to Aluminum Brass tubes preferably used now days for seawater desalination plants. Therefore, recommendations regarding chemicals injection rate and equipment design configuration are proposed to minimize the corrosion of Aluminum Brass tubes used for these plants.

Studies on the corrosion mitigation effect of biodegradable monomeric and gemini surfactants containing carbonate linkage for mild steel in 5% HCl

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Abstract

A biodegradable gemini surfactant and monomeric cationic surfactant having carbonate linkage namely, N,N'-((carbonylbis(oxy))bis(ethane-2,1-diyl))bis(N,N-dimethyldodecan-1-aminiumiodide) (referred as GS12) and N,N,N-trimethyl-2-(((hexadecyloxy)carbonyl)oxy)ethan-1-aminiumiodide (referred as THC) were synthesised and characterized employing elemental analysis, FT-IR, ^{1}H NMR and ^{13}C NMR. The corrosion mitigation effect of both the surfactants was for the first time studied on mild steel (MS) substrate in 5% HCl solution at temperatures 303, 313, 323, 333, 343, 353K and compared with the inhibition effect of THC obtained under identical conditions. Experimental investigations include gravimetric analysis, PDP, EIS, AFM, SEM, EDAX, XPS, FT-IR, UV- visible spectroscopy and contact angle measurements. Inhibition efficacy of each inhibitor was observed to be dependent on their concentration and electrolyte temperature. From the weight loss studies, at 303K, THC provided maximum inhibition efficiency of 93.2% at concentration of 1×10^{-4} M which was further raised to 98.1% at 353K whereas GS12 exhibited identical efficiency at relatively lower concentration of 1×10^{-6} M. PDP studies demonstrated that both GS12 and THC act as mixed-type inhibitor, lowering the partial anodic/cathodic reactions. Inhibition efficiency obtained from EIS and PDP are consistent with those obtained from weight loss measurements. The adsorption of GS12 and THC on MS surface mainly occur through chemisorption and is consistent with Langmuir isotherm. Surface studies such as contact angle measurement, AFM, SEM-EDX, and XPS justified the adsorption of GS12 and THC molecules on MS surface forming a protective coverage. The adsorption of surfactants on MS was also validated by FT-IR and UV- visible spectroscopy. The performance of GS12 was found slightly better than THC under identical experimental conditions.

Insight into the Corrosion Inhibition of L-tryptophanium picrate as Efficient Inhibitor for Mild Steel in 5% HCl: Experimental Studies and Theoretical Calculations

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Abstract

One of the worst corrosive attacks on mild steel occurs during acidizing, an industrial process used to increase petroleum recovery. The petroleum sector has to create very powerful inhibitors to lessen this problem. Herein, the corrosion inhibition performance of an amino acid derivative, L-tryptophanium picrate referred to as [Trp][Pic] for mild steel in 5% HCl was assessed by weight loss measurement, potentiodynamic polarization (PDP) and electrochemical impedance analysis (EIS). The findings of EIS investigations revealed that mild steel polarisation resistance increased numerically at 30°C, from 81.076 Ωcm2 in 5% HCl to 462.146 Ωcm2 in inhibited medium containing 100 ppm of [Trp][Pic]. This indicates an 82.46% inhibition efficiency. The chemisorbed [Trp][Pic] covering, according to surface micrographs obtained by atomic force microscopy (AFM) and scanning electron microscopy (SEM), protected the mild steel surface from corrosive ions, producing a smooth and seamless surface. While the findings of the EIS revealed the creation of an inhibitive layer on the MS surface, the PDP measurements obtained indicate that [Trp][Pic] functions as a mixed type inhibitor, primarily exhibiting anodic action. Strong interaction between MS surface and inhibitor was expected by activation parameters and thermodynamic calculations. Through the use of molecular dynamics (MD) modelling, potential binding sites for the molecular adsorption of [Trp][Pic] on the surface of mild steel were identified, providing insight into the fundamental process of corrosion prevention.

Keywords: Corrosion inhibitor · Langmuir · SEM · Mild steel · Acid corrosion

Synergistic Inhibitive Effect of a Hybrid metal Oxide-Benzalkonium Chloride Composite on the Corrosion of Carbon Steel in an Acidic solution

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Abstract

Metal oxide and quaternary ammonium-types surfactants have been separately recognized for their anti-corrosive efficiencies. Composite of them, not so far investigated, could provide a synergetic anti-corrosion effect. In this respects, in this study, a hybrid of zinc, iron, and titanium oxide and benzalkonium chloride composite was prepared in different mass ratios and its inhibitive potential against the corrosion of carbon steel in 0.5 M sulfuric solution was evaluated at room temperature. First, the chemical structure of the prepared composite was explored by both Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS). Then the corrosion inhibitive performance of the devised inhibitors were screened using electrochemical, hydrogen collection and weight loss measurements. The electrochemical measurements indicate that the prepared inhibitor exhibits a predominant cathodic inhibition behavior and the highest inhibition efficiency (about 91.9%) was obtained for one-to-one mass ratio.

Effect of Silver Nanoparticles synthesized using Aloe Vera leaf plant extract on the Corrosion Behaviour of API 5L in 0.5M of H_2SO_4

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Abstract

Good inhibitors have attributes like high inhibitory efficiency, low environmental toxicity, cost effectiveness, practicality, and eco-friendliness. This is because environmental conservation is becoming more popular worldwide. Synthesiszing nanoparticles with the use of organic extracts, which are biodegradable, eco-efficient, and reasonably priced is necessary because of environmental conservation and green chemistry. This study explores the use of silver nanoparticles (AgNPs) synthesized via Aloe Vera (*Aloe barbadensis Miller*) leaf extract as corrosion inhibitors for API 5L steel in sulfuric acid (H_2SO_4) environment. Characterization were carried out using Atomic Absorption Spectroscopy (AAS), Fourier-Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). These confirmed the metals in the extract; identified the functional groups and confirmed the size of the nanoparticles respectively. Four different concentrations of AgNPs solution (0% wt., 0.1% wt., 0.3% wt., and 0.5% wt.) were applied to 0.5M H_2SO_4 solution. Corrosion rate and inhibition efficiency of the steel samples were assessed using polarization techniques. The findings reveal that AgNPs act as effective corrosion inhibitors for the steel samples, forming a protective barrier on the steel surfaces. The optimal inhibition efficiency was achieved at 97% in the sulfuric acid environment, with concentration of inhibitor at 0.5% wt. This study highlights the potential of green-synthesized AgNPs for efficient corrosion protection in acidic environments.

Keywords: Corrosion Inhibitors, Aloe Vera, Polarization

Study of duplex oxide scales formation in binary metallic alloys at high temperatures through sequential isotopic oxidation tests coupled to SIMS analysis

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Understanding the parameters influencing the rapid formation of duplex oxide layers at high-temperature in metallic alloys is crucial for minimizing material degradation. Depending on variables such as composition, temperature or the oxidizing environment, either a "protective" single layer or a "non-protective" duplex layer may form.

Research conducted at CEA Saclay, inspired by Robertson's articles, introduced the "Available Space Model (ASM)" theory. The oxidation process initiates with the external oxide formation at the oxide/environment interface through the outward diffusion of the metal. This triggers the creation of metal vacancies at the metal/oxide interface, which leads to pore formation. The internal oxide layer grows within the available volume of these pores, facilitated by the rapid penetration of the oxidant through short-circuit diffusion paths. Despite observations of this phenomenon across diverse systems and conditions, a comprehensive generalization of the model is yet to be established.

To understand the growth mechanism of duplex oxide layers, a methodology was established, conducting sequential isotopic oxidation tests complemented by SIMS and nanoSIMS analysis. This methodology was experimented on pure metals and alloys having Cobalt (Co), iron (Fe) and nickel (Ni) as base elements. The obtained results will offer valuable insights into the generalization of the ASM mechanism during high-temperature oxidation, establishing a foundation for further in-depth studies in the future.

Enhancing Oxidation and Nitridation Behavior of Chromium Silicon Alloys under Cyclic Exposure at 1200 °C

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Chromium Silicon alloys become promising candidates for high temperature applications, because of outstanding mechanical strength at elevated temperatures [1] and high oxidation resistance [2]. In the context of increasing combustion temperatures due to alternative fuels and efficiency optimizations, the resulting content of nitrogen in the exhaust gases rises. However, caused by their poor resistance against nitridation and unstable oxide layer formation above 1000°C [2] the Cr-Si-alloys must be improved by alloying [3] and coating with an aluminum oxide layer. This prevents cracking or spallation of the oxide layer and the nitridation as a performance-limiting factor, especially during cyclic oxidation as in the subsequent application.

In this study, the effect of an Al-diffusion coating, reactive element additions (e.g. Y, Zr), A15-phase formers (e.g. Ge, Mo), and additions of glass phase formers (e.g. B, Ge) on the high temperature corrosion resistance of Cr-Si-alloys are evaluated using cyclic oxidation testing. Therefore, the alloys were manufactured using an arc furnace and a vacuum inductive melting machine. Pure chromium and $Cr_{89}Si_6Mo_5$ (Cr-Si-Mo) were sanded, and slurry coated with a polyvinyl alcohol-based aluminum slurry to form an Al-diffusion layer as reservoir for Al_2O_3 scale formation. The cyclic oxidation testing was performed at 1200 °C for a total duration of 30 h with heating cycles of 1 h, 5 h, and 10 h in air.

While pure chromium shows a mass decrease during oxidation of 3.8 ± 3.7 % due to spallation and nitridation, reactive elements, such as Yttrium, almost halve this mass loss. Also, Yttrium and A15-phase former cause a significantly reduced nitride formation in the alloyed samples. The resulting aluminum diffusion layer thickness of 25.03 µm ± 1.21 µm on pure Cr and Cr-Si-Mo was homogeneously and evenly distributed across the samples. Even if some cracks in the layer were detected the resulting alumina layer was continuously formed upon the samples.

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High temperature oxidation and corrosion behavior of chromized Ni-based superalloys – by pack cementation and slurry

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Ni-based superalloys are commonly used in high temperature applications because of their outstanding creep properties. In the temperature range of 650-950 °C, long term hot corrosion resistance of Ni-based alloys is typically insufficient and therefore protective diffusion coatings are required, which Cr_2O_3- being beneficial even over Al_2O_3-forming coatings.

Cr-based diffusion coatings are largely achieved using pack cementation where the parts/substrates are usually fully embedded into a powder mixture, which is energy- and labor-intensive. Alternatively, slurry-based coatings are a much more economical option. For sufficient diffusion rates during the heat treatment, the existence of a liquid phase at the interface of the substrate surface and the slurry particles is necessary. Because of the high melting point of Cr, Cr-based diffusion coatings by the slurry technique have been challenging. As demonstrated in this work, Cr-Si slurry coatings have been successfully developed. Higher Cr-activities, due to the partial liquid state, enable higher coating thicknesses when compared to similar coatings applied by pack cementation, by a factor of ~10).

The high temperature oxidation and corrosion performance of these novel Cr-Si slurry coatings applied on Rene 80 and Inconel 740H were investigated and compared to pack cementation-coated and uncoated materials. Oxidation exposures were carried out at 900°C in lab air. The hot corrosion behaviour was investigated by the deposition of 42.5 mg/cm^2 Na_2SO_4 salt. Afterwards, the samples were exposed at 700°C and 900°C for 300 h in a gas mixture of synthetic air containing 0.1 % SO_2. The slurry-coated samples showed significantly reduced attack by oxidation and corrosion during the exposures due to the formation of a slow-growing Cr_2O_3 scale and an Al/Si-rich subscale.

The effect of K and Cl concentrations on corrosivity and melting behavior of synthetic sulfate deposits

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There is a great interest in using renewable biomasses and waste-derived materials as sustainable substitutes for fossil fuels. Superheater material corrosion risk in CHP plants is high when combusting such low-grade fuels of complex chemical compositions. Thus, the maximum steam temperature in the superheaters is limited to clearly lower values than in coal-fired boilers. Potassium and chlorine in agricultural and forest biomass ashes have been identified as the main cause of high-temperature corrosion. However, the deposits forming on heat-transfer surfaces during combustion do not consist of potassium and chlorine only. The amounts of these elements in the deposit may vary, which affects the melting behavior and, through that, the corrosivity of these deposits.

This study addresses the corrosivity of two sulfate-based mixtures with different amounts of added potassium and chlorine in laboratory-scale furnace exposures with commercial heat-transfer materials. The exposures were carried out at two different temperatures, one below and the other above the calculated first melting temperature (T_0) of the studied mixtures. After the experiments, the mass loss of the samples was recorded/measured, and the damaged surfaces were studied with profilometry. Furthermore, the morphology, thickness, and composition of the formed oxide scale were characterized from cross sections with SEM-EDS. Additionally, the melting behavior of the salt mixtures was studied with TG-DTA and modeled thermodynamically.

The work sheds light on the impact of the following factors on superheater material corrosion: 1) Deposit composition on T_0 and the amount of formed melt at T_0; 2) Melting behavior and corrosivity of a deposit with varying composition. In addition, different approaches are used to measure the corrosion.

Hot corrosion assessment: a critical review on the effect of experimental parameters

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Hot corrosion of refractory metallic materials by molten salts is a common issue when it comes to high temperature processes. In the aeronautic field, the severity of the degradations is usually explained by the presence of molten sulfate – rich deposits found at the surface of some engine parts. Many methods have been developed and employed at lab scale or in industry to assess the corrosion resistance of Ni-based superalloys and to reproduce the observed attack in service.

Some of these methods are based on half or full immersion of the specimen to be tested in the molten sulfate; in others the sulfate-coated specimens are exposed to air or air+SO_2(g) at high temperature; others use various electrochemical techniques w/wo air+SO_2(g). Indeed performing electrochemical measurements has been judged to be an appropriate approach to investigate the behavior of alloys in molten salts since these techniques allow the *in situ* determination of many kinetic and thermodynamic parameters that are impossible to acquire otherwise.

However, all the experimental methods employed have to be critically considered when interpreting the results, because of the specificity and the high complexity of the chemical systems encountered in hot corrosion phenomenon: redox reactions involving several species, acido-basic reactions, equilibria between the liquid and the gaseous phase. If these are not properly taken into account, the determination of representative data can be impossible or the interpretations incorrect. Thus the objective of the communication is to present and discuss advantages and limitations of a few methods employed up to date to determine the corrosion behavior of Ni-based superalloys in type I and type II hot corrosion conditions.

Hot corrosion behavior of Mo-Si-B and its derivates with Ti or Cr at different temperatures

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The efficiency of gas turbines can be enhanced by increasing the turbine inlet temperatures. The state-of-the-art structural materials, Ni-based alloys are currently operating at temperatures close to their melting point. Hence, a further temperature increment leads to the requirement of new alloy systems. Due to their high melting point and creep strength, refractory elements such as Mo are promising candidates to be used in gas turbines. However, their utilization is usually restricted due to their insufficient oxidation and corrosion resistance.

The hot corrosion behavior of the Ni-based alloys is extensively studied. It shows two mechanisms which are attributed to the melting of Na_2SO_4 (type I) and the formation of eutectics with lower melting points (type II). In contrast for Mo-Based alloys, it is shown, that even nder sulfate deposits, Na_2MoO_4 will form. It has melting point of 687 °C and is able to dissolve the surrounding material. In addition, it can form an eutectic with MoO_3, which melts at around 500 °C. Therefore, the corrosion mechanism for these alloys shifts from a Sulfate-based attack to a Molybdate-based.

In this work, hot corrosion resistance of four Mo-based alloys, Mo-20Si-52.8Ti, Mo-21Si-34Ti, Mo-13.5Si-54.3Cr and Mo-9Si-8B, is investigated in a SO_2-containing atmosphere at temperatures between 500 °C and 900 °C. After the hot corrosion tests, the samples are analyzed by XRD, SEM and EPMA. The objectives of this study are to observe the development of the corrosion rate and to determine the temperature regimes (like type I and type II for Ni-base) for each alloy as well as to define the temperature ranges, which promote degradation mechanisms of pesting and hot corrosion. This fundamental research on the hot corrosion behavior of these alloys is needed to develop hot corrosion mitigation strategies e.g., protective coatings, which can enable the usage in gas turbine applications.

Effect of oxygen on high temperature corrosion of pure iron in ammonia environment

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Introduction

Attempts are being made to convert fossil fuels to hydrogen energy. Hydrogen as a pure gas is difficult to transport or store. This problem can be overcome if hydrogen is in the form of ammonia which can be easily liquefied. The use of ammonia as a hydrogen carrier offers the prospect of a relatively low-cost solution for the efficient and safe storage and transport of carbon-free energy. When ammonia is used as fuel, it reacts with oxygen to create thermal energy. Many unknowns remain about the environmental resistance of materials in such environments. The aim of the study is to investigate the corrosion behaviour of materials in an oxygen and NH_3 atmosphere using craft made oxygen pump sensors and oxygen and hydrogen probes.

Experimental details

To understand the fundamental mechanisms of corrosion, pure iron (99.99%) is used as a study material. Fig. 1 shows a diagram of the device. Ar-5% NH_3 gas was used as the introduced gas, and the flow rate was 30 ml min^{-1}. The oxidation temperature was 900°C. After raising the temperature for 1 hour, it was held for 4 hours, and then the electric furnace was turned off. An oxygen sensor and an oxygen pump-sensor were installed in the front stage of the electric furnace to adjust the amount of ammonia

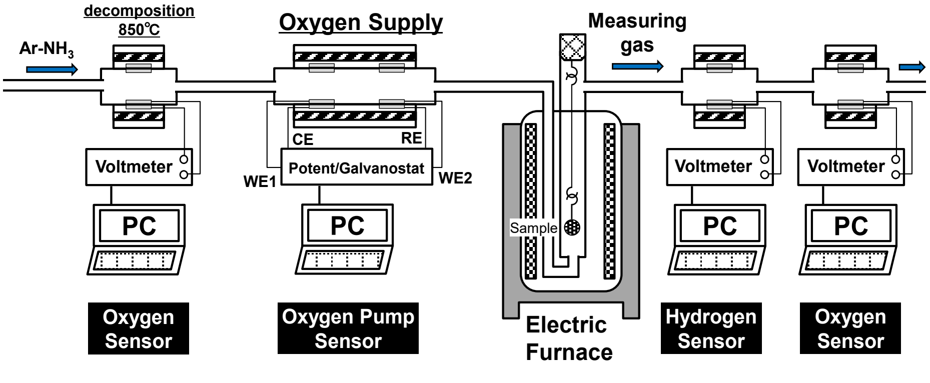

Fig.1 Diagram of the experimental setup.

decomposed and supply oxygen to control the reaction. The oxygen pump sensor was operated at 850 °C to ensure sufficient diffusion of oxide ions. A tubular oxygen sensor and hydrogen sensor were installed downstream of the electric furnace, and the hydrogen and oxygen partial pressures in the exhausted gas atmosphere were measured. The hydrogen sensor was operated at 500°C and the oxygen sensor at 700°C.

Results

Fig.2 shows the relationship between the current applied to the oxygen pump sensor and the amount of oxygen supplied calculated using Faraday's law. It can thus be seen that as the applied current increases, the amount of oxygen supplied increases. It can also be seen that at 240mA, 0.014mL s^{-1} of oxygen is constantly supplied.

Fig.3 shows the time dependence of oxygen partial pressure and hydrogen partial pressure. At 0 mA without supplying oxygen, the oxygen partial pressure was as low as 10^{-21} atm, and the hydrogen partial pressure was as high as $10^{-1.6}$ atm. By applying current, the oxygen partial pressure increases and the hydrogen partial pressure decreases. At 240 mA, the oxygen partial pressure is 10^{-7} atm and the hydrogen partial pressure is $10^{-3.1}$ atm, indicating that ammonia decomposes and generates hydrogen, and that hydrogen and oxygen react.

Fig.4 shows the dependence of the mass gain of Fe oxidized at 900°C as a function of oxygen partial pressure measured just upstream of the corrosion chamber (electric furnace in Fig.1). The mass gain does not change until the oxygen partial pressure reaches 10^{-19} atm. The dotted line shows the mass gain at 900 °C in an ammonia environment without oxygen supply. Therefore, it was found that when the oxygen partial pressure is lower than 10^{-21}atm, the mass gain was similar to that in an pure ammonia atmosphere. The oxygen supply amount at 200 mA is 0.012 mL s^{-1}. However, at 240 mA, the mass gain increased rapidly. The amount of oxygen supplied at this time is 0.014 mL s^{-1} from the current value, and the amount of ammonia supplied is 0.025 mL s^{-1}. For 10^{-19} atm of oxygen, ammonia and oxygen do not react completely ($4NH_3+3O_2 \rightarrow 2N_2+6H_2O$), so a reducing atmosphere is created by the hydrogen generated by the decomposition of ammonia. However, at 240 mA, the hydrogen and oxygen in ammonia reacted, so it is considered that accelerated oxidation occurred without creating a reducing atmosphere.

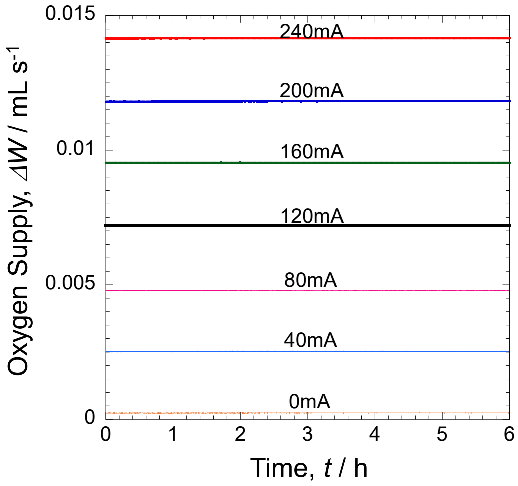

Fig.2 Relationship between applied current and amount of oxygen supplied.

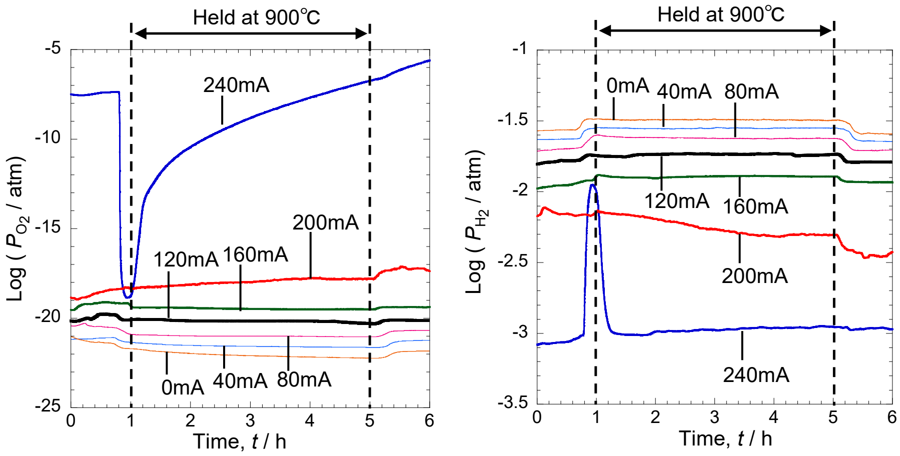

Fig.3 Time dependence of oxygen and hydrogen partial pressures during oxidation experiments.

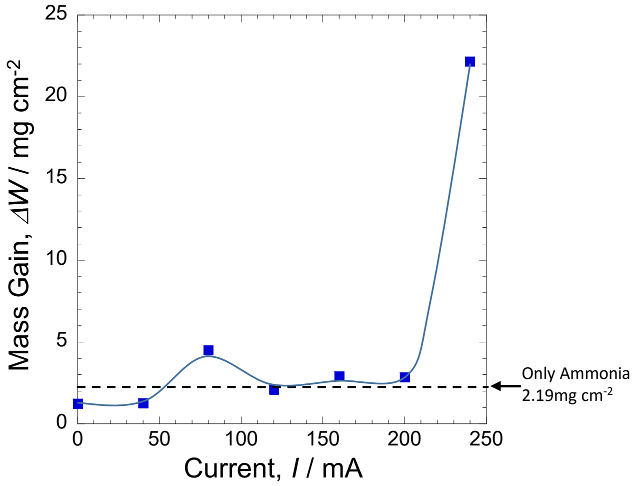

Fig.4 Relationship between applied current and mass gain.

Conclusion

The combined use of oxygen and hydrogen probes/pumps enabled the kinetics of ammonia decomposition in the presence of oxygen to be measured. This will be presented as a function of temperature and oxygen partial pressure. In addition, the threshold value of oxygen partial pressure generating a net increase in pure iron oxidation kinetics was determined. Finally, the oxidation mechanism will be presented.

Effect of N and S on the oxidation of Rene 80 in a high temperature CO_2 environment.

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The Allam cycle, a climate-friendly novel power generation cycle, utilises CO_2 as its working fluid whilst minimising emissions thus contributing to the future of net-zero goals. Allam cycle operates at temperatures up to 1100 ºC and 300 bar pressure, and these extreme operating conditions pose challenges to the material selection for turbomachinery. Rene 80 is a superalloy designed for gas turbine blades that could be a candidate for use in the Allam cycle. Contaminants such as N_2 and SO_2 are typically found as a result of combustion which are deleterious for the turbine components. Thus, there is a necessity for evaluation of materials' performance under these conditions.

This paper investigates the influence of contaminants in a baseline Allam cycle. It evaluates the influence of sulphur and nitrogen species on the oxidation and carburisation performance of Rene 80 at 800 ºC for 1000 h in two distinctive environments: CO_2 + 2.7 mol% H_2O + 0.17 mol% O_2 with and without 300 ppm SO_2 + 1.43 mol% N_2. The samples were exposed for 1000 h in 5 cycles and then analysed using an optical microscope, scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDX) for characterization of oxide scale and surface morphology, and atom probe tomography (APT). APT analysis highlights the internal sulfidation and nitridation in the sample.

Analysis using these techniques reveals a thicker external Cr - Ti oxide scale and extensive internal alumina precipitation (24.4 μm) along grain boundaries in the presence of sulphur and nitrogen contaminants compared to the CO_2 – H_2O – O_2 environment. It is hypothesized that the alumina forming along the grain boundary (GB) regions enabled enhanced transportation and localized nitridation. Further analysis using the APT along the GB indicates the localisation of nitrogen, however sulfidation potentially occurs in a non-uniform manner across GB.

Keywords: Rene80, CO_2, Oxidation, carburization, Allam cycle, APT.

Material Degradation in H_2 post combustion environment in gas turbine.

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The EU made the commitment to achieve climate neutrality by 2050 and reduce the emissions of pollutant gases by 2030. The power generation sector needs to help to achieve these targets and gas turbines will need to play their part. One way of doing this, is using unconventional fuels, such as H_2. The adoption of H_2 (from 30% up to 100%) will presents multiple challenges i.e., flame stability, flashbacks, NO_x emissions and understanding of the materials' behaviour. Understanding the impact of the combusted environment on the hot gas path materials will be crucial in terms of maintenance, repair and overhaul strategies. It is reasonable to think that small amounts of trace elements, such as S and Cl containing molecules could be present in the post combustion stream, these would play a crucial role in the degradation of turbine materials. For this reason, it is crucial to assess the behaviour of conventional materials in H_2 post-combustion environments, especially in comparison to conventional natural gas post-combustion environments.

In this work different superalloy and ceramic materials were compared in both, natural gas and H_2 post-combustion environments. The materials were exposed to corrosive atmosphere at 950°C in horizontal furnaces, using the deposit re-coating technique, to simulate the condensation of vapours from the gaseous environments. Samples were exposed for up to 5000h and then analysed using dimensional metrology techniques, SEM, EDS.

The study analysed the differences between the two post-combustions environments, in particular for the effect of the water content, as well as S content. The amount of damage observed has been linked to the chemical composition of the material, as well as the composition of the gaseous environment. The findings have been confirmed by SEM, which showed the migration of S from the gas to the alloy. Internal damage was also found, which can be linked to the microstructure of the materials.

Hot corrosion in post-H_2 combustion environments featuring HCl contamination.

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Abstract

Hydrogen is widely viewed as a possible substitute gas turbine fuel that can provide power generation without releasing CO_2 to the atmosphere. Compared to natural gas, the combustion of H_2 is hotter and results in higher levels of water vapour. Contaminants may also be present either in the H_2 fuel or ingested into the turbine from the local atmosphere. For example, H_2 produced from the electrolysis of seawater could contain traces of Cl_2 as a contaminant which would oxidize to HCl post-combustion. Such post-combustion atmospheres require study to understand their effects on materials degradation and how that can affect turbine component lifetimes.

This research investigates the response of superalloys to a simulated atmosphere that results from the combustion of H_2 with trace HCl contamination. Hot corrosion tests were carried out at 700 °C for up to 500 hours in an atmosphere of N_2 with 100 ppm HCl, 13% O_2, and 20% H_2O. A sea salt depost was applied to half the samples every 100 hours at a flux of 1.5 $\mu g/cm^2/h$ using a pnematic spray gun.

Dimensional metrology shows that carrosion rates are much higher when a sea salt deposit is present, but some metal loss still occurs in the absence of the deposit. Scanning electron microscope analysis shows reveals pitting morphologies even over short exposure times. The superalloys with higher concentrations of Cr tended to perform better than those with a lower concentration.

Material performance and metal dusting challenges in novel syngas conversion processes

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Abstract

The conversion of biogas resources into value-added products like methanol, synthetic liquid fuels or chemicals are enabled by technologies that reform the biogas into syngas as an intermediate step. To maximize the utilization of biobased carbon, it is necessary to also convert the CO_2 contained within the biogas. For this approach, dry reforming is an attractive process that may be catalyzed over carefully designed materials. The key challenge for the catalyzed process is to avoid carbon formation, both on the catalytic material and metal carbidization of enclosing vessel or tube walls, either in the reactor itself or in downstream tubing or heat exchangers. The latter process is well known as metal dusting and takes place at elevated temperatures and pressures when the carbon activity is high (a_c>1), such as in the case of a biogas reformed largely in the absence of added steam.

eQATOR is a Horizon Europe funded project aiming to demonstrate scalability of electrically heated catalytic reactor technologies for biogas conversion to bridge the gap between this renewable carbon resource and downstream syngas conversion technologies. The syngas generated by these reactor technologies via dry reforming is typically reducing $(H_2+CO)/(H_2O+CO_2) > 1.0$, and with sufficient carbon activity to promote aggressive metal dusting within the right temperature and pressure range. Material selection is therefore critical to enable long-term safe and reliable operation.

Understanding the impact of and mechanisms driving the degradation process on different materials is fundamental to proper material selection. Therefore, selected materials, considering both material properties and commercial aspects, have been screened at SINTEF in our laboratory equipment at relevant pressure and syngas composition. The selected candidate alloys included 602CA (UNS N06025), 699XA (UNS N06699), Inconel 601 (UNS N06601), Incoloy 800 (UNS N08800) and Inconel 617 (UNS N06617). The materials were first polished, followed by exposure to steam at ambient pressure and 550 °C, and then subjected to a syngas mixture at 4 barg and

650 °C; the composition of which corresponded to equilibrium by dry reforming at 4 barg and 850 °C. The pre-treatment and exposure conditions were selected based on a literature review of metal dusting combined with conditions relevant for the eQATOR project.

The extent of metal dusting was studied by means of gravimetry, optical microscopy, FIB SEM/EDS and other advanced characterization techniques.

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PVD MAX-Phase Coatings on TiAl for High-Temperature Applications

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Titanium aluminides have already used to replace conventional Ni-based alloys in low-pressure areas of turbines. They are characterized by a high specific strength, but their oxidation resistance decreases above 700°C and they are susceptible to various wear mechanisms. The application range of titanium aluminides could be significantly extended by the deposition of protective MAX-phase coatings, which combine metallic and ceramic properties. These coatings combine a high melting point, oxidation resistance and wear resistance. Compared to Al-rich coatings they also showed a higher strain tolerance. Using physical vapor deposition two MAX-phase coatings (Cr_2AlC and Ti_2AlN) are deposited on Ti-Al 48-2-2 and TNM-B1 alloys. Via magnetron sputtering flexible and accurate coating compositions are ensured and the optional reactive sputtering enables the incorporation of nitrogen. Upon heat treatment the deposited coating crystalizes and the interdiffusion of Al into the substrate and formation of Kirkendall pores is observed. During cyclic oxidation tests (up to 50 cycles) of Cr_2AlC-coated TiAl 48-2-2 at 900 °C the formation of a protective Al_2O_3 layer and an enlargement of the IDZ with an increasing number of cycles is observed. The MAX-phase coatings additionally display crack-healing capabilities. A comparison of the oxidation rates reveales an improvement of the oxidation behavior over the uncoated material. In high-temperature wear and erosion tests the mechanical properties of the coated samples will be further evaluated.

Behavior of High-Velocity Thermal Spray vs Alloy 625 in High-Temperature Erosion/Corrosion Environment

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A Secondary Smelter Plant treats complex lead/copper materials, containing valuable minor elements in an ISASMELT™ furnace, which utilizes a two-step smelting and converting process to produce various metals, including copper, lead, tin and precious metals. The batch process operates 20-24h cycles, with pressure oscillating between 20 and 28 bar. The temperature inlet 1st pass ~1200°C, then top of 1st pass ~800°C, then water quench in 2nd pass to get 350°C on the outlet.

High-Temperature Erosion/Corrosion

The process conditions in the furnace contributes to the generation of corrosive species causing metal wastage in the furnace and off-gas system. The flue gas is fed into the waste heat recovery steam generator (WHRSG) to reduce the temperature of the gas from the furnace. Due to the harsh process conditions the WHRSG surface experiences high erosion/corrosion rates leading to premature thickness loss of bare tubes and even the pre-installed Alloy 625 weld overlay (WOL). The time required for the weld repairs, together with any potential new panel installation in areas of damage, extended turnaround schedules, impeding on plant availability and resulting in associated production losses.

High-Velocity Thermal Spray (HVTS) Alloy Upgrade

In 2021, the plant installed 100m^2 of HVTS Cladding to the WOL, a NiCr-based alloy that is specifically designed for use in high temperature corrosion environments. This material offers a low stress, very dense corrosion resistant layer. The following year, in 2022, an inspection showed that while HVTS cladding successfully protected most of the installed WOL and bare metal surface, localized areas indicated HVTS cladding thickness loss. This was due to the gas velocities and higher temperatures in these specific areas. After evaluation, the cladding has been upgraded to combat both corrosion and erosion. An early 2024 inspection delivered good results, preventing any metal wastage of the base material and a decision was made to apply HVTS surface solutions again in 2024.

Interfacial Fracture Toughness Determination of 7-8 wt.% Yttria-Stabilized Zirconia Thermal Barrier Coatings After Oxidation

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This study aimed to determine the main failure mechanism of the TBC systems under severe conditions namely cyclic and isothermal oxidation. Understanding the failure mechanism at the topcoat and bond coat interface is crucial because the TBC spallation mostly occurs on this interface. An 8 wt.% yttria stabilized zirconia (YSZ) topcoat with a Ni22Cr10Al1Y bond coat was applied on IN 718 substrate. Fracture toughness and residual stress measurements were performed using the Vickers Indentation method. Multiple Vickers indentations were applied with forces of 3, 5, and 10 kgf at the coating interface, each with a dwelling time of 15 seconds. Consequently, radial cracks formed along the edges of the Vickers impressions. The lengths of these cracks were subsequently utilized for fracture toughness and residual stress evaluations. The radial crack lengths were measured on SEM images. The elastic modulus of the topcoat and the bond coat was measured using a depth sensing indentation instrument. Hardness values (0.3HV) of top and bond coat was also measured using a micro-Vickers instrument. These values were then used in the following expression (A model proposed by Lawn):

$$\frac{P}{c^{\frac{3}{2}}} = \frac{K_{\iota c}}{X_i} + \left(-\frac{2\sigma_r}{\sqrt{\pi}\ X_i}\right) c^{\frac{1}{2}}$$

Where P is the critical force to create sufficient cracks, c is the median crack length. As coated 8YSZ interfacial fracture toughness was calculated to be 0.79 MPa.m$^{-1/2}$, and the residual stress was estimated to be around -60 MPa. The isothermal oxidation tests were conducted at 1150°C in a muffle furnace. Sample weight gain was monitored every 24 hours with a 0.1mg accuracy digital balance. After oxidation the fracture toughness and residual stress values of the 8 YSZ coating system were investigated, and the results were discussed.

High Entropy Oxides ($A_6B_2O_{17}$) for Thermal Barrier Coatings

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The strive for turbine engines with better efficiency, lower fuel consumption and lower emission values requires advanced material solutions to handle increasing operating temperatures. With gas temperatures above the melting point of commonly used metallic materials in the hot section of gas turbines thermal barrier coating systems are crucial to protect the metal components from the hot gas. In the present work, we study five different high entropy oxides with the general formula of $A_6B_2O_{17}$ (A = Zr, Hf; B = Nb, Ta) as a promising alternative for the state-of-the-art yttria stabilized zirconia. The phase $Hf_6Ta_2O_{17}$ was shown to exhibit excellent phase stability in combination with low thermal conductivity. Substituting the cations in this structure will alter the material properties and potentially increase phase stability and lower thermal conductivity even more. These new materials could then be used either as a single material coating or as a filler material to optimize new coating approaches such as polymer derived ceramic nanocomposites (PDC-NCs). For this study $A_6B_2O_{17}$-type oxides are synthesized using the co-precipitation route. Phase and chemical composition as well as morphology of the synthesized materials are be examined by X-ray diffraction (XRD), scanning electron microscopy (SEM), and electron probe microanalysis. Phase stability and sintering of the materials is investigated to identify temperature ranges for operation of these new coating approaches.

Structural materials for nuclear reactors cooled with liquid Pb or Pb-Bi: behavior and damage of the metallic materials in contact with the liquid metal and under mechanical stress

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The durability of the structural materials at high temperature, under irradiation, under mechanical stress and in the presence of the heat transfer fluid, is one of the challenges in the development of 4th generation nuclear reactors, especially reactors cooled by liquid lead (LFR) or for the development of Accelerator Driven Systems which use liquid lead-bismuth eutectic (LBE). For these reactors, in addition of damage due to irradiation, one of the major damages to structural materials could be due to corrosion by liquid metal. Additionally, under stress (mechanical stress or stress due to temperature fluctuations), structural materials can be susceptible to liquid metal embrittlement (LME) or liquid metal accelerated damage (LMAD), i.e. partial or total loss of ductility in the presence of liquid metal and therefore an earlier fracture. Thus, although tough and ductile metallic alloys are selected, they may become brittle when stressed in liquid metal exhibiting thereby the so-called LME. The objective of the presentation is to summarize the knowledge acquired at UMET over more than 20 years on the mechanical behavior of coated or uncoated metallic alloys (martensitic and austenitic) in the presence of liquid Pb or LBE and then to present the main conclusions and the main issues for future researches. LME sensitivity of the materials has been investigated by mechanical tests (monotonic tests (Small Punch Tests and tensile tests) and Low Cycle Fatigue tests), in temperature, in air and in liquid LBE or/and liquid lead and then the study of fracture surface, cracking and damage by SEM-EDX-SEM-EBSD or ToF-SIMS analysis. In general, Body-Centered Cubic studied materials are more sensitive to LME than Face-Centered Cubic (FCC) steels especially at temperature lower than 450°C because of their low ductility while FCC alloys are more susceptible at temperatures higher than 500°C. Note that, strain rate, roughness of the surface, microstructure, temperature, oxygen content in the liquid metal appear as parameters that influences LME sensitivity. Taking into account the mechanisms to explain LME occurrence, challenges to avoid LME of the materials will be presented.

Peculiarities of corrosion appearances on austenitic steel Fe-15Cr-15Ni-1.2Mo-1.8Mn-0.5Si-0.4Ti under the short-term high-temperature (800-1000 °C) interaction with liquid Pb-Bi eutectic

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Heavy-liquid metals (HLM), such as Pb, Pb-Bi and Pb-Li eutectics, are quite corrosive media with respect to the steels as structural materials in novel liquid-metal bearing reactors. HLM leach the main steel constituents such as Ni, Mn, Cr, and Fe, resulting in the formation of mechanically weak near-surface layers with a phase-structural state different from that of the steel bulk. Most literature on the corrosion interaction between steels and HLM pertains to moderate temperature ranges, usually between 350 and 650 °C. This work is focused on the high-temperature (800-1000 °C) corrosion interaction between austenitic steel Fe-15Cr-15Ni-1.2Mo-1.8Mn-0.5Si-0.4Ti, with 24% of cold work, and static liquid Pb-Bi eutectic with low concentration of dissolved oxygen. The study specifically examines the very initial stages of interaction. The steel underwent dissolution corrosion, resulted in the formation of a near-surface corrosion zone infiltrated by Pb-Bi. Corrosion at high temperatures is accompanied by a recrystallization process that might be reason for the observed formation of ferrite protrusions above the initial solid metal / liquid metal interface (Figure). The structural, morphological and composition peculiarities of formed corrosion zones are detailed depending on the interaction temperatures. The results are compared with those obtained at moderate temperatures of interaction (< 700 °C).

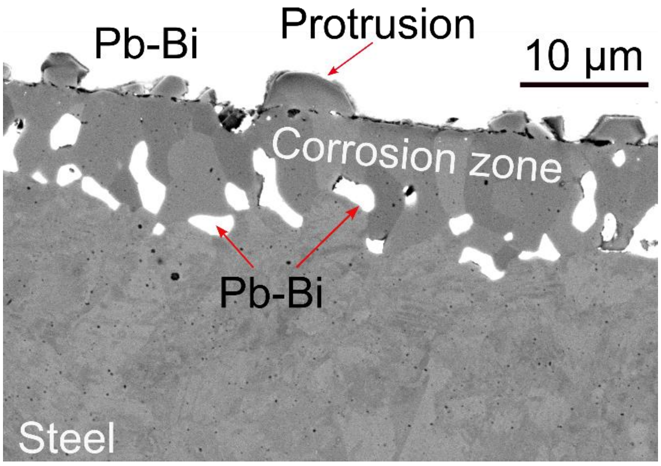

Figure. Morphology of corrosion zone formed on the surface of austenitic steel Fe-15Cr-15Ni-1.2Mo-1.8Mn-0.5Si-0.4Ti after exposure at 800 °C to static liquid Pb-Bi eutectic with low concentration of dissolved oxygen for 10 h.

Effect of surface condition and microstructural features on early stages of liquid metal corrosion of austenitic stainless steels 316L in liquid lead-bismuth eutectic

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Previous studies have discussed the influence of surface state and microstructural features on liquid metal corrosion. However, the impact of these parameters on the initial stages of LMC remains unclear. Therefore, the aim of this study is to investigate the effect of surface preparation and microstructure on the initiation and development of LMC of austenitic stainless steel 316L in liquid lead-bismuth eutectic (LBE). Flat samples were prepared with one side polished (up to 0.25 µm) and the other side ground with #800 paper. The surface roughness of the polished and ground surfaces was 0.123 and 0.257 µm, respectively. After exposure to static liquid LBE at 500 and 400 °C, it was observed that the areas affected by dissolution were higher and the average corrosion depth was greater on polished surfaces compared to ground surfaces. However, in terms of maximum corrosion depth, the difference between the two surfaces was significantly smaller. The surface analyses revealed that the corrosion process was delayed on ground surfaces compared to polished surfaces. However, once initiated, localized corrosion was frequently observed on ground surfaces, while polished surfaces exhibited a more uniform corrosion front. Regarding microstructural effects, clear evidence of preferential crystallographic directions in dissolution was observed on polished surfaces exposed to low dissolved oxygen concentrations (< 10^{-10} wt.%) at 500 °C. EBDS analyses performed before the exposure allowed us to correlate different corrosion morphologies with specific grain orientations.

Nickel oxide formation in liquid lead-bismuth eutectic

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Austenitic stainless steels are the main structural and functional steels foreseen for the nuclear reactor MYRRHA, an accelerator-driven system cooled by lead-bismuth eutectic (LBE), under development at SCK CEN, Belgium. To minimize aggressive dissolution-corrosion of steel components into LBE, control of the dissolved oxygen concentration (DOC) is necessary during operation. A constant DOC ensures the formation of a passivating oxide scale onto steel surface, which drastically slows down dissolution corrosion. However, even if released in LBE at a slower rate, the main steel elements – Fe, Ni and Cr – could potentially react with dissolved oxygen in the LBE bulk, thus further reducing the DOC available for the surface passivation.

This research focuses on preliminary kinetic evaluations of nickel oxide (NiO) formation; in particular, conditions under which NiO is stable in LBE are investigated. Three sets of tests after dissolution of known Ni amounts (0.02, 0.05 and 0.10 weight %) were conducted in LBE-containing alumina crucibles under controlled temperature and DOC. Comparison of obtained experimental results with thermodynamic calculations has revealed formation of NiO at all the three Ni concentrations. At 0.05 wt.% Ni, the ratio of experimentally estimated supersaturation of the DOC to nucleate NiO to its calculated equilibrium DOC was substantially higher – compared with PbO – and increased as temperature decreased (e.g. $19 \cdot 10^{-5}$ wt.% versus $6 \cdot 10^{-5}$ wt.% at ca. 450 °C). Moreover, thermal cycling tests at 0.5 °C/min have demonstrated slow NiO formation kinetics compared to PbO, whose kinetics is well defined in LBE.

The maximum total nickel concentration in MYRRHA's LBE is estimated to be below 0.001 wt.% Ni due to corrosion of structural materials by the end of operation. Given our observations made at much higher Ni concentrations, we can conclude that NiO formation should not be expected in the MYRRHA operating conditions: 10^{-7}-10^{-6} wt.% DOC and 200-400 °C.

Isolating radiation effects on lead-bismuth eutectic corrosion of pure Fe in multi-scale irradiation-corrosion experiments

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Understanding the effects of the simultaneous exposure of materials to irradiation, corrosion, stresses, high temperatures, and high temperature gradients is key to the development of new effective and safe materials that can be deployed in advanced Gen IV nuclear reactor systems. Since access to Gen IV reactors is scarce or non-existent, research and accelerated testing of materials in these novel environments requires experimental facilities capable of exposing samples to one or several extreme conditions to illuminate potential materials evolution in a real reactor environment.

One such experiment is the Irradiation-Corrosion Experiment III (ICE III), a static corrosion chamber designed for the exposure of metal foils (50 µm or thinner) to corrosion by heavy liquid metals or molten salts and radiation damage simultaneously. The primary focus of ICE III is to study pure metals and binary alloy model systems in this combined extreme environment to gain a better understanding of the interplay between radiation damage and corrosion as radiation-induced defect production and defect evolution affects the base metal and the corrosion layer and influences the latter's development.

Early ICE III results showed that corrosion of pure Fe by Pb-Bi eutectic (LBE, 450 °C) is drastically accelerated by the presence of a 4 MeV proton beam (~1e-5 dpa/s). However, it is difficult to ascribe this acceleration solely to the presence and evolution of radiation-induced defects, given several compounding factors, such as accelerated corrosion kinetics due to beam heating and potential changes in LBE chemistry due to hydrogen injection. In recent experiments, several steps were taken to attempt to isolate the impact of radiation damage. In this talk, we will show the results of this ongoing work and discuss the degree to which the various compounding factors in irradiation-corrosion experiments may obscure the effects of radiation damage on the corrosion process in ICE III and other similar experimental setups.

Liquid metal embrittlement sensitivity by LBE of Face-Centered Cubic austenitic steels and Complex Concentrated Alloys

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One of the challenges in the development of Lead Fast Reactors (LFR) or Accelerator Driven Systems is the reliability of the structural materials in contact with the coolant, so the lead or the Lead-Bismuth Eutectic (LBE) and in temperature. In addition of damage due to irradiation, one of the major damages to structural materials could be due to corrosion by liquid metal. Additionally, under stress (mechanical stress or stress caused by temperature fluctuations), structural materials can be susceptible to liquid metal embrittlement (LME), i.e. partial or total loss of ductility in the presence of liquid metal and therefore an earlier fracture. Because of the LME sensibility of the Body-Centered Cubic alloys, the most ductile Face-Centered Cubic (FCC) alloys could be preferred because of their low LME sensitivity below 450 °C and despite the corrosion observed, in particular the selective dissolution of Ni and possible LME sensitivity at high temperature (500 °C and more). The objective of the presentation is the study of the LME sensibility of 5 different FCC alloys (15-15Ti steel, two alumina forming austenitic (AFA) steels and two Complex Concentrated Alloys (CCA) of the family of the FeCrNiMn alloys, susceptible to be used in presence of LBE and Pb. Small Punch Tests were performed in air and in LBE saturated in oxygen at different temperatures between 200 °C and 500 °C. Then, the fracture surfaces and cracking were observed by Scanning Electron Microscopy. The influences of a lower strain rate and the composition of the liquid metal (tests in Pb, Bi) were investigated too. All the materials present ductile behavior and ductile fracture in air. The steels are less susceptible to LME by LBE that the studied CCAs. In case of LME occurrence, intergranular cracks were observed. The LME occurrence is discussed taking into account the microstructure, the hardness and the composition of the alloys. The study was supported by the GEMMA and INNUMAT projects (Euratom research and training programme: respectively 2014-2018 - grant agreement No 755269, and 2021-2022 - grant agreement 101061241).

Liquid Metal Embrittlement sensibility
of a FeCrMnNi alloy in presence of liquid Pb, Bi or Pb-Bi eutectic

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This communication presents a better understanding of the Liquid Metal Embrittlement (LME), Pb, Bi or lead-bismuth eutectic (LBE), of the Faced Center Cubic alloy FeCr15Mn17Ni22 at%, which could be used as structural material for LFR (Lead Fast Reactor). This study is carried out through mechanical testing, microscopic characterizations, thermodynamic analysis, and kinetic modeling. Tensile tests have been conducted in air and in liquid Pb, Bi and LBE saturated in oxygen at temperatures between 300°C and 500°C at the deformation rate equal to 5.10^{-5} s^{-1}. After tests, fracture surfaces and cross sections of the fractured specimens have been observed employing SEM (Scanning Electron Microscopy), EDX-SEM (Energy Dispersive X-ray), SEM-EBSD (Electron Backscatter Diffraction) and TEM (Transmission Electron Microscopy) to analyze the effects of liquid metal on the fracture mode, the microstructure (phases and composition) and the cracking.

The material presents, whatever the temperature, a ductile behavior and ductile fracture in air. In presence of Pb, Bi, and LBE, the sensitivity to LME varies depending on the temperature. The material exposed to Pb shows no sensitivity to LME at 400°C; but exhibits at 500°C a mixed-type fracture with ductile zones in the center of the fracture surface and brittle intergranular fracture at the edges. The material in contact with Bi or LBE exhibits sensitivity to LME at all tested temperatures (300,400 and 500°C) with intergranular brittle fracture. The presence of micrometer particles has been observed inside some cracks (400-500°C); these particles are rich in Fe and Cr, indicating a possible loss of Mn and Ni. On the other hand, zones rich in Ni have been observed next to the Fe-Cr particles using TEM. Phases equilibrium have been investigated and Dictra simulations, a thermodynamic and kinetic-based modeling approach, have been performed. These results will be presented and discussed to highlight the connection between the microstructure and the LME mechanisms.

Effect of coating composition on the corrosion resistance of 316L steel

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Abstract

The aim of the work was to verify the behaviour of materials under the working conditions of the pump impeller of a small lead-cooled modular reactor. Specimens of 316L stainless steel in as-received state and coated were exposed to liquid lead with 10^{-8} wt.% oxygen at 520 °C for 3500 h. Three various coatings based on Al, Ti, and W were applied by PVD. The post-test microscopic analyses revealed different mechanisms of degradation of the coatings and confirmed the improved corrosion resistance of the coated steel compared to the uncoated steel.

For 316L steel, the corrosion attack occurred on 92 % of the surface, with an average depth of the damage of 8.5 μm. Considering the fact, that this was a low oxygen environment, mainly solution-based attack (SBA) and Pb penetration into the material structure was found. The outer oxidation was negligible as small nodules of the oxide were visible only on 4 % of the surface. The evaluation of the cross-section of the coated specimens showed that SBA and Pb penetration were minimal, and the main damage mechanism was internal oxidation. Minimal corrosion damage occurred on the AlTiN coated specimen. In this case, AlTiN formed a protective barrier against the Pb penetration and there was also minimal oxygen penetration through the coating and negligible oxidation of the base material. Only 6 % of the 316L surface was attacked by internal oxidation with average depth of 0.1 μm. AlTi protective layer was more permeable to oxygen and internal oxidation of the base material occurred on 30 % of the surface with an average depth of 1 μm. The coating structure proved to be less dense and Pb penetration through the coating also occurred. The worst results were achieved with the metallic coating containing W. In this case, even the low oxygen concentration in the corrosive environment was sufficient to oxidize the coating and forming a mixed oxide with Pb. Similarly, to AlTi oxygen penetrated to the coating and the internal oxidation was found on 36 % of the base material surface with an average depth of 1.5 μm. SBA was found on 13 % of the base material surface.

Stability and corrosion of MAX phases in concentrated nitric acid environments

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Objectives

The lifetime of equipment used in reprocessing of spent nuclear fuel is limited by their exposition to concentrated nitric acid under oxidizing conditions. Protective coatings may be used to enhance the durability and corrosion resistance of these structural materials, but the protection efficiency depends on the stability of the coating materials in these conditions. Hence, a preliminary investigation of candidate materials under service conditions is desirable. This study was focused on MAX phases, i.e. ternary carbides of general formula $M_{n+1}AX_n$ (here X = C), owing to their known self-healing properties and stability in strong acid conditions.

Results and conclusions

Two MAX phases (Cr_2AlC and Ta_2AlC) were immersed in 7 M HNO_3 at 20°C (room temperature) or 110°C (boiling condition). For Cr_2AlC at 20°C, a low corrosion rate was observed after two weeks of immersion (3.2 µm/year), suggesting that the material is able to form a stable and protective passive film. This passivation was confirmed by anodic polarization curves of Cr_2AlC coupons. However, the sample rapidly corroded under boiling conditions, with a calculated damage thickness of 433 µm after only one week. Microscopic investigation revealed that the coupon actually underwent crevice corrosion, with most damage occurring via internal dissolution. The extremely high rate suggested a catalysis reaction, presumably chromium dissolution.

Relatively low corrosion rates (≤ 50 µm/year) were observed for Ta_2AlC at both 20°C and 110°C. Microscopic investigation confirmed that surface damage was limited, suggesting that Ta_2AlC may be a promising coating material.

Atomic emission spectroelectrochemistry study of a Ni-Cr-Mo alloy in acidic environments at various temperatures

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A Ni-Cr-Mo alloy have shown a better corrosion resistance than austenitic and super austenitic stainless steels in nitric acid environments. However, conventional electrochemical (cyclic voltammetry, linear sweep voltammetry, electrochemical impedance spectroscopy) and gravimetric measurements are insufficient to understand the mechanisms involved behind this improved corrosion behaviour.

The aim of this study is to use an approach using the Atomic emission spectroelectrochemistry (AESEC) technique, which allows measuring *in situ* and in real-time the elemental dissolution rates and the corresponding electrochemical response [1]. This work involves the study of the passive and transpassive domain of a Ni-Cr-Mo alloy in acidic environments at various temperatures.

The first results suggest a temperature-dependent selective dissolution of molybdenum in the passive domain, as well as congruent dissolution in the transpassive domain in a sulfuric acid environment.

In addition, chronoamperometries coupled with XPS analyses may be carried out to provide further insights into the corrosion behavior of the Ni-Cr-Mo alloy.

[1] K. Ogle, Atomic emission spectroelectrochemistry: real-time rate measurements of dissolution, corrosion, and passivation, Corrosion 75 (2019) 1398–1419, doi:10.5006/3336.

Stainless steels corrosion modelling in nitric acid in presence of oxidizing ions

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Sustainability of the fuel reprocessing plants is an important challenge for nuclear industry. Therefore, a constant effort is made to model corrosion in order to predict accurately the ageing of the plants. One challenge concerns corrosion of stainless steels (SS) in contact with the fuel dissolution solution, containing nitric acid and oxidizing ions. In these conditions, the corrosion kinetics is governed by two aspects. The first one is the stability of the oxidizing ions in the nitric acid solution, which is controlled by the redox reactions of the oxidizing ions with the nitric species. The second one corresponds to the corrosion reactions of nitric and/or oxidizing ions with the SS. The corrosion model developed takes into account these both aspects. Simulations are performed with different oxidizing couples: Np(VI)/Np(V), Pu(VI)/Pu(IV), V(V)/V(IV), Cr(VI)/Cr(III) and Ce(IV)/Ce(III). Input data (kinetic constants of the redox reactions in solution, corrosion rates) are taken from experimental works [1-2]. All these simulations allow illustrating the influence of the kinetics of redox reactions in solution and kinetics of corrosion, respectively, on the degradation of SS.

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[2] Fallet, A., Influence of oxidizing ions from the dissolution of the behavior of structural materials: experiments and kinetic modeling. PhD, 2015.

The corrosion of stainless steel in nitric acid liquors relevant to nuclear fuel reprocessing operations and storage conditions.

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Reprocessing of spent nuclear fuel at Sellafield, UK, incorporates evaporation and storage of nitric acid based liquors. Corrosion of the associated stainless steel vessels and pipework is a potentially life limiting process.

Numerous years of experimental work have been carried out at NNL to develop an understanding of the corrosive effects of the liquors. The work includes:

- Small scale testing, including immersion experiments in simulants containing potential corrosion accelerator species e.g. Neptunium and Cerium.
- Radiolysis experiments carried out to investigate the generation of nitrous acid in nitric acid.
- Large scale rigs, which incorporate the effects of a hydrostatic head and are designed to produce more representative plant conditions e.g. low nitrous acid concentration liquors under reduced pressure conditions and high surface temperatures.

The specific corrosion challenge has engendered the application of the bespoke corrosion testing regimes to generate meaningful results.

The data and information generated from the experiments have been used to support on-going plant operations at Sellafield.

Modelling of Flow Accelerated Corrosion in pipes of French nuclear power plants with BRT-Cicero^{TM}

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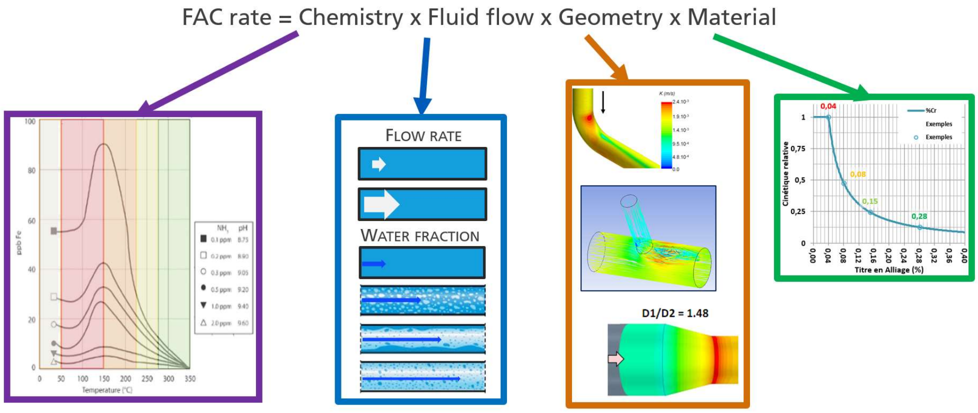
Flow Accelerated Corrosion (FAC) is a very important concern for nuclear power plants (Ref [1] & [2]). FAC degradation mainly affects carbon steel piping and equipment in the nuclear power plants and especially the secondary loop from high pressure turbine to steam generator. Dramatic accidents have occurred in the past due to this phenomenon and thus EDF developed the software BRT-Cicero^{TM} to calculate and monitor wall thickness wear of pipes due to FAC on susceptible materials. This software enables the operator to calculate FAC rates by taking into account all the influencing parameters (temperature, pH, moisture of the fluid; geometry, flow rate, alloy composition).



The latest version 4.3 of the software, currently being implemented on the French fleet incorporates new functionalities such as a local chemistry module and a power variation module, in order to consider the recent operating experience and in some cases reduce conservatism. The aim of this paper is to develop these recent improvements.

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[2] S. TREVIN – "Flow accelerated corrosion (FAC) in nuclear power plant component" in Nuclear Corrosion Science and Engineering – Ed. D. FERON – Woodhead Publishing Series in Energy, n° 22, p. 186- 229 (2012).

The difficulty of correctly modelling turbulent flow: its implication on Single and Two-Phase Flow-Accelerated Corrosion (FAC)

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Flow-Accelerated Corrosion, FAC, is one of the most common forms of degradation of carbon and low alloy steel pipes exposed to water flow. In a liquid-vapor two-phase flow environment, additional characteristics affect this complex corrosion phenomenon. Among them, phase redistribution, turbulence, and chemical partitioning have a major influence over the kinetics and/or the localization of extensive degradation. CFD-combined approaches have become increasingly popular as they are thought to be effective tools to increase predictions accuracy and reliability especially in situations involving local variations of corrosion and flow disturbances. Despite decades of investigations, some difficulties arise in the predictions in such environment partially due to a remaining gap in the proper understanding of the corrosion mechanisms and interactions. Moreover, aspects related to the nature of these flow regimes remain little addressed. The work carried out in this study aims to acquire a numerical methodology to improve predictions, which rely both on an appropriate modeling of the two-phase flow and the choice of a relevant corrosion model. In single-phase flow, the turbulence modeling approach has been shown to be determinant to evaluate the mass transfer between the wall and the flow with models providing incorrect estimations. Therefore, it is first verified that the simulations are able to capture this process in two-phase flow as well based on comparisons with experiments of wall dissolution in different flow patterns (stratified, annular, slug) [1]. In a second step, the mass transport model is coupled to a mechanistic corrosion model to provide wall thinning data. This type of study is particularly insightful to identify regimes and dimensionless numbers which may characterize FAC-prone situations. Using measurement available in the literature, the global performance of the method will be assessed and compared to simpler predictive models.

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Flow-assisted corrosion of carbon steel in simulated steam generator conditions – experiments and modelling

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The aim of our project is to develop, verify and validate a deterministic model of single-phase flow-assisted corrosion in s nuclear power plant team generators by using dedicated experiments in well-controlled hydrodynamic conditions and molecular dynamics calculations. In this paper, we communicate results of monitoring of flow-assisted corrosion with electrochemical methods at temperatures 130-240 °C and pressure of 10 MPa. First, a laboratory made re-circulation loop with a novel design to simulate flow-assisted corrosion is described, together with finite element hydrodynamic and current distribution calculations. Next, electrochemical measurements (corrosion potential vs. time and electrochemical impedance spectroscopy) in ammonia and ethanolamine secondary coolants are discussed. Finally, a model of flow-assisted corrosion processes based on molecular dynamics simulations of ammonia and ethanolamine adsorption on magnetite is outlined and a quantitative comparison with experimental data to extract kinetic and transport parameters is described.

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An experimental (SIMS and TEM) and computational (DFT and MD) study of internal corrosion of copper in synthetic groundwater

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The corrosion of copper as canister material has been debated for many years and successively gained more and more attention. A study has been initiated wherein copper was subjected to simulated groundwater conditions at both room temperature and 60 ^{o}C. The penetration of corrosive species, encompassing S, O and Cl was examined using Time-of-flight secondary ion mass spectrometry (ToF-SIMS). The findings demonstrated a significant penetration of corrosive species into the microstructure of copper (1). This penetration primarily occurs locally along specific fast pathways, most likely grain boundaries. Notably, after a four months exposure at 60 ^{o}C, S penetrated approximately 500 nm along these pathways.

Further investigations are being conducted in which copper samples, exposed to synthetic groundwater, have been prepared through FIB-cutting and subjected to correlative Nano-SIMS and Transmission electron microscopy (TEM) analyses. Nano-SIMS method offers a higher lateral resolution compared to ToF-SIMS, enabling more detailed chemical information. TEM is employed to unveil the microstructure of grain boundaries. Both Nano-SIMS and TEM provide lateral resolution at the nm scale.

In all, these efforts aim to unravel the mechanisms underlying the penetration of corrosive species containing S, O, Cl and H into copper, which turns out to be much faster at 60 ^{o}C than at room temperature. O is observed along the grain boundaries while S and H exists within confined areas of the copper matrix.

To obtain a more fundamental understanding of this internal corrosion behaviour of Cu exposed to simulated underground water, a computational study has more recently been implemented which uses density functional theory (DFT) calculations with machine learning combined with molecular dynamics (MD). This experimental and computational approach provides new insight into the ramifications for considering copper as a canister material for the long-term storage of nuclear waste.

(1). X. Yue et al, Corrosion Science, 210 (2023) 110833

Particle-boundary corrosion of cold spray Cu in HNO_3: corrosion mechanism, effect of oxygen content, and mitigation strategies

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Cold spray (CS) has been considered one of the two techniques for applying Cu as the corrosion-resistant layer on the Canadian-designed used (nuclear) fuel container (UFC). The resulting CS Cu must maintain its integrity in its lifetime, contemplated to be more than 10^6 y, in a deep geological repository (DGR), where the UFCs will be emplaced. Therefore, it's important for the corrosion of CS Cu to be investigated and evaluated under the various conditions corresponding to different periods in the DGR. Previous work reported the possible production of HNO_3 droplets on the UFC due to the radiolysis of humid air during the early stages of the DRG[1]. Thus, work is being carried out in HNO_3 bulk solutions with higher-than-anticipated concentrations as an accelerated approach to study the corrosion of CS Cu.

In preliminary work, CS Cu exhibited particle-boundary corrosion (PBC), but the mechanism was not elucidated[2]. In this study, we show that the PBC is initiated by the Cu^+ supplied via the dissolution of the oxide inclusions at the particle boundaries and sustained by the confined geometry left behind. Given the importance of the oxygen inclusions, the effect of the oxygen content in CS Cu on the PBC is also investigated. It has been discovered that PBC propagates faster and longer for CS Cu with higher oxygen content. In all cases, PBC terminates by itself. However, the time it takes depends on the oxygen content. We will discuss possible rationales for such behaviour.

Moreover, strategies are developed to mitigate the PBC. Microstructural engineering of the oxide inclusions by employing a higher annealing temperature leads to the consolidation of the oxide inclusions, thereby reducing the corrosion penetration depth. Besides, Cl^- is found to be an effective inhibitor for PBC. PBC is completely blocked even when $[Cl^-]$ is as low as 1 mM.

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Corrosion behavior of copper according to the hydrogen sulfide, chloride, pH, and temperature

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Abstract: Most countries have adopted permanent disposal in underground repository for the disposal of nuclear waste. At this time, nuclear waste disposal canister are required to have a lifespan of more than 10,000 years, considering the half-lives of high-level radioactive waste (HLW). Despite the canisters being shielded by backfill and isolated from the soil environment, groundwater infiltration can occur over time. Therefore, corrosion of the canister in groundwater are important.

Korea, Sweden, and Finland selected copper as a material for the canister. Copper corroded uniformly at a relatively low rate, making it a suitable as a canister material. Accordingly, the corrosion properties of copper have been studied under various environmental factors (eg., pH, HS^-, Cl^-, T). However, most studies investigated each environmental factor individually. Since these factors coexist in the actual soil environment, it is necessary to evaluate the complex effects of each environmental factor.

In this study, the corrosion behavior of copper according to the environmental factors was investigated in both aerobic and anaerobic environments through electrochemical tests and surface analysis. In the aerobic environment, environmental factors were set to temperature, Cl ion, and pH, and in the anaerobic environment, they were set to HS ion, Cl ion, and pH. To investigate the single and combined effects of these environmental factors, response surface methodology (RSM) was used to obtain a model for the corrosion behavior of copper according to each environmental factor. Therefore, the influence of environmental factors on copper corrosion was evaluated. It can provide good guidance for related research on the corrosion behavior of copper according to geological conditions.

Keywords: copper, disposal canister, corrosion, response surface methodology

The effect of microstructure of an advanced duplex stainless steel on the pitting corrosion and chloride-induced stress corrosion cracking

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Chloride-induced stress corrosion cracking (CISCC) is a significant concern for the integrity of dry storage canisters made of austenitic stainless steels (ASSs). To deal with the issue, an advanced duplex stainless steel (ADCS) was developed as a potential dry storage canister material. The chemical composition of ADCS was carefully determined to enhance its resistance to pitting and CISCC while maintaining a balance of strength and ductility. In this study, the corrosion behavior of ADCS alloys with different microstructures was evaluated. Two types of heat treatment conditions were applied to ADCS alloys to form equiaxed austenite and elongated austenite embedded in the ferrite matrix. To evaluate the effect of austenite morphology for ADCS on corrosion properties, the pitting corrosion and CISCC tests were conducted. The potentiodynamic polarization results revealed better pitting corrosion resistance of ADCS with equiaxed austenite than elongated austenite. It seems that the pitting corrosion is more affected by the pitting resistance equivalent number (PREN) of phases rather than the morphology. The CISCC tests using U-bend specimens showed that the ADCS with equiaxed austenite is more susceptible to CISCC. The length of cracks and selective dissolution of ferrites in ADCS with equiaxed austenite is longer than that with elongated austenite. Also, the depth of cracks in ADCS with equiaxed austenite was deeper than elongated austenite. As the elongated austenite retards the propagation of cracks, the susceptibility to CISCC is low in ADCS with elongated austenite. Overall, ADCS with equiaxed austenite represents high pitting corrosion resistance, while more susceptible to CISCC.

Evaluation of the lifetime of the materials considered in the Czech SNF disposal package concept

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Abstract

The safety of the Czech deep geological disposal system will be ensured by a multi-barrier system that comprises both the natural geological barrier and so-called engineered barriers that will act to prevent the escape of radionuclides from the disposed of spent nuclear fuel into the biosphere. The Czech waste disposal package (WDP), which is referred to as “UOS” in the Czech radioactive waste disposal concept, consists of a double-layered steel package with an outer casing made of carbon steel (EN 10219-1, ASTM A53B) and an inner casing made of stainless steel (EN 10297-2, AISI 316L). The design of the WDP is based on the knowledge provided through experimentation that indicates that the carbon steel outer casing will protect the inner casing until the temperature of the package decreases to 40-50°C. Stainless steel exhibits slow corrosion and fulfils the required service lifetime criteria; however, temperatures above this threshold may lead to the occurrence of pitting corrosion. Hence, the carbon steel outer casing will protect the inner casing until the deep geological disposal (DGR) environment becomes thermally suitable for the inner stainless steel. Consequently, one of the most crucial parameters in terms of the safety of the Czech DGR concept concerns the lifetime of the waste disposal package. Following extensive discussions and the study of international experience, SÚRAO determined that the WDP will be required to provide a safety function for up to 1 million years. In line with international experience and recommendations, the assessment of the viability of the Czech WDP includes the conducting of long-term anaerobic in situ experiments, the study of archaeological analogues, the examination of natural analogues, and the creation of predictive models. One such example concerns the Pilot Corrosion Experiment (2023-2035) underway at the Bukov underground research facility (Bukov URF), corrosion processes under conditions similar to those expected in the future Czech DGR are under examination. Furthermore, the results obtained from research projects that considered archaeological and natural analogues have provided important knowledge for the research of the WDP.

Corrosion rate of steel radioactive waste from the NPP decommissioning in cementitious matrixes

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The paper is focused on decommissioning radioactive waste behaviour in order to specify the rate of radionuclide release and their migration in the matrix, focusing on evaluation of matrix safety functions. Four different matrixes based on cementitious binders have been selected as an infill for disposal intermediate and high level waste from nuclear power plant decommissioning. The matrixes include cement paste I based on Ordinary Portland Cement (OPC), cement paste enriched with bentonite or nano-iron, and finally a geopolymer. The S355J2 unalloyed steel, AISI 420 and AISI 321 stainless steels were exposed in the matrixes under simulated repository (anaerobic groundwater) conditions for 6, 12 and 24 months of incubation in anaerobic conditions. In parallel, the materials were exposed to non-carbonated and carbonated slurries of all the infill materials for 6 and 12 months. The results showed extremely low corrosion rate of all the steels, which further decreased as the exposure continued. Thin layers of corrosion products were analyzed by means of XRD and Raman. The paper will also present results a microbial activity monitoring inside the matrixes and slurries as well as the dissolved metal ions sorption ability of the infill materials.

Key words: deep geological repository; decommissioning; cementitious materials; geopolymer

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Combined protection strategy applied to metallic drums intended for direct conditioning of decontamination sludges

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Abstract

Currently, in Spain, low and intermediate-level wastes are conditioned in carbon steel drums by immobilization in Portland cement matrices. These waste packages are exposed to the chemical environment generated both, by the cementitious barriers of storage and by the aggressive species present in the waste. For this reason, both sides of the drums are coated with a protective layer of epoxy-phenolic paints to prevent corrosion.

The role of complexants as both, mobilisers of radionuclides and enhancers of metallic corrosion, is one of the key issues included in Performance Assessment exercises of disposal sites. For that reason, this research aims to dispense with the current anti-corrosion treatments based on organic-based paints, but guaranteeing the design lifetime defined for these metallic drums.

This study proposes the use of a combined strategy based on the development of a new alkali-activated cement formulation and the use of different stainless steels as an alternative to carbon steel plates (austenitic 316-L and two duplex 2001 and 2205).

A blast furnace slag activated with carbonate and sodium silicate with three different liquid/solid ratios are selected to confine the maximum volume of decontamination sludge is selected.

The results indicate that the two alkaline formulations and the reference matrix with l/s=0.55 meet the mechanical acceptance criterion (compressive strength ≥10MPa) and allow the direct immobilization of 9% wt. sludge. Corrosion indicators show that both 2205 and 2001 in the carbonate-activated slag specimens and 316-L, in the silicate-activated slag specimens, present a moderate risk of corrosion, which may be associated with the corrosion process itself or with the effect of the sulfide anions present in the slag on the surface of the steels.

Anodic dissolution of iron in bentonite slurry- a mechanistic insight

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Bentonite is a clay material proposed as a buffer in underground radioactive waste disposal in many countries. The corrosion of iron/steel in contact with bentonite is a key factor affecting the disposal system's long-term performance and safety. Previous studies have mainly focused on the formation of corrosion film and metal corrosion rates after long-term burial in bentonite. However, the corrosion mechanisms and the product formation during the anodic dissolution of iron in bentonite are still unclear.

In this study, we performed accelerated corrosion experiments on pure iron in basic bentonite slurries (pH 9-10) using electrochemical techniques, such as potentiodynamic polarizations and potentiostatic tests. The use of bentonite slurries allows having access to the metal-bentonite interface which combined with the electrochemical measurements provided valuable information about the corrosion process, kinetics and corrosion product formation.

The anodic dissolution of iron in bentonite slurry resulted in the formation of a bentonite gel with acidic pH. The role of gel formation in the evolution of corrosion was identified.

Highlighting aluminium-magnesium alloys passivation in magnesium potassium phosphate cement: a step forward towards the conditioning of such metallic waste

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The reprocessing of spent nuclear fuel designed for natural uranium – graphite – gas reactors has produced some waste with aluminium alloys, which need to be stabilized and solidified before their final disposal. Portland cement (PC), extensively used for the conditioning of this type of radioactive wastes, leads to the oxidation of aluminium due to its high alkalinity, with production of dihydrogen. Aluminium passivation only occurs for pH values within the range 3-9, with the formation of a protective layer of alumina. This work aims at investigating a new solution consisting in using magnesium potassium phosphate cement (MKPC) instead of PC.

The corrosion rate of several aluminium-magnesium alloys (Mg content varying from 0 to 5% by weight) is investigated using two experimental techniques: measurement of dihydrogen released by corrosion by gas chromatography, and investigation of the electrochemical behaviour of Al-Mg alloys using electrochemical impedance spectroscopy. Two different environments are studied: firstly a MKPC-based mortar, and secondly synthetic solutions mimicking the mortar pore solution at increasing hydration degrees of cement. This second environment makes it possible to characterize the corrosion products on the metallic surface using SEM/TEM-EDX and XPS.

The results confirm that using MKPC instead of PC strongly mitigates the corrosion of Al-Mg metal, both in cement matrix and in representative pore solution. Formation of a passivation layer made of an aluminium potassium phosphate is evidenced in a MKPC pore solution at thermodynamical equilibrium. Comparing the corrosion rates in cement matrix and in pore solution shows that the limited availability of water in the MKPC matrix, due to its large consumption by cement hydration, strongly contributes to mitigate the corrosion of metallic alloys. Eventually, the Mg content in the Al alloy has limited influence on its corrosion rate in the MKPC matrix.

Potential influence of microorganisms on the corrosion of the carbon steel in the French high level long-lived radioactive waste disposal context

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Microbially influenced corrosion (MIC) refers to the influence of the microorganisms on the kinetic of corrosion processes of metal, caused by microorganisms adhering to the surface or modifying the environment. In the context of the French high-level radioactive waste (HLW) disposal, the potential influence of the MIC must be evaluated. In France, it is envisaged to dispose of high and intermediate level long-lived radioactive waste at about 500 m depth in a deep geological disposal (Cigéo project), drilled in a very stiff Callovo-Oxfordian claystone (Cox). To do so, a carbon steel casing will be inserted inside disposal cells which are horizontal tunnels drilled in the Cox. In the current concept, a specific cement grout will be injected between the carbon steel casing and the claystone. The cement grout aims to neutralize the acidic transient, induced by destabilized sulphur-bearing minerals (pyrite), and prevent steel from high corrosion.

In this study, carbon steel corrosion and microbial growth, as well as their possible interaction are investigated in representative conditions of the HLW disposal. For this purpose, laboratory exposure at 30, 50 and 80°C were realized, with and without microorganisms from bacterial culture collections and microorganisms enriched from samples of Andra's Underground Research Laboratory (URL) (Bure, France). Different formulations of the cement grout were also studied in presence of Cox. The corrosion data are completed with surface and biological analyses including cultural and molecular characterizations. The obtained result highlights i) the benefit effect of the more alkali cement grout formulation to limit abiotic corrosion and potential MIC phenomenon ii) the influence of the temperature on the microorganism's diversity and growth, and iii) the occurrence of MIC under some conditions.

Real-time corrosion monitoring of HLW metallic liner demonstrator in the Meuse/Haute-Marne Underground Research Laboratory

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The French National Radioactive Waste Management Agency (Andra) is responsible for the Cigéo[1] project dedicated to store high-level radioactive waste in a deep geological disposal facility. Since 1999, Andra has been carrying out investigations at its Meuse/Haute-Marne laboratory site to study the possibility of implementing an underground repository for high-level (HLW) and long-lived waste. The geological formation under consideration consists of a stiff clay rock located at a depth of 500 meters. HLW disposal cell concept consists of a carbon steel (CS) lined micro-tunnel measuring approximately 60 - 70 centimeters in diameter and around 100 meters in length. The initial annular space between the outer surface of the sleeve and the host rock is filled with a cement grout called MREA. The MREA material imposes corrosion-limiting environmental conditions (cement and bentonite mixed-based grout).

Andra has developed an overall monitoring strategy and identified specific technical objectives to inform disposal process management on evolutions relevant to long term safety as well as those relevant to the reversible, pre-closure management of the repository. In this context, studies have been conducted focusing on corrosion and mechanical behaviour of the CS casing, with interest for real-time corrosion monitoring solutions as an alternative to the common gravimetric method. This including the electrical resistance (ER) technique, raising several challenges such as i) the use of a sensing material representative of the HLW liner to monitor, ii) a high accuracy and stability of the sensor and acquisition system due to the extremely low corrosion rates expected in the cement grout, iii) a tens year lifespan, and iv) a remote data collection compatible with the underground research laboratory data center. The present work focus on the development of a new ER sensor and data acquisition system and the results obtained on experiments as a part of the HLW demonstrators' program.

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[1] Industrial underground radioactive waste disposal[2]

Corrosion of metallic beryllium in contact with different cementitious matrices and pore solutions

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At SCK CEN, metallic beryllium is used as moderator in the Belgian Reactor 2. After use, activated beryllium waste will need to be disposed of in a geological disposal repository. Therefore, beryllium could come into contact with cementitious matrices and will corrode producing hydrogen, and beryllium oxide and/or hydroxide. Different cement matrices could be used. The most common one is the Ordinary Portland Cement (OPC) possessing a highly alkaline pore solution. However, other cementitious materials, such as the Magnesium Phosphate Cement (MPC) possessing a near neutral pore solution can also be of interest. Indeed, because beryllium is an amphoteric material, decreasing the pH to more neutral conditions could be beneficial to decrease the corrosion rate.

In this study, the corrosion rate and mechanism of metallic beryllium is investigated in solutions mimicking the cement pore solutions as well as in cementitious matrices.

Two different methods were used to investigate the corrosion of beryllium: (1) Electrochemical Impedance Spectroscopy (EIS) and (2) the measurement of the concentration of the hydrogen gas produced during the anaerobic corrosion. Both methods revealed similar results. The corrosion rate was lower in solutions representative of the OPC pore water (pH~13.5; 2-7 µm/y) compared to solutions representative of the MPC pore water (pH~8; ~12 µm/y). In cement pastes, the corrosion rate is much lower in both OPC and MPC and reaches rates lower than 1 µm/y.

Scanning Electron Microscopy was also performed to analyse the surface and the cross section of the metal before and after corrosion. The first analysis revealed a crater-like structure of the surface as well as the presence of pitting corrosion in OPC pore water, while a thicker corrosion product layer, covered by K- and P-based crystals is formed after immersion in MPC pore water.

Effect of Dissolved Oxygen on Stress Corrosion Cracking of 316L Stainless Steel in Nuclear Primary Environment

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Austenitic stainless steels are widely used in pressurized water reactors (PWR) primary environment for their excellent resistance to corrosion, but operating experience has shown several cases of intergranular stress corrosion cracking (IGSCC). The water is normally deaerated and hydrogenated, but dissolved oxygen can be added during shutdowns or water additions, and is suspected to increase the SCC susceptibility. Previous studies showed that oxides forms in both conditions are different, and that intergranular oxides, considered as precursors of IGSCC, grow slower in oxygenated conditions. The literature gives contradictory results on the effect of oxygen on SCC susceptibility, what could indicate a major impact of the loading mode. The effect of temperature on SCC in stainless steels is also unclear, even under nominal conditions.

The objective of this study is to address how the temperature and/or the mechanical loading could modify the effect of oxygen on oxidation and SCC of 316L in PWR primary water. Samples are exposed in an oxygenated or hydrogenated environment at different temperatures (320°C vs. 340°C for the precedent study), and with different mechanical stress states (Slow strain rate tests, constant displacement tests using U-bend specimens, constant load tests with a stress level around the yield stress, cold worked samples). Oxidation and SCC susceptibility are studied by SEM analysis by measuring layer thicknesses, cracks and intergranular oxide penetrations depth and density, and oxides composition.

Effect of helium ion irradiation on short-time corrosion behavior of two novel single-phase bcc-structure high-entropy alloys in simulated PWR primary water

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High-entropy alloys (HEAs) are potential alternative materials for accident-tolerant fuel cladding due to their excellent irradiation resistance and high-temperature corrosion resistance. In this work, two novel body-centered cubic (bcc) structured $Mo_{0.5}NbTiVCr_{0.25}$ and $Mo_{0.5}NbTiV_{0.5}Zr_{0.25}$ HEAs were fabricated. Helium-ion irradiation was performed on the two HEAs to simulate neutron irradiation, and the crystal structure, hardness, and microstructure evolution were investigated. The crystal structure of the $Mo_{0.5}NbTiVCr_{0.25}$ HEA remained stable at low fluences, while amorphization may occur at high fluences in the two HEAs. The irradiation hardening value of the $Mo_{0.5}NbTiVCr_{0.25}$ was 0.77 GPa at fluences of 1×10^{17} ions/cm^2 and 1.49 GPa at fluences of 5×10^{17} ions/cm^2, while the hardening value of the $Mo_{0.5}NbTiV_{0.5}Zr_{0.25}$ was 1.36 GPa at ion fluences of 5×10^{17} ions/cm^2. In comparison with most of the conventional alloys, the two HEAs showed slight irradiation hardening. The helium bubbles and dislocation loops with small size were observed in the two HEAs after irradiation. The voids and precipitates were not observed in the two HEAs which could be ascribed to the high lattice distortion and compositional complexity of HEAs. This research revealed that the two HEAs show outstanding irradiation resistance, which may be promising accident-tolerant fuel cladding materials.

The effect of helium ion irradiation on the short-time corrosion behavior of two novel high-entropy alloys (HEAs) was also investigated in simulated PWR primary water. The results revealed that a two-layers oxide film consisting of Ti, Nb and V oxides was formed on both HEAs, including outer oxide particles and a protective inner oxide layer with a maximum depth of ~500 nm. Irradiation up to 10.5 dpa may hardly promote corrosion kinetics since severe lattice distortion and sluggish diffusion in HEAs. The corrosion processes with and without irradiation were discussed in detail.

Oxidation kinetics of zirconium and its alloys - impact of stress and stoichiometry on the zirconium oxide polymorphs

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Abstract:

Nuclear facilities require materials that can withstand extreme conditions, including high temperatures, radiation doses, and corrosion. In nuclear reactors, zirconium alloys are used for fuel cladding as a barrier separating the fuel from the coolant [1]. During operation, a cyclic corrosion process occurs, resulting in continuous creation of a corrosion-resistant tetragonal phase that is then transformed into the monoclinic, which is less protective [1,2]. It would be beneficial for the corrosion limitation to maintain the pre-transition regime. Thus, it is worth studying the transformation phenomenon and the stabilization mechanisms of the tetragonal zirconium phase.

To address this, we conducted an experimental study comparing the corrosion behaviour of pure zirconium with two zirconium-based alloys, E110 and Zircaloy-2, oxidized in air and water steam. Raman spectroscopy was used to analyse the phase distribution in the oxide scale the percent content of the tetragonal phase at varying distances from the metal/oxide interface. These results were compared with the stress state in the oxide and stoichiometry levels. In addition, high temperature Raman measurements and TGA/DSC on pure Zr were performed for an in-situ comparison of the atmosphere's influence and its impact on the tetragonal to monoclinic transition during heating and cooling. The presented work provides valuable insights into the process of zirconium oxide creation, including the phenomena of phase transformation and the factors that influence it.

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Experimental Study of Iodine Stress Corrosion Cracking Of Zirconium Alloys

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Abstract

Zirconium alloys are widely used in the nuclear industry as fuel cladding material, because they offer good thermo-mechanical, chemical, and neutronic properties, along with excellent corrosion resistance. They are the primary containment barrier for fuel pellets and fission products in pressurised water reactors (PWR). Whenever the reactor power is increased, the combination of the mechanical loading imposed on the cladding by the fuel pellet expansion and the corrosive environment (presence of iodine) creates a risk of Iodine-Induced Stress Corrosion Cracking (ISCC). Several studies have shown that the quantities of iodine and oxygen have a very important influence on the phenomenology of ISCC. Studies have also shown that iodine can react rapidly with many materials and form iodides that can accelerate or inhibit ISCC during laboratory tests.

The goal of this project is to study the coupled effects of iodine and oxygen on the ISCC of zirconium alloys in a chemical environment that is as representative as possible of the conditions in PWR fuel cladding. In order to approach these conditions, the CEA has developed an experimental tool for studying the ISCC of cladding under different conditions. The device uses iodine vapour in an argon carrier gas, which can be used to perform tensile tests on a C-Ring specimen. In the present study, the device has been modified in order to allow oxygen partial pressures as low as 1 Pa to be imposed on the sample. Initial results indicate the possible existence of iodine and oxygen thresholds for ISCC. Further tests are currently being performed to confirm these results. SEM microstructural observations of the Zircaloy-4 specimens are being performed to study the nature of the corrosion due to iodine. These results have made it possible to propose an initial hypothesis on ISCC mechanisms.

Assessing the Effect of Strain on Stress Corrosion Crack Nucleation in Advanced Gas-cooled Reactor Fuel Cladding

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The UK's Advanced Gas-cooled Reactor (AGR) nuclear fuel is contained within 20%Cr/25%Ni/Nb stainless steel cladding, acting as a corrosion and creep resistant barrier to fission product release in storage. A small fraction of fuel pins could be sensitised in service, leading to possible intergranular corrosion (IGC) susceptibility in storage pond. pH-control of these ponds was introduced to avert this; however, it is not clear whether corrosion reactions can be suppressed for the projected duration of spent fuel storage. This provides the potential for stress corrosion cracking (SCC) to nucleate at locations where corrosion proceeds in a very slow manner, and stresses were prior introduced during fabrication or reactor service. Very limited research is available on the SCC behaviour of AGR fuel cladding, where standard testing cannot be conducted due to geometry constraints and the radioactive nature of the pins following reactor exposure. To understand the SCC behaviour of AGR fuel cladding is challenging and requires adaption of different corrosion and SCC test methods on thermally sensitised 20/25/Nb.

An Avesta cell was first used to probe cladding performance in storage relevant environments, to determine where corrosion initially occurs in the microstructure. A bespoke electrochemical cell was then interfaced with a micro-tensile stage to test thermally sensitised cladding under applied stress and electrochemical control, to induce SCC nucleation whilst optical micrographs are taken to monitor the electrode surface and examine local strains via Digital Image Correlation (DIC). Calibrated C-ring specimens were also prepared and exposed in storage relevant environments at temperature over longer periods. In absence of stress, localised pitting or crevice corrosion was observed adjacent to niobium-rich precipitates, or grain boundaries before propagating as IGC in the thermally sensitised alloy. SCC was found to nucleate in the base of pre-existing crevice sites under galvanostatic polarisation below 0.2% proof stress, where it is believed it could propagate further as IGSCC.

Influence of powder preparation on corrosion behaviour of ODS austenitic steels with Y_2O_3 addition

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Oxide dispersion-strengthened (ODS) steels are known because of their superior mechanical properties at high temperatures and increased resistance to neutron irradiation embrittlement which favours them for future applications as a fuel cladding for the next generation nuclear systems and blanket materials for fusion power systems [1]. Powder metallurgy techniques including mechanical alloying and subsequent consolidation of powders are the most extended paths of development of these materials [2]. During mechanical alloying performed under a protective atmosphere, Y_2O_3 is the most often added as dispersed particles and dissolved into the matrix [3].

The critical point of the ODS steels with nano oxides successful fabrication is the powder prefabrication. Therefore, the main goal of this work is to analyze how various parameters of mechanical alloying influences microstructural and corrosion properties of the austenitic ODS steels. The austenitic 316L stainless steel with the addition of 1 wt.% of two sizes of Y_2O_3 were manufactured from powders prepared under different conditions (time and intervals of mechanical alloying). The corrosion resistance of the materials in terms of microstructural changes was analyzed, and the main factors affecting corrosion behaviour of the austenitic ODS steels were systematically studied.

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Effect of surface nitriding on the hydrogen uptake of a Ti-6Al-4V alloy in flowing pressurized water at 300°C

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The use of titanium alloys in the primary circuit of pressurized water nuclear reactors (PWR) is gaining interest [1]. Despite a good corrosion resistance in PWR primary water, they absorb significant amounts of hydrogen, that could potentially lead to embrittlement [2-3]. Besides, as wear could be another issue, surface nitriding was considered. Present work focuses on the hydrogen uptake of surface-nitrided Ti-6Al-4V exposed to primary water.

1-mm thick flat samples were exposed up to 72 days in simulated primary water at 300 °C in corrosion loops at different fluid speeds (≈ 1 mm/s and 7 m/s). Weighing, hydrogen analysis and microstructure characterizations were performed.

After exposure, the global hydrogen concentration increased with time in both the nitrided and untreated samples, with higher values at higher fluid speed. Nitrided Ti-6Al-4V samples had the highest hydrogen uptake, i.e. 400 wt.ppm after 72 days of exposure at a fluid speed of 7 m/s. The hydrogen pick-up fraction (HPUF) informs on the ratio of electrons produced by the oxidation of titanium contributing to hydrogen uptake. For untreated Ti-6Al-4V, HPUF stays below 1, as expected. Interestingly for the nitrided Ti-6Al-4V exposed to high fluid speed, HPUF was estimated way above 1, meaning an additional hydrogen source is involved. The hydrogen uptake mechanisms and kinetics will be discussed in detail and linked with the oxidation behavior.

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Evaluation of the PWSCC susceptibility of Alloy 182/600 HAZ using calibrated welding defects

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Primary Water Stress Corrosion Cracking (PWSCC) of nickel-based alloys has been studied for couples of decades and the replacement of low-chromium Alloys 600/182/82 by high-chromium Alloys 690/152/52 has efficiently prevented Power Water Reactors (PWR) from further PWSCC events. However, tests performed by several laboratories have shown that high chromium nickel-based alloys might suffer from PWSCC but only in out of manufacturing specifications situations, highly cold worked (>25%), non-representative microstructure, high level of stresses, etc... Nevertheless, some components made of low-chromium alloys in welding or sleeves cannot be replaced from original power plants reactor vessel. Consequently, some randomly distributed welding defects emerging at the surface could still be source of concerns without further justifications. The first objective of this work was to qualify a capsule-like SCC specimen with calibrated welding defects, representative of lack of fusion or hot cracks emerging at inter-pass or root-pass welding bed.

A specific high load tensile test machine was developed to investigate the PWSCC susceptibility of calibrated welding defects exposed to primary PWR water under constant load. The test apparatus favours PWSCC propagation from welding defects and possibly from nominal section, continuously monitored by Acoustic Emission.

An experimental test program has been performed on Alloys 600/182 capsules at several dissolved hydrogen contents. A welding defect appearing as chemical (segregation) and geometrical (notch) singularities, the effect of this later was corrected using calibrated Electro-Discharge Machined defects.

After exposure, non-destructive X-ray tomography was used to locate the zones likely to exhibit SCC cracking. Cross sections were carried out on welding defects to correlate hardness and crystallographic features with PWSCC. A local chemical analysis was performed at some hot cracked specimens from a past study to compare with calibrated welding defects produced and exposed within this present program.

Exploring microstructural evolution in cavitation peened Alloy 182: Impact on oxide film formation in high-temperature water

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Alloy 182 is a widely used Ni-based weld filler metal that is prone to stress corrosion cracking (SCC) during long-term operation of light water reactors (LWRs). Cavitation peening (CP) is a potential mitigation method to prevent SCC initiation by introducing compressive residual stresses in the surface layers (up to approx. 1 mm). However, there may be accelerated relaxation of these stresses during long-term operation in the high-temperature water (HTW) environments inside the LWRs. CP also induces a highly deformed and thermodynamically unstable surface-affected layer that has a strong driving force for microstructural changes at operating temperature in HTW and inherently increases SCC susceptibility in absence of compressive residual stresses.

SCC initiation and propagation are surface-dependent phenomena driven by the cyclical formation and rupture of a Cr-rich protective oxide film at the substrate/ environment interface. Protectiveness (susceptibility to rupture) of this oxide film is influenced by its morphology, chemical composition and electronic structure, which, in turn, are affected by the surface state (including topography, microstructure, hardness and stresses) of the substrate. This study aims to investigate the time evolution of the microstructure in the surface-affected layer induced by CP in HTW simulating reactor operating conditions. It also seeks to compare the differences in oxides formed over industrially machined versus cavitation peened Alloy 182 surfaces as a function of time and oxidizing environment.

Three conditions for each surface state were examined: i) as prepared, ii) exposed to 400 °C air for two months and iii) exposed to 320 °C HTW for three months. Characterization of the near-surface microstructure was done using scanning electron microscopy (SEM) and electron backscattered diffraction (EBSD). Cross-sectional microhardness values were compared to estimate residual stress relaxation with thermal ageing. Additionally, oxides formed in HTW over three months were analysed using SEM, Raman spectroscopy and electrochemical techniques. Results are thoroughly discussed.

Corrosion of steam generator tubes: effects of lead and sulfur on the damage mechanisms

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The outer diameter stress corrosion cracking (ODSCC) is one of the main corrosion modes that affects steam generator (SG) tubes in nuclear power plants. This corrosion mode is due to the local chemistry on the secondary side of the SGs, but also to the build-up of some non-volatile components from the secondary side. Lead and sulfur are part of these components which can embrittle the SG tubes. Understanding the role of these two pollutants in the corrosion and ODSCC mechanisms of SG tubes is a major issue in the perspective of power plant lifetime extension.

This study focuses on the Ni-based alloy mainly used in SG tubes in French nuclear power plants: alloy 690 TT (Thermally Treated). U-bend specimens made of alloy 690 TT were exposed to different representative secondary polluted environments. The behavior of the specimens was therefore subject to the influence of two parameters: the physical state of the surrounding environment (solid deposits, liquid-phase or steam-phase secondary environment) and the presence or not of lead-and-sulfur-based pollutants (PbO, $PbSO_4$/PbS or Na_2SO_4/Na_2S).

The first specimens studied were tested in steam phase with the addition of sulfur-based pollutants. Their characterization highlighted different environmental degradation phenomena, such as intergranular attack and stress corrosion cracking. The addition of sulfur compounds, even in quantities potentially found in crevices (8000 ppm), seems to promote metal embrittlement by oxidation at the metal/oxide interface. Moreover, traces of sulfur were detected locally in the oxides at the surface and at the crack tip. Comparisons with sulfur-free specimens will provide further insight into the role of sulfur in the embrittlement mechanisms of alloy 690 TT.

Combined XPS/TEM studies of the chemical composition and structure of native oxides on the inner surface of Ni-based alloy steam generator tubes of Pressurized Water Reactor

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The activity of the Reactor Cooling System (RCS) of Pressurized Water Reactor (PWR) mainly comes from the release of corrosion products of the very large surface area developed by steam generator (SG) tubes made of Nickel-based alloy (alloy 690: 60% Ni, 30% Cr, 10% Fe). The released isotope ^{58}Ni is activated in the isotope ^{58}Co in the reactor that contaminates all surfaces of the RCS. In order to reduce this activity in operation, and thus the radiation exposure of PWR operators during the operations of maintenance, it is necessary to control and minimize the release. The characterization of the native oxide films present on the inner surface of the SG tubes before exposure to the primary water is crucial, as surface passivation during exposure is strongly dependent on the nature and composition of the native oxide films.

The characterization of the inner surface of two industrial SG tubes made of nickel-based alloy 690 was performed using two main techniques, namely X-Ray Photoemission Spectroscopy (XPS) and Transmission Electron Microscopy coupled with EDS (TEM/STEM/EDS). The chemical composition and nanoscale structure of the native film were studied. A duplex oxide structure of the native film was revealed for the two tubes, with some differences in chemical composition for the inner and outer layers. In addition to the native film, chemical heterogeneities were also present on the surface of the as-received tubes, and could play a role in the evolution of the surface exposed to primary water. The multi-scale description of the surface provided a better understanding of the various mechanisms implied in the release of corrosion products.

Evolution of the passive properties of nickel-based alloy steam generator tubes during exposure to primary water

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Exposure of the inner surface of Ni-based alloy steam generator (SG) tubes to primary water induces the release of corrosion products and the contamination of the primary circuit of pressurized water reactors. Indeed, the Ni-58 released from the SG tubes is activated into Co-58 under the neutron flux in the reactor core, then redeposited on the surface of the circuits. This contamination increases the dosimetry, which can then have an impact on unit operation. Analysis of surfaces exposed to primary water, in particular characterization of the oxide layers that play an important role in nickel release during exposure to primary water, is essential to reduce this issue and understand the mechanisms involved.

The inner surfaces of two industrial SG tubes of 690 alloy (60%Ni - 30%Cr - 10%Fe) were exposed to simulated primary water in Framatome “Plateforme d’ETudE du Relâchement” (PETER) loop. During exposure in the PETER loop, the concentration of Ni cations was measured in order to determine the kinetics of Ni release, and differences were observed between the two tubes. To understand these differences, the inner surfaces of these two 690 SG tubes were studied before and after exposure, using several techniques at different scales. In particular, their electrochemical behavior was studied *ex-situ* combining potentiodynamic curves, chronoamperometry measurements and electrochemical impedance spectroscopy (EIS) analyses. Equivalent electrical circuits were developed to fit the EIS data and to extract relevant parameters to characterize the passive layers. These experiments allowed the passive properties of the tubes to be properly described and compared. Finally, the differences in the passive properties and the electrochemical behavior of the surfaces were explained using complementary analyses (XPS, SEM-TKD/EDS, TEM/STEM/EDS).

Effect of microstructure, residual strain and geometric structure on stress corrosion cracking behavior of scratched alloy 690TT

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Abstract:

Stress corrosion cracking (SCC) is one of the main failure modes of steam generator tubes due to their long-term operation in high temperature pressurized water. So far, surface scratches have caused many SCC failures of steam generator tubes worldwide. Scratches with varying depths are inevitable formed on the surface of steam generator tubes during manufacturing processes, and have caused many SCC failures of steam generator tubes worldwide. In this study, two different heat treatments, namely stress relief annealing (RA) and solution + TT treatment (SATT), were applied. Firstly, for RA-scratched area, the residual strain is nearly eliminated in fine grain zone (FGZ) and severe deformation zone (SDZ), but microstructure stratification in FGZ and SDZ still exists. While for SATT-scratched area, the microstructure and residual strain are eliminated. Secondly, for RA-scratched area, cracks could still initiate at the interface between FGZ and SDZ, but the crack length significantly decreases. For the SATT-scratched area, no SCC is observed in all samples.

Keywords

Alloy 690TT; Scratch; Stress corrosion cracking; High temperature water

Hydrogen permeation in correlation to microstructural changes and residual stress induced by cryogenic processing of stainless steel

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Keywords: hydrogen permeation, stainless steel, energy sector, fusion, cryogenic processing, microstructure, residual stress

Abstract

One of the leading research areas in energy sector is the improvement of already well known and established materials, while at the same time exploring new options for prolonging material´s life cycle in demanding environments. Unique properties such as high corrosion resistance, toughness, strength, and machinability are required for materials used in various energy material applications, including fusion applications. For various stainless steels, a novel processing that provides improvements in properties is the application of cryogenic processing (CP). During CP, the material is exposed to sub-zero temperatures, which causes fundamental changes to the properties (hardness, toughness, strength, stress state, corrosive resistance, magnetism etc.) of selected stainless steel. This study investigates the induced microstructural changes of ferritic-martensitic stainless steel in relation to hydrogen permeation and trapping behaviour. Microstructure was analysed by SEM; hydrogen trapping was characterized by TDS and its permeation with inverted Kelvin probe. The residual stress state of steel was checked by XRD. The results indicate changed microstructure after application of CP, which indicated transformation of austenite into martensite, increased precipitation resulting in finer carbides and different values of residual stress states. Results obtained from hydrogen permeation measurements indicate the importance of microstructure and changes in dimensional stability (evidenced by changes in residual stress state) for explaining the role of voids and behaviour of hydrogen during testing. Microstructural defects (carbides, vacancies, and grain boundaries) play an important role in hydrogen trapping, however also the increased precipitation and reconstruction of the matrix within the CP sample may also play an additional role in potential hydrogen trapping during exposure. As such, the newly obtained microstructure has higher dimensional stability and with this, the space is maximally saturated with the precipitates, which could also have an important role in prolonged functionality of stainless steels in high demanding environments. Finally, the material modified with CP displays unique properties, which can be achieved for this price only with CP.

Exposure of two high entropy alloys to simulated PWR primary water

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High entropy alloys have received attention regarding potential applications in nuclear reactors, since in certain conditions microstructural evolution under irradiation is slower in these alloys compared with other alloys with similar cristalline structures. However, there are very few studies of the corrosion resistance of high entropy alloys in the high temperature aqueous solutions typical of the primary or secondary side of pressurized water reactors (PWRs).

In this study, two cobalt-free austenitic high entropy alloys (CrFeMnNi family, grades called ES1 and Y3, respectively), designed and elaborated at the MINES de Saint-Etienne laboratory, have been exposed to simulated hydrogenated PWR primary water at 360°C. Behavior in terms of general corrosion and in terms of stress corrosion cracking were characterized. Simple flat coupons were used to measure oxidation mass gains after 250 and 1000 hours of exposure to PWR medium. U-Bend specimens mechanically loaded up to 530 MPa were exposed to study the stress corrosion cracking sensitivity. Both alloys seem to show very good resistance to the two forms of corrosion, but the results in terms of SCC resistance shall be confirmed under more severe mechanical conditions.

Analysis of Kori 1 baffle former bolts failure

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600 MWe Kori 1 began commercial operation in 1978 and permanently shut down in 2017. Flow pattern in internal changed from down flow to up flow in 1986. The internal has 7 rows of formers and each row has 104 baffle former bolts (BFB). The BFBs have as 4 fold rotation symmetry and 8 mirror symmetry planes at 45° x n (n=1~8). BFBs 14, 15, 40, 41, 66, 67, 92, 93 in lowest row showed indication in UT test in 2015. The purpose of this work is to understand the cracking behavior of the BFBs in Kori 1. Bolt positions in internal were marked to identify crack initiation sites before removal from the internal. Looking at bolt head from fuel side, top was assigned to 12 o' clock (OC) and right to 3 OC. Computer tomography (CT, 3D) and DR (Digital Radiography, 2D) were used to identify crack morphology in the bolt before destructive analysis in an M1 hot cell. We obtained defect images while rotating the bolt 360° at a given height. And then repeated the process while increasing height by 0.1mm until no crack was detected. The CT scan showed preferential crack growth at 3 OC in BFBs 14 and 15. The failure mechanism of Kori 1 BFBs is discussed in detail in terms of baffle structure and displacement caused by neutron irradiation and temperature.

Effect of Cold Working on Stress Corrosion Cracking Behavior of 316L Stainless Steel

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316L stainless steel is widely used in nuclear power plants as primary water coolant pipes and other structural materials due to superior corrosion resistance. In many cases, cold working by swaging is applied during manufacturing process to increase strength of material and so on. For example, in the manufacturing process of pressurizer heater, swaging is applied to 316L stainless steel sheath to make better contact in between inner heating components and outer sheath. However, cold working is known as detrimental factor to decrease stress corrosion cracking (SCC) resistance.

In this study, the effect of cold working by swaging of 316L sheath on SCC behavior is investigated. For comparison, some samples were heat treated at 1045 C for 20 min in vacuum environment. SSRT (Slow Strain Rate Tensile) tests were conducted at 360 C and 20 MPa in primary water condition of nuclear power plant. Test results show that additional heat treatment could cause increase in SCC resistance as a factor of 5. Fracture surface and crack mode of SSRT tested specimens will also be investigated.

Influence of exposed length on the corrosion fatigue of stainless steel pipes: A case study on scale-based systematic error in standardized experiments

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The modern scientific community expects a large random error from fatigue tests, particularly when combined with the influence of a corrosive environment. The main factors in corrosion fatigue are well known, consisting mainly of loading conditions and environmental variables. In this study, we propose that part of the supposed large random error may be in fact due to systematic error and demonstrate the influence of specimen gage length (exposed area) as an example case study. For a variety of strain amplitudes and rates, environmental fatigue factors ($F_{en}=N_f/N_{ref}$) for hollow pipes made of 316L austenitic stainless steel carrying deoxygenated high temperature water at 300°C and 150 bar were calculated for gage lengths from 2-3.4d, where d is the inner diameter of the specimen, using solid cylindrical bar specimens in air as reference tests. Using a minimum of three low cycle fatigue tests per condition, we demonstrated the influence of gage length on the expected fatigue life. In the reference tests in air, the fatigue life decreased with increasing specimen gage length, which was expected due to an increasing number of candidate sites leading to easier fatigue crack initiation. This effect was more pronounced at low strain amplitude with slower crack initiation. In high temperature water environment, the fatigue life was almost constant with respect to specimen gage length for both different strain amplitudes and strain rates, the effect of the environment presumably dominating over the effect of the gage length due to faster crack initiation at both amplitudes. Combining the results in air and high temperature water, it became clear that the Fen factor depended on the specimen gage length due to the fact that the reference tests show a different trend than the tests in water environment. This resulted in a potential underestimation of the Fen factor when longer specimens were used. Decreasing the strain rate caused a decrease in fatigue life and increase in Fen factor, which made sense as the vulnerable crack surfaces remain open and exposed to the water environment for longer. It was established that while the influence of gage length on corrosion fatigue life was weak, it could still introduce an uncertainty of 15-55% on fatigue life within the confines of ASTM and ISO standards.

Electrochemical Crevice Mouth: Determination of the Boundary Between Bulk and Crevice Environments within Crevice of Stainless Steels in High Temperature Water

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Abstract

Inside the crevice structure represented by Stress Corrosion Crack of stainless steels in oxygenated high temperature water, impurities are concentrated and acidic corrosive environment is formed by differential oxidation cell. Up to a certain distance from the crevice mouth, dissolved oxygen (DO) is supplied by convection and diffusion from the bulk water, creating an environment equivalent to that of the bulk, while at greater distances, depletion of DO results in a crevice environment. However, it is not clear at which location inside the crevice the boundary between the bulk and the crevice environment (Electrochemical Crevice Mouth: ECM) is formed, as there is no experimentally determinable definition of the ECM itself. Location and time shift behavior of ECM is important for understanding the growth behavior of SCC. In this study, the ECM of Type-316L crevices in high-purity water at 288°C, were experimentally determined by analyzing the surface oxides formed in the crevice. Raman spectroscopy showed that the oxide composition inside the crevice changed with increasing distance from the crevice mouth (d), and it was clearly observed that at a certain d, major surface oxide changed from γ-Fe_2O_3 to Fe_3O_4, regardless of the various factors (crevice gap, bulk DO concentration, and immersion time). The conductivity of the crevice solution also increased more than an order of magnitude at the position greater than the certain d, and we defined this as the ECM. It was confirmed that the ECM gradually shifted toward the deeper side of the crevice with time for the two DO levels studied in this experiment (0.2 and 8 ppm). Numerical simulation of this behavior suggested that the growth of the surface oxide layer increased the electrical resistance of the differential oxidation cell and decreased the amount of DO consumption as cathodic current in the crevice. This caused increase in DO flux into the crevice and a shift of ECM toward deeper side of the crevice.

Hydrogen uptake kinetics of cathodic polarised metals in aqueous electrolytes

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There is a pressing need to quantify hydrogen absorption in cathodic polarised metals to predict hydrogen embrittlement and establish equivalence with gaseous hydrogen uptake. This work combines electrochemical techniques to gain new fundamental insights into hydrogen absorption from aqueous electrolytes. The experiments are conducted on Fe and Ni, two commonly embrittled metals that serve as model materials. First, their Hydrogen Evolution Reaction (HER) surface activity is investigated using steady-state cathodic polarisation and electrochemical impedance spectroscopy (EIS). Next, hydrogen production and absorption are investigated by analysing successive electrochemical permeation transients. The effect of pH on HER and hydrogen absorption is evaluated using the reversible hydrogen electrode potential. EIS measurements show the dominance of the Volmer-Heyrovsky reaction pathway over Volmer-Tafel. Cathodic polarisation slopes are in line with the rate-determining step of Volmer (low coverage) or Heyrovsky (high coverage), with limitations due to mass transport and bubbling at high overpotentials. The evolution of the steady-state permeation current density with the overpotential can be explained by new theoretical relationships developed from the single-step reaction rate equations. The results capture the similar surface activity of Fe and Ni, linked to their comparable work function, and the more favourable absorption into Ni due to its less negative heat of solution. The novel combination of electrochemical techniques used in this work has therefore led to new insights into the dominant mechanism of HER and the dependence of HER kinetics on the pH and potential of the electrolyte, which paves the way for the quantification of hydrogen absorption and equivalent fugacity using recently developed models.

Determination of Reaction Rate Constant of Hydrogen Entry into Steels in Aqueous Solutions by Alternating Current Method

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A Devanathan-Stachurski cell [1] was used to determine reaction rate constants of hydrogen entry into steels. In this method, a thin metal sheet is sandwiched between two independent electrochemical cells of three-electrode system, and two surfaces are polarized cathodically and anodically for hydrogen entry and detection, respectively. The hydrogen penetration rate can be evaluated by measuring the oxidation current of hydrogen atoms diffused in the metal sheet at the anode side. The electrochemical impedance spectroscopy (EIS) was used with the Devanathan cell in order to investigate hydrogen penetration reaction (HPR) mechanisms because the time constants of hydrogen evolution and entry can be discriminated [2-4]. In this study, we used a complex hydrogen penetration ratio (CHPR), which is a transfer function related to hydrogen entry and diffusion in metal sheet. The CHPRs of carbon steel sheet immersed in aqueous solution of different pH's were measured by imposing AC current on the surface of hydrogen entry side. The reaction rate constant of hydrogen entry was determined by comparing experimental results with ones simulated by the theoretical equation of CHPR, and pH effect on hydrogen entry reaction was discussed.

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Absorption of Hydrogen into Fe Covered with Rust Layer Containing $MgCl_2$ during Atmospheric Corrosion

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Abstract

Absorption of hydrogen into Fe covered with rust layer during atmospheric corrosion was investigated. Fe plates covered with rust layer containing $MgCl_2$ were prepared as specimens. The specimen was subjected to dry/wet repeat test beyond 50 cycles, and then subjected to electrochemical hydrogen absorption test under atmospheric corrosion in the air with controlled relative humidity (RH). In the case that the rust contained an $MgCl_2$ amount of 39.8 $g \cdot m^{-2}$, a hydrogen absorption rate (i_H) started to increase from an RH around 15%, steeply increased with increasing RH up to about 30%, steeply decreased up to about 35%, gradually increased up to 65% and gradually decreased up to about 92%. For the $MgCl_2$ amount between 0.514 and 39.8 $g \cdot m^{-2}$, a decrease in the amount caused a decrease in i_H in the whole RH range. The maximum i_H at an RH around 30% increased with increasing $MgCl_2$ amount in the rust layer. Besides, the RH where the maximum i_H was obtained beyond an RH of 40% increased with decreasing $MgCl_2$ amount. From theoretical relationship between RH and estimated thickness of $MgCl_2$ solution film on Fe plate without rust layer, it is found that the solution film thickness at the RH where the maximum i_H exhibited was about 0.18 mm, almost independent of $MgCl_2$ amount. In addition, a thickness of the rust layer was almost 0.18 mm for an $MgCl_2$ amount between 5.14 and 39.8 $g \cdot m^{-2}$. The trend of i_H depending on $MgCl_2$ amount was tried to be explained using nature of deliquescence for $MgCl_2$.

Influence of the Heat Treatment on the Hydrogen Uptake and Embrittlement of 42CrMo4 under Gaseous Hydrogen Charging

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Abstract:

In hydrogen storage and transport applications, steels come in contact with hydrogen at various pressures and temperatures. Under high pressures and temperatures, the hydrogen uptake of steel is increased, which can cause hydrogen embrittlement and lead to operation risks. The susceptibility to hydrogen embrittlement generally increases with increasing material strength, therefore high-strength quenched and tempered steels have very little tolerance regarding their hydrogen contents. To prevent hydrogen embrittlement, it is crucial to investigate the used materials under the conditions encountered during their application. Therefore, a high-pressure high-temperature autoclave test bench for constant load tests and charging experiments, with an operation range of up to 1000 bar hydrogen pressure and 200 °C was used.

In this work, the hydrogen uptake of three different conditions (quenched, quenched and tempered at 500 °C, quenched and tempered at 700 °C) of steel 42CrMo4 have been investigated with and without a constant load of 90 % yield strength as a function of hydrogen partial pressure and temperature. In addition, the effective diffusion coefficient has been determined by electrochemical permeation measurements to simulate uptake in the form of time-dependent hydrogen profiles. Furthermore, TDS analysis was used to investigate the trapping behavior of all material conditions. Results from experiments and simulations are compared and critically discussed.

Keywords: Hydrogen uptake, High pressure, Hydrogen embrittlement, Quenched and Tempered Steel, Heat Treatment

Mechanisms of environmentally induced crack initiation and short crack growth in humid air in AA7085 T7651 and AA7449 T7651

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Abstract

New-generation 7xxx-series alloys, that have a high Zn content and Zn/Mg ratios, have been shown to be susceptible to Hydrogen-Environmental Induced Cracking (H-EIC) on exposure to humid air. Here we present the initiation and short crack behaviour of AA7085 and AA7449, when exposed to 50% humidity under a range of temperatures. In-situ, time lapse, optical imaging over large areas has enabled accurate identification of initiation and short crack behaviour and allowed the exact initiation sites to be identified and investigated with high-resolution fractographic studies. This has revealed that only minute scale corrosion reactions, involving highly localised condensed water, are necessary for initiation but not necessary for crack growth. Surface-connected microscale gas pore-clusters and/or intermetallic particles that are subjected to high stress concentration and undergo mechanical damage are identified as the preferred initiation sites. The reduction of temperature leads to significantly longer initiation times and slower crack propagation. The preferred initiation sites in the microstructure remain the essentially the same but at higher temperatures it appears that high angle grain boundaries are also highly susceptible to crack initiation.

Low-temperature embrittlement of an alloy 82 during exposure to pressurized water reactor environment

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Literature data showed that a decrease in ductile tearing resistance could be measured at low temperature (<100°C) for Alloy 82 welds after exposure to environmental conditions typical of pressurized water reactor (PWR). Hydrogen present in the environment was suspected to contribute to the embrittlement. However, many questions remain unresolved. The objective of the present work is to evaluate the influence of an exposure to the PWR water environment on the tensile mechanical properties of an alloy 82 weld and the contribution of hydrogen to the damage.

Experiments were performed on an alloy 82 weld deposited using a GMAW process. Tensile tests were carried out in simulated PWR water environment in an autoclave at 80°C and at 10^{-5} s^{-1} after pre-exposure to this medium at 300°C for 200 h. Other tests were performed without the pre-exposure step, while additional tensile tests were performed in different conditions after the pre-exposure: either in air or in gaseous (steam water) environment. For all tests, the references corresponded to tensile tests conducted in air on an as-deposited alloy, and on samples heat-treated at 300 °C for 200 h to take into account the influence of the exposure to 300°C on the mechanical properties. Results showed a decrease in the flow stress when the tensile tests were performed in the PWR environment, for both water and steam water environment, with formation of cracks in the surface layer near the fracture surface. Pre-exposure to PWR water environment did not induce a significant reduction in mechanical properties compared to cases where the specimen was not pre-exposed but was submitted to tensile tests in PWR water environment. Analyses using a scanning kelvin probe force microscope were also carried out on samples after pre-exposure to the simulated PWR water environment. The results were helpful to clarify the influence of the pre-exposure period on the mechanical properties of the weld.

Development of an Experimental Approach to Study the Synergy and Damage Mechanisms of Corrosion Fatigue in Metallic Materials

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Corrosion fatigue *Environmentally assisted cracking* *Stainless steels*

Abstract

Pure tensile cyclic loading tests are conducted in a 5 g/L NaCl solution at 25°C. Multiscale postmortem observations of the samples and in-situ electrochemical tracking have led to the following conclusions. First, localized corrosion is enhanced by cyclic loading. The early stage of crack growth is strongly reliant on corrosion. Both material dissolution and applied stresses contribute to short fatigue crack propagation. As the crack is growing, the impact of dissolution is decreasing. Finally, the fatigue crack growth rate becomes mainly controlled by applied cyclic stresses. Considering the above, an accelerated corrosion fatigue testing method is proposed to estimate the fatigue limit of the material based on the free potential tracking during the test. The corrosion fatigue crack initiation and propagation parameters were identified by in-situ electrochemical measurements, and an analytical model to calculate corrosion fatigue life is proposed. The interaction with the microstructure of different stainless steels is studied. The role of hydrogen introduced during fatigue corrosion processes is still questioned.

Hydrogen Effects on the Fatigue Crack Growth and Fracture Toughness of a Ti Alloy

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Titanium alloys are more appealing than ferrous alloys in the world of design for critical components because of their outstanding specific tensile properties. Especially alpha+beta titanium alloys in annealed condition offer a good balance of strength and ductility.

The effects of hydrogen on the mechanical performance of titanium alloys are limited in the technical literature. Utilizing mechanical testing data measured in high pressure hydrogen gas is critical for predicting the life and integrity of components operating in hydrogen gas deploying tools such as fitness for service analyses. Critical inputs for these analyses are fatigue crack growth rate, fracture toughness, and yield stress. This work focused on measuring the fatigue crack growth rates per ASTM E647 of a novel annealed α-β Ti alloy (Ti-6Al-2Sn-4Zr-6Mo) in an H2 environment at ambient temperature. After region II of the fatigue crack growth rate curve, the crack growth rate (da/dN) was independent of cyclic crack driving force (ΔK). This behaviour is uncommon for a typical fatigue crack growth rate in inert environment, suggesting that hydrogen could have played a role. Further fracture toughness testing as per ASTM E399 yielded plane-strain fracture toughness (KIC) that coincided with the onset of the independent fatigue crack growth rates. Two different crack opening displacement rates were used during the fracture toughness tests to ensure a lower-bound fracture toughness value was measured. Test results will be showed along with fracture surface analyses to make a direct correlation between properties and fracture surface appearance. Especially the propagation area independent of applied stress seems to have a distinctive morphology, most likely related to the hydride formation at ambient temperature.

Influence of surface modification by shot peening on the hydrogen embrittlement behaviour of tempered martensitic steels

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In recent years with continuously increasing energy demands, hydrogen appears to be a promising clean energy carrier to substitute fossil fuels. However, exposure of high-strength steels to hydrogen-containing environments can have a detrimental influence on their performance due to the elevated susceptibility to hydrogen embrittlement (HE). Modification of the steel with surface treatments is one of the possible strategies to improve the mechanical behaviour of the steel and simultaneously increase resistance to HE. Shot peening (SP) introduces compressive residual stresses to the material as well as the formation of hydrogen trapping sites in the deformed layer. Although, SP is a well-known and utilized method, there is scarce knowledge about its influence in terms of HE, especially in the area of tempered martensitic steels.

In this study, the effect of SP treatment on the HE susceptibility of two high-strength martensitic steels has been investigated. Hydrogen trapping behaviour and diffusion were investigated using an Electrochemical Permeation Test and Thermal Desorption Spectroscopy (TDS). Slow Strain Rate Tests (SSRT) of electrochemically charged steels were performed to elucidate mechanical performance after SP in a hydrogen environment. The changes in the microstructure and fracture surface morphology were observed using Scanning Electron Microscopy (SEM) and Electron Backscatter Diffraction (EBSD).

SP-induced trapping sites in the plastically deformed layer reduced the mobility of hydrogen, resulting in a decreased effective diffusion coefficient. TDS analysis indicated a higher uptake of hydrogen and a low-temperature peak for both SP alloys. SSRT tests exhibited enhanced mechanical performance of the SP specimens exposed to hydrogen compared to the specimens in base condition.

Development of a hybrid high-entropy alloy – steel to mitigate hydrogen embrittlement

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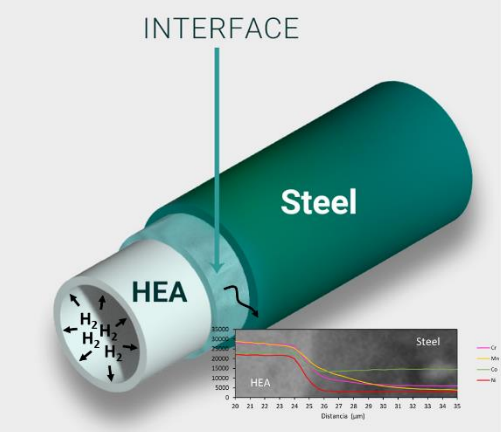
To move towards a future where hydrogen can be efficiently used as an energy carrier across countless industrial sectors, it is necessary to design and optimise materials to withstand high hydrogen pressures. Indeed, while hydrogen exposure drastically reduces the mechanical properties of traditional steels, some new metals, such as high-entropy alloys (HEAs), have recently demonstrated excellent performance in hydrogen-rich environments. However, the production of HEA-only components is not economically viable for extensive applications such as hydrogen transport and storage. That is why the development of multilayer structures - coating steel pipelines with HEAs - is becoming a promising option for the production of hydrogen-resistant components, allowing a reduction in weight, cost and carbon footprint. Therefore, this work aims to study the hydrogen embrittlement and diffusion behaviour of a hybrid HEA-steel material manufactured through near solidus forming (NSF). To do so, the mechanical behaviour of the interface was evaluated through tensile testing on hydrogen pre-charged samples. Furthermore, its effectiveness in acting as a barrier to hydrogen diffusion was assessed by means of hydrogen gaseous permeation and thermal desorption analysis (TDS). To gain a better understanding of the physical-chemical nature of the HEA-steel interface and its hydrogen trapping capabilities, a comprehensive characterisation of the joint was conducted through SEM, XRD and EBSD. Preliminary results suggest that the HEA-steel interface can effectively impede hydrogen diffusion without compromising the mechanical integrity of the component. Thus, the present work provides a cost-effective pathway for designing hydrogen-resistant metallic alloys.



Improved hydrogen resistance for high-strength fastener steels

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Keywords grain boundary strengthening, beneficial hydrogen trapping, titanium, vanadium, carbides

Abstract

This work focusses on the hydrogen embrittlement (HE) of high-strength, low-alloyed steels for the particular application of fasteners. The aim is to improve the HE resistance of quenched and tempered steels by targeting the specific hydrogen assisted fracture mechanisms. Intergranular and quasi-cleavage fracture will be counteracted by grain boundary engineering and beneficial hydrogen trapping by alloy design. Quantities of boron are added to improve grain boundary strength by segregation. However, the potential formation of boron nitrides might hinder this segregation. Therefore, additional titanium is added, as this element has a higher affinity towards nitrogen to form titanium nitrides. Furthermore, titanium also enables the formation of precipitates, i.e. carbides, that act as beneficial hydrogen traps. The intentional addition of precipitates to lower the amount of diffusible lattice hydrogen is a well-established approach. Finally, supplementary vanadium is added to provide vanadium carbides which act as additional traps. This alloying strategy will be applied on structural steel in a step-wise approach. A thorough microstructural analyses will be performed, combined with thermal desorption spectroscopy, melt extraction, and mechanical tests. The fracture surface will be investigated to elucidate the role of hydrogen upon fracturing. As such, a contribution to the development of H-resistant advanced high-strength steels is aimed for.

Effect of plastic deformation on electrochemical behavior of 316L manufactured by CMT-WAAM – Comparison with conventional 316L

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Wire and Arc Additive Manufacturing (WAAM) is extensively studied for its rapid deposition rates, cost-effectiveness, and moderate precision in constructing complex structures. However, like other additive manufacturing processes, WAAM yields a highly heterogeneous microstructure. In comparison with conventional manufacturing methods, 316L WAAM exhibits a heterogeneous microstructure. Unlike equiaxed austenitic grains, 316L WAAM displays an anisotropic grain morphology and a periodic δ-ferrite morphology associated with fusion lines [1], [2]. Recent research indicates that this multilayered structure lead to a reduction in ductility and an increase in tensile strength [3]. Regarding corrosion resistance, 316L WAAM demonstrates a correlation between pit potential and the observed plane, with a notable localization effect observed for pit formation along fusion lines created during the additive manufacturing process[4]. The 316L material is recognized to undergo a three-stage work hardening phenomenon, which leads to a non-linear evolution of dislocation densities and structures in response to the applied plastic strain[5], [6]. However, the effect of plastic deformation on corrosion sensitivity has not yet been developed.

This study investigates the effect of plastic strain on 316L SS corrosion resistance following the three-stage work hardening behaviour. To do that, wrought and WAAM-processed 316L specimens were first deformed at 4 plastic strain levels and were then subjected to corrosion tests (polarization curves, electrochemical impedance spectroscopy) and followed by surface observations.

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Hydrogen embrittlement re-understood: unravelling the role of hydrogen on plasticity

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Hydrogen is detrimental to the mechanical properties of a wide variety of pure metals and alloys, causing them to break in a brittle manner. However, evidence suggests that several metal-hydrogen systems still exhibit some degree of accumulated plasticity before fracture, indicating the non-negligible role of dislocation activity in final grain boundary separation. Based on this observation, recent explanations for hydrogen-assisted fractures consider a synergistic interaction between hydrogen-induced modifications affecting both plasticity and cohesive strength. Nevertheless, assessments of hydrogen effects on plasticity mechanisms have typically relied on TEM, offering a very localised measurement sensitive to microstructure heterogeneities. Therefore, the objective of this work is to provide insights into the effects of hydrogen on deformation behaviour over large scales, employing a novel approach. The texture that develops in a material after straining is explicitly linked to the active deformation process at the microscale. Consequently, we studied the influence of hydrogen on the crystallographic texture evolution after the deformation of hydrogen-charged and hydrogen-free nickel specimens. EBSD and XRD texture measurements reveal subtle differences in deformation texture between uncharged and hydrogen-charged samples, suggesting that hydrogen does not significantly impact grain-scale deformation behaviour at strains pertinent to hydrogen-assisted fractures. This contradicts current evidence regarding hydrogen-induced modifications of slip behaviour. To validate our experimental results, polycrystal plasticity simulations with different linearisation approaches - the number of slip systems active during deformation - are being conducted. The novel findings from this work enhance our understanding of the microscale processes responsible for hydrogen-induced degradation, a prerequisite for developing mitigation strategies and predictive models to address this engineering challenge.

Sensitivity of high strength steel bolts to hydrogen embrittlement under cathodic protection – influence of grade and process

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Rolling process to manufacture bolt threads is largely recognised as beneficial for the fatigue resistance of the component. A notable paradox concerns the use of rolled threads for subsea bolts under cathodic protection, emphasizing the challenges arising from the high local surface hardness on rolled threads, hydrogen trapping in the plastic zone, and the complex stress distribution around the thread root. The assumption that the rolling step might hinder the development of optimal resistance to hydrogen stress cracking (HSC) under service conditions[1] contrasts with the practices in subsea bolting and require a more careful exploration. From a pragmatic standpoint, both cut threads and rolled threads can be made for the same steel and bolting geometry. However, the advantages of rolling, particularly in mass production, are evident in terms of cost efficiency and reduced production time. Restricting the fabrication process solely to cut threads would, at least temporarily, impact the cost of subsea structures.

The aim of the study was to compare HSC risks for both rolled and cut threads of various steels grades compatible or not with subsea specifications. The experimental procedure was mainly conducted using incremental step load tests inspired from ASTM F1624 standard. The influence of stress relief heat treatment on the sensitivity of rolled bolts to HSC was also explored. The thread root area was inspected in terms of microstructure and micro-hardness to provide comprehensive insights, together with inspection of fracture surfaces. Complementary results were obtained on more conventional notch specimens, largely used in laboratories to investigate HSC. Higher grades were investigated to determine the limit of use of high strength steels (up to grade 12.9) under subsea conditions. For grades within the specifications of subsea applications, no deleterious impact from rolling was observed on the resistance to HSC, even a slight improvement compared to conventional machining. This behaviour was seen to be evident with and without a post threading stress relief heat treatment specified in API 20E.

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Effect of pre-strain on critical conditions for HIDC and crack nucleation characteristic of DP1180 steel

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Abstract: Hydrogen-induced delayed cracking (HIDC) represents a significant threat to the dependable performance of automotive steel. In this study, dynamic hydrogen charging constant load tensile tests were employed to measure the critical conditions for HIDC. The threshold stress values were obtained through the relationship between applied stress and fracture time, as illustrated in Fig. 1a. The assessment of the safe service area was determined by observing whether fracture occurs in the specimens within the specified time of 200 h, as shown in Fig. 1b. The objective of this work is to measure the specific critical conditions for HIDC of DP1180 steel plate [1] and establish the relationship between pre-strain, threshold stress, and critical hydrogen concentration, as shown in Fig. 1c. Additionally, the critical conditions for HIDC of another QP1180 steel plate [2] were also measured, and these findings provide valuable references for the safety assessment of high-strength automotive steels in hydrogen-exposed environments.

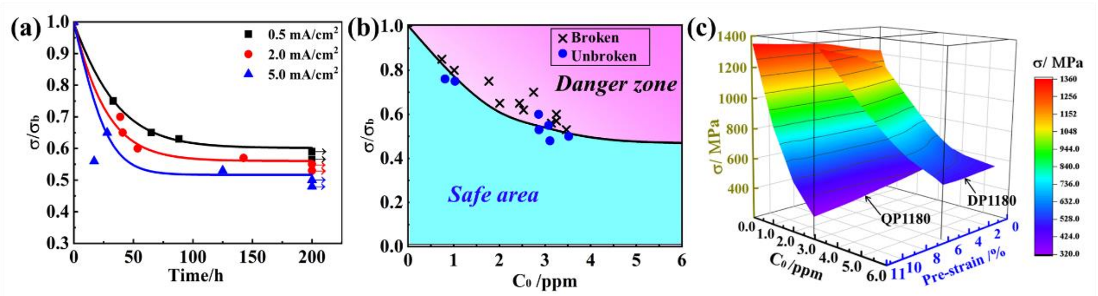

Fig. 1 (a) Relationship between applied stress and fracture time. (b) Relationship between applied stress and hydrogen concentration of the broken and unbroken specimens. (c) Relationship between the pre-strain, threshold stress, and critical hydrogen concentration.

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Corrosion behaviour under mechanical stress of austenitic stainless steel welded joints in chloride containing media

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Austenitic stainless steels (ASS) welded joints can be susceptible to stress corrosion cracking (SCC) in specific conditions [1]. However, a welded joint is a complex zone with microstructural, chemical, and mechanical gradients which can influence its SCC susceptibility. The surface finish (as weld geometry, mechanical polishing and pickling) also plays a role in this failure since the thermal oxides formed during welding, depending on the oxygen content and temperature, are less protective. To predict the SCC behavior of welded joints, it is therefore crucial to determine the conditions for which issues can be observed and to better understand the SCC mechanisms affecting ASS welded joints.

Welded zones (WZ) of two ASS, 304L and 316L, were studied. Two plates of the same ASS were welded by means of the Gas Tungsten Arc Welding (TIG) technique using a filler metal wire (W19 9L and W19 12 3L for 304L and 316L plates, respectively) varying the heat input (high and low) and the oxygen contamination in the backing gas (<100 ppm or 10 000 ppm). The microstructure and mechanical properties of the WZ as well as the thermal oxides formed were characterized. Slow strain rate tests (SSRT) were performed in 1 M NaCl, pH 4 and 60 °C solution with a strain rate of 10^{-5} s^{-1}. Specimens of different materials, weld conditions, and surface finish were tested. The mechanical properties in air and in the corrosive media were compared. Specimens fractured surfaces were analyzed to identify the failure mechanisms.

This work permitted the evaluation of the influence of different parameters (microstructural, chemical, mechanical and surface finish) on the SCC susceptibility of ASS welded joints.

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Study on hydrogen embrittlement sensitivity behavior and mechanism of high entropy metal materials

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Abstract

The issue of hydrogen-induced cracking in metallic materials has persistently afflicted the domain of engineering, exerting a substantial impact on equipment service life and safety. Throughout the years, scholarly efforts have been dedicated to investigating the mechanisms underlying hydrogen embrittlement. High-entropy metal alloys, distinguished by unique design paradigms and developmental attributes, have emerged as a result. These alloys exhibit exceptional material properties, including elevated hardness, superior strength, heightened thermal resistance, corrosion resistance, and more, surpassing those found in conventional metallic materials. Anticipated applications span across aerospace, nuclear power, oceanic exploration, shipbuilding, and other industrial sectors. In the present study, diverse analytical and characterizational methodologies were employed to observe the failure behavior and mechanisms inherent in several high-entropy metal alloys subjected to a hydrogen-laden environment. The findings elucidate that, relative to conventional alloys, high-entropy alloys manifest distinct characteristics concerning hydrogen cracking behavior and mechanisms. Beyond the established hydrogen-induced cracking mechanism, hydrogen-induced twinning has been identified within high-entropy alloys. This revelation not only contributes novel insights but also furnishes a conceptual foundation for the design of innovative alloys engineered to resist hydrogen embrittlement.

Controlled hydrogen-assisted pre-cracking to determine the fracture toughness of high-strength steels

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Abstract

The controlled initiation of observable cracks is critical in fracture mechanics studies. Typically, pre-notched specimens are employed, and fatigue-induced cracks occur at the notch root. In the specific case of circumferentially notched tensile (CNT) specimens, fatigue cracks originate from cyclic bending. Subsequently, the fatigued pre-cracked specimen undergoes tensile fracturing, from which fracture toughness (K_{Ic}) is determined based on the crack size and the applied stress at fracture. However, a significant portion of fatigue cracks initiated in this manner exhibits non-uniform radial lengths, resulting in eccentricity relative to the center of the fracture surface. Thus, accounting for both bending and tensile stresses is essential, thereby complicating fracture mechanics testing methodologies.

This study showcases the methodological approach for inducing hydrogen-assisted crack formation in CNT samples, resulting in the creation of a uniformly circumferential crack with a ligament concentric to the fracture surface. Consequently, critical stress intensity measurements can be obtained under both hydrogen-influenced (K_{Ic}^{H}) and hydrogen-free conditions (K_{Ic}). As expected, the investigation reveals a decline in K_{Ic}^{H} with prolonged hydrogen charging duration, correlating with increased absorbed hydrogen quantities. In conclusion, the development of controlled hydrogen-assisted crack initiation presents a promising avenue for advancing fracture mechanics research under both hydrogen-influenced and hydrogen-free conditions, providing a viable alternative to traditional fatigue-induced crack initiation methods.

Mitigation of hydrogen embrittlement in high-strength steel via hydrogen traps design: Progress and Prospects

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Under the background of carbon peaking and carbon neutralization, there is an increasing demand for advanced hydrogen embrittlement (HE) resistant high strength steels and novel mitigation methods. Among the proposed approaches, deep hydrogen trap design is a promising method that enable synergistically improve the HE resistance and strength/ductility. This report briefly reviews the discovery and recognition of hydrogen traps in steels, introduces the new methods in mapping hydrogen traps in metals, and summarizes the mainstream ideas of hydrogen trap regulation in steel. Furthermore, taking the HE resistant pipeline steels and ultra-high strength hot stamping steels as examples, the new progresses in the design and fabrication of second phases-induced deep hydrogen traps, such as inclusions and precipitates are described in detail. Finally, based on the above contents, the future research directions of deep hydrogen trap design in high-strength steels are prospected.

Effect of hydrogen charging on mechanical behaviour of Fe-Ni-Al alloys

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Fe-rich Fe-Ni-Al alloys consisting of bcc Fe_{ss} matrix and cubic NiAl precipitates are being increasingly recognized as a material system for important technological applications. Despite extensive studies on the Fe-Ni-Al system, little attention has been paid to describe the mechanical behaviour of the Fe-Ni-Al alloys in a hydrogen medium. In general, hydrogen diffuses and accumulates in metallic materials, influencing their properties, microstructure, and phase equilibrium.

The current study aims to investigate hydrogen influence on the microstructure and mechanical properties of Fe-Ni-Al alloys. The study seeks to address the following research question: What is the hydrogen influence on mechanical properties and fracture depending on the intensity of electrochemical hydrogen charging and alloy composition. The applied methodology comprises the following major stages: alloy fabrication using a vacuum induction melting with subsequent heat treatment, characterisation of alloy microstructure, cathodic hydrogenation in an electrochemical cell and determination of mechanical properties of the uncharged and treated alloy. The microstructural analysis includes employment of light and scanning electron microscopes, as well as an EDX detector and an X-ray diffractometer, while different charging modes were used to achieve the wide range of hydrogenation intensity.

Thus, the current project contributes to the growing area of studies on metallic materials characterisation by conducting fundamental research on the material properties of Fe-Ni-Al alloys subjected to electrochemical hydrogen charging.

Diffusion of Hydrogen in roll bonded clad plates

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Abstract:

The energy transition in Europe from fossil fuels to hydrogen will need tremendous storage and transport capacities for high-pressure hydrogen gas. Storage and transportation infrastructure is normally made of carbon steels, which are susceptible to hydrogen embrittlement. Elevated pressures demand either higher wall thickness or higher strength of the used carbon steels. With an increasing strength, the susceptibility to hydrogen embrittlement is increasing as well. Austenitic stainless steels are less susceptible to hydrogen embrittlement, in addition, they show a significantly lower hydrogen diffusion rate in comparison to carbon steels. Therefore, the use of austenitic stainless steel cladding is one way of increasing the service lifetime of storage facilities, especially if high-strength carbon steels are used.

Different carbon and austenitic stainless steels have been investigated regarding their hydrogen diffusion coefficients using electrochemical permeation testing in a Devanathan-Stachursky cell. The diffusion coefficients determined for bcc materials are between 3 and 5 orders of magnitude higher than those for fcc materials. These effective diffusion coefficients have been used to calculate hydrogen concentration profiles according to second Fick's Law as a function of time. During roll bonding several elements like carbon can diffuse from carbon steel to austenitic stainless steel cladding. Other elements like chromium and nickel might diffuse from fcc to bcc base metal. The influence of the resulting interface has been investigated using high resolution characterization methods. The results from experiments and numerical simulation are presented and critically discussed.

Keywords:

Hydrogen diffusion, Hydrogen embrittlement, Clad plate, Austenitic stainless steel, Carbon steel

Hydrogen diffusion and trapping in additively manufactured 316L stainless steel

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Additive manufacturing (AM) has been proposed as a strategy to produce 316L stainless steel components for the hydrogen economy. While it is well established that conventionally manufactured (CM) 316L stainless steel typically exhibits good hydrogen compatibility, there is significant interest in studying hydrogen-microstructure interactions in AM 316L to assess whether similar resilience to hydrogen embrittlement can be expected. Furthermore, dedicated studies examining the influence of post-build processing on hydrogen performance of AM 316L are limited. We address these knowledge gaps by assessing the effect of post-build processing on hydrogen diffusion (between 22 and 400ºC) and trapping of AM 316L. Thermal desorption spectroscopy (TDS) and finite element simulations were conducted on as-built (AB), annealed (ANN) and hot isostatic pressed (HIP) AM 316L samples charged with hydrogen. Results were compared to companion testing of CM 316L. Comprehensive microstructural characterisation through SEM, EBSD and XRD, including porosity and dislocation density analysis, was also conducted. Hydrogen trapping of the various AM conditions is discussed in the context of observed microstructure. Overall, the similar hydrogen contents and diffusion coefficients of CM and AB 316L revealed negligible influence of building direction or the unique dislocation and grain structure of AB 316L on hydrogen trapping. Conversely, ANN and HIP samples had reduced hydrogen uptake and increased hydrogen diffusivity, attributed to the annihilation of these as-built grain and dislocation structures. These results suggest that AM 316L can be post-processed to exhibit similar or improved resistance to hydrogen embrittlement relative to CM 316L.

Precipitation Strengthening and Hydrogen Embrittlement of High Strength Martensitic Stainless Steel

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In this research, the martensitic precipitation hardening stainless steels (17-4PH stainless steels) with different structures are investigated. High-density Cu-rich precipitates with different crystal structure were introduced by heat treatment. The crystal structure transformation process and strengthening mechanism of Cu-rich precipitates during heat treatment are explored by high-resolution transmission electron microscopy (HRTEM) and atomic probe chromatography (APT). It was found that Cu-rich precipitates with B2 structure are mainly formed in 17-4PH stainless steel after aging for 0.5 hours. After 1 or 4 hours of aging, the crystal structure transforms into BCC or 9R-Cu, repectively. When aged for 20 hours, it was found that the crystal structure of the Cu-rich precipitate is FCC. The dislocation-precipitation interaction changes from a cutting to a looping mechanism. The hydrogen trapping abilities of the four phases of Cu-rich precipitates (namely, B2, BCC, 9R, FCC) in martensitic steels are evaluated. It is found that the 9R-Cu/α-Fe matrix interface offers the deepest H-traps and best H-trapping capacity. First-principles calculations corroborate the experimental results and further reveal the tetrahedral sites on the 9R-Cu precipitate/matrix interface as favorable H-trapping sites. The findings unravel the perplexing H-trapping behaviours of Cu-rich precipitates, and propose a method to improve their hydrogen capture ability by regulating the precipitate structure. The HE sensitivity of 17-4PH stainless steel reduced from 89.6% to 40.1%, while the ultimate tensile strength of the steel changed a little.

Effects of multiple precipitates on resistance to hydrogen embrittlement in high-strength steel

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Multi-element microalloying is an effective approach to reduce the susceptibility of high-strength steel to hydrogen embrittlement (HE). By the multi-microalloying of 1.04 wt% Cr and 0.14 wt% V to high-strength spring steel, the rate of plastic loss after hydrogen pre-charging is significantly reduced, thus enhancing its resistance to HE. Through the regulation of heat treatment temperature, the formation of (Cr, V)C precipitates in the sample has been successfully achieved. The hydrogen trapping behavior of (Cr, V)C precipitates was analyzed in detail using scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM). V exists in the form of dispersed, small VC particles within the matrix, acting as weak hydrogen trapping sites. On the other hand, the addition of Cr results in the formation of (Cr, V)C composite nano-precipitates within the matrix. These composite nano-precipitates exhibit strong, irreversible hydrogen trapping capability and serve as effective hydrogen trapping agents. The essence of these precipitates lies in the semi-coherent misfit dislocations between (Cr, V)C and α-Fe. The high resistance to HE of the material was validated through slow strain rate tensile testing, with an improvement rate of 48.3%. This research provides experimental guidance for the design of high-strength hydrogen-resistant steels.

The effect of precipitate size on the hydrogen-induced stress cracking resistance of FeNi-based alloy A286

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The presence of hydrogen poses the risk of hydrogen-induced stress cracking (HISC) to pressurized or externally loaded components. Hydrogen can originate either from gaseous or liquid state energy carriers or from cathodic protection. In hydrogen exposed applications where high-strength and corrosion resistance are mandatory, the precipitation-hardened austenitic alloy A286 (SS66286) is a promising candidate.

The aim of this work is to evaluate the influence of precipitate size in alloy A286 on its HISC resistance under cathodic charging conditions. Hence, HISC testing by slow strain rate tests according to NACE TM0198 – App. C has been conducted for three different precipitation conditions: specified heat treatment according to ASTM A453/A453M (minimum yield strength of 105 ksi), under- and overaged state. Besides a basic mechanical characterization including macroscopic hardness, tensile and Charpy impact testing, the microstructure was investigated by high-resolution microscopy techniques such as atom probe tomography (APT). A particular focus was placed on the characterization of the morphology and chemical composition of the precipitates responsible for strengthening of the alloy, i.e., the gamma prime γ´ ($\sim \mathrm{Ni_3Ti}$) phase. Besides macroscopic HISC testing and nano-scale APT analysis, the characterization of the alloy was complemented by scanning electron microscopy (SEM).

Results show remarkably high HISC resistance of alloy A286 and basically confirm its suitability for use in hydrogen environments with external loads. The effects of under- and overaging in comparison to the specified heat treatment are discussed.

Optimising measurement of atmospheric stress corrosion crack growth rates of 316L stainless steel

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Atmospheric induced stress corrosion cracking (ASCC) is a potential concern for the integrity of containment materials (e.g. 304L and 316L Stainless Steel) for Higher Activity Waste (HAW)[1] at interim overground storage facilities in the UK, designed to last for many decades[2]. Although initiation of ASCC from corrosion pits formed from deposition of marine aerosols in the storage facilities is envisaged to be of low probability, there is a desire to delineate the exposure conditions for which crack development may ensue and, in that scenario, generate crack growth rate data to assess the likelihood of through-wall penetration during the storage and disposal period.

The growth rate of cracks developed from pits can be determined approximately by removal of ASCC test specimens at different time intervals and estimating average crack growth rates based on surface crack length measurement. However, there is an inherent uncertainty in the time to crack initiation. In situ monitoring by potential drop techniques provides a more incisive measurement of the time evolution of the crack size. However, a previous study[3] using direct current potential drop (DCPD) resulted in the probes located in the droplets disturbing the corrosion process. One of the novel features of the present research is the use of an advanced alternating current potential drop (ACPD) system with current focus technique for crack size measurement.

Test results supported by COMSOL modelling will be presented that compare ACPD and DCPD sensitivity, with a revised probe arrangement. The estimated crack growth rate data will be correlated with post-mortem optical and X-ray Computed Tomography measurements of crack size on specimens exposed for different periods. Conclusions will then be drawn about the efficacy of different techniques for crack size measurement under atmospheric exposure conditions and what this implies in assessing durability of HAW stainless steel containers.

[1] Higher Activity Waste (HAW): comprises High Level Waste (HLW), Intermediate Level Waste (ILW), and a small fraction of Low Level Waste (LLW).

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Understanding Welding-induced SCC of Type 316L Stainless Steel in HCl-containing Environment

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Nuclear products are stored in Type 316L stainless steel cans using a nested design with a closure-weld at the outer can. Previous research has identified that type 316L stainless steel can show localised corrosion (pitting) and stress corrosion cracking (SCC) with exposure to HCl vapour in high relative humidity environments and large applied stresses and strains using U-Bend samples. The overarching goal of our work here is to provide a fundamental understanding and identify threshold conditions for SCC to initiate in type 316L when exposed to HCl-containing liquids and vapours at elevated temperature. Potentiodynamic-polarisation (PDP) and electrochemical impedance spectroscopy (EIS) tests were conducted on ASTM G58 welded samples at various locations containing residual stresses. ASTM G58 plates were assessed with XRD to determine the magnitude of residual stress present, with these locations then probed with a small electrochemical pen (ec-pen) to understand the effect of residual stress on localised corrosion. The idea here is to produce local initiation points at the surface for SCC to nucleate. A setup was designed to simulate the HCl-containing vapour environment using type 316L samples at temperatures in excess of 100°C. The oxygen concentration was controlled by purging with nitrogen gas, with the sample surface investigated and characterised after HCl exposure. The sample showed a discoloured surface with difficult to remove surface layers.

Four-point bending test to evaluate sulphide stress cracking using sodium thiosulfate

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Abstract

Sulfide Stress Corrosion (SSC) is a complex environmental assisted cracking phenomenon and it causes trench formation due to localised corrosion perpendicular to the load axis under external loading. Due to the high toxicity and flammable effect of H_2S gas, it requires sophisticated instruments and dedicated laboratory facility to study the SSC. Thus a few specialised laboratories around the world can handle the H_2S and perform SSC studies safely. As a relatively safe alternative, in 1993, Tsujikawa et al proposed to use thiosulphate ($S_2O_3^{2-}$) for studying SSC in low alloy steel, stainless steel and corrosion resistance alloys (CRAs). Later many researchers expanded the knowledge of SSC using thiosulphate to study the fundamentals and claimed the effect of different alloys under the exposure of simulated H2S. In this study, we used the four-point bend test to evaluate SSC in thiosulfate environment with an inline monitoring of H2S production for the first time. This system was designed for atmospheric pressure, to study SSC with a leak proof flow line. Our extreme lab facility with added safety features enable to conduct the SSC experiments safely and confidently. Using this sophisticated setup, we have evaluated the SSC susceptibility for various steels and validated the $S_2O_3^{2-}$ test condition comparing to the use of H_2S gas using pit/trench morphologies. FeS was mainly identified in corrosion product using X-ray direction in both tests with H_2S gas and simulated $S_2O_3^{2-}$ test conditions.

Investigating stress corrosion cracking of ZK60 Mg alloy in a simulated physiological fluid environment

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Magnesium (Mg) and its alloys are recognized as potential temporary implant materials due to their attractive properties, such as high strength-to-weight ratio, comparable elastic modulus, biocompatibility, and non-toxic corrosion products. However, their higher rate of degradation than the rate of bone healing, severe pitting tendency in chloride-rich environments such as human body fluid, and susceptibility to stress corrosion cracking (SCC) are the possible shortcomings with Mg alloys as bioimplants. In this study, the corrosion and SCC susceptibility of a Mg-Zn-Zr alloy, ZK60, was investigated in a simulated body fluid environment (i.e., Hanks Balanced Salt Solution, HBSS). Slow strain rate tensile (SSRT) testing, followed by fractography employing scanning electron microscopy of the alloy tested in HBSS with and without the addition of glucose (1 g/L and 3 g/L), suggests that the alloy is susceptible to SCC at a strain rate of 3.1×10^{-7} s^{-1}. The electrochemical investigations on the addition of organic molecules like glucose and bovine serum albumin (BSA), identified that BSA (40 g/L) caused an acceleration, whereas the addition of glucose (1 g/L and 3 g/L) did not cause much significant influence in the degradation of ZK60 in HBSS.

Stress corrosion cracking behavior and mechanism of a high-strength corrosion-resistant rail steel

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Abstract

With the high-speed and heavy-load operation of railway transportation, as well as the complicated environment of railway laying, rail steel not only needs to withstand complex stress conditions such as extreme alternating stress, vibration, and friction, but also faces serious corrosion problems. Therefore, the stress corrosion cracking performance of rail steel requires special attention with the involvement of corrosion. In this study, slow strain rate tensile (SSRT) testing and U-bend testing with cyclic immersion corrosion tests were conducted to evaluate the Stress corrosion cracking behavior (SCC) of a new type of high-strength corrosion-resistant rail steel. Electron backscattered diffraction (EBSD) was used to investigate the crystallographic information of the material, while scanning electron microscopy (SEM) was employed to analyze the fracture morphology and crack propagation. The results indicate that the rail steel exhibited low stress corrosion sensitivity. The rapid passivation of cracks and the presence of the ferrite phase significantly reduced the crack propagation rate and enhanced the stress corrosion resistance of the rail steel.

Keywords

Rail steel; SCC

Development of low-cost, superhydrophobic coatings for solar panels

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Abstract

Solar panels can experience shading due to various factors, one of which is soiling. Soiling-induced shading can be classified into two types: (i) soft shading, caused by air pollution, and (ii) hard shading, which results from solid obstructions like dust accumulation that block the sunlight. Maintaining the cleanliness of the front glass of the solar unit is crucial to fully benefit from its properties, such as spectrum and light transmittance. However, cleaning techniques can be expensive, time-consuming, impractical or unsafe. To address this challenge, this work proposes to utilise Polydimethylsiloxane (PDMS), a fluorine-free polymer binder, to develop superhydrophobic coatings for solar panels. PDMS exhibits high chemical stability, abrasion resistance, water repellency, and adhesion to glass substrates. The addition of TiO_2/SiO_2 nanoparticles improved the mechanical properties of the coating without compromising high transparency and wettability. Similarly, heat treating the coating at 400°C for a couple of hours improves adhesion on the glass substrate. The coating system provides an innovative and low-cost solution to create superhydrophobic surfaces, which prevent dust and soil accumulation on the solar panel.

Combined in situ microscopic and spectroscopic study of stainless nature of low-alloyed Hybrid steel

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Recently, it was shown that Hybrid steel, with a concentration of about 5 wt.% of Cr, can show passive-like behaviour in Cl-containing aqueous solutions similar to 420 martensitic stainless steel with 14 wt.% of Cr *[Örnek, Cem, et al. npj Mater. Degrad. 71 (2023)].* With **ex situ** methods, it was revealed that a nanoscale passive film composed of mixed Fe-Cr oxides along with Al oxides may contribute to the stainless nature of Hybrid material. In this work, we use a combination of ***in situ*** techniques to further address the corrosion mechanism of Hybrid steel in Cl-containing environment.

Methods and Results

Standard laboratory microstructure investigation was combined with SKPFM, ***in situ*** AFM, and ***in situ*** ambient pressure XPS (AP-XPS) to characterize the Hybrid 60 steel (Ovako Sweden) and 420SS reference material. The SKPFM along with in-situ AFM allow to thoroughly characterise the native oxide forming on Hybrid 60 stainless steel and indicate the corrosion initiation points in relation to the material's oxide structure and its chemical heterogeneity. Synchrotron ***in situ*** AP-XPS helped us to follow the evolution of oxide composition in contact with electrolyte under anodic potential. The results of AP-XPS indicate that mixing of Cr and Al oxides affects dissolution kinetics of Cr oxide by stabilising the oxide layer at high potentials. When the Hybrid 60 is subjected to high anodic potentials, the chromium oxide content within the oxide layer is comparable to that of the native oxide. In contrast, the surface oxide of 420SS lacks chromium oxide under conditions similar to those mentioned.

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Electric double-layer and crystal-orientation sensitive model of corrosion damage

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Corrosion and stress corrosion cracking resistance are often life-limiting factors for pipelines and other water-facing metal components across many industries. Using stainless steel is the most common corrosion prevention method since these steels provide outstanding corrosion protection in neutral water and the absence of chlorides. A numerical model of corrosion damage is developed to address this problem. The model considers the migration of ions in the electrolyte and an EDL charging effect for the first time in a damage-prediction model. The model calibration to experimental data provided an excellent match for both pit depth kinetics and output current density. Also, the electric potential variations returned experimentally observed tendencies. The model was equipped with single-crystal mechanical properties of 316 stainless steel and further utilised to perform a statistical study of the influence of average grain size on corrosion and SCC propagation. The study considered three various grain sizes. A parametric sweep over three strains recreated the pit-to-crack transition tendency. Localised pitting and stress-enhanced dissolution are both considered for damage propagation. The grain size revealed no influence on average damage propagation. Instead, a higher variation in predicted damage could be observed for larger average grain sizes. The variation in the strength of crystallographic-driven directional dissolution was also tested to assess how different FCC metals might behave under the same activation overpotential. It was revealed that metals with lower polarisation variation to equilibrium potential ratio have a lesser tendency to develop sharp surface features inside the corrosion pit, which might lead to stress concentrations.

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Towards rational design of organic copper corrosion inhibitors: High-throughput computational evaluation of adsorption energy

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Designing environment-friendly, high-efficiency, and low-toxicity copper (Cu) corrosion inhibitors is an important topic in the field of corrosion inhibitors. The current design of organic corrosion inhibitors mainly depends on empirical trial-and-error approaches. New methods are needed to accelerate and rationalize the design of corrosion inhibitors. The possible correlation between standard adsorption Gibbs energy and inhibition efficiency provides an opportunity for the rational design of corrosion inhibitors. A high-throughput computational framework is established for automatic computation of adsorption energies of organic corrosion inhibitors. A correlation between adsorption energies and changed Cu-d band centers induced by molecular adsorption is established. Standard adsorption Gibbs energies were derived based on additional thermodynamical and solvation correction. Standard adsorption Gibbs energy cannot be directly correlated with the inhibition efficiency. While some of corrosion inhibitors show linear correlation with standard adsorption Gibbs energies and inhibition efficiencies, the rest do not due to their orientation-dependent adsorption mechanisms.

Passivation & Depassivation study of non-sensitized 316L ASS under PWR PW conditions via the polarisation technique

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Non-sensitized Austenitic Stainless Steels (ASS) exhibit a good corrosion resistance in nuclear Pressurized Water Reactor (PWR) Primary Water (PW) conditions. Nevertheless, under certain conditions, they can be susceptible to Stress Corrosion Cracking (SCC). The susceptibility to SCC, which implies the rupture of the passive film, is assumed to depend on the dissolution-repassivation kinetics. The literature contains limited results regarding the comprehension of the passivation and depassivation behavior of non-sensitized 316L ASS under PWR PW conditions.

In this context, the main objective of this study is to gain an understanding of the oxide film formation and dissolution through controlled electrochemical (EC) experiments at different potentials and temperatures. This would provide an insight into the time and frequency ranges where corresponding EC events would occur.

The experimental process, under PW conditions, involves a set of anodic potentiostatic (100, 200, 300, 400mV) and cathodic galvanostatic (-0.15µA/cm^2) polarizations to achieve the oxide film formation and dissolution, respectively. For each anodic potentiostatic experiment, the stationary current density is determined. The electric charge required to achieve this steady state is obtained by integrating the time-decreasing evolution of the current. Then, to return to the initial potential value, a constant cathodic current is applied.

The experimental findings have shown that higher anodic potential leads to a greater anodic charge due to the prolonged time required to reach the current steady state. Moreover, the cathodic charge required to return to the initial potential increases with anodic potential. An exponential-like decay of anodic current-time evolution has always been observed. On the contrary, two types of potential-time decay have been identified: exponential-like decay occurs at lower anodic polarisation, whereas a sigmoid-like decay has been observed at higher potential values. This difference in shape is likely linked to different oxide structures.

A novel approach for efficiently screening corrosion inhibitors on Mg alloys: a combination of high-throughput multi-well exposure with topographical volume loss quantification

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Efficient collection of coherent large experimental datasets presents a major bottleneck in the search for suitable alternatives for chromate-based corrosion inhibitors. Such big data is used as input for machine learning models that facilitate accelerated *in silico* exploration of the vast chemical space of potentially effective organic corrosion inhibitors. In this work, a novel high-throughput experimental method of inhibitor screening is proposed. Over 200 individual organic chemical inhibitors were tested for the AZ31 alloy. The volumetric material loss of the obtained 800 corrosion imprints was quantified by profilometric analysis and subsequently translated to corrosion inhibition efficiencies. The volumetric material loss of 29 randomly selected inhibitors, acquired by profilometric analysis, was further validated by traditional weight loss obtained by analytical balance. It has been shown that for magnesium alloys the combination of profilometric quantification with high-throughput corrosion exposure experiments significantly accelerates data acquisition by 3 factors, thus allowing for a more efficient exploration of large numbers of commercially available compounds for novel, efficient corrosion inhibitors.

The influence mechanism of Te treatment and heat treatment on the corrosion resistance of 15-5PH stainless steel

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Abstract: The effects of Te treatment and heat treatment on the localized corrosion mechanism of 15-5PH stainless steel were studied in simulated marine environment. Inclusions have good electrical conductivity in steel and are always dissolved electrochemically. Te increases the Volta potential of the composite inclusions and changes the local corrosion mechanism. Appropriate addition of Te can improve the corrosion resistance of steel. However, due to the continuous cathodic effect of Te in the inclusions and the destruction of the stability of the passive film by the dissolution of a large amount of TeO_3, excessive addition of Te will lead to the attenuation of corrosion resistance. After heat treatment, the dislocation density of the matrix of Te 15-5PH steel with a small amount of Te decreases, and the corrosion tendency decreases. Heat treatment significantly affected the potential difference between Te modified inclusions and steel matrix. The stainless steel changes from the activated to the passivation, and the corrosion resistance is improved. After heat treatment, the defect density of the steel passive film decreases. The repassivation ability of the passive film is improved by the insoluble or slowly dissolved tellurite film formed by the anodic oxidation of Te and the self-healing properties of TeO_3.

Keywords: stainless steel; Te treatment; inclusion; passive films; pitting corrosion.

Nitrogen Heterocyclic carbenes (NHC), a new class of organic molecules for the protection of metals

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The chemistry of N-heterocyclic carbenes (NHCs) is well-established in the organometallic field, owing to the remarkable reactivity of the carbon atom stabilized by the two nitrogen atoms within the aromatic ring. Additionally, NHCs exhibit high modularity, making them versatile building blocks [1]. Over the past two decades, NHCs have garnered significant interest in materials science. Notably, they play a crucial role in stabilizing nanoparticles and functionalizing noble metal surfaces for diverse applications, including sensors, molecular electronics, and microcontact imprints [2]. Despite their wide-ranging applications, there has been limited exploration of NHCs in the protection of metallic materials, particularly their interaction with oxidized surfaces.

The objective of this study is to investigate the interaction between NHCs and oxidized surfaces of different metals, exploiting their modularity to develop new inhibitors. To achieve this, we investigated the adsorption behavior of two model NHCs, generated in situ from (benz)imidazolium, on a variety of oxidized metals (Al, Ti, Fe, Cr, Mg, Zn, and Cu) using X-ray photoelectron spectroscopy (XPS). The results indicate that NHCs exhibit a strong affinity towards the oxidized metals, indicating their possible universal applicability. The XPS data show that the nature of the carbene/metal interaction is dependent on the chemical composition of the oxide layer and also the way used for the carbene generation. Additionally, corrosion tests conducted with a tailored NHC on an aluminum substrate demonstrated enhanced anticorrosion properties.

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Silicate corrosion inhibition study on common pipe materials – A comprehensive electrochemical study

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The degradation of piping and critical components due to corrosion remains a relevant issue in many industries. For cooling water systems, a frequently used solution is the addition of corrosion inhibitors to reduce the corrosion rate to an acceptable level. With the ongoing search for sustainable corrosion inhibitors, silicates show great promise as they are available, non-toxic, eco-friendly and provide excellent protection for steel components. In many existing systems, however, a mixture of materials is used and consequently should be compatible with the used corrosion inhibitor. In this study, steel, copper and zinc were subjected to a 3 wt.% NaCl environment with varying concentrations of $Na_2Si_3O_7$(SS). Here experiments were both conducted under static conditions and within a rotating cylinder electrode (RCE), which allows for a precise control of both temperature and flow speed (set to 0.5 m/s at the sample surface). To estimate the inhibition behaviour and effectiveness of silicate, potentiodynamic scans (PDS), electrochemical impedance spectroscopy (EIS) and Mott-Schottky (MS) were utilized. For copper and steel, protective layer was formed on the surface by the added silica. The zinc samples on the other hand, required a sufficient amount of silica to show some inhibition. Moreover, insufficient amounts of SS could even result in acceleration of corrosion. Further insight in the protective film formation and structure was obtained via analysis of the EIS spectra and the obtained MS curves. Here, a link was found between the improvement of the formed protective film properties (EIS/MS) and the resulting corrosion rate and film stability (PDS).

Ab Initio Study of the Stainless Steel/Passive Film Interface The Role of Alloying Elements

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In this study, we employ an ab initio computational approach to examine the interactions occurring at the interface between stainless steel (SS) and passive film, with particular attention to the influence of alloying elements on the electronic structure of the ferritic SS/Cr_2O_3 oxide interface. The aim is to elucidate the fundamental mechanisms governing the corrosion resistance of stainless steels, especially during the crucial initial passivation stages.

We conducted a comprehensive analysis of surface energetics, encompassing adhesion, segregation, and adsorption processes, to assess the impact of alloying elements on the passivation process. The investigation started with an examination of the bulk properties of Cr_2O_3 oxide when doped with various alloying elements. Subsequently, the study focused on the significant role of the inner SS/Cr_2O_3 interface, recognizing its importance in the early stages of passive film formation. The research yielded several key insights, including the intricate understanding of the electronic structure at the steel/passive film interface, highlighting the pivotal role of alloying elements in enhancing passivation effectiveness.

By exploring the interface and surface phenomena influencing stainless steel corrosion, this investigation advances our comprehension of passive film formation and stability. It highlights the critical necessity of considering both bulk and surface attributes in the alloy design process to achieve optimized corrosion resistance.

Investigation of enhanced passivity of stainless steels at the atomic scale by DFT modelling

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Inner barrier layers of passive films formed on the surface of stainless steels, mostly composed of chromium oxide, provide excellent corrosion resistance for these alloys. However, they still contain weak sites (less protective against corrosion), locally enriched in Fe instead of Cr and developing from the early stages of oxidation. Recent experimental studies have suggested that the Fe-rich weak sites could be cured by the presence of Mo in the inner barrier layers, resulting in the enhanced passivity in highly concentrated Cl-containing environments [1].

To investigate at the atomic scale the role of Mo in improving the corrosion resistance of passive films, substitution by Mo and its effects on vacancy formation were studied on (0001)-oriented anhydrous and hydrous Cr_2O_3 and Fe_2O_3 surfaces of different terminations using DFT modelling [2]. The substitution of a surface or subsurface cation by Mo is exothermic and energetically more favoured on Fe_2O_3 than on Cr_2O_3 surfaces, indicating that Mo is preferentially located in the Fe-rich zones of the Cr_2O_3 -enriched passive films. The substitutional Mo is preferentially located in the subsurface for anhydrous surfaces, but for highly hydroxylated surfaces, it is stabilized between the hydroxide and oxide layers, in agreement with the experimental observations. The presence of substitutional Mo disfavours the formation of O vacancies and favours metal vacancies, more significantly in Fe_2O_3 than in Cr_2O_3, suggesting a prevention of passivity breakdown in chloride-rich environment and a cure of the Fe-rich weak sites of passivity by Mo. Combined with the experimental data, these results provide atomistic insights on the Mo effects on enhanced passivity of stainless steels [3].

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Investigating adsorption behaviour and stability of benzothiazole derivatives for galvanised steel in NaCl solution

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In-depth investigation into adsorption behaviour of corrosion inhibitor governed by unique inhibitor features is the key premise to realising target-driven inhibitor discovery for pronounced metal protection. In this work, different adsorption behaviours induced by tuning the chemical functionality upon benzothiazole, i.e., 2-mercapto-benzothiazole (2-MBT) and 2-amino-benzothiazole (2-ABT), towards electro-galvanised steel (ZE) in NaCl were examined using both experimental and theoretical approaches. The underlying interactions of inhibitor candidates with the targeting metal, dissolved metal ions and corrosion products were determined by means of X-ray photoelectron spectroscopy, focused ion beam scanning electron microscopy and Raman Spectroscopy. It is revealed that 2-MBT initiates the precipitation upon the ZE by complexing with the released Zn^{2+} in solution, while 2-ABT promotes preferentially thin inhibitor film formation initiated by chemisorption. Density Functional Theory (DFT) calculations were performed to assess the adsorption of the two molecules on the main orientation {0001} of Zn surface at different concentrations. Both molecules adopted a parallel configuration at low concentrations as the most stable. However, at higher concentrations, they tend to form a self-assembled monolayer (SAM), oriented slightly tilted on the surface and stabilized by pi-pi stacking interactions among the SAM molecules. DFT results suggested that 2-MBT interacted strongly with the Zn surface, leading to more effective complex formation with 2-MBT. Furthermore, the adsorption stability on electro-polarised ZE surfaces indicates that 2-MBT forms a thick inhibitor layer at higher polarisation states, while 2-ABT dissociates from the surface as the surface overpotential increases. The findings of this study are anticipated to provide new knowledge and insight for rational inhibitor engineering to realise tailored corrosion inhibition properties.

Corrosion inhibition of copper by 2-mercaptobenzimidazole organic films adsorbed in an acidic chloride environment

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2-Mercaptobenzimidazole, an azole derivative compound, is often used as a corrosion inhibitor for copper and its alloys. Its protective capabilities are derived from its structure which contains a sulphur atom and two nitrogen atoms that aid in its bonding with metallic surfaces. Despite several advances in understanding the bonding mechanisms with copper, there is some ambiguity on how 2-MBI would interact with a partially oxidized surface. Moreover, the role of surface native oxides on the interfacial bonding and complex formation has not been explored. Finally, the inhibitive properties of the organic films formed under different conditions need to be scrutinized for a better understanding of the bonding configurations and their merits.

In the present work, the interfacial bonding, the layered structure, and the inhibition effects of 2-MBI organic films adsorbed on electrochemically controlled copper surfaces were investigated in acidic chloride aqueous solution using electrochemical and advanced surface analytical techniques.

The results show that bi-layered organic films are formed with a physisorbed outer layer and a chemisorbed inner layer. In the chemisorbed inner layer, 2-MBI is bonded primarily by its nitrogen atoms with metallic and oxidized copper surfaces. Sulphur atoms are also involved in the bonding when metallic copper is directly accessible to the 2-MBI molecules. The initial presence of native copper oxides promotes the formation of Cu(I)-2-MBI metal-organic complexes using cathodic reduction to dissociate the oxide. Metal-organic complexes also form upon anodic polarisation owing to Cu(I) ions generated by oxidation of the copper metal. 2-MBI effectively inhibits copper anodic dissolution in varying degrees depending on the pre-treatment used for the formation of the organic bi-layers. An enhanced protection of the copper surface is obtained by adsorbing the inhibitor on an initially oxide-free surface.

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Transient and spatial resolved modelling of passive films considering chloride-ion adsorption and injection

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Abstract:

In addition to experimental research, physical models can also contribute to check plausibility of partial processes governing passive film formation and breakdown. The model presented in this work is based on the fundamental assumptions of the well-known point defect model and its modification [1]. An extension considering the adsorption and injection of chloride-ions at the relevant interfaces and its transport process within the film was modelled. The model is applied to transiently simulate the formation and breakdown of passive films on the stainless steel AISI 316L under variation of pH, temperature, applied potential and chloride-ion content. This contribution was qualitatively verified in terms of reasonable behavior according to the literature and own electrochemical investigations.

Simulations predict the transient spatial distribution of crucial quantities within the passive film, such as vacancy-, ionic concentrations or the electrical potential, which can be referred to fundamentals of solid-state physics or published experimental work for critical discussion. The model also provides insights into the postulated film degrading processes induced by hydroxide- and chloride-ions. By simulating linear sweep voltammetry experiments with different chloride-ion contents, it can be shown, that the model captures major characteristics of the electrochemical system, especially regarding a shift of both open circuit potential and pitting potential.

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Fatigue crack initiation and growth monitoring in hollow stainless steel tubes using direct-current potential drop method in PWR environment

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Corrosion fatigue (CF) is an important material degradation mechanism that affects components in a wide range of industries where an aggressive environment is combined with mechanical loading at significant amplitude and suitable frequency. However, methods of in-situ crack initiation monitoring during the corrosion fatigue process has not been well explored. In this paper, we devise a procedure to integrate crack monitoring into corrosion fatigue experiments using a direct current potential drop (DCPD) setup on a hollow stainless steel specimen flowed through with deoxygenated and hydrogenated high temperature water containing boric acid and lithium hydroxide, as is typical in pressurized water reactor (PWR) primary coolant. An electrically isolated load cell is used to perform strain-controlled cyclic mechanical loading on hourglass-shaped 316L stainless steel specimens at 0.3% and 0.6% strain amplitude while electrical leads are fastened with conductive R-clips in order to avoid welding and subsequent weakening of the surrounding material. Using a 4-channel DCPD scheme with reference measurement on a thick section where cracks will not propagate, it was possible to observe the initiation and propagation of the crack throughout the corrosion fatigue experiment. After the full experiments, interrupted experiments were performed, stopping crack progression at a point after initiation and comparing the potential drop signal to actual crack length and geometry. Calibration of potential drop vs. crack characteristic length was performed using full and interrupted experimental data and these were compared to stress evolution during fatigue.

Inhibition of steel corrosion using imidazolium-based compounds

- Theory and Experiment

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In this contribution we investigate the corrosion inhibition of the mild steel in the 1 M HCl solution by 1-octyl-3-methylimidazolium hydrogen sulphate 1-butyl-3-methylimidazolium hydrogen sulphate, and 1-octyl-3-methylimidazolium chloride, using electrochemical, weight loss, and surface analysis methods as well as the full quantum- mechanical treatment. Polarization measurements prove that studied compounds are mixed-type inhibitors with a predominantly anodic reaction. The inhibition efficiency obtained from the polarization curves is about 80–92% for all of the 1-octyl-3-methylimidazolium salts with a concentration higher than 0.005 mol/l, while it is much lower for 1-butyl-3-methylimidazolium hydrogen sulphate. The values measured in the weight loss experiments (after seven days) are to some extent higher (reaching up to 98% efficiency). Furthermore, we have shown that the influence of the alkyl chain length on the inhibition efficiency is much larger than that of the anion type. We obtain a realistic model of a single molecule on iron surface Fe(110) by applying the Density Functional Theory calculations. We use the state-of-the-art computational approach, including the meta-GGA strongly-constrained and appropriately normed semilocal density functional to model the electronic structure properties of both free and bounded-to-surface molecules of 1-butyl-, 1-hexyl-, and 1-octyl-3-methylimidazolium bromide, chloride, and hydrogen sulphate. From the calculations we extract, the HOMO/LUMO gap, hardness, electronegativity, and charge transfer of electrons from/to molecules-in-question. It supports the experimental findings and explains the influence of the alkyl chain length and the functional group on the inhibition process.

Effect of Additive Manufacturing Parameters on 316L Mechanical and Corrosion Behavior

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Laser bed powder fusion (LBPF) has made it easier and faster to perform previously challenging complex design problems because of the freedom of design LBPF adds to additive manufacturing. Innovative design structures and intricate geometries can be formed in one processing step, unlike typical additive and other manufacturing methods where multiple steps are required. LBPF therefore reduces manufacturing costs, hastens time to market, and quickens replenishment of stock parts. To evaluate and qualify the additive manufacturing process for a wide range of applications, it is typically necessary to analyze the mechanical, microstructural, and, in some cases, corrosion behavior of the raw materials, in this case 316L stainless steel. Key effects of varying selective additive manufacturing laser printing parameters are investigated to improve speed of production and finish of parts made from 316L stainless steel, without sacrificing mechanical and corrosion properties. Selectively varying additive manufacturing parameters of laser power, hatch spacing, and laser speed for 20-micron layers, comparing to the typical 40-micron layers. Further, evaluation of metallurgical, mechanical, and electrochemical potentiodynamic (corrosion) properties are carried out. Faster scanning speeds resulted in greatly minimized defects, with similar finished product qualities, and without compromising mechanical properties. The paper will discuss in more detail the findings of along with unusual results not previously expected, encountered, or reported.

Effect of Chromium and Cobalt Contents on Type I Hot Corrosion Resistance of M (Ni, Co) CrAlY Overlay Coatings at 900^{O}C Under Na_2SO_4 Deposits

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In this research, the effect of Co and Cr contents on Type I hot corrosion resistance of MCrAlY overlay coatings at 900^{O}C under Na_2SO_4 deposits were investigated. Ni-based MCrAlY overlay coating alloys with different chemical compositions were produced via vacuum arc melting in bar form and heat-treated in 1100^{o}C for 16 hours. Optical Microscope, XRD, SEM and EDS characterization were performed after heat treatment to identify phases, observed phase fractions and chemical composition of the phases and these results were compared to the results calculated by ThermoCalc software. Hot corrosion tests were performed at 900^{o}C in static air after samples sprayed with Na_2SO_4 salt as surface film in 72 hours intervals. Weight change versus time graphs were plotted as sample weight, total weight and spallation weight changes. The weight change graphs and microstructural characterizations showed that increasing Cr content in NiCrAlY overlay coating did not improve the hot corrosion resistance of NiCrAlY coating alloy. Both Ni-22Cr-10Al-0.2Y (wt%) and Ni-30Cr-10Al-0.2Y (wt%) alloy resisted to hot corrosion up to 936 hours. Adding 10 wt% Cobalt to Ni-30Cr-10Al-0.2Y (wt%) alloy increased hot corrosion resistance of Ni-10Co-30Cr-10Al-0.2Y (wt%) coating alloy from 936 hours to 2088 hours drastically. These results were evaluated with respect to type I hot corrosion mechanisms.

The Influence of Hydrogen on Nickel Alloy 625 Manufactured using Direct Energy Deposition

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Abstract

Nickel Alloy 625 (UNS N06625) is an austenitic material which is primarily strengthened by solid solution. It is commonly used for high temperature applications and in corrosive environments. In subsea Oil and Gas applications, Nickel alloys such as UNS N06625 can be connected to less noble materials which are protected by cathodic protection (CP), because of this hydrogen will evolve from the surface of these materials and can adsorb and diffuse into the Nickel alloys which can lead to hydrogen embrittlement and ultimately a failure of the material. This study develops insight into hydrogen behaviour of UNS N06625 which is manufactured using Direct Energy Deposition (DED) and is compared with the conventionally manufacturing method. The hydrogen embrittlement susceptibility is assessed using step loading tensile tests (SLTT) based on ASTM F1624-12 standard. The tensile samples were pre-charged with hydrogen in a 0.6M NaCl environment at 50mA galvanostatic current, equivalent to -1.4 $V_{Ag/AgCl}$ and were continually charged in-situ during loading until failure. The results indicate that DED materials with an increased hydrogen embrittlement resistance compared to conventionally manufactured UNS N06625. Using fractography analysis and EBSD fracture characterisation indicating hydrogen behaviour differences between the two manufacturing methods. Moreover, hot extraction study confirmed that the DED material contain low diffusible hydrogen compared to the conventional material.

On the role of the parameter field of activity of hydrogen, mechanical stress and time for the risk of hydrogen embrittlement

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We investigated the combined parameter field of hydrogen activity, exposure time and mechanical stress influencing the risk for hydrogen embrittlement of high strength steels. Despite their relevance for engineering applications, especially the time of exposure to mechanical stress coupled with hydrogen activity of different levels has not yet been systematically studied. We performed our investigations on a designated Fe-5 wt.% Ni model alloy, which offers specific advantages especially in terms of highly controllable microstructural defect structures, hydrogen trap sites and strength levels.

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Pitting corrosion of stainless steels in acids: development of open and covered pits

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Pitting corrosion is a common form of attack in stainless steels (SS) in acidic high-temperature solutions involving chlorides, and the pit propagation is influenced by parameters, like chloride-to-sulfate ratio and temperature [1]. Further, it is well known that duplex and austenitic grades of SS may behave differently under identical operation conditions despite the equal pitting resistance equivalent numbers (PRENs). This work aims to shed more light on the initiation of pitting corrosion and propagation of open and covered pits under a range of operation conditions for several commercial SS grades, such as 1.4404 (PREN 24), 1.4162 (25), 1.4539 (34), 1.4462 (35), 1.4547 (43), and 1.4410 (44). The combination of [Cl^-], pH values, and acids (sulfuric, hydrochloric and formic) that cause pitting attack on SSs specimens was examined at 90 °C using cyclic polarization measurements with [Cl^-] ranging from 0 to 5000 mg/L, solution pHs 2.5 and 4. The findings demonstrate a correlation between operating conditions, material susceptibility to pitting corrosion, pit morphology (open/covered) and material properties (PREN, austenitic or duplex microstructure). Furthermore, the role of each acid has been identified for both pH values providing new insights into the shape and propagation mechanisms of pits. The pitting corrosion of materials is explained mechanistically using microstructure, alloy composition, and PRENs. The raking of materials based on the results assists researchers, engineers, and industrialists make proper material choices.

Keywords: stainless steel, pitting, chloride, pH, microstructure

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Application of SECM to detect a local electrolyte acidification due to the hydrogen flux desorption from a cathodic charged 316LN

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Different processes can lead to water reduction on a metallic surface, leading to hydrogen adsorption and absorption [1], which may in turn decrease mechanical properties [2]. Some studies have highlighted interaction between hydrogen and corrosion [3, 4]. In the case of austenitic stainless steel, hydrogen can attain extremely high subsurface concentrations [5], suggesting a potential alteration of metallurgical states and surface mechanisms such as dissolution and passivation. In this context, this study aims to investigate the impact of hydrogen/metallurgy interactions on the kinetics of dissolution and passivation in 316LN. Firstly, the concentration and distribution of hydrogen were explored following an electrochemical charging process in a sodium hydroxide solution with ammonium thiocyanate (poison). Hot extraction analysis was employed to quantify the total hydrogen concentration. Kelvin Force Microscopy was performed on cross sections, revealing that hydrogen is localized in a few tens of micrometers below the charging surface. Stationary and non-stationary electrochemical tests, coupled with Inductively Coupled Plasma, were conducted to evaluate the increase in dissolution kinetics after hydrogen absorption. The findings indicate that modifications in electrochemical properties are partially reversible with hydrogen desorption. An original approach, using SECM, enabled the assessment of the effects of hydrogen desorption on the local pH of the electrolyte over time (at a distance of 3 µm from the sample). These results provided an initial explanation for the previously observed reversible effects.

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Scrutinizing Zirconium Conversion Coatings: Understanding Zr's Aqueous Chemistry and Structural Foundations for Optimization

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Zr conversion coatings (ZrCCs) are promising alternatives to phosphate and chromate coatings. Yet, solution starting conditions (pH, concentration, complexing agent) significantly influence Zr's aqueous chemistry, resulting in various Zr- monomeric and polymeric species mixtures. Thus, a deeper understanding of Zr chemistry is crucial for understanding and enhancing the mechanisms of ZrCC coating formation.

A thorough review of Zr's aqueous chemistry resulted in the construction of equilibrium diagrams based on the experimentally validated Zr–OH and Zr–F species, highlighting the tetrameric Zr species as the fundamental building block of the ZrCC layer[1].

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)[2] measurements performed on ZrCCs deposited on cold-rolled steel samples confirm the effects of solution pH, conversion time, and H_2ZrF_6 concentration, already shown through Response Surface Methodology (RSM)[3]. Tetrameric structures are exclusively formed in ZrCCs at pH=4.0, with increased thickness over time[2].

Electrochemical Impedance Spectroscopy (EIS) in simulated acid rain further confirmed that optimal ZrCC formation needs pH=4.0 and extended conversion time, evidenced by a high-frequency loop[2], which is in line with prior Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy (SEM/EDS) surface analysis[3].

The described approaches lay the groundwork for predicting and explaining ZrCC formation, potentially expanding its uses with different conversion bath additives.

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Predicting the Locations of Corrosion Pit Formation through Reflective Microscopy Imaging

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Accurately forecasting the locations of future pit formation sites on stainless steels (SS) holds significant practical value in both fundamental science and the corrosion industry, yet it poses a significant experimental challenge due to the need to localize imperfections in the passive film at a sub-nanometer scale. In this study, we tackle this issue by utilizing the latest advancements in *in-situ* Reflective Microscopy (RM) instrumentation, optical modeling, and machine vision techniques, focusing on the prediction of pitting in SS316L alloy in chloride-rich media. Our findings indicate that the appearance of future pits is always linked to slight (~0.5%) decrease in the intensity of light reflection from the SS surface, yet this relationship is not always reciprocal. Optical modeling results suggest a chromium oxide deficiency in the surface films over these zones. There is also a tendency for pits to occur in closely spaced groups, with this clustering not influenced by chloride concentration, pointing instead to the initial surface state as a factor. This study provides proof of concept that RM can be used as an accessible, highly precise tool to define zones of preferential pitting corrosion on SS substrates.

Insights into the Zr-based conversion coating of aluminium alloy investigated by a novel element-resolved electrochemistry coupled with quartz crystal microbalance.

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A novel coupling between atomic emission spectroelectrochemistry (AESEC) and electrochemical quartz crystal microbalance (EQCM) is introduced to monitor Zr-based conversion coating formation mechanism on an aluminium alloy. The integration of these two techniques opens the possibility of monitoring in real-time kinetics of dissolution and conversion coating formation. This combined approach is then utilized for *in situ* monitoring of the Zr-based conversion coating surface treatment on an AA2024-composition aluminium alloy substrate.

The dissolution kinetics specific to each element during the activation and growth phases of the conversion coating, along with the corresponding mass changes, are simultaneously monitored. In the initial stage of surface activation, a higher dissolution of the elements constituting the alloy is monitored, leading to a net decrease in the mass of the substrate. Subsequently, during the deposition and growth phase of the conversion coating, a near steady-state elemental dissolution (AESEC) profile and increasing total mass (EQCM) are observed, which eventually plateaus, signifying a slowdown in conversion coating growth.

This simultaneous monitoring and the correlation between dissolution and mass changes provides valuable insights into the overall kinetic processes involved in the conversion coating step. Furthermore, this study highlights the ability of the coupled technique to complement AESEC, providing direct information on the quantity of insoluble product formed during substrate surface treatment.

D and ^{18}O, isotopic tracers of micro-infiltrating atmospheric corrosion of bell bronze

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The bronze bell is part of our tangible and intangible heritage. Atmospheric corrosion, combined with the mechanical stresses of percussion, degrades this heritage through invasive micro-infiltration of environmental fluids.

The corrosion facies of an old bronze bell (Cu-Sn-Pb alloy) in an urban atmosphere has been studied: (1) A micro-cracked outer layer of antlerite/cuprite and aluminosilicate elements, mainly derived from bell-making techniques, was observed: on the inner face of the bell, a layer of atacamite/paratacamite developed on the surface, and residual metallic inclusions were in the urban patina. On the outside of the bell, a copper oxy- chloride layer is observed at the corrosion layer/alloy interface. (2) Selective corrosion of the alloy's α phase takes place: on the outer surface of the bell, type I corrosion with inter-dendritic cracks of mechanical origin filled with copper/lead oxides connecting the corroded α phases; on the inner surface, type II corrosion stratified by copper oxy-sulfates/tin oxy-chlorides.

Using an original corrosion recovery protocol in a $D_2{}^{18}O$-labeled atmosphere and nano-mass spectrometry analyses, the micro-infiltration properties of urban corrosion were investigated. D and ^{18}O are adsorbed in the pores and microcracks of the outer corrosion layer. Deeper down, ^{18}O precipitates (cuprite) at the α-alloy/corrosion product interface. This is where cathodic/anodic corrosion reactions take place. The oxy-chloride layer acts as a selective barrier, blocking chlorine, sulfur and deuterium in the outer layer, but diffusing ^{18}O into the alloy. In its absence, D precipitates in the stratified corrosion products α (deuterated antlerite) and ^{18}O at the strata interface. Anodic/cathodic dissociation of the sites is suspected. This study is part of the BellACorr project (Project-ANR-18-CE27-0006).

Title Material design and CMAS corrosion behavior of rare earth silicate $(Er_{1/4}Tm_{1/4}Yb_{1/4}Lu_{1/4})_2Si_2O_7$ for environmental barrier coating

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Environmental barrier coatings (EBCs) have been developed to improve the durability of SiC_f/SiC CMC components against harsh combustion environment. Among the most promising EBC candidates, rare-earth disilicates ($RE_2Si_2O_7$) have been attracting attentions due to their low thermal expansion coefficient, excellent high temperature water vapor resistance, and good thermal and chemical compatibility with silicon-based ceramics and composites. However, the insufficient CMAS ($CaO-MgO-Al_2O_3-SiO_2$) corrosion resistance ability of $RE_2Si_2O_7$ has become one the critical drawbacks that limit the application of them as environmental barrier coating at higher temperature. Herein, we reported our recent studies on the material design and CMAS corrosion behavior of a novel $(Er_{1/4}Tm_{1/4}Yb_{1/4}Lu_{1/4})_2Si_2O_7$ silicate through strategic high entropy design and experiments. The present advancements demonstrate the merits of high entropy engineering for advanced EBCs for the improvement of CMAS resistance property in engine applications.

Investigation of Water Molecule Adsorption Behaviour on X2-RE_2SiO_5 Surface by First-Principle Method

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X2-RE2SiO5 has attracted extensive attentions as the top coating material in environmental barrier coatings (EBC), due to its good corrosion resistance and phase stability at high temperature. Resistance to water vapor corrosion in combustion environment is the critical protection function of EBC. However, the mechanism of water vapor corrosion of RE_2SiO_5 is still unclear. Investigation of the interaction between RE_2SiO_5 and water molecules at the atomic scale is essential for understanding the water vapor corrosion process at high temperature. In this work, the surface stability and water molecular adsorption behavior of X2- RE_2SiO_5 (RE= Lu, Yb, Tm, Er, Ho, Dy, Tb) were studied by first principles method. Based on the BFDH rule and the analysis of structural characteristics, 13 RE_2SiO_5 surface configurations covering 4 types of low index surfaces were selected, and the stability of these 4 types of surfaces was predicted by calculating the surface energy. The analysis of electronic structure shows that the high chemical activity sites on the surface are O and RE atoms with high unsaturated bond. The adsorption sites and adsorption energies of water molecules on the surface were compared, and it is found that there are two different adsorption mechanisms related to the different unsaturated state of O atoms on the surface. The results of this work show that the active O atom is the key factor of RE_2SiO_5 interaction with water molecules, which provides an important theoretical basis for establishing the mechanism of water vapor corrosion resistance.

Study on pitting corrosion behavior and semi in-situ pitting corrosion growth model of 304 L SS with elastic stress

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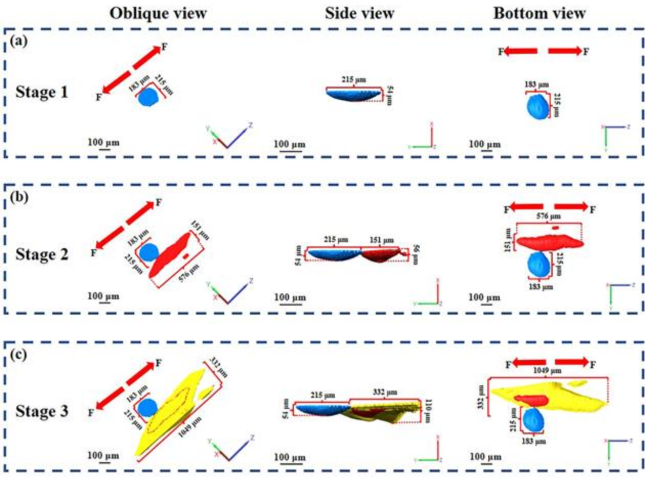
Abstract — The passive film characterization and pitting corrosion behavior of 304 L stainless steel (SS) with various elastic tensile and compressive stresses are investigated by electrochemical measurements, acoustic emission, and surface analysis methods. The elastic tensile stress could decrease the pitting corrosion sensitivity of 304 L SS at 16.63%σ0.2. As the elastic tensile stress further increases, the pitting corrosion sensitivity of 304 L SS increases. The compressive stress has the opposite effect on 304 L SS localized corrosion behavior. Furthermore, a four-dimensional spatiotemporal model of pitting corrosion development progress in 304 L SS with the elastic stress was established by X-ray computed tomography results for 304 L SS under the 63.24%$\sigma_{0.2}$ elastic tensile stress, **Figure 1**. In the initial stage of stable pitting corrosion process, independent corrosion pits would nucleate and grow on the 304 L SS surface. And new corrosion pits would not nucleate at the pre-existing pits area. Elastic tensile stress would cause the corrosion pits to turn into elongated shape when the corrosion pit grows to a certain stage. And finally, adjacent corrosion pits merge into a large pit and leading to the 304 L SS failure.

Figure 1.

Top, Side and Bottom of 3D morphology corrosion pits in different stages.



Repassivation of Ni-base superalloys by self-healing

Jinshan Pan[a], ***Xiaoqi Yue***[a,c], ***Alfred Larsson***[b], ***Dihao Chen***[a,c], ***Andrea Grespi***[b], ***Giuseppe Abbondanza***[b], ***Josefin Eidhagen***[a,d], ***Ulrich Lienert***[e], ***Zoltan Hegedüs***[e], ***Arno Jeromin***[f], ***Thomas F. Keller***[f], ***Mattia Scardamaglia***[g], ***Andrey Shavorskiy***[g], ***Chaofang Dong***[c], ***Edvin Lundgren***[b]

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Passivity is claimed to be the key to our metal-based civilization. Stability of the passive film on an alloy relies on repassivation ability of the alloy in corrosive environments. In this work, we have studied the mechanism of repassivation of Ni-base superalloy (Ni-Cr-Mo-Fe-Nb) covered by a defective passive film through a combination of multimodal *in situ* synchrotron X-ray measurements, electrochemical methods, and DFT calculations. The results reveal chemical and structural evolutions of both the passive film and the underlying surface alloy layer under transpassive condition. We elucidate a self-healing mechanism of the repassivation of the alloy, in which the surface alloy layer plays a crucial role. Upon passivity breakdown at high anodic potentials, the passive film becomes highly defective with vacancies, and metal dissolution leads to generation of metal (mainly Ni) vacancies in the surface alloy layer (Figure 1). This triggers a 'self-healing' process by enhanced outward Cr diffusion to sustain the passive film and by reinforced strength of Cr-Ni bonds to slowdown the metal dissolution, thus leading to repassivation when the high potential is removed.

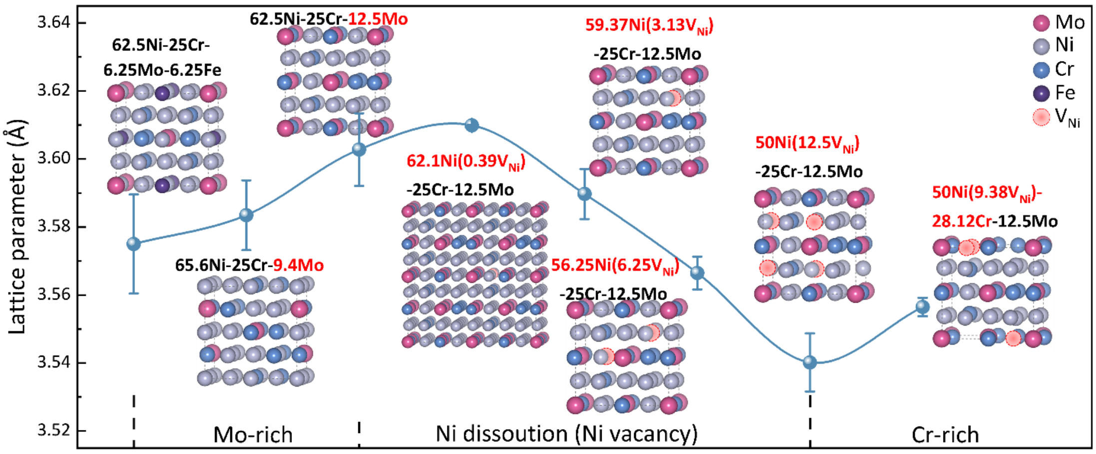

Figure 1. Lattice parameter calculated by DFT for the Ni-Cr-Mo-Fe-Nb alloy with vacancies vs. applied anodic potential, showing the same trend as that measured by in-situ GI-XRD.

Cu alloying and its impact on localized corrosion mechanisms in solutionized and aged model Ni-Cr-Fe alloys

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Abstract

Cu is commonly found in Fe and Ni-based corrosion resistant alloys as a minor alloying element or an uncontrolled impurity. Its effect on localized corrosion of these alloys is unclear. This study explores the impact of Cu on localized corrosion mechanisms in low Cr, model Ni-13Cr-10Fe alloys with Cu additions up to 5 wt.%. The Cu effect was studied in the solutionized and thermally aged conditions to understand the role of microstructural distribution of Cu.

In the solutionized condition, the pitting potentials and the incubation time for stable pitting in 0.1 M NaCl environment increased with Cu content in the alloy. A first-principles competitive adsorption model applied in a simulated pit environment, suggested that chloride adsorption was suppressed, and proton adsorption increased with pit surface Cu content. The suppressed chloride adsorption and enhanced proton adsorption on the pit surface inhibits pit stabilization, which can rationalize the effect of Cu on the measured pitting potential and incubation time trends. It may be inferred from the above results that Cu alloying is beneficial to the localized corrosion resistance of low-Cr alloys when Cu is present in the solid solution.

In contrast to the solutionized condition, the Ni-13Cr-10Fe-5Cu alloy aged at 700°C for 10 h was prone to intergranular corrosion (IGC) with possible detrimental effects on pit growth and repassivation, while the Cu-free Ni-13Cr-10Fe alloy did not show IGC susceptibility. The aging treatment resulted in Cu segregation and precipitation at the grain boundaries (GBs) in the 5Cu alloy, which induced Cr depletion as confirmed by scanning transmission electron microscopy. Cu-induced Cr depletion (sensitization)

in the 5Cu alloy can be explained based on a CALPHAD-assisted broken bond model of GBs, which captures the repulsive interaction between Cu and Cr at the GBs. The IGC susceptibility of the 5Cu alloy was confirmed based on double loop electrochemical potentiokinetic reactivation in 0.001 M sulfuric acid + 1 ppm KSCN and immersion testing in a 10:1:10 mixture of hydrochloric acid, nitric acid, and water. The post-mortem morphology characterization carried out after both tests indicated preferential attack propagating along the GBs.

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The Role of Accumulating Corrosion Products on the Behaviour of Copper and its Alloys

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While it is straightforward to evaluate the corrosion sussceptibility of Cu for a given set of thermodynamic conditions, the changing nature of the electrolyte can alter the mechanism by which Cu corrodes. Dissolved Cu ions can accumulate to saturation, stabilizing Cu even in acidic, oxygenated electrolytes. This effect, first typified by dealloying experiments conducted on brass in the 1980's, continues to be relevant in the long term corrosion of pure Cu and crevice corrosion of Cu alloys.

It has been asserted that Cu will not undergo pitting in acidic and near-neutral oxygenated electrolytes containing 3 M Cl^- due to the instability of Cu oxides which are a precursor to pitting. This research shows that Cu can pit in near-neutral electrolytes, providing enough Cu^{2+} and $CuCl_2^-$ accumulate in the electrolyte to stabilize Cu oxides. This was achieved simply by adding Cu turnings to the electrolyte which increased the Cu surface area relative to the electrolyte volume. Linear polarization resistance experiments in conjunction with electrochemical impedence spectroscopy evidenced the formation of unstable passive films.

Monel-400, a Ni-Cu alloy used in nuclear steam generators, underwent dealloying in service due to the accumulation of corrosion products in an occluded region. The accumulation of Cu ions stabilized alloyed Cu, resulting in the selective dissolution of Ni. This effect was recreated using immersion experiments and potentiostatic polarization experiments in simulated steam generator chemistries. Corrosion character was evaluated using scanning electron microscopy and energy dispersive x-ray spectroscopy.

This work demonstrated that Cu has the ability to pit in near-neutral electrolytes due to the accumulation of Cu ions, which is of significant importance in the long term corrosion of Cu. Similarly, accumulating Cu ions can promote dealloying in a Cu alloy which can lead to localized corrosion and accelerated failure.

Enhancing the longevity and durability of steel structures with recycled Al alloy coatings

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A conventional approach for corrosion prevention involves the application of a layer of sacrificial metals onto the material's surface, where these metals donate electrons, safeguarding the material from corrosion. Commonly employed metals for this purpose include aluminium (Al) and zinc (Zn). However, Al-based anti-corrosive coatings tend to passivate over time, diminishing their efficacy, owing to a lack of cathodic protection. Conversely, Zn-based coatings provide superior protection, yet they can induce hydrogen entry to steel in defects and increase the risk of hydrogen embrittlement of steel, and are derived through a less sustainable process. A recent idea to address this challenge involves using scrap Al (s-Al), promoting circular economy principles by providing a sustainable solution for contaminated Al. Although these contaminants make s-Al unsuitable for many applications, this very factor improves s-Al anti-corrosive performance. Our objective is to assess s-Al efficacy in preventing steel corrosion by employing a dual approach based on molecular and continuum models. On the one hand, molecular models, employing techniques such as density functional theory (DFT), yield physically meaningful solutions and can derive fundamental properties (Fermi level, work function), albeit at a computational cost unsuitable for practical applications. On the other hand, continuum models, while computationally more affordable, and able therefore to model large systems, are not capable of deriving fundamental properties of alloy systems. Our proposed strategy seeks to couple these two methodologies to obtain a reliable yet cost-effective continuum model, demonstrating its significance to the field. Such a model is called *physically informed* since input data are directly obtained from molecular calculations. A comprehensive examination of various s-Al-based alloys is undertaken to understand corrosion resistance for steel coverage.

Reactivity of Cr_2O_3 layers obtained by ALD on 2024 Al alloys

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Atomic Layer Deposition (ALD) is a technique for thin-film deposition that allows for atomic-scale control over the thickness of the deposited layer. It operates based on a sequential gas-phase chemical process, which involves the interaction between a substrate and various vapor-phase precursors introduced in sequence. This method facilitates the deposition of a wide range of materials, including metals, oxides, nitrides, and sulfides. ALD is mainly used in many industrial applications [1].

In the field of corrosion, several studies have reported a significant enhancement of the corrosion resistance for several metals and alloys (such as steel, stainless steel, and copper) protected by an ultra-thin metal oxide layer produced by ALD [2]. Also in the case of photocorrosion, protective layers based on metal oxides have been demonstrated e.g. for hematite protection [3].

This study aims to examine the behavior of a 2024 Al alloy coated with a Cr_2O_3 layer produced by ALD. The Cr_2O_3 layers were characterized using a combination of advanced surface analysis techniques, including X-Ray Electron Spectroscopy (XPS) and Time-of-Flight Secondary Ions Mass Spectroscopy (ToF-SIMS). The results indicate the deposition of a homogeneous Cr_2O_3 layer, with no observed interdiffusion (between Al and Cr) for the various thicknesses studied. The deposition of thicker Cr_2O_3 layers resulted in an increase of the Al_2O_3 thickness present on the Al surface.

Immersion tests demonstrated high corrosion resistance for film thicknesses of approximately 10 nm. Additionally, polarization curves obtained in neutral solutions containing chloride ions indicated some improvement in pitting corrosion resistance.

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[2] S. Mirhashemihaghighi et al. Electrochimica Acta, 193, 2016, 7
[3] T. Imrich et al., Journal of Photochemistry & Photobiology, A: Chemistry, 409, 2021, 113126

Hydrogen-induced stress cracking mechanism in coarse super duplex stainless steel revealed by in situ high-energy X-ray diffraction

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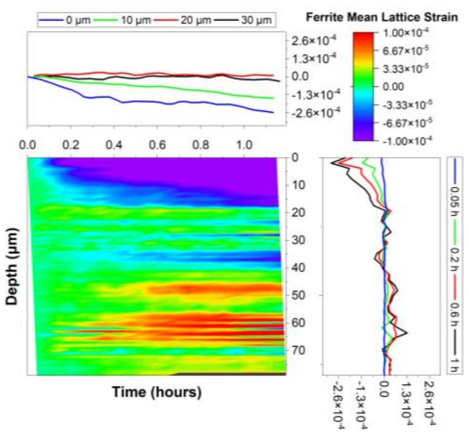
Super duplex stainless steel (SDSS) has been widely used in harsh conditions where a combination of high strength and high corrosion resistance is required. However, failures have been observed in SDSS used in seawater, which related to the presence of hydrogen and mechanical load, and hence raises the concern about the risk of hydrogen-induced stress cracking. The cathodic electrochemical protection during service can lead to the water reduction reaction in the exposure region for SDSS, and thus hydrogen charging on the SDSS. Therefore, with the mechanical load and addition hydrogen-induced stress, the fracture can occur very dramatically if the SDSS is loaded near the yield strength, especially for the coarse-grained SDSS.

The development of hydrogen-induced strain, especially the concentration of local strain within the microstructure, is closely related with the deformation damage in SDSS. In this work, the direct relationship between the hydrogen and tensile load induced microstructural evolution and macroscopic fracture behaviour of a SDSS has been investigated by in situ synchrotron high-energy X-ray diffraction (HE-XRD). Moreover, the hydrogen micro-print and microcomputed tomography measurements further demonstrate that the deformation damage, such as the crack initiation and propagation, occurred in the ferrite phase (α) in the SDSS and high concentration hydrogen accumulated at the crack front. The lattice strain development during deformation measured by the in situ HE-XRD measurement confirms the lattice deformation of Y{200} , Y{220}, Y{111}, and Y{311} austenite grains and α{200}, α{110}, α{211}, and α{311} ferrite grains under electrolytic hydrogen charging and elastic deformation (50% and 75% of the R_p, 484 Mpa). However, after raising the load to 81% of the R_p, hydrogen-induced microstructural evolution exceeds the critical threshold of cleavage cracks in ferrite. The increased plastic deformation of austenite and ferrite grains was observed from the interior to the surface of the sample after the release of the load.


Strain Evolution at Loading Direction

Influence of γ-FeOOH on corrosion behavior of Al

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The effect of γ-FeOOH on the corrosion behavior of Al alloys used in the multi-materialization of vehicles was investigated. γ-FeOOH is a well-known as the iron-based corrosion products formed on carbon steels. Immersion corrosion tests and polarization measurements of pure Al placed γ-FeOOH were performed using 0.5 wt% NaCl solution as test solution.

As the results of the immersion corrosion test, little corrosion damage occurred on the Al surface when γ-FeOOH was not present on the surface. However, the corrosion damage on the surface of the Al with γ-FeOOH was more severe, and the numerous pits was observed on Al surface. This result indicates that the corrosion resistance of Al is reduced by the presence of γ-FeOOH.

The effect of γ-FeOOH on the polarization behavior of Al in 0.5 wt% NaCl was researched. A passive region was observed in the anodic polarization curves of the Al without γ-FeOOH from 0 to 0.5V. In addition, the passive current density of the Al with γ-FeOOH was one order of magnitude larger than that of the Al without γ-FeOOH. This result means the presence of γ-FeOOH inhibited passivation. The presence of γ-FeOOH also gave an increase of the cathodic current density of Al. γ-FeOOH promoted both anodic and cathodic reactions.

Statistical Evaluation of the Uniform and Localized Corrosion of 2205 Duplex Stainless Steel for Hydrometallurgical Applications

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Hydrometallurgical processes involve aqueous solutions of acids such as sulfuric acid. Hydrometallurgical environments are aggressive. They are often characterized by low pH, high concentrations of oxidizing agents and ligands, elevated temperatures, and erosive agitation: in sum, everything needed to put and hold metals in solution. These conditions can result in significant corrosion to plant equipment if materials selection is not done carefully. Stainless steels are extensively used in hydrometallurgical applications. These alloys must resist both uniform and localized corrosion to ensure the longevity of process equipment.

This study evaluates the uniform and crevice corrosion behavior of 2205 duplex stainless steel in simulated copper leaching solutions. The response surface methodology (RSM) was used to evaluate the relative significance of four factors, including H_2SO_4 (lower and upper levels of 10 g/L and 50 g/L, respectively), H_2O_2 (lower and upper levels of 2 g/L and 10 g/L, respectively), Cl^- (lower and upper levels of 1 g/L and 10 g/L, respectively), and temperature (lower and upper levels of 25 °C and 85 °C, respectively) on the uniform corrosion rate of the alloy. All test solutions contained 10 g/L Cu^{2+} (added as $CuSO_4$). The uniform corrosion rate of the alloy was considered as the model's response, which was determined using the corrosion current density measured from potentiodynamic polarization. Analysis of variance (ANOVA) was used to analyze the statistical significance of the results. ANOVA showed that the model is significant, while the lack of fit is not significant, implying that the model accurately fits the data and can reliably be used to interpolate the response. Furthermore, ANOVA showed that temperature, Cl^- concentration, and the interaction between temperature and Cl^- concentration are significant.

The potentiostatic critical crevice temperature (CCT) of 2205 DSS was determined in different solutions. It was found that in 50 g/L H_2SO_4 + 10 g/L H_2O_2 + 10 g/L Cu^{2+}, increasing the Cl^- concentration from 1 g/L to 10 g/L decreases the CCT of the alloy from > 95 °C to 58 ± 3 °C. However, H_2SO_4 and H_2O_2 concentrations have little to no effect on CCT. This implies decreasing the Cl^- concentration increases the service temperature of 2205 DSS in the presence of H_2SO_4, H_2O_2, and $CuSO_4$ without the risk of crevice corrosion.

Corrosion evolution of aluminium-copper and aluminium-copper-lithium alloys in chloride solution

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Aluminium-copper and aluminium-copper-lithium alloys are widely used in the aeronautic industry. The precipitation of alloying elements such as copper, lithium, or magnesium, creates the well-known intermetallic particles that enhance the mechanical properties of the alloys but decrease their corrosion resistance. The objective of this work is to better understand the corrosion behaviour of AA2024 (aluminium-copper) and AA2050 (aluminium-copper-lithium) alloys – used in aircraft fuselage and wings – following their surface reactivity in a corrosive solution (NaCl, 0.01M) using electrochemical and surface science techniques such as linear sweep voltammetry, electrochemical impedance spectroscopy, and X-ray photoelectron spectrometry (XPS) or time-of-flight secondary ion mass spectrometry (ToF-SIMS) respectively. This study aligns well with the current era of developing ecologically responsible protection methods, particularly in response to the impeding ban on chromium VI by REACh regulations.

Various immersion times ranging from 0h (freshly polished reference) to 72h reveal that pitting corrosion is the predominant observed mode, and pits develop over time. However, the corrosion current density, coming from Tafel's slope extrapolation, decreases with time (from 2.10^{-6} A.cm^{-2} to 5.10^{-7} A.cm^{-2} for the AA2050 alloy) because the aluminium metal becomes progressively buried beneath an oxidized aluminium layer as evidenced by the evolution of Al 2p photoemission signal. In-depth ToF-SIMS profiles of Al_2^- and AlO_2^- ions, corresponding to the metal and oxide, respectively, show that the oxidized layer is thicker in the AA2050 alloy, despite exhibiting a lower corrosion current density than the AA2024 alloy. This indicates a different surface reactivity of these two alloys. The comparison of the photoemission areas of XPS peaks associated to the metallic elements of corroded surfaces reveals an enrichment in copper over time of the AA2050 alloy surface.

Differential Corrosion Behavior of UNS S32750 Duplex Stainless Steel Friction-Stir Weldment

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Friction stir welding (FSW) supresses the formation weld cast structure and potential phases that are normally encountered in typical fusion welded joints of metallic alloys. Thus, the detrimental effects of the latter type of weldments on corrosion are not anticipated in friction stir weldments. However, FSW introduces stresses in a differential manner across the friction stir weldment. Understanding the corrosion behaviour of such zones is critical for successful application of FSW technique for various types of alloys. Considering the importance of UNS S32750 for application in severe corrosive environments, this study addresses the ambient temperature corrosion behavior of three zones of friction weld namely the stir zone (SZ), the advancing side (AS) and the retreating side (RS) in chloride containing sulfuric acid (0.5 M H_2SO_4 + 3.5 wt pct NaCl). The alloy showed significant variations in the grain refinement both with respect to the austenite and ferrite phases in the three regions of the weldment in relation to that found in the base metal (BM), although less significant changes in the volume fraction of the two phases are found in these three zones. A notable variation is a significant raise in the coincident site lattice (CSL) in these three zones with respect to BM. Potentiodynamic polarization showed that the anodic dissolution and cathodic reaction rates on the metal surface significantly differed in the three zones of the weldment. Thus, the passive current density and the cathodic current density of the weldment followed the order BM >SZ>RS>AS. Such a variation seems to have been brought out by the formation of thicker passive films with lower defect density on the AS and RS as compared to that formed on the SZ and BM.

Molecular Level Thermodynamics and Properties of the Aqueous Hematite Interface from First Principles

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Undercoating corrosion and delaminaton is often difficult to predict, detect and mitigate. The complex feedback between polymer degradation, electrochemistry of the confined solution and interfacial chemistry is still poorly understood. On steel the formation of iron oxy-hydroxide (Fe-O-H) layers is evidenced and the solution interface to these surfaces is therefore of fundamental and technical interest. Molecular level characterisation, as for all buried interfaces, is extremely challenging.

The Fe-O-H system is characterised by strong electronic correlation producing a complex phase diagram in which charge, orbital, magnetic and geometrical degrees of freedom are strongly coupled. Here we present a detailed description of how these interactions affect the interfacial chemistry of the aqueous-hematite interface and propose a molecular level model of the reaction sites and chemistry of the adsorbed layer. The underlying thermodynamics is established using high efficient and large scale hybrid exchange density functional theory.

Effect of micro-alloying of Ca and Y on the corrosion resistance of AZ series Mg alloy

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An indispensable requirement for Mg alloys is excellent corrosion and ignition resistance as chemical properties. To achieve this, 'SEN' alloys were developed by micro-alloying of Ca and Y in Mg-Al-Zn-based alloys. Here, the letters ‘S,’ ‘E,’ and ‘N’ denote ‘stainless steel,’ environmentally friendly, and ‘non-flammable,’ respectively. The SEN alloy exhibited superior corrosion and ignition resistance relative to the commercial AZ series Mg alloys as counterparts. In this study, the effect of micro-alloying of Ca and Y on the corrosion behavior of cast-type AZ series Mg alloys was investigated; especially, the enhancement mechanism of corrosion resistance was discussed in terms of 2nd phase (i.e., the volume fraction, composition, and distribution) and solid solution elements. For the mold cast type alloy, the type of Al-containing intermetallic particles was changed by alloying with Y from Al-Mn-(Fe) to less noble Al-Mn-Y, which reduced the micro-galvanic reaction. Furthermore, a solid solution element Y produces a more stable surface film. The corrosion resistance of SEN alloy can be improved due to those two effects. A die-casting process with a high cooling rate led to further improvement in the corrosion resistance of SEN alloys because of the more continuous network of β-phase acting as a corrosion barrier and the decrease in volume fraction of eutectic α-Mg acting as a galvanic site.

A mechanistic model to predict the corrosion rate of carbon steel exposed to weak acids

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Weak acids are often encountered in industrial applications and represent a severe threat to metals, despite their relatively high pH with respect to strong acids. Indeed, the electrochemical interactions taking place in the presence of weak acids are complex and commonly difficult to interpret and predict. In the last decades, efforts in research directed at predictive modeling of acidic corrosion have primarily concentrated on two specific cases: sweet and sour corrosion, very common in upstream petrochemical plant. In this context, the Tafel-Piontelli model was designed to become an all-around tool for the prediction of acidic corrosion, applicable to several scenarios, as strong acid corrosion, weak acid as well as sweet corrosion. The model is mechanistically based on the kinetics and electrochemistry of the anodic and cathodic semi-reactions. Its theoretical description and latest developments are presented. Its performance is tested on carbon steel coupons exposed to a monoprotic, a diprotic and a triprotic weak acid. In particular, solutions prepared with formic, azelaic and citric acid were used in a wide range of pH (3, 3.5 and 4) and temperature (20°C, 40°C, 60°C) conditions. Potentiodynamic polarization tests were carried out to assess the kinetic parameters of the process: Tafel slope and exchange current density of iron dissolution and hydrogen evolution. Mass loss tests were used for the validation of the performance of the model in the estimation of the corrosion rate. The analyses show promising results and allow to extend the applicability of the Tafel-Piontelli model to weak acids.

Complexity at a Humid Interface:
Throwing Light on Atmospheric Corrosion

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Wetting of solid materials in humid environments drives various real world physicochemical processes, ranging from reduction of surface friction to substrate degradation. Concerning the latter, deterioration of metallic substrates through atmospheric corrosion has long been a topic of particular interest, as it can result in the loss of both cosmetic appearance and structural integrity. In the 1930s, Vernon undertook seminal work in this area, establishing that corrosion can become significant prior to surface condensation of bulk liquid water, i.e., the relative humidity (RH) of the environment does not need to exceed 100%. Commonly, this behaviour is proposed to result from the accumulation of adsorbed monolayers (ML) of water atop a substrate, which become sufficient in number to support corrosion chemistry once a critical RH (RH_{crit}) is exceeded. Experimental data supporting this hypothesis do exist, but nanoscale details of the water layers at pertinent RH values remain scarce, impeding full mechanistic understanding of atmospheric corrosion.

In this presentation, we apply both near ambient pressure X-ray photoelectron spectroscopy and vibrational sum frequency spectroscopy to elucidate the interaction of water vapour with zinc, a common engineering substrate for corrosion protection applications. Data acquired as a function of relative humidity indicate that water sorption is much more complex than expected, involving pore filling/capillary condensation in the adventitious carbon layer covering the zinc surface. These results suggest that current mechanistic models for atmospheric corrosion, as well as other interfacial phenomena occurring in humid environments, require extensive revision, and should embrace explicit consideration of the role of surface carbon contamination.

In situ gas measurement coupled with element-resolved electrochemistry: Effect of fluoride, chloride and nitrate on Mg dissolution kinetics

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A novel coupling between gravimetric gas measurement and atomic emission spectroelectrochemistry (AESEC) has demonstrated its analytical ability to simultaneously measure the anodic reaction rate (*i.e.* metal dissolution), cathodic reaction rate (*i.e.* gas evolution) and total reaction rate (*i.e.* electric current). This coupling has been applied to better understand the stoichiometry of Mg dissolution in NaCl solutions, particularly in the case of anomalous hydrogen evolution (AHE) in the anodic potential domain, often referred to as negative difference effect (NDE).

In this work, we used the gravimetric gas measurement – AESEC coupling to investigate the effect of anions in the electrolyte such as fluoride, chloride, and nitrate, on the Mg dissolution kinetics. The presence of fluoride has no influence on the hydrogen evolution in the cathodic potential domain, while no AHE was observed in the anodic potential domain, which may be attributed to the formation of MgF_2 species on the surface by dissolution-precipitation mechanism. When chloride is present in the NaF-containing solution, AHE is observed most probably due to local breakdown of the MgF_2-based passive film. This again confirms the previously proposed mechanism: AHE occurs at the local breakdown site of the passive film. In the presence of nitrate, no gas evolution was monitored in the cathodic domain because the dominant cathodic reaction is the reduction to nitrate. In the anodic potential domain, no AHE was observed again confirming that AHE is caused by local breakdown of the passive film only in the presence of chloride.

The reaction mechanism and stoichiometry of nominally pure Mg under different conditions, i.e., anions and cations in the electrolyte, will be discussed. This work would contribute to the understanding of the Mg dissolution mechanism by simultaneously measuring the anodic and cathodic reaction rates.

Elucidating the Corrosion Behaviour of Laves Phases in Mg-Al-Ca Alloys

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Mg-Al-Ca alloys are potential alternatives for Mg-Al-Zn alloys in lightweight applications. Ca causes the formation of Laves phases, which increase the resistance to creep at elevated temperatures. However, inconsistent phase activities and electrochemical properties in the different electrolytes indicate that such alloys are not yet well understood. We aim to unravel the mechanisms behind those discrepancies by mapping the electrochemical behaviour of all phases of the Mg-Al-Ca alloy system in solutions with different pH.

Therefore, three alloys with different Ca/Al compositions leading to the precipitation of the Laves phases Al_2Ca (C15), $(Mg,Al)_2Ca$ (C36) and Mg_2Ca (C14) were cast, heat-treated and their microstructures were characterized. These alloys were subsequently immersed in a borat buffer solution (pH 8) or in a passivating alkaline KOH solution (pH 11.5) and further analysed via Linear Sweep Voltammetry (LSV). Scanning Vibrating Electrode Technique (SVET) was used to study in-situ the surface activity in the different solutions. Prior and post immersion cross-sections were analysed with SEM, TEM and EDX to monitor the secondary phases and the layers of formed corrosion products. Furthermore, the dissolution behaviour was in-situ analysed by a custom-built flow-cell coupled to an Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS). This enabled the in-situ determination of ion-specific corrosion current densities and thus provided information beyond the standard electrochemical measurements.

In the end, we could link the different electrochemical activities of the material inherent Laves phases and their varying morphology to the overall alloy's corrosion resistances.

Acknowledgments:

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Atmospheric corrosion of carbon steel under droplet conditions

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Investigating metal atmospheric corrosion under thin film or droplet electrolytes has been a longstanding topic of interest. Past studies on atmospheric corrosion kinetics of carbon steel typically involve simultaneous monitoring of corrosion rate and environmental factors like relative humidity and precipitation (e.g. rain, snow) rather than descriptors directly related to the thin electrolyte layer or droplet. In contrast, mechanistic investigations focus more on understanding how electrolytes influence the formation of corrosion products. These studies typically involve controlled and simplified electrolyte layers, different from the complex electrolyte geometries, including discontinuous thin-film layer and multi-droplet conditions encountered in practice.

This research is founded on the assumption that atmospheric factors influence the corrosion rate of carbon steel by affecting the properties of the thin electrolyte deposited on its surface. We view the discontinuous thin electrolyte layer as a collection of droplets, where their size and distribution are considered. Utilizing a novel homemade experimental setup by which corrosion rate, droplet evolution and environmental conditions can be simultaneously monitored, we first study the analytical correlation between the environmental conditions and the corrosion rate, then dive deeper into the effect of droplet property and distribution. Preliminary findings show that localized corrosion is typically found under droplets, and the probability of corrosion initiation appears to be positively correlated with droplet size. NaCl concentration and sample surface roughness also play a crucial role in the kinetics of the process. In general, we find that at higher NaCl concentration and surface roughness will increase the probability of corrosion developing under fixed-size droplets. We have also observed that corrosion products can appear at inter-droplet areas, while most droplets surrounding this area do not induce corrosion on the sample beneath them. The results hint at possible ion migration between droplets, leading to behaviours that deviate from the typical Evans model.

Evaluate progress of steels corrosion in wet and dry condition with image analysis

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Infrastructures such as roads and bridges in Japan are aged more than 50 years after constructed in very soon. Proper evaluation and maintenance are required to use these infrastructures in safe and good condition for the future. A low cost and quantitative evaluation technique is needed to achieve the requirements. Recent technological advances in machine learning and AI have led to use in imaging analysis and other research area. If machine learning assisted image analysis can be used to easily diagnose corrosion conditions from images, social infrastructure can be maintained with efficiently and low cost. The purpose of this study is to evaluate progress of steels corrosion in wet and dry condition with image analysis.

Specimens used in this study was steel sheets cut into proper size for corrosion tests. Laboratory base wet and dry cycle tests were conducted to form corroded specimens. Exposure tests were carried out at two different atmosphere near the coast in Miyakojima and Choshi, Japan with different periods and conditions (direct exposure and shielded exposure). After the tests, optical images of specimen surface were taken for image analysis. Revised version of AlexNet and convolutional neural network (CNN) were used for image analysis. Train data of 180 images and validation data of 20 images, and test data of 50 images were randomly selected from obtained corroded sample images as one data set. Five data sets were created for impartial evaluation.

The CNN classifier created using corrosion images obtained in corrosion tests as teacher data succeeded in classifying the degree of corrosion with a probability of 60% to 80%, even for unknown image data. Therefore, it can be said that there is a possibility to evaluate the degree of corrosion of a structure by creating a CNN classifier based on corrosion images of the structure.

Effect of Grain Size on Corrosion Behaviour of Pure Magnesium

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Abstract:

It is widely known that the grain size variation can impact the electrochemical characteristics of the metals and alloys. In this regard, the literature on Mg and its alloys gives a very inconsistent view. Prior studies address the impact of grain size of pure magnesium on corrosion behaviour without separating the effect of texture and localized stresses. It is not very clear how the grain size actually affects the corrosion response. In this work, the impact of grain size on corrosion has been investigated using pure magnesium that has been rolled and annealed while maintaining a consistent texture. A wide range of grain sizes was considered while keeping localized stresses and texture consistent. The corrosion rate was calculated and the corrosion behaviour was studied using potentiodynamic polarisation testing, electrochemical impedance spectroscopy, and corroded surface characterization to get a broader insight into the corrosion mechanisms. It has been noted that as grain size decreases, the corrosion rate increases. This study contributes to the systematic and thorough understanding of the impact of grain size on the corrosion behaviour of pure Mg.

Effects of grain boundary segregation and misorientation on intergranular corrosion in Fe-P alloy

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Phosphorus (P) in iron and steel is known to segregate at grain boundaries (GBs) and tends to cause intergranular corrosion (IGC). The IGC was reported to be accelerated as P segregation at GBs increased in Fe-P binary alloys [1]. In addition, elemental segregation strongly depends on GB misorientation. Thus, it is important to investigate the relationship between the GB segregation, GB misorientation and IGC behaviour. In this research, immersion tests of Fe-P alloy with three different GB segregation were conducted. The GB segregation and misorientation were analysed with three-dimensional atom probe (3DAP) and electron backscatter diffraction (EBSD) measurements. Based on these results, the effects of GB segregation and misorientation on IGC in Fe-P alloy were discussed.

Fe-0.01P (mass%) alloy was used as a material. The specimens were annealed at 700 °C for 1 h, 600 °C for 24 h, and 500 °C for 960 h, respectively (hereinafter called HT700, HT600, HT500). Amount of P segregation at GBs of HT700, HT600, and HT500 were evaluated as interfacial excess to be about 1, 2, and 3 atom / nm^2, respectively. In addition to the P segregation, 1 atom / nm^2 carbon (C) segregation at GBs was detected only in HT500. GB misorientation distribution was analysed by EBSD measurement. The specimens were subjected to immersion tests in a 0.1 M Na_2SO_4 aqueous solution. After the immersion test, the corrosion products were removed, and the specimen surface was observed using an optical microscope.

From the comparison between HT700 and HT600 (without C segregation), IGC only occurred on HT600 with higher P segregation at GBs. These results indicated that IGC resistance deteriorated with higher P segregation at GBs. On the other hand, despite the highest P segregation in HT500, no IGC was observed. The improved IGC resistance on HT500 may be due to C segregation at GBs. In the presentation, the relationship between IGC and GB misorientation will be discussed.

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Hydrogen Permeation in Magnesium Alloys at Room Temperature

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Introduction

With the recent expansion of the use of light metals and alloys, hydrogen embrittlement studies of these materials are accelerating. However, unlike steel materials, electrochemical hydrogen permeation testing of light metals and alloys at room temperature is difficult. One reason for this is that these materials are more susceptible to corrosion than steel materials. The corrosion causes problems such as the large residual current on the hydrogen detection side, and corrosion wastage and formation of corrosion products on the hydrogen introduction side. In this study, we performed electrochemical hydrogen permeation tests of Mg-based materials, which are particularly susceptible to corrosion, by devising test solutions for the hydrogen detection and introduction sides.

Materials and Methods

Thin sheets of pure Mg, AZ31 alloy, and WE43 alloy with 25 mm x 25 mm x 0.3 mm were used as specimens. A Devanathan-Stachurski cell was used for electrochemical hydrogen permeation tests. The hydrogen detection side was filled with 2-propanol and the specimen was polarized at +200 mV (vs. SHE). After confirming that the residual current density on the hydrogen detection side was less than 0.1 $\mu A/cm^2$, the hydrogen introduction side was filled with saturated $Mg(OH)_2$ solution, and a current of -5 A/m^2 was applied to the hydrogen introduction side.

Results and Discussion

On the hydrogen detection side, the residual current was less than 0.1 $\mu A/cm^2$ immediately after the onset of polarization. The corrosion wastage and the formation of corrosion products on the hydrogen introduction side were small. The hydrogen diffusion coefficient of the samples was so small that it took about three months to complete the electrochemical hydrogen permeation measurement, during which time the sample surfaces were protected from corrosion, allowing the measurement of hydrogen diffusion coefficients in Mg-based materials at room temperature.

Quantification of Hydrogen Absorbed in Steel Sheet during Electrochemical Hydrogen Permeation Tests

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While demand for high-strength steel is increasing as a measure for energy conservation in transportation equipment, there is concern about the occurrence of hydrogen embrittlement in high-strength steel due to atmospheric corrosion. The precursor process of hydrogen embrittlement in the steel has been studied by electrochemical hydrogen permeation tests using the Devanathan-Stachurski (DS) cell [1] to investigate hydrogen permeation in the specimen and diffusion behavior within the specimen. However, it has been difficult to quantify the amount of hydrogen absorption and trapping, which are directly related to hydrogen embrittlement, and to discuss the detailed absorption and trapping mechanisms. In the previous study [2], some of the authors developed a new electrochemical hydrogen permeation testing method that combines a flow-type double-electrode technique. Here we will report the hydrogen absorption and trapping mechanisms by in-situ evaluation of the amount of hydrogen absorbed into the high-strength steel specimen.

The thickness dependence of the amount of hydrogen absorbed into the steel specimen resulted in the showing two linear relationships between the gradient of hydrogen amount and hydrogen charging time with slopes of 1 and 1/2 in the double logarithmic plot. It was suggested that most of absorbed hydrogen into the steel are initially trapped at the trapping sites in the steel, and after the trapping the hydrogen mainly diffuses into the steel specimen. Charging time of trapping sites was dependent on hardness of the specimen as well as the charging condition such as the entry electrode potential.

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Ti6Al4V and Ti6Al4V-Cu alloys for biomedical applications prepared by additive manufacturing

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Infection of orthopaedic and dental implants remains one of the most severe complications of implantology, and the search for viable solutions to reduce the infection incidence has been an ongoing research activity for decades. The scientific challenge is to develop a material with inherent antibacterial properties that do not jeopardise other biomaterial properties. This study aimed to develop and characterise novel material based on the most crucial commercial material, Ti-6Al-4V alloy, used in orthopaedic and dental medicine. The material was prepared using the additive manufacturing (AM) method of direct energy deposition by adding copper, a known antimicrobial agent and an essential element in the human body, to obtain Ti-6Al-4V-Cu alloy. Materials characterisation was conducted using SEM/EDS and XRD methods, and electrochemical measurements were carried out in a simulated physiological solution. Commercial wrought Ti6Al4V alloy prepared by the classical metallurgical method was used as a benchmark. The composition of AM Ti6Al4V alloy is aligned with that of the wrought alloy. The microstructure of wrought and AM alloys differs, with the former showing α-Ti phase and intergranular β-Ti phase and the latter with lamellar widmanstatten pattern. Copper was added to the Ti6Al-4V-Cu without jeopardising the alloy's microstructure. Both wrought, and AM Ti6Al4V alloys passivate in simulated physiological solution and show no susceptibility to localised corrosion. Adding copper does not deteriorate the alloy's protective behaviour in the simulated physiological solution. These results confirmed that the properties of both additive-manufactured Ti alloys (Ti6Al4V and Ti6Al4V-Cu) are comparable with commercial wrought alloy and thus offer great potential for further corrosion and biological studies.

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Role of the late transition metal on the passive film properties and pitting susceptibility of Zr-based ternary bulk metallic glass.

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The possibilities offered by metallic glasses, whether in thin-film or bulk form, have aroused growing interest in various fields such as energy, biomedical and sports. Their excellent mechanical and wear properties are the main reasons for this enthusiasm. Depending on their composition, these metallic glasses can also provide better corrosion resistance than their crystallized counterpart. From a corrosion point of view, they are of particular interest due to the absence of grain boundaries or microstructural defects, enabling in-depth study of the effects of alloying elements and their synergy on corrosion behavior. However, these materials turn out to be more complex than they initially appear. Glassy structure and chemical heterogeneity must also be taken into account. Recent works have revealed the susceptibility to localized corrosion of Zr- and Ti-based metallic glasses in mildly aggressive saline solutions, depending on the alloying elements while Zr or Ti alloys generally exhibit high corrosion resistance.

In this study, the corrosion behavior of ternary bulk metallic glasses $Zr_{56}Co_{28}Al_{16}$ and $Zr_{60}Cu_{30}Al_{10}$ is examined and compared with that of pure Zr in a 9 g/L NaCl saline solution at 37°C (pH=7.4). The choice of this solution is motivated by the potential biomedical applications of these glasses. The properties of the passive film formed are mainly studied using electrochemical impedance spectroscopy measurements. These measurements, performed at different potentials, are then analyzed following a graphical protocol and using recently proposed model taking into account the bi-layer structure of the film and the distribution of the resistivity through the passive film thickness. The structure of passive films is also examined by X-ray photoelectron spectroscopy. These results are then compared with the susceptibility of these alloys to localized corrosion, enabling a discussion of the role of late transition metal on the glass structure and reactivity.

The effect of calcite deposits on the hydrogen uptake of carbon steel: The dual behaviour of calcite

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Abstract

While cathodic protection (CP) is commonly employed to safeguard submarine steel from corrosion, it may increase susceptibility to hydrogen embrittlement due to the prevalence of the hydrogen evolution reaction. Additionally, CP can generate OH^- ions near the metal surface, causing the precipitation of calcium carbonates ($CaCO_3$) and magnesium hydroxides ($Mg(OH)_2$) on the metal.

There is significant controversy regarding the influence of calcareous deposits on the hydrogen uptake of carbon steel during CP, and the mechanism remains unclear as to whether calcareous deposits inhibit or promote hydrogen uptake. The aim of this research is to clarify the mechanism of calcite (one of the crystal structures of $CaCO_3$) on the hydrogen uptake of carbon steel. To do this, the Devanathan-Stachurski cell has been used to measure the resulting hydrogen permeation current and to obtain information about deposit formation at the entrance cell, electrochemical impedance spectroscopy has been applied every 2 hours. Furthermore, the deposits formed on the surface are evaluated by scanning electron microscopy and X-ray diffraction, obtaining the structure and chemical composition of the deposits. The findings indeed reveal a dual behaviour of calcite in relation to hydrogen uptake, acting as a inhibitor at higher CP currents and as a promoter at lower CP currents. Permeation tests on samples with preformed deposits confirm calcite's inhibitory effect on hydrogen permeation.

Assessing inhibitor/metal electrified interface in an aqueous environment: the case of MBI@Cu

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Innovative technological solutions are proposed daily to mitigate corrosion, but one of the most efficient, green, and cost-effective alternatives is using small organic molecules as corrosion inhibitors. A significant effort is made worldwide to propose and test new inhibitors. However, a question remains: What properties must a molecule have to be an effective inhibitor? Molecular modeling can be determinant in answer to that question. Most of the theoretical results in the literature either under-explore their potential by following standard procedures or apply overly simplistic models that neglect fundamental aspects of the corrosion process. With the objective of overcoming that issue, we present a novel approach by creating an accurate model of the interface between the inhibitor, metal, and solvent. The quantum character of the metallic slabs and inhibitor molecules attached to them are considered via the non-equilibrium Green's functions (NEGF) method, allowing for applying a potential to the electrodes. Yet, the corrosive medium is considered by explicitly incorporating water molecules at a molecular mechanics level using the quantum mechanics/molecular mechanics (QM/MM) method. We showcase our approach by investigating the interaction between 2-mercaptobenzoimidazole (MBI) and Cu slabs. Our findings demonstrate that the inhibitor film acts as a physical barrier, displacing the water molecules from the metallic surface. Besides that, we could access the charge redistribution at the interfaces due to the presence of the inhibitors, demonstrating that our methodology can include the effect of a voltage applied to the electrodes, thus going far beyond standard DFT simulations. As a perspective, we are now increasing the complexity of the metallic slab and the corrosive media by considering Cu oxide films at the metal's outermost layer and the presence of a realistic electrolyte by including counter ions in the solution. In summary, this work's significance lies in introducing a method that considers all the necessary ingredients to simulate corrosion properly, significantly improving how we approach this critical problem.

Nitriding effect during ammonia-based direct reduction of iron oxides and its implications on the re-oxidation protection

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Keywords: ammonia, microstructure, re-oxidation, solid-state reduction, saline water corrosion, nitriding

Abstract

Ammonia is a promising alternative hydrogen carrier that can be used for the solid-state reduction of iron oxides due to its ease of liquefaction, transportation, and high volumetric energy density. The main challenge for its utilization in the steel industry is to understand the reaction kinetics for different process parameters and the effect of nitrogen uptake from ammonia (as nitride or solute) into the reduced material. In this presentation we discuss the nitrogen uptake that occurs through both spontaneous and in-process nitriding, which fundamentally affects the microstructure and chemistry of the reduced material. In this regard we explore the effect of nitriding on the re-oxidation properties of the final reduced material and compared with the reduced iron via solid-state hydrogen reduction. Re-oxidation is explored via analysis of the oxide development on the material surface with exposure to a saline solution that mimics common water solutions to which the reduced material can be exposed during transportation. It is worth noting that this aspect of the study pursues an approach of 'corrosion by design', as corrosion occurs here by purpose and the layers formed act as a protective means for unwanted and uncontrolled oxidation of 'green steel' feedstock. The results provide fundamental understanding of the reduction behaviour of iron oxides in ammonia and the associated nitriding phenomena, particularly highlighting the protective role of the nitriding against re-oxidation. As such, the presented work provides a critical understanding of how ammonia direct reduction can be used to develop and tailor a re-oxidation protection of the solid-state reduced iron. The re-oxidation is particularly crucial for world-wide transportation as the reduced iron on its own is highly active to oxidation and can pose a thermal risk due to the exothermic character of the reaction. To reduce this effect, postprocessing of the reduced iron is performed with hot briquetting, which increases the costs and processing time of the iron ore reduction process. With the investigated nitrogen-based protection against oxidation, the ammonia reduction opens a new option to produce and intentionally protect the reduced iron in one single process. This way, the ammonia-based reduction provides the means to reduce the transport costs and simultaneously increasing the technological flexibility of the solid-state iron oxide reduction processing chain.

Electrochemical Sensing for Steering of the Process Steps Degreasing, Pickling and Passivation in Galvanic Process Lines for ZnNi Plating

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Abstract

The paper shows that open circuit potential (OCP) transients allow real-time electrochemical sensing of the process steps degreasing, pickling and passivation in ZnNi plating lines. According to the developed methodology the steel component to be treated is submerged as an electrode into the treating bath at its usual environmental conditions and the course of the OCP is measured against a reference electrode from the moment of submersion into the bath. The treatment is finished when the slope of the potential/time curve reaches a value close to zero ($dU/dt \rightarrow 0$) at a potential plateau. The time elapsed to reach this criteria can be used to steer the cycle time of the corresponding treatment step, to assess the efficiency of the treatment bath, and in case of the process steps degreasing and pickling also to range the contamination intensity of the metal surface with grease or rust.When the ($dU/dt \rightarrow 0$)-criteria is reached in the alkaline degreasing bath, the metal surface exhibits its optimum wettability (proof: contact angle measurements). In the pickling bath an optimum surface activity is achieved (proof: adhesion strength of the ZnNi coating). In the Cr(III)-based and in the Zr-based passivation bath the optimum protectiveness of the passivation layer is obtained (proof: corrosion resistance in the salt spray test).

The industrial applicability of this monitoring methodology, for which an innovative measuring technology has been specifically developed, is demonstrated with an industrial Cr(III)-based ZnNi passivation bath. The sensing methodology which has been developed within the international ZIM-project MONACO-PLATE provides a fundamental contribution to the digitalization of galvanic processes.

Respirometric measurements combined with electrochemical methods

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The Respirometric method is based on monitoring the changes in H_2 and O_2, which enables to quantify the H_2 evolution reaction (HER), the O_2 reduction reaction (ORR), as well as the O_2 evolution reaction (OER). With this universal in situ method, it is possible to gain insights into the cathodic reactions and consequently also to reliably determine the corrosion rate [1]. Combining well established electrochemical measurement techniques with respirometric measurements provides further insights into the occurring mechanisms. By polarizing different working electrodes, the respirometric measurements were confirmed and validated [2]. This enables deconvolution of polarization curves and measure effects such as the negative difference effect or superfluous H_2 evolution on Mg or Al [3]. Furthermore, this also allows investigating transpassivity and secondary passivation, which will be demonstrated on the prominent material stainless steel.

Another common method is Electrochemical Impedance Spectroscopy (EIS), a powerful technique which is not always straightforward in interpretation. Simultaneous respirometric measurements show good correlation on Zinc and could provide helpful parameters for corrosion kinetics and complement the EIS. The entirety of cathodic reactions on Zinc is complex, because it corrodes not exclusively with the regular 4-electron ORR pathway, but can also lead to H_2O_2 formation. Additionally, HER was monitored and confirmed. A thorough analysis of the Zn reaction mechanisms will be presented.

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Corrosion Behavior of Cu, Ni, Zn and Mg in Ionic Liquids Assessed by High Resolution Respirometric Monitoring, Mass Loss, EIS, and Laser Profilometry

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The aim of this work is to identify critical factors that govern the corrosiveness of (functionalized) ILs towards different metals and to investigate the corrosion and protection mechanisms at the metal–IL interfaces. Therefore, the corrosion behavior of Cu, Ni, Zn and Mg under droplets of ionic liquids was investigated by respirometry, Electrochemical Impedance Spectroscopy (EIS), mass loss and laser profilometry. 15 different ILs were investigated in this study with imidazolium, ammonium, pyridinium or pyrrolidinium cations combined with triftlate-, bistriflimide-, chloride-, nitrate-, BF4-, or cyano-based anions. In addition, functionalized ILs with sidechains containing sulfonic acid, nitrile and fluorinated groups were tested.

A new high resolution respirometric electrochemical droplet cell was designed to monitor the rate of the O_2 reduction reaction (ORR) and H_2 evolution reaction (HER) simultaneously during EIS series. The agreement between both monitoring methods proves that as in aqueous corrosion, ORR and HER are the main cathodic processes that accompany metal oxidation in the IL electrolyte. The overall corrosion trends correlated with mass loss results after 30 days exposure and the localization of the attack could be assessed by profilometry.

From the results it can be concluded that both the nature of the anion and the cation are important for the corrosivity. Most ILs were corrosive for Cu where protic ILs and functionalized ILs tended to show higher corrosion rates compared to aprotic and non-functionalized ILs. Ni and the less noble metals Mg and Zn were corroding only in few ILs and were otherwise passive. The differences in the corrosivity for the different combinations of anion, cation and metal are discussed in terms of the availability of protons, the O_2 solubility and diffusivity and surface film formation. Apart from the degradation of the metals, also the degradation of the IL constituents due to corrosion reactions can be induced by reduction, pH induced hydrolysis or deprotonation. The formation of protective surface layers that include IL decomposition products was studied with surface analytical techniques.

An Updated Review on High Temperature Hydrogen Attack: Attack Mechanism, Mechanical Property Degradation, Remaining Life, Fitness for Service and Nondestructive Examination

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One of the most critical and insidious types of hydrogen degradations is the High Temperature Hydrogen Attack (HTHA). In 2014, the U.S. Chemical Safety and Hazard Investigation Board (CSB) published an alerting investigation report due to a catastrophic incident caused by a refinery heat exchanger massive rupture. This rupture was attributed to HTHA. Due to the criticality of HTHA in refining and petrochemical industry and the several research developments, this paper is devoted to provide a comprehensive and updated literature review on HTHA, to help point out the current industrial and research status. Background and recent developments in the THA mechanism identification and degradation levels of different mechanical properties, including tensile strength, ductility and creep resistance, are discussed. In addition, THA susceptibility and rate factors such as metallurgical microstructure, operating parameters, loading and residual stresses and heat treatment are detailed and reviewed. In addition, the recent developments and capabilities in remaining life prediction, fitness for service evaluation and non-destructive examinations are also evaluated and introduced.

Corrosion of infrastructure metals and alloys: effect of inorganic and organic road salts

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Snow and ice control is essential to maintaining the safety and mobility of various roads and sidewalks during the winter months in Canada. Sodium chloride (NaCl) remains the most used de-icing material in Canada. Road salt use is causing significant corrosion to infrastructure and vehicles, which are made of various material classes including different steels, galvanized steel (zinc-coated), aluminium alloy, and reinforced concrete. This research tested the effect of nine different road salts, both chloride-based and organic salts, on the corrosion of mild steel, high-strength steel, stainless steel 304, galvanized steel, and aluminium alloy in field and laboratory tests including mass loss, microscopic investigations, X-ray micro-computed tomography, electrochemical investigations, and metal release tests. For steels and aluminium alloy in atmospheric conditions or neutral solutions, the chloride-based salts were significantly more corrosive than organic salts. In contrast, galvanized steel (zinc) was more attacked by organic salts. This was also predicted from chemical speciation thermodynamical equilibrium modelling. Mixed salts, containing both organic and chloride-based salts, were able to attack all material types significantly. To prevent catastrophic failure of critical infrastructure, there is an urgent need to 1) reduce salt use to a minimum, and 2) consider specific salt-metal interactions as a function of pH value and material classes.

Operando ORP-EIS as a direct (in situ) monitoring of Electrochemical Surface Processes

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Electrochemical Impedance Spectroscopy (EIS) is employed to study the electrochemical processes that satisfy the causality, linearity and stationarity requirements [1]. These requirements hinder the application of the conventional EIS to investigate ongoing electrochemical processes including anodizing and conversion treatments. However, in situ monitoring the oxide film formation can provide an opportunity to better control the properties of the oxide layer. Hence, in situ monitoring of the surface treatment processes is of prime importance.

The Odd Random Phase Electrochemical Impedance Spectroscopy (ORP-EIS) technique, developed in our research group, can measure the time-resolved impedance of non-stationary systems [2]. This methodology was recently extended to quantify nonlinear distortions and obtain Best Linear Time Varying Approximation (BLTVA) of nonlinear time-varying processes like the corrosion process [3]. In the current research, the operando ORP-EIS technique is applied for in situ monitoring of the anodizing of aluminum (Al) [1] and the conversion treatment of zinc. For the anodizing process, according to figure1, the capacitive time constant can correspond to the barrier properties of the oxide layer and enables us to follow the growth of the barrier oxide layer. Moreover, the inductive time constant may be an indication of the surface charge accumulation [4]. On the other hand, this technique makes it possible to monitor the conversion treatment of metals and the role of organic and inorganic additives on the barrier properties of the conversion layer in situ in the bath and look at corrosion and protection protection of unstable metals such as Mg, Al are co. Therefore, the operando ORP-EIS plays a key role to study and better control the ongoing electrochemical process.

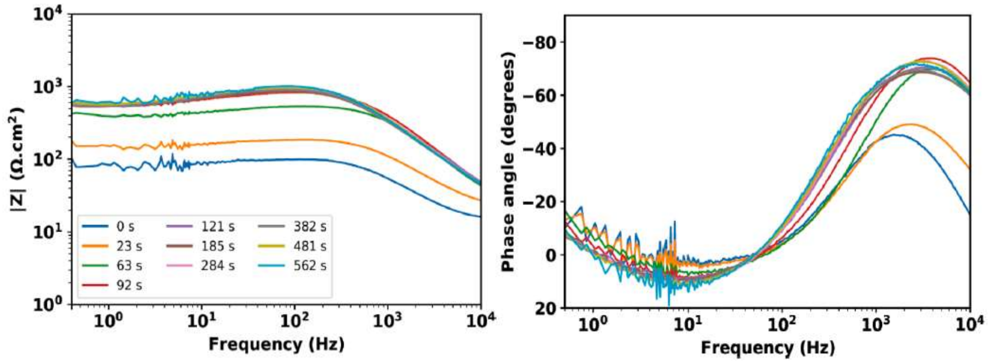

Figure1: Bode plot during the anodizing of AA2024 in the 0.1 M H_2SO_4 solution at room temperature. The anodizing DC potential 20 V (1 min sweep at a rate of 20 V/min and 9 min plateau at 20 V).

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Design of an EIS-based sensor for non-invasive in-field corrosion monitoring

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In-field electrochemical measurement is of great interest for corrosion monitoring of metallic structures. However, traditional laboratory assemblies such as three-electrode electrochemical cells are no longer suitable due to limitations in the size and shape of the analyzed facilities. In addition, the commonly used liquid electrolytes are highly inconvenient because of liquid flow and cell air-tightness issues. This study aims to develop a non-destructive and immersion-free sensor based on electrochemical impedance spectroscopy (EIS), designed to provide detailed electrochemical information about the system while being applicable for in-field measurements.

The proposed sensor consists of two transparent 3D-printed cells connected to a potentiostat. One cell has a 99.99% platinum foil counter electrode and a low-profile Ag/AgCl reference electrode, while the other cell has a platinum foil working electrode. Both cells are filled with solid electrolyte using 0.1 M Na_2SO_4 gelled with 3% w-v agar and placed side by side on the studied surface. In the preliminary work, this EIS-based sensor was applied on different substrates and the results were compared with conventional measurements to validate the sensor's measurements. One particular attention was given to the response of the sensor itself on the measured impedance signal. When necessary, the data were processed to subtract the sensor impedance. The corrected results were close to conventional measurements, with the modulus approximately doubled since the two-cell sensor measures twice the interface.

The proposed "non-invasive" sensor, designed specifically for in-field measurements, has proven capable of obtaining reproducible and accurate high-quality EIS spectra from laboratory samples and, given its unique non-invasive characteristic and versatility, may ultimately serve as a useful tool for various outdoor corrosion monitoring applications.

Modelling anaerobic microbial iron corrosion with direct electron transfer

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The study provides theoretical evidence on how the reversible electrical connection to the bacterial metabolism via cytochromes enables the microbial use of electrons from Fe^0 dissolution to supply the bacterial catabolism. The bidirectional exchange of electrons can interface with a natural corrosion cell, thus influencing the iron corrosion rate.

The model combining electrochemical and biological reactions with the transport of ions explains the mechanism of anaerobic iron corrosion by coupling the bacterial metabolism of *Geobacter* sp. The model bacteria can both deliver electrons from the carbon-based metabolism to an external metal surface coupling with hydrogen evolution, the classic EET metabolism (1), or take electrons from the iron dissolution and couple with inorganic carbon reduction, which can provide the bacteria with energy while interacting with the corroding metal.

Based on recently reported experimental data, we analyzed different scenarios function of local environmental conditions. We calculated corrosion potentials and currents explaining those determined experimentally.

(1) Nature Reviews Microbiology, volume 14, pages 651–662 (2016), doi.org/10.1038/nrmicro.2016.93

The role of shrinkage defect in the corrosion resistance of ductile iron

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Abstract: Ductile iron pipes, widely favored in urban water supply networks worldwide, now confront a formidable adversary—corrosion. This insidious threat jeopardizes both water quality and the integrity of pipe infrastructure. This study investigated the coupling mechanism of shrinkage defects and graphite on the corrosion resistance of ductile iron by electrochemical measurements, quasi-in-situ immersion tests and numerical simulations. The detrimental impact of shrinkage defects was confirmed by elevated corrosion current density and the formation of a porous corrosion product layer. Multiple-galvanic coupling effect among the matrix, graphite, and shrinkage defects serves as corrosion triggers, which is verified by scanning Kelvin probe force microscopy (SKPFM) and numerical simulations. Additionally, quasi-in-situ observations corroborate the deposition of corrosion products and Cl enrichment at defect bottoms, expediting occluded cell formation and corrosion propagation.

Novel dynamic method based on voltammetric modes in SECM for the in situ characterization of copper degradation

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Scanning Electrochemical Microscopy (SECM) has gained reputation for the local determination of species involved in corrosion reactions [1]. However, limitations remain for the detection of ions whose amperometric conversion leads to non-soluble species, as occurs when Cu^{2+} is reduced into metallic copper, thus changing the probe morphology and compromising the accuracy of the image. Therefore, scanning procedures have been developed based on potentiometric sensors or mercury-modified probes. However, it is also possible to implement operation with the microelectrode probes to perform anodic stripping voltammetry, either cyclic (CV) or square wave (SWV), as accurate electrochemical methods for Cu^{2+} quantification [2].

The objective of this contribution was to develop and optimize a dynamic anodic stripping voltammetric method enabling the detection of copper cations released upon copper corrosion, using gold microelectrodes as SECM probes. Deposition and redissolution steps were carried out while the probe was scanning continuously, by the appropriate coupling of the repetitive voltammetric operation and the rasterization routine, avoiding the withdrawal of the probe for the copper reoxidation. CV-SECM and SWV-SECM are proposed as methods to characterize the different reactivities of copper samples when exposed to aggressive and protective corrosion conditions, while additional information on the ability of the surface towards electron donation was simultaneously surveyed with CV-SECM following the addition of a redox mediator. The results are consistent with a heterogeneous nature of copper degradation and the development of protective films or passive layers.

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Influence of microstructure and pore saturation in measuring corrosion rates of a carbon steel API 5L X65 in contact with cement grout in future nuclear waste disposal program

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In the future deep nuclear waste disposal for highly radioactive waste in France (Cigéo), the radioactive waste will be placed in API 5L X65 linings, separated from the Callovo-oxfordian argillite by a cemento-bentonitic type filling material (CBM), composed of CEM III-A cement, bentonite, hydrotalcite, silica fume and water, allowing the steel to be in a passive state thanks to its basic pH (>12). During pilot laboratory tests, a demixing of CBM occurs when the bentonite used is not sufficiently hydrated. The two distinct phases obtained (supernatant bulk phase (b), and solid phase (s)) thus allow us to study and compare the corrosion rate of steel samples in these phases. Linear polarization resistance, chrono-amperometry, voltammetry around open circuit potential and electrochemical impedance spectroscopy were redundantly used at regular intervals for 243 days to measure the corrosion rate both in the supernatant bulk and the solid medium, using a robust Ag/AgCl solid electrode as reference. The high water/solid ratio (w/c=3) of CBM makes the pores saturated with electrolytes. With a porosity of the solid phase of 0.7-0.72 during the first two days of the experiment, the ratio obtained between the corrosion current of the solid phase and the supernatant bulk (s /b = 0.35-0.55), in the range of the ratio obtained by applying the mechanistic model of steel corrosion in a dense porous and saturated medium, with interconnected pores. After the hydration of the cement and solidification of the grout, the porosity decreases below a critical porosity, losing its interconnectivity and decreasing its diffusive properties. The new ratio measured is then significantly lower (s/b=0.07-0.075). Taking into account the microstructure of the pores and mechanisms of capillary condensation, we find a new porosity of 0.22-0.3. This study therefore highlights the variation in the corrosion rate between bulk and porous medium, which depends not only on the properties of the electrolyte, but also on the microstructure of the solid medium, directly related to the electrochemically active surface.

Monitoring of current distribution on a polarized electrode measured by coupled multielectrode array technique

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Coupled multielectrode array (CMEA) sensor represents a macroscopic-size electrode divided into multiple sections. Each section is electrically insulated from other and connected to the common ground via its own zero resistance ammeter. Simultaneous measurement of partial currents allows the spatiotemporal monitoring of corrosion pattern, while all sections are at the same electric potential – common ground. In the present experimental work the CMEA sensor consists of 5x5 array of carbon steel wire electrodes (diam. 0.5 mm).

The objective of the study is to investigate the actual current distribution of CMEA sensor during its cathodic / anodic polarization in water-based electrolyte. Preliminary results indicate that majority of protective cathodic current flows towards the CMEA sections with highest corrosion activity (anodic current) measured beforehand during open circuit potential conditions.

Various experimental conditions will be tested such as electrolyte chemistry and conductivity, and the initial corrosion state of CMEA sensor. Moreover, the critical cathodic protection potential that warrant corrosion protection to all sections of CMEA sensor will be addressed, as well as the onset of corrosion activity after the cathodic protection has been switched off. In the case of anodic polarization we seek to elucidate whether the onset of localized corrosion may act in a protective way for the remained sensor's surface.

Besides measuring partial currents from CEMA sensor and its common corrosion potential, the time lapse macro photo imaging provides additional source of information. The exact location of corrosion products build-up can be determined from these images. Imaging therefore gives additional information for the explanation of the observed partial currents distribution and intensity.

Localized corrosion behavior of Tubing Steels under complex water injection conditions

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Abstract text - The corrosion of injection well is an urgent problem restricting water injection. The injection well environment contains Sulfate Reducing Bacteria (SRB) with a content of 0-1000 cell/mL; the dissolved oxygen content is high with a content of 0.2-5 ppm; it also contains residual H2S/CO2 with a maximum content of 500 mg/L; the water injection temperature is in the range of 40℃-75℃; salinity is high with a maximum content of 130,000 mg/L of Cl- in Middle East H oil field. Four factors (SRB, DO, H2S/CO2, temperature) and three-level orthogonal tests were designed and carried out to study the low alloy steel L80, which is the most widely used as tubing in H oil field. The results show that in SRB-DO-H2S/CO2 environment with different levels of factors, serious general corrosion and pitting corrosion occur on L80, and the maximum pitting corrosion rate is 8.84mm/a. According to the calculation of 4 1/2" tubing, it will be corroded and holed in about 8 months. Through the analysis of orthogonal test results, SRB and dissolved oxygen are the main controlling factors of pitting corrosion of L80. Dissolved oxygen causes pitting corrosion. The local acidification of SRB accelerates the development of pitting corrosion. The influence weight of temperature and H2S/CO2 on pitting corrosion of L80 steel is lower. The general corrosion rate of martensitic stainless steel 13Cr and super 13Cr in simulated injection well environment is lower than 0.1 mm/a, but the pitting corrosion rate is higher, up to 5.7 mm/a. The general corrosion rate of 22Cr and 25Cr, duplex stainless steel in simulated injection well environment is also lower than 0.1 mm/a, and there is no obvious pitting corrosion. Comprehensive analysis shows that the super duplex stainless steel 25Cr can meet the water quality requirements under the poor water quality level; in order to improve the water quality and reduce the corrosion of injection tubing, the priority is SRB, dissolved oxygen and H2S / CO2. After the addition of a system inhibitor-bactericide, the general and local corrosion of L80 under such complex water injection condition was significantly controlled.

Predicting corrosion under natural (charge-conservation) conditions

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Laboratory and numerical corrosion experiments typically impose an electric potential on the metal surface, differing from natural corrosion conditions, where corrosion generally occurs in the absence of external current sources. In this work, we present a new computational model that enables predicting corrosion in the absence of external current sources (i.e., under natural, charge-conservation conditions) [1]. The metal potential, an output of the model, is allowed to change, capturing how the corrosion and cathodic reactions must produce/consume electrons at the same rates, as in natural conditions. Finite element simulations are performed over typical pit geometries and a large range of concentrations. The results highlight the notable influence of the charge-conservation assumption and pioneeringly quantify corrosion rates under realistic conditions. They further show: (i) the strong coupling between the corrosion rate and the hydrogen and oxygen evolution reactions, (ii) under which circumstances corrosion pits acidify, and (iii) when corrosion can become self-sustained lacking oxygen. Oxygen was found to be required to develop acidic pits but it was also shown that pits can sustain corrosion lacking oxygen. The results are relevant to a wide range of corrosion phenomena, including the corrosion of reinforced concrete structures.

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Phenomenological model for estimating corrosion kinetics information and anodic current

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The current study utilizes measured corrosion rates of mild steel and chemical oxygen demand (COD) to estimate parameters of the Butler-Volmer (BV) equation adapted for concentration dependence of the exchange current density. Hence, enabling to obtain corrosion kinetics from raw data and further facilitating to measure the anodic current at any given time. The concentration of metal ions at the metal surface, which can be estimated using the anodic current, and the oxidizing species at the metal surface could help analyze phenomena such as corrosion fouling.

Corrosion rates were obtained from a cooling water system containing multiple corrosion inhibitors, antiscalants and ions. The BV equation was individually fitted to events highlighted in Figure 1, as the transfer coefficient is affected by concentration of ions and inhibitors. The sweep rate was set to 0.1 mV/s over a scan period of 100s. The diffusion coefficient D (m^2/s), shown in Figure 1 is for of metal ions from the surface to the bulk solution. Oxygen was considered as the oxidizing species. COD was assumed to be equivalent to oxidizing activity due to microbial corrosion, i.e. the concentration of Oxygen was estimated to be the same value as the COD. It should be noted that the values of the BV parameters differed with the type of oxidizing species (e.g. Cl_2, NO_3^-) considered. How the accumulative effect of all oxidizing species could be quantified is yet to be determined. Charge transfer coefficients are generally accepted to be higher in regions with high inhibition efficiency. However, criteria for evaluating the validity of parameters is yet to be refined.
The values of the parameters of the BV were determined based on the minimum value of the error function within 200 iterations. The error function was set to $\left\{(i_{a,\min(i_{net})} - i_{corr}) + i_{net,E-E_{eq}=0}\right\}$, where i_a is the anodic current, i_{corr} the corrosion current and $i_{net,E-E_{eq}=0}$ the net current at 0 overpotential.

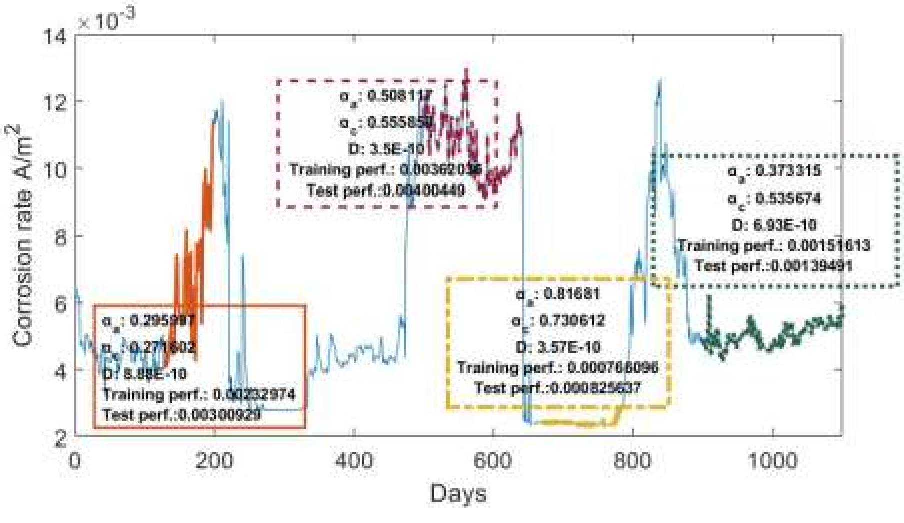

Figure 1 - Parameters of the BV equation. α_a(0.25< anodic charge transfer coefficient<1), α_c (0.25< cathodic charge transfer coefficient<1), D (diffusion coefficient, m^2/s)

The training and test data sets were defined per region highlighted, such that the statistical properties of the two data sets are similar.

Under strain: Using data analytics to unearth the relationship between geohazards and pipeline corrosion

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Prediction of external corrosion using data from in-line inspections (ILI) can be instrumental in making proactive pipeline integrity management decisions, especially when integrated with geospatial data. Recent studies have shown the effectiveness of machine learning algorithms in this area. Understanding pipeline corrosion, which initiates from failures in protective mechanisms like coating defects or insufficient cathodic protection, is critical. This work investigates how a relationship may be established between the presence of bending-strain areas and the progression of external corrosion. As the initiation of external corrosion requires both failure of the external coating and failure of the cathodic protection system, it may be possible to limit the damage that is caused in areas of bending strain. Additionally, the study examines how integrating geohazard characteristics into machine learning models may improve the prediction of external corrosion. ILI data for inspections completed in the United States is sourced from the Integrity Data Warehouse (IDW), a global repository with over 26,000 ROSEN's ILI operations. This data is combined with geohazard spatial information to analyze the relationship between geohazards, external corrosion, and the susceptibility of pipelines to bending strain-related corrosion. The research emphasizes the role of data-driven insights in maintaining pipeline safety and reliability. The paper provides insights into the complex interplay of geohazards, bending strain, and corrosion, informing better integrity management strategies. This study suggests a shift towards a holistic, automated, machine learning-assisted approach for pipeline integrity, highlighting the importance of data-driven approaches for safety and reliability.

Modelling of lead corrosion in contact with a HCl solution, influence of the corrosion product presence

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Hydrochloric acid is the hardest common acid in terms of corrosion. However, it is widely used in the industry for regulating the pH level of a wide variety of manufacturing processes (production of drinking water, pharmaceuticals, disposal of slaughter house waste). But the main fields of HCl application are in cleaning, pickling, and wastewater treatment. Intensive care in choosing materials is required to deal with the acid itself, whether in slightly dilute concentrations or actual solutions containing a known amount of hydrochloric acid. Everyday uses for HCl acid tend to focus on the corrosive effects of this acid on material in general, and particularly on lead. In fact, the elimination of lead (Pb) in many areas has become a major problem for a variety of items, including electronic devices, paint, and hydrometallurgical. That is why the lead corrosion behavior in the acid liquid phase is particularly studied. The dissolution of lead with acidic fluids is a complex process involving the interplay of transport and chemical reaction processes. Even if the modelling of the different equations made it possible to establish the main stages of the corrosion mechanism, there is no numerical model allowing the behavior of lead in HCl to be simulated. In fact, the numerical tools are more dedicated to simulate the thermodynamic equilibrium of the leaching, to model soil solid-solution phase distribution of Pb, or to examine corrosion inhibitors. However, having a practical tool that is useful for simulating the different stages of the Pb corrosion process or to help data interpretation would be an important asset, which could be used in many domains.

The lecture outlines the first stages in modelling lead corrosion upon contact with an anaerobic and aerobic HCl solution. These developments are carried out with COMSOL Multiphysics. , When lead is immersed in a deaerated HCl solution, its dissolution leads to saturation of the electrolyte with the consequent precipitation of corrosion product. The PbCl2 corrosion product is simulated with a porous domain using either fixed or variable porosity. The results show a PbCl2 development that takes place through growth in space as well as through densification. The simulation highlights the fact that the PbCl2 layer is more compact near the surface of the electrode in accordance with the place of creation of the lead ions. Moreover, The presence of oxygen modifies the chemistry of the environment and its influence is studied numerically by taking into account an aerobic environment, confirming that it is possible to form other oxides as observed experimentally.

Fractal Modelling of Pitting Corrosion Activity from Polarisation Curves Datasets

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Fractal geometry, widely applied in various scientific/engineering fields, has crucially clarified the complexities of material structures. However, its use in corrosion science has not been fully realized, particularly from the electrochemical perspective. This study represents a pioneering application of fractal analysis to electrochemical responses in pitting corrosion, focusing on 316L stainless steel. The novelty of this research lies in its application of the Mandelbrot model to pitting corrosion, a first in the domain. While fractal analysis has been utilized to describe the pit morphology[1–3], the Mandelbrot-Zipf distribution's role in modelling the complex, autocatalytic nature of the electrochemical processes at play represents uncharted territory. Our study examines the statistical distribution of pitting current activity through a comprehensive dataset (N=84), encompassing large sample populations across 3 NaCl concentrations. Our data suggest robust statistical features and multifractal patterns in the higher ranks of current density distribution. Through the Mandelbrot-Zipf function, a power-law distribution adept at describing frequencies in varied phenomena[4,5], we interpret the steep decline at higher ranks as indicative of the rarity of pit formation during the anodic branch of potentiodynamic polarization curves. This characteristic rapid fall-off in the distribution's tail is essential for understanding pitting as a rare event in electrochemical processes. These findings suggest a scale-invariant pattern in log(j) distribution, indicative of a potential fractal nature in pitting corrosion.

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The Importance of Corrosion to CO_2 Emission of Steel: Research on carbon emission calculation method of steel pipelines based on the coupling of life cycle model and corrosion model

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Steels not only have carbon emissions in the manufacturing, transportation, installation, service and recycling stages, but also determine the consumption of steel materials per unit time by the life of steel materials, thus affecting the overall carbon emissions. Our research has specified a method for accounting for the total life-cycle carbon emissions of steel materials from manufacturing, transportation, installation, service to recycling, puts forward the idea of reducing the average annual life-cycle carbon emissions of steel structures through corrosion control technology. Taking steel pipelines in chemical industry, oil and gas fields industry and long-distance natural gas transportation as examples, with the life prediction methods we proposed, the life-cycle carbon emissions of steel pipelines in typical industrial conditions were calculated. Although the use of appropriate corrosion protection will bring additional carbon emissions, it can significantly prolong the service life and effectively reduce the average annual life-cycle carbon emissions, with the maximum emission reduction potential of more than 80%. The results of our research provide a theoretical basis and quantitative method for reducing carbon emissions of steel materials by using corrosion protection, and propose a new measurement method for carbon emissions of steel materials throughout the life cycle.

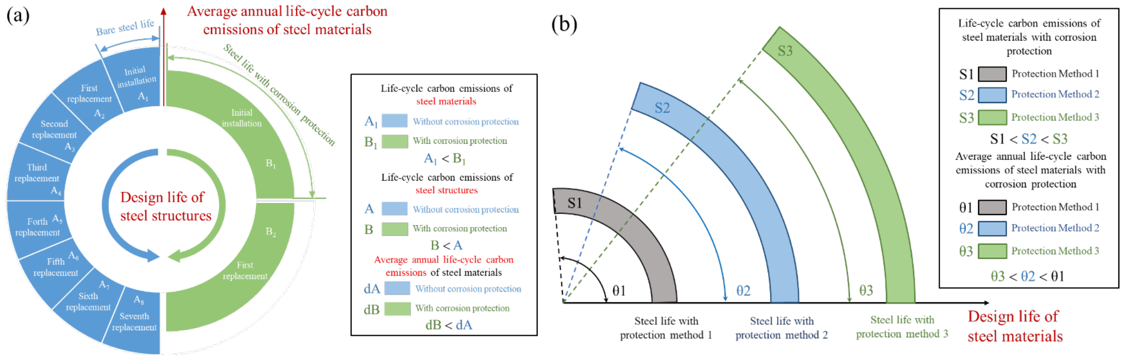

Fig. 1 The life-cycle carbon emission model of steels considering corrosion

Making the Transition Smoother: From University Corrosion Education to Field Corrosion Expectations

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Abstract

There has naturally been a gap between the corrosion education one receives in a university (where corrosion engineering is taught) and the corrosion control practices routinely carried out in any particular field or operating company.

Such a gap is believed to be further widening as more operating companies are adapting to the newer asset integrity management systems which are based on the corrosion management approach, rather than the corrosion engineering discipline.

Unfortunately, the relevant curriculum of universities where corrosion engineering discipline is taught, solely focuses on the corrosion engineering subject Thus, for the pertaining graduate corrosion engineers it would increasingly take longer time to adjust themselves to the typical field corrosion expectations which are becoming more corrosion management orientated.

The recommended solution could be rather easy and straightforward: either the corrosion management subject could be incorporated into the current curricula or the graduate corrosion engineers could attend a short-term corrosion management training course just prior to or immediately after their graduation. Such complementary corrosion management education or training would not only significantly improve their chances of finding their first job more quickly, but also would help them to perform better and create greater added value at the start of their professional career.

Corrosion Education - From Rust, Degradation and Deterioration to Electrolysers, Batteries, and Steam Reforming Reactions

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The education of corrosion engineers entails a number of natural science-based modules, based on the fundamentals of chemistry, physics, and metallurgy/materials science. These are then interlaced with engineering disciplines, the likes of chemical, mechanical, civil and electrical/electronic engineering, with programming/computer science featuring nowadays as a standard addition. Application of all these diverse topics and disciplines make the field of corrosion science and engineering quite challenging to grasp, and people interested to learn more about this exciting field get often overwhelmed by multi-topic based challenges. In contrast, understanding how all these disciplines can successfully be synchronised, provides ample opportunities to generate a broader picture of (potentially) disruptive technologies. Corrosion science and engineering is certainly at the heart of shaping the net-zero engineering landscape.

This presentation will combine traditional ideas of oxidation, redox reactions, and materials performance, with a view of how to map those onto the rapidly emerging renewable energy landscape. A number of short case studies will be presented, demonstrating how the field of corrosion is successfully applied to drive net-zero innovation. Topics include, for example, the application of simple battery technology to drive the decoupling of water splitting reactions, and how knowledge of rust formation is applied for hydrogen synthesis in chemical looping reactions. A view of how these ideas can easily be incorporated in corrosion teaching will also be discussed.

An international corrosion mentorship program – insights from the first year

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The Canadian-funded "NSERC CREATE training program for Excellence in Canadian Corrosion Education through internationalization, equity, and interdisciplinarity (CORRECT)"[1] is an international corrosion training program that, among others, aims at increasing the number of trainees and the participation of underrepresented groups in corrosion science and engineering. As part of their missions, CORRECT and the Young European Federation of Corrosion (YEFC) joined efforts to launch and administer a new global corrosion mentorship program (CORmentor)[2]. Mentorship programs have been shown to positively intervene with biases and stereotypes hindering the career aspirations and progress of underrepresented groups in Science, Technology, Engineering, and Mathematics (STEM) fields.[3] Such programs on a global scale are rare in the field of corrosion science and engineering. 50 pairs of mentees and mentors were matched from 16 countries (9 European countries, Canada, Colombia, Ghana, Nigeria, India, Qatar, and Iran), in both academia and industry. More than 80% of these pairs were actively meeting. The program offers meeting guidelines, is rigorously evaluated, and includes a whistleblower system to mitigate negative relationships. A virtual workshop with attractive topics and possibilities to network is also offered. Here, we evaluate the first year of this program and present our insights and future revisions and plans.

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An academic laboratory course on corrosion and protection of metals at Politecnico di Milano: teaching experience and students' feedback

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In this work, the teaching experience and students' feedback of the course "Laboratory of Corrosion and Protection of Metals" are discussed. The course is held for the students of the Master's degree program in Materials Engineering and Nanotechnology at Politecnico di Milano, Italy. It consists of 50 hours, divided in laboratory activities (30 hours, 60%) and ex-cathedra lessons for the remaining part (introduction to the practical experiences and final remarks). The course is currently held for a maximum of 25 students. The aim of the course is to provide an experimental-laboratory approach to the study of metal corrosion and its prevention, supporting and consolidating the theoretical and phenomenological knowledge acquired by students in a propaedeutic course in the Bachelor's in Materials Engineering and Nanotechnology. Practical experiences cover all the main aspects related to corrosion of metals and its protection: corrosion mechanism, electrochemical techniques, accelerated and field testing, selected corrosion forms in different environments, protection techniques, corrosion monitoring. Laboratory activities are anticipated by a brief theoretical introduction by the teacher. Moreover, seminars on specific topics are offered to students by corrosion experts from industry. An introductory seminar on philosophy of science is also proposed during the course to improve sensibleness of students on epistemology, semantics, and ontology; the connection between corrosion and art by a seminar on the interference colours on titanium is discussed, too.

During the course, students have the opportunity to be hosted by the virtuous Italian company Snam S.p.A. in San Donato Milanese (Milan), whose main core business is related to the transportation of natural gas in all the country and by the company M-I stadio S.r.l, which manages the activities of the "G. Meazza S. Siro" stadium on behalf of the two football clubs of Milan. During the visit to the structure, students can carry out some monitoring measurements to the reinforced concrete structure as part of the program of corrosion assessment and its protection.

In both situations, the discussion of the main aspects related to the design of anti-corrosion systems, their inspection and monitoring (from technical to economic considerations) stimulate a positive Q&A session which generates curiosity in students. The connection between theory, experimental activity from one side and management and monitoring of real structures/infrastructures on the other side generates a virtuous learning outcome in students.

Among the positive aspects of the course, there are the strengthening and improvement of the knowledge with an experimental approach, not always easy to transfer with numerical exercises in classroom, and the interaction among students and with the teacher, which helps the self-evaluation of knowledge and the social interaction.

EUROCORR 2024

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Title: How to define corrosion for medical community? A case study and some perspects.

Corrosion is not well defined and known from the doctors and pharmacists. Euro-Pharmat, from 2015, wanted to develop the interaction between 'corrosion doctors', engineers and researchers, and pharmacists especially. Most of the time there is no corrosion but it is not. The challenge was in 30 mins to define from the scientific point of view the corrosion and to get some current examples, in the daily life practise, to pharmacists. This practise is firstly innovative in France that is the reason why we want to exchange about this practise. The assembly was constituted from more than thousand attendees.

First, we stated the thermodynamic and kinetic concepts. The question was: How to explain shortly these concepts but accurately? We are suggesting a pathway.

Secondly, we are speaking about the implants that the pharmacists are dealing with from buying by the hospital to manage the incidents from the patients. In France, we are speaking about Matério-vigilance. Stainless steel, titanium alloy and cobalt-chromium-molybdenum alloys would be presented from the view of comparison of properties, chemical and mechanical. It sounds relevant for pharmacists to have a right order of magnitude.

Thirdly, we are presenting the grey matter for scientists and pharmacists. Are we able to find by calculation some electrochemical values like resistivity? The patients are different for size-length, medium constitution, etc. We were discussing about this issue. A learning process is starting for pharmacists from life learning. The feedback sounds good from pharmacists. We may wonder about the efficiency of this kind of lecture. A group of scientists and pharmacists may be constituted for improving this kind of learning process.

Mastering the climate challenges in corrosion education: Implementing strategies for well-trained next-generation engineers

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Abstract

The preparation of well-trained next-generation corrosion experts, engineers for fulfilling green deal, climate ambition, zero emission, decarbonisation of heavy industry, mobility and smart cities presents several challenges and opportunities for high innovation, research-based education. Rapid increase in clean technologies such as batteries, battery storage and hydrogen technologies require a workforce that can understand the risks, adapt as necessary to new risks, and respond when it counts most. Lithium-ion batteries, fuel cells and hydrogen storage unlock great opportunities for the clean energy transition but also come with the rare but serious risk of failures, esp. joined with material degradation which can lead to explosions etc. We see tragic cases of battery fires causing injuries, such as the French warehouse in January 2023 or the Dutch cargo ship in July 2023. Battery fires are a risk for consumers as well, as the e-cars fires after floods or hurricanes, such as in Florida in September 2023. It needs to be verified if corrosion place o role here and what is behind these incidents and how could be prevented within innovative, interdisciplinary and broad safety training including corrosion. Ideal collaboration on new training/educational modules is within industrial associations from these sectors. We are working together with EIT InnoEnergy Skills Institute and Batteries Europe task forces on on-line courses and next step will be practical exercises in R&D centres and in dedicated corrosion and battery labs at university level.

Acknowledgments:

This work was carried out within the frame of the project KEGA 006TUKE-4/2021 "Preparation of new hybrid engineers for battery systems, energy storage and hydrogen technologies" and project VEGA 2/0072/22 "Research of the resistance and prevention of modern structural materials against hydrogen embrittlement".

An effective approach to teach corrosion fundamentals and assess students learning outcomes

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Awareness and fundamental understanding of corrosion become more and more crucial for next generation scientist and engineers who are involved with any materials selection, design and discovery in any industrial sector of energy, transportation, healthcare and communication construction. Corrosion fundamentals teaching is often delivered for general material science students in a limited teaching hours by different approaches 1) Lecturing corrosion theories with some relevant case studies for assessment, 2) Demonstration corrosion fundamental theories through lab practices, and 3) Combining corrosion fundamentals lectures with lab practices. In this paper, the reflections in different approaches are summarized from the past practices, and an approach on effective delivery of corrosion fundamentals and assessment student learning outcomes with some well-designed lab practices will be discussed.

Ballast Tank Corrosion: Studying Tubercles Microbiome

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Ballast tank corrosion is a critical concern in maritime engineering, impacting the structural integrity and longevity of vessels. Corrosion reactions release iron into the bulk waters that can re-precipitate, forming mound-like features known as tubercles, that can exacerbate localized corrosion. The role of microorganisms in tubercle formation remains debated, with limited evidence to support their participation. This study delves into the microbiome of tubercles, seeking novel insights into the intricate relationship between microbial communities and the formation of these structures on the ballast tanks of an offshore platform in Australia.

High-throughput DNA sequencing from tubercles revealed substantial variation in microbial community structure and composition across samples, even within tubercles from the same ballast tank. The microbial diversity within tubercles was high, with over 40 phyla detected. Predominant phyla included *Proteobacteria, Actinobacteria,* and *Firmicutes*, aligning with previous observations in tubercles from reclaimed and drinking water systems. Variations in the microbial populations indicated that the tubercles' growth and composition can be affected by the specific conditions of the surrounding environment, including material substrate, water chemistry, oxygen level, and location within the tank.

Remarkably, despite the microbial composition varied across samples, the metabolic capabilities of the communities were very similar in all tubercles. This suggests that, despite microbial variations, the communities inhabiting the tubercles can use the same metabolic pathways to survive in the environment. Positive correlations between tubercle mineralogy and the abundance of specific taxa supported the hypothesis that microorganisms contribute to tubercle formation, particularly those with metabolic capabilities that promote corrosion processes. The findings of this study suggest that microbial contamination in ballast tank water contributed to the corrosion processes leading to the formation of these iron structures.

Effect of zinc anodes on the behavior of antifouling coatings applied on copper alloys

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This work targets the investigation of anti-fouling coatings for corrosion protection of bronze propellers in marine applications. Propellers are usually protected by zinc alloy sacrificial anodes. Moreover, these systems are coated antifouling varnishes to prevent bio-fouling development and become a barrier for corrosion protection. Several commercial anti-fouling paints work by releasing chemical biocides with the aim of reducing the adhesion of organisms on submerged surfaces. However, when sacrificial anodes are employed with coated metals cathodic delamination can occur. This is one of the main failure mechanisms for organic coatings in seawater, the outcome is the weakening or the complete loss of bond at the interface coating-substrate. The reduced adhesion is related to electrochemical reactions (cathodic disbonding).

This work investigates the cathodic delamination resistance of anti-fouling systems. In particular, different formulations of primers with their antifouling topcoats for copper alloy substrates are investigated in order to evaluate the resistance to delamination. This behaviour was assessed by electrochemical methods (Potentiostatic Polarization, Electrochemical Impedance Spectroscopy). Besides, immersion tests of coated panels in natural marine environments are used to compare laboratory results with in-field results. Moreover, the efficacy of different biocides is considered in this work.

Discontinuous development of pitting and localized corrosion for steels in marine immersion

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Pitting corrosion sometimes is claimed to occur only for metals and alloys that have a passive film. However, detailed experimental observations have shown pitting of mild steels almost immediately after first exposure, even in triply distilled water (Mercer & Lumbard 1995). Both for passive-film metals and others, including mild steel, the initial pitting develops in depth and spatial extent and may form localized corrosion that then develops further with renewed pitting (Melchers & Jeffrey 2022). The result is a process that is discontinuous in development and in time. Although largely ignored in the corrosion literature, extensive digital scanning over large surface areas with clear evidence of corrosion pitting has produced large trances of data from which the most extreme depths of pits and localized corrosion can be extracted. Analysis of the data in principle requires the use of the Gumbel Extreme Value (Gumbel EV) distribution. Data from the exterior of cast iron pipes buried in soils, the interior surfaces of water injection pipelines and crude oil production pipelines and also for steel coupons exposed to seawater all exhibit, repeatedly and consistently, highly non-linear patterns on Gumbel EV plots. These patterns are proposed as showing discontinuous pit depth development, both for shallower and for deeper pitting. The mechanisms potential involved are considered in the light of modern theories for pit depth initiation and development.

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Corrosion impeding concretion layers formed on shipwreck steel in the Belgian North Sea

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Steel shipwrecks submerged along the Belgian and French North Sea coast exhibit concretion, which results in remarkably low corrosion rates. The primary objective of this study was to investigate the developed concretion layers and gain a more complete understanding of the gradual deposition processes in the North Sea. Detailed microstructural examination by scanning electron microscopy, energy dispersive X-ray spectroscopy and X-ray diffraction of two distinct specimens reveals the presence of an intricate multilayered structure within the concretion. Nearest to the metal surface, a layer of 100% akaganeite is found. This layer originates from corrosion products exhibiting elevated concentrations of Cl^- ions at the metal surface. Subsequently, various iron oxides, including goethite, lepidocrocite and magnetite are observed. Moving further outward, layers emerge that encompass both corrosion products and compounds from the environment. These layers feature calcium carbonates (calcite and aragonite), calcium sulphate (gypsum) and quartz (sand). Additionally, a displacement of calcium by iron results in the formation of an additional phase consisting out of hard, dense siderite mixed into calcite. Ultimately, the concretion's surface is coated with a biofilm.

Keywords: Concretion, conservation of shipwrecks, corrosion rate, marine infrastructure, microbial induced corrosion

Corrosion of World War I ammunition at the Paardenmarkt, North Sea

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After World War I, a substantial quantity of residual toxic German ammunition was deposited on the "Paardenmarkt," a sandbank near the Zeebrugge port. To evaluate the physicochemical condition of munitions buried for over a century, due to the prohibition of bringing certain grenades to the surface, an experimental approach was employed. Subsequent modelling will be applied to extrapolate results over the extended time span. The experimental setup aimed to closely mimic "Paardenmarkt" conditions, including seabed characteristics (a mixture of silt and sand) and potential freshwater influx altering seawater salinity. Brass, steel, and zamak were selected to represent commonly used ammunition construction materials. Samples, including galvanic couples of steel/brass and steel/zamak, were exposed to soil and water in various configurations to simulate burial conditions (buried in the sand, laying on the sand and upright) and assess the effects of different water types (salt water, brackish water, fresh water and salt water with a weekly addition of sodium acetate to stimulate bacterial growth). Sampling occurred at intervals of 2, 6, 12, 24, and 36 months, with eight repetitions per time point. XRF analysis was conducted on coupon surfaces before and after corrosion product removal, and corrosion rates were calculated using the weight loss method.

For zamak, the corrosion rates range from 0 to 0.021 mm/year after 6 months of submersion and from 0.003 to 0.014 mm/year after 24 months of submersion, depending on water type and configuration. For iron, the corrosion rates range from 0.012 to 0.050 mm/year after 6 months of submersion and from 0.018 to 0.042 mm/year. The decrease of average corrosion rate with longer submersion periods is as expected. The most elevated corrosion rates are observed when the coupons are positioned in an upright orientation within the sand and water. This phenomenon is readily explicable due to the establishment of a differential aeration cell, which accelerates localized corrosion at the sand/water interface, consequently raising the average overall corrosion rate.

Formation of Mg-Fe layered double hydroxide on carbon steel at OCP in artificial seawater

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Layered double hydroxide (LDH) can form on the surface of steel as a result of corrosion in seawater. The most reported corrosion products in the seawater environment are different types of green rust. Such products are the hydroxide of $\mathrm{Fe}^{\mathrm{II}}$and $\mathrm{Fe}^{\mathrm{III}}$ that incorporate anions like sulfate, carbonate, and chloride within their layers. Moreover, the abundance of Mg^{2+} cations in seawater and high interfacial pH in cathodic protection can promote the formation of Mg-Fe LDH. Regarding the fact that Mg-Fe LDH formation is a consequence of pH augmentation, the present study focuses on the possibility of the formation of Mg-Fe LDH at open circuit potential (OCP) with pH variation. For this purpose, tests were performed on construction steel in artificial seawater (ASW), which was prepared based on ASTM Standard D1141. The samples were immersed in ASW for a few days and linear polarization resistance (LPR) measurement was applied hourly around (OCP) during immersion time. The influence of pH and temperature on the corrosion products was investigated by X-ray photoelectron spectroscopy (XPS). The XPS elemental scanning showed the presence of Mg on the surfaces. The formation of Mg-Fe LDH in certain conditions after a few days of immersion was approved by scanning electron microscopy (SEM), and grazing incidence X-ray (GIXRD).

Keywords: Corrosion products, Mg-Fe LDH, XPS, GIXRD, artificial seawater.

Marine corrosion of carbon and micro-alloyed steel: comparison between specific natural conditions (La Rochelle seaport) and laboratory conditions

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Carbon steel and low alloy steel coupons were immersed for 6 to 9 months in natural marine medium (Les Minimes seaport – Atlantic Ocean, La Rochelle, France) and in laboratory conditions, but using natural seawater sampled in the seaport. The corrosion processes were studied by open circuit potential (OCP) measurements and polarization resistance (R_p) measurements. At the end of the experiments, the corrosion product layers were characterized by µ-Raman spectroscopy and X-ray diffraction. Various steel grades with increasing Cr content (from 0.02 to 1.1 wt.%) were considered, some of them also containing various amounts of Al, Cu, Ni and/or Si.

R_p measurements showed that the resistance to corrosion was significantly improved in seaport conditions only for the low alloy steel containing 1.1 wt.% Cr and 0.5 wt.% Al. In laboratory conditions, the low alloy steel containing 0.8 wt.% Cr but no Al also showed improved resistance to corrosion. The analysis of the corrosion product layers after 6 and 9 months of immersion revealed significant differences between natural and laboratory conditions. In natural conditions, besides the specific presence of FeS due to bacterial activity, the formation of the sulfate green rust ($Fe_6(OH)_{12}SO_4\cdot 8H_2O$) was favored with respect to that of magnetite (Fe_3O_4), and that of goethite (α-FeOOH) with respect to lepidocrocite (γ-FeOOH). Finally, the improved resistance to corrosion was associated with corrosion product layers enriched with FeOOH compounds.

If results obtained in laboratory and natural conditions may differ, laboratory studies remained necessary to provide the information related to the main electrochemical processes and interpret the origin of the discrepancy with "natural" conditions whatever its origin (influence of micro-organisms, organic matter, sediments, local variations of seawater composition, etc..)

Saline resistant weathering steel for saline applications

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Abstract

Protection of steel structures against corrosion in offshore environments is a challenging task compared to rural or industrial environments, mainly due to the harsh conditions induced by the high load of chlorides in the seawater and the atmosphere. The offshore market is seeking to reduce its huge maintenance cost, therefore, a new plate steel product – with enhanced corrosion resistance to atmospheric marine/saline weathering conditions – is being developed for applications in saline environments.

The development of the metallurgical concept resulted in steel compositions with a good combination of corrosion-resistance, mechanical properties and weldability. Industrial trials in a heavy-plate mill have proven the feasibility and robustness of the concept. The results of mechanical characterisation showed that a S420 strength level is comfortably achieved for plates of 20 mm thick, and this is within reach for plates of 50 mm thick as well.

This work focusses on the results of corrosion testing of saline resistant weathering steel. Since only real exposure corrosion tests can provide conclusive information concerning the corrosion performance of the steel product, multi-year exposure tests have been launched and are currently running. The corrosivity of the exposure sites in this research are in the range of C3-C4 until CX. Besides bare steels also welded and painted steels are tested. The corrosion results show the improved corrosion resistance of saline resistant weathering steel compared to the conventional S355MLO grade.

Since the enhanced corrosion resistance of weathering steel is attributed to the formation of a patina, an in-depth characterization of the rusts formed after corrosion testing is performed by advanced surface analytical tools.

Developments in 20 years of coating maintenance on the Rion-Antirion Bridge, in marine and coastal environment.

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The Charilaos Trikoupis Bridge in Greece is a multi-span cable stayed bridge linking the continent with Peloponnese, crossing the Corinth gulf between Rion and Antirion towns. This large bridge, with 9 international awards, has been designed & built by a joint venture of VINCI Construction and 6 Greek construction companies. Inaugurated in 2004, the bridge is built in a very adverse location: deep seabed, intense seismic activity associated with large tectonic movements, strong currents, winds & waves, ship collision risk, and high corrosivity due to the marine and coastal environment. The Concessionaire, Gefyra SA, with major shareholder VINCI Concessions set-up a specific monitoring and maintenance plan to fulfil the service life of 120 years.
Supported by fully digital data from visual monitoring (from 2005) and detailed records from maintenance projects, the technical dept of the Concessionaire plans and executes corrosion protection operations on the steel structure and equipment that are optimized for each section of the bridge. The maintenance approach relies substantially on in-house resources for supervision and implementation within QHSE values. The team develops internally: inspection attributes, defect criteria, maintenance triggers, durability testing to validate coating systems, parametric cost forecasting tools to optimize the life cycle cost for the Concession period (till 2039) and specific work procedures to deal with challenging construction details. Furthermore, since 2021, the Concessionaire has introduced a pilot program with a water based coating which, apart from the environment benefits, is being reviewed for durability, workability and productivity.

Focusing on protective coatings, this paper describes the developments over 20 years of maintenance of this major infrastructure in a marine and coastal environment, that combines the preservation of the asset with engineering best practices and cost optimization.

Photogrammetry for FPSO Mooring Chain corrosion Monitoring -

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Mooring lines for permanently moored Floating Production and/or Storage and Offloading Units (FPSO) are critical components to ensure that the floating units remains on station at all to times and therefore are a key contributor to their integrity. The mooring line of a floating unit moored in deep water environment is usually consisting of a chain - synthetic wire rope - chain assemblies, attached to piles at the bottom and connected at the top to the FPSO. Mooring chains are made of carbon steel (CS) and exposed to harsh seawater environment and high corrosion risks. Corrosion control of the mooring chains is then essentially based on corrosion allowance (CA) when uniform or generalized corrosion is the expected type of corrosion for CS exposed in seawater. However, under specific conditions, localized corrosion with higher corrosion rates have been experienced on mooring chains in submerged near-surface zone. This paper will focus on severe localized corrosion observed on the top chain links and the use of Advanced Photogrammetry Technique used to monitor the corrosion on several lines of a FPSO offshore Angola.

This presentation will first explain the “Video Laser Scan” methodology, and the way this photogrammetry tool works and calculates the depths, lengths, and widths of the localized corrosion. Then the following will be developed:

- Accuracy of the acquired data. Real results will be displayed and discussed.
- Comparison with traditional methods (diving activities). The natures of the measurements for the different methods lead to results similar or quite different, depending on the different corrosion situations.
- Lessons learnt and way forward. The presentation will focus on the way to use the technology in the future.

Corrosion protection for very long lifetimes – are 35 years or more possible for offshore wind?

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DNV Renewables Certification – Energy Systems,

Abstract:

There are plans to expand offshore wind power generation capacity worldwide significantly. Additionally, the turbines are expected to have a longer service life to increase economic efficiency, with discussions currently underway for periods exceeding 35 years. Corrosion protection is crucial in achieving these goals.

DNV Renewables Certification is involved in most of the offshore windfarms worldwide. A very broad overview of the problems arising during the design of corrosion protection systems and the applied solutions and approaches for these issues have been gained over recent years.

DNV will present strategies for finding optimized corrosion protection methods for different site conditions and how to overcome the challenges that arise.

We will present and discusses methods to achieve extended lifetimes for offshore wind structures beyond current designs. The topics of coatings and cathodic protection will be addressed.

Guidance in the currently valid standard for coating systems ISO 12944 is given for durability very high (VH) of 25 years, while the relevant part 9 of this standard series is only valid for durability high (H) 15 years. Within the latest revision 7 of NORSOK M-501:2022 Surface preparation and protective coating guidance is given for the selection of coating systems that have experiences durability of more than 25 years.

Within ISO 2063 (all parts) Thermal spraying — Zinc, aluminium and their alloys additional guidance on the protection of steel in offshore environments is given while durability definitions are slightly deviating.

What are the site-specific categories of corrosivity according to ISO 9223, both internally and externally? Recent investigations by EnBW and Bundesanstalt für Materialforschung und -prüfung (BAM) in Germany suggest that deviations from current standard approaches may be justifiable.

Organic and metallic coatings degrade over time. Within the very aggressive offshore environment this is accelerated and is a relevant design issue. No guaranteed lifetimes for coatings can be set from a technical viewpoint, inspection and possible maintenance shall always be part of a corrosion protection philosophy of an offshore wind farm. Current investigations indicate that operating and maintenance costs account for approximately 20-30% of the total costs and could be reduced through the implementation of robust and maintenance-friendly design solutions.

DNV will present solutions for the challenges mentioned above, considering the latest guidelines and standards. We will demonstrate how to establish a comprehensive corrosion protection plan for offshore wind projects, using the latest developments and experience from global wind projects, and achieving lifetimes of over 35 years in offshore environments.

Integration of sensors in coating systems for structural health monitoring on offshore structures

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Offshore structures, such as platforms and foundation structures, are exposed to extreme environmental conditions, including salt water, waves, wind and temperature changes. These adverse conditions can lead to structural challenges that require early detection and monitoring to ensure system safety and reliability. The integration of sensors into coating systems on maritime structures provides an innovative solution to monitor structural integrity and health in real time.

The Fraunhofer IGP is part of the research group SOT (Smart Ocean Technology) and is actively involved in the Smart Coatings project, focusing on the sensor integration of coating systems for offshore applications. The SOT is developing appropriate sensors for structural health monitoring. The current state of the art shows that retrofitting sensors for Structural Health Monitoring (SHM) is challenging and that long-term durability under offshore conditions is particularly difficult. Therefore, the coating integration of sensors is being researched as an alternative to increase durability. This involves considering geometric integration and material selection. The sensitive electronics consist of circuit boards and cables, which were cast into molds based on different designs and initially bonded to steel sheets. The samples were subjected to a mechanical test to derive suitable geometries regarding resistance to mechanical stress. After ensuing weathering of the samples in the field, a sensor belt was engineered. This belt was integrated into the coating of a demonstrator for long-term tests in brackish water, with data being read out at regular intervals.

The evaluation of the long-term tests is still outstanding. However, it is already clear that this promising technology can enable efficient remote monitoring of offshore structures in the future. This eliminates the need for divers, resulting in cost and personnel savings.

Surface Optimization of Maritime Weld Seams for Enhanced Corrosion Protection

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The maritime industry faces significant challenges in effectively protecting structures from corrosion. This applies particularly to weld seams, which are highly susceptible to deformation and degradation (Fig. 1). Current coating processes often fall short in adequately addressing the unique demands of these high-stress areas. This deficiency highlights the need for a comprehensive study and for the development of more effective corrosion protection strategies, tailored to the specific needs of maritime structures [1,2]. The ongoing project, supported by national funding and collaboration from industrial and academic partners, is dedicated to advancing corrosion protection at weld seams of maritime structures. Utilizing cyclic accelerated aging tests (ISO 12944-9), the study examines the influence of various factors on the coating performance. Key to the research is the categorization of weld seam defects according to ISO 8501-3 and DIN EN ISO 5817, including pores and notches, and their correlation with coating failure. The project employs 3D scanning to quantitatively map defect geometries. Weld seam treatment methods, such as grinding and laser technology, are evaluated for their impact on coating adhesion. The coatings under investigation include a solvent-free, two-component epoxy resin and a low-solvent, high-durability two-component epoxy. Electrochemical Impedance Spectroscopy (EIS) measurements on coated welds are performed to assess the electrochemical behavior and protective efficacy of these coatings.

A comprehensive factorial experimental design, supplemented by Analysis of Variance (ANOVA), enables a detailed evaluation of the factors to enhance the corrosion protection of weld seams in maritime environments.

Effect of flow velocity on the corrosion performance of thermally sprayed aluminium coating in synthetic seawater

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Abstract

This work focuses on the effect of flow velocity on the corrosion performance of Thermal Spray Aluminium (TSA) Coating obtained by twin-wire arc spraying. Cylindrical electrodes (12 mm diameter) were machined from an S355 steel rod and coated with 300 µm thick TSA (AA 1050). An analytical rotator was employed for testing the coupons in synthetic seawater at 50 rpm and 600 rpm for 10 d. Testing under stagnant conditions was also included. Open Circuit Potential (OCP) and Linear Polarisation Resistance (LPR) measurements were carried out at 18 ±2 °C to assess the flow velocity effect and calculate the corrosion rate. Within 5 days of immersion, the OCP became more positive at higher rotation speeds. White corrosion products and calcareous deposits were observed on the coupon surfaces after 5 days, and the corrosion rate decreased in all cases.

Impact of deaeration and residual chlorine on the corrosion resistance of stainless steel in natural seawater

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Stainless steels and nickel base alloys are often used for seawater-handling applications. However, for the lowest grades, localized corrosion can be caused by the high chloride content combined to the so-called biofilm-induced ennoblement. This explains why stainless steels grades with PREN below 40 are generally not recommended in natural seawater. Several studies have demonstrated that it exists a dissolved oxygen threshold value under which ennoblement on stainless steel due to biofilm settlement does not occur. Then, the risk of localized corrosion is significantly lowered, and the use of lower grade alloys may be considered for seawater applications in such conditions. The combination of deaeration with other treatments such as chlorination, which is sometimes required (e.g. for some injection well) raises questions regarding the corrosion resistance of stainless steels. For this reason, several stainless steel grades have been tested under specific conditions of dissolved oxygen and chlorination to assess their limit of use.

To assess the limits of use, the crevice corrosion susceptibility of S41500, S32202, S32101, S32205, S32750 and S31052 alloys has been investigated in renewed natural seawater at different controlled chlorine and dissolved oxygen levels. Results showed that in presence of chlorine, regardless of the DO content, a significant increase of the OCPs occurred for all material. This potential increase for low-grade alloys leads to a higher susceptibility to initiate localized corrosion. All grades with PREN lower than 40 showed corrosion in chlorinated seawater even for DO content of about 20ppm. High grade alloys showed good resistance for residual chlorine tested (0.5 and 1ppm) at 30°C but corroded at 50°C. The impact of the chlorination on the crevice corrosion rate was also discussed in this study.

Using random sampling statistical method to optimize pickling parameters in order to maximize corrosion resistance of stainless steel in high-chloride environment

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Pickling process, defined as removal of undesired metallic oxides and other surface contaminants and establishment of new, uniform passive layer, is the step defining corrosion resistance of stainless steels. Necessity of pickling to achieve good resistance is well known, however there is not a broadly accepted process established for individual stainless materials.

Presented work explores the relationship between picking parameters and corrosion performance in various environments. For optimization, RSM (random sampling method) was employed. The input for the method defines the border value for each variable. Then, values for all studied variables are selected at random and output test is carried out. Values of individual variables leading to maximize output are then extrapolated. In this particular instance, time of pickling, concentration of pickling acids and temperature served as input variables and output variable was pitting potential. This whole process performed for AISI 304, 316 and superaustenitic 904L.

The results showed that the as-received surface, while having been pickled in production, is usually not in its optimal state and improvement of several hundreds of mV in pitting potential can be achieved using optimized picking. The improvement was even greater for improperly produced surface, such as after welding or brushing/grinding without chemical pickling.

Further, effect of optimized pickling was shown to have effect in exposures. Corrosion rate of stainless steel in high chloride was measured using CorrSen sensor. Comparing the optimized and non-optimized pickling, increase in up to 80 % was found. Also, the non-optimal samples quickly developed red rust in modified salt spray test providing method for visualisation of surface state.

Stainless steel rebars in concrete exposed to marine environment

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Abstract

After 10 years, rebars of different stainless steels as integral part of reinforced concrete in marine environments are studied.

Search for innovative and sustainable alternative technologies for construction is the main objective of this research, especially to achieve compatible components based on new materials for marine environments. Experience shows the need to carry out actual test on structures, due extrapolation from accelerated laboratory test to tangible durability conditions, may be different to that determined by real aggressiveness of the environment. According to this, structures of stainless steel rebars and concrete are install on a beach of Huelva (Spain) with direct contact with seawater. Throughout the exposure time, the behaviour of stainless steel reinforcement in marine environment by measurements of corrosion potential in-situ, as well as other specific variables, are evaluated. The long-term study reports the actual behavior and gives a more accurate view for the proper material selection in marine environments.

The results obtained show how stainless steel presents much better behavior as a reinforcing material in concrete reinforcements exposed in a marine environment, compared to carbon steel, not exceeding after 10 years of test, the critical value of current intensity of 0,1 μA/cm².

Keywords

Stainless steel, rebar, concrete

The effects of corrosion product films on the degradation behavior of magnesium alloys in aqueous environments

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Abstract

Magnesium alloy is the lightest structural material, and it has been widely used in consumer electronics, automobile, and aerospace industries. However, Mg alloy is prone to corrosion due to its high electrochemical activity, hindering its integrity safety during long-term services. It is of great importance to investigate the degradation behavior of Mg alloys in various environments for development of corrosion-resistant Mg alloys. In this work, the corrosion behavior of pure Mg and Mg-Al alloys is investigated in bulk solutions and thin electrolyte layers to simulate corrosion in seawater and atmospheric corrosion, respectively. The electrochemical measurements, SEM, TEM, XRD and XPS characterizations were conducted on the specimens. It is found that the integrity of the surface film, which consists of corrosion products, is the dominant factor affecting the corrosion rate of Mg alloys. A compact corrosion product film results in a high corrosion resistance. In the case of Mg-Al alloy, the measured corrosion current density can be decreased to 2.3 μA/cm^2 due to the existence of a protective surface film, which consists of MgO, $Mg(OH)_2$, and Al_2O_3. However, since nano-scaled pores are formed at the interface matrix/film interface, the stability of this surface film is not high enough for long-term protection. Moreover, compared with the specimen in a bulk solution, a more compact surface film forms on the specimen in a thin electrolyte layer. The formation of a surface film in thin electrolyte layers might be attributed to inhibited mass transfer of corrosion products in limited space. The results show that the corrosion resistance of Mg alloys can be improved by modification of the corrosion product films, which might be a promising approach to corrosion-resistant Mg alloys.

Suitability of nickel aluminium bronze alloy fabricated by laser powder bed fusion to be used in the marine environment

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Nickel aluminium bronze alloy (NAB alloy) specimens were produced using laser powder bed fusion (LPBF) and subjected to heat treatment to understand their corrosion behaviour when exposed to a 3.5 wt% NaCl solution. Electrochemical analysis, including impedance spectroscopy and polarization curves, was performed to characterize the samples after 30 days of immersion.

The main conclusion is that the alloy in the condition as-built (AB) responds better to corrosion than its heat-treated counterpart because the temperature causes a phase transformation that increases the intermetallic phases, sites where the oxide layer does not develop. In this way, the treated sample surfaces are partially covered and protected, while AB samples have a more homogeneous oxide layer. Moreover, impedance spectroscopy analysis reveals that the oxygen reduction reaction plays a substantial role in the impedance response.

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Author[1]**, **Author[2], Author[3] (underline the presenting author)

1) Organization, City/Country

2) Organization, City/Country

3) Organization, City/Country

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Microbial corrosion fingerprinting: a challenge

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A new project [1] is proposed in the EFC HUB within the Microbial corrosion Session, aiming to create a common, free, and open platform where discuss together about microbial fingerprints of biofilms. The idea is to critically discuss biofilm profiles that characterize microbial corrosion (MIC) cases and/or relevant conditions for MIC risk assessment.

Molecular analyses from gene pyrosequencing (Next-generation Gene Sequencing NGS) are revolutionizing the analyses of microbial pools, as they can detect and name every kind of organism, not only the minority of cultivable ones. The cost of analysis has decreased (to under 30 €/sample), and collecting samples for molecular analysis has become simpler. Furthermore, there are now many labs skilled in NGS analysis and related data analysis, which has facilitated this process.

Why putting effort in this project?

The study of a specific group of "corrosive" micro-organisms has already been shown to be generally inconclusive in characterizing a large proportion of MIC cases. The microbiological fingerprint indeed captures the complexity of the microbial communities on samples (and different metabolisms) in a single (but complex) image.

One of the most ambitious targets is to demonstrate that a complex pool of microorganisms, rather than single components, may pose a significant challenge for MIC. This topic can be explored through the collaboration of human intelligence and artificial intelligence (AI).

[1] https://efcweb.org/WP10.html

Steering FPSO Integrity: Unveiling Microbiological Corrosion and Strengthened Approaches- A Field Case.

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Managing Floating Production, Storage, and Offloading vessels (FPSOs) in the offshore oil and gas sector is challenging. Operators rely on decision-support tools for maintenance and inspections. This paper presents a field case study on Microbiologically Influenced Corrosion (MIC) in an FPSO off the coast of Western Australia. The study examined turret lines with corrosion issues, potentially related to ineffective chemical treatments.

The investigation identified key microbial metabolic pathways linked to MIC, especially iron oxidation and reduction, nitrate, and sulphate reduction processes. Active MIC-assisted corrosion was found in severely affected lines, attributed to MIC-reg flag microorganisms known for their corrosive impact on steel assets. Molecular analysis and bioinformatic analysis revealed a diverse active microbial population, possibly indicating issues with biocide treatments. The unique microbial community structure suggested environmental influences.

Historical data suggested damage resulted from the combined under-deposit corrosion (UDC) and microorganisms, or under-deposit microbial corrosion (UDMC). Operational factors like CO_2 fluctuations, interruptions in corrosion inhibitor application, changes in biocide use, elevated oxygen levels, scavenger shortages, and rising sulphate levels contributed to corrosion.

To address the MIC challenge comprehensively, the study included screening, detailed MIC assessment, and a comprehensive set of recommendations to enhance existing strategies. By mitigating the impact of microbial-induced corrosion on overall performance and maintenance costs, FPSO operators can enhance operational efficiency and safety in the challenging offshore environment.

Field Microbial Corrosion Assessment Through Adoption of An Optimized Monitoring Approach

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Widespread oil fields have been in production for years with unknown risk of microbiologically induced corrosion (MIC). Due to the nature of the scattered and complex network of production pipelines, it was impractical to establish the risk level by conducting a field sampling from all trunklines.

This paper discusses the MIC risk assessment methodology which was adopted with stringent guidelines, established in collaboration with microbiologists, after conducting an intensive field sampling and microbial analysis over around a two-year interval. The monitoring approach was also optimized by selecting 13 sampling locations to represent 120 oil trunklines distributed over three (3) fields.

The initial results confirmed that the risk of MIC is low in ten (10) areas while further monitoring was required for three (3) others. The additional data verified that the remaining three (3) areas have also a low risk of MIC which resulted in eliminating the need for corrosion control requirements (i.e., biocide injection) for a total of 120 trunklines. These efforts resulted in ensuring the pipelines' integrity by addressing a major corrosion threat through a cost-effective approach.

Why Effective MIC Control is Still a Major Challenge in the Oil and Gas Industry

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Abstract

Microbiologically influenced corrosion (MIC) still remains as a major integrity threat and cause of failure for many upstream, midstream and downstream, oil and gas assets – in spite of the continuous technological advances in the areas of oilfield microbiology, metallurgy and chemicals.

Systems most susceptible to bacterial contamination and MIC include, but are not limited to sea water injection, fire water, drains, cooling water, wet product transfer pipelines and wet product storage tanks.

Extensive field experience from both the UK's North Sea Sector and the Persian Gulf Region indicates that the main root cause of the encountered MIC leaks, failures and issues, has been either inadequate knowledge and expertise in relation to bacterial and MIC basics and fundamentals among the pertinent personnel.

More precisely, MIC incompetency has been the main culprit behind the encountered MIC leaks and failures. In general, the observed MIC incompetency can be divided into the following four subject areas:

1. Bacterial nourishment and growth conditions
2. Bacterial and MIC monitoring
3. Bacterial and MIC assessment
4. Bacterial and MIC control

Simultaneously, it has also been observed that oil and gas assets which successfully managed and controlled the MIC integrity threat were the ones whose relevant personnel possessed adequate MIC competency, mainly due to MIC training they had received.

While MIC incompetency remains the main root cause of bacterial and MIC problems, timely, practical and adequate MIC training is regarded as the main solution and the way forward for tackling the existing MIC issues for the oil and gas assets concerned.

Corrosion of API XL 65 steel in presence of *Clostridium senegalense* isolated from produced water

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Hydrogen sulfide (H_2S) produced by sulfidogenic bacteria promotes pitting corrosion through a combination of electrochemical effects caused by galvanic coupling between iron sulfide deposits in the biofilm and the metallic surface. For this reason, existence of sulfidogenic bacteria is a major concern in the oil industry. This type of microbial corrosion is commonly attributed to sulfate-reducing bacteria. However, knowledge about the corrosive effect of sulfidogenic *Clostridium* sp. is limited. Therefore, the first objective of this study was to isolate *Clostridium* sp. from the produced water. The second objective was to investigate the potential corrosive effect of the isolated *Clostridium* sp. on API 5L X65, which is widely used material for piping in the oil and gas industry due to its low cost and easy availability.

In this study, an anaerobic sulfidogenic enrichment culture was first obtained from an oil field with corrosion problems. Denaturing gradient gel electrophoresis (DGGE) of PCR-amplified 16S rDNA fragments was used to explore the bacterial community in the mixed culture. A sulfidogenic bacterium was then isolated from this culture and, then identified by biochemical techniques, and by 16S rDNA amplification, and sequencing. Finally, API 5L X65 steel coupons were exposed to the isolated sulfidogenic bacterium for 20 days in a lab-scaled test system. Test and control coupons were removed for corrosion rate measurement by the weight loss measurement method.

Biochemical and 16S rDNA sequence analyses identified the isolate as *Clostridium senegalense*. Weight loss of API 5L X65 test coupons in the presence of *C. senegalense* increased with time and the test coupons showed significantly higher corrosion rates than the control coupons. Thus, *C. sen*egalense was found to cause corrosion in API 5L X65 steel. The results obtained indicate that sulphidogenic *C. senegalense* may be a potential contributor to corrosion in the oil industry.

Use of Advanced Materials Techniques to Characterize Reverse Osmosis Membranes to Support Failure Analysis in Refineries and Gas Plants

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ABSTRACT

This paper describes a laboratory-based case study for the characterization of the reverse osmosis membranes by using the microbiological investigation (quantitative polymerase chain reaction (qPCR, Rotor-Gene Q, Qiagen)) - the spectroscopy techniques (Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric analysis (TGA), and environmental scanning electron microscopy-Energy-dispersive X-ray spectroscopy (ESEM-EDS)) - and the diffraction techniques (X-ray powder diffraction data and Rietveld method) - to support the failure analysis in determining the root cause(s) of performance loss and pre-mature failure of the membranes in water treatment plants serving diverse operations. Additionally, it correlates the Rietveld quantitative phase analysis of high-resolution X-ray powder diffraction (XRD) data of samples to the microbe compositions, so that rapid in-field microbiological assays could be carried out to assess the potential of microbiologically influenced corrosion. The results revealed that the microbial contamination of the virgin (new) and the fouled reverse osmosis membranes was confirmed, however no evident contribution of biofouling was confirmed. Moreover, the deposition of $CaCO_3$ scales was confirmed as the main inorganic foulant responsible for reverse osmosis membrane failure. Finally, quantitative phase analysis of XRD data of inorganic crystalline materials part of the samples by Rietveld method revealed that the sample consisted of calcium carbonate in the form of calcite. Additionally, the measured and calculated XRD patterns agreed well, and the refined structural parameters agreed well with the reported XRD single crystal data. These findings can guide the field engineers at the refineries and gas plants to overcome the problems of the affected equipment by drawing up the right procedures and taking preventive action to stop the generation of those particular samples.

Corrosion performance of S235 carbon steel exposed to live anaerobic digestion reactors

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Anaerobic digestion (AD), a well-established organic waste management technology, is utilized to recover biomethane and simultaneously converts waste nutrients into a valuable renewable digestate. Metallic AD reactors are constructed using either enamel- or epoxy-coated carbon steel, with design lives of several decades. The AD digestate, in the form of a slurry, contains an aqueous mixture of organic matter and a microbial consortium, while directly above the slurry there is a raw biogas mixture of CH_4, CO_2, water vapour, H_2S and other trace gases. Despite being well-established, the harsh AD environment will challenge any coating flaws and in-service deterioration that exposes the bare carbon steel. Short-term AD carbon steel corrosion is often studied in simplified media or with specific bacteria/archaea, but rarely in a biotic AD reactor, especially over extended exposures.

Bare S235 carbon steel samples were exposed to the gas and digestate phases in four continuously stirred tank reactors for 15 months. Two reactors were fed with food waste (FW) and maintained at 35°C and 55°C, respectively. The other two reactors were fed with municipal solid waste (MSW) and operated at 35°C and 55°C, respectively. X-ray diffraction and scanning electron microscopy were used to identify the corrosion products. Ex situ electrochemical tests combined with cross-sectional analysis were conducted to identify corrosion kinetics and rust film formation. Uniform and compact rust films formed on the carbon steel surfaces both in the gas and liquid phases in the four reactors. Along with siderite ($FeCO_3$) widely found in previous studies, both crystalline and amorphous iron-based corrosion products containing phosphorus, oxygen, magnesium, calcium and iron were found on the retrieved samples. In the gas phase, both the FE and MSW feedstocks and operating temperatures resulted in similar corrosion rates (0.006 – 0.013 mm y^{-1}). Samples removed from the liquid of the FW-fed reactor at 55°C have the highest corrosion rate, within the range of 0.04 – 0.10 mm y^{-1} of the four reactors. This will provide insights into carbon steel corrosion mechanisms in live AD reactors, thus assisting the resilience of the AD industries.

X-Ray Absorption Spectroscopy study on methanogens influenced corrosion of metallic components from the natural gas network

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The presence of hydrogenotrophic microorganisms as methanogens in natural gas reservoirs storing electrochemically produced hydrogen can significantly affect both the fuel stability and the degradation rate of metallic pipelines, resulting in significant economic losses. In this context, corrosion of metallic materials can manifest as a parasitic reaction in which the metallic substrate acts as an electron donor in competition with H_2. However, the relationship between this corrosion mechanism and the methanogenesis process remains poorly documented.

The aim of this study is to understand the corrosion mechanism affecting metallic components used in the natural gas network for hydrogen storage purposes by assessing the mechanism of crystallization of the corrosion products. To achieve this objective, preliminary corrosion experiments have already been carried out on carbon and copper-based alloys commonly used in the distribution network (carbon steel, a stainless steel, copper and brass) to verify the effect of methanogens on their electrochemical behaviour. An abiotic condition was also set up to define the effect of the solution (dissolved gas, ions).

Biotic and abiotic coupons were then analyzed using sub-μm surface-sensitive X-ray absorption spectroscopy (XANES) and extended X-ray absorption fine structure spectroscopy (EXAFS) to verify the oxidation states of the main alloying elements and the degree of crystallinity of the corrosive patina. Chemically different corrosion products and variations in the degree of crystallinity due to methanogens were detected depending on the material and the conditions, which helped indicating the type of corrosion mechanism (direct or indirect) they underwent. Important information was also obtained on the evolution of the oxidation states of metals related to different electrochemical pathways for the production/degradation of methane.

Iron surface modifications induced by marine bacterial adhesion

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Metal surfaces exposed to natural marine environments rapidly develop biofilms, leading to the interrelated key issues of biocorrosion and biofouling. These issues significantly impact the performance, maintenance, and service life of ship hulls. In an aggressive medium with high concentration of chloride ion, such as seawater, metal dissolution occurs simultaneously with the formation of biofilm. This work focus on the early stage of biofilm formation to understand the mechanisms involved in the bacterial adhesion process. Furthermore, the aim is to investigate surface modifications resulting from biofilm formation and evaluate their impact on corrosion behaviour. The proposed innovative approach involves the observation and characterization of iron surface modifications induced by the adsorption of *Pseudoalteromonas* NCIMB 2021. This is achieved through the application of advanced surface chemical analysis techniques, including X-ray Photoelectron Spectroscopy (XPS) and Time-of-Flight Secondary Ions Mass Spectrometry (ToF-SIMS). To assess modifications of the corrosion behaviour, electrochemical corrosion tests (OCP, $1/R_p$, impedance) were conducted, combined with ICP-OES to measure the dissolution of iron.

Corrosion tests reveal a decrease in the iron corrosion rate in artificial seawater when bacteria are present. There is a correlation between this phenomenon and the adhesion of organic compounds from extracellular polymeric substances secreted by the bacteria at the surface. XPS and ToF-SIMS analysis points out a modification of the oxide/hydroxide layer in the vicinity of bacteria, resulting in a modification of the corrosion resistance properties of the passive film.

Corrosion and microbiome analysis of galvanic coupled austenitic stainless steel with dissimilar microstructures in natural freshwater

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In some previous studies, we evaluated the microbiome formed on the surfaces of various structural materials in an industrial freshwater environment where MIC (Microbiologically Influenced Corrosion) risk was suspected. Based on these findings, we were motivated to elucidate the microbial dynamics that drive cathode reactions on corrosion-resistant steels during the induction of potential ennoblement.

From the viewpoint shown above, we planned series of studies on dynamics of microbiome related to the cathodic site formation on stainless steel. In this study, we examined the corrosion behavior of galvanic coupled austenitic stainless steel with dissimilar microstructures and the differences in microbiome formed on the anodic and cathodic surface using next generation sequencing.

Type-304 stainless steel was prepared to 20 x 50 x3^t mm size and the surface was finalized with 600-grit emery paper. The test specimens were prepared by galvanic contact between the as-received 304 SS (stainless steel) and the sensitized one in order to provide a potential difference in natural fresh water. The test was conducted using a water storage tank installed at an LNG terminal.

After a one-month exposure test, the gravimetric analysis based on ISO 84074 was performed. The sensitized 304 SS showed a greater reduction in mass than the galvanic coupled as-received one. The microbiome of the surface layer of the sensitized 304 SS and the as-received one was investigated. The correlation between the microbial dynamics observed here and the electron consumption activity on the as-received 304 SS is of interest.

Modelling the effect of semi-conductive iron sulfide in localized MIC-SRB of carbon steel

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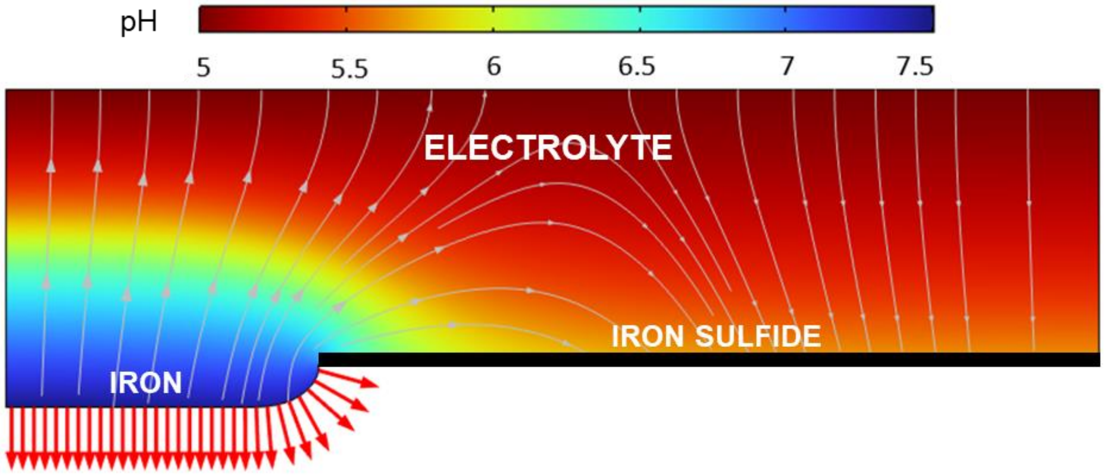
Microbiologically influenced corrosion caused by sulfate reducing bacteria (MIC-SRB) has been debated by researchers believing that H_2S excreted by SRB acidifies the environment enhancing the dissolution of the metallic substrate. However, it can be demonstrated that the sulfate microbial respiration ends up in a considerable consumption of protons, which means other causes of MIC-SRB must be investigated. MIC-SRB of carbon steel can be analyzed from a localized corrosion point of view. The formation of semi-conductive FeS layers in biogenic H_2S-containing environments provides a partial passivation on the metal surface. We developed a 3D numerical model demonstrating how a fractured FeS film in the presence of SRB provides anodic sites for iron dissolution, thus enhancing pitting corrosion. Time dependent studies accounting for growth of sulfate-reducing microbes and iron dissolution were conducted to compute corrosion indicators such as local currents, potential drops and pitting rates. As an example, the figure shows pH evolution in a pit generated after 100 days of exposure to SRB.



Biobased antifouling solutions for sea water applications

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Biofilm initiation is induced by the adhesion of bacterial cells producing extracellular polymeric substances (EPSs) and then a biofilm matrix is formed. This matrix is a complex mixture comprised of exopolysaccharides (EPS), proteins, nucleic acids, and lipids. EPSs play a crucial role in the bacterial adhesion process on a surface, mediating the transition from weakly reversible to strictly irreversible adhesion. The most effective biofilm mitigation strategy is the inhibition of biofilm formation in the early stage. Adhesion of *Pseudoalteromonas* NCIMB 2021 has been investigated on Cr surfaces covered or not by EPSs secreted by *Pseudoalteromonas* NCIMB 2021. A 15 nm thick EPSs conditioning film inhibits bacterial adhesion on Cr, demonstrating the anti-adhesive properties of this organic film. Understanding the role of Extracellular Polymeric Substances, including exopolysaccharide interactions with a well-defined chromium surface, is of importance to master anti-adhesive processes. Adsorption of EPSs secreted by *Pseudoalteromonas* NCIMB 2021 and exopolysaccharides (EPS) synthesized by two marine bacteria belonging to *Vibrio sp* and *Alteromonas sp,* respectively strain Mo245 and strain Mo169 was investigated on Cr surfaces using an original approach combining *in situ* kinetic measurements by quartz crystal microbalance (QCM) and detailed surface chemical analysis using X-ray photoelectron spectroscopy (XPS). We show that adsorption of different tested EPS is an irreversible process. The amount of adsorbed EPSs increases with increasing EPSs concentration in solution. For low concentration, the surface is only partially covered by EPSs, whereas a continuous organic film of around 15 nm is formed at the surface for high EPSs concentrations. An in-depth structuration of this organic layer is evidenced by angle resolved XPS, revealing a strong enrichment of proteins in the inner part and polysaccharides in the outer part.

Light-driven extracellular electron transfer accelerates microbiologically influenced corrosion by *Rhodopseudomonas palustris* TIE-1

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Abstract

This study investigates the microbiologically influenced corrosion (MIC) mechanism on X80 steel accelerated by *Rhodopseudomonas palustris* TIE-1 photorespiration. The photosynthetic electron transport chain (PETC) plays a key role in promoting extracellular electron transfer (EET)-induced MIC. Compared to the sterile anaerobic medium, *R. palustris* TIE-1 accelerated X80 steel corrosion, with a significantly higher corrosion rate under light conditions, approximately three times that of the dark conditions. The corrosion manifestation under light conditions primarily involved pitting corrosion, while uniform corrosion was observed under dark conditions. Inhibition of the PETC or cessation of photostimulation resulted in a pronounced reduction in the corrosion rate.

Keywords: Extracellular electron transfer; Microbial corrosion; Photosynthetic electron transport chain; *Rhodopseudomonas palustris* TIE-1

Microbiologically Influenced Corrosion in Nutrient Limited Environments

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Microbiologically influenced corrosion (MIC) is a complex phenomenon that compromises the integrity of metallic infrastructure by inducing localized attacks, commonly resulting in deep penetration into the base metal. The extent of MIC is known to be influenced by various factors, including characteristics of the environment and operational conditions of the systems. Despite some progress, a complete understanding of all factors affecting the kinetics of corrosion reactions induced by microorganisms is still lacking. For instance, while a nutrient-rich environment tends to favor microbial metabolic activities that lead to metal oxidation, MIC has also been observed in nutrient-limited conditions. Nonetheless, several MIC prediction models suggest that locations with organic content below 20 ppm pose a LOW risk of MIC. This study investigates the feasibility of using this approach to assess the risk of MIC. The initial evaluation focused on uniform and localized corrosion rates induced by a known corrosive bacterium across a range of organics from 0 to 1600 ppm.

Results indicated a lack of a linear correlation between the concentration of organics and MIC rates. Notably, nutrient-limited conditions exhibited a steady increase in corrosion rates over exposure period, while conditions with higher nutrients tended to decrease over time and were not significantly different from nutrient-limited conditions at the end of the test. A second set of experiments, assessing the behavior of an oilfield multispecies consortium under nutrient scarcity (10 ppm) compared to high nutrient levels (1000 ppm), was conducted to validate results obtained with the corrosive isolate. Remarkably, the consortium triggered higher MIC rates in nutrient-limited conditions, challenging the accuracy of estimating MIC risk solely based on metabolic rates and nutrient levels. This investigation enhances our understanding of the effect of nutrients on MIC and underscores the potential of native field microorganisms to corrode carbon steel in nutrient limited environments.

Assessment of the biodeterioration of coated cast iron

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Waters transport ductile iron pipes are protected from the external environment by specific layers. In particular, Saint Gobain PAM developed an active BioZalinium coatings (Zn-Al, Cu) and a polymeric Aquacoat®. These coatings must guarantee the durability of the pipes in contact with the ground by bringing into play self-healing mechanisms. Is the repair effectiveness still maintained in the presence of microorganisms?

In order to answer this question, we monitored the corrosion evolution of various ductile iron coupons, artificially injury or not, covered or not with protective layers, in the presence of iron-reducing bacterial suspensions or bacteria rich-soil suspensions. Experiments were carried out under anoxic conditions to be as close as possible to the conditions of burying of pipes. The behavior of the pipe samples in our different environments was followed by analyzing, both the “released iron” in solution (i.e. the soluble or insoluble oxidized iron detached from the surface) and the surface corrosion products by Raman spectroscopy.

As expected, the amount of “released iron” was 20 and 10 times lower for the coated coupons compared to the bare sample (0.1 - 0.8 mg cm^{-2} for coated cast iron compared to 2 - 8 mg cm^{-2} for bare cast iron after 7 months). In some cases, it cannot be excluded that the presence of bacteria reinforces the stability of the cast iron coupons. The repair effectiveness of an artificial injury through the protective layers of coated cast iron remains unaffected by the activity of iron-reducing bacteria or soil consortia. On corroded coupons, Raman spectroscopy showed clear differences of the surface products and in good adequation whether the inoculum was *S. putrefaciens* or the bacterial consortium from the soil. Vivianite, green rust, mackinawite were unambiguously observed.

Effects of extracellular electron transfer on biomineralization by *Shewanella putrefaciens* in damaged organic coatings

Xiangping Hao*[1,2,3], *Yixin Qian*[2], *Yun Bai*[2], *Ning Wang*[2], *Hongchang Qian*[2], *Yuntian Lou*[2], *Luning Wang*[1,3], *Dawei Zhang*[2,3]

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In contrast to microbiologically influenced corrosion (MIC), biomineralization can inhibit the corrosion of metal substrates by forming dense and uniform biomineralized films with barrier effects against corrosion. Compared with traditional corrosion inhibition techniques involving physical and chemical approaches, biomineralization is considered a “greener” approach for corrosion mitigation in marine environments and has received increasing interest in recent years. In this study, we investigated the effect of extracellular electron transfer (EET) on the biomineralization behavior of *Shewanella putrefaciens* (*S. putrefaciens*) in coating scratches as well as the relationship between biomineralization and corrosion processes by adjusting the carbon source concentration in 2216E media. The results indicated that *S. putrefaciens* was able to obtain energy from metal surfaces to support metabolism via EET when the carbon source was insufficient. Under these conditions, bacteria colonized the coating scratches, resulting in accelerated corrosion instead of mineralization. The EIS results revealed that biomineralization was most significant in the 75% carbon source medium after 7 days of incubation. Interestingly, the pH of the medium increased with an abundance of carbon sources, which promoted biomineralization.

Keywords: Corrosion, Microbiologically induced corrosion inhibition, Biomineralization, Extracellular electron transfer

Impact of Al and Mn ions' Synergistic Toxicity on the Microbiological Corrosion by Manganese Oxidizing Bacteria

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Manganese oxidizing bacteria (MOB) oxidize soluble Mn ions and form solid Mn-oxides, thereby increasing cathodic reactions in the metal and causing corrosion. Research on the microbiologically induced corrosion (MIC) of different kinds of metal by MOB in various industrial systems has increased recently. However, it is also important to investigate Mn concentrations that should not be suppressive the MOB in MIC studies. It has been reported by Arkan et al. (2022*****) that MOB isolate belonging to the *Sphingomonadaceae* family, isolated from aviation fuels, caused MIC of 7175-T7351 aluminum alloy in the highest Mn concentration (1g/L) that promotes the growth of the isolate. Afterwards, it was noticed that the bacterial growth density in the presence of coupons was lower than in the coupon-free conditions.This awareness brought to the fore the hypothesis that dissolved Al ions from the coupons and the Mn ions in medium may have been caused a synergistic toxic effect on the MOB isolate.

In the current study, Al ions dissolved from the coupons in the lab-scale system containing 1 g/L Mn were measured by ICP-MS. The minimum inhibitory concentration of Mn and Al combined on the MOB isolate was investigated by the Al concentration range (0.004-4 g/L), determined according to the analysis results, and different Mn concentrations (0, 0.5, 1and 2 g/L). The MIC of the MOB isolate on 7175-T7351 aluminum alloy coupons was investigated for 60 days in the lab-scale systems established with 0.5 g/L Mn concentration by gravimetric method.

In the presence of the MOB isolate, the corrosion rate of the coupons was determined as 2.40 ± 0.46 μm/y, which was 6.75 times higher than the values of control system. Moreover, the data obtained from the system was 1.86 times higher than the value (3.62) obtained from the lab-scale system containing 1 g/L Mn. This indicates that at 0.5 g/L Mn concentration, the MOB isolate can behave more aggressively. The results unequivocally reveal that high Mn ions at a concentration that promotes bacterial growth in typical conditions and metal ions dissolved from the alloy have a synergistic toxic effect on MOB, resulting in reduced microbial activity and MIC in bacteria.

Keywords: Microbiologically induced corrosion; gravimetric method; 7175-T7351 aluminum alloy; manganese oxidizing bacteria; minimum inhibitory concentration.

* S. Arkan-Ozdemir, T. Tüccar, N. Cansever, E. Ilhan-Sungur, Microbiologically Induced Corrosion of Aluminum Alloy by Manganese Oxidizing Bacterium, European Corrosion Congress-EUROCORR, Berlin, Germany, 2022.

Methodological guide for diagnosing corrosion in reinforced concrete structures

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Abstract

Within three French associations (i) Centre Français de la Corrosion (CEFRACOR, Commission Corrosion des Aciers dans les Bétons (CABs)), (ii) the Association Française du Génie Civil (AFGC) and (iii) the Ingénierie de Maintenance dans le Génie Civil (IMGC), we are writing a "Methodological guide for diagnosing corrosion in reinforced concrete structures".

This "Methodology Guide" is primarily intended for project owners, and is designed to respond to their concerns as asset managers, with regard to the diagnosis of reinforced concrete structures that are degraded or likely to be degraded by pathologies linked to the corrosion of reinforcement.

The guide consists of 7 parts which will be explained during the presentation.

1. Introduction
2. Corrosion of Reinforced Concrete Structures
3. Corrosion Diagnosis Procedure
4. On-site corrosion diagnosis methods
5. Laboratory Analysis for Corrosion Diagnosis
6. Corrosion Monitoring of reinforced concrete structures
7. Load-bearing capacity assessment of using corrosion diagnosis data
8. Conclusions and outlook
9. Case studies

Ex-situ and in-situ electrochemical methods for steel wire corrosion rate estimation in post-tensioned tendons

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Predicting the lifespan of old post-tensioned structures remains a major challenge. Difficulties in using the standard procedures commonly adopted and coded for rebars in ordinary reinforced concrete structures severely limit the opportunities to perform a non-destructive estimation of the corrosion rate of steel wires or strands inside a metal tendon duct. Even if electrochemical methods (EM) have been suggested in the literature for application in such conditions they still face unresolved issues. This research combines on-site and lab experiments to highlight the limitations and uncertainties of EM for assessing post-tensioned structures. A critical element is crevice corrosion of the innermost wires. Proper knowledge of the embedding environment (grout) as well as of its passivating properties is of foremost importance in integrating the information obtained by EM.

The study also explores scenarios with defective or ungrouted ducts, discussing the challenges and durability implications of accessing and assessing tendons in such situations.

DiaCor: innovative probes to assess the corrosion rate in reinforced concrete structures

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Around 80% of the damage observed on reinforced concrete structures is generated by corrosion of the rebars. In the most severe cases, this damage can lead to significant risks of loss of bearing capacity, or even collapse of the structure. It is therefore crucial to assess the state of corrosion of the rebars and to evaluate the kinetics of the corrosion phenomenon once it has initiated. With this in mind, two types of corrosion rate measurement probes, called DiaCor probes, were developed as part of the DIAMOND project (2016-2019) of which Setec LERM was one of the pilots (https://www. project-diamond.com/). Unlike existing devices, DiaCor probes allow joint and collocated measurements of the corrosion rate of the rebars (Vcor), the corrosion potential and the resistivity of the concrete cover by having direct and controlled access to the different parameters influencing the measurement of Vcor. 3D digital twins were produced using COMSOL to optimize the probes design. Furthermore, charts making it possible to apply correction coefficients to the measurement of Vcor have been produced taking into account the joint influences of the diameter, the spacing and the concrete cover subjected to a current of controlled intensity. The first type of probe (called “DiaCor surface”) was designed to take measurements from the concrete surface. It makes it possible to assess the level of corrosion of the rebars at a given time. The second type of probe (called “DiaCor monitoring”) was designed to continuously measure Vcor by installing the probe inside the concrete. It makes it possible to monitor Vcor values over time and to evaluate the kinetics of loss of section of the rebars. Since 2020, several DiaCor probes tests have been carried out on-site by Setec LERM assisted by LMDC and EDF. These tests made it possible to produce more robust versions of the DiaCor probes, both on a practical level and in terms of data processing and valorization. After a quick overview of the context and objectives of DiaCor probes, this talk will present some examples of on-site implementation of DiaCor surface and monitoring probes.

Marine reinforced concrete test site equipped with advanced corrosion monitoring techniques.

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In marine environments, reinforced concrete structures face diverse exposure conditions, including seawater spray, tidal influence, and constant submersion. These zones of exposure exhibit varying levels of humidity, water contact, salt deposition, chloride ion migration, temperature fluctuations, and oxygen levels. While existing? studies assessed mainly the corrosion damage in marine structures over decades of exposure, less is understood about the initiation and propagation of corrosion across different exposure zones.

This experimental test site aims to monitor corrosion from its initiation to propagation in specimens exposed to immersed, tidal, and splash zones. Reinforced concrete columns, standing at three meters tall, were constructed and embedded with 16 steel coupled electrodes (CME) and 5 electrical resistance (ER) sensors. These electrodes and sensors were evenly distributed along the column height to cover all mentioned exposure zones. Throughout the exposure period, CME and ER sensors are electrically coupled to simulate rebars spanning multiple exposure zones. Custom-designed measuring equipment is used to continuously monitor thickness reduction on ER sensors and corrosion currents on CME electrodes.

The 4-year long ongoing study will present the effects of changing water levels and harsh environmental conditions on corrosion rates across different exposure zones. The results obtained will highlight critical areas with varying corrosion conditions, providing deeper insights into corrosion processes in marine environments.

Non-invasive 3D Electrical Tomography for corrosion diagnosis of reinforced concrete materials

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Multi-channel probes-based non-invasive electrical devices bear practical relevance for corrosion diagnosis of reinforced concrete (RC) materials [1, 2]. Injecting current between two electrodes from the surface induces indirect polarization of the rebars, while the resulting potential difference (ΔV), between a set of reception dipoles, is simultaneously recorded. A transfer function permits to compute the apparent resistivities (ρ_{app}) profiles. When ΔV reach steady state, ρ_{app} depends on the concrete resistivities (ρ_c) and on the corrosion current densities (J_{corr}).

The novel Corimager switch device (CSD) developed by IRIS Instruments is an Electrical Resistivity Tomograph (ERT) adapted to contact impedances measurements on cement-based materials thanks to 96 electrodes evenly distributed over the 4 fronts of an iron maiden probe [2]. CSD was successfully applied for 3D ERT measurements on passive RC beams of dimensions 10 x 10 x 40 cm² [2].

In this study, CSD is used on RC beams (10 x 10 x 40 cm²), that were submitted over 10 years to tidal conditions, on the experimental site of La Rochelle. Measurements were performed in laboratory, under controlled temperature and relative humidity. The device provided 3D images of ρ_c and j_{corr} distributions. J_{corr} were compared to those provided by four conventional electrochemical techniques: EIS, LRP, VaOCP and GP. X-ray Tomography was used to comfort the spatialization.

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Pit Morphology Characterization in Chloride-Exposed Reinforced Concrete

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Abstract

Chloride-induced corrosion stands as one of the most prevalent mechanisms causing damage to reinforced concrete, leading to a rapid loss of steel cross-section. In the evaluation of load-bearing behavior in existing structures, chloride-induced corrosion is typically assumed to result in an idealized loss of cross-sectional area in the reinforcement. This simplification arises due to a lack of understanding of the corrosion pit morphology. However, addressing this knowledge gap regarding the pit morphology is crucial for assessing the durability and quantifying the remaining service life of reinforced concrete structures.

In a preliminary step, the pit morphology of over 400 corrosion pits on six actual structures has been documented and analyzed. 168 pits in an early corrosion state were documented on specimens from previous laboratory experiments. Subsequently, ten concrete specimens, each embedded with one reinforcement bar, were fabricated and exposed to a chloride solution in a controlled laboratory environment. The objective was to compare the corrosion pit morphology observed in the lab setting with that found on actual structures. Corrosion initiation was monitored using potential measurements, while corrosion kinetics were tracked through Linear Polarization Resistance (LPR) measurements. The examination of the first specimen after three months of active corrosion revealed a similarity between the pit morphology observed in the lab specimens and that identified on real structures. Notably, corrosion pits exhibited a tendency to grow in width and length rather than in depth. The remaining specimens are scheduled for opening and in-depth analysis in the near future.

The insights gained into corrosion pit morphology in chloride-exposed reinforced concrete will contribute significantly to refining the calculation of the actual limit state of structures. This understanding will ultimately enhance the maintenance practices of reinforced concrete structures exposed to chlorides, offering benefits from both an economic and ecological standpoint.

Keywords: Steel corrosion; Chlorides; Pit morphology; Service life modelling.

The role of internal and external environmental conditions on corrosion of steel in concrete macro-defects

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The experimental work aims to describe and discuss the environmental conditions that can occur within macro-defects in reinforced concrete structures. Inside these defects, the steel reinforcements are not protected by alkalinity, because they do not come into direct contact with the concrete. They thus remain in conditions of active corrosion and are exposed to microclimatic conditions which can induce an entirely internal attack inside the concrete matrix. This corrosion morphology has an entirely endogenous nature, not induced by the typical corrosion phenomena from exogenous causes, such as carbonation or penetration processes. of chlorides from the external surface. The internal environmental conditions of macro-cavities artificially created in concrete specimens are discussed in in terms of hygrometric and temperature variations inside the cavity itself and the external environmental parameters, i.e. relative humidity, temperature, exposure conditions and concrete surface temperature. The amount of water vapor in the macro-defect was observed in summer, as a function of the inversion of the thermal flow induced by the cyclical variation of the external surface temperature caused by solar irradiation and night-time natural cooling. The experimental data are interpreted based on models of humidity and heat transport within the concrete, assumed as a porous medium, consisting of a solid matrix and interconnected air voids. The effect of daily cyclical heating of the surface layers on the vapor flow inside the concrete was evaluated. Depending on the physical state of the fluid in the pores, the transport mechanisms change. In concrete not saturated with water, it is possible to identify vapor diffusion phenomena that can be described by the Fick's theory and thermal transients in concrete matrix. The temperature gradients result in vapor partial pressure gradients in the pores of the concrete which can promote a flow of vapor towards the innermost layers. Internal visual inspection of the artificial cavity confirmed the presence of corrosion products on reinforcements.

Influence of Stress Level on Susceptibility to Hydrogen-induced Stress Corrosion Cracking of Prestressed Steels

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From 2020 to 2022, the BAM developed a new test method for assessing susceptibility to hydrogen-induced stress corrosion cracking (HiSCC) of prestressed steel, especially for wires and bars. The setup contains polished specimens pre-stressed to a constant 80% R_m stress level. The specimens are constantly charged with hydrogen during the test by an electrochemically applied cathodic current density. The time to brittle fracture is measured.

The new test method can provide a sensitive separation between different kinds of susceptible prestressed steels by fracture times. This enables further parameter studies with load level and cathodic current density variation. Therefore, known as high-susceptible quenched and tempered prestressing wires of “old-type” (without alloying Cr and manufactured before 1965), *Hennigsdorfer* and *Neptun* were tested.

The influence of the different parameters was investigated by a design of experiments approach. A statistical model of time to fracture was calculated for both wires. Testing *Hennigsdorfer*, a significant susceptibility change appears in the load level range from 50% R_m to 40% R_m, where times to fracture significantly begin to rise. The variation of cathodic current density cannot show a related effect. The findings with *Hennigsdorfer* specimens limited the parameter area in the *Neptun* experiments, which show similar influences of the investigated parameters.

Damaged prestressed bridge structures will be reduced in load to ensure the remaining service life. Based on the findings, it will be discussed if these measures for bridges built with susceptible prestressed steels could ensure the remaining service life.

Insights on the mechanism of corrosion products precipitation in voids at the steel-concrete interface in reinforced concrete

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Even though corrosion of steel in concrete is one of the main degradation mechanisms affecting civil infrastructures, a fundamental understanding of several micro-scale processes relevant to corrosion is still lacking. In this context, the influence of micro-scale defects (such as air voids) at the steel-concrete interface (SCI) on the susceptibility of the steel to corrosion has not been understood yet, and it has been hypothesized that local moisture conditions may be a crucial factor in this process. Since the precipitation of corrosion products is controlled by ionic diffusion and local concentration gradients, the moisture conditions at the SCI may in turn influence the mechanism of corrosion propagation as well. However, the destructive nature of many techniques commonly used in the literature has not allowed the validation of these hypotheses yet, nor a formalization of the micro-scale processes occurring at the SCI. In this study, X-ray Computed Tomography (XCT) is applied to reinforced mortar specimens to gather deeper insights into the precipitation mechanism of corrosion products at the SCI triggered by the exposure to wet-dry cycles with 3.5% NaCl solution. XCT acquisitions capturing the specimen in its undisturbed state and undergoing corrosion are reported herein. The results of this study show that after corrosion onset, corrosion products build up inside the corrosion attack at the steel surface and along the edges of the interfacial void as a thin layer (roughly tens of µm). At this stage, the void at which corrosion occurs is uniformly filled with solution in which iron ions diffuse from the steel surface, while other voids in the matrix are filled by air. Hence, the thin layer of precipitates at the edges seems to hinder the desorption of solution from the void, in which precipitation of corrosion products occurs over time. These findings may contribute to a better understanding of the processes occurring during corrosion propagation of steel in concrete, which is comprehensively discussed.

Model of Reinforcement Corrosion Based on the Concentrated Electrolyte Theory and 3D Hierarchical Structure of Concrete

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The corrosion of reinforcement in concrete structures is a serious problem due to safety and economy reasons and affects directly the sustainability and life-time of reinforced structures.

3D Corrosion model of reinforced concrete structures based on theory of conjugate transport in multicomponent concentrated electrolytes is formulated. A three-dimensional hierarchical structure of concrete containing aggregates, interfacial transition zones (ITZ), air pores, cracks and capillary pores was determined based on X-Ray Computed Tomography (XCT) measurements and is an essential and novel element of the proposed model. Model is solved numerically using the finite element method solvers in COMSOL Multiphysics by implementation the user defined governing equations together with proper initial and boundary conditions based on Butler-Volmer kinetics. The influence of model parameters on a rate of reinforcement corrosion is shown. Experimental verification of the reinforcement corrosion model in concrete samples of real 3D hierarchical structure is demonstrated. Corrosion tests on reinforced concrete specimens prepared from CEM I 42.5R and/or CEM III/A 42.5N cements with various w/c, aggregates sizes, capillary porosity and concrete cover thicknesses in chloride containing environment are performed. The samples were examined by non-distractive methods: potential mapping on the concrete surface, electrochemical impedance spectroscopy, galvanostatic pulse and X-Ray Computed Tomography.

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In situ synchrotron characterization of corrosion products of iron in carbonated concrete pore solution

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Abstract

To address the gaps in our understanding of the propagation phase of corrosion and precipitation of corrosion products at the steel-concrete interface (SCI), it is imperative to fundamentally study these processes in situ after corrosion initiation. To this end, we employ a model SCI simulated within a capillary setup to investigate the transport behaviour of iron ions and characterise, spatially and temporally, the corrosion products in situ through advanced synchrotron techniques, namely µXRF, µXRD, and µXANES. The glass capillary contains an iron wire immersed in a pH 8 buffered solution, mimicking the pore solution of carbonated concrete. Over 9 months and in the presence of oxygen, corrosion products precipitated and were characterized as a more crystalline goethite phase near the iron, and predominantly an amorphous 6L-ferrihydrite phase further away from the iron-solution interface. Quantitative analyses allowed estimating the average corrosion rate based on iron volume loss and corrosion product formation, which was found to compare well with instantaneous corrosion rates measured electrochemically in parallel experiments of iron in bulk solution. These findings help us gain mechanistic insights into processes occurring locally at the SCI and clarify aspects such as the phase transformation of corrosion products and its kinetics, diffusion of Fe(II)/Fe(III) ions in solution, and the role of oxygen. Such new and fundamental knowledge will be instrumental in ensuring the long-term durability of environmentally friendly, low-carbon cementitious systems.

Keywords: Iron corrosion; Corrosion products; Synchrotron; In-situ characterization; Carbonated concrete pore solution.

Corrosion Properties of Reinforcing Steel Between Past and Present — Effect of steel manufacturing

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The growing demand for more durable and sustainable structures has raised the necessity for improved mechanical and corrosion resistant structural steel. Presently, reinforcing steel bars are manufactured through various production processes, including mechanical or thermo-mechanical treatments, influencing steel metallurgy and, consequently, the mechanical properties to meet the standard requirements. However, the investigation into the effect of different production processes on the corrosion properties of the produced reinforcing bars is still limited.

The current study aims to bridge the gap between steel fabrication processes and its corrosion properties. Therefore, several types of modern and century-old steel bars are examined by electrochemical methods, such as potentiodynamic polarization and electrochemical impedance spectroscopy in an alkaline medium. The results reveal a clear correlation between the type of steel bars and electrochemical properties. Corrosion potential, and impedance measurements suggest that thermo-mechanically treated steel exhibit lower corrosion susceptibility in the absence of mechanical stresses. Furthermore, the study characterizes the physical, chemical, and microstructure differences between modern and older steel.

Corrosion of Steel in Concrete: effect of inorganic and organic road salts

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Snow and ice control is essential to maintaining the safety and mobility of various roads and sidewalks during the winter months in Canada. Sodium chloride (NaCl) remains the most used de-icing material in Canada. Unfortunately, the high release of chlorides, particularly from de-icers, is causing significant corrosion to infrastructure and vehicles. Also, road salt penetrates concrete structures and corrodes the embedded steel rebars, which can compromise the structural stability of transportation facilities, most notably bridges. This research tested the effect of nine different road salts, both chloride-based and organic salts, on the corrosion of steel-reinforced concrete in field tests and control experiments in the laboratory. The research used X-ray micro-computed tomography, immersion tests, surface analysis, and solution analytical methods. Organic salts were, however, significantly more corrosive than chloride-based salts inside concrete, which is an alkaline and confined environment. This is not explained by pH since control experiments showed no corrosion by organic salts at high pH. Mixed salts, containing both organic and chloride-based salts, were able to attack the steel significantly. To prevent catastrophic failure of critical infrastructure, there is an urgent need to 1) reduce salt use to a minimum, and 2) consider specific salt-metal interactions as a function of pH value and material classes.

Chloride induced corrosion of reinforced concrete as a function of the climatic conditions and the exposure classes.

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Abstract

As part of the French Perfdub project, a study of the corrosion of reinforced concrete prisms exposed to different climatic conditions and in different exposure classes was initiated in 2019. Three concrete mix designs were tested: B01 (OPC cement, w/c=0.6), B04 (CEM III/A, w/c=0.6) and B31 (CEM III/A, w/c=0.4). The reference concrete (T) was a sound concrete. For chloride induced corrosion (G), chlorides were added to the mix. The prisms were exposed to different conditions depending on the controlled temperature and relative humidity (20°C with 80% or 92% relative humidity, 45°C with 60%, 80% or 92% relative humidity) and outdoor exposure classes (XC4, XS3 and XS2 from NF EN 206/CN). In XS3 and XS2, chlorides also penetrated in the concrete from the sea water.

The aim of this study was to evaluate the corrosion behaviour of reinforced concrete prisms over time using electrochemical measurements (half-cell potential, linear polarisation resistance, impedance) and to calculate the corrosion current density. Visual corrosion defects and kinetic results will also be presented.

The results show that the more corrosion resistant concrete mix design was B31 (as expected because slag cements usually slow down the penetration of chlorides into the concrete and its water/cement ratio was very low). The behaviour of B04 was somewhat unexpected as some cracks appear after 13 months in the climatic conditions (45°C and 92% RH).

The questions that arises from these results are: (1) Why is B04 corroding so soon? (2) Can we use the Rilem recommandations to assess the corrosion or reinforced concrete with common electrochemical methodology of mix design that are not based on OPC?

Diffusion potentials as error source in corrosion-related investigations of reinforced concrete – Outcome of research project

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Corrosion-related investigations of reinforced concrete structures often rely on measuring the half-cell potential of the steel embedded in concrete (e.g. half-cell potential mapping, corrosion onset monitoring). Furthermore, the application of potentiometric sensors in concrete has gained increasing attention to observe the chloride ingress or the pH decrease due to progressive carbonation or leaching of concrete. Differences in chloride concentration or pH cause diffusion potentials, which result from diffusion and simultaneous charge separation of the diffusing anions (Cl^-, OH^-) and co-diffusing cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) owing to their different intrinsic mobilities. However, the diffusion potentials in concrete may significantly interfere with the potential measurements. Therefore, it is important to enhance the accuracy when predicting the diffusion potentials in order to adequately take account of them in the potential measurements.

This requires an improved understanding of the diffusion potentials that arise in concrete, which is the aim of the research project (DFG project number 276790461). The research study employs the laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) to analyze the concentration profiles of the species in concrete with a very fine spatial resolution in the micrometer range. This enables the investigation of the permselective property of concrete (i.e. differences in ion mobility are more pronounced in concrete pore structures compared to solutions), and its implication for the arising diffusion potential. Despite of the permselective property of blast furnace cement pastes upon chloride exposure, the diffusion potentials are in the range of a few millivolts due to the high pH values of the pore solutions. In contrast, there are diffusion potentials of several hundred millivolts when pH differences of 5-7 units result from carbonation of concrete. This particularly affects the potentiometric sensors, which are highly sensitive to potential deviations. The outcome of the research project will be presented at the European Corrosion Congress 2024. The significance of the diffusion potential error will be demonstrated for various corrosion investigation methods.

Passive layer formation of steel in alkali-activated slag/fly ash mortars

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Within the current task of realizing durable concrete structures with a lower carbon impact, alkali-activated binders represent a promising alternative. Apart from making a significant contribution to reducing the CO_2 emissions caused by cement production and use, they offer technical benefits that are particularly relevant in building preservation, such as increased chemical resistance. For the use of alkali-activated binders in reinforced concrete structures exposed to chlorides or carbonation, the ability of the steel to reach and maintain the passive state is highly important. Research has shown that the processes of surface layer formation of steel in alkali-activated materials can differ from those in Portland cement. The pore solution of alkali-activated ground granulated blast furnace slag concrete contains sulfides, which affects the electrochemical properties of the steel surface and makes it difficult to use conventional standards.

The present contribution describes the results of a research project, focusing on the passivation behavior and corrosion initiation of steel in alkali-activated slag/fly ash mortars, as well as in standard blast furnace slag mortars. Throughout the course of the study, it became evident that the formation of the surface layer in the examined alkali-activated binders is notably extended compared to the conventional binders. The evolution of the open circuit potential was therefore monitored over a period of several months, accompanied by the determination of polarization resistances and EIS measurements at critical stages. The electrochemical results are contextualized with aspects of the analyzed pore solution of the binders. In addition, the first results of a test series with chloride ingress are presented, in which the stability of the passive layer is evaluated electrochemically. The results contribute to a better assessment of the corrosion resistance and durability of steel in alkali-activated slag/fly ash mortars.

Corrosion behavior of steel in low carbon mortar based on C-S-H phases from the autoclave

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The high CO_2 emissions associated with cement production require the use of binder types that can be produced in a more climate-friendly way than ordinary Portland cement. A novel type of hydraulic binder, that is produced on the basis of CSH phases synthesized by autoclaving a mixture of calcium oxide and silica, was developed by researchers from the Karlsruhe Institute of Technology (KIT) and is called Celitement. It is currently only being produced in small quantities in a pilot plant and was provided for our research project regarding the influence of alternative binder types on the corrosion behavior of embedded steel. In a first step, corrosion relevant material properties, like the pH of the pore solution, the pore size distribution, the specific electric resistance of the mortar, and the chloride migration coefficient, were characterized. In addition, electrochemical tests in a three-electrode setup in terms of the open circuit potential, anodic polarization curves, and impedance spectroscopy were carried out to investigate the passivation of the steel over 28 days.

Corrosion behavior of reinforced concretes containing recycled plastic exposed to wet/dry in chlorides solutions.

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Abstract

Due to its extreme versatility, plastic has become particularly important in our lives, causing its production to increase and, with it, unfortunately, the volume of waste as well. Disposal of plastic waste has therefore become an urgent issue. With growing concerns about sustainability and impact on the environment, the use of recycled plastic in construction is becoming a viable strategy within a circular and sustainable economy. Therefore, the possibility of partially replacing conventional aggregates with regranulated plastic waste was considered in this research for the preparation of lighter concrete, helping to address the disposal challenge presented by these non-degradable wastes.

The main objective of this investigation is to understand the influence of recycled plastic grains additions on the corrosion behavior of steel reinforcements in concrete. Results are presented in terms of corrosion potential and polarization resistance measurements and electrochemical impedance spectroscopy analysis during wet/dry cyclic exposures to chloride-containing solutions. After specific cycles, the total chloride concentrations (as wt.% versus binder) in contact with the reinforcing bars were determined according to standard methods. Moreover, at the end of wet/dry exposure, visual observations of the bars and scanning electron microscope (SEM) analyses were carried on sections of concrete samples in order to gain insight on the corrosion mechanism.

This research was carried out in the scope of the IMPRESA project supported by POR-FESR 2014-2020 funds (Call 2018).

Electrochemical analysis of industrial wastes as supplementary cementitious materials in reinforced mortars

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The cement industry's impact on greenhouse gas production is significant, accounting for approximately 5-8% of global emissions[1]. It is important to explore environmentally friendly alternatives to cement in construction. In Chile, the copper industry has seen a rise in waste production due to declining mineral quality. The global mining industry generates billions of tons of waste annually, including 14 billion metric tons of mining tailings[2]. This research used copper tailings and slag as cementitious materials in reinforced mortars. The copper residues were examined using scanning electron microscopy and X-ray diffraction. Enhanced mortar specimens were produced employing 0-20 wt.% of copper residues as a substitute for cement with water-cement ratios of 0.5. Specimens were subjected to a saturated calcium hydroxide solution for 120 days. The electrochemical measurements of enhanced mortar specimens, including open circuit potential, electrochemical impedance spectroscopy, and linear sweep voltammetry. The XRD analysis revealed the influence of pretreatment on the amorphous and crystalline phases. Mechanical tests showed optimal properties were reached using 5-10 wt.% of industrial waste as cement replacement. The electrochemical examination uncovered that the passivation of carbon steel was affected by the type of industrial refuse and its pre-treatment, which had a more noteworthy impact for a more prolonged exposure duration.

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Corrosion of steel in concrete: effectiveness of preventative measures evaluated by Monte Carlo simulation

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Prevention of rebar corrosion is achieved in the design and construction phases, by suitable mix design, casting and curing, and adequate cover depth; this approach can be defined as "prescriptive" and is present in international standards, such as EN 206, and design codes (Eurocode 2). Preventative methods, such as cathodic protection and stainless steel rebars can be used in very aggressive environment, especially in presence of chlorides, or when increased service life is required.

In this work, the service life of reinforced concrete structures exposed to chlorides has been evaluated in a conservative way considering only the corrosion initiation. Atmospheric and splash zone (classes XS1 and XS3 according to EN 206 standard) have been considered.

Chloride transport was modelled by 2nd Fick's law and the service life was estimated by means of Monte Carlo simulation. The input data for the calculation were the distribution of surface chloride content, chloride diffusion coefficient, critical chloride content (literature data). Concrete cover and maximum water/cement ratio were selected in agreement with Eurocode 2 and EN 206 standard respectively considering different cement type (CEM I, CEM III and CEM IV according to EN 197 standard).

The results enable to rank the preventative methods in term of effectiveness. Cathodic prevention and stainless steels rebars are the most effective protection methods in severe environments in presence of chlorides. The use of pozzolanic or slag cement is effective to slow chloride transport and by this way to increase the service life. The results have been compared with those obtained in literature using FIB Model Code for service life design (2016): a fair agreement was demonstrated.

Keywords Corrosion in concrete, chlorides, corrosion initiation, service life, Monte Carlo simulation

Investigation of corrosion product layers in chloride containing mortars

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Hot dip galvanized reinforcing steel forms surface layers depending on the ion composition and concentration in the mortar or concrete/galvanized reinforcing steel interface. For the formation of stable surface layers on hot-dip galvanized reinforcing steel, an equilibrium concentration of zinc ions, zinc oxides and zinc hydroxides is required, as already investigated by Fulton and Swinehart (Zn(OH)2) or Ziegler and Johnson for Ca(Zn(OH)2)3)·2H2O. These surface layers in solid electrolytes such as mortar or concrete describe a diffusion-controlled corrosion system. If chlorides are in sufficient quantities in the phase boundary region, there is no depassivation as known from non-galvanized reinforcing steels, but a surface layer transformation and formation of Simonkolleite (Zn5(OH)8Cl2·H2O). With the formation of this surface layer component, the corrosion system changes from a diffusion-controlled corrosion system to a permeation-controlled system, which could be determined by the phase shift with constant frequency observation The presentation will show how these corrosion systems can be investigated and interpreted.

Effect of Calcium Nitrate as Concrete Admixture to Mitigate Carbonation

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Abstract

Over the years, calcium nitrate has been used as a concrete admixture, primarily as a setting accelerator. Past studies have shown that, in addition to improving the long-term durability of concrete, it also reduces corrosion, especially when exposed to chloride. Initial preliminary tests have also demonstrated that the carbonation resistance can be increased by adding calcium nitrate.

Therefore, in this study, we primarily wanted to investigate the effect of calcium nitrate on the carbonation of concrete and cement paste. For this purpose, cement pastes and concretes from Portland cement (CEM I) and Portland composite cement (CEM II/A-S) were prepared with the addition of 0, 2, and 4 % bwoc calcium nitrate, respectively, and stored in accelerated (2% CO_2) and non-accelerated carbonation conditions. The compressive strength and carbonation depth of the concrete samples were then determined. The effect of carbonation on cement pastes was investigated using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and thermogravimetric analysis (TGA). Additionally, porosity and effect on pore solution were tested by Mercury Intrusion Porosimeter (MIP) and pore water analysis. Finally, X-ray diffraction (XRD) should provide insights into incorporating calcium nitrate into hydrate phases.

Concrete and cement paste experiments have shown that adding 4% bwoc calcium nitrate significantly reduces the carbonation depth compared to a reference without calcium nitrate and, simultaneously, leads to a similar compressive strength after 28 and 180 days. MIP, pore solution analysis, and XRD indicate nitrate incorporation to form a nitrate-AFm phase, which could stabilize ettringite and thus densify the cement matrix.

Key words: calcium nitrate, admixture, carbonation mitigation

"SACI Utilization in the Reconstruction of a World-Class Sporting Heritage and Football Stadium"

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Abstract:

One of the world's largest football stadiums required refurbishment. Profound carbonation reduced the concrete's protective alkaline pH, aggravated by a shallower-than-average concrete cover. The project encompasses the refurbishment of the lower two levels of the stands, with the upper third stage set for demolition and reconstruction. The new construction area spans approximately 220,000 m2, while the renovation area covers approximately 75,000 m2.

A migratory corrosion inhibitor has been selected for the repair and protection of exposed concrete, drawing upon 45 years of experience and its alignment with specified repair design requirements. The choice of an amino-based corrosion inhibitor is grounded in its efficacy in safeguarding reinforcing elements within carbonated concrete, thereby effectively diminishing the corrosion rate and delaying the onset of corrosion.

This paper aims to outline the application of migratory corrosion inhibitors and an "in situ" monitoring system. The fieldwork in this context involves conducting on-site carbonation profile assessments following UNE EN 14630 standards on exposed reinforcement to ascertain the location of the carbonation front.

Electrochemical corrosion measurements will be conducted using the Gecor 10 portable corrosion equipment. This involves mapping corrosion potential, corrosion rate, and resistivity to assess the corrosion state of the study structure. The primary goal of these measurements is to identify areas where corrosion may be occurring. The interpretation of corrosion potential measurements involves assessing the risk based on criteria established in the UNE 112083 standard.

Key words: migratory corrosion inhibitor, concrete, carbonatization, "in situ" monitoring, corrosion potential, corrosion rate

Long-term corrosion behavior of reinforced concrete structures in acid aggressive environments: Case studies.

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Abstract

The paper presents the results of research on the corrosion behavior of reinforced concrete structures subjected to the corrosive action of acid aggressive agents, after a long-term service in a strongly aggressive environment. To evaluate the damage state of reinforced concrete elements / structures, both "in situ" investigations of structures and laboratory tests on concrete samples extracted from some elements damaged by corrosion, using a specific investigation methodology were performed. The results of the research revealed the existence of a severe corrosion-induced damage of the structural elements, which affected the resistance, stability and durability of the structures. Based on case studies on the service behavior of reinforced concrete elements/structures, there are pointed out the specific damages generated by the corrosive action of the acid aggressive agents, the causes of their occurrence and presents considerations on the mechanisms of the corrosion processes of concrete and steel reinforcement in acid aggressive environments. Finally, there were proposed intervention measures in order to assure normal service conditions of the reinforced concrete structures located in such aggressive environments.

Operational feedback of cathodic protection and prevention for a reinforced concrete structure in a coastal environment

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Abstract

As part of a major rehabilitation scheme, an impressed current cathodic protection (ICCP) has been implemented in conjunction with concrete repair and structural strengthening of a coastal reinforced concrete structure.
The structure consists of a pedestrian corbelled promenade anchored to the cliff and has been exposed over the last 60 years to a harsh and corrosive environment and has exhibited severe concrete damage due to chloride-induced corrosion. Due to the selected structural rehabilitation and concrete repair strategy both cathodic protection and cathodic prevention system were installed.

The paper presents the overall CP design philosophy and gives accounts of operational data for various project phases which underlines the heterogeneous operating CP current densities of similar CP systems with identical anode distribution amongst the various concrete elements along the seashore. The paper also discusses the effect of the CP current distribution between multiple layers of steel, CP current density for prevention in temperate climate in and key design factors to be considered in the CP design process.

Modeling and optimization of ICCP for reinforced concrete protection

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This study investigates the performance of impressed current cathodic protection (ICCP) on a reinforced concrete structure through a combined experimental and numerical approach applied on a laboratory slab. More particularly it aims at bringing quantitative information concerning the number, arrangement and effective radius of protective anodes.

For this purpose, a laboratory-produced reinforced concrete slab (1m×30cm×15cm) is made. The concrete is formulated closely to that used in the segments of the Saint Cloud Viaduct and initially polluted by addition of chloride ions (3% by mass of cement) to the mixing water. The slab is crossed along its highest dimension by a single steel rebar. Three reference electrodes are embedded in the vicinity of the rebar and two anodes are placed in holes drilled from the slab surface. Experimental tests are carried out to evaluate the initial state of the system and explore different ICCP scenarios.

A numerical finite element model, coupling ohmic conduction, electrochemical phenomena and oxygen diffusion, is built to estimate the spatial distribution of the potential and current fields in the whole domain and more particularly along the rebar. To describe the imperfect interface between steel and electrolyte, a term related to the surface resistivity is introduced into Ohm's law. Numerical simulations clearly put in evidence the radius of action of the injection anodes according to experimental scenarios. The levels of polarization can indeed be compared to the standard criterion.

Finally, using a least-squares optimization technique, some parameters which are difficult to obtain experimentally, are determined, ensuring the consistency of all the simulated scenarios with experimental results. The robustness of the model is particularly underlined by similar trends obtained for experimental and numerical potentials at reference electrodes close to the steel/concrete interface during impressed current cathodic protection.

Alkali-aggregate reactivity of concrete and the corrosion of reinforcement

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Mass concrete structures have long been known to be prone potentially to alkali-aggregate reactivity (AAR). Over long periods of time the expansive reaction so caused produces, typically, crazed surface cracking. Less well-known is that the concrete in steel-reinforced concrete structures also may be prone to AAR. Particularly where the reinforcement is in the vicinity of the exterior concrete surfaces the cracking effects of concrete expansion due to AAR may appear, superficially, as induced by expansive corrosion products, even in environments where chloride-induced or carbonation-induced reinforcement corrosion is extremely unlikely or there is no evidence to support such mechanisms. Several practical examples are given to illustrate the point. A critical overview is given also of a number of cases originally ascribed to chloride-induced corrosion that more likely were due to AAR causing concrete cracking prior to reinforcement corrosion rather than the other way round. The analysis is supported by a number of finite element analyses showing the stress state set up by the aggregate-induced concrete expansion. For this, the locations of the highest surface stress states correlate with field observations of concrete cracking. The results suggest that AAR may be an underestimated practical contributor to deterioration of reinforced concrete structures.

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Crevice corrosion assessment of steel liners and cement interface in nuclear power plants under oxic conditions

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Nuclear Power Plants (NPP) contain numerous concrete structures with embedded steel reinforcement, barrier and carbon steel liners. Although concrete environment provides the alkaline nature that enables passivation of the steel surface, corrosion has been observed in carbon steel liners in NPP. The concrete and steel liner interface can act as a crevice former and the environmental conditions may change in time due to the carbonation of the concrete and/or the presence of chloride ions. These changes at the interface can generate crevice corrosion but there is no sufficient information available to predict or model such a mechanism in this application. In this paper, potentiodynamic polarisation (PP), Tsujikawa Hisamatsu Electrochemical (THE - ASTM G192) method and open circuit potential (OCP) were applied to assess crevice corrosion of carbon steel liners. PP data provided information on the passive current density, which was an input for the THE method. The THE method was performed to induce crevice corrosion and determine the crevice repassivation potential (CREV), while the OCP monitoring over a long period was used to compare with CREV and assess crevice corrosion without applying accelerated techniques. Tests were performed in a high pH solution (sat.($Ca(OH)_2$, pH ~12.7) and a low pH solution (0.005 mol/L Na_2CO_3 + 0.015 mol/L $NaHCO_3$, pH~9.5) under oxic conditions to mimic the concrete environment. The crevice was formed by pressing a flat cement paste block (Ordinary Portland Cement OPC) on the surface of the steel. To accelerate the corrosion process, tests with high pH solutions containing 0.01 and 1 mol/L of chlorides (Cl^-) were also performed. The PP results showed a passive current density region for all the solutions studied in this work except at high pH in addition of 1 mol/L Cl^-. The THE results showed no corrosion attack nor CREV in high pH solutions, except if 0.01 mol/L Cl^- is added. In low pH solution, some corrosion attack was observed outside the crevice region but no CREV was obtained.

Crevice corrosion of steel in concrete pore solution

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Abstract

Concrete is an essential material in nuclear power plant (NPP) structures. Often, concrete structures envelope steel in various forms, such as rebars, anchors and supports, or liner plates. The latter is particularly important in NPP containment structures, where it ensures the integrity and leak-tightness necessary for the NPP safety. However, several cases of liner plate perforation by corrosion have been reported globally [1]. Recent research [2] has demonstrated that crevice corrosion could explain the high local material loss rates in embedded liner plates, and that crevice corrosion can also be triggered in reinforced concrete [3]. Consequently, it is apparent that greater attention must be given to understanding the phenomenon of crevice corrosion in steel embedded in concrete. This constitutes the main goal of this study. Two types of experiments were performed: immersion experiments and electrochemical measurements. Immersion tests involved crevice formers of various materials: concrete, carbonated concrete, and a piece of wood, and they were carried out in three electrolytes: concrete pore solution, carbonated concrete pore solution, and concrete pore solution with chlorides. Duration of the tests was 6 months, after which the liner plate specimens were subjected to thorough characterization. In parallel, electrochemical measurements were performed for steel in the electrolytes in the presence and absence of oxygen. The results are presented and discussed for elucidating the probability and drivers of crevice corrosion in concrete structures.

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Electrochemical multi-technique measurement of corrosion rate for geological disposal application

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The French National Radioactive Waste Management Agency (Andra) is responsible for the Cigéo project (Industrial underground radioactive waste disposal) dedicated to dispose high and intermediate level long-lived radioactive waste in a deep geological disposal facility at 500 m depth drilled in a very stiff clay Callovo-Oxfordian claystone (Cox). Since 1999, Andra has been carrying out investigations at its Underground Research Laboratory (URL), in Meuse/Haute-Marne, to study and support the design and development of the underground disposal facility.

High Level Waste (HLW) disposal cell concept consists of a hundred meters long micro-tunnel, with a carbon steel (CS) casing measuring approximately 60 - 70 cm in diameter. The initial annular space between the outer surface of the casing and the host rock is filled with a cement based grout called MREA. The MREA imposes corrosion-limiting environmental conditions. This cement grout aims to buffer the acidic transient resulting from the release of acidity in the pore water due to the oxidation of sulfur-based minerals. Real-time Monitoring of Carbon steel corrosion in this low-pH material is required.

A non-destructive electrochemical monitoring system has been developed. The system is based on a unique three-electrodes device elaborated with the same metal as the micro-tunnel casing of the cell, namely API 5L X65. Corrosion rates are measured using an electrochemical multi-technique capabilities instrument.

In this paper, measurements conducted in the URL on a specific demonstrator will be shown. Results of non-destructive methods such as Open Circuit Potential (OCP), Linear Polarisation Resistance (LPR), Electrochemical Impedance Spectroscopy (EIS) and Harmonic Distortion Analysis (HDA) will be discussed as well as the performance obtained with 70 m electrodes cable.

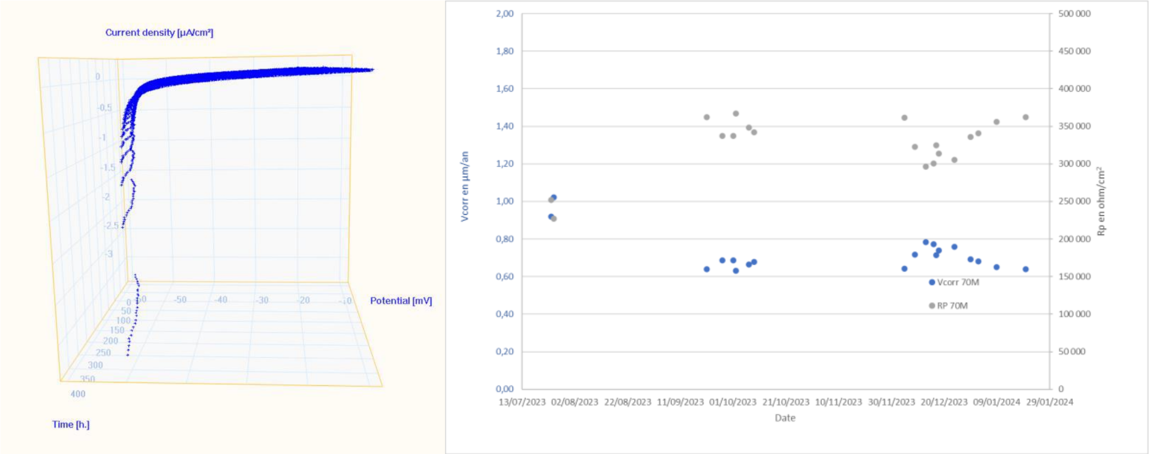

Figure 1 : Evolution of corrosion rate and polarisation resistance of an API 5L X65 electrode immersed in a cement as a function of time.

Over a year follow-up of parameters of a cemento-bentonitic filling material (CBFM) and of the corrosion potential of a carbon steel lining submerged by the CBFM, in an underground gallery cell.

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Abstract

Radioactive waste-management programs today mainly focus on deep geological storage, as this is currently the most appropriate strategy for ensuring the long-term safety of people and environment. “Cigeo” is the name of a future deep geological disposal facility for high-level, long-lived radioactive waste, to be built in France, at 500 m depth within the clayey Callovo-oxfordian formation (Cox). The radioactive wastes will be placed in horizontal pipes made of Carbon Steel API-5L-X65 (CSX65), separated from the Cox by a cemento-bentonitic filling material (CBFM). The CBFM will permit the steel to be maintained at passive state, thanks to its alkaline pH (>12).
For a better insight into physical and chemical behavior of materials, experiments were conducted in laboratory, using pluri-centimetric scale pilots, and in the underground research laboratory (URL) of Andra at Bure) at plurimetric scale. In the URL-conceived experimental set-up, two multi-parametric probes (MPPs) were placed on a horizontal tube, at 12.6 and 32.1 m from the gallery, into a sealed cell, previously submerged by the CBFM. Each MPP is composed of four electrodes: a Sb_2O_3/Sb solid as pH electrode, a robust $AgCl/Ag_{(s)}$ solid reference; a robust $Ag_2S/Ag_{(s)}$ solid as S^{-II} selective electrode and a redox Pt electrode. A cable connected to the CSX65 lining close to each MPP permits to monitor the CSX65 corrosion potential ($E_{corrX65}$) vs $AgCl/Ag_{(s)}$. The measurements over a year, *in situ* (URL), of $E_{corrX65}$, pH, redox potential and S^{-II} content enabled without interruption, the monitoring of the tube in contact with CBFM and the evolution of the physical and the chemical parameters of CBFM. These *in situ* results, compared to those of the previously implemented pilot in laboratory [1], shown excellent similarities and illustrated how accurate and rigorous was the pilot simulation.

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Nickel base alloy solutions for oil and gas applications – a review

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Nickel is an element that alloys easily with other metals, allowing for a variety of combinations that form the different nickel base alloys available on the market. These can be divided in three main groups according to their microstructure and processing condition: solid solution, cold worked and precipitation hardened nickel alloys.

Solid solution nickel alloys are composed mainly by nickel, iron, chromium and can have additions of copper and molybdenum. These alloys are characterized for a very good environmental cracking resistance and localized corrosion resistance, as predicted by the PREN-number[1]. The weakness of solid solution alloys are their low mechanical strengths, which limits their usage.

When high mechanical strengths are needed, solid solution nickel alloys can be hardened through cold working, what reduces ductility and creates a state of residual stresses that can lead to earlier corrosion. Additionally, properties may vary through the section thicknesses. Big dimensions or complex shapes might be difficult or even not possible to be processed.

In order to get around the processing limitations of cold working, precipitation hardened alloys can exhibit very high strength levels that are more homogenous and do not have the same limitations that are associated with cold worked alloys. It is granted by the addition of alloying elements like niobium, aluminum and titanium. Through a precipitation hardening heat treatment, extremely small uniformly dispersed particles of a different intermetallic phase that are the result of additions of alloying elements such as niobium, aluminum and titanium. These act then as a barrier for the movement of dislocations, increasing the strength resistance of the alloy, which can exhibit good localized corrosion resistance and environmental cracking resistance.

The aim of this presentation is to review nickel alloys available in the market focusing on the solutions for the oil and gas industry applications, briefly touching the most recently alloy developments.

Material selection for sour gas wells: definition of test conditions

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Abstract

A new sour gas field will be developed and material selection for well producers was conducted. Several grades of martensitic stainless steels were tested with regards to their resistance to SCC and SSC. The tests were conducted according to NACE TM0177-2016 Method A (uniaxial tensile test), at various partial pressure of H_2S. The specific environment was defined in order to be as much as possible representative for the in-situ conditions. The testing program was completed with electrochemical tests to assess the pitting potential and repassivation potential of these materials in the selected environment (Figure 1). The results showed that some of the tested materials are borderline for the defined test conditions due to susceptibility to localized corrosion. How to define more accurately the test conditions to avoid any unnecessary over-conservatism and the relevance of the test method itself are discussed too.

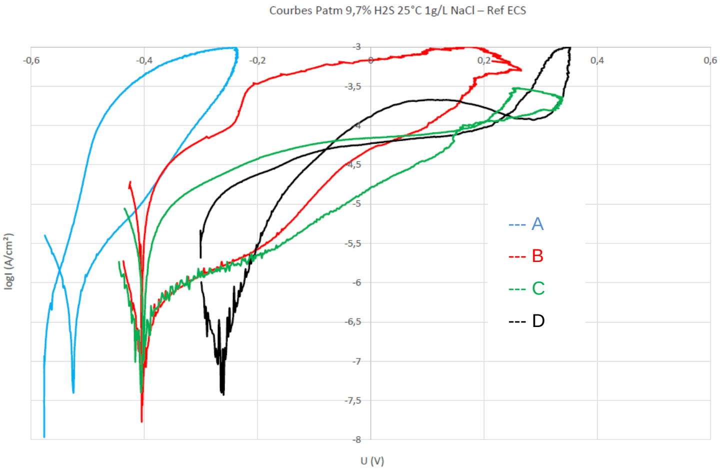

Figure 1. Polarization curves at ambient pressure, 9.7%H2S, 1g/l NaCl

Effect of CO2 on the corrosion mechanism of carbon steel

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Understanding the effect of the CO_2 on carbon steel corrosion mechanism is important to improve the models that provide estimations of uniform corrosion rate, important in the oil and gas industry.

Almeida *et al.*[1], using electrochemical impedance at OCP and calculation, demonstrated that, if CO_2 was able to act on the free iron surface, producing $(FeCO_2)_{ads}$ as reported in the literature[2] its relaxations would appear as a capacitive loop. Thus, two consecutive capacitive loops should be seen. This diagram has never been observed, which means that the CO2 is not able to act on free iron surface. Nonetheless, if CO_2 are able to play any role in the corrosion mechanism, this can only be seen by polarizing the system.

Considering the above, electrochemical impedance was used to investigate the effect of CO2 on X65 carbon steel corrosion in different pH values. An experimental methodology was performed to polarize anodically and also cathodically the system, with small and fixed quantities of chloride, in the presence and absence of CO_2, separating the chloride effect from any other that can be played by CO_2.

The preliminary results at pH 4, show that in general, the impedance has two faradaic loops: An inductive followed by a capacitive in a smaller frequency range. The inductive loop is associated with relaxation of FeOHads[3]. Hering, the impedance diagrams clearly showed that CO2 does not act directly on the free iron surface, showing that the mechanism is not changed. However, a change in the characteristic frequency of the inductive loop in the medium containing CO2 was observed. In order to understand this behavior and the real influence of the CO2 on the corrosion mechanism of the carbon steel, measurements of electrochemical impedance at more anodic and also more cathodic potential in different pH values are carrying out.

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Failure due to CO_2 Corrosion in Gas Lift Compression Unit: Operational Feedback and Lessons Learnt

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A corrosion failure was experienced in the gas lift compression module of an offshore asset of the Gulf of Guinea. The carbon steel discharge pipe from inter stage cooler failed leading to a gas leak. An investigation of the corrosion mechanism showed that the corrosion seen downstream of the cooler elbow outlet was caused by CO_2 corrosion. Following the root cause analysis (RCA), several actions were conducted:

- The design of the equipment was modified
- The material was upgraded from carbon steel to stainless steel
- The inspection program hence the Risk Based Inspection philosophy was updated to reflect the management of change

Although the material selection for a project is performed considering preliminary design and operating conditions (temperature, pressure, CO_2 content, etc.), the corrosion assessment needs to be updated based on the actual operated conditions and this shall be correlated with the inspection results.

Keywords: CO_2 corrosion, material selection, gas compression, root cause analysis

An Overview of Top of Line Corrosion In the Subsea Gas Pipelines- Abstract

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Top of the Line Corrosion (TOLC) is a pervasive challenge in Oil and Gas Sector. TOLC is an insidious corrosion phenomenon typically encountered in the transportation of wet gas. TOLC occurs mainly when the flow regime is stratified and when significant temperature gradient exists between the pipeline and its external environment. This temperature gradient can result in internal water condensation at the top of the pipeline. The condensed water phase contains dissolved acid gases (e.g., carbon dioxide and hydrogen sulfide) and which can results in internal corrosion.

Through this paper, authors intent to share EPC CONTRACTOR's experience in dealing with the potential threat of the TOLC for the Subsea Rich Gas Pipelines.
The base case design, process parameters and client requirements along with the sample laboratory testing results will be discussed.

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Should Stress Assisted Grooving in H_2S Containing Environment Be Considered as Artifact?

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Addition of controlled quantity of iron (II) chloride ($FeCl_2$) in a test solution allows a tight control of the pH of Sulfide Stress Cracking (SSC) tests for low alloy steels. The natural buffering capacity is a consequence of the precipitation of iron sulfide corrosion products at a very early stage during the corrosion test. In previous works, it has been established a reduction of the corrosion rate in such environments while the susceptibility to SSC keeps high, even higher than in standardized solutions presenting a significant pH drift during the test. This led to the conclusion that iron (II) chloride solutions allow a fair assessment of the SSC susceptibility of a material because both applied stress and key environmental parameters (pH and P_{H2S}) keep constant during the whole test duration. This work investigates the impact of iron (II) chloride solutions on the occurrence of stress assisted grooving on the surface of NACE TM0316 four-point bend specimens sampled in linepipe grades after exposure to sour environments. Results are interpreted in light of the current knowledges on the mechanism of formation of grooves and the interest of the usage of iron (II) chloride solutions for the qualification of the SSC resistance of linepipe grades is discussed.

Environmentally Assisted Cracking of Cleaning Pig Brushes in sour conditions

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For several decades, oil and gas industries have relied on pipelines for ease of transportation of petroleum liquids and gases. Integrity of these pipelines is of utmost importance as a Loss of Primary Containment (LOPC) event could result in economic losses, and environmental issues. Corrosion products accumulated in the pipeline can reduce the corrosion inhibitor effectiveness, leading to under deposit corrosion (UDC) issues. Therefore, these pipelines are regularly cleaned using cleaning pigs to remove the sludge/corrosion products. Usage of metallic cleaning brushes instead of plastic brushes have gained momentum as they can deliver a better cleaning efficiency due to their higher hardness, specifically reaching into small pits.

This work details an attempt to understand the environmentally assisted cracking behavior of metallic cleaning brushes in sour service conditions. Carbon Steel (ASTM A228), Stainless Steel (SS) 302 (UNS30200) and 304 (UNS30400) materials were tested using U-bend specimens in condensed water composition of 3500 mg/l (Cl^-) with a TDS of 5785 mg/l at pCO_2 (3.2 bar) and pH_2S(1.7 bar) at 75 ^oC and 25 ^oC for several exposure conditions (4h,8h,24h and 48h). The materials evaluated are cold rolled with a hardness of 50-52 HRC. Carbon steel samples failed in 4h exposure due to sulfide stress cracking (SSC) whilst the stainless-steel samples did not fail during the exposure test. Microscopic examination of stainless steel samples post exposure in 25 ^oC test condition revealed that several pits and cracks were initiated in samples exposed to 8h test duration potentially due to sulfide stress corrosion cracking (SSCC). The number of pits and the crack length increased with increased exposure duration. However, no pits were found in the 4-hour duration sample. At higher temperatures (75 ^oC), the SS samples showed deeper pits with higher mass loss and cracks originated from them. These exposure tests assisted in defining an integrity operating window and paved way for selection of cleaning pig brush materials for sour conditions.

The Effect of Oxygen on Crevice Corrosion of CRA OCTG Material in HT/HP Natural Gas Well Condition

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Localized corrosion was observed on the tubing made of 22Cr duplex stainless steel (DSS) that was retrieved from a high-pressure and high-temperature (HP/HT) natural gas well that had undergone workover operations. The produced natural gas contains 6% CO_2 and 3 ppm H_2S. The cause of corrosion is considered to be insufficient deaeration during the injection of a large amount of brine due to well packer trouble.

To evaluate the effect of localized corrosion in aerated and deaerated HP/HT environments, immersion tests and electrochemical measurements were conducted on 22Cr DSS and 17Cr SS at 90 ˚C and 180 ˚C. Test solutions used in the immersion tests contained 50,000 ppm Cl^- and 12 wt% NaCl to simulate brine conditions. In addition, the influence of $CaCO_3$ was also evaluated.

The average corrosion rate of 22Cr DSS was lower than that of 17Cr SS, and this trend was consistent in an oxygen-containing environment. Selective corrosion in crevice areas was observed on the martensitic phase of 17Cr SS and the ferrite phase of 22Cr DSS. The concentration of Cl^- had a significant effect on the average corrosion rate. However, the pitting corrosion depths of both 17Cr SS and 22Cr DSS were independent of Cl^- concentration. In a deaerated environment, both the corrosion rates and the pitting depths were decreased. The addition of $CaCO_3$ resulted in a decrease in the corrosion rate but an increase in pitting corrosion. These findings suggest that the pitting corrosion is accelerated by potential differences caused by dissolved oxygen concentration between the inside and outside of the crevice, and a decrease in pH due to the leaching of ionic components such as Cr during corrosion.

Effect of Ni on Fissure and Sulfide Stress Cracking in Carbon Steel

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In the oil and gas industry, pipelines transporting oil and natural gas get exposed to wet H_2S environments (sour environments), causing sulfide stress cracking (SSC) in low-alloy carbon steel in some cases. Recently, a judgment flowchart was proposed to determine SSC susceptibility based on the shape of the corrosion or microcracks on steel surface observed in the early stages of SSC. A crack-like corrosion morphology called “fissure” occurs in Ni-containing steel materials. Reports have highlighted that fissure formation is different from SSC, but fissures are extremely similar to cracks in terms of shape; however, the initiation and growth mechanisms remain unclear. Furthermore, if a fissure were to be determined by the SSC judgement flowchart, all steel materials with Ni above a certain concentration may fail the SSC test.

This study investigated the effects of Ni on fissure and SSC. Constant-load tests and double cantilever beam tests (DCB tests) were conducted under various sour environments using TS 800 MPa grade steel with and without 1 % Ni addition. Fissures were observed in Ni-added steel and their characteristics were classified into various shapes such as stress groove, cracklet, and deep corrosion pit, which can be judged as either “fail” or “pass” on the SSC judgment chart. These fissures were not observed on the cathodic side but on the corrosion potential and anodic side. Additionally, these fissures were confirmed to be active path corrosion based on the relationship between the fissures and crystal orientation of the microstructure. In the presentation, the effect of Ni on absorbed hydrogen concentration and fracture toughness values (K_{ISSC}) will be demonstrated and the stress intensity factors at the tips of fissures and the SSC judgement flowchart for Ni-added steel will be discussed.

Material Selection Experience for Offshore Wet Sour Gas Pipelines

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Selection of materials for high pressure gas pipelines should reflect the overall philosophy regarding design life, failure risk evaluations, inspection and maintenance philosophy, safety and environmental profile, and cost profile. For an offshore wet sour gas field, designers calculate the expected corrosion rate per year based on the reservoir conditions, and material selection is performed. At a minimum, reservoir corrosivity evaluation should include CO_2 content, H_2S content, elemental sulfur content, halide metal ion content, operating temperature, operating pressure, organic acids presence, flow regime and condensing conditions. Also, the feasibility of top of line corrosion (TLC) should be evaluated as the wet gas pipeline will get cooled by seawater. When corrosion is expected to exceed a certain level, Corrosion Resistant Alloy (CRA) material or CRA weld overlay on carbon steel are selected. When top of line corrosion is a concern, and temperature limits are suited, fusion bond epoxy (FBE) coated pipelines are selected. In cases of lower corrosion rates, carbon steel with a higher wall thickness is selected.

This paper summarizes cases of five different reservoir conditions, the challenges with material selection and lifecycle costs, material selected, and testing regime for FBE coating when applicable. Further, FBE coating testing regime for applicable reservoirs are articulated where the type of tests included dry film thickness (DFT) testing, hardness testing, holiday detection, pull-off adhesion testing, electrochemical impedance spectroscopy (EIS) and autoclave testing. The paper also examines the effect of different hydrate control methods on FBE coating and top of line corrosion (TLC).

Qualification Testing of UNS R53475 Titanium for Stress Joints

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A new titanium alloy UNS R53475 (475) has been developed to meet the requirements for riser tapered stress joints (TSJ) using on FPSO's operating in the Campos basin. TIMETAL® 475 is a moderately alloyed grade Ti-0.4%Ni-3.6%Mo-0.75%Zr designed for superior corrosion resistance with good high temperature strength combined with ease of manufacture. The alloy can be heat treated to a wide range of strength and toughness in either the alpha-beta or beta microstructural conditions. The alloy is designed to replace alloy UNS R56404 without the requirement of costly Ruthenium additions.

The FPSO operator experienced corrosion issues with existing flexible risers that are to be replaced with steel catenary risers (SCR). Installation requires a unique titanium pull tube design (TiPT) with five individual flange bolted forgings to be inserted though the existing porch structure with significant bending. Qualification requirements were based on the specific specifications set out by the operator. Forged and trepanned bar was produced to simulate the dimensions of actual components. A heat treat matrix was carried out to determine to meet basic mechanical properties as well as fatigue and fracture toughness. Fatigue testing was performed in air to establish base properties. Environmental testing focused on corrosion fatigue crack growth rates (FCGR) under conditions designed to mimic ocean frequency. A fatigue frequency scan was conducted in NACE A solution to determine if the alloy was in was susceptible to localized corrosion. Slow strain rate tests were conducted based on NACE TM-0198 Appendix C. J-R toughness curves were produced according to ASTM E1820. Finally, stress-life measurements were made to validate against published TSJ curves. This paper summarizes these results.

In-Situ Electrochemistry in Applied Load Tests to Further Understand CO2-SCC in a Flexible Pipe Annulus Environment

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The annuli of flexible pipelines represent a unique corrosive environment due to the low ratio between the volume of electrolyte and the exposed steel surface. This specific environment is associated with extremely low corrosion rates of the carbon steel wires because of the formation of protective corrosion product films. However, it has been observed, under certain conditions, that this same environment is susceptible to CO_2-induced Stress Corrosion Cracking (CO_2-SCC).

In this work, the initiation and propagation of CO_2-induced Stress Corrosion Cracking (CO_2-SCC) on flexible pipe carbon steel armor wire specimens were investigated, simultaneously, under applied stress and using Electrochemical Impedance Spectroscopy (EIS). This complex experimental technique of carrying out electrochemical measurements on a sample under tensile load in a high-pressure CO_2 environment is rather innovative and helped track the corrosion behavior of the stressed test specimen. Multiple tests, carried out over different time durations, demonstrates that the formation of a protective “pseudo-passive” film is a necessary pre-cursor to the initiation of CO_2-SCC. Furthermore, electrochemical data showed changes in the impedance behavior resulting from the initiation and propagation of cracks on the steel surface well before final sample fracture.

Investigation into the CO_2 SCC mechanism in tensile wires of flexible pipes

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Abstract

In the recent years, CO_2 stress corrosion cracking (CO_2 SCC) was identified as a potential cause of failure of carbon steel wires used in the tensile armour of flexible pipes. This research initiative aims to expand the knowledge of this failure mechanism through an extensive testing programme dedicated to study the CO_2 SCC mechanism and investigate how different parameters might influence the CO_2 SCC susceptibility of these wires. Small-scale tests have been carried out with wire specimens stressed by four-point bending. They were exposed at different CO_2 partial pressures to artificial seawater solutions supersaturated with iron carbonate ($FeCO_3$) to simulate the annulus conditions. The high content of dissolved $FeCO_3$, artificially achieved prior to the exposure, compensated for the relatively large water volume to steel surface area ratio (V/S) in the experiments in comparison to the V/S in the annulus of the pipe, which is typically very low. In some of the tests, the specimens were subjected to electrochemical polarisation to examine the nature of the CO_2 SCC mechanism. The results have shown that the CO_2 SCC susceptibility is strongly affected by the characteristics of the $FeCO_3$ film formed on the steel surface, which in turn is influenced by the surface condition of the steel (history effect) and the environmental conditions. The results of tests with polarised specimens suggest that CO_2 SCC is an anodic dissolution mechanism.

Keywords: carbon steel, CO_2 stress corrosion cracking, flexible pipes, galvanostatic polarisation, iron carbonate

Prediction of pH and iron ion concentration in the annulus of flexible pipes compared to results from full- and small-scale corrosion tests

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The annulus of a flexible pipe constitutes a very confined environment (low liquid volume to available steel surface area), normally characterized by diffusion of only a few chemical substances and water. In most cases, the corrosive environment within the annulus may be described by modelling of CO_2 and H_2S fugacities in combination with annulus water composition and ionic strength. During the last 25 years a vast amount of small- and full-scale tests were carried out and published by industry to characterise corrosion and environment of the highly confined annulus. Recent findings from the new NOV full-scale test facility combined with results from small-scale testing provided new insight in annulus environment evolution. Carbon steel armour wire corrosion rates were measured by weight loss as well as hydrogen evolution measurements, and pH was measured in-situ and ex-situ. Due to the confined environment, the annulus liquid becomes highly super saturated with iron ions. After a short initial period of relatively high corrosion rates and a maximum in iron carbonate supersaturation, the corrosion rates decline due to passivation, and the iron ion concentration and pH decline, but stabilizes at higher levels than for saturation. Based on experiments and theoretical considerations, correlations and trends in corrosion rates, iron ion concentrations and resulting pH as a function mainly of fugacity and temperature are presented and discussed.

Keywords: Flexible pipe, annulus pH, carbon steel, iron carbonate, super saturation.

EIS study of carbon steel corrosion in presence of viscosifying polymers for EOR application

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Polymer flooding is an Enhanced Oil Recovery (EOR) technique that allows to extract 8 to 20 % more crude oil during oilfield exploitation SAV10, an Acrylamide Tertiary Butyl Sulfonic (ATBS) based polymer may be used to viscosify the injected brine in a wide range of high temperatures and high salinities. In such conditions, corrosion control is a key parameter to ensure integrity of the facilities.

Objectives

The aim of the study is to determine the corrosion rate and the corrosion mechanism of carbon steel over a wide range of concentration (0.06 mol/L to 4.1 mol/L) through electrochemical techniques and to evaluate the impact of polymer.

Results

Corrosion rate is not monotonous, with a maximum around 0.5 mol/L Deep analysis of Electrochemical Impedance Spectroscopy – EIS, permits to determine that below this value corrosion rate is dominated by a faradic reactivity involving adsorption phenomenon and the charge transfer resistance is decreasing with increase of chloride concentration. At higher concentrations, mechanisms correspond to anodic and cathodic reactivity in parallel with limitation of the cathodic reactivity by mass transport. In presence of SAV10, mass transport limitation of faradic impedance limit drastically corrosion rate, especially at concentrations lower than 0.5 mol/L of chloride.

Conclusions

Then electrochemical techniques permit to determine the evolution of corrosion over a wide range of chloride concentrations (from 0.06 mol/L to 4,1 mol/L), to explain this evolution by a modification of the mechanism. With any chloride concentrations, SAV10 shows, at least, a slight inhibiting effect ensuring no additional detrimental effect on carbon steel injection structure and completion equipment.

Flexible pipes-corrosion when H_2S is consumed

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Flexible pipes used in oil and gas production are composed of densely packed steel armour wires enclosed in an annulus confined by inner and outer thermoplastic sheaths. Hydrocarbons, water, CO_2 and H_2S from the bore permeate through the thermoplastic sheaths. When the steel corrodes, Fe^{2+} and alkali are produced (Eq 1&3), $FeCO_3$ and FeS precipitate when a certain supersaturation is reached (Eq 2&4), and CO_2 and/or H_2S are consumed depending on the solids that are formed.

$$2H_2CO_3 + Fe = Fe^{2+} + 2HCO_3^- + H_2 \qquad \text{(Eq 1)}$$

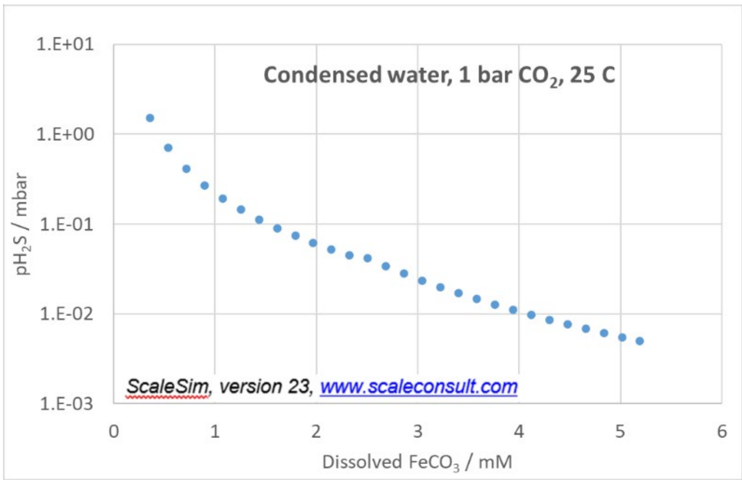
$$Fe^{2+} + CO_3^{2-} = FeCO_3\,(s) \qquad \text{(Eq 2)}$$

$$2H_2S + Fe = Fe^{2+} + 2HS^- + H_2 \qquad \text{(Eq 3)}$$

$$Fe^{2+} + S^{2-} = FeS\,(s) \qquad \text{(Eq 4)}$$

The FeS solubility is much lower than the $FeCO_3$ solubility and the precipitation kinetics much faster. The consequence for the flexible annuluses and for corrosion testing in the lab is that H_2S is consumed instead of the CO_2 until very low H_2S concentrations are achieved. The fast precipitation of FeS makes it challenging to perform experiments at low H_2S partial pressure as the concentration of H_2S in the gas phase (i.e. gas bubbling) can be quite different from the equilibrium concentration of dissolved H_2S in the water phase due to consumption in the water phase.

The H_2S consumption was documented/studied in confined environments where carbon steels were exposed to water and various CO_2/H_2S gas mixtures. When the concentration of dissolved $FeCO_3$ (Fe^{2+} and HCO_3^-) increased due to corrosion, the H_2S partial pressure decreased up to several orders of magnitude as illustrated in the figure where the equilibrium pressure of H_2S has been calculated with the ScaleSim model assuming a saturation ratio of 1 for FeS.



Corrosion Fatigue Test Philosophy for Lifetime Extension of Unbonded Flexible Risers

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Abstract

Safely prolonging infrastructure lifetime is essential for efficient operations and maintenance as the oil and gas industry is facing lower margins and pursuing to reduce the CO_2 footprint. Equinor has a significant portfolio of dynamic unbonded flexible risers in operation that are approaching the original design life of 20-25 years. Risers assessed to be in good technical condition and have a low risk of failure/leak are suitable candidates for lifetime extension studies.

Comparing the operational history to design premises may reveal conservative assumptions in design which represent a potential to utilize the remaining capacity. The flexible pipe suppliers' SN-curves for the individual armour wire qualities used in fatigue life design is typically chosen based on conservatively predicted annulus environment and dynamic loads.

Equinor has developed a modified corrosion fatigue test methodology, together with IFE, to better simulate a steady state annulus environment and wire surface condition of a long-operated flexible pipe compared to the widely used Marintek JIP test protocol [Catalogue for SN Curves JIP Corrosion Fatigue of Armour Wire for Flexible Pipes, Final report, 2019]. Sour service SN-curves generated for a pipe-specific wire quality in a corrosive environment with realistic H_2S flux incorporated into the methodology have been proven to give more accurate and less conservative fatigue life analyses than some of the Marintek JIP curves, enabling lifetime extension of several risers. The Equinor corrosion fatigue test methodology and 1-2 field cases will be presented, demonstrating the benefits of the new test methodology.

Black powder management in KOC West Kuwait facilities: establishing probable causes and mitigation strategies

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Abstract

This paper presents initial work in the remit of an R&D project focused on understanding and reducing the adverse effects due to black powder formation in West Kuwait (WK) petroleum production and distribution facilities. The so-called black powders are comprised of iron-based corrosion products, oxides, water, mineral scales, asphaltenes and may be dry powders or bulky sludges. Their formation in sour oil and gas production facilities presents unique challenges for maintenance, corrosion, instrumentation plugging, equipment damages that may eventually affect the product quality and result in production losses.

Initial efforts in this work have focused on thoroughly reviewing historical operations data of WK facilities (i.e. production flow-charts, fluid analyses and black powder composition reports), as well as maintenance and inspection reports. This meta-analysis has helped identify some of the most critical areas affected by black powders, as well as aspects of their nature. Thermodynamic calculations have been employed to examine the changing conditions in the gathering center during gas and water separation operations, and hydrodynamic simulations of solid particles transport was conducted to check the risks of black powder accumulation in gas and liquid pipelines using operational fluid dynamics data.

This paper intends to share the main findings of this investigation and to describe some of the solutions that will be explored to mitigate black powder issues.

The Use of the Ultraviolet Accelerated Weathering Tester to Study the Effect of UV Exposure on the Performance of FBE Coatings

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Abstract

Pipelines are among the safest, most cost-effective and efficient ways to deliver energy liquids and gases across nations. For example, 16.2 billion barrels of crude oil and petroleum products were transported by US transmission pipeline in 2014. These pipelines are crossing different environments such as salty soils, sand dunes, and seabed while others are directly exposed to sun lights. The most common technique to mitigate the environment corrosivity is by applying external coatings on these pipelines. In the oil and gas industry many of the coated pipes are exposed to the sun's UV light, which might have a detrimental effect on the unburied pipe's external organic coating, impacting its corrosion protection performance. Therefore, this study was conducted to investigate the effect of 1000 hours of intensive UV light on the performance of the fusion bonded epoxy (FBE) coating that is commonly utilized in the oil and gas industry as an external coating for steel pipes. A comprehensive test program was established to investigate the effect of UV light on the FBE coating after and before exposure in the Q-Lab Ultraviolet (QUV) Accelerated Weathering Tester. The program included several methodologies such as Electrochemical Impedance Spectroscopy (EIS), Adhesion Test, Impact Test, and hardness measurements.

Keywords: FBE, Organic Coating, Pipeline, UV Weathering Tester

Reviewing Three Pipeline Internal Corrosion Case Studies

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Abstract

Pipeline internal corrosion is a major integrity threat for many wet product transfer pipelines in the upstream, midstream and downstream oil and gas sectors. Severe pipeline internal corrosion rates could lead to pipeline leaks and failures with consequences such as: human injuries, environment pollution, deferred production, wasted product and extra labour, logistics and repair costs.

However, post-failure reviews illustrated the fact that a considerable portion of such pipeline issues were largely due to inadequate competency levels associated with corrosion, integrity and inspection disciplines. Thus, they could have been simply avoided by improving competency levels among the aforementioned disciplines. That is, providing relevant and timely training for the pertaining personnel could have easily prevented a significant portion of the pipeline internal corrosion incidents encountered. This paper reviews three pipeline internal corrosion case studies from the UK's North Sea Sector and the Persian Gulf Region. The main conclusion is that all such three cases (as well as many other similar ones) could have been avoided, if the relevant personnel possessed the required competency levels in the first place through proper and timely training; thus, also saving considerable amount of resources.

Driving Corrosion Monitoring Through Deployment of Customized Risk Based Inspection for Offshore Top-Side Operating Facilities

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Recently, the chemical, petrochemical and refinery sectors have been facing tougher safety, environmental and mechanical integrity regulations as well as challenges associated with the need for cost reduction to improve competitiveness. Under these circumstances, it has become crucial to manage operational risks and corrosion threats especially for offshore oil and gas facilities, through the use of cost-effective technologies and best practices for inspection and maintenance planning. To meet this intent, a customized Risk-Based Inspection (RBI) methodology is developed and discussed in this paper to assess offshore top-side operating facility in line with the concepts and fundamentals of RBI industry standards. The methodology enables effective corrosion damage mechanism management and involves measurement and calculation of risk through determination of a probability of failure (POF) combined with the consequence of failure (COF) which was tested and validated through a pilot RBI assessment performed on a Gas Compression Unit. The pilot was carried out for 40 pressure vessels, 80 heat exchangers and 418 piping systems. It revealed that 14% and 15% of the equipment/piping are at high risk and medium-high risk levels, respectively, due to Wet H_2S Damage, Corrosion Under Insulation and CO_2 Corrosion. To manage corrosion and risk of failure, a total of 663 internal and external corrosion, 23 stress corrosion cracking damage mechanism inspection tasks have been listed. Furthermore, the pilot assessment revealed the Turnaround internal inspection interval can be extended from 5 to 7 years which results in a business cost avoidance.

How to avoid CUI.
Experience with pipe insulation in the Barents Sea after 8 years in operation

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Corrosion Under Insulation (CUI) is regarded as one of the most critical safety risks for oil and gas processing plants.

Can the CUI problem be solved? My respond is that we have the technology to eliminate the problem, may not remove CUI completely, but down to a level that it is not regarded as a problem.

This paper will focus on experience with the pipe insulation solutions on the Goliat FPSO installation in the Barents Sea after 8 years in operation. What steps was taken and what are the result related to avoiding CUI.

The Goliat installation is far north in a cold climate which required an extensive insulation scope due to winterisation of piping systems with heat tracing and insulation. The offshore oil and gas industry need to select robust and long-lasting solutions.

Pipe insulation solutions based on NORSOK M-004 “Piping and equipment insulation” will be presented and also DNV-RP-G109 “Risk based management of corrosion under insulation“, and how this is used to define inspection location and intervals.

Content in existing standards and possible “new” insulation materials will be discussed.

Key words: CUI. Insulation

Materials integrity assurance for carbon capture and storage injection wells

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Abstract:

Carbon Capture and Storage (CCS) technology is currrently the most important techology available to mitigate emissions from large scale fossil fuel use. It is essential to develop a good understanding of CO2 composition and phase behaviour to understand material threats and corrosion. Impurities in the supercritical CO2 stream can react and cause dropout of highly corrosive liquids which could be detrimental for the metallic materials. Selection of materials plays pivotal role in each of the main steps involved in CCS such as CO2 capture, processing, transportation and injection for ensuring asset integrity and optimization of cost. CO2 is compressed to supercritical pressures for transportation to its final injection and storage facility. Supercritical CO2 along with the presence of various contaminants/impurtities can be very corrosive to metallic materials in the presence of water. Intent of this paper is to discuss the effect of O2 as contaminant in supercritical CO2 environtment on metallic materials to determine the integrity operating window for CO2 injection wells. An electrochemical methodology was used to evaluate the critical crevice temperature (CCT) of the corrosion resistant alloys such as 25CRW [UNS S39274], G3-110 [UNS N06985], SM2550 [UNS N06255], P750 [DIN 1.4675] , 955 [UNS N09955] and HC276 [UNS N10276]. The effect of chlorides and gaseous impurities on these alloys are also studied in the presence of supercriticalCO2. The current study developed safe operating envelope for these alloys under supercritical CO2 conditions with various contaminants. Supercritical CO2 corrosion testing capabilities in the form of electrochemical measurements and exposure studies have been developed, which would be used as an effective screenging method for materials selection for various sections of CCS processes.

Failure analysis: a galvanic influenced corrosion in very salty environment leading to a pipeline replacement

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Only a few weeks after the startup of a 16’’ pipeline in the middle east a very quick and unexpected corrosion issue was experienced. Following successive in line inspection runs where up to 80% loss in thickness was recorded, it has been concluded that the corrosion cannot be successfully mitigated with a regular chemical treatment. The pipeline was shut down and preserved 18 months after startup and before any leakage was detected due to the loss in wall thickness of the pipeline.

Following an investigation and a root cause analysis, the mechanism of corrosion threat that occurred cannot be definitively confirmed but it is believed to be galvanically influenced CO2 corrosion in a high chloride environment. To our knowledge such a mechanism and associated massive weight loss corrosion has never been experienced nor reported in the past by any Operator.

It is worth noting that this, has yet unexplained rapid loss in thickness, is a significant threat observed in the oil and gas industry. The objective will be to present the main data collected and propose a mechanism.

Best Practices of Designing a Laboratory Test Matrix for Corrosion Inhibitors Evaluation

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Abstract

Chemical corrosion inhibition (CI) is one of the most common ways to control corrosion in a pipeline. They are widely used as an effective mean for controlling corrosion of carbon steel in oil and gas production and processing facilities. The mechanism of corrosion inhibition is attributed to the adsorption of the inhibitor on the pipe wall. A large number of commercial CI products are available with chemical formulations that are application specific and new products are being continually introduced to handle increasing corrosion severity. Currently, there are no internationally accepted standard test protocols to qualify and compare the performance of candidate inhibitors for the oil and gas service. Each user develops its internal guidelines based on own specific application, testing cost, resource availability, etc. Establishing a laboratory best practice for corrosion inhibitors to optimize the selection process, minimize evaluation cost, and ensure consistency in the selection process is discussed in this paper.

Key words: prescreening tests, accelerated tests, corrosion, chemicals dosage, performance ranking, corrosion inhibitor.

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3) Organization, City/Country

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Characterizing a cost-effective impeller-agitated system for corrosion testing using computational fluid dynamic (CFD)

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Laboratory tests are commonly used to evaluate the performance of materials and corrosion inhibitors in the oil and gas (O&G) industry. However, the current standard methodologies for assessing corrosion inhibitors under flow conditions have limitations, such as the centrifugal force effect on the rotating electrode, non-representative results of localized corrosion using the jet impingement technique, and the need for large fluid volumes in flow-loop systems. To address these limitations, this work focuses on investigating the effect of baffles on a 45° pitched blade turbine (PBT) stirred tank as an alternative to standardized laboratory methodologies. Computational fluid dynamics (CFD) simulations were used to estimate the wall shear stress on the samples, analyse flow patterns, and investigate the effect of baffles in the vessel. The results showed that the stirred tank model with an upper baffle showed less disturbance due to the absence of vortex formation, leading to a more uniform distribution of velocities inside the vessel. A uniform distribution of wall shear stresses (τ_W) on the samples was also observed. A flow test was performed to obtain mass transfer coefficients using the stirred tank model with an upper baffle. The mass transfer coefficients were determined by investigating the dependence of the Sherwood number (Sh) on the Reynolds number (Re) and the Schmidt number (Sc) in a coupled ferri-ferro cyanide system. By utilizing the Sherwood correlation, the corresponding velocities for varying impeller speeds in a pipe with a diameter of 0.1 m were determined. The results demonstrate that the proposed system is a simplified, cost-effective, and easy-to-adapt system that can be characterized using CFD simulations and mass transfer tests. Therefore, the impeller-agitated system can be considered a suitable alternative to standardized methodologies.

Keywords: CFD, pitched blade turbine, mass transfer, laboratory methodology

Influence of the specimen profile geometry on rotating cage corrosion mechanism

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The ASTM G170-06 standard addresses the rotating cage (RC) as a laboratory methodology to simulate environments in the oil and gas (O&G) sector and evaluate the corrosion resistance of materials under flow conditions. Nevertheless, there is a consensus regarding the conservative nature of this technique, mainly attributed to the non-uniform distribution of wall shear stresses on the specimens. This study aims to assess the impact of the geometric shape of the specimen profile on the wall shear stress uniformity by characterizing the flow patterns inside the autoclave, especially around the samples to a better understanding of the corrosion mechanisms. Utilizing the Computational Fluid Dynamics (CFD) technique, three specimen profiles were evaluated: a rectangular one, as specified in the ASTM G170-06 standard, and two aerodynamic profiles - one with rounded edges and another with a rounded leading edge and streamlined trailing edge. Simulations were conducted at 1000 rpm in an autoclave with an upper baffle. The results indicate that aerodynamic profiles promote a notable alteration in the flow patterns inside of the autoclave, particularly around the specimens. The most significant changes were observed for the rounded edges profile. The velocity profile on the specimen was strongly influenced by the profile's shape, it becomes larger near the wall, therefore modifying the distance between the boundary layer and the outer flow region. Turbulent kinetic energy values and predicted streamlines around samples were also significantly modified. All these modifications result in an increase in the wall shear stress uniformity index ranging between 7.54% and 2.54% from both rounded edges and another with a rounded leading edge and streamlined trailing edge, respectively, when compared with rectangular profile. It is concluded that altering the specimen profile in relation to the standard ones provides a more uniform distribution of the wall shear stresses on coupons surfaces which leads to a more homogeneous distribution of corrosion rates along the samples.

Advancement in Vapor Corrosion Inhibitor Delivery for Aboveground Storage Tanks: Case Studies and Best Practices

***Jessica Davis*[1], *Juan Dominguez Olivo*[1], *Terry Natale*[1]**

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A comprehensive exploration of state-of-the-art methods for delivering vapor corrosion inhibitors (VCIs) beneath aboveground storage tanks (ASTs) is presented in this conference proceeding. Advantages associated with VCIs, such as ease of application and reapplication, the capability to provide corrosion protection both in direct contact with the tank bottom and indirectly through airspace, and the potential to establish a more alkaline environment under the tank, are discussed. The latest technological advancements in this critical area of corrosion prevention are showcased through a series of case studies and laboratory data. Topics covered include the utilization of dry delivery systems, application techniques for weldable plates, and the integration of corrosion monitoring by electrical resistance probes. The application of corrosion inhibitors is targeted toward each asset depending on foundation type, operating conditions, and access to the tank. Real-world scenarios and best practices are examined, providing valuable insights into the optimization of corrosion inhibition strategies for ASTs. Asset longevity and operational reliability are ultimately enhanced through the application of these findings.

Oil Field Production Chemical Qualification for Umbilical Usage in Deepwater Applications

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ABSTRACT

Umbilical functionality is critical to the proper operation of subsea production systems to eliminate risks and downtime. The importance of preventing deepwater operational issues has led to more stringent chemical quality requirements. These applications have gone deeper in depth, further from shores, and more demanding as far as Health, Safety & Environment are concerned. Production chemicals such as corrosion inhibitors to provide protections for deepwater systems from flow assurance to integrity management have become more demanding concerning product performance, stability, deliverability, and compatibility with the materials of construction. The present work describes various laboratory testing protocols used for certificating oil field production chemicals including corrosion inhibitors designed for subsea applications via umbilical in deepwater applications.

Keywords: corrosion inhibitors, water-soluble corrosion inhibitors, deepwater chemical, umbilical application, corrosion inhibitor testing

An Overview of Vapor Corrosion Inhibitor Delivery for the Protection of Pipelines

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This presentation aims to give an overview of the application of Vapor Corrosion Inhibitors (VCIs) as a method for preserving pipeline integrity during both operation and in storage. Application of Vapor Corrosion Inhibitors inside pipe assets is demonstrated to provide effective protection against internal corrosion and can be tailored to individual assets based on operating conditions as well as concerns based on geometry of the asset. A summary of different approaches for the use of VCIs in pipelines for preservation, protection of casings, and preparation for service is outlined. The discussion includes a description of the chemistries employed, including information on Vapor Corrosion Inhibitors, Soluble Corrosion Inhibitors (SCI), and gel used in casings. Examples will be included from laboratory data as well as real-world scenarios, showcasing how the corrosion inhibitors are able to protect the asset through direct contact and airspace. This presentation also highlights the advantages of the use of VCIs in relation to personnel safety, cost-effectiveness, and ease of application.

Effect of Preferential Welding Corrosion on The Lifetime of Mooring Chains

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The mooring system is responsible for ensuring that floating offshore production units remain positioned within a safe region, keeping the unit in place during storms and other environmental conditions during the operation phase. A critical failure in this system can lead to significant accidents with environmental, human, and economic consequences. Therefore, it is essential to have a proper mooring system integrity management.

Subsea mooring lines inspections often identify the presence of preferential weld corrosion (PWC) on chain links. The phenomenon affects the flash weld zone, generated during the welding process. The presence of PWC raises concerns about the structural integrity of the mooring chains, necessitating an assessment of its effects during the operational phase.

This paper discusses the effect of PWC on mooring chains in operation and performs an assessment of the effect of this phenomenon for a particular case, using fracture mechanics and hot spot fatigue assessment.

Fitness-for-service and hot spot fatigue methods were adapted for evaluating the integrity of mooring chains. The presence of PWC has a negative effect on the fatigue life of mooring lines. The extent of this negative effect depends on the geometry (depth and width) of the PWC, and the loads experienced by the mooring chains. Field observations show that the geometry of the PWC varies and can be presented as a W shape or a groove.

The presence of PWC can significantly reduce the fatigue life of mooring chains. It is crucial to further explore methods for assessing localized defects in mooring chains to enhance integrity management. During the design phase, the use of fatigue life safety factors greater than the minimum recommended by standards is advised to account for this type of uncertainty. Additionally, mitigation measures during the manufacturing phase, such as improving welding and heat treatment procedures, should be evaluated. Cathodic protection in mooring chains can also be employed to prevent PWC.

Field Cases - Pipeline Corrosion/Erosion Monitoring and Management

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Erosion, sometimes combined with corrosion, is a challenge in many industries, such as conventional oil and gas production, oil sands production and mining. Erosion can be caused by sand particles produced with oil and gas and by slurry transport in oil sands processing and mining industry. Strategies to manage erosion can be early warnings if erosion rates exceed a certain level, tuning of flowrates to optimize sand amount versus production rates and predict estimated pipe life and plan repairs/replacements. Another strategy can be rotating pipelines to extend the operating life.

High accuracy ultrasonic wall thickness monitoring is a valuable tool for efficient erosion management. Sensor and configuration examples of distributed UT sensors used in Oil & Gas production and UT sensor belts for slurry lines are presented. Field Data examples are shown, explaining how data is used for real life erosion management and extending asset life – contributing to safer and more sustainable operations.

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Study for a corrosion inhibitor for extreme sour conditions

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Corrosion poses safety and operational challenges in the oil and gas field, particularly in sour environments. Corrosion inhibitors (CIs) are therefore used to protect the integrity of industrial assets. The anticorrosion effect of different formulations of alkoxylated amine based CIs on carbon steel (CS) was investigated by electrochemical and gravimetric techniques. The corrosion process was monitored both in static and in high flow rate conditions (τ=200Pa). Weight loss tests were performed with specimens immersed in a sodium chloride (1600ppm) sodium acetate (450ppm) brine with the addition of 1% kerosene exposed to a highly sour atmosphere (P_{H2S} 15bar, P_{CO2} 5bar) at temperature up to 85°C. Although all the compounds exhibit very good performance as inhibitors of CS corrosion in dynamic tests (corrosion rate <0,1mm/y), under static conditions some of the formulations promoted localized corrosion phenomena. Further investigation of the adsorption properties, studied by electrochemical measurements, and other physical parameters such as high cloud point and water/oil repartition allowed to understand that the poor protection in static conditions can be attributed to the loss of emulsion stability at elevated temperature.

Advancing Environmentally Responsible Zinc Electrodeposition using Halide Free Non-Aqueous Electrolytes: Insights from the INHALE Project

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Metallic zinc coatings are indispensable in various industries, especially transportation, where electroplated zinc and zinc-alloy coatings provide essential corrosion resistance for mechanical components like fasteners and brake calipers. However, traditional aqueous solutions used for zinc electrodeposition pose environmental and safety challenges due to their toxicity, corrosiveness, and propensity to induce hydrogen embrittlement. The investigation of halide free ionic liquids for the electrodeposition of zinc and zinc alloys (INHALE) project addresses these concerns by focusing on the development of environmentally responsible alternatives. By exploring halide-free ionic liquids (ILs), deep eutectic solvents (DESs), and organic solutions, the project systematically evaluated and downselected electrolyte systems, successfully producing halide-free electrolytes and zinc coatings with performance comparable to conventional approaches. The primary objective is to present an overview of the INHALE project, emphasizing its comprehensive evaluation of different non-aqueous halide-free electrolytes' impact on zinc and zinc-alloy electrodeposition. Key considerations include environmental impact, corrosion resistance, scalability, and cost analysis. Additionally, the comparative assessments between traditional aqueous electrolytes and halide-free alternatives, providing valuable insights into alternative electrolytes for electroplating applications will be discussed. Through its research and findings, the contributions from the INHALE project towards advancing environmentally friendly solutions for zinc electrodeposition, addressing critical environmental concerns will be discussed.

This research has received funding from the European Union’s Horizon 2020 research and innovation program under the Marie Sklodowska-Curie grant agreement No. 885793.

Effect of Mg and Al on Microstructure and Corrosion Resistance of High Contents Zn-Al-Mg Alloy Coated Steel Sheets

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Zn-Al-Mg alloy coated steel sheet has been developed since the early 2000s with the purpose of replacing the galvanized steel sheets (GI) in areas where high corrosion resistance is required. The Mg content contributes to corrosion resistance by forming such as eutectic phase and $MgZn_2$ phase. The Al content contributes to the formation of ternary eutectic phase and dense corrosion products. On the other hand, the Mg and Al contents of the Zn-Al-Mg alloy coated steel sheets are inevitably limited due to high oxidation properties and dross generation on the process. For areas exposed to more severe corrosive environments, some steel makers have developed Zn-Al-Mg coated steel products by increasing Al and Mg content. However, the research is not well known that the effect of high contents Zn-Al-Mg alloy coated steel sheets on the microstructure behaviour and corrosion resistance.

Investigation in this paper focuses on microstructure and corrosion resistance of Zn-Al-Mg coated steel sheets by increasing Al and Mg contents. As increasing Mg contents, corrosion resistance improves as the $MgZn_2$ phase fraction increases, but the $MgZn_2$ phase formed on the surface cause coating crack. Increasing Al can decrease Mg oxidation, but if excessive, it accelerates growth of inhibition layer due to Fe-Al diffusion reactions. The corrosion resistance of Zn-Al-Mg coated steel sheet was evaluated following the ASTM B117-16 salt spray test. Microstructure and surface morphology of bending sample were investigated using Field Emission Scanning Electron Microscopy (FE-SEM).

Keywords: Zn-Al-Mg coated steel, corrosion resistant, microstructure

Study into corrosion resistance in marine environments or Cold Metal Sprayed Aluminium components.

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Cold Metal Spray (CMS) technology has operated in marine environments, primarily in the oil and gas industry and in shipping. The primary purpose of this technology is to produce a sacrificial coating onto steel platforms/shipping to impart corrosion protection. A variety of alloys can be applied using this technology, but this study primarily uses an aluminum/alumina coating.

The advantage of this coating method is that it can be applied in situ by applying powder at supersonic speeds which provides:

1) a very high bond strength
2) a better enclosed working environment

The supersonic speeds produce mechanical interlocking of the powder onto the substrate utilising nitrogen/helium imprinting. This produces a very strong bond strength without the need for heating. Not needing a large inventory of heating equipment lends this technique to working in confined spaces. The process does not damage the substrate at all, because it involves no heat, so there is no heat affected zone problems on the surface.

The nature of the coating means that it will be galvanically sacrificial to the steel substrate. Particularly for marine shipping applications, the key question that needs to be answered is the lifetime of this coating. Especially for the internal areas within shipping, where the coating can be brought into contact with a number of different sea water based solutions contaminated with a variety of oils, solvents and other chemicals.

The work detailed in this presentation acts as an extended lifetime trial has imitated typical exposure conditions in a variety of locations in a ship, looking at the rate of degradation and the nature of the chemical attack onto the surface.

Making hot-dip galvanizing usable as a corrosion protection system for steel hydraulic structures in Germany

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Abstract

in Germany, the Federal Waterways and Shipping Administration (WSV) is responsible for the operation, maintenance, upgrading and construction of federal waterways. According to the WSV guideline, the steel hydraulic structures must be passively protected against corrosion by coatings in compliance with the ZTV-W, LB 218 guideline. The approval of corrosion protection for the WSV is carried out by the Federal Waterways Engineering and Research Institute (BAW) as the federal authority in the department of the Federal Ministry of Transport and Digital Infrastructure (BMVI) based on its own experiments in accordance with the RPB-guideline. If the respective limit values of the analysis method are adhered to, the system is classified as "suitable" for the respective corrosion protection category. So far, only organic coating systems have been listed in the BAW's approval lists, but no corrosion protection systems based on hot-dip galvanizing. Making hot-dip galvanizing usable as a corrosion protection system for steel hydraulic structures in future is the motivation of the current work. The results based on initial long-term exposure test presented in this study are to become the basis for systematically identifying and solving open questions. Nevertheless, supplementary experiments regarding chemical parameters of water, abrasion and ecotoxicological effects and development a new approach should be considered.

Keywords:
Steel hydraulic structures, breakwater, hot-dip galvanizing, corrosion resistance, zinc coatings, coating systems

Electrochemical and corrosion behaviour of new AlSiZnMg coatings

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Hot-dip galvanizing is largely used to improve the corrosion protection of steel. In the last decades, the steel industry has proposed to improve the performance of coatings, either by alloying the Zn with other elements or completely replacing Zn galvanizing by Al based galvanizing, generating complex microstructures containing multiple phases with varied chemistry and electrochemical behavior. The objective of this work is to understand the correlation between the microstructure and the corrosion mechanisms of new AlSiZnMg metallic coatings. Special focus is made on the effect of corrosive environment (Cl^- containing with NaCl and Cl^- free with Na_2SO_4).

Coatings with the composition of Al from 33 wt.% to 55 wt.% and the amount of Si and Mg ranging from 0 to 5 wt.% were studied in the configuration of intact coating and in the presence of the scratch, allowing galvanic coupling with the underlying steel. Samples were subjected to accelerated corrosion tests in climatic chamber and to electrochemical tests, in both NaCl and Na_2SO_4 environments, with following chemical and microstructural characterizations. Scanning electron microscope (SEM) with an energy-dispersive spectrometer (EDS) analysis were used to observe the corroded microstructure and the morphology and chemistry of the corrosion products, complemented by X-ray diffraction (XRD) and Raman spectroscopy. Accelerated corrosion with NaCl highlighted a significant difference in the behavior of the coatings when coupling with steel is made. Samples with high Al content presented better behavior if tested without the scratch, while samples containing more Mg-rich phases presented a better behavior when scratched.

Electrochemical dissolution tests were performed to understand how different phases would behave in the environments with and without chloride. In both environments, the binary ZnAl phase corroded first, while the dendrites of α-Al were the last phase to corrode. The corrosion potential of the dendrites was higher in Na_2SO_4 than in NaCl, and was close to the corrosion potential of steel.

Controllable release of Cu ions contributes to the enhanced environmentally-friendly performance of antifouling Cu-bearing stainless steel coating prepared using high-velocity air fuel

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Organic antifouling coatings represent an economical and efficient solution for addressing the marine biofouling. However, their application is constrained by issues of durability and toxicity. Therefore, this study has developed a metal-based antifouling coating by utilizing pre-alloyed copper-bearing stainless steel (Cu-bearing SS) powder in conjunction with high-velocity air fuel (HVAF) technology, aiming to achieve an environmentally-friendly and long-lasting antifouling coating. The results showed that the Cu-bearing SS coating exhibited enhanced bonding strength, hardness and wear resistance compared to the self-polishing copolymer (SPC) coating. Furthermore, the coating demonstrated strong inhibitory effects on typical fouling microorganisms and algae adhesion due to Cu ions release process environmentally-friendly. The electrochemical techniques coupling with surface morphology observations were used to elucidate the antifouling mechanism. The three-stage evolution of surface morphology, accompanied by the controlled release process of Cu ions, had become a distinctive feature of antifouling properties for a metal-based coating.

Corrosion behavior of SiC/Cu and Al_2O_3/Cu composite coatings deposited by cold spray coating process

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Dynamic cold gas spraying is one of the most innovative thermal spraying processes. It enables the production of metal matrix composite (MMC) coatings from mixtures of metal and ceramic powder projected at very high speeds (500 to 1200 m/s) by an inert propellant gas flow. Solid metal particles undergo intense plastic deformation well below the melting point, leading to the rupture of thin oxide layers formed on the substrate and particle surfaces, thus allowing close contact and strong bonding between chemically active material grains.

Studies have shown that these metal-ceramic composite coatings exhibit significantly higher density and mechanical properties compared to pure metal coatings without the addition of ceramic particles. Among the various available metallic materials for the matrix, copper is interesting due to its corrosion resistance, especially in a deaerated environment.

The objective of this work is to conduct a comparative study of the corrosion resistance of high-purity solid copper and SiC/Cu or Al_2O_3/Cu composite cold spray coatings produced by cold spraying, depending on the ceramic particles proportion. Corrosion behavior is assessed using classical electrochemical methods: measurement of open circuit potential, potentiodynamic polarization and mass loss measurements in naturally aerated saline solution and synthetic ground water. The results have allowed estimating the different corrosion rates of deposits and solid copper. Analysis of corroded surfaces revealed the more or less localized nature of corrosion depending on deposit density, notably the presence of porosities. Corrosion localization was also interpreted in relation to microstructure gradients within the particles through EBSD analyses.

Empowering PVD for corrosion protection: TiMgGdN coatings with game-changing corrosion performance

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Abstract

Today, PVD technology is not the 1st choice for surface functionalization under corrosive conditions. Sate of the art for corrosion protection are multilayers of electroplating or chemical corrosion protection layers, followed bv a PVD top layer. This effects sustainability and economic factors in a negative way.

The authors successfully developed PVD-TiMgGdN coatings, sputtered with a powder metallurgical target in an industrial DC-magnetron PVD unit. With an only 5 µm coating thickness, corrosive mild steel substrates can be protected for at least 1000 h in the salt spray test against corrosion [1].

After experimentally improving the mechanical, microstructural and corrosive properties of these coatings, the mechanism of alloying MgGd into the TiN matrix will be explained. Therefore, binary TiN coatings were compared with TiMgGdN coatings regarding their microstructural, chemical, physical and corrosion properties. Corrosion properties were investigated by different corrosion tests. The coating surfaces were also analyzed by nanoidentation measurements and chemical analysis to gather knowledge of the coating stability during corrosive stresses.

It will be shown that the excellent corrosion performance is mainly influenced by the MgGd amount inside the coatings, which influences the open circuit potential between substrate and coating significantly. Moreover, the outcome of the investigations will show, that the MgGd amount has a minor influence on the coatings mechanical properties but a major influence on the resulting microstructure and the chemical stability of the coating during corrosive stresses, which directly correlates with the corrosion performance.

[1] Ulrich, T., Pusch, C., Hoche, H., Polcik, P., Oechsner, M., Surface and Coatings Technology 422 (2021) 127496

Electrochemical measurements for investigating cold-sprayed tantalum coatings performances

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Stainless steels (SS) are usually corrosion-resistant in nitric acid environment. However, in severe conditions, SS present a high dissolution rate and, in most cases, intergranular corrosion is observed. The use of coatings is a promising way to improve the anti-corrosion properties of SS under such severe conditions.

This study deals with the corrosion behaviour of high-pressure cold-sprayed Ta coatings, compared with Ta bulk material and SS 304L substrate material. Polarization curves and electrochemical impedance spectroscopy measurements were carried out in 5 M HNO_3 solution at 80 °C with the addition of oxidizing species. The effect of the SS substrate material and of the cold-spray process on the coating formation was investigated using FESEM, EBSD, micro-hardness and X-ray tomography. The electrochemical measurements showed that the presence of the coating significantly influenced the corrosion of the SS: the passive domain was extending towards higher potentials. However, the passive current of the cold-sprayed coating is higher than the Ta bulk material. To explain this, we investigated the potential relationship with the microstructure of the cold-sprayed coating which is composed of homogenous hard splats (resulting from the cold-prayed powder). The presence of an inter-splats porosity would increase the real corroded surface, which could affect the electrochemical measurements.

The unique corrosion behaviors of magnetron-sputtered alloys

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Magnetron sputtering is a thin film deposition method known for its versatility and precise control over material characteristics. One of its key features, the high control of ad-atom diffusion, can be used to deposit non-equilibrium materials with phase compositions and microstructures that cannot be achieved through bulk synthesis. The corrosion resistance of these films has been reported to differ from, and often be higher than, bulk samples of the same composition. One suggested explanation is that the films are often nanocrystalline, which can greatly affect the corrosion processes [1]. However, this effect is not well understood and is difficult to isolate from other typical characteristics e.g. the lack of inclusions, high elemental homogeneity, highly oriented crystals, and sub-nanometer scale roughness.

In a series of studies, the effects of these characteristics were explored for several high entropy alloys. A method was developed to deposit films of the same composition with and without nano-spaced twin/grain boundaries and elemental segregation, as well as a range of crystal orientations. The samples were tested with multiple electrochemical methods, including scanning electrochemical cell microscopy to understand localized corrosion effects. The results showed that the microstructure can affect both the rate of active dissolution and the passive behavior. The mechanisms behind these effects will be described. Furthermore, films with sub-nanometer roughness displayed unusual wetting effects, e.g. superhydrophilicity during cathodic polarization. These insights can be used to optimize the corrosion resistance of alloys without changing their composition.

[1] R. K. Gupta, N. Birbilis, Corrosion Science. 92, 1–15 (2015).

Investigating the corrosion mechanism of high-velocity oxygen-fuel (HVOF) hard-facing materials using bipolar electrochemistry

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HVOF deposited hard-facing materials consist of tungsten carbides (WC) embedded in a Co, Ni, CoCr, and NiCrMo binder phase. Not much research has been conducted yet to assess the corrosion performance of this material group, with conventional corrosion tests so far only focusing on the corrosion nucleation threshold parameter. Material failure is to corrosion propagating through the microstructure. To improve our understanding of the corrosion mechanism of this alloy group, a bipolar electrochemistry corrosion screening test was employed, allowing for the estimation of critical corrosion potential and corrosion growth kinetics to be obtained. The findings reveal that the binder phase preferentially corrodes in HCl and NaCl, while WC is the primary cause for failure in NaOH. In acidic and neutral environments, modifying the binder composition enhances corrosion resistance. It was found that porosity is the key factor controlling corrosion propagation, irrespective of the binder composition.

Nanostructure Coatings for Protection Against Corrosion Applied to Oil Transporting Trunk Lines

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Abstract

Effective coatings of pipelines in oil and gas industries plants is vital in ensuring safety availability, increased production, reduced repair cost, and minimize the none productive time. Due to the high cost of coating used in oil and gas sectors, there is a need to enhance the coatings performance through choosing a strong and hard feedstock material by reducing the particle size to nanostructure size. The paper explores existing problems in pipeline due to corrosion and shows the different mechanisms occur. This paper also identifies the recent developments of WC-12Co nanostructured coatings and how they have performed when deposited using different thermal spray techniques, such as some of the successful spray techniques such as high velocity oxy fuel (HVOF) and cold gas dynamic spray. The research focuses on assessing such deposits (HVOF WC-12%Co nanostructured and HVOF WC-12%Co microstructured) against mechanical performance and corrosion performance. These results demonstrate that the significant improvement in nanostructured WC-12Co coating performance can be achieved by utilizing proper controlling parameters for each technique.

The microstructure and corrosion behavior of high entropy metallic layers deposited by selected electrochemical methods at low and high temperature.

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The crucial aim of this work was to analyse the effect of the manufacturing process on the chemical composition and morphology of the CoCrFeMnNi multi-component metallic layers (High Entropy Films, HEF) deposited by different electrochemical methods at low- and high temperature. The second goal was to optimize the parameters which allowed to obtain the CoCrFeMnNi layer with homogeneous and equimolar composition as close as it possible. The low-temperature electrodeposition process was carried out at ambient or elevated temperature (up to 100 ^{o}C) in organic electrolyte. The high-temperature electrodeposition (several hundred Celcius degrees), in turn, allowed to form the layer by electrochemical reduction of metals from molten salts. In order to analyse and compare the chemical composition and microstructure of the coatings, XRF, SEM/EDS, TEM and XRD techniques were employed. During these studies, a strong relationship between the electrodeposition method and the quality, microstructure and properties of the coating has been revealed. Morover, the determination of corrosion resistance of the layers in selected electrolytes (i.e. organic and non-organic liquids) was no less important than the above mentioned objectives.

Room Temperature Synthesis of Hydrogen Permeation Barrier for Storage and Transportation Application

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Abstract text

Distribution of hydrogen in future hydrogen-based economy requires a dense pipeline network for its safe delivery. Natural take is to consider the existing networks of natural gas (NG) infrastructure. However, the main issue is that hydrogen-embrittlement on NG pipes' steels significantly reduces their fracture toughness and threatens their structural integrity1. Besides developing a new grade of steels less susceptible to embrittlement, effective hydrogen permeation barriers (HPBs) remain an important solution for re-purposing of the existing NG infrastructure for hydrogen transport. We employed a strategy for HPB synthesis based on electroless Cu-deposition process. Electroless solution chemistries explore a wide range of reducing agents. These include formaldehyde, glyoxylic acid, Na2HPO2 … and others. Variety of complexing agents were considered as well; EDTA, sodium citrate, sodium potassium tartarate and others. Our optimum solution design favored a large driving force for Cu reduction providing high nucleation rates and films with fewer defects and dense grain boundaries. The comparative analysis between hydrogen permeation rates through steel samples and steel samples coated with Cu HPB films is performed using Devanathan - Stachurski permeation technique. More than 30 samples have been evaluated. Our results exceed theoretical predictions by a factor of 2-5.

Superhydrophobic surface on MAO-processed AZ31B alloy with zinc phosphate nanoflower arrays for excellent corrosion resistance in salt and acidic environments

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Corrosion caused by the active chemical properties of magnesium (Mg) alloys seriously restricts their applications in aerospace, transportation, biomedicine, and other fields. Although micro-arc oxidation (MAO) coatings can provide some corrosion protection for Mg alloys, their microporous structure is prone to localized corrosion. Herein, nanoflower-shaped zinc phosphate is prepared and hydrophobically modified. The commercial glue is used to bond the nanoflower-shaped zinc phosphate particle arrays to the MAO-coated AZ31B alloy substrate to produce a two-layer composite coating with superhydrophobic properties. The composite coating exhibits obvious repulsive effects in salt and acidic solutions as indicated by contact angles of 160° and 156°, respectively. The composite coating has improved electrochemical properties and immersion corrosion in both the salt and acidic solutions compared to the substrate and MAO-coated sample. Moreover, the composite coating retains the long-term superhydrophobic effects under different conditions such as immersion in salt and acidic solutions, water scouring, and sunlight exposure, which well indicates commercial applications.

Bridge for the thermodynamics and kinetics of electrochemical corrosion: design of self-densified plasma electrolytic oxidation on magnesium alloys

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Abstract A new idea was proposed to design the self-densified plasma electrolytic oxidation (SDF-PEO) coatings on magnesium alloys based on the dissolution-ionization-diffusion-deposition (DIDD) model. The main considerations of the new PEO electrolyte include the establishment of a thermodynamics diagram, the construction of a liquid-solid sintering system and the regulation of plasma sparkling kinetics. The SDF-PEO coating exhibited a homogeneous and dense microstructure, a superior corrosion resistance and a good technological adaptability. The significant contribution of this study is to present a novel theory to design surface treatment with superior corrosion resistance and promising application prospect.

Keywords: self-densified coating; plasma electrolytic oxidation; corrosion resistance; Mg alloys

High-throughput screening of stabilization treatment agents for promoting the growth of rust layers on weathering steel

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High-throughput experimental techniques can accelerate and economize corrosion evaluation, and thus, have great potential in the development of new materials for corrosion protection such as corrosion-resistant metals, corrosion inhibitors, and anticorrosion coatings. In this work, a novel high-throughput screening method of the stabilization treatment agents for promoting the growth of rust layers on weathering steel surface is developed by depositing microarrays of droplets containing different stabilizer solutions on a Q420 MPa low-alloy weathering steel. This method can test up to 200 channels of stabilizer solutions with a miniaturized setup. In addition, the method allows the independent control of droplet compositions and concentrations. Different combinations and concentrations of Na_2WO_4, Na_2MoO_4, and $NaNO_2$ were dropped on the steel surface, and the growth behavior of the rust layer and the corrosion resistant property were assessed using the wire beam electrode (WBE) technology and surface observations. The combination of 0.6 g/L Na_2WO_4 and 1.2 g/L Na_2MoO_4 could promote the generation of a dense rust layer with a high percentage of α-FeOOH, which is conductive to strengthen the corrosion resistant property of the rust layer. WBE electrochemical results demonstrate the highest impedance modulus among all the stabilizer combinations.

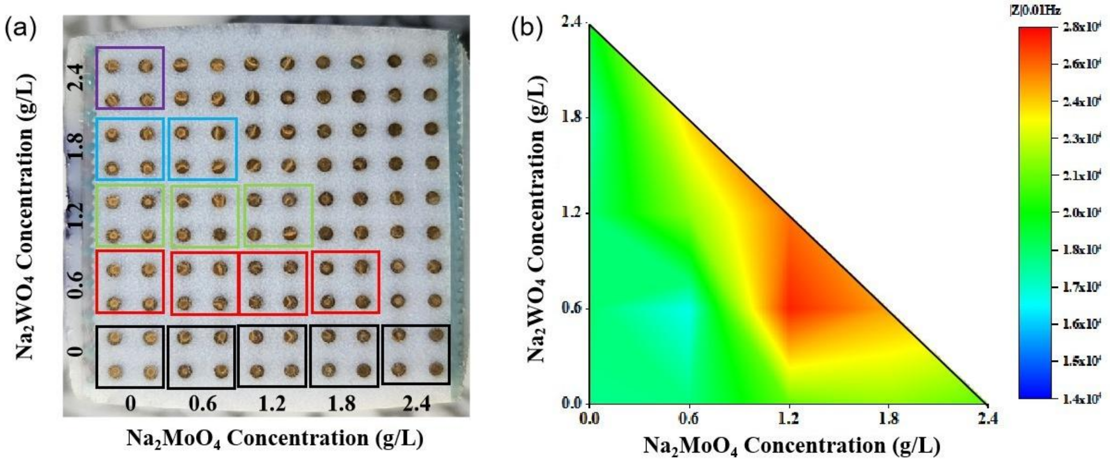

Figure. (a) Photograph of rust layers on Q420 weathering steel with Na_2WO_4 and Na_2MoO_4 addition; (b) 0.01 Hz impedance modulus measured on each wire beam electrode.

Study on the Growth Mechanism and Thermal Stability of Nanotwin Ceramic Coatings

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We break through the extremely high stacking fault energy potential barrier and successfully achieves the controllable preparation of high-density nanotwins in ceramic coatings. And the following research is carried out on the growth mechanism, mechanical properties, and high-temperature stability of nanotwins in ceramic coatings: (1) By doping B element in TiN, NT-TiBN coatings with high-density nanotwins were prepared, including incoherent twin boundaries (ITBs) and coherent twin boundaries (CTBs). Boron doping promotes the orientation transition of the coating from [200] to [111], providing an orientation advantage for the formation of twins. B segregates at the grain boundaries of [111] oriented grains, reducing the ITB interfacial energy, which is thermodynamically favorable for its formation; on the other hand, segregation forms a large internal stress, making ITB more stable and suppressing its detwinning. The coupling of these two effects not only promotes the formation and stability of ITB, but also provides a possible precursor structure for the formation of CTB. Driven by the minimization of system energy, some grains undergo in-plane rotation during the growth process, thus forming CTB.

(2) The structural evolution behavior of nanotwins in ceramic coatings at high temperatures and its effect on mechanical properties were studied. The results show that the twin density is positively correlated with the thermal stability of the coating, and the NT-TiB0.11N1.16 coating with the highest twin density exhibits ultra-high thermal stability. Even after annealing at 1100 °C for 60 minutes, the twin density and grain size did not change significantly. Thanks to the ultra-stable structure, the nanotwinned coating after annealing maintained a super-high hardness of 44.5 GPa, which did not decrease compared with the as-deposited state, and was significantly higher than the TiBN coating without twins (the hardness after annealing was only 19.6 GPa) and other TiN-based multicomponent coatings after high-temperature annealing. The study shows that the combined effects of B segregation at the interface, the network structure composed of CTB and ITB, the orientation constraint between the columnar crystals, and the still high stress after annealing ensure the stability of the coating structure at high temperatures.

Conversion post-treatments for PEO coated substrates

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The plasma electrolytic oxidation (PEO) is considered as a state of the art technique in many industrial applications to confer inorganic protective or functional conversion layers on top of light structural materials such as aluminium or magnesium alloys. However, the obtained PEO layers are normally characterized by highly developed porosity, which compromises the barrier properties and overall corrosion protection. Sealing of anodic layers is often used to close the porosity and confer additional active protection functionality to the PEO coatings.

The current paper focuses on several recent approaches towards sealing the PEO layers by inhibitor containing compounds or structures such as layered double hydroxides (LDH) or metal-organic frameworks (MOF). Both LDH and MOF treatments offer possibilities for sealing PEO layers on Mg, Al and Zn alloys, enhancing their corrosion resistance. Roles of PEO composition and conversion solution are analysed. The obtained results demonstrate the possibility to use hydrothermal treatment for a partial conversion of PEO layer into LDH or MOF structures. The formed active compounds are partially sealing the porosity and offer reservoir for potential corrosion inhibitors. The possibility to achieve PEO layers with active corrosion protection functionality in defects through such conversion post-treatments is demonstrated.

Sealing post-treatments of coatings produced by plasma electrolytic oxidation (PEO) on aluminum alloy

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Ceramic coatings produced by plasma electrolytic oxidation (PEO) are affected by the presence of defects whose formation is intrinsically related to the occurrence of energetic plasma events during the process. Consequently, the corrosion resistance of the treated component may be reduced since corrosive substances could penetrate through the defective oxide layer. To solve the problem a sealing post-treatment aimed at closing the porosity of the coating could be carried out. One of the simplest sealing treatments is the hydrothermal one. A disadvantage of this sealing is that it is run at high temperatures requiring a huge amount of thermal power. It is possible to modify the chemical composition of the sealing bath by adding reagents able to produce at lower temperatures insoluble compounds that precipitate into defects of the oxide layer clogging them. In the present work, different types of sealing treatments are compared. PEO is performed on disks made of an aluminum alloy (AA2024) using NaOH and KOH alkaline solutions containing Na_2SiO_3 and glycerin. The applied signal consists of an AC-pulsed duty cycle, 60 % anodic and 40 % cathodic with a cathodic peak of 7 %. The resulting PEO samples are post-processed by hydrothermal sealing, sealing with sodium acetate, layer double hydroxide (LDH) sealing, and sealing with cerium nitrite. The sealing duration varies from 15 to 60 min and the working temperatures range from the 100 °C of the hydrothermal process to 30-40 °C reached when sealing based on $Ce(NO_3)_3$ is performed. The SEM analysis shows the structure modification of the PEO coatings due to the sealing treatments. The major change is observed when the LDH sealing is carried out since the final surface of the coating is characterized by the presence of lamellas mainly containing the elements coming from the sealing bath. It is found that all the sealing techniques improve the corrosion resistance of the coatings as highlighted by the results of electrochemical tests: linear polarization resistance (LPR), electrochemical impedance spectroscopy (EIS), and potentiodynamic polarization (PDP) carried out in a 3.5 wt.% NaCl solution. In particular, the larger enhancement of the polarization resistance and the lower corrosion current density are obtained for LDH and cerium nitrite-sealed samples.

Plasma Electrolytic Oxidation (PEO) corrosion resistant coatings on aluminium 2024 texturized with a riblet-like surface for aeronautical applications

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Aluminium 2024 is one of the most widely used alloy in aeronautical applications. Despite its excellent specific mechanical properties, this alloy shows a lower corrosion resistance with respect to pure aluminium, especially in marine environment. Corrosion resistance can be improved by means of a multi-layered protection system, consisting of a porous anodic coating, a corrosion inhibited organic primer and an organic top coat. Alternatively, an aluminium clad, conversion coatings or plasma electrolytic oxidation (PEO) coatings can be used. PEO-coatings, to this date, only have niche applications in the industry, but several efforts to optimize PEO-coatings are ongoing. The aim of this research is to improve the corrosion resistance of aluminium alloy 2024 by optimizing the anodic PEO treatment, together with the formation of a nature-inspired texture on oxidized aluminium. The goal of the activity is twofold: i) to mimic the scales (the so-called “riblets”) of the mako shark skin on aluminium for aeronautical application in order to improve the fluid-dynamic features by texturing its surface; ii) to improve the corrosion resistance by the optimization of the anodic PEO process.

In the first part of the work, the definition of the proper bio-inspired surface texture is discussed. Then, preliminary results about the texture-making of the riblet-like surface on aluminium 2024 substrate are discussed. The texture has been obtained through high-resolution photochemical etching performed on the metal surface. The formation of the blade-like structure was performed as follows: (i) application of a photocurable polymer coating to protect portions of the aluminium surface by means of a 2D printer; (ii) curing of the polymeric materials by means of UV light; (iii) immersion of the sample in the etching solution; (iv) stripping of the photocured polymer coating.

In parallel, PEO treatments on aluminium 2024 specimens (not-texturized) were carried out in order to optimize the process parameters, as the electrolyte composition and the electric regime. In particular, pulsed voltage mode and a wide spectrum of signal frequency were considered, in order to investigate the effect on plasma formation and thickness of the growing oxide. Microstructural analyses and electrochemical tests were carried out to characterize the PEO coating varying the experimental parameters. Finally, the optimized PEO treatment was applied to the texturized aluminium specimen, checking the maintaining of the texture of the metallic substrate. The results presented in this work are part of the research project “MAKO - biomimetic corrosion resistant aluminium for aeronautics”, funded by European Union – Next Generation EU, PNRR - Missione 4 “Istruzione e Ricerca” - Componente C2 Investimento 1.1 “Fondo per il Programma Nazionale di Ricerca e Progetti di Rilevante Interesse Nazionale (PRIN)” D.D. n. 104/2022 “Bando PRIN 2022”.

HVAF ceramic coatings for improved performance of L-PBF printed stainless steel in harsh conditions

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Abstract.

Ceramic-metallic coatings represent an attractive solution for application conditions where corrosion threat is associated with wearing concern. Different coating chemistries (and deposition parameters) were studied by several authors to determine the optimum parameters for the best performance when applied on conventional materials. On the other hand, additive manufactured materials limitation in abovementioned application conditions can be solved through cermet coatings. In the present work, the corrosion behaviour of cermet coatings in acidic saline medium was studied. Different cermet coatings were sprayed by High Velocity Air fuel (HVAF) on laser powder bed fusion (L-PBF) printed 316L stainless steel substrate and exposed in stagnant acidified 3%NaCl at ambient temperature. The studied coatings include WC and CrC matrix based that were sprayed using the same HVAF parameters. Electrochemical methods were combined with surface chemistry and microscopy to understand short-term behaviour of the proposed coatings. Promising performance was observed for WC-CoCr coating compared to the L-PBF printed 316L substrate (reference). Both general and localized corrosion resistances were improved using WC-CoCr. The multiphase microstructure of the coatings showed complex behaviour where the passivation process is affected.

Can machine learning help us to generate new coating formulations for corrosion protection?

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Abstract

Organic coatings (i.e. paints) are ubiquitous in imparting aesthetics (e.g. color) and function (e.g. corrosion protection) to surfaces. Coatings are complex formulated products, akin to polymer matrix particulate composites, and contain multiple ingredients making it challenging, costly and exceptionally time-consuming to cover the entire formulation space. Corrosion protective coatings comprise a high-value subset of the coatings product portfolio and impart essential longevity to the assets that they protect. In this work we use Machine Learning to connect historic test data with formulation information to identify the key factors that optimize corrosion protection performance. The search comprises a 151-dimensional Euclidean space where optimization is hindered by incomplete coverage (sparse data) and is consequently computationally challenging. The search strategy constructs a supervised learning model, using Random Forests, in which the formulation ingredients are the inputs, and the corrosion performance metrics comprise the output, producing a multi-dimensional landscape of the search space. The landscape is then navigated towards potential optimal locations using Differential Evolution Active Learning, whereupon the Random Forest model is invoked to evaluate the predicted corrosion performance metrics. Results from this proof-of-concept located several prototype formulations which were then verified by prohesion testing. One of these was found to provide excellent corrosion protection from a combination of ingredients that was outside current formulation space and entirely novel. In further work we will expand the data space and limit the quantity and types of ingredients to prevent the Machine Learning model from suggesting formulations that cannot be made into a viable paint system.

Image recognition for lifetime prediction of epoxy coating in the deep-sea environment

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Image recognition technology is used to extract information from SEM images of epoxy mica coatings serving for different periods of time in the simulated deep-sea fluid-pressure environment. A targeted approach containing convolutional neural networks and post-processing has been established for the crack area detection of coating surface. The length distribution and the statistical evolution of cracks were summarized, to obtain the kinetic equation of the cracks related to coating structure degradation. Based on this achievement, a comprehensive failure model combining coating properties and coating structure degradation is developed. The relative weights of three dominant factors in coating failure, including water diffusion, coating adhesion, and crack length were calculated by the gray relational analysis method. A relatively accurate prediction of coating lifetime was performed through the established "performance-structure" failure model.

Incorporation of biopolymer nanocomposite coating into epoxy matrix and its corrosion studies

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Metals are protected from the environment by organic coatings, which act as a physical barrier. Epoxy, urethane, silicones, and other materials that are frequently used in ship hulls are among the various materials used for organic coatings. These organic coatings can also serve as reservoir for various inhibitor-containing containers, adding another degree of protection for metals. One of the most commonly used inhibitor are the biopolymers. During the prolonged exposure of corrosive media on metal surface, these biopolymer containing epoxy coatings are subjected to stresses that creates nano or micro sized pores. To avoid this, biopolymers can be functionalised using nanoparticles.

The present study aims at the evaluation of corrosion property of prepared zinc oxide tailored biopolymer nanocomposites incorporated epoxy coating. The synthesised biopolymer nanocomposites are characterised using fourier transform spectroscopy (FT-IR), x-ray diffraction studies (XRD) and thermogravimetric analysis (TGA). The surface morphological analysis of the prepared coatings was performed using transmission electron microscopy (HR-TEM) and scanning electron microscopy along with elemental mapping using energy-dispersive x-ray analysis (SEM-EDX). Electrochemical impedance analysis (EIS) and potentiodynamic polarisation technique (PDP) were utilised for the determination of corrosion rate of the prepared coatings. It was found that the Zinc oxide modified biopolymer epoxy coatings exhibited higher inhibition efficiency than the biopolymer incorporated epoxy coatings. The hydrophobic character of the prepared coatings was determined using contact angle measurements. Enhancement in the hydrophobic character was observed for zinc oxide modified epoxy coatings. This study thus demonstrates the feasibility of creating epoxy coating with nanofiller integration in the future, which will expand its use in the coating industries.

Sustainability in Corrosion Control: Bio-Based Acrylic VCI Coating vs. Traditional Inhibitors

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This paper presents a study on the development and evaluation of the corrosion resistance of a bio-based acrylic VCI direct-to-metal (DTM) coating. In line with the growing demand for environmentally friendly alternatives in the coatings industry, the coating formulation incorporates sustainable and biodegradable raw materials. The research focuses on comparing the corrosion resistance performance of the bio-based acrylic coating with different types of corrosion inhibitors. Specifically, three different corrosion inhibitors were investigated: a contact & vapor corrosion inhibitor (VCI), e.g. an aromatic acid salt, a metal complex corrosion inhibitor, e.g. zinc sulfonate, and an amine carboxylate salt. The experimental methodology involved incorporating these inhibitors into the biobased acrylic coating matrix, followed by various tests to evaluate their corrosion mitigation efficacy on metal substrates. Various corrosion resistance parameters were used to quantify and compare the protective capabilities of each inhibitor, including salt spray & humidity testing, electrochemical impedance spectroscopy (EIS), and scanning electrochemical microscopy (SECM). This work contributes to ongoing efforts in developing sustainable coatings with enhanced corrosion protection properties and provides valuable information for industries seeking green alternatives without compromising performance.

Predictive Maintenance by in-field EIS using the CQM-method

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S. Kuniewski, C-Cube international, Delft, The Netherlands

Over the last 16 years, a new approach was developed to the application of Electrochemical Impedance Spectroscopy (EIS) in the field using the Coating Quality Measurement (CQM) Method. In the Eurocorr 2023 lecture, the two main parameters derived from the EIS data were presented: Barrier Index (BI) and Permeability Index (PI). In this presentation, the added value of the method for asset management and predictive maintenance is discussed.

For this, typical in field CQM projects are discussed, for example for a tank external and internal coating, a 1,5km long steel bridge and surge barrier gates. For these structures the added value along with other inspection techniques the current condition is determined using a large set of data obtained from many measurements, sometimes 1500 measurements for a structure. The approach, the data collection and the standardized graphical representation of the results are given.

The bode plots, histograms, boxplots and mapping point out that EIS can produce logically explainable data on the current condition of a coating system, adding to the pallet of other inspection techniques. Moreover, the relations between the graphs and objective maintenance decisions will be discussed.
The presentation opens the way for degradation modelling and prognoses, which will be discussed in a later lecture.

The Role of Organophosphate groups in Corrosion prevention in Coil Coatings

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Abstract

An organophosphate additive has significantly improved adhesion and anticorrosive performance when used within coil coatings, particularly when used in conjunction with a substrate pre-treatment. Electron and X-ray imaging, electrochemical analysis and spectroscopic techniques have been used to characterise the system microstructure. With focus on the coating structure, interfaces, the interactions of the additive with the binder and other coating components, in addition to the corrosion propogation fronts. These outputs have been correlated to the coating kinetics and degradation processes following accelerated aging conditions. The findings of the present work will aid in the development of sustainable commercial coil coating products.

Polyoxometalate-polypyrrole Synergism: A New Approach to Boost Oxide Film Formation for Fabricating Self-passivating Organic Coatings

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Developing efficient anticorrosion coatings has become a prominent focus in materials science. Conductive polymer (CP) composite coatings can offer passivation functionality for active metal substrates, but their capability often does not persist long enough. Herein, a polyoxometalate ($Mo_7O_{24}^{6-}$)-polypyrrole (PPy) synergism is proposed to develop the PPy/epoxy composite coating (PPy-POM/EC) with exceptional passivation capability. Experiments and theoretical calculations demonstrate that compared to conventional dopants, redox-active $Mo_7O_{24}^{6-}$ dopants effectively improve and stabilize the conductivity and redox activity of PPy backbones. Benefitting from the dual electroactivity of PPy and $Mo_7O_{24}^{6-}$ dopants, PPy-POM/EC can induce a continuous and solid protective oxide film on the aluminum substrate, exhibiting excellent defense behavior and corrosion control. Therefore, PPy-POM/EC still maintains a low-frequency impedance of 1.7×10^{10} Ω cm^2 even after 150 days of immersion in a 3.5 wt.% NaCl solution. The long-lasting anti-corrosion performance ranks among the best ever seen in CP composite coatings. This study demonstrates the potential of polyoxometalate-assisted CP in facilitating metal passivation and paves the way for developing highly durable anti-corrosion coatings in the future.

A deeper understanding of the passivation mechanism

A novel passivation mechanism is proposed that the protective oxide film formation is associated with the dual redox process provided by $Mo_7O_{24}^{6-}$ dopants and PPy backbones, and this synergism not only promotes the formation of $Al(OH)_3$ intermediate but also accelerates the transition from $Al(OH)_3$ to Al_2O_3 film.

A new strategy for corrosion protection of porous stainless steel using polypyrrole films

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This work presents a methodology to improve the corrosion protection of porous sintered stainless steel. For this purpose, polypyrrole (PPy) layers doped with dodecylbenzenesulphonic acid (DBSA) have been electrodeposited on 316 L stainless steel (SS) samples. PPy is a conducting polymer with high corrosion resistance and good biocompatibility [1,2]. The efficacy of PPy coating depends on the adequate adhesion between the metal substrate and the coating layer. In order to evaluate the effect of the conditions of fabrication on the corrosion resistance, the 316 L SS has been sintered at different atmospheres (nitrogen and vacuum) and cooling rates (furnace and water). In addition, two electrochemical deposition techniques (chronopotentiometry and chronoamperometry) have been tested to select the most adequate. The corrosion protection in phosphate saline medium has been studied using different electrochemical techniques such as open circuit potential evolution, anodic polarization measurements and electrochemical impedance spectra. The results showed that a more homogeneous and stable coating was obtained in the case of porous stainless steel and the corrosion potential shifted to nobler values and the anodic polarization branch became more stable (Fig. 1). Therefore, coated porous samples have a good passivation performance with a lower stable passive current density and a higher breakdown potential [3]. Finally, the porosity of sintered stainless steel is seen as an advantage for the improvement of the adherence of PPy coatings.

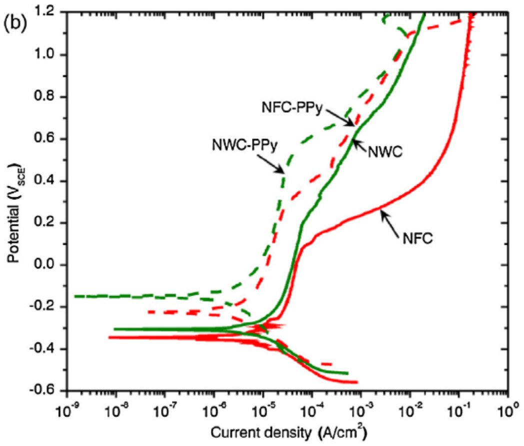

Fig.1. Effect of PPy coating on anodic behavior of nitrogen sintered samples, in PBS solution, with WC (water cooling) and FC (furnace cooling).

[1] *Acta Biomater.* **10** (2014) 2341–2353.

[2] *Prog. Org. Coat.* **78** (2015) 21–27.

[3] *J. Mater. Sci. Technol.* **37**, (2020), 85-95.

Synergistic assembly of MXene nanosheets and covalent organic frameworks (COFs) with self-healing and enhanced anti-corrosion properties

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MXene nanosheets have emerged as a hotspot in corrosion applications thanks to their 2D sheet-like structure and inherent physicochemical properties. Despite their potential, challenges such as restacking and oxidation narrow down their practical application. Moreover, even highly exfoliated MXene nanosheets lack a sufficiently large surface area, which is crucial for self-healing and protective coatings. To address these limitations, we present a novel tailored hybrid skeleton through the in-situ growth of a highly porous covalent organic framework (COF) on MXene nanosheets. This systematic design aims to prevent oxidation and restacking while augmenting the surface area of MXene. Such an advanced structural design is vital for corrosion-protective coatings, as it improves the barrier properties and facilitates hosting corrosion inhibitors to provide self-healing features. As proof of concept, an imine-based COF was grown on the MXene nanosheet via an in-situ method, resulting in a 128 $m^2.g^{-1}$ surface area. Subsequently, the loading of zinc and glutamate molecules as inorganic and organic inhibitors into the porous MXene nanosheets demonstrated 88 % corrosion mitigation over a prolonged period (96 h), showcasing promising results among counterparts. Moreover, introducing these innovative nanoplatforms into an epoxy coating provided self-healing properties, exhibiting over 200% improvement in active corrosion prevention compared to the unfilled coating. Additionally, the total impedance value of the proposed coating remained stable at 10.64 $\Omega.cm^2$ after 11 weeks in a 3.5 wt% saline solution, indicating sustained resistance to electrolyte diffusion. In brief, this work not only proposes a novel structural design for superior anti-corrosion coatings but also a concept that can potentially be applicable in various MXene-related fields. **Figure 1** illustrates the synthesis procedure of the MXene modified porous nanosheets.

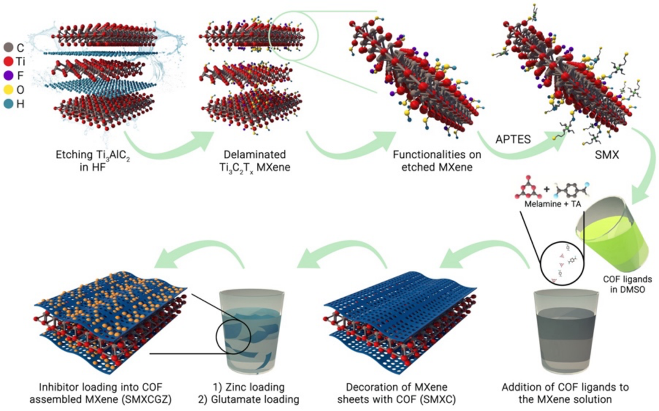

Figure 1. The schematic illustration of different synthesis steps

Evaluation of corrosion protection and antifouling efficiency of fouling-release coatings on copper alloys

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This study targets the development of environmentally friendly fouling-release paints for safeguarding bronze propellers against corrosion in marine applications. Traditionally, propellers rely anti-fouling systems, based on the chemical release of biocides to reduce the adhesion of micro-organisms on submerged surfaces. However, escalating environmental concerns have spurred the development of non-toxic coatings, such as fouling-resistant and fouling-release systems. These systems aim to reduce fouling by minimizing adhesion strength between organisms and the metal surface, facilitating easy removal through mechanical or hydrodynamic means. Nevertheless, these silicone-based paints often display poor mechanical properties and often require the application of a primer to improve their adhesion to the metal substrate.

This study investigates the corrosion protection properties of eco-friendly fouling-release paints. In particular, different primer formulations in combination with several formulations of silicone topcoats are investigated in order to first evaluate their corrosion protection. This is assessed by Electrochemical methods (Electrochemical Impedance Spectroscopy) together with immersion tests in marine environment that are employed to evaluate the antifouling behavior too.

Evaluation of Wax Based Tape coating exposed to atmospheric conditions over 20 years

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Wax based tape systems have been used for buried and atmospheric pipeline corrosion protection from over four decades. For atmospheric conditions, it is widely used to rehabilitate paint system when application conditions are not suitable for paint. This paper shows two inspections done on rehabilitation with wax based tape respectively 20 and 37 years after the rehabilitation.

20 years rehabilitation on a Penstock in the French Alps

A Penstock pipe paint in the Alps was renovated in 2004 with wax based tape system. The pipe made of carbon steel is 1200 mm diameter located in underground gallery at 2100 m of altitude with a first part of weak slope (less than 16°) and second part outside of the gallery with heavy slope (36°). The tunnel is underneath a lake so there are permanently water drops falling onto the pipe.

In 2023, the gallery was visited with penstock inspection for corrosion risk analysis. It appears that most of the wax based tape coating was in great shape and still operational. Some inspection windows have been cut to evaluate the substrate protection at various points.

The inspection also included the protection at the concrete pipe support area.

37 years old bridge span decommissioned and inspected

Analyses were conducted on a 37-year-old wax-wrapped natural gas exposed main as part of an ongoing effort to collect data on long-term performance of self-firming anticorrosion wax wrap. An 8" diameter natural gas line, approximately 30 linear feet in length, was removed from service in Ann Arbor, MI in October 2020. The gas line was originally installed in the late 1950s. Primer and anticorrosion wax wrap were applied in 1983.

Electrochemical Impedance Spectroscopy as a method to evaluate the electrochemical properties of zinc rich epoxy primers

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Anders W. Skilbred, Jotun AS, Sandefjord/Norway

Abstract

When testing and developing zinc rich primers (ZRPs) it can be challenging to differentiate with respect to their galvanic protective properties. One of the most common assessment methods today is to evaluate the rust-creep development under the coating during exposure e.g., in neutral salt spray - ISO 9227. However, this gives only a limited view of the electrochemical properties of the ZRPs.

Electrochemical Impedance Spectroscopy (EIS) is a well-known assessment method for evaluating the barrier properties of protective coatings/primers. What is less known is that EIS has potential as an assessment method for the galvanic protection properties of zinc rich primers.

This work aims to describe how EIS can be established as an assessment method to evaluate the electrochemical properties of zinc rich primers. This could potentially help to save time in the development phase of new ZRPs, be used to give predictions on their lifetime as well as serve as a comparative technique when comparing product performance. Selected ZRPs with 80 weight % zinc in dry film have been evaluated. Their electrochemical properties have been assessed through EIS and then linked to their performance in accelerated corrosion testing like neutral salt spray. The EIS evaluation includes performing potentiostatic and potentiodynamic EIS measurements, as well as monitoring the open-circuit voltage (OCV) of the ZRPs with exposure time.

In conclusion, the work shows that EIS has good potential as an additional assessment technique when evaluating the electrochemical properties of ZRPs. Specifically, the potentiodynamic EIS mode and OCV measurements over time seem to correlate with the performance of the zinc rich primers when tested in neutral salt spray as single coats.

Real-Time Low-Frequency Impedance Monitoring with Predictive Value for High Durability Atmospheric Coatings

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The purpose of real-time low-frequency impedance monitoring of coatings is to facilitate informed coating selection and to optimize coating repair and renewal intervals while reducing costs and extending asset lifetime. We define real-time measurement as a measurement that is able to repeatedly record the impedance at low frequencies (0.1 or 0.01 Hz) without affecting the coated sample equilibrium with its environment. Periodic or continuous monitoring provides a set of data that can be interpreted in terms of reversible impedance variations associated with water ingress and egress, temperature sensitivity of the polymer and permanent impedance loss correlated to the physical and chemical degradation of the coating. Ideally, a coating should be thin, adhesive and flexible, impact, abrasion and UV resistant and impermeable to water and corrosive substances. From a formulation perspective, some of these properties are contradictory and a compromise is sought, dictated by the stressors present in each application. Therefore, we present a novel approach to impedance interpretation that considers the relevance of coating Tg, permeability, water-induced plasticization, structural polymer relaxation, and mechanical properties of the coating relevant to adhesion. We use commercial surface-mounted devices that employ electrodes with quasi-solid-state and solid-state contact between the electrode and the coating for repeated impedance measurements on surfaces of different geometries and orientations. The predictive value of periodic and continuous impedance monitoring is demonstrated by comparing data obtained in the field with reference impedance charts generated from monitoring a large number of coated samples during a two-year exposure in an offshore-like atmospheric environment and from accelerated and long-term laboratory exposure data. We conclude that the monitoring data can help match the coating system to a particular environment and provide early warning of premature coating failure.

Exploring the Dual Diffusion Dynamics of Water and Ions in Organic Coatings: Leveraging Impedance Spectroscopy for Comprehensive Insights into Coating Barrier Properties

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The performance of protective coatings relies on their barrier properties against the diffusion of corrodents, i.e., water and ions. Water uptake has been extensively studied using diverse methodologies given its adverse impact on the durability of hybrid structures. Contrary to water uptake, monitoring the independent diffusion of ions poses a more intricate challenge. Obtaining reliable experimental data together with robust data treatment/modelling approaches using odd random phase electrochemical impedance spectroscopy (ORP-EIS) in combination with spectroscopic techniques has proven to be a potent tool in providing comprehensive insights into the dual diffusion dynamics of water and ions [1,2]. To broaden the application of this methodology in more complex systems, a series of model coatings is designed, incorporating different pigment volume concentrations (PVC) as a parameter that can significantly alter the transport properties of organic coatings. Hence, a correlation has been sought between the transport properties of the coatings and their morphology/structure changes as a function of PVC. It was demonstrated that increasing the PVC enhanced the water uptake and ion diffusion in the system under study, ultimately leading to accelerated degradation of highly pigmented hybrid systems. This approach enables the *in situ* and non-destructive determination of the ion diffusion front velocity in different systems, supported by glow discharge optical emission spectroscopy (GDOES) elemental depth profiles [3].

[1] N. Madelat et al., Corros. Sci. 212 (2023) 110919.
[2] N. Madelat et al., Electrochim. Acta. 455 (2023) 142400.
[3] N. Madelat et al., Corros. Sci. 227 (2024) 111699.

The degradation mechanism of polyester powder coating exposed to cyclic corrosion test (CCT)

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Kaivalya Borwankar[1], Suzanne Morsch[1], Xiaorong Zhou[1], Stuart Lyon[1], Yanwen Liu[1],
Gianfranco D'Ambrosio[2], Niek Hijnen[3], Simon Gibbon[3]
1) Dept. of Materials, The University of Manchester, Manchester, M13 9PL, UK
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3) AkzoNobel, Stoneygate Lane, Felling, Gateshead, NE10 0JY, UK

Abstract

Defect formation around pigment particles, formed under cyclic corrosion testing, leading to crack formation and propagation have been identified as a major cause for degradation and failure of polyester powder coatings. This degradation leads to coating damage which will eventually lead to blistering and even delamination. Coating degradation was characterized at the microstructural level through the use of Scanning Electron Microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and Focused Ion Beam (FIB) microscopy. A mechanism linking the initiation of cracking to localized microstructural features inside and around pigment particles was proposed based on observations of a powder coated sample before and after exposure to cyclic corrosion testing. Pigment clusters within the coating system led to premature localized corrosion taking through local micromechanical conditions introduced by the cyclic corrosion testing.

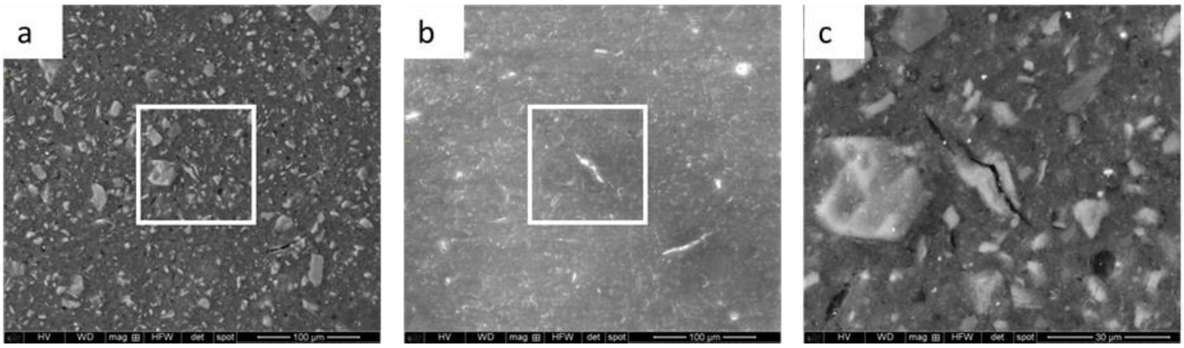

Fig. 1 Scanning electron microscopy of the top surface of a powder coated panel exposed to 4 months CCT showing crack formation.

Nano metal-organic frameworks towards the high-performance anticorrosion epoxy resin coatings

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3) Zhongshan Photoelectric Materials Co., Ltd, Zibo/China

Abstract

Metal-organic frameworks (MOFs) have been extensively utilized in the development of high-performance anticorrosion organic coatings. Specifically, MOFs are prepared using imidazolate organic ligands and the coordinated transition metal. The inclusion of the imidazole group not only enhances the barrier property of the coating through improving the crosslinking with the epoxy group but also the effectiveness as an inhibitor to metals when decomposed into the ligand.

In this work, novel aminated MOF nanoparticles are designed based on the ZIF-8 and using the 2-Aminobenzimidazole (2-ABI). The proportion of 2-ABI within the imidazolate organic ligands led to nanoparticles in various sizes and active hydrogen content, consequently influencing the reaction between the MOF nanoparticles and epoxy resin. The epoxy resin coating modified by MOF nanoparticles containing 15 % 2-ABI (ZA-15/EP) exhibited the most effective corrosion resistance during prolonged immersion in NaCl solution.

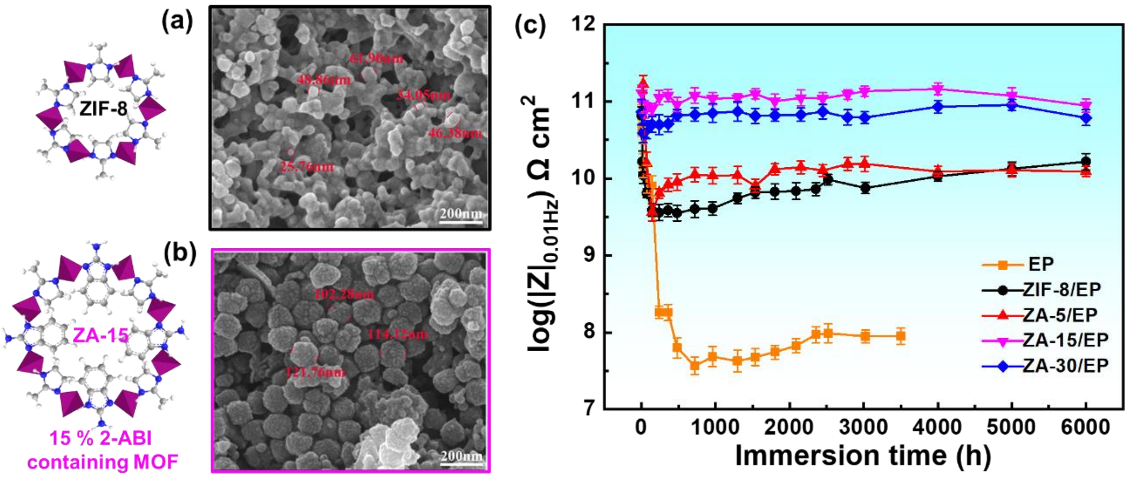

Figure 1. SEM image of ZIF-8 (a), 15 % 2-ABI containing MOF (ZA-15) (b) and (c) impedance moduli at 0.01 Hz ($|Z|_{0.01Hz}$) as a function of immersion time in 3.5 wt. % NaCl solution.

Evaluation of corrosion inhibition capability of graphene phosphate and amine modified resin-based coatings on mild carbon steel

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3) Institute of Coating Technologies, 52 Chalkidonos St., Athens, GR-11527, Greece

The main goal in this work, is the reduction of corrosion protection coating thickness by the incorporation of pigments that act as corrosion inhibitors. The corrosion protection of mild carbon steel was studied using two types of coatings: a solvent-borne short-oil alkyd resin primer and a solvent-borne 2K epoxy resin primer. Each primer was reinforced with pigments based on: Graphene, hydrophobic compounds, zinc phosphate and magnesium salts, amine derivatives. Three different nominal dry film thicknesses (DFT) of 50μm, 100μm and 200μm were produced and examined with respect of their morphology, elemental analysis, and their corrosion behavior via salt spray test (SST) and electrochemical impedance spectroscopy (EIS). The obtained results revealed the superiority of epoxy primers over alkyds. According to the EIS analysis, the epoxy samples demonstrated no signs of corrosion after immersion for 55 days in a 3.5 wt% NaCl solution. On the other hand, the alkyds-based coatings presented severe blisters, cracks and corrosion products. This outcome is attributed to the better adhesion and coverage of the epoxy primers onto the metal surfaces. It also appeared that the thickness is a very important factor for the resistance of the coating in the aggressive corrosive environment. The SST on the alkyd samples showed that the incorporation of either hydrophobic compounds or zinc phosphate pigments improves the anti-corrosion properties of the coatings for the average DFT of 50μm. This outcome is due to the hydrophobic compounds' properties of the alkyd sample to repel the aqueous solution; preventing the corrosive agents to reach the metal substrate. In addition, the phosphate group acts as a corrosion inhibitor by creating a film on the surface of the steel. In larger thicknesses, both the reference alkyd and the other alkyd primers presented similar enhanced corrosion protect performance.

Development of Graphene-Polyether Ketone Ketone Composites as Corrosion-barriers: Mechanistic Probing for Practical Applications.

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Monolayer graphene is impermeable for gases such as helium, oxygen, nitrogen, and exhibit exceptional impermeability for ions such as Na^+, K^+, Li^+, and Cl^-, leading to profound implications for gas separation, water desalination and corrosion resistance. Achieving this high impermeability of monolayer graphene over a large surface in practical applications is challenging. Graphene developed over the larger surface have discontinuities that can cause localised corrosion. With a view to plugging such discontinuities, we investigated the application of a coating of polyether ketone ketone (PEKK) embedded with mechanically exfoliated graphene over copper surface. Our studies aimed to demonstrate the superiority of the blade-coated graphene-polyether ketone ketone (Gr-PEKK) composite coating over a few layers of pristine graphene synthesised by chemical vapour deposition (CVD), for corrosion-resistant coating applications. Here we report composites of graphene with PEKK using a solvent-mediated approach by matching the Hansen solubility parameters of the composite and its components. Electrochemical studies of corrosion inhibition conducted under simulated sea water environment on Gr-PEKK-coated copper surfaces, reveal a corrosion rate of 3.2×10^{-8} mmpy, which is lower than the corrosion rate of copper metal coated with pristine graphene grown by CVD. Compared to a PEKK alone coating, the corrosion resistance of the composite coating is superior by twenty times. The Gr-PEKK composite coating performs better because the polymer matrix comprises of well-dispersed graphene nanoplatelets, which hinders the transport of the electrolyte across the coating. This inference is supported by electrochemical impedance spectroscopic studies, which indicate increase in charge transfer resistance due to the composite coating. Mechanistic understanding of percolation pathways across Gr-PEKK coating is obtained through Positron Annihilation Lifetime Spectroscopy. PEKK has not been used in coating applications due to its strong resistance to solvents. To our knowledge, this is the first time that a solvent-based Gr-PEKK composite has been synthesized and implemented as a corrosion-resistant coating.

Visualization of coating degradation after mechanical formation and humidity exposure

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Ion beam milling has during the past years become the state of the art in cross-section preparation of delicate samples. This paper highlights the benefits of SEM imaging and modern high-resolution EDS element mapping of ion beam milled cross-sections of coil coated samples after mechanical formation and humidity resistance.

Two-layer coatings were applied on hot dip galvanized steel specimens with different zinc compositions. The samples were imaged after mechanical formation (T-bend), and subsequent humidity exposure. After T-bend, the coating with good formability (polyurethane) was basically intact, but deviations were observed at structuring agent particles and zinc coating (Figure 1). The residual stresses within the coating were released during humidity exposure, seen as cracking of the coating, which allowed humidity to initiate metal corrosion. Imaging of samples facilitates prediction of long-term coating degradation and corrosion and allows tailoring the coating system to meet the specifications for various applications.

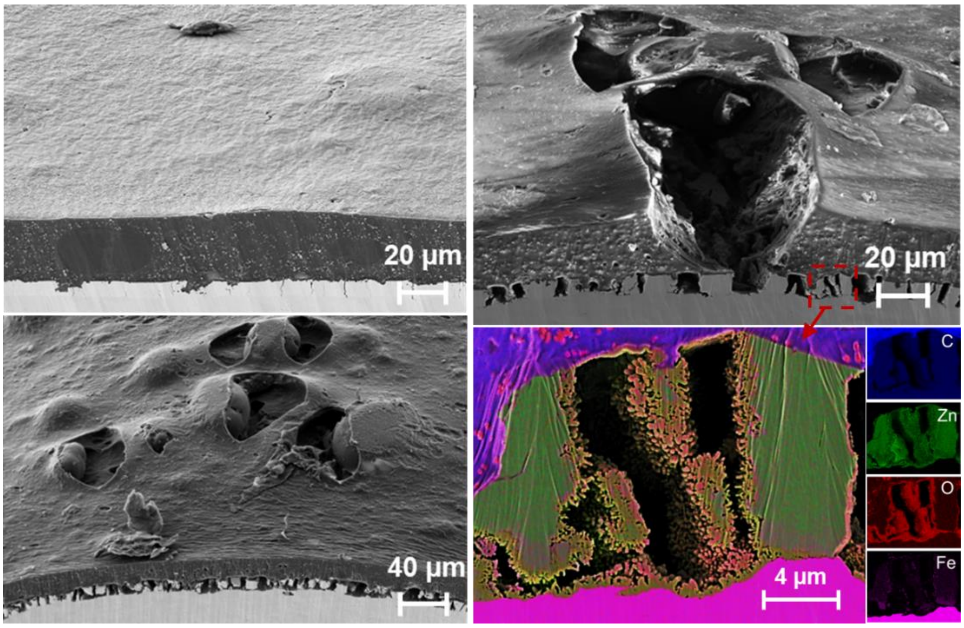

Figure 1. Cross-sections of coated panels: reference (up left), after T-bend (down left), after T-bend and humidity exposure (up right), and EDS element maps (down right).

Under-Film Corrosion Monitoring by Painted Electrodes in High Humid Environment

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Most steel structures such as transmission towers, bridges, plants, etc. are painted to prevent corrosion. Most steel structures and plants except bridges have very thin paint system with dozens or several hundred micrometers order thickness. Moisture penetrates thin paint system easily and aged paint system keeps moisture at the interface between under coat and metallic substrate resulting under-film corrosion. The top coat has been degraded by ultraviolet radiation and the bottom layer has peeled off by moisture penetration. Increasing of peeled area of paint system caused by under-film corrosion are the main reason of re-painting. The sea salt deposition and time of wetness are the main factors of atmospheric corrosion and under-film corrosion.

The main acceleration factors of under-film corrosion are the penetrated moisture to the interface between under coat and metallic substrate and the remaining corrosion products and remaining sea salt depositions according to the surface treatment before painting, However, the corrosive condition at the interface between under coat and metallic substrate has not been explained.

Therefore, the relationship between surface preparation condition and under-film corrosion was evaluated quantitatively by the painted electrodes. Atmospheric Corrosion Monitor, ACM. Sensors and Intelligent Corrosion Monitor, ICM, sensors were used as under-film electrodes.

KEYWORDS

steel structure, under-film corrosion, surface preparation, moisture, deposition, sea salt

Impact of surface preparation on marine paint systems performance for maintenance work

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Surface protection against corrosion continues to attract research interest since all materials are subjected to degradation in the form of costly corrosion. Several solutions are proposed to end-users to correctly protect the surface with aim to slow down corrosion and the application of organic coating remains a favored choice. However, to obtain good long-term performance of organic coatings a good and adequate surface preparation is required. Up to 75% of observed coating failures are found to originate from a non-adequate surface preparation.

The critical parameters of surface preparation are surface cleanliness and anchor profile of the surface. Surface cleanliness is designed to remove oil, grease or other contaminants whereas the anchor profile, achieved either by abrasive blasting or with ultra-high pressure water jetting, produces roughness offering better mechanical anchoring/adhesion for the coating. Most adhesion theories consider a rough surface to be favorable for achieving a high level of adhesion with a given organic coating. However, there has also been studies showing no relationship or inverse relationship. Therefore, the impact of the surface preparation and in particular the roughness on interface quality remains an attractive research topic especially when considering the economic and environmental impacts in steel coating process. Even more, when less stringent surface preparation as the one recommended by usual standard like ISO 12944-4 are considered like in the case of maintenance work.

In this study, six painted systems applied on five different surface preparations were tested using one accelerated test (ISO 12944-6 – 2688h) and field exposure. The results showed that the major parameters to consider in surface preparation are the surface homogeneity and the cleanliness (salt contamination + presence of iron corrosion products). Both parameters have shown to have an impact on the adhesion of the organic coating whereas only the surface homogeneity had a significant impact on the corrosion scribe line. Difference in the sensibility of barrier primer compared to zinc rich primer to surface preparation was also highlighted.

Advancing Coating Science: Non-Destructive Methods for Coating Degradation Evaluation and Breakdown Mechanism Investigation

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In the pursuit of robust solutions to augment the durability and performance of coated structures, non-destructive testing techniques have become indispensable tools in unravelling the complexities of coating systems. This study centres on the innovative application of advanced non-destructive methods, encompassing optical 3D Profilometry, Scanning Acoustic Microscopy (SAM), and a comparative analysis with the ISO 12944-9-based approach, for a comprehensive evaluation of coatings degradation from a damage. The research spans two coating systems, namely an epoxy-primed (EP/PUR) system and a zinc-rich epoxy-primed (ZnEP/PUR) system, undergoing accelerated laboratory testing and real-field testing environmental conditions.

This investigation provides a nuanced understanding of coating breakdown mechanisms, offering insights into the factors influencing material resilience. It emphasizes the effectiveness of non-destructive methods in providing real-time insights into coating performance without compromising material integrity. This, in turn, propels the advancement of non-destructive methods for coatings evaluation and the investigation of coating breakdown mechanisms. The findings presented herein significantly contribute to the continual evolution of methodologies aimed at enhancing our understanding of coating behaviour, ensuring the longevity and efficacy of coated materials.

Regulatory Landscape and Compliance Requirements for Zinc Dust in Coatings for Corrosion Protection

Guy Decelles

DEC Solutions, Fully/Switzerland

Zinc rich coatings play a pivotal role in corrosion protection across various heavy-duty industry, offering a robust defense against environmental degradation of metallic substrates. As the demand for effective corrosion prevention rises, understanding the regulatory landscape governing zinc dust coatings becomes paramount. This paper explores the diverse regulations attributed to zinc dust coatings, highlighting key compliance requirements mandated by regulatory bodies. The paper underscores the imperative for stakeholders within the corrosion protection industry to remain vigilant, adaptive, and proactive in navigating the evolving regulatory landscape surrounding zinc dust coatings.

Principal investigation on the surface chemistry of phosphated zinc coatings treated by hot active plasma

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The effect of hot active plasma (HAP) on phosphated zinc coated steel was studied in detail by means of electron microscopy and spectroscopy, with x-ray photoelectron (XPS) and scanning Auger electron spectroscopy (AES) used in a complementary way. In order to extend the scope of the methods from the surface down to the bulk of the investigated coatings, Ar^+ ion sputter depth profiling coupled with XPS was utilized. The results showed, at first, a strong relationship between the intensity and the impact of the HAP treatment on the coating chemistry and structure. While a mild surface cleaning effect was observed for weak treatments, with increasing HAP intensity the coating underwent significant chemical and structural changes on the surface as well as down to the bulk of the treated material. Initially, a partial decomposition of zinc orthophosphate ($Zn_3(PO_4)_2$), as the sole surface constituent of the untreated coating, led to a mixed zinc metaphosphate ($Zn(PO_3)_x$) and zinc oxide (ZnO) phase, highly localized in randomly distributed micrometer sized spots on the treated surface. Finally, the most intensive HAP treatment, leading to a temperature rise of the treated sample up to 700 ºC as revealed by in-situ temperature measurements, caused a complete transformation of the zinc phosphate material into a porous and rough ZnO layer. Moreover, the heat contribution of the HAP treatment induced remarkable modifications within the bulk of the coating – diffusion of zinc into the steel substrate – an effect mimicking a galvannealing process.

Interplay of Pearlitic Steel Corrosion and Zinc Phosphate Conversion Coating Formation

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Zinc phosphate conversion coatings are pivotal in the cold-drawing industry for high carbon steel, providing corrosion protection and lubrication. The coating forms via corrosion of steel substrate and a chemical reaction at steel / solution interface, resulting in a layer of crystalline phosphate. Two major theories regarding the formation of zinc phosphate crystals were postulated, one states that it occurs on micro-anodic areas where there is high ion concentration, and the other one describes micro-cathodic areas due to local pH increase from hydrogen evolution [1]. Using pearlitic steel, where a lamella of ferrite and cementite is mixed with MnS inclusions, this study focuses on the phosphating fundamentals. Temperature variations during the deposition process indicated kinetic differences in coating formation, while pH adjustments revealed a critical point for zinc-iron phosphate crystallization. The study is supported by thermodynamic considerations to distinguishe soluble and insoluble phosphate formation. A novel finding of this study is the observation of spherical nano-sized phosphate precipitates forming an unprecedented porous network, identified through focused ion beam (FIB) cross-sectioning and EDS analysis. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) and X-ray photoelectron spectroscopy (XPS) at different stages of phosphating process unveiled initial MnS corrosion with subsequent phosphate and zinc accumulation, aligning with FIB findings.

Compared to the steel, phosphating on pure iron showed a kinetical difference. Pearlitic steel achieved more efficient coating due to its corrosion behaviour, even with a simple bath of phosphoric acid and zinc, without additives. Similar characterization on pure iron indicated a slower and a less effective coating; this may be explained by different corrosion mechanisms and kinetics compared to the pearlitic steel. This study not only presents a fresh perspective to the phosphating process but also emphasizes the critical role of substrate microstructure in coating efficiency.

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Sustainable Atmospheric Plasma Deposition of Thin Films on Aluminum Alloys for Corrosion Protection

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Sustainability has been of high priority for Chemetall in recent years as we strive to make our surface treatment technologies continuously more environmentally sound. In our pursuit of more sustainable solutions, we have been investigating atmospheric plasma technologies since 2019. Our main objectives are to reduce water consumption, chemical waste, and the use of hazardous chemicals.

Since 2023 we are developing an atmospheric plasma pretreatment together with the University of Paderborn. The development is focused on a unique remote atmospheric plasma process that activates complex organosilane precursors through kinetic interaction (collision between charged particles and organosilane molecules) rather than heating. This approach allows us to work with heat-sensitive organic compounds and to apply the plasma process in combination with traditional Chemetall products, like Oxsilan® without the need for solvents and with almost zero chemical waste.

The presentation presents initial results of the Atmospheric Plasma project, demonstrating the performance of Oxsilan® MG-0611 in terms of corrosion resistance of thin-film coated aluminum alloys. Oxsilan® MG-0611 is a multi-metal surface treatment which leads to the formation of electrically conductive layers on lightweight metals in aerospace and electronics industries. Typically, the treatment bath consists of 90% solvents. However, by applying Oxsilan® MG-0611 by atmospheric plasma deposition, we could eliminate the use of solvents and even enhance the corrosion resistance.

The results of atmospheric plasma film deposition will be compared with performance of traditional solvent based process.

Growth and corrosion mechanisms of Zr-Ti-Mo-based conversion coatings on Al-6082 alloy

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Conversion Coatings (CC) represent one of the main strategies for corrosion protection of Al alloys in transport applications, among them aerospace, either as a stand-alone protection or as a treatment before primers and topcoats. The gold standard of CC treatments in terms of corrosion protection is that in which Cr-based formulations are used. However, these have arisen environmental and human health concerns and their use has been already restricted. Formulations containing Zr, Ti and Mo represent promising alternatives, but their corrosion protection do not meet the acceptance criteria. Therefore, the aim of this work is to apply a Cr-free Zr-Ti-Mo-based CC process on an Al-6082 alloy and to study its nucleation and growth as well as its corrosion resistance as a function of its morphology at microscale and the deposition process parameters.

The influence of different Al-6082 intermetallics on the nucleation and growth of the CC has been studied by means of scanning electron microscopy (SEM), elemental analysis, and scanning kelvin probe force microscopy (SKPFM). The impact of different pre-treatments was also considered due to their action on the substrate microstructure. Monitoring of the open circuit potential has been used to define the stages of the CC process: initial dissolution, nucleation and growth. The microscale morphology and chemistry of the CC was systematically investigated at these stages and correlated with the microstructure of the substrate. The corrosion protection offered by the CC under different process parameters was evaluated by means of electrochemical impedance spectroscopy and correlated with the CC process parameters and microstructure. The results from this study will enhance the understanding of Zr-Ti-Mo conversion coating treatments aiding to the optimization of the formulation and the process parameters to comply with the necessary corrosion protection requirements.

Flash-PEO on AZ31B magnesium alloy coated with a Phosphate Conversion Coating

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Abstract:

Surface treatments are needed to improve the corrosion resistance of AZ31B magnesium alloy. Usually, several strategies are used based on the combination of several protective systems: e.g., conversion coatings (CC) or plasma electrolytic oxidation (PEO) among others surface treatments, prior to the application of organic coating as topcoat layer.

Phosphate CC (PCC) are characterized by their low cost and user-friendly implementation at industrial level. On the other hand, PEO requires high voltages (and therefore high energy consumption, usually up to 600 V) to growth an oxide layer having various species from the electrolyte into its composition. However, to hinder the main drawbacks of PEO coatings, short time treatments (<100 s) called Flash-PEO can provide relatively thin (3-7 μm) coatings.

This research intends to combine both surface treatments, PCC and Flash-PEO (using several electrolyte compositions) to build up a thin protective coating on AZ31B magnesium alloy. PCC was processed during 30 minutes on bare AZ31B prior to transform the surface by flash-PEO (60 s). The substrate was characterized before and after both surface treatments by X-ray diffraction (XRD), optical microscopy (OM), scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS). The performance of the coatings was evaluated by means of open circuit potential (OCP) and electrical impedance spectroscopy (EIS) measurements up to 7 days in 0.5% wt. NaCl. Results have shown different surface morphology as well as the synergistic effect of the PCC coating in the overall protective system, revealing different evolution of the OCP and impedance values up to 10^7 Ohm·cm^2 at low frequencies.

Comparative assessment of corrosion protection of an intelligent coating versus conventional epoxy-based coatings for corrosion under insulation

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Corrosion under insulation (CUI) is a costly and dangerous issue faced by many industries. CUI can go undetected due to its inability to be detected by visual inspection and limits to other inspections techniques and maintenance cycles. The degradation caused by CUI can lead to many consequences including personal safety, production loss and environmental damage.

To counteract CUI, protective barriers and cathodic protection are sometimes used, individually or in combination. Both mitigation strategies have limitations and to improve safety and increase production, new methods for detecting, monitoring, and protecting assets covered by insulation are needed. An integrated ICCP system combining the benefits of both barrier coatings and ICCP could dramatically change the approach to asset protection from corrosion under insulation.

Copsys Intelligent Digital Skin (CIDS) is a new paint-based digital technology that integrates impressed current cathodic protection within a barrier coating and enables remote detection and location of coating failure in real time while not impacting the attributes of a commercially available coating systems.

To understand the capabilities of an integrated technology a rigorous three phase experimental plan was conducted in partnership with Suncor energy, Fisheries and Marine institute (MI) and Dalhousie University. Phase 1 of this plan, completed at MI, compared the mechanical behaviour and corrosion protective nature of the CIDS technology to an industry approved, commercially available coating. Phase 2 was conducted at the Marine Institutes Asset Integrity Field test site in Holyrood Newfoundland and in laboratory facilities in St. John's, NL. The results of this comparison show a significant improvement in corrosion protection for assets under insulation with no reduction in coating performance. Phase 3 was not completed by MI and is not included in this work.

Polymers with self-healing and anticorrosion properties enabled by dynamic covalent bonds and responsive linkages

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Coating metallic structures with a protective material is a popular strategy to hinder their deterioration by corrosion.[1] However, maintaining their functions after mechanical damage is necessary for prolonging their lifetime. Herein, we design a coating displaying simultaneous self-healing and anticorrosion properties after damage. The coating is prepared by blending a redox-responsive copolymer[2] with the ability to release a corrosion inhibitor and a self-healing polyurethane containing disulfide bonds[3]. The functions of the polymers are enabled by disulfide exchange reactions upon heating. The healing efficiency of the anticorrosion properties is exceeding 95% after damage, which induced a corrosion rate of steel ~ 24 times lower than for a steel substrate coated with the sole self-healing polyurethane (without redox-responsive polymer).

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A pH-responsive and NIR photothermal self-healing coating for metal protection

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Abstract: A novel pH-responsive and near-infrared (NIR) photothermal composite coating was fabricated to improve the anticorrosion performance of the shape memory coating. The mesoporous silica nanoparticles (MSN) acted as the nanocarrier to load the BTA molecules, and the PDA shell has the pH-responsive property and acts as the gatekeeper to control the BTA release. Under NIR irradiation, the PDA shell not only facilitates the release of corrosion inhibitors to suppress the corrosion activity but also raises the coating temperature to repair the coating scratches. The anti-corrosion performance of the composite coating was investigated by electrochemical impedance spectroscopy (EIS) measurements. The coating resistance of composite coating with 1.0% MSN@BTA@PDA loading could be maintained above 10^8 $\Omega\cdot cm^2$ after 35 days of accelerated corrosion test, which was two orders of magnitude greater than the pure EP coating. Furthermore, the scratched composite coatings could be healed after 300 s of NIR irradiation. These pH-responsive and NIR curing endowed the composite coating with a short-time self-healing ability and an excellent anti-corrosion performance.

Advancing corrosion protection of steel with Biobased Polyurethane Coatings

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Abstract

Biobased coatings are attracting a lot of attention because they can be a commercially viable alternative to conventional chemistries based on fossil fuel-derived chemicals. One advantage is that the chemistry of these coatings can be tailored by adjusting the ratio between chemicals, resulting in matrices that can range from very rigid to softer, accommodating various types of additives, such as corrosion inhibitors. Thus, these biobased coating formulations are emerging as sustainable, functional, and tailored solutions for the corrosion protection of steel substrates.

In this study, bio-based polyols were derived from the thermochemical liquefaction of biomass feedstocks. Together with a commercial biobased polyisocyanate, they were utilized to produce bio-based polyurethane (BioPU) coating formulations that were subsequently applied onto steel plates using a bar coater. These formulations were modified with tannin, a green corrosion inhibitor to create a coating with enhanced corrosion protection. Additionally, a functional molecule was incorporated into the coating formulation to introduce corrosion sensing functionality. This sensing capability is activated by changes in local pH and the release of iron cations in active corrosion areas.

Electrochemical Impedance Spectroscopy (EIS) measurements were carried out on the coated panels immersed in NaCl solutions.

The influence of the addition of the corrosion inhibitor addition and the self-sensing molecule on the coating barrier properties was assessed in conjunction with the corrosion inhibition effect. The experiments demonstrated that tannins offer effective corrosion protection and also provided evidence of self-sensing capabilities. Additional studies utilizing localized electrochemical techniques and physicochemical characterizations yielded valuable insights into the protective performance of the coatings.

The results demonstrate that biobased polyurethane coatings formulated from biomass waste and modified with corrosion inhibitors and functional molecules can provided important corrosion protection and carry potential to design a self-sensing matrix.

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Challenges of converting potential corrosion inhibitors identified by ML into useful anticorrosive pigments

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The search for efficient and environmentally friendly corrosion inhibitors is a constant activity for most researchers in academia and industry working on the active corrosion protection topic. Testing all the available molecules experimentally is physically impossible, thus it is necessary to use machine learning models to support and accelerate this activity and identify potential molecules that must be confirmed experimentally. Although this process saves time and resources from trial and error attempts, the transition from an identified molecule into a useful anticorrosive pigment is also challenging.

In this work, a group of potential molecules was identified by ML followed by its experimental validation and selection according to specific KPIs, like toxicity, price and ability to be immobilized into inorganic carriers. The developed anticorrosive pigments were tested according to their compatibility and stability in different coating components, namely solvents and resin types. Some problems like color modification of the resin and loss of crystallinity in the presence of specific solvents were identified. Therefore, new customized strategies were developed and optimization steps were performed in order to increase the compatibility and workability of the tested coating formulation.
The optimized systems were incorporated into coating formulations and applied to AA2024.

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The influence of pigment particle size on the leaching behavior of inhibitors in active corrosion protection coatings

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The performance of active corrosion protection coatings depends on the release of inhibitive species from inhibitor pigments that are incorporated into the organic coatings. The leaching kinetics play a key role in effective protection. Ideally, the leaching rate is sufficiently high to provide adequate concentrations of inhibitive species within the defect to form a protective film, but not so high as to lead to a rapid depletion of inhibitive species in the coating. In the present study, the leaching rate as a function of inhibitor pigment particle size and the associated leaching mechanism are investigated. Model organic coatings loaded with calcium sulfate pigment with 4 different particle size distributions were immersed in deionized water for various time intervals up to 720 h. The leaching rates were determined by measuring the concentrations of the leached species using ICP-AES, which are correlated to the microstructure changes in the coatings in order to gain insight into the leaching mechanism.

It is found that reduced particle size results in an increased leaching rate. Further, 2D electron microscopy of the coating shows that the dissolution of calcium sulphate pigments starts from the coating defect and progresses inwards, resulting in cavities in the coating. Observations of the distribution of the cavities after the leaching process suggest that the soluble inhibitor particles must be connected with each other through a network of interconnected particles. This connectivity hypothesis will be verified by our currently ongoing nanotomography work on the coatings before and after exposure.

Corrosion behavior of AZ31 magnesium alloy coated with aluminate ion-loaded layered double hydroxide

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Abstract

As an anti-corrosion coating for Mg alloys, layered double hydroxide (LDH) coatings are receiving attention because LDH can be a reservoir of corrosion inhibitor and/or an absorber of chloride ions. Loading of corrosion inhibitor is generally carried out by ion exchange after coating LDH with interlayer NO_3^- or CO_3^- ions ($LDHNO_3$ or $LDHCO_3$). In this study, aluminate ions were loaded to LDH particles ($LDHAlO_2$), and then a $LDHAlO_2$ coating was formed on AZ31 by electrophoretic-co-deposition (EP-co-D) method [1]. Effect of aluminate ion loading on the corrosion behavior was examined.

AZ31 plates were used as a substrate. Aluminate ions were loaded to LDH particles by reconstruction process. $LDHAlO_2$ and $LDHCO_3$ particles were fixed to AZ31 surface with Mg-Al double hydroxide gel by the EP-co-D method. Anodic polarization tests in 0.1 mol/L NaCl solution and wet-dry cyclic corrosion tests were performed.

The $LDHAlO_2$- and $LDHCO_3$-coated AZ31 showed the quasi-passive current density which was about 10 times lower than the anodic current density of uncoated AZ31. The quasi-passive current density of the $LDHAlO_2$-coated AZ31 was slightly higher than that of the $LDHCO_3$-coated AZ31. However, the weight gain in the cyclic corrosion tests of the $LDHAlO_2$-coated AZ31 was less than half of that of the $LDHCO_3$-coated AZ31. It was revealed that the aluminate ion loading to the LDH coating was effective to enhance the corrosion protection ability of LDH coatings in the atmospheric corrosion environment.

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Fabrication of multifunctional Epoxy/PVDF coating using ZIF-8 nanosensor for corrosion protection of mild steel

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Abstract

Mild steels are prone to atmospheric corrosion, particularly in marine environments. Its corrosion can lead to a variety of issues, including huge financial loss, detrimental effects on safety, pollution of the environment, and depletion of natural resources. Coating is a conventional way to retard metals from corrosion as they have strong adhesion, excellent chemical stability, and mechanical properties. However, the demand for corrosion protection in aggressive environments is still a challenge and conventional coatings are not enough as they have high susceptibility to corrosion. As a result, smart multifunctional coatings are required for long term protection of mild steel.

The present study reports the fabrication of Epoxy/Polyvinylidene fluoride (EP) coating with self-healing, corrosion sensing and superhydrophobic properties. The EP coating has been modified with Zeolitic imidazole frameworks-8 (ZIF-8) nanoparticles which act as corrosion inhibitor as well as sensor. Zeolitic imidazole frameworks (ZIFs) a sub-family of MOFs are considered as emerging functional materials. Metal-organic frameworks (MOFs) are a new class of functional porous materials with high porosity, variable pore size, large specific surface area, and high stability. In this study, benzotriazole, phenanthroline, and stearic acid are used to provide the self-healing, sensing and super-hydrophobicity to the coating. XRD, FTIR, FESEM, TEM, UV-VIS and water contact angle studies are performed for structural, morphological and wettability measurements. The electrochemical impedence spectroscopy and potentiodynamic polarization are performed to investigate the corrosion performance in 3.5 wt% NaCl solution. The overall results show that EP/ZIF-8 coatings have excellent corrosion resistance and could be a promising smart coating strategy.

ZIF-8 /Ti3C2 MXene sheets for improvement of corrosion resistance of eco-friendly epoxy-silica composite coatings

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Currently, 75% of global epoxy polymers rely on bisphenol A (BPA), a well-known reprotoxic substance. This not only poses environmental challenges but also hinders progress toward sustainable solutions. Our research focuses on changing this landscape by developing an environmentally benign alternative based on a green epoxy coating formulated with vanillin alcohol diglycidyl ether (DGEVA), a derivative of wood lignin. Based on this approach, the objective of the work focuses on further enhancing the performance of our preliminary composite coating. The incorporation of MXene nano-sheets as carriers for inhibitors, would increase the overall efficacy of the coating. The critical aspect of our investigation lies in the functionalization of MXene surfaces through the in-situ growth of ZIF-8 (zeolitic imidazolate framework-8) nanoparticles. This intricate modification not only preserves the intrinsic properties of MXene nano-sheets but also adds additional functionalities, making it an ideal carrier for inhibitors in our composite coating. The release ability of corrosion inhibitors in saline solution resulted in 81% improvement of recorded inhibition efficiency of ZIF-8/MXene nanoparticles in comparison with the MXenes. Electrochemical impedance spectroscopy (EIS) was applied to coatings to evaluate their passive/active inhibition efficiency. The results obtained from the Nyquist diagrams indicated that the total resistance of the coating reinforced with ZIF8-modified MXene sheets was noticeably improved compared with the blank sample and the coatings containing only MXene or ZIF-8 nanoparticles.

Stability of tannic acid in aqueous media of different pHs and implications for anticorrosion systems

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Abstract

Carbonaceous materials, such as graphene oxide (GO) and carbon nanotubes (CNTs), have gained significant attention as anti-corrosive nanocontainers. The 2D GO nanosheets exhibit impermeability to corrosive substances such as oxygen, water molecules, and various corrosive ions. In recent times, researchers have shown a growing interest in using natural resources to obtain organic inhibitors. This change of direction is mainly motivated by the potential benefits that these inhibitors offer to the pigments industry, such as the fact that they are non-toxic, renewable, cost-effective, and efficient raw materials. In this work, oxidized graphene (GO) was functionalized with tannic acid (TA) to confer an active protection mode to the nanocarbon pigment. XRD analysis revealed the self-assembly of TA molecules on the GO surface. The stability and release of TA was studied at different pHs. Tannic acid is stable at acid pH, but hydrolyzes and oxidizes at high pH. Long-term release was observed at both acidic and neutral pH, which may be beneficial for long-term corrosion protection. The effect of pigments on corrosion protection of a polyvinylbutyral matrix in NaCl medium was studied by electrochemical impedance spectrometry. GO-TA pigments provide superior protection to GO. Tests on scarified specimens showed the formation of TA-Fe complexes in the artificial defect, confirming the release of TA during immersion.

Innovative Industrial Coatings: Graphene Oxide (GO) Nanoplatforms Reduced with Cerium Zinc Phosphate (CZPGO) as Potent Corrosion Inhibitive Coating Additives

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Abstract

In industries requiring robust corrosion protection solutions, the development of novel nanopigments presents a promising avenue for enhancing coating performance. In this research, from an industrial perspective, novel corrosion inhibitive nanopigments were synthesized using graphene oxide (GO) nanoplatforms. To reduce GO nanosheets and increase their hydrophobicity, a modified version of zinc phosphate nanopigments containing cerium was synthesized in-situ on graphene oxide nanosheets using hydrothermal co-precipitation method. Next, CZPGO nanoplatforms were loaded with Zn^{2+}/lignosulfonate complexes as corrosion inhibitors. The characterization of CZPGO nanoplatforms were performed using FT-IR, Raman, XRD, and FE-SEM techniques, proved the successful reduction of GO nanosheets. In the coating phase, first, loaded CZPGO nanopigments were dispersed in a water-borne epoxy and applied on steel substrates. Results confirmed no blister/delamination for scribed nanocomposite coatings after 1000 h of salt spray and almost 70% increase in coatings adhesion in comparison with control coatings. After successful optimization and evaluation of CZPGO nanopigments performance in pure epoxy coatings, CZPGO nanopigments were dispersed in a commercial aerospace coating (AkzoNobel) and applied on aluminum A2024 substrates. Salt spray and cyclic corrosion tests results confirmed the enhanced corrosion properties in the presence of CZOGO nanopigments.

Keywords: Industrial coatings; graphene oxide; Cerium zinc phosphate; Coating additives; Aerospace coating.

Corrosivity of biofuels and engine fouling: a review

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The use of fuels from biomass is one of the paths to the transition toward the non-fossil energies. In bio-refineries, different processes (biological, thermochemical, etc.) transform feedstocks of very different compositions (vegetable oils, wood, straw, residues, etc.) to obtain alcohols, esters and synthetic fuels. The presence of some specific compounds (alcohol, oxygenated products, bacteria) in these new fuels can lead to corrosion and fouling in storage equipment and in the internal combustion chambers of heat engines and turbojets. Careful selections of metallic and polymer materials or inhibitors have to be made in order to fulfil the reliability of tanks, pipe and engines components. Specific corrosion and scaling methodologies are required. A review and some guidelines will be presented.

Optimizing Management of Corrosion Under Insulation with Humidity Sensors

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Corrosion Under Insulation (CUI) presents a major challenge in industrial operations, demanding proactive measures to prevent potential equipment damage, safety hazards, production delays, and financial burdens. For the oil and gas Industry, CUI is considered one of the main threats to its facilities' mechanical integrity and one of the main drivers for major accidents and maintenance costs.

The deployment of wireless humidity and temperature sensors offers a tremendous opportunity for proactive risk management in addressing the negative effects of CUI. By detecting wet and dry insulation, these sensors eliminate uncertainty in existing strategies, by strategically placement to map humidity levels and optimize inspections for effective CUI management.

This study aims to establish a connection between humidity sensor field data and an optimized inspection/maintenance scope, drawing from a large dataset of over one thousand sensors. Analysis reveals that areas with high wet insulation are a small percentage of the total insulated area (<10%). It also shows that areas with irregular cladding geometry and intrusive elements in the cladding tend to have higher humidity levels, indicating increased susceptibility to CUI. On the other hand, segments with uniform cladding on straight horizontal pipes show fewer occurrences of high humidity sensor readings. Proactively addressing identified risks in high humidity areas and adjusting inspection/maintenance frequency in dry areas allows end users to optimize their scope for CUI management. Furthermore, the study's insights offer short-term benefits, including enhanced workmanship confidence and timely identification of water ingress points for prompt repairs.

The study concluded that the use of humidity and temperature sensors for CUI management in this particular gas processing facility could result in safer operations, reduced maintenance costs, and lower carbon emissions.

Comparative Analysis of Mineral Wool and Calcium Silicate Insulations: Effects on Humidity Monitoring and CUI Management

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Corrosion under insulation (CUI) is a persistent concern in the oil and gas and petrochemical industries, demanding innovative approaches to improve the management of this issue. This paper presents a study that sheds light on how the characteristics of two different insulation materials affect the interpretation of humidity monitoring data.

The study explores the behavior of two distinct insulation materials, namely mineral wool, and calcium silicate, with a controlled introduction of water/humidity. Importantly, the research examines how the unique properties of each material impact humidity migration and, consequently, the effects on data interpretation.

The study underscores the importance of humidity monitoring for all insulation materials by uncovering these material-specific nuances in humidity behavior. The insights gained from this research have implications for developing more precise and targeted risk assessment and mitigation strategies, thereby addressing the issue of CUI more effectively within the industry.

Abstract :

With climate influence, water availability and water restrictions, recycled water or reclaimed water use as make up water for recirculating cooling systems have become more frequent or even more dynamic in nature. These sources of makeup water experience wide variability in water quality. As a result, the deposition stress seen in the cooling system heat exchangers can vary widely. This paper outlines a novel patented technology that is used to monitor deposition stress in cooling systems. The technology is able to operate at multiple temperatures simultaneously giving insight into the stress seen across a range of heat exchangers in a cooling system, this system is able to identify different type of fouling (biofouling or mineral fouling) or scaling. Information will be provided from laboratory testing as well as applications in the field.

Cold Spray coating for sulfiding environment

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The durability of a thin metallic coating thanks to COLD SPRAY technology is investigated. The metallic coating is made of Nickel based Alloy 625 and specimens for qualification and testing are made of carbon steel substrates. Severe conditions with high temperature (450°C) and highly corrosive H_2S containing fumes are considered for downstream application. The use of cold spray in these conditions is not common, and therefore, its resistance to high-temperature gaseous corrosion is not well-documented. The test was performed in laboratory in response to severe sulfidation discovered on a section of the flame tube in a Claus heater of a refinery.

Key outcomes from the study include:

1. Homogeneity: For simple shapes, the COLD SPRAY coating demonstrated homogeneity, with very low porosity and minimal thickness variability. Depending on substrate size and shape, variation in coating thickness (or homogeneity) can occur (with limited impact on sulfidation tests)
2. Adhesion: The interface Carbon Steel / Cold Spray made of Alloy 625 displayed good adhesion even after exposition at high temperatures of 450°C. No disbonding, separation or cracks were observed after testing in the environment.
3. Corrosion Rates: Relatively low penetration rates were recorded (10 µm/year), although higher than those of raw Alloy 625 materials (4 µm/year). These corrosion rates are considered suitable for the service.

The study concluded that COLD SPRAY coating is a highly promising technique for repairing and/or applying a corrosion-resistant thin metallic film for high temperature gaseous corrosion.

The success of the application heavily relies on the application parameters and the choice of a qualified subcontractor.

Lessons Learned from Premature Corrosion of Storage Tanks in Refining and Petrochemical Megaprojects

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The tank farm is an integral part of any refining and petrochemical industrial complex. Storage tanks provide operational flexibility, buffering unit operations from sudden loss or shortage of feedstock and allowing for change between different modes of operations. The design, procurement and construction of storage tanks are well established activities in the relevant international standards and Operators' specifications.

This paper discusses unique challenges that arise before, during and after the simultaneous / consecutive construction of large number of storage tanks in megaprojects. A comprehensive preservation strategy was developed and deployed which protected the majority of tanks against massive corrosion, yet premature damage still occurred specifically in the tanks' bottom plates. A multi-disciplinary investigation ensued to map out all related activities. Also, a formal root cause analysis was conducted to identify all associated causal factors and root cause to provide corrective actions and protect against recurrence of storage tanks' premature damage in future megaprojects prior to placing them in service.

Key words: Storage Tanks, Premature Corrosion, Preservation, Megaprojects, Root Cause Analysis, Lessons Learned

Using Acoustic Emission for damage detection or In-service monitoring of Equipment

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The Acoustic Emission (AE) technique has been successfully used for damage detection with a focus on mechanical integrity and corrosion diagnosis.

The paper deals with recent successes within TotalEnergies as follows:

1. An AE test conducted during a hydraulic test of a column (built in 1940s). This tower, made of Sa 212Gr.B known for its potential brittleness, was tested “out-of-service” as part of a comprehensive Fitness-for-Service (FFS) assessment.
2. An AE test of water wash of ammonium chloride salts at high temperatures (>150°C) in stainless steel pipes. This test was used to monitor chloride stress corrosion cracking (ClSCC) of the welds.
3. AE on a reactor nozzle with a thermal fatigue issue. This test demonstrated the damage mechanism in service and confirmed that insulation modifications fixed the problem.
4. AE on a tube sheet of an exchanger with cracks found on the weld overlay. This test, conducted during a hydrotest and startup, revealed that the cracks were the result of a previous operation. These cracks did neither propagate into the base metal nor evolve during service.
5. AE on a blistered low-pressure drum. The number of blisters was too high for a Fitness-for-Service calculation, leading to overly conservative assumptions. The solution was to conduct an AE to assess the integrity at that time and apply a coating to temporarily prevent from further wet H_2S damage.
6. AE on a Pressure Swing Adsorption (PSA) unit for fatigue assessment.

Historically, AE was used for the diagnosis of mechanical integrity. However, it has proven to be a useful tool for a wide range of applications like detect or monitor damages (localized corrosion, fatigue, cracking, etc.) on a broad spectrum of materials, including metals, and composites, yielding excellent results. For corrosion monitoring, as there are no standards, the success relies entirely on the experience of the AE contractor.

Carburization resistance in carburized gas atmosphere for UNS S34752

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Product gases can be generated from refinery residues via thermal decomposition during the final stages of petroleum refinery processes. Carburization resistance is critical and superior creep strength for reaction tubes used during the process. In addition, excellent carburization resistance is required for heat-resistant materials in hydrogen reformer plants to prevent carburization derived from the feed gas. In this study, carburization resistance was evaluated to consider the applicability of the developed low-C 18Cr-11Ni-3Cu-Mo-Nb-B-N steel (UNS No. S34752) and other austenite stainless steels. Specimens were subjected to 650 °C for 100 h in a CH_4-CO_2-H_2 atmosphere. The carburization resistance was determined by measuring carbon concentration profiles of the cross-section around the surface using field emission–electron probe microanalysis.

S34752 exhibits excellent carburization resistance with a lower amount of penetration carbon content than conventional TP347H (UNS No. S34709). The amount of carbon content in S34752 is lower than that in conventional S34709. In addition, the thickness of the carbide layers formed around the surface of S34752 specimens is thinner than that of S34709. The precipitation of chromium carbide can be reduced owing to the lower carbon content of S34752, and a high chromium concentration occurs at grain boundaries. Consequently, a uniform protective Cr_2O_3 layer can be formed in S34752. Therefore, UNS S34752 can be used in petroleum refinery and hydrogen reformer plants as a heat-resistant material for several tube applications at elevated temperatures.

How corrosion can be prevented with fiber optic sensors

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2) BASF, Antwerp/Belguim

3) Fluves, Gent/Belguim

Objectives:

Corrosion Under Insulation (CUI) poses significant challenges in the maintenance of insulated pipelines across industries. Distributed Fiber Optic Sensing (DFOS) has emerged as a viable solution, surpassing traditional monitoring techniques. The system developed by Fluves uses a fiber applied at the outside of the cladding and connected to a laser source. From the fiber optic readings and the Fluves algorithms, insulation defects which could lead to corrosion are detected and localized with a precision of 0.5 m. Following successful laboratory and small-scale field tests, the system was subjected to a comprehensive trial over a 4 km stretch of piping at BASF's Antwerp plant. The aim was to evaluate the system's effectiveness in a complex network featuring varying heights, insulation materials, and pipe sizes.

Results:

The large-scale field test reaffirmed the findings from earlier lab and smaller-scale tests. Over three months of monitoring, the Fluves corrosion detection system identified several potential corrosion points along the pipeline. While some areas showed minimal moisture with low corrosion risk, others exhibited fully saturated insulation, posing significant corrosion threats. The system enabled BASF to prioritize maintenance actions based on the varying degrees of corrosion risk.

Conclusion:

The large study at BASF was a resounding success, demonstrating the system's capability to detect even minor defects, thereby identifying corrosion risks at an early stage. The consistent performance across different insulation types underlines the system's adaptability and effectiveness in diverse industrial settings. Future work will focus on rolling out the system on a plant-wide scale and further integrating the system into the day-to-day maintenance operations.

Abstract

Ferritic-martensitic steels are ideal for high temperature applications compared to other materials because they have better combination of mechanical and high temperature properties such as toughness, hardness, strength, low thermal expansion coefficient, and higher thermal conductivity. One of the main uses of these steels is in hydroprocessing reactors in refining industry. The reactor's technology evolved throughout the years starting in mid-1920s where the industry started using 2.25Cr – 1Mo, then moved to 2.25Cr – 1Mo – V and 3Cr – 1Mo – V, where these two materials dominated the market since mid-1980s. However, Stainless Steel overlay is needed because these materials cannot provide the needed resistance to high temperature corrosion. Other materials such as 9Cr – 1Mo – V are receiving attention for potential application in hydroprocessing reactors construction as they proved to operate efficiently at high temperature processes in other industries where high temperature corrosion is not a concern. Therefore, as a step towards understanding the performance of 9Cr – 1Mo – V in hydroprocessing conditions, the main objective of this sturdy is to evaluate 9Cr – 1Mo – V in simulated high temperature oxidation environments and compare it to the conventional materials.

Acid Salt Corrosion on Carbon Steel Pipe in a Diesel Hydrotreating Unit

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In 2017, during the corresponding period of a scheduled shutdown, a significant loss of thickness was detected along a horizontal section of a 14" carbon steel pipe that formed part of the system downstream of an HDT-Diesel reactor, which had been in operation since 2003. This loss was limited to the upper half of the pipe, which led to the decision to install a reinforcement plate on that half along the entire length, allowing the plant operation to continue. Considering the possibility of leakage becoming a critical scenario, as this system carries mixtures containing basically hydrocarbons, hydrogen, hydrogen sulfide, ammonia and hydrogen chloride., at high pressure and intermediate temperatures (~90kgf/cm^2, ~200°C), the text discusses the possible causes that could justify such an occurrence and concludes by proposing hypotheses: the ineffectiveness of the washing water, flow stratification, and the precipitation of NH_4Cl salt.

Application of novel flexible resistometric sensors for real-time corrosion monitoring under insulation

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Corrosion under insulation (CUI) is a form of corrosion typically occurring on steel piping and vessels covered with thermal insulation. CUI is a critical problem in chemical and petrochemical industry which leads to significant financial losses and severe environmental hazards in case of the failure. For this reason, reliable inspection and monitoring procedures are required for the effective CUI management. Few inspection approaches have been established; however, all of them possess certain drawbacks including high price, necessity of the equipment shutdown, or impossibility to serve as early warning and prevent thus costly repairs.

To avoid these limitations, a novel real-time CUI monitoring system based on the resistometric technique was developed. The solution includes flexible sensors tightly attached to the pipe under insulation undergoing the same climatic conditions as the monitored equipment, small wireless loggers placed outside the insulating system preserving its integrity, and data transmission and processing system. The operating principle allows the direct real-time corrosion rate measurement.

The developed monitoring system was used to study the effect of insulation properties, pipe geometry, and presence of a defect on the actual corrosion rate of carbon steel. Five flexible sensors were attached to the pipe on top and bottom positions, covered with two different insulating materials and exposed to cyclic condensation conditions. The results showed the immediate corrosivity increase caused by wetting and drying induced by moisture condensation and evaporation. Water collection on the bottom position resulted in wetting prolongation and a higher corrosion rate. The insulation material showed the most complex effect as its properties linked to corrosion performance were contradictory to the insulating efficiency. The state-of-the-art flexible sensors showed high sensitivity and provided invaluable information on the actual corrosivity, proving the large potential of the technique to be used for CUI monitoring in industrial facilities.

EFFECTS OF CH4/H2 GAS BLENDS ON THE TOUGHNESS AND FATIGUE CRACK PROPAGATION PROPERTIES OF A CNG TANK STEEL

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In the framework of biomethane standardization, the European GERG group set different pre-normative research studies since 2016. Among them, the applicability of Compressed Natural Gas (CNG) tank to gas blends containing biomethane and a small percentage of hydrogen is of particular attention. Up-to date standards EN 16723 part 1&2 advise not to exceed a percentage of 2% hydrogen in volume inside the gas mixture. But the effect of greater hydrogen concentrations close to 2% on the tank steel susceptibility to hydrogen embrittlement isn't well documented. Within the scope of BIOSTAR2C HORIZON Europe project on which GERG group is working along with ENGIE lab CRIGEN and other partners, the fatigue crack propagation and toughness resistance of low-alloy 34CrNiMo6 steel used in CNG type I tanks were investigated at the *Institut P'* laboratory using the *Hycomat* platform. The results of this will be used to provide recommendations to CEN TC 408 on the revision of the aforementioned standards. The study mainly consisted of fracture toughness and fatigue crack propagation tests under various blends with different concentrations of hydrogen at 26MPa pressure. A special attention was paid to the fatigue crack growth enhancement induced by the presence of hydrogen, one order of magnitude higher than in air, and the decrease of toughness properties KQ, CTOD and Jm in hydrogen-containing environments. However, the results indicate almost no influence of the hydrogen percentage, in the range 2% to 6%, on the fatigue crack growth rates, and little effect on fracture toughness properties KQ, CTOD and Jm. The fracture mode is brittle in the presence of hydrogen, characterized by intergranular failure and lath decohesion. The obtained crack growth rates served as inputs for residual fatigue life assessment in the presence of a semi-circular crack type defect in CNG tanks. The simulations using Afgrow® software highlighted a decrease in the number of cycles to failure, defined as a leak before rupture, by over an order of magnitude in hydrogen-containing environments than in air or methane.

Corrosion under insulation (CUI) at lower end of CUI susceptible temperature range

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CUI is considered to be temperature dependent. For carbon steels, the CUI susceptible temperature ranges from just below freezing temperature up to 175 °C. At the lower end of the CUI susceptible temperature range; particularly between the freezing point and the ambient temperature, CUI corrosion rate is generally assumed to be low. However, a number of severe CUI cases were encountered in such operating conditions.

It has been found that a number of environmental, design and operating factors could affect the CUI corrosion rate in practice. High ambient temperature and relative humidity, deteriorated insulation and prolonged shutdowns increase CUI corrosion rate. It is important to analyze all the factors in CUI risk assessment and provide adequate corrosion protection for piping and equipment operating in this temperature range. A case study is presented to illustrate the effect of environmental and operational factors.

VDM Alloy 31 Plus® / DMV4692 – Mastering corrosive environments in the production of fertilizer and other chemicals with a cost effective material

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Denise Caspar[2], Patrik Schraven[2]

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VDM Alloy 31 Plus / DMV4692 is a nickel base alloy which has been developed to close the gap between high-alloyed 6-Mo stainless steels and the highly resistant nickel base alloys of the C-family. Owed to its well-matched composition, the alloy is very resistant under aggressive conditions like salt crystallization, sulphuric acid, nitric acid, phosphoric acid, even in the presence of halide impurities.

The production of phosphoric acid as pre-material for fertilizers, pharmaceuticals and battery electrolytes is an essential industry segment for the globalized world. The common application conditions during the manufacturing of phosphoric acid are very aggressive due to the media used and the elevated temperatures. The presence of impurities such as chlorides may cause even more corrosive conditions. The selection process for a suitable material especially for critical components is therefore essential.

At the same time, this alloy, which is available in the product forms seamless tubes, strip, sheet, rod, bar and wire, is readily machinable and also weldable using matching or over-alloyed filler metal. Thus, the application components such as heat exchangers, reactors, agitators, etc. can be easily manufactured and maintained. Additionally VDM Alloy 31 Plus / DMV4692 can offer advantages regarding lifetime and costs compared to other alloys or non-metallic solutions.

In this paper, the performance of VDM Alloy 31 Plus / DMV4692 in typical media connected to fertilizer / phosphoric acid and other applications will be displayed and for reference compared to metallic alloys from different families. Furthermore, application examples and fabrication of this material will be depicted.

Elevating Corrosion Protection: The Efficacy of an Advanced Hybrid Polymeric Coating for Gas Sweetening Units

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Abstract

The resolute pursuit of enhanced corrosion protection solutions is a critical imperative in industries where the efficient removal of contaminants and impurities is essential. In gas refineries for instance, corrosion can result from various factors, including the presence of contaminants such as hydrogen sulfide (H_2S), the destructive contributions of impurities like carbon dioxide (CO_2), temperature, pressure, and the specific materials used in equipment and pipelines. All of these factors significantly accelerate equipment deterioration. Moreover, corrosive mechanisms are further accelerated by high-pressure steam, high-temperature vapor/solution flows, condensation of acidic vapor media, heat-stable salt formation, the presence of oxygen, and the most severe agents like amine solutions and degradation products due to their interaction with other chemicals and gases.

This study meticulously assesses the performance of the high-tech hybridized polymeric coating system, aiming to establish its efficacy in corrosion protection as compared to conventional methods.

Through a series of comprehensive tests and regular monitoring, our findings reveal the remarkable corrosion resistance and durability exhibited by this innovative coating system. It not only provides a robust barrier against the corrosive agents prevalent in gas sweetening units but also offers a sustainable, long-term solution for repairing and safeguarding these critical components.

The single-layer application of the cutting-edge coating system, HEGGEL Corr 212, with its advanced properties and exceptional protective capabilities, emerges as a promising contender for corrosion mitigation in gas sweetening units. This paper not only contributes invaluable insights into the field of corrosion protection but also underscores the significance of embracing innovative coatings in industrial settings, ensuring the reliability and longevity of gas sweetening equipment.

CUI mitigation by the application of corrosion inhibitors

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Extended Abstract

Insulated pipelines are widely used in the industry to preserve the temperature of the internal fluid, reducing heat exchange, and preventing heating or cooling depending on the process. When thermal exchange with the environment occurs, the plant loses energy, and its operation may decrease efficiency.

The major issue with Corrosion Under Insulation (CUI) is that it occurs unnoticed, silently, and tends to concentrate in certain areas of the pipes (localized) and can occur with any type of steel or insulation used.

Corrosion can cause catastrophic damage to the unit, posing risks to operators and the environment such as burns, asphyxiation, explosions, leaks, and contamination of rivers and lakes.

Special chemical molecules called Volatile Corrosion Inhibitors (VCIs) or Contact Corrosion Inhibitors (CCIs) can help reduce problems with this type of corrosion. The use of self-fusing sealing tapes with Corrosion Inhibitors will be discussed, which can be applied to areas of the pipes that present potential issues.

Data from various installations will be presented, demonstrating the effectiveness of corrosion inhibitors in mitigating corrosion under insulation in petrochemical facilities.

Keywords:

Volatile Corrosion Inhibitors (VCI), Contact Corrosion Inhibitors (CCI), Corrosion Under Insulation (CUI), ZIF, ZSF, Insulated Pipelines.

Driving Efficiency in Pipeline Maintenance: Digital Twins for Extended Inspections & Life Expectancy

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Aging pipeline assets are a concern for many pipeline operators. As pipelines age, external corrosion control becomes more challenging and often results in more aggressive monitoring and maintenance activities such as more frequent in-line inspections (ILI) and direct examinations.

A pipeline case study is discussed demonstrating how a digital twin based on mechanistic modeling was utilized as a proof of concept for identifying possible cathodic protection remedial actions to decrease external corrosion growth rates (CGR) with the goal of extending the ILI inspection interval from 3 to 5 years. Various remediations such as adjusting or adding cathodic protection and resolving interference are modeled and compared with the existing corrosion control configuration. An economic analysis is included to determine if theoretical remediations can reduce monitoring and maintenance costs while maintaining asset integrity.

Key words: Pipelines, Computational modeling, In-line inspections, corrosion monitoring, assessment, remediation, growth rate predictions and economic analysis

Long term testing of monitoring systems for cathodic protection applied to buried tanks

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Buried tanks used for the storage of Liquefied Petroleum Gas (LPG) or any other fluid that may lead to HSE hazards are protected against external corrosion by an organic coating supplemented by cathodic protection (CP). A better knowledge and better mastering of the various measurement methods for testing CP will avoid possible harmful effects of overpolarization on coating adherence. In conjunction with the existing return of experience since the early 90ies, this will provide the industry and the authorities solid technical elements supporting potential extension of the inspection and requalification regime according to the latest French regulation on pressure equipment. Following a 3D numerical modelling study, a long-term experimental study was launched using the opportunity of a new project of LPG storage tanks where it was possible to install various CP instrumentation tools during construction. A large database has been accumulated after more than 6 years of measurements. Results show a very low protection current requirement due to the low corrosivity of sand, the excellent insulation characteristics of the coating and the perfect electrical isolation of the tanks. The main lessons are the following: it is imperative to calibrate the permanent reference electrodes prior to perform measurements, potentials measured with permanent saturated copper sulphate electrodes (CSE) are systematically more negative than the theoretical value, CSE of the conventional or long-duration types give similar results, Ag-AgCl/KCl 0.5M and Zn-$ZnSO_4$ electrodes are relatively more stable than CSE, the location of the permanent reference electrodes does not seem decisive, the “optimized” probe (coupon in the centre of which a small electrolytic bridge communicates with a CSE located on the opposite side) shows promise for monitoring without needing off-current measurements, the risk of degradation of the coating by cathodic overpolarization is negligible if the coating is specified and applied in accordance with the recommendations.

C.P. remote monitoring by Teréga

<u>François CASTILLON, Jesus VIU</u>

Teréga/Teréga Solutions, Pau/France,

Teréga/TIGF/GSO has equipped its cathodic protection installations (rectifiers and drainages) with remote monitoring since 1970 using different techniques according to the evolution of transmission technologies :

- BIT through pipes,
- RTC network,
- GSM and GPRS, 2, 3, 4G
- and now with radio transmission.

Technological advances have allowed us to evolve from simple remote alarm to increasingly complex and precise telemetry, to assess the cathodic protection efficiency.

With its new POLCat project, TEREGA has opted for telemetry on operating values on rectifiers and drainages and Eoff values on coupons at the drainages and on tests points.

To be representative, Teréga continues to deploy telemetry on its network to have a telemetered point every 8 km of pipeline on average. This new approach to remotely operate cathodic protection system (for TEREGA), allows real-time monitoring of the cathodic protection efficiency, but does the philosophy of the CP management shall be changed ?

Polcat is powered by IO-BASE, the digital cloud solution developed by Teréga Solutions and used today to collect all of Teréga's industrial data in real time.

This solution has the advantage of limiting the risks of dependence on a hardware supplier. We use 4 different brands of equipment whose data is valued in a single database.

It's strategically very interesting !

How can we manage and use this data, is it possible to use modules from various sources (different suppliers), what credibility can we give to these measurements ? these are the different questions that the presentation will be expected to answer.

Electrical safety measures in cathodic protection systems

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Abstract

The contribution of cathodic protection to preserving the integrity of steel buried and submerged structures is unquestionable, however, knowing that they use low-voltage electricity during the exploitation, the systems must be designed to work safely. Dangers during the operation of the cathodic protection system, as well as various external influences, can cause the following threats on the manually accessible parts of the installation; electric shock, electrical sparking, overheating of the conductor and overheating of the short circuit. In doing so, the consequences can be fire, explosion, plant stoppage, harmful impact on the environment, material damage and ultimately the lethal consequences on workers and third parties. Related to the above, the parent norms from cathodic protection refer to the application of national electrical safety regulations that should be applied in the design, implementation, and maintenance of the cathodic protection system. Electric safety in cathodic protection refers to low voltage installations and equipment (AC and DC), potential equalization systems, grounding and lightning protection systems, protection systems against induced voltages caused by nearby EE plants and areas threatened by explosive and flammable atmospheres. The paper interprets the minimum safety requirements and presents examples of mistaken solutions in cathodic protection systems.

Keywords: cathodic protection, electrical safety, design, low-voltage, mistaken solutions, explosive atmosphere, flammable atmosphere.

Systematic and repetitive failures in cathodic protection designs: lessons learned from power plants' piping systems

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Abstract

While conducting assessments of cathodic protection (CP) systems for power plant piping across Southeast European countries, identified is a pattern of common and repetitive failures. These issues consistently lead to poor system performance. Coincidence or not, gotten data sets clearly have shown generic and one-size-fits-all approach of installing discrete and proximity sacrificial anodes along the piping. This paper reveals the shortcomings in CP design through a detailed examination of close interval potential survey data, among which, at least one of them resulted in pipeline perforation.

Keywords: cathodic protection, design failure, Southeast Europe, proximity anodes, CIPS, pipeline perforation.

Degradation of grounding conductors for AC mitigation: influence of backfill composition, conductor material and AC current level

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Buried pipelines protected against corrosion by cathodic protection (CP) systems can be influenced by alternative current (AC) flowing from various sources. These influences can result in significant corrosion phenomena. To mitigate AC corrosion risk, GRTgaz installs grounding systems, such as galvanized steel, to counteract AC effects and discharge induced current into the ground. Depending of their nature and composition, grounding systems can rapidly degrade over time as a result of their function. RICE (Research and Innovation Center for Energy – GRTgaz) conducted laboratory tests to investigate this phenomenon.

The laboratory tests involved exposing copper or galvanized steel conductors to AC influences in different media: coke breeze, bentonite, and a mix of gypsum and bentonite. Weekly electrochemical measurements (OCP and polarization curves) were conducted to monitor the degradation of the conductors. Post-experimental characterizations, including visual observations and mass loss measurements, were also performed.

Results revealed that experiments conducted in coke breeze exhibited the fastest degradation rates. This can be essentially explained by a galvanic coupling between conductor materials and the coke breeze medium. In contrast, conductors are better preserved in the gypsum/bentonite medium, even when exposed to AC influences. Regarding conductor materials, the results show that galvanized steel appears to be more susceptible to AC influences than copper. However, differences in geometry between samples made of galvanized steel and those made of copper may have significant effects. Finally, some tests have been performed with stainless steel and showed, as expected, very good durability.

Keywords: grounding, backfill, AC mitigation, galvanized steel, stainless steel, copper.

Stray current corrosion of pipelines: An assessment of limiting critical conditions

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SGK Swiss Society for Corrosion Protection, Zürich/Switzerland

The concepts associated with stray current interference are well understood and described in EN ISO 21857. DC interference represents a possible risk for the integrity of buried infrastructure and assessing potentially critical conditions is of highest relevance. In order to understand the limiting influencing factors, laboratory investigations have been performed under extreme soil and interference conditions. These include very low soil resistivity, increased chloride content and anodic current densities of up to 100 A/m^2. These represent extreme conditions that may indeed be encountered in field applications. The associated results are presented and the possible implications with respect to the integrity of pipelines and mitigation methods are discussed.

Well Casing Cathodic Protection Practices and Challenges

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With ever increasing energy demand oil & gas companies are meeting these energy demands with enhanced production. To support this more and more well casings are added to the oil & gas fields making it a complex network of systems. It is a challenge for the asset owners to cathodically protect these complex networks of well casing structures and associated pipelines.

In Saudi Aramco, metallic well casings are installed for oil, gas and water wells and provided with cathodic protection for external well casing corrosion protection. Practices followed include independent systems for each of the well casings, shared system for more than one well casings and then a bonded system. When multiple wells are drilled in the same area and further share the right of way with multiple pipelines, conventional approaches are no longer adequate for these complex networks and these additional challenges needs specials measures to overcome these challenges and to ensure proper protection as well as to address potential interference situations.

This paper presents approaches followed in Saudi Aramco and how the data from field survey is used combined with existing cathodic protection system operating parameters as well as simulation modeling to manage external corrosion of Saudi Aramco's well casing systems. We will share some field data, network details, challenges, and solutions provided what future improvements are possible. This paper will show from the performance of actual installed cathodic protection systems that how the design of cathodic protection has to consider all scenarios as found from past experience, field surveyed data, combined with simulation modelling to provide an effective system to be assured of proper protection of well casings and associated network.

Keywords: Well Casing; Cathodic; Protection; Current; Corrosion; Interference; Stray Current; Simulation, Modelling; Complex.

Research on the corrosion behavior and mechanism of pipeline steel under dynamic AC interference

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Based on the field test data, the dynamic fluctuation characteristics of AC interference parameters on pipelines near AC electrified railways were systematically analyzed. Field and laboratory simulation experiments were conducted to determine the dynamic AC corrosion laws of pipelines near AC electrified railways under various interference cycles, interference amplitudes, and cathodic protection levels. In addition, the corrosion mechanism under dynamic AC interference was obtained by combining electrochemical testing and surface analysis techniques, which provided a reference for understanding the corrosion behavior and mechanism under dynamic AC interference.

Cathodic Protection Enhancement for Cross-country Pipelines Corridor at Saudi Aramco

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External corrosion of cross-country pipelines is being controlled by the use of latest technologies in protective coatings and by maintaining adequate levels of cathodic protection (CP). Pipelines face challenges to maintain the cathodic protection systems' performance of hydrocarbon cross-country pipelines that run in complex pipeline corridors of different ages, different coating types and conditions and wide variety of soil and terrain. This paper discusses challenges in selecting, monitoring and maintaining the cathodic protection for six pipelines running in same corridor in different geological areas. They cross different types of soil including rocky mountains, wadies and very corrosive subkha soils. The paper focuses on the enhancement of CP current distribution and resolving low CP potentials along the pipelines corridor. Furthermore, the external corrosion controls for these pipelines are analyzed and enhanced considering all factors including coating condition, CP system performance, soil corrosivity and ILI results.

Key Words: Cathodic Protection, Cross-country Pipelines, Reliable Remote Power

Supply, CP Potentials, Current Distribution, Inline Inspection

Passive film characterization on buried gas pipelines after cathodic polarization interruption

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The corrosion protection of buried gas pipelines is achieved through both coating and cathodic protection (CP). The CP is a method consisting in shifting the pipe potential towards cathodic values to reach the passivity or immunity domain of iron [1]. In service, interruption of the CP can occur because of maintenance operation for example, thus leaving the pipeline unpolarized and supposedly unprotected. It was observed that after interruption of the CP, the metal potential became more anodic than its free potential, which is characteristic of a passive state [2]. This residual protection (RP) is caused by the concentration polarization mechanism [3][4]. During CP, the reduction of O_2 and H_2O are increased, leading to a local alkalinization of the metal/soil interface and the metal passivation [3]. This protective film can last several days after the CP interruption in the case of proper soil conditions (density, humidity, etc..). To our knowledge, no work focused on the characterization (chemistry, thickness) of the protective layer formed during CP in soil medium.

In this work, the main objective was then to characterize the passive film formed during CP. Several soil compositions, soil humidity, CP time and CP potential were tested to evaluate their influence on the thickness and composition of the protective layer. The nature and thickness of the protective film was evaluated using X-ray Photoelectron Spectroscopy (XPS). XPS measurements showed a thickness of the passive layer comprised between 4 and 8 nm. It was demonstrated that several parameters resulted in an increased film thickness: a higher CP time, a lower humidity level, a finer granulometry and a less electronegative CP potential. Regarding the chemical nature of the film, XPS revealed a composition based on different ratio of ferrous oxide and hydroxide (Fe_2O_3, Fe_3O_4 and $Fe(OH)_3$). These ratios were altered by the changing test conditions. The two main factors influencing the surface chemical composition were the soil humidity (which significantly increased the hydroxide content) and the soil granulometry (a finer one reduced the Fe_3O_4 content). Moreover, it was also observed that increasing the potential of CP towards more cathodic values did not influence the film composition. The role of the chemical composition of the passive film on the material properties are discussed.

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Internal cathodic protection of water turbine
–
Polarization data in extremely high flow rate for modeling

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Abstract

Cathodic protection can be used for a wide range of applications to prevent corrosion of metallic materials in conductive electrolytes. For inner surfaces of pipes, the use of cathodic protection can be challenging since its efficiency is strongly limited by the ohmic drop induced by the pipe geometry. The flow rate in pipes is another unfavorable factor since it greatly increases the current demand to protect the metallic surface. Despite these difficulties, internal cathodic protection of a high-pressure water turbine was evaluated to mitigate the existing corrosion. Within this case, extremely local high flow rates (up to 60m/s) are reached, and the electrolyte had rather low resistivity. This configuration is out of standards for CP design and the first step was to get reliable polarization data in extreme flow rates since no data were found from standards. Polarization curves were built experimentally from 0 to 2 m/s and extrapolated up to 60 m/s using Eisenberg equation. In a second step, the efficiency of the specific cathodic protection system has been assessed by finite element modeling using the polarization curves obtained and considering local specificities of the designed water turbine including differential local flow rates and dissimilar materials.
This work has allowed to assess current demands for atypic environment which was not documented in the literature so far. The model built using relevant entry data has allowed to verify and optimize the cathodic protection design of the carbon steel and stainless-steel elements of the water turbine as a function of the local flow rate.

Designing an unidirectional drainage bond

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EN ISO 15589-1 and EN ISO 21857 does not provide any satisfying requirement for designing an unidirectional drainage bond. Consequently, some French pipeline operators design higher cable section than needed because they apply requirements defined in NF A05-610, an old French standard. Therefore, the increase of the costs can be very significant. This French standard is no longer applicable and the French pipeline operators now apply EN ISO 21587 requirements.

How can we design the drainage bond according to a clear set of rules while taking the context into consideration?

During 2008 EUROCORR congress in Edinburg, JM Vernet presented the XY method for analyzing the efficiency of an unidirectional drainage bond. And this method is now widely used and applied in France by the pipeline operators. Consequently, when a drainage station has a good balance, the pipe potentials are much more stable (reduced range) and the pipe over polarization risk decreased near the drainage station.

The first step of cable section design is based on the YX analysis carried out on the drainage bond. The goal is to measure or anticipate the level of dc influences by linear correlation. When this is done, it’s easy to calculate the balancing resistance.

The second step is to choose a part of balancing resistance which will be introduced in series with the bond. It is possible to choose a conservative resistance value (expressed in percentage, such as 10 or 1%) and calculate the section.

The final step is to calculate the current density flowing through the cable. It shall be under 3 to 4 A/mm².

In conclusion, this method can be used to consider the geographical and electrical environment of railways and pipelines in design of the drainage bond. With conservative hypothesis, it’s also possible to design of the drainage bond before works.

Proactive Managing Pipeline Safety and Corrosion Threats in the Evolving Energy Landscape

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The dynamic evolution of the energy sector, driven by the expansion of renewable wind and solar energy sources, long-distance high-voltage direct current (HVDC) systems, and high-speed AC trains, presents pipeline operators with a complex set of challenges to ensure the integrity and safety of their infrastructure. While these third-party systems can lead to various operational risks, including corrosion on the pipeline and hazardous shocks to personnel, most of them are not announced in advance, requiring operators to adopt innovative and proactive approaches in their risk mitigation strategies.
Mechanistic modeling solutions can support operators in navigating this shifting landscape effectively by empowering them to make informed decisions, enhance safety, and optimize their infrastructures.

Among the many benefits of adopting mechanistic modeling solutions in today's operators' toolkit, one can highlight the following. *Accuracy and Precision*: mechanistic or deterministic models are physics-based providing results at joint level. *Real-time Monitoring*: Integrating with IoT sensors, mechanistic models offer real-time assessments of AC/DC-induced risks. The creation of this digital twin enables operators to respond proactively to emerging threats, minimizing downtime and maintenance costs. *Market Adaptability*: These models can adapt to fluctuations in power generation sources and demand patterns, enabling operators to optimize infrastructure and reduce operational expenses. *Cost-efficiency*: By offering precise predictions and targeted mitigation strategies, mechanistic models assist operators in resource allocation, minimizing maintenance overhead while ensuring asset longevity. *Compliance and Safety*: As regulatory requirements tighten, mechanistic models provide comprehensive data and evidence of compliance, enhancing overall safety.

Different case studies will demonstrate the ability of mechanistic modeling to deliver high-value and empowering insights to operators on how to prevent threats from solar and wind farms, HVDC, and conventional AC energy corridors.

Optimization of Zinc Addition in Fin Metal on Cathodic Protection for Galvanic-Coupled Fin-Tube Aluminum Heat Exchanger

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Aluminum(Al) based alloys have preferred properties for heat exchanger applications due to their high thermal conductivity, good mechanical properties, and low density. Al heat exchangers are used in various applications, including air conditioning, refrigeration units and heat pumps. For the reducing size and weight of Al heat exchangers, the current trend involves using thinner and smaller tubes. In the case of thinner tube, corrosion resistance is a crucial factor in enhancing the lifespan and efficiency of the heat exchanger. Therefore, preventing corrosion of heat exchangers is essential to increase both their efficiency and lifespan.

The fin-tube heat exchangers are manufactured in such a way that the Al tube is expanded, and fin and tube are physically bonded. Since fin-tube heat exchangers consist of two different metals, galvanic corrosion occurs, causing a significant reduction in the lifespan of heat exchanger. To extend the lifespan of heat exchanger, fin has a more negative corrosion potential than the tube by adding zinc(Zn) to provide sacrificial anode cathodic protection for tube. However, accelerated fin consumption with increasing Zn content can cause debonding of fin-tube, diminishing thermal efficiency and causing localized corrosion of tube, ultimately reducing the lifespan of heat exchanger. Therefore, minimizing the consumption rate of fin and protecting the tube is essential for extending the lifespan of the heat exchanger.

In this study, we aim to increase the lifespan of heat exchanger by considering both corrosion potential and anodic current density of fin. To achieve this objective, the corrosion of Al fin-tube heat exchangers, composed of fins with varying Zn content, was evaluated by using potentiodynamic polarization tests, zero resistance ammeter (ZRA), sea water acetic acid test (SWAAT) and boundary element method(BEM) simulations. Finally, we propose an optimal fin metal design to prevent galvanic corrosion and increase the lifespan of the Al heat exchanger.

Keywords: aluminum, heat exchanger, galvanic corrosion, cathodic protection

Investigation of the of cathodic disbondment of pipeline coatings in seawater and soils

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To ensure the integrity of offshore and onshore buried structures against corrosion, a complementary approach combining cathodic protection and organic coatings is used. Following the ISO 15589-1, the efficiency of the CP for onshore pipes is ensured by maintaining the CP potential within a protective range with a critical limit potential value of -1.200 V/$CuCuSO_4$. This latter, beyond the hydrogen embrittlement risk, was mainly defined to limit the cathodic disbondment (CD). However, lower potentials might be observed in the field. At the other hand, an overprotection risk exists with an impact on coating that remains complex to be studied. Indeed, the influence of over cathodic protection on the coating depends on several factors such as the nature of the coating, the media, the temperature, the electrochemical processes and the kinetic involved. In the literature, many CD testing procedures are discussed in terms of testing parameters. For instance, existing procedures are usually limited to chloride containing electrolytes that are not representative of underground environment.

In the present study, CD tests were realized in different soils and natural seawater at ambient temperature for 28 days and 12 months. The effect of polarization potential and current density were studied on typical pipeline coatings including Fusion Bonded Epoxy (FBE) and three layers Polyethylene (3LPE). Different CD rates were observed in these medias, highlighting a reduced CD rate in soils that can be related to the reduced active surface area and other parameters.

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Title: CFR by the CEFRACOR – a new certification dedicated to contractors applying coating systems on-site for the corrosion protection of buried pipelines

Abstract:

The purpose of this presentation is to introduce the background of this certification, especially the observations and expectations from the French oil & gas pipeline operators, towards their subcontractors, involved in the maintenance of their assets, in particular for the rehabilitation of coatings on buried pipes. This presentation describes the process involving pipeline operators, coating manufacturers, training centers and inspection companies, to establish the specifications of this new certification and the conditions to certify applicators. It presents the today situation after more than 4 years of certification and the benefits of its implementation, especially with a recognition by the French administration.

Corrosion severity mapping based on real time data acquisition in Europe

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In this study, real time data acquisition is used to forecast corrosion severity in Europe.

Whilst the damage of cars by rust is anecdotally known, there are few thorough studies on the effect of weather on automotive corrosion. Consequently, this study aims to substantiate these claims through a systematic examination.

The project uses commercially available sensors (Aircorr O, Luna Acuity LS) to gather atmospheric (temperature, RH, contamination) and corrosion data (free and galvanic) from the vehicle and combine them with weather forecast data to build a regression model that can forecast corrosion severity. Data was collected in Belgium and Norway.

Experiments were conducted to find the best model for predicting corrosion events, combining the key features that correlates to corrosion severity. The predictive model can predict corrosion using weather data. The best feature configuration, using an ensemble algorithm, achieved an R^2 around 0.6.

The project has the potential to remotely monitor the quality of vehicles and monitor the onset and development of corrosion on cars.

A Proven Roadmap for Developing State-of-the-Art Corrosion Predictive Models in the Automotive Industry

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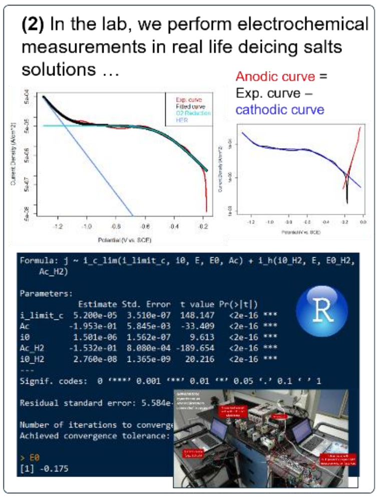
Leveraging ten years of experience in in-service corrosion testing on instrumented vehicles, the National Research Council Canada (NRC) has developed an advanced corrosion model using Finite Element Analysis (FEA) and Machine Learning (ML). Calibrated with real-world data from on-the-road testing, this FEA/ML-based model is now used by automotive companies to improve component designs and hasten their time-to-market.

Objectives

The objective is to showcase the strategy implemented by the NRC for conducting in-service testing and incorporating data on temperature, relative humidity, time-of-wetness, and galvanic currents into time-transient FEA/ML models.

Results

(1) We collected millions of data from the road using instrumented vehicles…



(2) In the lab, we perform electrochemical measurements in real life deicing salts solutions …

```
Formula: j ~ i_c_lim(i_limit_c, i0, E, E0, Ac) + i_h(i0_H2, E, E0_H2,
    Ac_H2)

Parameters:
           Estimate Std. Error  t value Pr(>|t|)
i_limit_c  5.200e-05  3.510e-07  148.147   <2e-16 ***
Ac        -1.953e-01  5.845e-03  -33.409   <2e-16 ***
i0         1.501e-06  1.562e-07    9.613   <2e-16 ***
Ac_H2     -1.532e-01  8.080e-04 -189.654   <2e-16 ***
i0_H2      2.760e-08  1.365e-09   20.216   <2e-16 ***
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Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1

Residual standard error: 5.584e-

Number of iterations to converge
Achieved convergence tolerance:

> E0
[1] -0.175
```

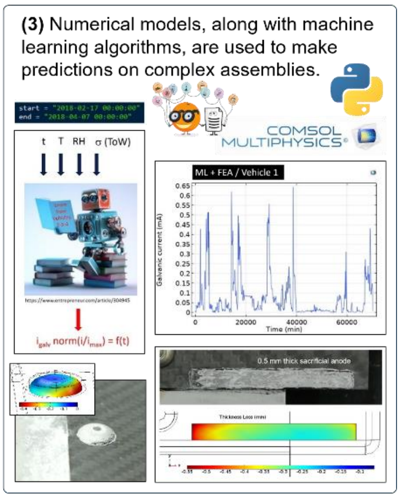

(3) Numerical models, along with machine learning algorithms, are used to make predictions on complex assemblies.

Conclusions

This presentation will focus on the importance of using FEA and ML as complementary tools. It is crucial to recognize that the growing excitement around ML should not overshadow the proven strengths of FEA. As will be shown, employing FEA/ML models without proper calibration and integration of in-service results can lead to significant misinterpretations, potentially hindering the development of innovative designs.

Corrosion Performance of an Al-Mn Alloy for Production of Battery Base Plates

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In the dynamic landscape of e-vehicles, the efficiency and the service-life of batteries play a pivotal role. One of the critical parts of the battery cooling systems is the base plate. Corrosion of the base plate can be a concern, especially when different metals are in direct contact with each other. The base plate is typically manufactured out of Al-Mn aluminum alloys. The corrosion performance of the aluminum base plates is affected by its production route and twin-roll casting (TRC) is a promising technique for producing these components.

The utilization of copper rolls in TRC to take place in a faster solidification, therefore it is worth to investigate the change in the material characteristics, especially the corrosion behavior of the base plate. The potential difference between the aluminum matrix and the intermetallic particles is the driving force for the onset and the progress of corrosion. The alterations in the micro-chemistry and the morphology of the intermetallic particles, which is affected by the thermal conductivity of the roll material, influences the corrosion performance of the strip. Furthermore, iron content of the intermetallic particles is another important factor dictating the cathodic reactivity of the particles with respect to the matrix and generally increased iron content of the alloy deteriorates the corrosion performance of the strip since iron has a very limited solubility in aluminum solid solution and diffuses from the intermetallic particles.

In this study, the influence of the copper roll application on the corrosion behavior of a modified Al-Mn aluminum alloy was investigated and compared with the results of standard steel roll application. Subsequently, iron content of the alloy was increased to observe whether a faster solidification provided by using a copper roll compensates for the detrimental effects of increased iron content. The strips, cast via an industrial twin-roll caster, were processed with lab-scale instruments and then characterized by measuring open circuit potentials and polarization curves. SEM-EDS analysis was performed to observe the morphology and the micro-chemistry of the intermetallic particles. Complementary analysis was conducted with SKPFM-AFM measurements to correlate the corrosion performance of the strip with microstructural features. It was concluded that the application of copper rolls in TRC can be used as a tool to improve the corrosion performance of Al-Mn alloy base plates. From the corrosion perspective, it has an unexplored potential to be exploited since it provides extra space for iron in the alloy. This potential can be utilized to develop recycling-friendly alloys, which encourages the consumption of secondary aluminum and aluminum scraps containing iron.

New generation of sustainable waterborne zinc flake coatings

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Zinc flake coatings have been successfully used as anticorrosive coatings for steel substrates for the past decades. Indeed, the zinc flakes embedded in the film grant an excellent sacrificial protection, while the binder combined with the lamellar shape of the zinc ensures a good barrier effect. As a result, these coatings offer good corrosion resistance at low thickness, even in severe environments.

The binders used for this technology are often based on organic resins, requiring the use of volatile organic solvents. However, these solvents are harmful both to the environment and to the human life. That's why NOF Metal Coatings has developed waterborne formulations using sol-gel technology to provide a safe and sustainable solution for corrosion protection. These coatings exhibit very good performances, even at thicknesses from 6 to 10 µm. Nonetheless, they require a curing step at relatively high temperature to achieve both total evaporation of the water and reaction of the sol-gel binder. In line with NOF's sustainable development and CSR policy, a new generation of water-based products with lower curing temperature has been developed. This new formula offers similar corrosion protection capabilities, while consuming 25-30% less energy during the application process.

The corrosion properties of this new coating are investigated using different accelerated corrosion tests, such as Salt Spray Test (SST) and cyclic corrosion tests, as well as outdoor exposure. Moreover, electrochemical measurements like potentiodynamic polarization and electrochemical impedance spectroscopy (EIS), combined with microstructure analysis through electron microscopy (SEM) provide insights on the mechanism involved in the corrosion protection process of these systems.

This study shows that the new formula exhibits excellent anticorrosion properties thanks to a strong sacrificial protection. In addition, a self-healing effect is granted by the formation of a zinc corrosion products. This layer enhances the barrier effect of the coating once the zinc has been consumed, leading to long-term protection of the substrate, even at a lower curing temperature.

X-ray photoelectron spectroscopy studies on different zinc flake systems after exposure to several corrosive environments

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The corrosion protection mechanisms of metallic zinc coatings such as hot-dip galvanizing and electroplated zinc coatings on steel have been extensively studied, yet the corrosion mechanism of inorganic zinc flake coatings has not been investigated to the same extent.

In this study, we provide an insight into the corrosion mechanism of different zinc flake systems by exposing steel components coated with these systems, mainly consisting of zinc, aluminum and zinc alloy flakes embedded into an inorganic binder, to different corrosive atmospheres. The resulting different corrosion products are compared using X-ray photoelectron spectroscopy (XPS) analysis in order to draw conclusions about the oxide formation and the associated cathodic corrosion protection by the zinc (alloy) flake systems. The different behavior of zinc flake coatings is also analyzed via scanning kelvin probe (SKP) measurements.

Various corrosion tests such as salt spray tests, humidity tests, cyclical corrosion tests and outdoor weathering were carried out. The resulting corrosion products help us to understand the mechanism of protective layer formation of zinc flake systems in different corrosive atmospheres. Based on this approach tailor made zinc flake systems can be developed.

Development of Accelerated Corrosion Test Methods Using Wet-Dry Cycling of Varying Salt Solutions and the Study of Coating Damage Evolution via Electrochemical Test Methods

Victor Ponce[1], Shaik Merkatur Hakim Marjuban[1], Heather Eich[2], Allison Mahood[2], Rishi Gupta[2], and Homero Castaneda[1]

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ABSTRACT

Wet-dry cyclic testing has been used to accelerate corrosion failure mechanisms by exposure to harsh conditions in a controlled laboratory environment. The stress parameters in the cycling environment include temperature, salt composition, and humidity, in an effort to replicate real-world conditions while increasing the degradation rate. With the current accelerated methodology corrosion is characterized by visual analysis. This work studies the characterization of automotive coating/substrate systems after exposure to an accelerated corrosion environment via electrochemical testing, mechanistic analysis, and mathematical framework. The methodology included different temperatures, salt compositions, and monitoring setups. The cycling process included a wet condition, with four days (96 hours), and a dry condition lasting three days (72 hours), completing a 1-week cycle. Corrosion testing was conducted using a Cyclic Corrosion Test (CCT) chamber with varying solutions including ($NaCl$, $NaCl+CaCl_2+MgCl_2$). Three distinct coating types with different corrosion control mechanisms were studied. Electrochemical assessments were conducted in real time via electrochemical impedance spectroscopy (EIS) to quantify different degradation stages. The phase angle data was analyzed over 30 days of exposure and provided valuable insights into the corrosion mechanisms based on the damage evolution stages previously developed using steady-state methods. These findings underscore the importance of accelerating protocol to simulate field conditions and supported the development of new accelerated corrosion testing methods to quantify corrosion performance using damage evolution modeling.

Predictive Tools of Corrosion Evolution in Automotive Coatings Using Electrochemical Testing and Artificial Neural Networks

Victor Ponce[1*], Shaik Merkatur Hakim Marjuban[1*], Heather Eich[2], Allison Mahood[2], Rishi Gupta[2] and Homero Castaneda[1]

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ABSTRACT

The corrosion performance of three different automotive surface coatings (physical barrier, sacrificial, and barrier/sacrificial hybrid) was characterized and monitored with time. The corrosive conditions faced by vehicles in the field, such as deicing, were simulated using different salt compositions (NaCl, $NaCl+CaCl_2+MgCl_2$). The coating/metallic substrate interface experiences various degradation stages during exposure to harsh conditions. Each stage was defined based on the dominant mechanism and correlated with the exposure time. Different interfacial processes were defined based on the electrochemical testing and validated with high-resolution surface tools.

In this work, we use electrochemical and surface experimental data with mechanistic analysis to develop a model that can fit the monitored laboratory and field data and be used as a predictive tool. A mathematical framework based on mechanistic principles and machine-learning concepts was developed to predict each performance stage. Water uptake and substrate activation have been used to define the initiation of a potential coating failure. The phase angle plots from EIS were utilized to monitor and quantify the state of the coating and substrate surface during steady-state conditions and train an Artificial Neural Network (ANN) as an arrangement of Time Series Prediction (TSP). The transport processes, activation, and interface interaction with the corrosive environments were analyzed as a corrosion mechanism and were predicted via the ANN concept. The ANN has predicted the coating performance for several years, and the experimental results have been validated by scanning electron microscopy (SEM) imaging of cross-sectioned samples. The model has been able to predict ten years of performance for each coating/substrate interface.

Effect of drying on the corrosion of technically important metallic materials during the accelerated corrosion tests

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1) Technopark Kralupy, University of Chemistry and Technology Prague, Kralupy nad Vltavou/Czech Republic

Cyclic accelerated corrosion tests (CACTs) widely used in automotive industry for material testing and lifetime estimation usually simulate the real operation conditions with the regularly repeated phases of salt contamination, wetting and drying. Drying is particularly critical as the relative humidity (RH) decrease first results in the formation of thin concentrated surface electrolytes with rapid oxygen supply creating highly corrosive conditions, and suppresses corrosion in the later stages due to the electrolyte evaporation. Most of the standard CACTs simulate the drying process within a range from 50 to 70 % RH. However, in real outdoor exposures much lower (< 30 %) RH is regularly reached during warm days. Moreover, hygroscopic salts, if present on the surface, retain moisture and require significantly lower RH to dry fully.

The current study aimed to evaluate the effect of drying RH on the corrosion behaviour of carbon steel, zinc, aluminium and magnesium AZ31 alloy. Metallic coupons and resistometric (ER) sensors were exposed under the conditions of modified ISO 16701 CACT. The test was repeated three times, with all the parameters kept unchanged except for the dry phase RH set at 30 %, 50 %, or 70 % RH. After the test, real-time corrosion rate measured with ER sensors, average corrosion rate of the coupons, morphology and composition of the corrosion products were evaluated. Possible corrosion mechanisms were considered and the data compared to the results of real outdoor and on-vehicle exposures to propose the optimal drying conditions.

The results revealed that 70 % RH was not sufficient to fully dry the surface leading to corrosion under- or over-estimation for different materials and altering the material ranking compared to the real exposures. Milder drying under 50 % RH reflected carbon steel and zinc corrosion in aggressive industrial and marine atmospheres. Low drying RH effectively simulated the material ranking and corrosion morphology for all the tested materials in the wider environment scale, and could be thus recommended as optimal for accelerated corrosion testing.

The effect of chemical composition of High Strength Steel on the mode of corrosion in accelerated testing was investigated. Mass loss rates were determined and linked to SEM/EDX mappings of the oxide layer.
The SAE J2334 test generates a layered oxide structure, while the VDA 621-415 and VDA 233-112 tests generate the classical inner oxide – outer oxide structure.
While the tests are designed to mimic urban/industrial conditions, the SAE J2234 test invokes corrosion associated with marine conditions in some cases. The result is a distinct difference in the mass loss rate between steels of comparable properties, or the same steel depending on the exact execution of the test. Whether the switch occurs depends on the chemical composition of the steel.

The role of the elements added to High Strength Steels on the corrosion mechanism is discussed, especially with respect to the interpretation for Automotive applications.

Corrosion Mechanism of Galvanized Press-Hardened Steel in Atmospheric Conditions

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Over the last 20 years, galvanized press-hardened steel (PHS GI) have become an important material in the automotive industry because of exceptional mechanical properties and good corrosion resistance. Due to the specific manufacturing process, the resulting zinc coating is composed of a combination of Zn-Fe intermetallic phases with different potentials. The corrosion mechanism of this material is thus significantly different compared to conventional galvanized steel.

This work describes the mechanism of formation and evolution of corrosion products on PHS GI under atmospheric conditions and the influence of each formed phase on further corrosion properties. During simplified accelerated corrosion tests, analysis of soluble and insoluble corrosion products in time was performed by techniques such as ion coupled plasma – optical emission spectroscopy (ICP-OES), Fourier transformed infrared spectroscopy (FTIR) and X-ray diffraction analysis (XRD). A model for the composition of corrosion products is proposed.

It is shown that PHS GI exhibits very good corrosion resistance under atmospheric conditions. A strong tendency to form insoluble corrosion products was observed. Except of akaganeite, the insoluble corrosion products such as simonkolleite, hydrozincite and dawsonite serve as a barrier and slow down corrosion. Altering of wet-dry cycles led to a rapid formation of simonkolleite due to high chloride consumption, and promotion of dawsonite and hydrozincite due to a better transport of CO_2 to the surface. Rate of the corrosion process increased after dissolution of the zinc-rich phase, when corrosion of the iron-rich phase accelerated akaganeite formation. However, the model showed that akaganeite was still represented by less than 20%, whereas simonkolleite accounted for nearly 50% as a dominant corrosion product.

Exploring Hydrogen Activity Distribution in Press Hardened Steel: Insights from EBSD, Nanoindentation, Reflective Microscopy, and Scanning Kelvin Probe

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The attractiveness of Press Hardened Steels (PHS) has grown due to their mechanical properties, notably an ultimate stress of up to 1500 MPa in tensile strength. This trend is particularly evident in the transport industry, where emerging trends emphasize weight reduction and more rational, cost-effective manufacturing. However, it is important to note that PHS exhibits high sensitivity to hydrogen embrittlement and stress corrosion cracking. Hydrogen uptake studies have traditionally focused on generalized mechanisms without considering localized phenomena. Nonetheless, due to the spatial separation and localization of anodic reactions during atmospheric corrosion, hydrogenation is undeniably a local phenomenon, as demonstrated by Nazarov et al. [1] in advanced high-strength steels using Scanning Kelvin Probe (SKP). Regions with increased hydrogen concentration and elevated levels of local residual or applied stress are prone to cracking. The distribution and accumulation of hydrogen could depend on the presence of voids, inclusions, and traps in steel. In this contribution, our focus will be on establishing a correlation between three local techniques to better understand hydrogen distribution within PHS and to define the microstructure features related to the localization phenomena. Initially, PHS thin membranes were cathodically charged in a sodium chloride solution. Subsequently, the permeated side of PHS initially characterized by EBSD was investigated using *ex-situ* SKP, *in-situ* Reflective Microscopy and Nanoindentation.

[1] A. Nazarov, Corros. Mater. Degrad. 4 (2023) 158–173.

A study of hydrogen embrittlement mechanism for Zn coated high strength steel

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With increasing global attention to environmental regulations and automotive safety, the lightweight steel is being demanded to simultaneously achieve fuel efficiency and vehicle stability. However, as the strength of steel increases, the issue of hydrogen embrittlement, where rapid fracture occurs due to hydrogen, becomes problematic. The most fundamental way to address hydrogen embrittlement issues in high strength steel is to minimize the ingress of hydrogen during steel making processes and in corrosive environments occurring during automotive operation.

Recently, Zn coated high strength steel has been applied to automotive components to enhance their resistance to corrosion. However, it is known that hydrogen diffusion rate of Zn is significantly slower compared to iron (Fe). Furthermore, Zn coated steels are prone to localized galvanic corrosion, which can lead to an increased inflow of hydrogen in corrosive environments. As a result, hydrogen embrittlement issues in Zn coated steel have become more significant.

In this study, we confirmed the differences in hydrogen diffusion rates among different types of Zn coating through electrochemical hydrogen permeation experiments and analysis of morphology in Zn coating layer. Additionally, by conducting electrochemical polarization experiment, permeation experiment, and observing morphology changes of Zn coating layer in corrosive environments, we identified the differences in hydrogen generation and inflow behavior due to corrosion among various Zn coated steels.

Ultimately, by understanding the mechanisms of hydrogen generation, inflow, and diffusion specific to each type of Zn coated steel (GA/GI/EG), we demonstrated that relative differences in hydrogen embrittlement characteristics can arise during the steel making processes and automotive application corrosive environments based on the Zn coating types.

The effect of Zn-Fe coatings on hydrogen absorption to press hardened steel

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In recent years, press hardened steel (PHS) became a key material for construction of vehicles, mainly for passive safety components. The potential risk of PHS components lies in the possibility of hydrogen embrittlement (HE) during their lifetime. Hydrogen can be introduced to the material by atmospheric corrosion and, in the extreme case, may precipitate a reduction in both yield strength and ductility.

PHS components are commonly protected with metallic coatings in order to enhance their corrosion resistance. Multiphase Zn-Fe coating forms by annealing of zinc-galvanized steel plate followed by quenching in cooled dies. The process introduces defects in the coating, where the steel/coating galvanic couple forms in corrosive environment. The cathodic polarization of steel during this process may result in hydrogen evolution and permeation to steel substrate. The hydrogen entry depends on the coating's morphological characteristics, phase structure and corrosivity.

In the present study, three types of coatings with three different annealing times were compared in terms of their effect on hydrogen absorption to steel. The microstructural features of the coating were characterized using scanning electron microscopy (SEM). Furthermore, their elemental composition was analyzed by energy-dispersive X-ray spectroscopy (EDS) in combination with inductively coupled plasma mass spectrometry (ICP-MS) analysis of solutions obtained after electrochemical dissolution.

The coatings were exposed under immersion conditions in NaCl electrolyte with composition corresponding to a thin electrolyte film that forms on the metal surface during atmospheric exposure. Galvanic couples steel/coating were systematically monitored with the zero resistance ammeter (ZRA) technique. Subsequently, the hydrogen content within the steel cathodes was later evaluated with thermal desorption analysis (TDA). The content of hydrogen was compared to that in samples exposed in atmospheric conditions.

Influence of Oil Residues of 6xxx Aluminium Surfaces and Evaluation of Cleaning Strategies for Adhesive Bonding

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Exploring the Impact of Dry-Film Lubricants on 6xxx Aluminium Alloys

AMAG is a manufacturer of semi-finished aluminum products in premium quality. Knowledge and a deeper understanding of our material under different environmental conditions and how it can be further optimized is an essential part of our research. An increasingly important function of our surfaces, especially those for automotive applications, is the ability for adhesive bonding. In addition to many specific influencing factors such as surface texture, oxide composition or chemical coatings, factors from our customers' processes are essential for this surface function.

The use of lubricants as an aid for forming processes is one example that will be examined in more detail in this study. Lubricants are widely used in metal forming and contribute significantly to the successful completion of precise and demanding forming operations. However, remaining residues of these lubricants can influence subsequent joining methods such as adhesive bonding. This work investigates the effect of lubricant residue on bonding performance.

Various test methods and climatic simulation techniques can be used to investigate the factors influencing the degradation at the interface between the adhesive and the metal surface. Under these climatic conditions, residuals (e.g. from lubricant) can trigger chemical reactions that have a considerable impact on the durability of bonded joints. The present study shows the influence of oil / lubricant residuals on the bonding performance of Ti/Zr passivated 6xxx aluminum alloys under different aging conditions. The effects of cleaning strategies were investigated and evaluated. The existing damage mechanisms were characterized and explained.

Effect of low concentrations of Cu and Zn on precipitate crystal structures and intergranular corrosion in 6082 Al-Mg-Si-T6 alloys

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Abstract

Al-Mg-Si alloys are widely used as extruded profiles, e.g., architecture, aerospace, marine, and automotive application, due to their good formability, high strength to weight ratio, and good corrosion resistance. Given that Zn is one of the trace elements that might potentially exist in Al scrap metals throughout the recycling process, it is important to understand to which degree different levels of Zn can influence the microstructure and corrosion resistance of Al-Mg-Si-Cu alloys. Microstructure and susceptibility to intergranular corrosion (IGC) in Al-Mg-Si-T6 alloys with different Zn content (0.003, 0.022, 0.041, and 0.059 wt.%) were investigated. Scanning Electron Microscope (SEM), Electron Backscatter Diffraction (EBSD), and Scanning/Transmission Electron Microscopy (S/TEM) are employed to investigate the microstructure and the role of grain boundary precipitates and chemistry on IGC.

Material showed a dual microstructure with recrystallized surface layer and deformed centered layer. The results revealed that the IGC is noticeably influenced by a minor addition of Zn. The higher the Zn content, the less the susceptibility to IGC. The TEM results revealed the presence of Cu film at the GBs in the alloy containing 0.05 wt.% Cu while Cu and Zn films were detected in the alloy containing 0.05 wt.% Cu and 0.06 wt.% Zn. In addition, the results also showed less penetration depth as a function with Zn content.

Selective corrosion protection coating deposited on Aluminium using Atmospheric pressure plasma processes

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Substituting conventional steel alloys with titanium, magnesium or aluminium offers substantial weight savings which leads to reduced emissions, increase fuel economy of enhanced vehicle performance. Aluminium alloys represent today a primary choice for the manufacture of automotive components due to their mechanical properties, their low specific weight and also their recyclability. However, in the presence of a corrosive environment, the thin aluminium oxide layer formed on the metal surface can be depleted and lead to corrosion propagation and attack of the metal substrates. Several type of coatings can be considered to protect aluminium metal substrates from corrosion such as anodizing coating, sol-gel coatings, electrochemical deposition, physical vapor deposition (PVD) chemical vapor deposition (CVD) and also most recently developed atmospheric pressure plasma enhanced chemical vapor deposition.

Atmospheric plasma processes have been used in several type of application as a surface preparation method on metal or polymers to clean the surface by oxidizing the contaminants and at the same time improve the surface energy enabling reliability and process control on the adhesion. Moreover, it is also possible to introduce a specific siloxane precursor in the plasma discharge and deposit a thin barrier coating used to prevent corrosion of the aluminium surface. The atmospheric pressure plasma deposition of anticorrosion coating can be easily integrated in the production line and have been identified as an ecofriendly solution to protect motor pump in comparison with anodizing process. Even after 1200 h in the salt spray chamber, the optimized plasma coatings provided a leak-free corrosion penetration fulfilling the customer's requirements.

In this work, the influence of the precursor type and the deposition parameters on the corrosion protection of aluminium using Electrochemical impedance spectroscopy and salt spray tests will be presented. A correlation between thin film composition using FTIR characterization and thickness evaluation obtained using SEM and Ellipsometry measurements will be discussed. Additionally, process control and industrial integration of the anticorrosion solution will also be highlighted.

Accelerated corrosion tests of AA1050 in contact with E27 biofuel

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Abstract

Recently, biofuels have gained global interest as a substitute for fossil fuels in transportation, aligning with international policies aimed at reducing greenhouse gas emissions and crude oil consumption. Among available biofuels, bioethanol stands out for its abundant resources, simple production processes, and compatibility with existing infrastructures. Its application in automotive fuels can serve either as an additive or as a substitute for gasoline, offering environmental benefits and reducing fossil fuel dependency. While flexible-fuel vehicles (FFVs) have been developed to accommodate bioethanol content up to 100% (E100), standard vehicles typically utilize bioethanol blends as additives, posing corrosion risks to lightweight aluminum alloy components. Limited empirical evidence exists on the corrosiveness of bioethanol blends, especially beyond 10% (E10), which can induce unpredictable non-linear corrosive effects on aluminum alloys, exacerbated by the high engine temperatures. This study investigates the corrosion characteristics and mechanisms of AA1050 aluminum alloy in contact with a mixture of gasoline with 27% bioethanol (E27). Experiments were conducted in an autoclave at 100 °C for three days, under oxygen exposure. Samples were then analysed using X-ray diffraction, scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS) to examine surface oxide formation. Corrosion studies were conducted by means of polarization curves, Open Circuit Voltage measurements and Electrochemical Impedance Spectroscopy (EIS). The corrosion rate was measured accordingly with the experimental conditions. Additionally, chemical analysis of E27 biofuel were performed before and after interaction with the alloy The actual corrosion of the alloy with oxide and alcoholate formation was observed. Analysis of the samples and fuel enabled tracing the causes of corrosive phenomena back to temperature and the presence of oxygen, which reacts with the water content of the biofuel.

Optimizing Electrochemical Sensing in Low-Conductivity Environments: Methodologies and Applications

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Addressing the unique challenges of electrochemical sensing in low-conductivity environments is vital, especially concerning applications in environmental monitoring. This extends to crucial assessment such as evaluating the material compatibility of various fuel vessels and analyzing the electrochemical behavior of coolants in fuel cells. Understanding these challenges is critical to, for example, ensuring proper thermoisolation within systems, particularly in the context of e-mobility.

However, the high resistivity intrinsic to low-conductivity electrolytes presents hurdles in electrochemical sensing. Constrained charge transfer kinetics hinder electron exchange at the electrode interface, contributing to voltage drop and thereby impeding accurate detection of electrochemical activities. The presence of contaminants, which could obscure the desired response by manifesting as shifts in voltage or current, along with other external interfering agents, e.g., temperature fluctuation, further complicate the measurements, necessitating tailored strategies to overcome these problems.

This work investigates methodologies tailored to optimize electrochemical sensing techniques specifically designed for low-conductivity electrolytes. The initial findings indicate a propensity for salt-based contaminants to leach into the electrolyte from the salt bridge, rendering the utilization of conventional reference electrodes like Ag/AgCl and standard calomel electrode impractical. To address this issue, the optimization process involves integrating a pseudo-reference electrode. The electrochemical stability of both silver and platinum rods were tested in various environment in temperature range of 30 °C to 60 °C for this purpose. Furthermore, factors contributing to measurement inconsistencies, such as surface area and precise electrodes placement, are expected to be significantly reduced. Through reviewing established methodologies, this study aims to elucidate the complexities involved in measurement within these environments. The potential for monitoring electrochemical behavior in low-conductivity settings, as well as their inherent limitations – which encompass challenges in measurement sensitivity and interpretation ambiguity – are highlighted.

INFLUENCE OF HYDROGEN ON FRACTURE RESISTANCE OF ADVANCED HIGH-STRENGTH STEELS

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Advanced High Strength Steels (AHSSs) play a key role in the automotive industry. These steels, characterized by very high strength, good global formability and high crash performance, have become the dominant materials of choice for the lightweight construction of structural and safety-related automobile components.

However, the implementation of such high-performance steels has brought new challenges related to their limited damage tolerance and higher cracking susceptibility compared to conventional mild steels. Furthermore, because of their high strength, AHSS may be susceptible to hydrogen embrittlement (HE) increasing the risk of delayed fractures after forming or catastrophic failure in a crash event. Therefore, evaluating the influence of hydrogen (H) on fracture properties is of primary importance to assess the HE susceptibility and predict potential fractures that can compromise formability and structural integrity.

In this work, the influence of H content on the fracture resistance of different AHSS is assessed by means of Hole Expansion Tests (HETs) and Essential Work of Fracture (EWF) tests with hydrogen-charged samples. HETs are well-established in the automotive industry to evaluate the stretch-flangeability and edge-cracking sensitivity of high-strength metal sheets. The Hole Expansion Ratio (HER) is an indicator of edge fracture resistance.

On the other hand, the EWF methodology allows the evaluation of the crack initiation and propagation resistance of thin metal sheets. In this work, a novel rapid testing tool for EWF sample preparation is presented. The results show that H concentration may have a detrimental effect on edge cracking resistance and fracture toughness even at concentrations of 0.5 ppm. The proposed novel testing methodology based on the EWF is shown to be a fast and simple tool to readily measure HE susceptibility. Since the method measures the propagation resistance of a well-defined and confined crack, the local effects of H in the material crack initiation and propagation resistance are effectively determined.

Progress in sol-gel coating: Optimizing formability and corrosion resistance for hot forming of galvanized medium manganese steels

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Safety-critical components in the automotive industry, such as B-pillars, presently rely on press-hardened manganese-boron steels like 22MnB5 or 20MnB8. While this method allows to produce robust components from cost-effective alloys, there are persistent manufacturing challenges that warrant attention. The hot stamping process, integral to this manufacturing, results in the formation of an oxide scale on the steel surface. This not only increases wear on the pressing tool but also necessitates the subsequent removal of the oxide scale.

In addressing these challenges, contemporary strategies often involve the application of Al-Si layers to mitigate steel oxidation. However, these layers bring their own set of issues, including adhesion to oven rollers and a lack of active corrosion protection. As an alternative, zinc coatings are considered for safeguarding the substrate against corrosion. However, adapting the press-hardening process becomes essential to prevent issues such as liquid metal embrittlement and the formation of brittle Zn-Fe phases.

The primary goal of this research is to significantly elevate the existing 5% market share of galvanized press-hardened steels and facilitate smaller companies access to this cutting-edge technology.

This presentation will outline the approach taken in developing a sol-gel based layer that enhances formability and provides active corrosion protection for medium manganese steels. Utilizing sol-gel chemistry and inorganic micropowders, SiO2-based layers are formed with low sintering temperatures. The dispersions are meticulously characterized through solid content determination via re-drying, measurement of particle size distribution using dynamic light scattering and assessment of viscosity. The coatings, applied through dip-coating, undergo thorough characterization through light microscopy and SEM, both on the substrate surface and in cross-sections. The evaluation of their performance, specifically in terms of corrosion protection, is a key focus of the study.

Graphene barrier coating industrialisation for Al/Cu foil used in Li-B Electrode

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Abstract:

Removal of 100 to 1,000 giga tonnes of CO_2 this century may be needed to achieve **deep decarbonization** and avoid exceeding the 1.5°C climate target. Carbon Nano materials and nanotechnology is playing a key role. CNT and Graphene has found its use in numerous industrial applications due to its unique properties. While its impermeable and conductive nature can replace currently used anticorrosive toxic pigments in coating systems, graphene can be an important component as a next-generation additive for many industrial applications (1). The current bottleneck in using conductive graphene is the availability of cost-effective, high-quality materials manufactured from graphite and their effective incorporation into the industrial product matrices.

On overcoming these factors, graphene may attract significant demands in terms of volume consumption. Graphene can be produced on industrial scales and cost-effective top-down routes such as high-pressure and shear mechanical exfoliation. Graphene depending on end applications can be chemically tuned and modified via functionalization so that easy incorporation into product matrices is possible. This talk discusses graphene with an average thickness below five layers, which were produced with almost no defects. Graphene additives with siloxane crosslinking chemistry play a key role in barrier layer on Li B Aluminium substrate in energy storage applications.

Keywords: Graphene application barrier coating, Few Layer Graphene, Graphene industrial scale up production, Graphite, Li-Ion Battery additives

Reference:

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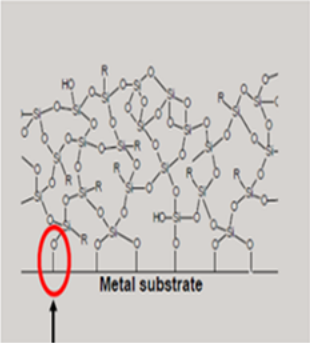

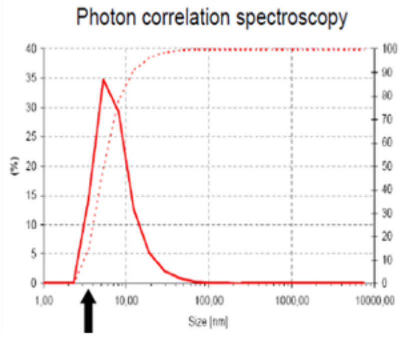

Key Benefits of Graphene/Siloxane system:

- Barrier for ingress of Li+ ion to Al foil and acid (H+)
- Hydrogen bonding with Aluminium metal surface of Silane
- Compatible Cathode or Anode coating subsequent layer
- Remove dendrite formation during lithiation and Di lithiation cycle.
- Excellent adhesion.

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Dr Sivasambu Bohm received his first degree in Chemical Engineering, followed by an MSc at Hahn Meitner Institute (Max Planck Institute) in Berlin. After gaining his PhD at the University of Bath in Chemistry, he worked at different academic institutions, University of Swansea, TU Delft, The University of Birmingham and India Institute of Technology, Bombay, University of Cambridge, and Imperial College London. Siva has 20 years of industrial experience (TATA, Talga, CAMI, VEMS, Ceylon Graphite and AM) in various research fields; metallurgy, protective coatings, energy storage in the automotive industry, nanotechnology, and applications of graphene. Dr. Bohm has published 40 patents and 98 scientific publications and implemented 12 commercial products globally. He is a Fellow of the Royal Society of Chemistry and a Fellow of Technical Surface Coatings. Dr. Bohm has been awarded the Royal Society Industry Fellowship initial at the University of Cambridge, Cambridge Graphene Centre from 2017 and continued fellowship at Imperial College London and Graphene Expert at AM Global R&G & AM Commercial UK Ltd, also Chief Scientific Officer of Ceylon Graphite Corp. Dr. Bohm. Zhejiang torch national talent award winner and Director of R&D in Zhejiang Hanano R&D till Aug 2024 and about to start Graphene industrialisation project in Europe and carbon materials global product implementation.

Smart active/barrier anti-corrosion coating system based on PEO and sol-gel process for AZ31B Mg alloy.

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Magnesium alloys have become promising materials for different applications due to their comparably light weight. The use of lightweight materials to replace structural parts in airplanes or cars would be a viable method to reduce the overall weight of vehicle bodies, the fuel consumption and thus the greenhouse gas emissions (GHE). Shifting to lightweight vehicles will help in the transition towards zero carbon emission which is a target included in the Sustainable Development Goals (SDG) 2030 of the EU. Nevertheless, the high chemical reactivity makes them highly susceptible to corrosion, limiting their widespread use.

Under this perspective, the aim of this work is to develop a smart self-healing protective system to provide a long-term protection to the Mg alloys. The integrated system was performed by a first deposition of an oxide layer using PEO technique followed by a post-sealing process using a glass-like Ce_xO_Y film and inorganic-organic hybrid SiO_2 coating. The PEO coating was obtained using a phosphate-carbonate based electrolyte. The glass-like Ce_xO_Y coating was developed using cerium acetate and the SiO_2 hybrid coating was obtained by hydrolysis and condensation reactions of tetraethoxysilane (TEOS), 3-(glycidyloxypropyl) trimethoxysilane (GPTMS). Electrochemical Impedance Spectroscopy (EIS) and scanning Kelvin probe microscopy (SKPFM) were performed to characterize the corrosion resistance performance of the coating. The EIS and the SKPFM characterization confirmed that the integrated multilayer coating not only provide long-term corrosion protection in a highly concentrated 3.5% wt. NaCl solution (more than 20 days) but is also capable of self-repairing defects due to the presence of cerium ions (Ce^{3+}/Ce^{4+}).

Keywords: AZ31B Mg alloy, PEO, sol-gel, self-healing, Glass-like Ce_xO_y coating.

Multifunctional Plasma Electrolytic Oxidation TiO_2 coatings on TiNbZrTa alloy for dental applications

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Abstract

Although in the last years, the use of titanium implants has become a common treatment, a considerable number of failures are still reported. Among other factors, failure of dental implants strongly depends on the implant/bone interfacial mechanical properties and on the biological events occurring at the interface, including the formation of microbial biofilms, fibrous tissue and/or the presence of wear debris or corrosion products. Micro-movements between the implant and the bone are unavoidable leading to formation of debris and release of metal ions, causing an adverse cellular response, which can result in implant loosening and pain. In the same way, during surgery, the implant is screwed into place at a precise torque and wear debris can be created. Consequently, the tribological properties of the surface of the implants are important. In this sense, although the titanium alloys are the most promising biomaterials due to their excellent biocompatibility and properties close to the bones, they have a poor tribological behaviour. To solve the most typical problems that lead to a failure of a dental implant, the development of TiO_2 coatings by means of Plasma Electrolytic Oxidation technology on a superelastic TiNbZrTa alloy has been studied. These coatings, due to their ceramic nature, present excellent wear and corrosion resistances. In order to provide not only tribological properties but also bioactive and biocide properties to the films, additional elements such as Ca, P, or Ag have been also fixed into the matrix of the layers to create multifunctional structures. The new coatings were characterized by means of tribological and tribocorrosion studies. Additionally, their microstructure, chemical composition and their biocide and cytotoxic effects were analysed by means of in vitro tests.

Keywords:

Plasma Electrolytic Oxidation, TiNbZrTa, Tribocorrosion, Antibacterial

Investigating the relevance of TiNbTaZr high entropy alloy for orthopaedic applications

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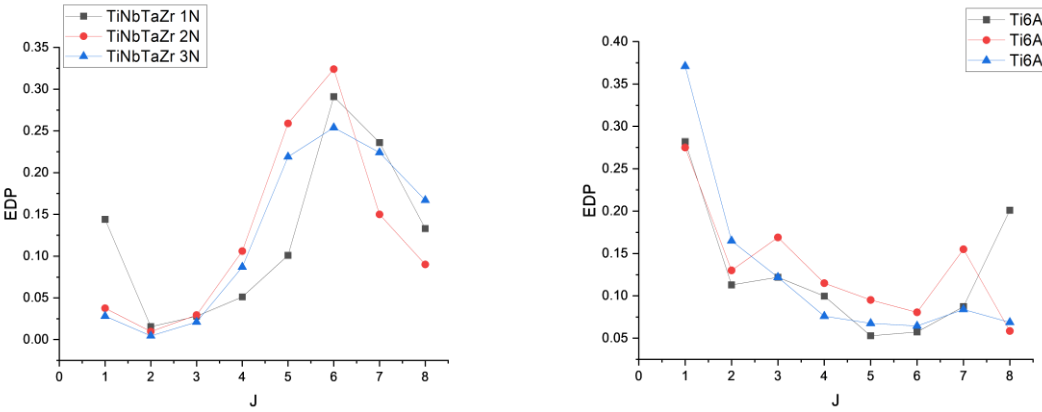
Abstract

The drawbacks of commonly used metallic biomaterials, like the release of toxic ions for the CoCrMo alloy and poor wear resistance for Ti-based alloys, make it necessary to find a better metallic material as a new candidate for orthopaedic applications. In this work, different characterisation techniques were employed to investigate the relevance of a recently suggested TiNbTaZr HEA for orthopaedic applications. TiNbTaZr exhibited excellent mechanical properties and outstanding electrochemical behaviour. However, no significant enhancement in tribocorrosion behaviour is observed of TiZrNbTa over Ti6Al4V alloy, but the two materials exhibit different in-situ repassivation behaviour during tribocorrosion testing. A new approach of using the electrochemical noise EN technique in tribocorrosion investigation and data analysis is suggested.



The above figure shows using the wavelet transform in the analysis of EN technique data to investigate the tribocorrosion degradation mechanism and detect the passivation behaviour. Ti6Al4V alloy showed the ability to repassivate in the course of tribocorrosion testing, while this did not happen with TiNbTaZr HEA.

Bioinspired Ti oxide nano-structures for antibacterial purposes. Wear and mechanical accommodation issues under tribochemical conditions.

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Bacterial infection is one of the most critical challenge of health systems, which can lead to prolonged pharmacological treatments, high cost to social care systems, as well as several health complications for patients, including death. In addition, the increasing antibiotics resistance creates a complex situation that needs to be addressed. From the materials science discipline, bioinspired surface structure is one of the most explored ways to obtain antibacterial or bactericidal properties. Nevertheless, the behavior of those nanostructures under tribochemical conditions, to which prostheses are subjected is unknown. Moreover, if those structures are broken during implantation surface or service, the effect of particles generated on wear and mechanical accommodation remains unclear.

In this work, nanospikes (NSP) structures of different length were obtained on Ti6Al4V through a thermochemical process of acetone pyrolysis followed by a high temperature oxidation. NSP samples undergo tribochemical test in 0.9% NaCl solution, under applied passive potential, as well as a normal load of 1.25N, sliding speed of 60mm/min and 3600 cycles. It was found that the length of the structures created play an important role in the material wear and COF evolution, which in turn has an impact on the tendency of the particles to remain or to be ejected from the contact, under the same mechanical and electrochemical action. In addition to characterizing the morphology and the amount of material lost in the wear tracks, measurements were made of how far into the surface the ejected particles can reach. Furthermore, nanospikes surfaces were characterized by SEM, DRX, TEM, FIB. Biological test, such as cellular and bacterial adhesion and proliferation were conducted, in which the impact of wear on the antibacterial properties of NSP was considered.

Tribocorrosion properties of DLC coating deposited by PACVD on ZK60 Mg alloy

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ABSTRACT

Magnesium alloys are presented as a great alternative for applications such as biomedical implants or automotive components to lightening weight. Their good mechanical properties combined with low density and biocompatibility are a great advantage over other materials such as stainless steel, titanium, or polymers. However, the high corrosion rate of magnesium in the presence of a corrosive medium has limited its application and has forced searching for solutions for ensure its applicability. Furthermore, relative contact with other components, such as bone in the case of implants, can lead to synergy between mechanical wear and corrosion, which would further accelerate the degradation of the Mg alloy. Different surface treatment and coating strategies have been studied in order to overcome this problem, but it is still necessary to find a coating that ensures good adhesion to the substrate and sufficient protection against corrosion. In this study, DLC coatings have been deposited into ZK60 magnesium alloy via Plasma Assisted Chemical Vapor Deposition (PACVD). This technique is designed to achieve a coating with a high adhesion to the substrate and free of defects that will prevent the corrosive solution from passing through to the substrate. Dry and wet tribology tests have been carried out to evaluate the wear and tribocorrosion resistance of the coatings. In addition, static corrosion has been analyzed by potentiodynamic polarization tests, and nanoindentation and scratch tests have been carried out to characterize the coating. The results have shown coatings with good adhesion to the substrate and capable of improving the tribocorrosion resistance of the substrates.

In vitro assessment of metal release in CoCrMo partial implants during sliding against articular cartilage

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Osteoarthritis is a chronic disease that results in pain and worsen the quality of life of patients. The only effective procedure during late-stage osteoarthritis is surgery, consisting in the replacement of damaged knee cartilage and bone by medical implants. There are two different options for knee replacement surgery: total or unicompartimental (UKR), with the latter focusing on the removal of the most affected bone regions and thus being much less invasive than the former. UKR is thus a less severe type of surgery, leading to faster rehabilitation, better function of the knee and higher quality of life for the patient. However, despite its obvious advantages UKR still represents less than 10% of total knee replacement surgeries, due to high revision surgery rates.

The aim of this work aims to assess and quantify metal release of CoCrMo specimens under reciprocating sliding motion against bovine osteochondral plugs using an *in vitro* test rig. The experiments are performed with controlled electrochemical conditions using a floating cell with a three-electrode set up coupled to a nanotribometer. Phosphate buffer saline is used as an electrolyte. Throughout the experiment, the coefficient of friction and the open circuit potential is monitored. Afterwards, the electrolyte is analyzed using Inductively Coupled Plasma Atomic Emission Spectroscopy and mass spectrometry in order to measure the amount of released Co ions and correlate it with the electrochemical measurements. Additionally, the structure of the molecules present on the cartilage surface after the experiment are unveiled using high resolution mass spectrometry. The results showed the occurrence of biotribocorrosion during sliding between a CoCrMo alloy and bovine articular cartilage. Co concentrations of up to 22 ppb were measured along with the presence of Co and compounds on the cartilage surface in form of organometallic complexes with amino acids.

Tribocorrosion of Stainless Steel 304 in Food Environments

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The manufacturing and processing of food using machines and processing units helps to make food production faster and easier. However, the continuous processing of food and the effect of friction/wear can lead to the combined mechanical and chemical material deterioration (tribocorrosion) of these processing units and machines. Tribocorrosion is the deterioration of a material resulting from the simultaneous action of wear and corrosion. Tribocorrosion can lead to the degradation of processing units and machines, and this can result in the release of metal ions and particles from the food contact material, such as stainless steel, into food. We studied the tribocorrosion of stainless steel 304 in the presence and absence of cassava using different analytical techniques such as optical microscopy, scanning electron microscopy, X-ray photoelectron spectroscopy (XPS) and confocal microscopy. Cassava, characterized by its tuberous roots, is a perennial woody shrub known for its high energy content, and it is packed with vitamins, minerals, and dietary fiber. It is the third most significant calorie source in the tropics with a reported production of approximately 303 million tons in 2020. This study revealed that cassava acted as a lubricant against mechanical friction, but it also hindered the repassivation process of the stainless steel 304 and ultimately caused corrosion of the stainless steel. The hindrance of the repassivation of the stainless steel was confirmed by an insufficient potential recovery in open circuit potential over time measurements before, during and after the sliding process. This increased corrosion tendency upon friction and chemical interactions with cassava also correlated with an increased fraction of chromium(III) hydroxide in the surface oxide, as confirmed by XPS. Further, XPS and metal release tests confirmed that cassava increased the content of chromium in the surface oxide and the metal release (through chemical processes) even without friction. The results of cassava will be compared with other protein-based foods (soy and pea proteins).

Enhancing Titanium's Tribocorrosion Performance through Innovative Surface Hardening

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Titanium and its alloys are prominent in medical, aerospace, sporting goods as well as in the wearables industry. Properties such as specific strength, corrosion resistance and biocompatibility are justifying its position as material of choice. However, titanium's low hardness, poor wear resistance, and its limited fatigue properties restrain its field of use especially when subjected to loaded sliding contact scenarios.

This study redresses the mentioned limitations by gaseous surface hardening at low temperatures, increasing the hardness of the surface as well as sub-surface layer of near net-shape machined parts, while retaining the metallic luster without severe grain growth, brittle layer formation, deformation, or changes in dimensional and topographical features. The hardened surfaces were characterized by means of microscopy and X-ray diffraction throughout the processing route. Mechanical properties of low temperature surface treated commercially pure titanium specimens were evaluated by hardness and ball on disc wear investigations. Corrosion and laboratory-scale tribocorrosion investigation of treated titanium showcased superior performance over untreated titanium and conventionally used CoCr.

The findings suggest that surface-modified titanium holds promising potential for applications within both dental implants and implants in various contexts, such as arthroplasty.

Influence of duration on the tribocorrosive lubricating behavior of stainless steels in an alkaline environment

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The aim of the presented research is to investigate the relationship between the concept of electrochemical lubrication and the duration of passive film formation mechanisms encountered during the cleaning process in the food industry. In pursuit of this objective,experimental tribocorrosion campaigns were carried out on stainless steel (316L/316L) in sodium hydrogen carbonate solution (pH=8.4) to study the influence of time on tribocorrosive behavior.

Wear traces resulting from these tribocorrosion experiments were examined using various microscopic and spectroscopic characterization techniques such as SEM, AFM, Raman spectroscopy, and ToF-SIMS. Electrochemical results, obtained by measuring the open circuit potential, align perfectly with tribological findings. The physico-chemical analysis revealed the morphology and chemical composition of the passive film formed on the surface. These results serve as a foundation to deepen the fundamental understanding of the electrochemical lubrication phenomenon in stainless steels exposed to a long-term basic environment. Tribocorrosion tests aim to replicate industrial cleaning conditions, with the goal of reducing energy consumption related to component friction and increasing the lifespan of equipment.

Elucidating the effect of surface films on the wear of steel in oil lubricated contacts through tribocorrosion concepts

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Tribocorrosion deals with tribological contact operating in chemical reactive environments. So far, tribocorrosion was mainly investigated in aqueous solutions as typically found in technological applications such as biomedical implants, marine equipment, mining. Aqueous environments also offer the possibility to use electrochemical techniques as powerful tool for the quantification of wear and corrosion as well the investigation of degradation mechanisms. For example, by comparing the tribological response under applied passive or non-passive electrode potentials it was possible to observe that surface films, despite their thinness, can significantly affect the strain accumulation in the metal surface and thus influence wear.

Formulated engine oils contain additives, such as ZDDP likes molecules, that, under friction, chemically react on worn metal surfaces to form protective boundary films. The responsible mechanism is generally attributed to the lowering of friction and thus the overall stress field by the soft boundary films. The subsurface strain accumulation induced by boundary films was however never investigated despite the relevant role of surface films observed in aqueous tribocorrosion.

This study was initiated with the aim to assess the influence of boundary films on the tribologically induced deformations of metals in oil lubricated contacts and their effect on wear. For this, the tribological behaviour of a carbon steel contact was studied in a commercial fully formulated engine oil with and without blending it with a specific commercial additive package. Surface analysis by AES and XPS revealed that the first oil led to the formation of an iron–zinc oxide surface film while the second to a calcium–carbon–oxygen rich film. The results show that, without influencing the coefficient of friction, the nature of the formed films significantly affect, similarly to passive films, the metallurgical transformations (characterized by SEM and FIB) occurring in the near surface region of the metal and the corresponding wear response. This shows that tribocorrosion concepts can be applied to other tribosystems such as oil lubricated contacts.

Corrosion and tribocorrosion performance of selected coatings sliding against internally epoxy coated pipes in CO_2 corrosive environments

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Materials and components used in the energy sector are often exposed to highly aggressive CO_2 anoxic environments in applications such as oil and gas, geothermal energy or carbon capture and utilization, among others. The aggressiveness of these environments in terms of corrosion is very high and results in fast material degradation and premature component failure. This holds particularly true for components such as pipelines and tubings that need to be made of carbon steel for the sake of cost-effectiveness. In order to mitigate their corrosion rates in some critical applications, there is a current trend in increasing the use of corrosion resistant epoxy internal coatings. The use of epoxy internal coatings effectively serves for mitigating not only corrosion but also wear since these epoxy coatings typically contain hard particle reinforcements. Their drawback is that their higher abrasivity results in excessive wear of components sliding against them, such as couplings used to connect sucker rods in the oil and gas industry.

The present work aims at evaluating the corrosion and tribocorrosion performance of wear and corrosion resistant coatings for sliding against epoxy internal coatings in CO_2 corrosive environment under anoxic conditions. The coatings are selected in order to cover a wide range of relevant technologies, such as chemical vapor deposition, electroless plating and thermal spraying. The coatings are evaluated using model tribocorrosion experiments under controlled electrochemical conditions and also using close-to-reality component tests, both in 3 wt.% NaCl brine under 3 bar CO_2 pressure. The results reveal that the use of epoxy internal coatings requires a careful selection of a suitable coatings in order to have a contact pair that operates successfully under combined sliding and CO_2 corrosion conditions in order to prevent excessive wear and premature coatings failure.

Innovative Way to control Inhibitor Release from Corrosion Protection Films

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Volatile corrosion inhibitors are incorporated into PE films. The effectiveness of these VCI films depends primarily on the physico-chemical properties of the inhibitors and their concentration in the film. The rate of release of polar inhibitors from the non-polar PE matrix is in many cases temperature dependent. An anticorrosive atmosphere builds up in the packaging volume, which must be maintained by the VCI depot of the VCI film over the limited application period.

EXCOR introduces ICB (Intelligent Corrosion Blocker) to extend the active phase of the corrosion protection film: non-volatile precursors are converted into volatile inhibitors in an upstream reaction with air humidity.

In a statistical test approach (DOE 2^2 with the factors of temperature and relative humidity), ICB films were artificially aged for a period of 7 days. The concentrations of the remaining inhibitors were measured at fixed times.

The inhibitors were released in two steps. In the first stage, after one day of ageing, volatile inhibitors already formed by water in the film were released from the matrix at a temperature-dependent rate. This step is comparable to the release of inhibitors from VCI films.

In the second stage, non-volatile precursors reacted with humidity to form additional volatile inhibitors. As expected, increasing both temperature and relative humidity increased the release rate. The main effect of temperature on the release rate was 1.3 times higher than the main effect of humidity. In the experiment, temperature and humidity showed a significant interaction: at low temperatures, the effect of humidity on the release rate was twice as high as at higher temperatures, i.e. the effect of relative humidity decreases with increasing temperature.

The new ICB film couples the release of volatile inhibitors more strongly to environmental conditions via humidity. More humid and therefore more corrosive conditions during transport or storage deliberately increase the release rate of volatile inhibitors; conversely, release decreases in drier and cooler conditions, protecting the film's active ingredient depot.

Study of Physical Aging of Polyvinyl Chloride (PVC)

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Abstract. The insulating properties of the polymers are widely used in electrical engineering for the production of insulators and various supports, as well as for the insulation of electric cables for medium and high voltage, etc. These polymeric materials have significant advantages both technically and economically. However, although the insulation with polymeric materials has advantages, there are also certain disadvantages such as the influence of the heat which can have a detrimental effect on these materials.

Polyvinyl chloride (PVC) is one of the polymers used in a plasticized state in the cable insulation to medium and high voltage.

The consequences of increasing the temperature of a polymer are modifications; some of them are reversible and others irreversible. The reversible changes do not affect the chemical composition of the polymer, or its structure. They are characterized by transitions and relaxations. The glass transition temperature is an important feature of a polymer. Physical aging of PVC is to maintain the material for a longer or shorter time to its glass transition temperature. The aim of this paper is to study this phenomenon by the method of thermally stimulated depolarization currents. Relaxations within the polymer have been recorded in the form of current peaks. We have found that the intensity decreases for more residence time in the polymer along its glass transition temperature. Furthermore, it is inferred from this work that the phenomenon of physical aging can have important consequences on the properties of the polymer. It leads to a more compact rearrangement of the material and a reconstruction or reinforcement of structural connections.

SolRec2: Innovative digital watermarks and green solvents for the recovery and recycling of multi-layer materials

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Abstract

Figures for plastic waste which end up in landfill are alarming - globally, only 9% of plastic waste is recycled while 22% is mismanaged [1]. It is time for a paradigm shift in our approach to packaging waste, and recycling flexible, multi-material packaging systems is a key part of the solution. Sol-Rec^2 project funded by the EU is looking at developing ‘Green solvents’ to enable multi-material recycling of blister packs and laminate food packaging. The purpose of the experimental work was to evaluate non-toxic, stable, deep eutectic solvents (DES) and ionic liquids (ILs) for the separation and recovery of polymer-aluminium laminates. The findings revealed that some DESs and ILs were successful in delaminating effectively the constituent films, resulting in good separation and excellent recovery of the polymer and aluminium layers. Reactor trials with different conditions aim to build a DoE model for the process at lab-scale and in a scaled-up procedure. Finally, experimental results reveal the impact of DESs and ILs on the corrosion performance of aluminium.

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[1] OECD Global Plastics Outlook Database

Acknowledgements

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Materials in contact with drinking water – A review

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Corrosion of metallic materials in contact with drinking water can cause failures of distribution pipes or other components (water loss, water damage, blockage of valves etc.). But on the other hand it is also possible that the metallic materials leach metal ions into the water which can result in hygienic problems when limit values (drinking water directive, technical guidelines, WHO recommendations etc.) are exceeded. In this case it can be seen as a corrosion damage of the water itself. This paper is intended to maintain awareness of this kind of corrosion damage by giving a review of the various material-water-interactions as well as the development and advancement of regulations and guidelines regarding this topic.

The coupling mechanism of shrinkage defects and graphite on the corrosion resistance of ductile iron

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Abstract: Cast iron has historically upheld a steadfast reputation as a preferred material due to its advantageous blend of ubiquity, material properties, cost-effectiveness, and recyclability. Shrinkage defects, a common issue in ductile cast iron components, are challenging to eliminate due to the intricate design of parts and process fluctuations. Despite these prior investigations, the specific role of shrinkage defects in influencing the corrosion resistance of ductile iron and the mechanisms underlying corrosion initiation have remained elusive.

This study investigated the coupling mechanism of shrinkage defects and graphite on the corrosion resistance of ductile iron by electrochemical measurements, quasi-in-situ immersion tests and numerical simulations. The detrimental impact of shrinkage defects was confirmed by elevated corrosion current density and the formation of a porous corrosion product layer. Multiple-galvanic coupling effect among the matrix, graphite, and shrinkage defects serves as corrosion triggers, which is verified by scanning Kelvin probe force microscopy (SKPFM) and numerical simulations. Additionally, quasi-in-situ observations corroborate the deposition of corrosion products and Cl enrichment at defect bottoms, expediting occluded cell formation and corrosion propagation.

The presence of shrinkage defects elevates the corrosion current density in NaCl solution, consequently diminishing the corrosion resistance of ductile iron. Notably, the presence of defects leads to the formation of loose and incomplete corrosion products, while also fostering the enrichment of corrosive ions, such as Cl^-, within the defects. Early-stage corrosion of sample with shrinkage defect manifests that the corrosion around the defect is more serious than that of the matrix. In addition, the results of SKPFM and numerical simulation suggest that the order of potential is graphite > matrix > shrinkage defects, indicating that corrosion initiation is triggered by shrinkage defects due to the multiple-galvanic coupling effect. Quasi-in-situ observation provided evidence of corrosion product deposition on defect surfaces, along with Cl element enrichment at the bottom of defects, consistent with numerical simulation results. The formation of occluded cells and an acidification autocatalytic effect emerged as the primary factors contributing to the propagation and exacerbation of corrosion due to shrinkage defects in ductile iron.

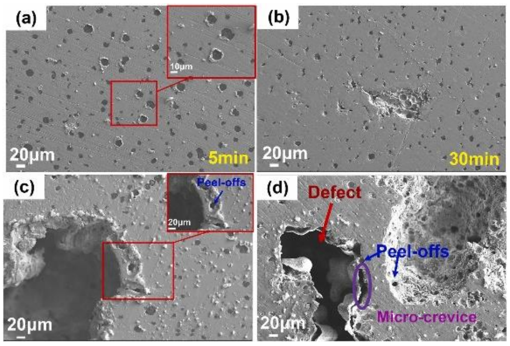

Fig.1 Corrosion morphology of ductile iron after immersion in 3.5 wt% NaCl for different time

Influence of styrene-butadiene rubber on adhesion, abrasion resistance and corrosion properties of polymer-modified cementitious coatings

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Abstract

Many studies report the influence of latex addition in cementitious systems (mainly mortar or concrete), but few concern their effect on the properties of cement paste coatings on ferrous substrates. Such cementitious coatings have been used to protect the inner walls of tanks (sand filters, contact towers, hot water tanks, etc.) against corrosion. The water/cement ratio has been adjusted to ensure that each formulation has the same consistency for easy application. The curing conditions (dry, wet or a combination of dry and wet conditions) and the styrene-butadiene copolymer content (varying between 0 and 10 phr) have a strong impact on the coating's adhesion, mechanical properties, and electrochemical behavior in a 3.5% NaCl environment. The addition of copolymer greatly improves adhesion properties in both wet and dry cure, as well as abrasion resistance and damping properties. These results were analyzed in relation to the impact of the copolymer on the morphology, crystallographic composition, and degree of porosity of the coatings, determined respectively by SEM observations, XRD and TGA analyses and density measurements.

Pipe interior rehabilitation of drinking water pipes with a glass-like coating

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Water pipe damage is by far the biggest risk in the context of residential building insurance. In 2008, around 1,040,000 claims occurred, which corresponds to 45% of all reported claims in residential building insurance. The costs per claim have been rising for years, so that a total claim amount of € 1.710 billion had to be paid in 2008. The proportion of damage caused by corrosion is well over 50%. The causes of corrosion are manifold, but it is certain that in the case of damage caused by corrosion, a breakthrough usually occurs first at one point, but the damage to the rest of the pipeline is also well advanced and is about to break through. This means that the pipeline must either be replaced or the inside of the pipe must be protected.

As part of a research project, a process with a new coating based on organic silicon compounds was developed. The results will be presented.

The corrosion resistance was determined by electrochemical tests, e.g. with the aid of impedance spectroscopy, aging tests and adhesion tests. The whole process of rehabilitation of the pipe will be regarded. The cleaning of the surface before coating was intensively investigated and optimized. The application of the coating inside the pipes was examined and illustrated

The tests were carried out on pipes made of galvanized steel and copper. In summary, it can be stated that the corrosion protection of the coating on galvanized pipes is inadequate, but copper pipes can be excellently protected.

Development of the new APM 316A stainless steel grade: Investigation of its corrosion resistance for water applications

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Thanks to their good corrosion resistance, ease to shape and weld, austenitic stainless steel grades are standard materials generally used in the different water compositions encountered in numerous water applications. In drinking water networks, corrosiveness of the fluids is mainly influenced by the concentration of halides (more specifically chlorides), low pH, temperature and their combination. In most of the cases, the chloride concentration doesn't present major issues for 304L grade. However, in certain conditions, chloride concentration exceeds the 304L tolerance and a superior alloy such as 316L is needed.

Considering the economic and ecological costs due to the Ni and the Mo contents, a new and cheaper grade APM 316A has been developed to reach not only close mechanical behavior to 316L but also a similar corrosion resistance in all media and temperature.

The present study deals with the localized and the general corrosion resistance of the APM 316A austenitic grade compared with the most commonly used austenitic stainless steels 304L and 316L. Corrosion behavior was assessed using electrochemical methods: pitting potential was determined at different chloride contents at 23 and 50°C; polarization curves were also performed in different acidic solutions in order to assess uniform corrosion.

Effect of Intermetallic Phases on Cast Stainless Steel Corrosion in Drinking Water

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Traditionally, water supply components have been made of brass; however, corrosion failures have become more prevalently reported in water distribution systems. Flowmeters, measuring water flow through an ultrasonic principle, find application in various places within water distribution. The durability of these flowmeters could be improved by applying an alternative flowmeter body material. In this regard, stainless steel is expected to have superior corrosion and erosion resistance compared to brass. These stainless steel flowmeters are commonly produced by casting due to their intricate geometry. Therefore, it becomes important to understand how the casting process impacts microstructure and corrosion resistance.

This research combines corrosion investigations with metallurgical characterization to pinpoint important casting parameters impacting the final surface appearance and corrosion properties of flowmeters. The flow induced corrosion resistance of brass and stainless steel flowmeters was compared in aggressive drinking water in a flow loop setup. Thermodynamic calculations were used to simulate the precipitation of different phases at various temperatures. Based on this input, heat treatments were selected at 700 °C and 800 °C temperatures to induce intermetallic precipitates, such as sigma phase, and carbides.

Immersion pitting corrosion tests and electrochemical tests were carried out to characterize pitting initiation and progression and to understand the effect of intermetallic phases on the corrosion behavior and stainless steel passivation layer. After corrosion tests, scanning electron microscopy revealed that localized corrosion, starting as pitting, is more severe in areas where intermetallic phases are present, particularly around the ferrite grains where the attacks initiate.

Corrosion behavior of different brass grades in different EU drinking waters

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Abstract.

Brass alloys are common materials in installations for drinking water, mainly for domestic use (taps, valves, couplings etc) but also in the water distribution network (water meters, valves etc). Following stricter EU regulations related to the quality of drinking water, manufacturers of brass are facing business sustainability challenges related to the presence of lead in their products. The brass industry is currently adapting the industry to meet the stricter requirements on lead release from the material to the drinking water. At the same time, corrosion performance of leaded and lead-free brass grades remains not fully explored and conclusive in the context of different EU drinking water qualities. Scientifically, the mechanism and factors of lead release in drinking water needs further investigation. In the present work, different brass grades were subject to corrosion study in water testing rig using two representative EU drinking waters with different corrosivity levels. A combination of electrochemical, water analysis and microscopic characterization methods was adopted to explore mechanistic aspects. Initial results support a lead release following oxidation of surrounding matrix and exclude its oxidation. The contribution of this element as an additional cathodic site is confirmed. The different brass grades were ranked in terms of both general and localized corrosion performance. The impact of the obtained results on the long-term behavior is discussed.

Dezincification of brass couplings in potable water

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Abstract:

Brass couplings are widely used in the plumbing industry due to their durability and corrosion resistance, which is greatly influenced by its chemical composition. Copper-zinc alloys containing more than 15% zinc are generally susceptible to dezincification. Dezincification selectively removes zinc from the alloy, leaving behind a porous, copper-rich structure that has reduced mechanical strength. It can occur as a uniform or localized process. In this paper, the case study on the cause of brass couplings damage in the water silo was conducted. Microstructural analysis revealed that couplings are damaged due to selective corrosion, type uniform-layer dezincification. SEM/EDX cross-section analysis of the brass coupling confirmed selective leaching in the form of dezincification.

Key words: brass, selective corrosion, dezincification, testing

Titanium Dioxide-Coated Glass Beads: Photocatalytic Degradation and Corrosion Behavior in Drinking Water with Disinfection Byproducts

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Titanium dioxide (TiO_2) stands out in the realm of photocatalytic bead development for its exceptional efficiency and stability across diverse pH levels. These beads, crafted by enveloping substrates such as glass, silica, or alumina with delicate TiO_2 films, exhibit remarkable prowess in decomposing organic pollutants under UV irradiation. Apart from its renowned hardness and wear resistance, TiO_2 assertions superior corrosion resistance. This attribute renders components coated with TiO_2 resilient against corrosion in saline and mildly acidic environments. Nevertheless, comprehensive studies probing into the corrosion dynamics and the formation of calcareous deposits on TiO_2-coated beads due to interactions with natural organic matter (NOM), as well as calcium (Ca) and magnesium (Mg) salts prevalent in drinking water, and their correlation with photocatalytic degradation, are notably sparse.

The primary objective of this research is to fabricate TiO_2-coated glass beads and analyze their photocatalytic degradation and corrosion behavior in drinking water containing disinfection byproducts (DBP). This endeavor aims to elucidate the impact of synthesis and post-treatment conditions on three key aspects: (i) photocatalytic activity, (ii) corrosion behavior amidst calcareous deposit formation on TiO_2-coated glass beads, and (iii) controlling corrosion through local pH engineering. Additionally, the study will look into optimizing TiO_2-coated glass bead morphology and composition for effective DBP removal.

Funded by the European Union, under the Grant Agreement GA101081953 attributed to the project H2OforAll—Innovative Integrated Tools and Technologies to Protect and Treat Drinking Water from Disinfection Byproducts (DBPs). Views and opinions expressed are, however, those of the author(s) only and do not necessarily reflect those of the European Union. Neither the European Union nor the granting authority can be held responsible for them.

ENDURE – Sustainable preservation of underwater wreck sites

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UNESCO estimates that there are over 3 million shipwrecks on the world's ocean floor including both wooden and metal wrecks. These wrecks are a particularly challenging heritage asset as they are hidden from view and difficult to access and assess. Although many wrecks over 100 years old are formally protected by the UNESCO Convention for the Protection of Underwater Cultural Heritage, this and other treaties do not take into account the efficacy and long-term sustainability of their central tenet of 'in situ preservation' (preserving sites where they lie). More modern wrecks from World Wars I and II are of increasing concern due to the risks of pollution from fuel oil and ammunitions, causing a dilemma for preservation of this heritage as well as protecting the natural environment.

The key aims of the EU-funded ENDURE project (2022-2027) are fourfold: 1) to detect, visualize and interpret accumulated decay of shipwrecks based on remote sensing techniques, where the results are subsequently correlated to environmental conditions and anthropogenic impact at the shipwreck sites. 2) to determine key natural processes and rates of decay of materials in the shipwrecks, using state-of-the-art metagenomics to map the diversity of degrading microorganisms in combination with respirometry studies of the microorganism's metabolism. 3) to identify and rank simultaneous decay processes, combining different types of chemical, physical and anthropogenic processes. 4) to propose novel intervention methods to mitigate threats to the shipwrecks, including both physical protection and corrosion protection. Further details are available on www.endureerc.com

ENDURE's work will benefit stakeholders, conservators and ultimately future generations by helping to preserve our common heritage. Furthermore, shipwrecks are excellent examples for studying long-term corrosion in the marine environment.

Corrosion, damage and value in archaeological iron

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Of all archaeological metals, iron presents the most challenging ongoing corrosion and interpretation problems post-excavation. During burial, it is disfigured by corrosion that takes various compositional and physical forms and which retains varying degrees of information about object shape and surface detail. Post excavation corrosion mechanisms and the characterisation of corrosion profiles have been investigated by French and British researchers. This has identified how corrosion layers form and the role of chloride in this process and in post excavation corrosion, as well as the impact of environmental humidity on corrosion rates. The resulting physical damage and its impact on heritage value has received less attention but is important when assessing the value of an object to the archaeological record and for planning management regimes for large archaeological archives and for museum displays.

The work reported links data from a large study of the corrosion rates of archaeological iron nails (Watkinson et al. 2019) to the resulting physical damage produced in objects. This is carried out by semi-quantitative and qualitative assessment of the corrosion-related damage sustained by the nails during the study period. Extent of damage is linked to the fixed environmental humidity during the corrosion processes, the chloride content of a nail, the corrosion rate of individual nails (measured quantitatively using oxygen consumption), and the nature of the corrosion product layers. The resulting data provided information on how corrosion rates influence damage according to the type of corrosion product layer present on an object. This is discussed relative to its meaning for the value of objects as an archaeological record, the management of archaeological iron collections and definitions of corrosion for the heritage sector.

Watkinson D. E., Rimmer M. B. and Emmerson N. J. (2019) The Influence of Relative Humidity and Intrinsic Chloride on Post-excavation Corrosion Rates of Archaeological Wrought Iron. Studies in Conservation, 64; 8, 456–471. https://doi.org/10.1080/00393630.2018.1565006

Conservation of an underwater vehicle "Delfin II". Interdisciplinary and collaborative approach as a key element of successful projects.

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Objectives

The aim of this work was to perform conservation of an underwater vehicle named "Delfin II" by conservators and technical staff of the National Maritime Museum in Gdansk. An approach involving particular stages of a surface preparation and a coating system's application specific was applied in the museum's environment. A reason for that was decision of exhibiting the object after completion of the project in front of one of the branches located by the Baltic sea. Thus it was required to provide the appropriate protection in demanding conditions.

Results

The first stage was to remove minor components from the interior of the vehicle, including portholes, entrance and emergency hatches and a seat. The ballast fins, in the form of skids, attached to both sides of the vehicle were in poor condition, hence it was decided to replace them. Once cleaning of the vehicle's interior had been completed, the next step was to remove the old paint from the exterior. The welds were then repaired followed by reinstallation of all the smaller components. The final stage was accomplished through the application of a coating system providing protection for years to come.

Conclusions

Restoration of the underwater vehicle was carried out in close cooperation with coatings inspectors, external consultants from the Gdansk University of Technology and Jotun Polska Sp. z o. o. In many cases, budget of museums planned for objects' conservation is limited. Thanks to involvement of various institutions and individuals, conservators were able to complete the project and apply some aspects of cleaning and the coating system's protection from industry to museum needs.

A multi-analytical characterisation of a collection of Chinese bronzes

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4) Museum of Oriental Art, Torino, Italy

This study deals with the investigation of a selection of Chinese votive bronze sculptures belonging to the collection of the Museum of Civilisation (Museo delle Civiltà, Rome, Italy). In details, the analyses have been taken on ten small statues, six of which are gilded and four of them are coated by brown and green surface layers. A multi-analytical diagnostic campaign has been carried out with the final aim of collecting information on the conservation state and manufacturing techniques of the ancient artefacts. The elemental composition of the sculptures was investigated by means of X-ray fluorescence (XRF), both to detect the alloy composition and obtain information on the gilding technique. Moreover, Raman spectroscopy was employed to analyse the corrosion products. XRF analyses allowed detecting the presence of different Cu-based alloys used for manufacturing different parts of the sculptures. Mercury was also identified on the surface of the gilded artefacts, suggesting the application of an amalgam of mercury and gold to the bronze surface. Raman spectroscopy allowed identifying several corrosion products on the sculptures surface, mainly copper oxides (CuO and CuO_2), with small amounts of copper chlorides and hydroxychlorides, and nitrates, highlighting however a good conservation state. Moreover, photogrammetry and multispectral imaging were employed for an accurate reconstruction of integrated 3D digital models of the Chinese sculptures. Integrating data from different spectral bands (VIS/UV/IR) and data collected by the diagnostic techniques (XRF, RAMAN) opens up new perspectives in the study and documentation of the artefact conservation state, allowing information to be combined in a three-dimensional object of more immediate consultation.

Toward prediction of corrosion protection by data-driven modelling

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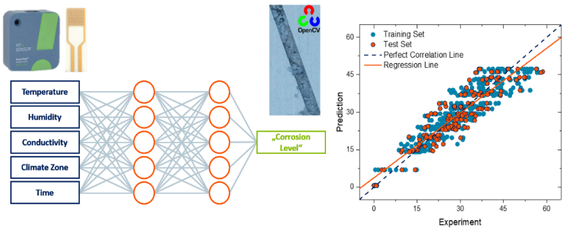
Current philosophy of Aircraft maintenance in relation to corrosion occurrences claims that all damages have to be immediately repaired once observed. Therefore, the necessary unanticipated and unscheduled maintenance actions lead to unexpected down time, leading to high costs and time loss.

The development of reliable prediction methods and approaches is an essential part of the future Condition Based Maintenance (CBM) concept. They would deliver the information about onset and propagation of corrosion and, thereby, fill the gaps between corrosion detection or monitoring and estimation of its structural impact.

During a collaboration between AIRBUS CRT and Helmholtz-Zentrum Hereon, a data-driven machine learning (ML) approach was successfully employed to predict corrosion of 2024 TSA samples by its correlation with environmental conditions at the lab scale. Different climate zones inside a corrosion chamber have been implemented to increase the volume of data and corrosion sensors have been customised to log the environmental factors which are subsequently used as input features for the development of a predictive model. The model was trained on the corrosion progression in the exposed specimen which was quantified by computer vision-based image analysis and employed to predict the corrosion progression in samples that have not been used for training of the model.

The transfer of this approach to in-service environments is a promising option as well as a big challenge to predict the corrosion behaviour of aerostructures.



Correlation of the corrosion onset with the environmental conditions based on an AI approach.

Insights on the application of tannic acid as corrosion inhibitor for corrosion protection of aluminum alloy 2024-T3

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The search for active corrosion protection coatings based on eco-friendly corrosion inhibitors to replace Cr(VI)-derived technologies has been under consideration over the last decades.

Across the innumerous species found in literature, one may highlight bio-based, relatively small compounds such as amino acids and vitamins. More recently, studies have started to focus on the use of larger molecules with antioxidant properties such as polyphenols. In the case of AA2024 alloy, an alloy used in the aerospace industry, the available literature is quite scarce, since only a few tannin-derived molecules have been studied as additives in anodizing baths and on polymeric coatings. Although some level of improvement with respect to corrosion protection of the underlying substrate has been reported, the fundamentals of the inhibiting action are still missing.

Therefore, the present work aims to study the corrosion inhibiting performance and corrosion mechanism of tannic acid on AA2024, in a stepwise manner, first as a corrosion inhibitor directly available in solution, then as an additive to different types of organic coatings.

Automated Management of AA2024 Electrochemical Data: An Algorithm for Polarization Curve Analysis and Prediction

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The advance of data science has instigated a paradigm shift in corrosion science, leading to innovative approaches in accelerated coating development and predictive maintenance. This transformation emphasizes the need for efficient and robust data (pre-)processing and utilization, especially in comprehending the corrosion behaviour of materials. In this study, our primary focus is on tackling challenges associated with the electrochemical corrosion behaviour, specifically emphasizing AA2024 - an aluminium alloy widely used in the aerospace industry for its commendable damage tolerance and high specific strength [1].

However, persistent inconsistencies in the literature regarding the designation of characteristic descriptors for AA2024, mainly derived from polarization curves related to steel, hinder a comprehensive analysis [2]. To bridge this gap, we introduce the **Al**uminium **P**ol**a**rization **C**urve **A**nalyser (ALPACA), an algorithm designed to automatically extract key features from polarisation curves experimentally recorded, for instance, at scan rates of 1, 10 and 20mV/s in varying sodium chloride solutions. ALPACA ensures a consistent analysis specific to AA2024, considering different heat treatment states, and thus lays the groundwork for a robust foundation in machine learning (ML) applications. In synergy with a ML script utilizing either a random forest or the XGBoost algorithm, ALPACA facilitates the consistent extraction and prediction of polarization curve descriptors across varying scan rates. To illustrate the methodology's efficacy, we showcase its application by predicting characteristic polarisation curve parameters of experimental AA2024 polarisation curves recorded at a scan rate of 5 mV/s, demonstrating the potential of ML for corrosion science.

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[2] DIN EN ISO 17475:2008-07, 2008.

Evaluation of Degradation and Protective Mechanisms of Post-Service Chromate-based Structural Aerospace Coatings

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Substituting chromates in structural coating systems within the aerospace industry with environmentally friendly alternatives remains a persistent challenge. A major hindrance to this transition is the absence of a standardized methodology that facilitates a comprehensive performance comparison between chromate-containing coatings and their proposed alternatives. To address this critical gap, the present study is focused on identifying key degradation factors that are essential for such a methodology. In this study, pivotal degradation factors are scrutinized for intact coated structural aluminium alloy aircraft parts that have been in service for over 35 years. This approach deviates from a conventional research methodology, wherein the predominant focus typically revolves around the corrosion inhibition of defects in newly applied active inhibiting coating systems.

This investigation employs advanced electrochemical, microscopic and spectroscopic techniques to analyse the degradation of coating systems, including Electrochemical Impedance Spectroscopy (EIS), Scanning Electron Microscopy - Energy Dispersive X-ray (SEM-EDX) analysis, and Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR). The results indicate a significant impact of coating constitution and thermo-oxidation on the ageing process of these structural coatings.

Concurrently, this study explores the protective mechanisms provided by macroscopically-intact chromate-containing coating systems. The detection of aluminium within the coating indicates the formation of aluminium hydroxides inside the transport pathways. This aluminium hydroxide shows to form a chromate-adsorbing gel. This process results in a reduced electrolyte mobility effect, contributing to an increased pore resistance, ultimately resulting in a coating with higher resilience and increased performance.

Stress corrosion cracking and hydrogen embrittlement of very high strength maraging stainless steels. TRIP effect of reverted austenite

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In aeronautic, stress corrosion cracking (SCC) and hydrogen embrittlement (HE) can lead to in-use properties degradation of maraging stainless steels in service. These martensitic steels, hardened through an aging heat treatment, exhibit high mechanical strength and a complex microstructure (i.e. martensitic matrix, residual and reverted austenite, hardening precipitates). The objective of this study is to investigate the role of those microstructural elements on SCC and HE mechanisms.

To address this challenge, the Transformation-Induced Plasticity (TRIP) effect of reverted austenite is studied on different maraging stainless steels. A small amount of reverted austenite is formed during aging, especially as films located at interfaces (lath/block/packet boundaries and prior austenite grain boundaries). Reverted austenite initially improves toughness resistance, particularly in environments prone to SCC and HE phenomena. Indeed, it is believed to serve as a hydrogen trap, limiting the flux of hydrogen to sites susceptible to embrittlement, such as crack tips. However, reverted austenite is suspected to be unstable under mechanical deformation. During the transformation into fresh martensite, it releases accumulated hydrogen into the matrix of the maraging stainless steel. Consequently, the matrix becomes locally oversaturated with hydrogen, leading to increased material embrittlement.

In this work, several maraging stainless steels with different compositions were studied. To better understand the properties of this reverted austenite and improve our comprehension of its stability across the studied grades, detailed analyses have been conducted. Observations using TEM (Transmission Electron Microscopy) were performed, examining spatial distribution and morphology. Austenite composition was determined from thermodynamic calculations. The TRIP effect was investigated through X-ray diffraction (XRD) analyses of tensile samples after deformation. Finally, the sensitivity to the TRIP effect is correlated to the austenite composition. The impact of TRIP effect on prior austenite grain boundary fracture under hydrogen is discussed.

Corrosion hot-spots of a metal-based combat aircraft and the impact of Airforce Sites

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A multi-role combat aircraft generates a database during its operational life through regular maintenance. For example, any damage or corrosion that occurs is recorded in such a database in the form of error messages. These data allow a statistical analysis of the parts most susceptible to corrosion and grants insights on the environmental impact at the different stationing locations. Furthermore, the analysis allows the identification of corrosion hot spots with relation to critical material pairings and surface protection systems. The gained knowledge shall be used to modify common cyclic corrosion tests to more accurately simulate the operational stress specifically in combat aircraft.

A salt spray corrosion detection based on acoustic emission tested on witness coupons representing damaged AA 2024 painted panels

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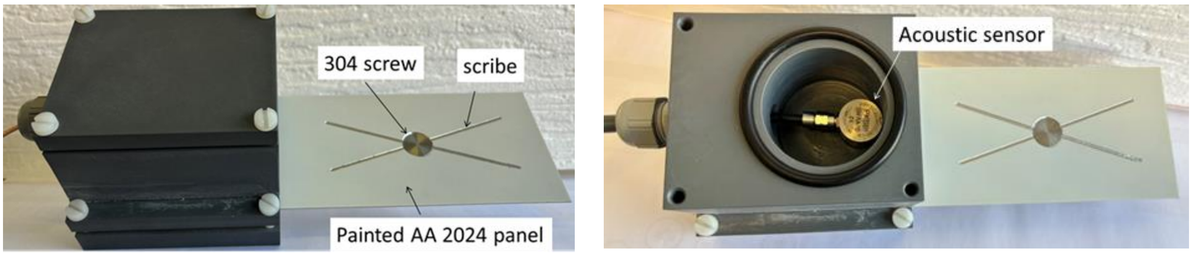
There is always a debate on the correlation between accelerated tests (i.e., salt spray, field exposure) and the behavior of aircraft structures in service conditions. But this debate is not enough based on the comparison of a common approach of the sensing of corrosion processes whatever the exposure framework (laboratory cabinet, outdoor rack, aircraft structure).

The aim of the presented work was to demonstrate that a non-destructive sensing technique, acoustic emission, could be used to monitor in real time the corrosion steps on witness coupons mimicking riveted aircraft panels, during chloride salt spray exposure after calibration in full immersion conditions.



(a) (b)

Figure 1- *Corrosion sensing on AA 2024 panel (255x75x4 mm). (a) top view of the “galvanic” coupon consisting of an active X-scribe (100x2x0.15 mm) coupled to a more noble head of 304 screw; (b) the acoustic sensor is located inside a sealed box to avoid any damage during spray exposure.*

Acknowledgments: this work was supported by EU H2020 Grant agreement ID: 864905 (Early detection and progress monitoring and prediction of corrosion in aeronautic Al alloys through calibrated Ultrasonic-CorROSion Sensor application)

Investigation of hydrogen trapping in model aluminium alloys by thermal desorption analysis and positron annihilation spectroscopy

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***Tomáš Prošek**[1], **Pavel Novák**[1], **Jakub Čížek**[2], **František Lukáč**[2], **Ivan Procházka**[2],*

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2) Charles University, Czech Republic

Aluminium alloys play a vital role in the automotive and aerospace industries. Aluminium on its own is a soft and lightweight material, unsuitable for these demanding applications, but the addition of other metals as alloying elements, followed by a precipitation hardening process, yields alloys with excellent mechanical properties and low weight. However, high-strength aluminium alloys may be susceptible to hydrogen embrittlement. Cracks typically initiate in corrosion pits that form due to galvanic coupling between anodic or cathodic precipitates and the matrix. Localized corrosion is then accompanied by the generation of hydrogen, which is absorbed into the material. This can cause hydrogen embrittlement, promoting crack initiation and growth.

Intermetallic particles in aluminium alloys enhance the material's strength and act as effective hydrogen traps with high binding energy. Therefore, modifying the shape, morphology, or chemical composition of the precipitates through different heat treatments and alloying can affect the resistance of aluminium alloys to hydrogen embrittlement.

In the present study, a model Al-2Cu alloy was prepared. Precipitates were characterised using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and scanning Kelvin probe atomic force microscopy (SKPFM). The amount of diffusible hydrogen entered during *ex-situ* electrochemical charging was measured by thermal desorption analysis (TDA) which provides information about energy of trapping sites. Positron annihilation spectroscopy (PAS) was used to localize hydrogen in the metal structure. In combination with TDA, the hydrogen binding ability of specific hydrogen traps was determined.

Improving corrosion resistance in plasma electrolytic oxidation (PEO) coatings through the integration of a modified sol-gel layer incorporating hexagonal boron nitride (h-BN) nanosheets

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Abstract

Sol-gel sealing is recognized as a straightforward and efficient method to enhance the protective performance of PEO coatings. While sol-gel coatings are reliable and corrosion-resistant, the addition of nanoparticles has shown improved barrier properties. Our objective was to validate the positive impact of nanosheet incorporation and the influence of h-BN functionalization in the sol-gel/PEO coating system on AA2024. The PEO layer on AA2024 was acquired at 5 A constant Anodic current, 100 Hz frequency, and 30% duty cycle in an electrolyte containing sodium silicate and potassium hydroxide. Specifically, we utilized as-received, oxidized, and functionalized nanopowders at different concentrations. (3-Aminopropyl)triethoxysilane (APTES) is a suitable candidate for the h-BN functionalizing as the sol-gel layer is the combination of tetraethyl orthosilicate (TEOS) and (3-Glycidyloxypropyl)trimethoxysilane (GPTMS). Some chemical techniques such as Fourier-transform infrared spectroscopy (FTIR) and Zeta potential measurement confirmed the successful oxidation and functionalization process. Rheology measurement affirmed the influence of the h-BN functionalization on its compactness and the network viscosity. The presence of nanosheets was visualized by Field Emission Scanning Electron Microscopy (FESEM) in the sol-gel coating over the PEO layer. The electrochemical impedance spectroscopy (EIS) analysis reported the greatest corrosion resistance found in the modified sol-gel coating with the functionalized h-BN after three weeks of immersion in 0.1 M NaCl solution.

Local electrochemical analysis of the formation stages and corrosion of a lithium-based conversion layer on AA2024-T3

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Lithium salts have been recognized as a promising substitute within the scope of green and sustainable inhibitors for the corrosion protection of aerospace aluminum alloys[1]. Lithium ions play a critical role in stabilizing the reaction products, leading to the formation of a protective multilayer structure[2]. Prior studies have focused on a detailed characterization of the structure and composition of the protective layer[3]. However, local electrochemical characteristics of the conversion layer formation process and its final protective behavior upon exposure to corrosive conditions was yet unknown.

Using Scanning Electrochemical Microscopy (SECM), the progressive formation stages were studied through measuring the local reactivity. During the conversion layer growth, the entire surface presented an initial reactivity increase followed by a decrease up until final passivation. Three intermetallic particle types (IMPs), including Al_2CuMg (S-phase), Al_2Cu (θ-phase), and constituent particles serve as active cathodic areas during the entire conversion layer formation process. The passivation over θ- and constituent phases preceded that on the S-phase. Bubbles generated by hydrogen evolution attached to the alloy surface and locally hindered the conversion layer formation, weakening the corrosion protection of the conversion layer at these locations. Exposing the mature lithium-based conversion layer to a corrosive NaCl solution showed that the areas surrounding IMPs were prone to corrosion attack, especially around S-phase and large constituent particles.

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2. Kosari, A. *et al*. *Corros. Sci.* **190**, 109651 (2021).

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Assessment Tool for Galvanic Compatibility of Aerospace Materials

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Luna Labs USA, LLC, Charlottesville Virginia, USA

Recent experimental, modelling, and method development efforts have been focused on establishing tools for more accurate and rapid assessment of aerospace materials. These capabilities address the need for improved materials selection and design tools that are readily accessible to engineers without expert knowledge of corrosion. The US Navy has recently revised the galvanic compatibility standard practice to account for both potential differences and corrosion kinetics of mixed material couples. A web-based tool has been developed for rapid determination of compatibility and comparison of galvanic couples according to the MIL-STD-889D. This capability forms the basis for establishing component models that provide information on damage distribution on basic part geometries and characterizing the extent of damage for environments of different severity. The methods and models utilize anodic and cathodic polarization curves measured in immersion and environments representing atmospheric conditions. These data inform finite element method (FEM) corrosion models. Corrosion measurements in outdoor tests with multiple material combinations, thin electrolyte film theory, and FEM modelling have been used to establish and evaluate approaches for determining galvanic compatibility and expected corrosion damage in atmospheric conditions. This ongoing work has resulted in a FEM corrosion model and a complimentary interactive web application that is being used to rapidly determining galvanic compatibility according to MIL-STD-889D.

Effect of galvanic couple strength on the kinetics of local corrosion inhibition

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Galvanic corrosion of AA2024 typically occurs in aircraft joints where it is connected to more noble materials (e.g., CFRP, steel). This leads to increased dissolution of the aluminium matrix on top of the intermetallic particle-induced local pitting. Recent works on active corrosion protection for AA2024 galvanic couples analysed the viability and inhibition mechanism of different inhibitor chemistries based on the electrochemical behaviour of the coupled materials. Meanwhile, our recent study showed that the kinetics of local corrosion processes (i.e., intermetallic particle dealloying) also play a role in the corrosion inhibitor activity. Understanding the interplay of inhibitor activity and intermetallic particle dealloying when there is galvanic corrosion can further improve the active corrosion protection strategies for AA2024.

In this work, we analysed local corrosion and inhibition of AA2024 galvanic couples (i.e., AA2024/AA7075, AA2024/low carbon steel, AA2024/Graphite) exposed to 0.05 M NaCl and 0.001 M Ce(NO3)3. An in situ optical-electrochemical technique with high spatial and temporal resolution was used to observe the surface changes of the AA2024 intermetallic particles during the exposure to the electrolyte. Operando observations were further supplemented with post-exposure ex-situ characterization with SEM-EDX.

The results suggest that the strength of the galvanic coupling measured in terms of the potential difference between the materials can affect the kinetics of local surface changes. Furthermore, the extent of inhibitor precipitation appears to be influenced by the coupling as well.

Surface modification of diatomite to improve the loading and release of organic corrosion inhibitors

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Organic corrosion inhibitors have shown remarkable corrosion inhibition efficiency in solution for AA2024 alloys. They also suit the requirement of non-toxic, lighter pigments (instead of heavy metal elements) in primers in industry, makes them the ideal replacement for Chromium VI. Encapsulating corrosion inhibitors in carriers is widely known to avoid the possible interactions between inhibitors and coating matrix. In our previous work, mineralized diatom exoskeletons (i.e. diatomite), which are highly nanoporous microparticles with a hollow inner pill-box structure, were used as carriers for corrosion inhibitors in anticorrosive coatings. We filled up to 15% of the total free volume of diatomite via in-situ precipitation of inhibitors from their saturated solutions. However, when an organic inhibitor, 2,5-dimercapto-1,3,4-thiadiazole (DMTD) was loaded in the diatomite, it showed some good behavior but below another Ce-carrier system which suggests an inactivation or insufficient loading of DMTD in the diatomite. [1]

Inspired by the pharmaceutical field, it is possible to increase the loading and release capacity of diatomite carrier. In this work, we choose different types of silane to modify the diatomite in solution. The morphology and chemical composition of the modified diatomite were characterized by fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX). After the loading of DMTD, the loading and release capacity of DMTD from surface modified diatomite was studied by ultraviolet-visible spectroscopy (UV-vis). Finally, the modified diatomite with DMTD was incorporated into the epoxy coating and applied on the AA2024 substrate. The release capacity and inhibition efficiency of the coating was studied by UV-vis and opto-electrochemical measurement.

The results show that the hydrophobic surface modification improves the loading and release capacity of the diatomite and the corrosion inhibition at the damage sites.

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Effect of condensation and high voltage on Electrochemical Migration

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With the widespread use of electronics today, reliability concerns have increased significantly. As the electronic devices are exposed to varying climatic conditions, the transient conditions often result in condensation on the Printed Circuit Board Assemblies (PCBA). The issue related to condensation is alarming now, as the distances between oppositely biased components have reduced with miniaturization. The condensed water, thus can easily bridge between the oppositely biased components and form an easy path for Electrochemical Migration (ECM), in the presence of an applied operational voltage. As the trend towards electrification is rapidly increasing, the operational voltages are on the rise (>400V).

This study uses an in-house set-up using the gravimetric method, in order to measure the average water-film thickness on the PCBA surface. Tests were carried out with PCB laminates placed in humid environments (90%RH) and cooled to different temperatures below dew point. The droplet morphology has been visually recorded with an in-situ digital microscope. In order to understand the effect of high voltage, applied bias starting from 10V to upwards of 100V have been used. This electrochemical test is supplemented with image analysis as well as characterization techniques such as SEM-EDS to analysis the dendrites and corrosion product formed as a result of the applied bias.

The study provides a holistic understanding of the combined effects of high voltages and water layer formation observed in high-powered electronic devices, on ECM and dendrite growth characteristics.

Key Terms: Condensation, Electrochemical Migration, Dendrite Formation, High Voltage, Humid Environment, Printed Circuit Board Assemblies (PCBA)

Numerical Modeling of Electrochemical Migration Process in Case of Copper

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Electrochemical Migration (ECM) failure is gaining increased attention in the microelectronics sector as miniaturization continues, heightening the risk of short circuits resulting from dendrites induced by ECM. Most ECM investigations primarily concentrate on experimental measurements. Nevertheless, there is a scarcity of previous studies that elucidate the ECM process by conducting numerical simulations of its various stages. This study proposes a numerical model for ECM involving pure copper electrodes in the presence of contamination. The model encompasses the depiction of metal dissolution, alterations in the properties of the contaminated electrolyte, ion transport within it, ion reduction, and dendrite growth. The model's effectiveness is examined using pure copper electrodes and a contaminant electrolyte with varying types and concentrations. Validation of the model's results is conducted through experimental water-drop tests.

USE OF AI TO PREDICT THE COMPATIBILITY BETWEEN SOLDER PASTE RESIDUES AND COATINGS

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The electronic industry has always had to adapt to many challenges, such as the complexification of circuits, miniaturization, growing demands in terms of performance or lifespan, and product reliability, even with harsh environmental conditions. To ensure higher reliability, Printed Circuit Board Assemblies (PCBAs) must be protected against the environment. Therefore, conformal coatings have been used for years in automotive, military, aerospace and energy industries.

For optimum performance of these coatings, it is advised to clean the PCBAs before application. Market constraints in terms of cost and time are forcing manufacturers to reduce the number of steps in the process. Sometimes, the cleaning stage is not considered as an option and the use of no-clean residues is preferred. An incompatibility between the solder paste residue and the coating applied could generate more harmful effects than without coating. Then physical and chemical compatibility between the two products must be ensured. These requirements triggered a new challenge: on one hand, there are many types of coatings on the market; on the other hand, there are numerous techniques for solder paste formulations. The ingredients of these two products are most of the time confidential and different from one manufacturer to the other. Today, there is no simple way to determine the reliability between a solder paste and a conformal coating. It requires physical and reliability measurements which often consist in long and costly qualification processes with many trials required.

For these reasons, it would be very useful to have a simple test to predict the compatibility between solder paste and coating. Artificial Intelligence can help to determine a model to assess the compatibility. This paper shows how AI is used to predict compatibility results between solder paste residues and coatings. A full physical compatibility study is carried out to benchmark some combinations of solder pastes and coatings of the market. Residues surface energy, coating surface tension and physical application tests are used as input data for the AI calculation. Results between AI prediction and the physical tests are compared to choose the right AI model for a good prediction of the compatibilities.

Influence of Microstructure in the Evolution of Galvanic Corrosion of SAC-Bi-xMn Solder Alloys in Simulated Marine Atmosphere

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The ban on the use of lead in electronics manufacturing has created a demand for the development of lead-free solder alloy candidates. One of the reliability challenges faced by these candidates is their ability to withstand the harsh environments in which they are installed. Electrochemical corrosion (ECC) constitutes a crucial challenge for the reliability of lead-free alloys, particularly when exposed to harsh environments like chlorides, exacerbating the issue. Various methods were employed to enhance the corrosion resistance of lead-free solder alloys by focusing on microstructure refinement. These methods include but are not limited to appending the specific alloy with more alloying elements, controlling the cooling process during solidification, applying permanent magnetic stirring (PMS) during the solidification, and obtaining a native oxide film on the solder surface with better corrosion resistance. Therefore, the present work represents an investigation of the ECC of novel lead-free alloys SAC-Bi-xMn compared to the commonly used SAC305 solder alloy prepared by two different methods of sample preparation.

Liquid metal-solid metal symphony: Unveiling the corrosion at Copper-Galinstan interconnects in flexible electronics

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Liquid metals as soft conductors have emerged to be an excellent choice for flexible electronic sensors. On a fundamental level, these devices/sensors consist of copper-based solid metals connected to a liquid metal alloy, for example the alloy Galinstan (an alloy of Gallium, Indium and Tin), with the whole system embedded in a stretchable polymeric resin. The reliability of these sensors highly depends on the interaction between the solid copper contact and the liquid Galinstan. In this study, we observed that there is a very rapid (inter)diffusion happening between the two metals, already observed after one day of contact. The interaction leads to the formation of an intermetallic compound (IMC) composed of '$CuGa_2$'. However, formation of this IMC is not homogenous; instead it nucleates already during 1 day of exposure at specific sites. With increasing exposure time, a dense collection of misoriented blocks of IMC was observed. When aged samples (~2 years) were analyzed in cross-section, the propagation of this interaction results in a complex interaction morphology with 3 different layers: the bulk Cu, the IMC with In and Sn diffused in the grain boundaries (with a concentration gradient towards the bulk Cu), and an outer In-Sn region (with the In and Sn clearly expelled from Galinstan alloy) with $CuGa_2$ IMC blocks suspended in this region. We hypothesize that when these sensors are stretched and relaxed, the interaction layers can compromise the flexibility. The conductivity can also be aggravated by formation of oxides of Galinstan. This will be tested in further research.

Vapor phase corrosion inhibiting biodegradable and compostable packaging for the electronic industry

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Abstract: In the world of corrosion and antistatic protection, packaging is a material that contains vapor phase corrosion inhibitor (VpCI) and/or electrostatic discharge (ESD) additives that protect the object during transport and storage as well as allow an extension of the lifespan of the item. Once-discarded packaging is a major environmental issue since it forms a sizable portion of solid waste. The goal of reducing the problem of packaging waste can be achieved by reusing, recycling, and other forms of recovery of packaging waste. Another solution is the use biodegradable packaging that does not have a negative impact on the environment. There are several materials that can be used to create corrosion inhibiting biodegradable packaging, including paper and blown film.

This paper will discuss the benefits of using VpCI biodegradable packaging in the form of natural 100% recycled content fully recyclable/repulpable paper and biodegradable and compostable coextruded blown film with an ESD additive. Experimental testing will include corrosion protection according to the VIA NACE TM0208 standard, testing of antistatic properties: surface resistivity and static decay requirements of MIL-PRF-81705D (Static Dissipative Packaging Materials), testing of tear strength and tensile strength according to ASTM D1922 and ASTM D882-02 test methods for both products.

Keywords: rust preventatives, biodegradable packaging, compostable packaging, ESD protection, corrosion testing

Corrosion characteristics of lead-free solder alloys under bias voltage

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(written in Arial 12 pt., cursive, centered, 1,5 line space)

Abstruct

In the electronic field, lead-free solder has become a mainstream development trend as a replacement for the traditional Sn-37Pb alloy. However, as electronic circuits continue to develop toward miniaturization, solder joints exposed to the environment are affected by electrochemical migration and cause device failure, which can no longer be ignored.

The first step in the electrochemical migration of alloys is the dissolution of the anode metal. This work takes the Sn-3Ag-0.5Cu alloy (SAC305), which is currently the most widely used, as the research object, and analyzes it from the perspective of the electrochemical corrosion behavior of the solder alloy under different bias voltages. Comprehensive microstructural characterization was performed using various advanced microstructural characterization techniques, such as electron backscatter diffraction (EBSD) and transmission electron microscopy (TEM). Scanning Kelvin probe force microscope (SKPFM) and Conductive Atomic Force Microscope (C-AFM) were used to characterize the potential and conductive characteristics of the alloy surface micro-region. The dissolved products were analyzed using X-ray photoelectron spectroscopy (XPS). The composition of the corroded liquid was tested using Inductively coupled plasma mass spectrometry (ICP-MS).

The results show that when IMCs with high thermodynamic stability are exposed, they do not have the protection of a passivation film similar to β-Sn, and induce corrosion in the form of microgalvanic couples. When a bias voltage higher than the pitting corrosion potential is applied, the alloy will be damaged and develop in the form of pitting corrosion. The matrix β-Sn phase is preferentially dissolved, and the IMCs particles fall off or dissolve in water at a later stage to complete migration.

Keywords

lead-free solder alloys, bias voltage, corrosion

Correlation of reflow solder flux-humidity interaction with surface-mount component level reliability issues

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Electronic devices, particularly smartphones, energy control systems, electric vehicles and their increasingly complex connectivity infrastructure play an important role in modern life, which emphasizes the critical necessity for reliable electronic systems. The demand for uninterrupted high-level performance despite geographical climate variations is challenged by the effects of condensation that can be brought about by rapidly changing temperature and humidity. This causes failures like high leakage currents and Electro-Chemical migration (ECM). Industrial focus is now shifting to design and material selection on Printed Circuit Board Assemblies (PCBAs), with an extension to electronic component packaging. Different PCBA-level components have varying connector shape, pitch distance, standoff height and other such design parameters, which give rise to distinct climatic reliability concerns.

Climatic testing of test cards containing quintessential PCBA components like BGA, QFN, and QFP has been carried out, with the first point of interest being to develop a methodology of electrochemical characterization involving a combination of AC impedance spectroscopy and DC chronoamperometry, to track humidity performance changes in-situ. The second focus has been to study the humidity interaction of three industrially prevalent “No-clean” reflow solder pastes with the different component designs. Flux analysis after humidity exposure has also been caried out using Ion chromatography.

The study involves a combination of Scanning electron microscopy (SEM) and X-ray imaging to visualize flux morphology changes. This shines a light on the effects of flux chemical activity and physical spreading on component connector-driven flux outgassing obstructions, and idiosyncrasies such as component warpage on electrochemical migration phenomena. This test process has additionally been carried out with a glass substrate PCB, to optically visualize changes in flux morphology and any associated reliability issues like corrosion, which is otherwise impossible with FR4 PCB substrates. Put together, the results present a holistic understanding of both the synergistic and counter-indicative effects of flux choice based on electric component design parameters.

Keywords: Ball Grid Array, Chronoamperometry, Humidity, Impedance, Quad-Flat No-lead, Quad-Flat Package, Reflow, Scanning Electron Microscopy, Solder paste, X-ray, Warpage

Evaluation of Moisture Behavior and Delamination Behavior of Printed Wiring Boards

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Moisture absorption in printed wiring boards (PWBs) can lead to the occurrence of the conductive anodic filament (CAF) due to applied voltage during equipment operation and the delamination between water vapor generated by heating during component mounting or repair. In the present study, we clarify the effects of moisture absorption behavior on delamination and establish the standard for baking processes for preventing delamination in various PWBs.

The prototype PWBs with and without copper solid pattern were exposed to various temperature and humidity conditions, and the change in moisture absorption of the PWBs over time was measured by the gravimetric analysis. Assuming that moisture diffusion follows the Fickian diffusion process, the temperature dependence of the out-of-plane diffusion coefficient and solubility coefficient were determined from the moisture absorption data of the PWB without copper solid pattern. The in-plane diffusion coefficients were also determined from the moisture absorption data of PWBs with copper solid pattern. Using these diffusion coefficients and solubility coefficients, we confirmed that the moisture diffusion analysis method for PWBs with anisotropy can be used to estimate the moisture absorption distribution of PWBs.

We exposed the moisture absorbed PWBs to the reflow soldering environment and clarified the effect of moisture absorption on delamination. In addition, the maximum amount of moisture absorption of the exposed PWB was determined by moisture diffusion analysis. Using maximum amount of moisture absorption as an indicator of delamination on PWB, the allowable amount of moisture absorption that prevents delamination on various PWBs was determined, and the baking treatment temperature and treatment time were determined.

Dew Condensation Evaluation by Atmospheric Corrosion Monitoring Sensors in Electronic Control Cabinets

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Electric power equipment, factories, etc. are monitored and controlled by electric and electronic devices. These devices and electric equipment are installed in electronic control cabinets and boxes which have the function of the prevention from water and dusts according to the International Protection Code of IEC 60529, “Degrees of protection provided by enclosures”. The IP code may be spreading widely as if it is the proof of the moisture protection. However, the code is not assured on the moisture ingress protection in high humid environment. The moisture can be permeated through organic materials such as gaskets and sealants resulting in dew condensation on the electronic devices in the control cabinets and boxes. Atter long usage, the moisture accumulated in the cabinets and deliver the corrosion of electric and electronic devices and the decreasing of the insulating performance.

In this study, the invasion phenomenon of high humid air from gaskets and sealants of the electronic control cabinets and boxes was monitored by Atmospheric Corrosion Monitor, ACM, sensors which can detect wetness produced by dew condensation. on the electric and electronic devices and to evaluate corrosion environment. The moisture accumulation phenomena in electronic control cabinets with and without countermeasures to prevent moisture penetration were evaluated quantitatively.

KEYWORDS

electronic device, control cabinet, corrosion, moisture, gasket, sealant

Enhancing Humidity Robustness of Electronics: Understanding the Crucial Role of PCBA Cleanliness

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Abstract- The dependability and service life of electronic devices are fundamentally linked to the cleanliness of Printed Circuit Board Assemblies (PCBAs). Our research critically examines the impact of various soldering techniques, such as wave, selective, and reflow soldering, on PCBA cleanliness and subsequent device reliability. Residual solder flux, if not properly managed, can degrade device functionality or induce corrosion, leading to outright failure. Wave soldering, unless paired with comprehensive cleaning, may leave behind significant residues, while selective soldering can form superior connections with minimal residual material when applied adeptly. Similarly, reflow soldering is capable of producing pristine and durable joints with appropriate materials. The judicious selection of soldering and subsequent cleaning protocols is imperative to forestall device failures and extend their operational life. Our study underscores the critical interplay between PCBA cleanliness and ambient humidity, which is essential to ensuring the sustained quality and dependability of electronic components. We endeavor to explicate the vital function of activators in solder fluxes concerning humidity's influence on PCBA cleanliness, thereby impacting the manufacturing process. Leveraging an extensive dataset from the Center for Electronic Corrosion (CELCORR) at the Technical University of Denmark (DTU), which spans numerous years, our investigation highlights the necessity of comprehending these intricate interactions for the advancement of electronic product manufacturing.

Effect of bias potential amplitude and capacitor size on electrochemical migration (ECM) behaviors of printed circuited boards (PCBs) for implantable electronic devices

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Abstract- Dendrite formation induced by electrochemical migration (ECM) is a common reliability problem occurred on printed circuit boards (PCBs), thus significantly threatening the long-term safe operations of current implantable electronic devices. Although several factors (i.e., contaminations, humidity, temperature) are proved to be closely related to ECM susceptibility under climate environments, further targeted research still need to be conducted as ECM is highly environmental-dependent. Herein, the effect of bias potential and capacitor size on ECM sensitivity are systematically studied using an actual PCB. Finite element method firstly prove that a DC voltage pattern could be regarded as an accelerated test compared to other waveforms. Subsequent chronoamperometry tests using the DC potential further indicate an ion-amount dominated and ion-migration-speed controlled ECM process under low and high bias potential, respectively, based on which an empirical plot is also conceived to predict the ECM possibilities of PCBs. Benefited from electrochemical impedance spectroscopy technique, the capacitor reliability under different corrosion states is also, for the first time, evaluated in a detailed manner. This work offers great value both in electronic corrosion mechanism and future rational design for reliable IEDs.

Comparative analysis between corrosion experiments of steel under CO_2 conditions captured in industrial facilities and simulation results using OLGA.

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Recently, as part of energy transition for carbon neutrality, research is actively underway on CCS technology that capture CO_2 released from industrial facilities, transfer and inject to the underground reservoir. The Republic of Korea, aligning with this global initiative, is actively preparing for the establishment of a 1.2 million metric tons per annum (MTPA) CO_2 injection plant. That project involves utilizing an underground reservoir located in the East Sea, specifically within a depleted gas field.

However, a critical challenge in implementing this technology arises from the impurities (water, hydrogen, etc.) present in the captured CO_2, sourced from diverse industrial processes like power plants and steam methane reforming reactors. These impurities cause corrosion and embrittlement of steel pipeline and equipment for transportation of CO_2.

The study in this paper focused on experimentally evaluating the corrosion rate by circulating a fluid similar in composition to the captured CO_2 by installing a closed-loop experimental system and comparing with simulation results using OLGA software. The corrosion rate of steels such as API 5L on a high-pressure CO_2 was experimentally evaluated. The corrosion rate was evaluated by measuring the weight loss per surface area by manufacturing specimens in the same shape as the 1inch steel pipe. Then the corrosion rate was evaluated according to the change in the concentration of the impurities. Finally, the simulated corrosion rates, derived using OLGA software under similar conditions, were compared with the experimental findings to validate the accuracy of the simulation results.

CCS corrosion risk assessment: focus on acid dropout

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The emerging CCS *(Carbon Capture & Storage)* business brings specific corrosion concerns. Among those corrosion threats, the acid dropout is particularly investigated, to define a safe CO_2 specification, specific to each project. This dropout results from impurities reactions (H_2O, O_2, H_2S, SO_2, NO_2), within the CO_2, leading to strong mineral acid formation (e.g., sulfuric and nitric acids). Once enough acid is produced, and exceeds the solubility limit inside CO_2 stream, acid droplets appear.

The aim of this presentation is to present a philosophy that helps evaluating the corrosion risk associated with acid dropout mechanism. The methodology will be similar for both cryogenic and dense anthropogenic CO_2 (HP). The approach is split in three steps:

- Estimation of the acid concentration and quantity via thermodynamic model
- Identification of process conditions leading to dropout & associated critical areas
- Material compatibility & corrosion rate forecast considering acid concentration and temperature

Thermodynamic assumptions and limitations are also discussed. The outcomes highlight the need to generate more kinetic data in that field, with the aim to define the corrosion risk and associated mitigation solutions more accurately.

Regarding corrosion data, limitations on available figures and key missing information are listed. Further R&D works with additional dedicated corrosion tests and way forward is discussed too.

Corrosion rate of steel exposed to dropout of strong acids in dense phase CO_2 systems

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In carbon capture and storage (CCS), certain impurity combinations and concentrations can result in formation of strong acids in the CO_2 stream [1]. If the concentration of the acids exceeds the solubility limit, an aqueous solution with high concentration of sulfuric and nitric acids may drop out [1]. Establishing realistic corrosion rates for such conditions is needed. However, corrosion testing under high pressure is expensive and time-consuming; therefore, simplified glass cell experiments at ambient pressure (1 bar CO_2) were carried out as part of a larger project.

A critical aspect of understanding corrosion caused by acid drop-out in dense phase CO_2 systems is the unknown distribution of acid dropouts across the CO_2 transportation system, which is currently not well understood. This study simulated different scenarios for distribution of acid dropout by varying the liquid volume to steel surface area ratios (V/S-ratios). Although this was a simplified test, due to the high acidity of the test solution, it is assumed that the reduced CO_2 pressure (1 bar instead of 100-150 bar) has limited effect on the corrosion rate, which will be verified by experimental testing at high CO_2 pressure. It is planned to verify a few of the simplified test results with high pressure testing in future work.

This study was carried out for 14 days in 3-liter glass cells with CO_2 purging (1 bar CO_2). Low temperature (+4°C) experiments were carried out in double mantled glass cell connected to a cooling bath for temperature control, while ambient temperature experiments were carried out in single walled cells without temperature control. Each glass cell contained 6 small beakers (~50 ml volume) with one X-65 pipeline steel coupon each. The exposed coupons were characterized with mass loss, photography, 3D profilometry, XRD and SEM/EDS.

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Electrochemical study of carbon steel exposed to CO_2 hydrate

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Implementation of Carbon capture and storage (CCS) will require transportation of large quantities of CO_2. It is expected that subsea pipelines often will be used to transport the CO_2 from shore to the injection point (permanent storage site). No separate or corrosive phases are expected to form in the pipelines during normal operation. However, a water phase could be present in certain special cases, for example because of small quantities of water remaining from hydro-testing after commissioning. This could result in both corrosion and hydrate formation. While CO_2 corrosion of carbon steel [1] and CO_2 hydrate formation [2] has been well studied, there is limited information on the combination of hydrates and corrosion.

The present work studied corrosion of carbon steel in conditions with and without hydrates. The corrosion coupons (X65 pipeline steel) were exposed in a 300 ml autoclave with transparent windows. A camera was used to observe corrosion and hydrate formation etc. inside the cell. The autoclave was placed inside a chamber with temperature control (freezer). CO_2 was provided from a normal CO_2 bottle with pressure regulator. The corrosion rates were measured with mass loss and linear polarisation resistance (LPR) using a standard three-electrode setup.

The temperature was +4°C to simulate seabed temperature. It was shown that the corrosion rate in water without hydrate (18 bar CO_2 pressure) was relatively low for these conditions, although it was probably high enough to require some form of mitigation. The corrosion rate in CO_2 hydrate (20 bar CO_2 pressure) was much less. Reduced corrosion in hydrate was assumed to be related to most of the water being converted to hydrate. Thus, there was not much water available for the corrosion process.

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Development of standard test method for corrosion rate measurement of pipeline steel in dense phase CO_2

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Carbon capture and storage technology has significant potential to decarbonise fossil-fuelled power plants and other carbon-producing industrial sectors by limiting CO_2 release into the atmosphere. It is essential to characterise the corrosion behaviour of pipeline steels in impurity-containing dense phase CO_2 for implementation of CO_2 transport infrastructure. However, the corrosion rate data in the literature are scarce and, sometimes, contradictory. One reason for such inconsistency is the lack of a standard test method. In this work, a procedure for corrosion rate measurement in dense phase CO_2 with on-line impurity monitoring is developed. Critical factors influencing repeatability of test data, such as incubation time for attainment of steady state impurity concentrations and contact of liquid water with test specimens, are established. The improved repeatability of the procedure is demonstrated by evaluating the impact of key impurities, such as water, O_2 and SO_2 on corrosion rate of a pipeline steel.

Investigating the Influence of CO_2 Partial Pressure on the Rate of Formation and Protective Properties of $FeCO_3$ Corrosion Products

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The presence of dissolved carbon dioxide (CO_2) in geothermal process fluids acidifies the environment and accelerates the corrosion of the carbon steel pipes. Under certain conditions, iron carbonate ($FeCO_3$) corrosion products can form a protective layer on internal pipeline walls and significantly reduce the corrosion rate of the underlying metal surface. For the accurate prediction of corrosion rates in geothermal environments, an improved understanding is required of the operating conditions conducive to protective $FeCO_3$ formation, the mechanisms by which $FeCO_3$ protects the underlying carbon steel surface, and the physical properties exhibited by a protective $FeCO_3$ layer.

This study investigates how CO_2 partial pressure affects the characteristics of the $FeCO_3$ layers that form on X65 carbon steel. Autoclave corrosion testing is performed using CO_2-saturated, 3 wt.% sodium chloride solution at an operating temperature of 80 °C and CO_2 partial pressures ranging from 5.5 to 15.5 bar. In-situ linear polarisation resistance analysis demonstrates how operating pressure influences the rate of formation of $FeCO_3$. The evolution of the $FeCO_3$ layer is also investigated using Electrochemical Impedance Spectroscopy (EIS). This technique demonstrates how the mechanism for protection offered by the $FeCO_3$ layer transitions from initially blocking active sites, to providing additional corrosion suppression by restricting the diffusion of ions to the underlying metal surface. The formation of an effective diffusion barrier is accelerated at high CO_2 partial pressures. A combination of ex-situ analysis techniques and equivalent electrical circuit fitting to experimental EIS data is used to investigate how physical properties of the corrosion product layer contribute towards the different mechanisms for corrosion protection.

Corrosion Behavior of Materials for CCS Infrastructure under Diverse Impurity Scenarios

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Abstract

Carbon Capture and Storage (CCS) technology, while effective in reducing greenhouse gas emissions, faces significant hurdles, chiefly in terms of the durability and longevity of materials used in its infrastructure. Corrosion, driven by various impurities present in the CO_2 stream, poses a significant threat to the structural integrity of CCS systems, particularly affecting different grades of steel used in construction. While some of the studies related to this topic have been explored recently, the systematic testing of different materials under different CCS environments as well as proper correlation of the observed corrosion rate with the mechanism of corrosion is missing. This research aims to fill the knowledge gap in this area, offering insights into the corrosion mechanisms of steels in CCS environments by investigating the interplay between material composition, impurity levels, and corrosion rates.

This study focuses on the investigation of corrosion behavior in various grades of steel (materials with varying chromium contents:1%, 13%, 25%, 29%, and 32%) used in CCS infrastructure. To achieve this, corrosion tests were conducted in two different environments: impure dense phase supercritical CO_2 and aqueous CO_2-saturated brine with impurities. The steels were exposed to CO_2 streams mixed with varying concentrations of oxygen, nitrogen dioxide, and sulfur dioxide. The study employed conventional electrochemical techniques such as DC polarization and AC impedance spectroscopy for monitoring corrosion. Additionally, the nature and composition of corrosion products were analyzed using Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD), respectively. The research further utilized X-ray (micro-) computed tomography (CT) to examine the surface morphology beneath the corrosion scale and to obtain a 3D visualization of the scale structure.

Corrosion under CO_2 storage conditions: Predictive analytics-based data analysis of effect of impurities

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Abstract

CO_2 Capture and Storage (CCS), a crucial strategy in reducing atmospheric CO_2 levels, is often hindered by material degradation, particularly corrosion. In addition, the presence of impurities in the CO_2 stream (such as H_2O, H_2S, SO_x, NO_x, etc.) can considerably lower the solubility of water resulting in water dropout with lower pH values and further increase corrosivity. Traditional methods for predicting and studying corrosion have been an area of focus, however, they often fall short in addressing the complex, multifaceted nature of corrosion processes under varying environmental conditions. This gap underscores the necessity for a more advanced, efficient, and predictive analytics approaches. By leveraging predictive analytics techniques, this research aims to predict corrosion rates in CCS applications, taking into account the diverse and dynamic nature of impurities present in CO_2 streams.

To understand the influence of impurity and predict corrosion rates, systematic experimental corrosion measurements of L80-1Cr (most commonly used tubing material) was conducted under aqueous CO_2-saturated solution as well as supercritical CO_2 with different impurity concentrations and environmental conditions as derived from the design of experiment (DOE). The corrosion rate was determined using conventional electrochemical techniques (e.g. polarization resistance, electrochemical impedance) and weight loss measurements using ASTM standards while scanning electron microscopy and X-ray diffraction was employed to analyze the corroded surface. The extensive dataset obtained from these measurements was utilized to develop predictive analytics models. These models estimate the impact of critical factors on corrosion rate and predict corrosion rates under various conditions.

Development of Novel Materials and Coatings for Carbon Capture, Utilisation and Storage (CCUS) Applications

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In the global effort to mitigate carbon emissions without impeding economic growth, the technical feasibility of reducing CO_2 emissions is apparent in many instances, albeit not universally achievable. Sectors engaging in energy-intensive processes, like cement production, inherently emit CO_2 due to the associated chemical reactions. CCUS technologies emerge as a crucial solution for mitigating CO_2 emissions from such industries. The key to ensuring the economic viability of CCUS in numerous cases lies in the development of cost-effective materials tailored to the specific needs of the industry. Many instances reveal that the presently employed materials have reached their functional limits, underscoring the need for new materials derived from non-critical raw materials to deliver optimal performance.

Compositionally complex alloys (CCAs), an umbrella term inclusive of high entropy alloys (HEAs) and multi-principal element alloys (MPEAs), represent a novel class of materials characterised by a broad compositional spectrum. This expansive field presents an opportunity for the design of alloys with enhanced combinations of properties. The application of these materials, particularly in the form of coatings, allows for the creation of functional surfaces, thereby offering a cost-effective alternative to traditional cast or forged components.

This paper presents research conducted within the framework of the Horizon 2020 project 'FORGE,' focused on the 'Development of novel and cost-effective coatings for high-energy processing applications.' Novel alloys were developed in thin film form and subjected to testing in simulated environments. The down-selected material compositions were processed into powder for subsequent coating production through various methods, including thermal spray. These coatings underwent testing in simulated CCUS environments to ascertain their performance. The paper will present findings from corrosion studies conducted on the recently developed alloys.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 958457

Corrosion and Chemical Reactions in Impure CO_2

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Abstract

To reduce CO_2 emissions for the industry projects have been initiated that aim to capture CO_2 from multiple industrial emitters (sources). Each emitter brings a different spectrum of impurities. It has been identified that due to these impurities separate phases can form that comprise of water or reaction products including strong acids, that can cause severe corrosion.

To ensure long term integrity, a safe CO_2 specification needs to be identified. Tight control of CO_2 stream composition and operating conditions together with the selection of suitable materials are essential to ensure the integrity for all operating scenarios including upsets.

This paper focuses on the effects of impurities on corrosion, mechanisms involved and the challenges that require understanding to control it.Sound understanding of the mechanisms that stand behind these chemical reactions, phase behaviour and potential consequences are needed to be able to identify or/and adjust impurity limits for a CO_2 specification in projects. This work aims to improve understanding provide guidance and to reveal knowledge gaps that require addressing in order to identify a safe CO_2 specification for a CCS project.

Key words: Corrosion, Carbon Capture and Storage, Impurities, Impurity reaction in CO_2, CO_2 corrosion, CO_2 specification

Effect of Cl^-, O_2 and SO_2 on the Corrosion Resistance of Duplex Stainless Steels for CCS Application in Supercritical CO_2 Environments

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In Carbon Capture and Storage (CCS), CO_2 containing various impurities (emitted from various industries) is transported injected underground through OCTG material in dense or supercritical phase. To evaluate corrosion resistance of various OCTG materials exposed to supercritical CO_2 environment contaminated with oxygen (O_2) and sulfur dioxide (SO_2), corrosion tests were conducted at 100 °C in solutions containing 5 and 25 mass% sodium chloride (NaCl) under a total pressure of 130 and 200 bar, with different amounts of O_2 and SO_2.

Super Martensitic Stainless Steel (UNS S41426, 13CR SMSS), Duplex Stainless Steel (UNS S82551, 25CR DSS), and Super Duplex Stainless Steel (UNS S39274, 25CR SDSS) were tested under these environments.

As a result of these tests, localized corrosion was observed on S41426 material, in 25 mass% NaCl, even when no contaminant gases in CO_2 were present.

On the other hand: - S82551 showed good corrosion resistance (corrosion rate less than 0.1 mm/year and no localized corrosion) up to 0.039 bar O_2 in the 5 mass% NaCl environment, whereas in the 25 mass% NaCl environment the material suffered corrosion.

- S39274 showed good corrosion resistance up to 0.01 bar O_2 in both 5 mass% and 25 mass% NaCl solutions, suggesting that S39274 is a suitable material for CCS environments.

In addition, while it is expected that environments containing SO_2 will be more severe due to a reduction in pH, the duplex stainless steel did not show any de-passivation up to 0.13 bar SO_2. Therefore, it is believed that the effect of SO_2 is considered negligible up to a certain amount on duplex stainless steel materials.

Damage investigation of Aluminum Conductor Steel-Reinforced (ACSR) cables used in overhead power lines.

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Electrification and energy transition is challenging all the Transmission System Operators (TSO) with a significant increase demand for electrical energy. RTE is the French TSO responsible for trading electricity with its European neighbors and operating and maintaining the French grid. Electricity is partly transmitted by overhead conductors (unburied lines supported by pylons). At present, the lines are designed to be renewed after 85 years of service, which implies major renewals by 2030-2035. RTE is therefore seeking to develop tools within its R&D asset management department to prioritize the replacement of lines. The understanding of the damaging mechanisms is a key to create models. As transmission lines are bare metal strands without any paint, grease, or polymer sheath, the assembly is completely exposed to the environment (rain, atmospheric pollutants, condensation…) and subjected to atmospheric corrosion while being mechanically cycled by the wind (inducing fatigue and fretting phenomena). In order to have a better understanding of the in-service degradation mechanisms, our study is focused on a 48-year-old aluminum conductor steel-reinforced cable (ACSR), composed of a core of galvanized steel wires surrounded by two layers of aluminum wires and based on the strand cross section analysis. A new and original approach consisting of the achievement of an occurrence map of all the observed corrosion and mechanical phenomena (uniform corrosion, pitting, galvanic coupling, fretting-fatigue induced cracks) at the strand scale is carried out.

Atmospheric corrosion of aluminium based alloys containing Zn, Fe, Sn and Bi for the sacrificial protection of steel

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Abstract

To replace zinc coatings over steel, aluminium based coatings are increasingly being investigated due to beneficial properties such as lower weight, increased circularity and lower hydrogen embrittlement risk. In this work, different aluminium alloys Al-Fe, Al-Fe-Zn, Al-Fe-Bi-Sn and Al-Fe-Zn-Bi-Si and Al-Bi-Sn are exposed in a controlled climatic chamber to investigate their atmospheric corrosion properties. Different methods of evaluating corrosion are utilized such as weight loss experiments, galvanic current measurements, microstructural analyses (with SEM-EDS) and corrosion product analyses (with FTIR). A comparative study is presented showing the effect of different alloying elements on the corrosion properties of the aluminium alloys and their ability to protect steel cathodically.

Factors controlling corrosivity in swimming pool atmosphere

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The air quality in halls of indoor recreational swimming pools is controlled to keep the relative humidity (RH) below 50 %. Although the temperature is elevated to 25-30 ° C, air corrosivity can be expected to be negligible at such low RH. However, rapid corrosion degradation of both metallic and plastic materials is often experienced in swimming pool halls, which is explained by the presence of small quantities of specific products of water disinfection in the air.

Two monitoring campaigns have been conducted in a pool room and in technical rooms of two newly opened swimming pool establishments. In addition to corrosivity class evaluation using steel, zinc, and copper coupons according to EN ISO 11844-1, collection of solid deposits and their analysis, RH and temperature monitoring, and sampling of ozone and chloramines from the air, real-time corrosion rate data were obtained using high-sensitivity *CorrSen* corrosion monitors. These measurements provided unique insights into the distribution and duration of corrosive events during the measurement period. It was found that a few short periods of high corrosivity were responsible for the majority of metal loss. For example, in the pool hall, 85 % and 56 % of the mass loss of carbon steel and zinc took place in less than 1 % of the monitoring time when the air conditioning system did not work properly. The data also clearly showed different modes of activation for the exposed metals; while carbon steel was protected by a passive film initially and activated only after many days of exposure, copper activated almost immediately. The role of specific gaseous air pollutants and recommendations for minimisation of corrosion losses are discussed.

Risk of wet corrosion under chloride deposits of stainless steels and nickel-based alloy weldments in incinerator systems

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The incineration of organic industrial wastes produces specific corrosive species, notably $ZnCl_2$, $CaCl_2$, and NH_4Cl. These highly water-soluble compounds can induce wet corrosion even at low humidity levels, thereby complicating the management of corrosion risks associated with such equipment. To address this risk, various methods, including the use of corrosion-resistant materials, can be employed. Ni-Mo-Cr and Ni-Cr-Mo alloys such as Hastelloy® C276 and C22 are widely recognized as excellent choices for constructing or lining equipment exposed to acid dew-point corrosion in flue gas environments due to their superior corrosion resistance. However, welded joints pose significant challenges from a corrosion perspective, as they exhibit microstructural heterogeneity leading to local modifications in material properties. Specifically, changes in phase composition, grain size, precipitate formation, stress concentrations, and the presence of built-in stresses can substantially decrease the corrosion resistance of the material.

Weldments done on 316L, UR66™, and Hastelloy® C22 were characterized in terms of microstructure in the fusion zone and heat-affected zone, and the potential difference between the weld and base material was measured using the Scanning Kelvin Probe technique. To evaluate their behaviour under conditions of salt deposits, with a focus on $ZnCl_2$, a specific cyclic corrosion test was applied to the welded specimens.

In this context, AISI 316L welds exhibited some resistance to pitting but were susceptible to severe stress corrosion cracking. Conversely, UR66™ displayed only pitting in the heat-affected zone of the weld. As anticipated, Hastelloy® C22 demonstrated superior performance, manifesting localized corrosion only in the fusion zone of the weld. The extent of this corrosion degradation was notably influenced by the composition of the filler materials and welding process employed.

This project is a partnership between Orano, CEA and Andra. It is supported by the French government program “Programme d’Investissements d’Avenir” whose management has been entrusted to Andra.

Corrosion Inhibition Effects of Corrosion Products on High-purity Mg and AZ91D under Thin Electrolyte Layers

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Abstract

Magnesium (Mg) and its alloys are the lightest structural metallic materials, which are widely applied in automotive, 3C (Computer, Communication, and Customer Electronic), aerospace and other fields with high requirements for lightweight to reduce energy consumption. However, the structural integrity of Mg and its alloys in the atmosphere will gradually decay during service due to corrosion. Atmospheric corrosion is the electrochemical corrosion under thin electrolyte layers (TEL) or even adsorbed water layers formed on the metal surface. Different from the corrosion in bulk solutions, the diffusion of corrosive species and deposition of corrosion products in limited space can play very different roles in the corrosion rates of metals under TEL.

In this work, electrochemical corrosion of AZ91D and high-purity (HP) Mg were investigated under TEL with various thicknesses and in bulk solution for different immersion times. Electrochemical impedance spectroscopy (EIS) and polarization curves measurements were conducted in 3.5 wt.% NaCl solution to analyze the stability of the corrosion products. Scanning electron microscopy (SEM), energy dispersive spectrometry (EDS), X-ray photoelectron spectroscopy (XPS) were also employed to characterize the composition and morphology of the corrosion products films.

The competition of dissolved corrosive species and deposited corrosion products under TEL are investigated. Compact corrosion product film forms on HP Mg in thin electrolytes instead of bulk solution. Deposition of compact corrosion product films under TEL contributes to low corrosion rates and pseudo-passive behavior of HP Mg, especially under extremely thin electrolytes (100-μm-thick and 200-μm-thick TEL). The pseudo-passive films of HP Mg are stable under TEL. However, there is almost no stable pseudo-passivation on AZ91D due to micro-galvanic corrosion of AZ91D under TEL. The AZ91D alloy has a higher corrosion rate under TEL that in bulk solution because of lower pH value induced by dissolved CO_2.

Evaluating the corrosion behaviour of copper during deliquescent drying/wetting cycles in humid air

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Copper and its alloys are highly valued for their moldability, heat/electricity conduction, and corrosion resistance, making them widely used in various industrial applications. One potential application of copper is as the corrosion barrier for used nuclear fuel containers (UFCs) within a deep geological repository (DGR) in Canada. The UFC's copper coating will experience different conditions in the evolving DGR environment, which will transition from warm, dry, and oxic to cool, wet, and anoxic. Deliquescence is a known process in forming the initial corrosive solutions/droplets that may occur as a result of adsorption of moisture by salt particles at the UFC surface during the DGR cooling period. The duration over which the surface will remain wet will be impactful on the extent of corrosion. To investigate this phenomenon, the quartz crystal microbalance (QCM) technique is being used. The QCM consists of a quartz plate, covered by gold electrodes on both sides onto which a layer of copper is deposited using E-beam deposition. In this technique, the change in the resonance frequency of a vibrating quartz crystal is linearly proportional to the change in weight on the crystal's surface (Δm) under certain conditions. We used this effect to monitor the adsorption and evaporation of water and to quantify the extent of corrosion on copper surfaces.

To study wetting and atmospheric corrosion of copper surfaces, controlled amounts of different salts (NaCl, $CaCl_2$, and $MgCl_2$) and those derived from CR10-E simulated groundwater were loaded onto copper-coated QCM crystals using an inkjet printer, and then corrosion tests were performed at different relative humidity (RH) values at 75 °C. These experiments indicated that, for $CaCl_2$, the surface remains wet for a relatively brief period after deliquescence; during this period corrosion transforms all the salt on the crystal surface into non-deliquescent corrosion products. We found that a higher amount of salt results in a longer duration of wetness on the crystal surface. Moreover, the salt loaded on the crystal is depleted more rapidly at higher RH values, and the corrosion rate stabilized at a level comparable to that observed on bare copper exposed to the same conditions. Additional experiments are underway, focusing on NaCl and $MgCl_2$ salts and CR-10E simulated groundwater.

Atmospheric corrosion and runoff of zinc and copper – A field and laboratory study

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Atmospheric corrosion and runoff of zinc and copper were investigated for one year in an urban and rural environment on hot dip galvanised steel, zinc, and copper samples. Laboratory experiments, utilising a purpose-built rainfall simulator, were also conducted to examine the influence of selected environmental conditions on corrosion characteristics in detail, namely rainfall intensity, pH, and inclination.

Linear polarisation resistance (LPR) tests during the field studies indicated the formation of a protective surface layer after one month for zinc and galvanised steel, and after six months for copper. These observations were supported by the chemical composition of the corrosion products, as determined by X-ray diffraction (XRD). Corrosion products were predominantly hydrozincite $Zn_5(CO_3)_2(OH)_6$ for zinc and galvanised steel and cuprite Cu_2O for copper. The corrosion rate decreased with time at all study sites, whereas the runoff rate varied with time and among locations, ranging between 1.7 and 4.8 g/(m^{2}y) for zinc and galvanised steel, respectively. For both, zinc and copper, the annual runoff rate was lower than the corresponding corrosion rate. Compared to zinc, a significantly higher corrosion rate was determined for copper at all locations, but contrary to expectations, a slightly lower runoff rate (< 1.0 g/(m^{2}y)). Besides the composition and density of the different surface layers, the main reasons are specific impact factors like the volume and intensity of rainfall and the sulfur dioxide concentration in the different environments.

Laboratory studies showed inclination and rainfall intensity to have a detrimental effect on the runoff rate with high runoff rates from samples of low inclination from horizon and low rainfall intensities. The laboratory data can be used to explain variations in runoff rate between different sampling periods observed in field data.

Numerical Simulation of Anode Cathode Patterns in Atmospheric Corrosion

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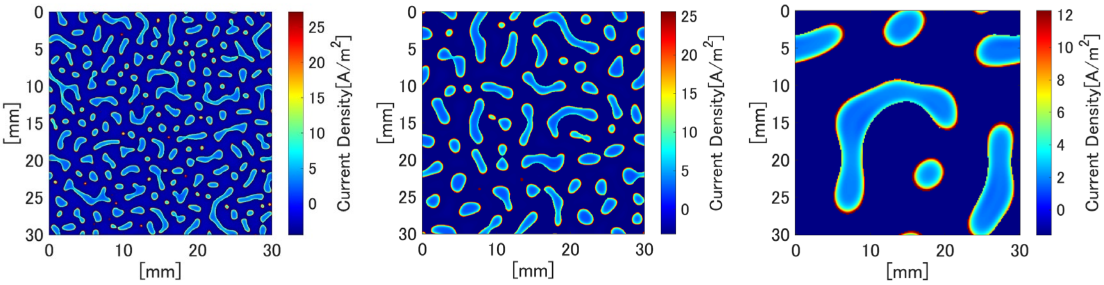
In this study, the numerical simulation of atmospheric corrosion was conducted. Atmospheric corrosion was mathematically modeled as a 2D multi-physics problem involving electric field, concentration field, and reaction field. By employing a polarization curve model with a continuously and dynamically changing Anode-Cathode boundary, the mathematical model capable of analyzing corrosion progression patterns within a two-dimensional plane was developed. Numerical analyses were performed under various conditions of saltwater film thickness. The relationship between the thickness of the saltwater film and the size of corrosion progression patterns was identified. The reaction-diffusion equation was non-dimensionalized and quantitative explanation of the relationship between saltwater film thickness and corrosion progression pattern size is provided.



(a) film thickness10μm, (b) film thickness 30μm, (c) film thickness 100μm

Figure 1 Current density distribution for various water film thickness

Dissolved oxygen in salt solution at low temperature

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Hokkaido and other northern regions of Japan are cold regions with low temperature and heavy snowfall in winter. Large amount of snow-melting chemicals are sprayed on roads, creating an environment that promotes corrosion of automotive bodies and steel structures. It is necessary to collect detailed data on corrosion and environment under low temperature and high salt-concentration conditions. However, concentration and diffusion coefficient of dissolved oxygen (DO) at low temperatures are not well reported. Thus, it is difficult to predict corrosion rates below 273 K in general.

This study was conducted to determine the diffusion coefficient and concentration of DO as functions of temperature and salt-concentration, respectively, in order to predict corrosion rate of steel in salt solutions at low temperatures. The diffusion coefficient of DO that was obtained from the solution viscosity measured using a rotational viscometer decreased with increasing salt-concentration or decreasing temperature. Concentration of DO measured by a chemical titration (Winkler method) tended to decrease with increasing salt-concentration while increased with decreasing temperature of the solution. The authenticity of these data of DO was confirmed by diffusion limiting current measurements using a micro-disc electrode.

In NaCl solutions at temperatures from 258 to 298 K, the corrosion current of iron decreased with decreasing salt-concentration and with decreasing solution-temperature. The corrosion current also was in good agreement with the limiting current for DO reduction calculated using Cottrell equation with the obtained DO data.

Development of a Double-Head Scanning Kelvin Probe for Analysing Atmospheric Corrosion and Hydrogen Permeation Behaviour

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High-strength steel is required to meet the increasing demand for weight saving and extending the service life of steel products. However, hydrogen embrittlement of steel products in service due to atmospheric corrosion needs to be mitigated. Recently, numerous methods, such as the Kelvin probe technique (a local detection method), for detecting hydrogen permeation during corrosion have been reported. However, a method for simultaneous detection of local corrosion potential and hydrogen permeation has not yet been developed. In this study, we developed a double-head scanning Kelvin probe (DHSKP). Each probe can simultaneously measure the corrosion potential on the corroded side and surface potential on the hydrogen-permeation side.

A steel sheet was machined to obtain a sample with a diameter and thickness of 25 and 0.1 mm, respectively. The sample was loaded into the DHSKP equipment, and an NaCl aqueous solution was dropped on the corroded side. The potentials of the corroded side and hydrogen permeation side of the samples were measured using the DHSKP manufactured and modified by Wicinski-Wicinski GbR.

The DHSKP facilitated simultaneous measurement of the corrosion potential and the surface potential of the hydrogen-permeation side. The surface potential of the hydrogen-permeation side locally decreased at the opposite area, where the corrosion potential showed less noble than that of the surrounding area, during the drying process. The relationship between atmospheric corrosion and hydrogen permeation behaviour will be discussed on site.

ATMOSPHERIC EXPOSURE TEST IN URBAN AND MARINE ATMOSPHERE: CORROSION RATE ANALYSIS AND COMPARISON WITH ISO STANDARD EQUATION

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In the last decades research and field test programs have been carried out by international research groups to investigate the corrosion behaviour of metals exposed to atmosphere. These efforts led to the development of ISO standards (9223-9226) which allow the definition of the corrosivity class and the corrosion rate of the most used industrial metals, such as carbon steel, galvanized steel, copper and aluminium.

The aim of the present work is to measure the corrosion thickness loss of metals exposed to both urban (Milan, Lombardia) and marine (Bonassola, Liguria) atmosphere in Italy. Politecnico di Milano is included in the recent "Exposure site catalogue" of the European Federation of Corrosion (WP25 Atmospheric Corrosion).

Two years ago, a renewed exposure rack was designed according to specification reported on ASTM G50, and installed in the two sites. Nowadays a wide number of coupons (100x150 mm) of carbon steel, hot-dipped galvanized steel with X-shaped and L-shaped defects (in accordance with EN ISO 17872), weathering steel with both natural and artificial patina, and different grades of stainless steel are exposed.

At fixed period of time, some samples have been characterized by means of LPR, mass loss tests and corrosion products analysis. The corrosion rate on carbon steel exposed to urban atmosphere obtained by means of mass loss test and LPR are in a good agreement with the value estimated by the dose-response function. The three methods gave values in accordance with corrosivity class C2 of ISO 9223. Similar measurements on galvanized steel exhibited a coherent average corrosion rate. Higher values were measured for samples exposed to marine atmosphere. Stainless steel samples exhibited only superficial spots of corrosion in the case of marine exposure, even after just few months.

Analysis of dynamic chloride ion permeation behavior in rust layer by using stable isotope

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Weathering steel is widely applied for steel bridges as one of the useful methods to reduce life cycle cost of bridges and shows superior corrosion resistance by formation protective rust layer on its surface under atmospheric condition. However, it is reported that the weathering steel is rather corroded than conventional steel under atmospheric corrosion condition such as costal area. Under the condition, the protective rust layer of weathering steel does not form on its surface and particularly β-FeOOH is often observed in rust layer.

It is considered that the protection of rust layer has electrochemical reduction resistant and chloride ion interception property. Although the chloride ion interception property has been studied by determination of membrane potential, this method needs to remove rust layer from steel sample and does not fully simulate the real chloride ion interception property of rust layer. In this study, we have studied the chloride ion interception property by using stable isotope $Na^{35}Cl$ and $Na\ ^{35-37}Cl$. 250 μl of 0.01 M $Na^{35}Cl$ solution was dropped on the surface of test samples, and the corrosion cycle test was carried out under 40 ^{o}C, 40%RH, 4 hours ↔ 40 ^{o}C, 80%RH, 4 hours. After 7 days, 250 μl of 0.01 M $Na^{35-37}Cl$ solution was dropped on the surface of corroded test samples, and the corrosion cycle test was continued 2 more days. After preparation of cross section sample including interface between rust layer and steel, mapping data of ^{35}Cl and ^{37}Cl in rust layer was acquired by TOF-SIMS. In the case of carbon steel and weathering steel, ^{37}Cl reached into the interface through the rust layer. For Ni advanced weathering steel, ^{37}Cl did not pass through the rust layer and stayed on the surface of rust layer.

Consequently, we found that Ni advanced weathering steel showed a superior corrosion resistance with protective rust layer having chloride ion interception property even under the atmospheric corrosion containing high amount of chloride ion such as costal area. By using stable isotope, it became possible to observe dynamic chloride ion permeation behavior in rust layer.

Hydrophobicity and Improved Corrosion Resistance of Weathering Steel with Natural Rust Film

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Weathering steel, which has a protective corrosion product film, is widely used in various construction and landscaping applications. However, it causes metal contamination to the receiving ecosystem by corrosion-induced metal dissolution and rust run-off. Traditional corrosion prevention methods, such as surface coating, also suffer from environmental pollution and high maintenance costs. This study provides a facile method for a hydrophobic surface preparation of weathering steel with natural rust layer. Based on the microscale flower-like structure of the rust substances, the sol-gel method was used to form nano-SiO_2 particles on the rust flakes as nanoscale bumps. After treating the as-prepared micro-nanostructure with low surface energy substances, the as-synthesized film shows strong corrosion resistance, with the corrosion current density is four orders of magnitude lower than that of the samples without hydrophobicity. The hydrophobic surface also reduces the risk of contamination through its self-cleaning properties. Therefore, the weathering steel with hydrophobic rust film can be more stable and environmental-friendly for multi-scenario applications.

Keywords

weathering steel; hydrophobic coating; self-cleaning; corrosion resistance; micro-nano structure

Data-Driven Identification and Experimental Verification of Optimal Sn Microalloying Composition for Corrosion Resistance in Low-Alloy Steel

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Abstract

The primary method to improve the corrosion resistance of low-alloy steel is by adding Cr, Ni, Mo, and rare earth elements. However, these elements face challenges such as poor substitutability and low recovery rates, posing potential supply risks. Tin (Sn) is a potential novel corrosion-resistant element, but its mechanism in low-alloy steel remains unclear. Microalloying low-alloy steels with varying Sn content gradients were prepared for long-term outdoor exposure experiment in the two different atmospheric environments at Beijing and Guangzhou, China. Corrosion currents were monitored using novel corrosion sensors simultaneously. Later, the corrosion mechanisms of Sn in low-alloy steel were explained by experimental techniques such as SEM, XRD, XPS and EPMA, combined with machine learning methods.

The results indicate that corrosion sensor technology can determine the optimal Sn content at different environments. In the early stages of corrosion, Sn can promote corrosion. Its role is primarily manifested in raising the corrosion potential of the steel, forming stable Sn oxides incorporated into the rust layer, and facilitating the transformation of protective corrosion products such as a-FeOOH, thereby increasing rust layer stability and slowing down the uniform corrosion process of the steel.

Keywords

Sn microalloying; Corrosion resistance; Machine learning

(How) do laboratory corrosion tests compare to outdoor exposure of a street lighting unit?

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Looking for a correlation between salt mist tests and real-life performance, a painted aluminium luminaire housing for street lighting applications has been exposed to 5 different laboratory tests and 2 years of outdoor exposure at the Dutch coast. In this short lecture, the results of this investigation are being presented.

Moving Toward a Sustainable Society: Corrosion Issues and Challenges

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The Paris Agreement and the United Nation's 2030 Agenda for Sustainable Development stimulated a global transition towards a more sustainable society. “To end poverty, protect the planet and improve the lives and prospects of everyone, everywhere, 17 Sustainable Development Goals (SDGs) were adopted by all UN Member States” (https://sdgs.un.org/goals) in 2015. Several of these SDGs are directly related to the long-term behaviour of structural materials (mainly metals and alloys) and are challenges for economic, industrial, university and decision-making actors.

One of the first challenges, common to all the STGs, is the “protection of the planet”. Even if corrosion prevention follows already several principles of the “Green Chemistry”, a significant change in practices is necessary to move toward environmentally friendly systems. The 12 principles of the Green Chemistry outlines a framework for the design of corrosion protection processes which involve evolutions of technologies, education, training and international cooperation.

To illustrate these concepts, a series of cases underlines the importance of corrosion awareness and management in the development of the low-carbon energy technologies.

Analysis of microbiologically induced iron corrosion of offshore platforms

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Corrosion of iron is a global problem that causes significant financial damage in the offshore industry. Approximately one third can be attributed to microbiologically induced corrosion (MIC). Improving MIC resistance therefore has a direct positive effect on profitability and sustainability, especially for offshore wind turbines with a relatively short service life.

In situ incubation experiments and corrosion mechanisms inside the monopile

The investigation of this study is produced as part of the joint project “MiCorFe”, which is funded by the BMWK. To study MIC inside of a monopile, commonly used as foundation for offshore wind turbines, we performed in situ incubation experiments by deploying structural steel 1.0570 for three months near the surface and 1 m above the seafloor. In situ sensor systems demonstrate that the water column inside the monopile is subjected to environmentally dynamic conditions. While near the surface, the water is fully oxic, at the ground it is anoxic, which leads to different corrosion mechanisms. The corrosion rate is determined gravimetrically depending on the position within the monopile. In addition, the corrosion products are analysed with regard to their topography and chemical composition using 3D microscopy, scanning electron microscopy and X-ray diffraction. The results show a significant influence of the water environmental conditions on the samples. This is accompanied by different microbes colonizing the steel structures likely facilitating corrosion. The findings are used to determine the structural condition of corroded monopiles and to detect a suitable coating to protect monopiles of MIC. Therefore, the findings of this study confirm the importance of research on MIC for offshore applications.

Effect of ammonium carbamate on corrosion behaviour of carbon steel in liquid ammonia

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Abstract

In recent years, ammonia is expected to be use as a fuel because it does not emit CO_2 during combustion, and its demand may increase. High strength steel is required for large storage tanks that contribute the supply chain of the fuel ammonia. On the other hand, stress corrosion cracking (SCC) is one of the major issues of high strength steels exposed to liquid ammonia. In view of environmental aspects, it has been reported that CO_2 contamination in ammonia prompts ammonia-SCC. In laboratory studies, ammonium carbamate has been usually used as a CO_2 source. However, the mechanism of the effect of ammonium carbamate on ammonia-SCC is not fully clarified.

This study focused on localized corrosion, which is considered to be the initiation site of SCC, and investigated the effect of ammonium carbamate on the corrosion behaviour of carbon steel in liquid ammonia. It was found that ammonium carbamate plays a role in destroying the passive film and promoting the dissolution of iron. The corrosion conditions were different depending on the amount of ammonium carbamate and stirring condition. General corrosion was observed when supersaturated ammonium carbamate was added and stirred during the immersion test. On the other hands, localized corrosion was observed without stirring during the immersion test and under low amount of ammonium carbamate. These results suggests that the concentration of ammonium carbamate on reaction surface affects depassivation and repassivation of the passive film. Furthermore, the active-passive behaviour of iron dissolution was evaluated from static and dynamic polarization behaviour with varying amounts of ammonium carbamate. In this study, the mechanism of the effect of ammonium carbamate on corrosion behaviour is discussed.

High temperature corrosion of steels by nitridation in ammonia

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Hydrogen economy has emerged as an attractive prospect for green energy in the shift towards a carbon-free society. Ammonia is an integral part of hydrogen economy both as an efficient energy carrier but also as a direct fossil-free combustible for energy, free of carbon dioxide emissions from combustion. Hence, ammonia is an attractive green fuel for example in marine transportation. High temperature processes, such as energy conversion, in environments with high nitrogen activity can lead to corrosion of materials by nitridation. The aim of this research was to study the ammonia-steel interactions at high temperatures to provide understanding of the behaviour of steels in ammonia combustion applications.

In this study, three steel grades: 34CrNiMo6, X40CrSiMo10-2, and 316+, were exposed to ammonia-containing gas mixtures at temperatures of 400 °C and 500 °C for various durations. The development of nitride layers on the steels was observed by weighing the specimens and studied using scanning electron microscopy, energy dispersive X-ray spectroscopy, X-ray diffraction and microindentation. All test materials experienced nitridation on the surface. The major changes caused by nitridation were limited to some tens of micrometres below the surface. Microindentation results showed that the nitride layer is harder and more brittle than the steel itself. Based on the results, it can be concluded that the composition of the gas atmosphere, time under exposure, and temperature all influence the extent of nitridation and the behaviour of the three steels. The results from the ammonia experiments are presented and discussed from the perspective of ammonia combustion applications.

Offshore wind structure internal corrosion and oxygen availability

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Abstract

Dissolved oxygen is a critical factor for internal corrosion of monopile foundations for wind turbines. The long-term experience has shown that complete isolation of the inside of monopiles is not a realistic assumption, and some degree of daily water replenishment must be expected. Seawater circulation changes the available oxygen and the profile of the water column inside the monopile. As a result, seawater replenishment is expected to affect the corrosion rate and even the corrosion protection messures.

In the first step, dissolved oxygen and the potential profiles from inside monopiles operating in the North Sea were measured and extracted. The field data is used as a boundary condition input for the secondary current distribution simulation to check the level of correlation between potential and oxygen profiles. Based on the collected data, cathodic corrosion protection (CCP) will be designed and implemented in the next step. The performance of the cathodic corrosion protection system is monitored for a period of one year after implementation.

The preliminary analysis confirms that a constant oxygen profile is not a correct assumption, and the free corrosion potential profile shows a clear correlation with available oxygen. Moreover, based on the numerical simulation combining field data and cathodic protection data, the oxygen profile is an essential factor in CCP design, but the sensitivity is less than the values mentioned in ISO 24656.

Durability and performances of ferritic stainless steel interconnects for Solid Oxide Electrolyzer Cells

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In the context of sustainable hydrogen production, CEA in collaboration with GENVIA are developing Solid Oxide Electrolyzer Cell technologies (SOEC). SOEC devices operate at temperatures between 650-800 °C and are composed of stacked solid electrochemical cells separated by stainless steel interconnects allowing current conduction from one cell to the next. During SOEC operation, the AISI 441 interconnects suffer from high temperature degradation which leads to a decrease of the overall SOEC performances with time. Especially on the oxygen rich side, there are two major degradation phenomena: (1) the growth of a Cr rich oxide scale that increases the Area Specific Resistance (ASR) of the interconnect and (2) the formation of chromium volatile species able to diffuse through the electrode and poison it.

The objective of this presentation is to discuss the long-term ($t > 5000$ h) electrical (ASR) and oxidation performances of bare and coated interconnects in air and fuel (H_2/H_2O) environments. The ASR is measured in a home-made facility that accounts for any effect of the current direction (SOEC or SOFC mode). For uncoated interconnects, after 2500 h at 800 °C in air, a drastic ASR increase is observed for the SOFC mode but not for the SOEC mode. On the same time scale, such ASR increase is not observed for coated samples. This phenomenon will be discussed in lights of electrical characterizations, Cr volatilization resistance and post-mortem microstructural analysis of the interconnect material. These results will be compared to electrical and oxidation behaviour measured in the fuel environment.

This project has been funded by CEA and GENVIA.

Study Of The Glass Seal - Interconnect Interactions In Solid Oxide Electrolysis Cells For Green Dihydrogen Production

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Context

In the context of the environmental transition, the decarbonization of the industry is a crucial goal. The use of decarbonized hydrogen produced by High Temperature Electrolysis (SOEC) is part of the solution.

In this device, the solid electrolysis cells are separated by stainless steel interconnects that allow the electric conduction in the whole stack. A glass seal is used to separate the gas flows (O_2 enriched air and H_2/H_2O fuel environments) and to ensure gas tightness for the whole device. This project aims to study the interactions between the glass seal and the steel interconnects and to investigate potential protection solutions in case of detrimental interactions.

Methods and results

The interactions were studied by applying glass samples on thin steel foils with different coatings. The samples were then heat-treated at 700, 800 and 850 °C for 1000 h under laboratory air. After this, the reaction products were analyzed using SEM, EDS, DRX and Raman.

The first observations at 850 °C showed the presence of bubbles in the glass and that the glass had spread onto the surface of the sample during the test. The SEM and EDS analysis revealed reaction zones at the steel-glass interface. In the presence of air, $BaCrO_4$ phase was identified as corrosion product despite the coatings supposed to prevent the interaction. This could be problematic as $BaCrO_4$ has a CTE gap with the rest of the materials of SOEC. The formation of $BaCrO_4$ is in agreement with the thermodynamic predictions obtained using FactSage.

The results of the experiments at 700 and 800 °C will be also presented to have a better understanding of the interactions and their kinetics.

TiN_x based protective coatings for corrosion protection of 316L stainless steel bipolar plates under PEMWE anode-like conditions

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Proton exchange membrane water electrolyzers (PEMWE) electrochemically split the water molecules in order to produce high-purity oxygen (at the anode) and hydrogen (at the cathode). The elevated capital expenditures (capex) deriving from the use of expensive corrosion-resistant materials undermine the economic competitiveness of this technology [1]. In this contribution, we will focus on the corrosion protection of anodic 316L bipolar plates titanium nitride (TiN_x) films. The thin coatings were grown by reactive magnetron sputtering and characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, atomic force microscopy, X-ray reflectivity, energy dispersive X-ray spectroscopy, electron energy loss spectroscopy and interfacial contact resistance measurements. The corrosion resistance of the TiN-coated stainless steel was evaluated *ex situ* using open-circuit potential monitoring and electrochemical impedance spectroscopy in dilute H_2SO_4 solution in a three-electrode electrochemical cell at 60-80°C. The solutions were also analyzed after the tests by inductively coupled plasma Optical Emission Spectrometry to detect the dissolution of 316L elements.

[1] M. Prestat, *Corrosion of structural components of proton exchange membrane water electrolyzer anodes: A review*, J. Power Sourc. 556 (2023) 232469.

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Corrosion protection of 316L stainless steel by TiOx thin films for porous transport layer application in PEM water electrolyzers

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Proton exchange membrane water electrolysis (PEMWE) is one of the low-temperature technologies to produce hydrogen from water splitting. Its high capital costs resulting from the implementation of expensive corrosion-resistant components, which negatively affects the economic competitiveness of this technology compared to industrial hydrogen production methods based on fossil fuels [1]. Notably, the porous transport layers (PTL) in contact with the anode catalyst layer are usually composed of titanium protected by precious metal (Pt, Au, Ir) layers so as to endure the harsh oxidizing conditions combined with the highly positive electrochemical potential.

This contribution investigates the corrosion resistance of 316L stainless steel, as prospective cost-effective material for anodic PTL application, coated with ALD and PVD TiO_x thin films. Both uncoated and coated 316L samples underwent examination using open circuit potential (chemical stability), anodic polarization and electrochemical impedance spectroscopy in H_2SO_4 solution (pH 0-2) at 60-80 °C for test periods ranging from one day to several weeks. *Ex situ* interfacial (PTL/catalyst) contact resistance measurements before and after polarization and surface state assessment with electron microscopy and scanning kelvin probe are used as key-indicators of the coatings' anti-corrosion performance as a function of their chemical composition, thickness, and microstructure [2].

[1] M. Prestat, J. Power Sourc. 556 (2023) 232469.
[2] T. Srour *et al.*, Int. J. Hydrogen Energy, 58 (2024) 551.

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In Operando Stability of NixMoyFez Bifunctional Electrodes for Alkaline Water Electrolysis: Insights from In Situ Characterization Techniques

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Alkaline water electrolysis (AWE) is considered one of the most promising methods for hydrogen production due to its lack of greenhouse gas emissions and relatively high efficiency [1]. In these systems the materials, based on Ni, demonstrate excellent electrocatalytic performance towards both HER and OER, so can be considered as bifunctional. It has been shown that the surface state of the Ni-based electrode (whether oxidized or reduced) largely determines their electrocatalytic activity [2].

This study focuses on degradation mechanisms of new bifunctional $Ni_xMo_yFe_z$-based electrodes during electrocatalytic activity by combining electrochemical tests with in situ and ex situ surface analysis. Electrochemical properties and durability of binary and ternary $Ni_xMo_yFe_z$ materials synthesized via the DC-sputtering technique were examined and compared in both half-cell and full-cell configurations. The chemical and electrochemical stability of these catalysts was investigated using in situ electrochemical analysis, combined with in situ Raman and X-ray Absorption Spectroscopies (XAS) for a comprehensive understanding of the electrode's behavior under working conditions. The results of in situ electrochemical Raman experiments revealed the formation of γ-NiOOH on NiMo, NiFeOOH on NiFe and NiMoFe at the electrode surface during OER, which was confirmed by XPS. No Raman-active species were detected under HER conditions. Therefore, in situ electrochemical XAS experiments were carried out to monitor the evolution of the electrode during HER. The knowledge gained from this multi-technique in situ characterization can be helpful to optimize the catalyst composition, thus promoting the development of efficient and stable electrodes for green hydrogen production.

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[2] Oshchepkov A, et al., ACS Catalysis. 10(13) (2020) 7043-7068.

Galvanic corrosion in latent heat storage systems using sodium acetate trihydrate.

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Abstract

Sodium acetate trihydrate (SAT) is a promising phase change material (PCM) for use in latent heat storage (LHS), for hot water applications due to its melting temperature (58 °C) and high energy storage density.

To implement LHS in a sustainable way, it is desirable to retrofit existing hot water systems to include LHS. However, old, and existing hot water systems are not designed to handle a situation where SAT leaks into the heating water. Since the distribution system can be made from different material combinations galvanic corrosion must be avoided.

Some preliminary compatibility studies have been performed by others with SAT on several common engineering materials like aluminium, steel, stainless steel and copper. However, whereas some materials like aluminium and stainless steel are considered suitable for SAT, other studies recommend caution when using these combinations. These studies were conducted on single materials in pure SAT. However, no studies on corrosivity in hot water with different amounts of PCM dissolved in the water are known to the authors. More research is therefore necessary to facilitate robust and sustainable use of LHS using SAT for hot water applications.

To facilitate wider use of LHS, this work[1] investigates common engineering metals behavior in different SAT-solution with focus on corrosion and galvanic corrosion performance in hot water applications.

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Laboratory testing, evaluation, and qualification of suitable metallic materials for underground hydrogen storage projects aiming to decarbonization solutions

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Underground hydrogen storage (UHS) has been identified as a technology for the practice of storing hydrogen aiming to reduce the carbon fossil footprint. Hydrogen injection in depleted Oil&Gas reservoirs requires a careful evaluation of the material integrity degradation.

The objective of the testing activity is to evaluate materials commonly used for gas and oil wells, in the context of UHS. The tests are performed on standard OCTG carbon steel metallurgies API/ISO grades J55, L80, T95 and P110.

The compatibility was evaluated through tests in autoclaves for 720 hours with a combination of two pressures (30-300 bar), two temperatures (4°C and room temperature). The environment was properly designed considering different concentrations of hydrogen (20% and 100%) and contaminants (H2O and CO2).

Eight different conditions in pressure, temperature and mix of gas were analyzed. Environment and test procedure were specifically addressed for the scope.

Before the aging, the metallurgies are pre-cracked according to ASTM-E1820 and after the exposure time, metallographic investigations are performed to assess the crack propagation due to Hydrogen and KIH is determined (as per ASME B31.12, ASME BPVC Sec. VIII, ASTM-E1681 procedures requirements).

Crack propagation was observed only for P110 steel, the measured KIH decreases increasing the H2 pressure and descreasing the temperature.

Overall, the study highlights the need for careful selection of materials and quality control for underground hydrogen storage facilities.

Evaluation of Corrosion Behavior of L80 Carbon Steel Casing Material in Simulated Superhot Geothermal Well Environment

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In recent years interest and efforts in drilling deeper and hotter geothermal wells, often referred to as superhot wells have increased substantially to increase the availability of geothermal energy production around the world. The conditions of these deep and superhot wells are more challenging than for typical high-temperature geothermal wells due to higher temperatures, higher pressure, and increased corrosiveness of the geothermal fluid present in the wells. The corrosion behavior of a commonly used carbon steel casing material such as API L80 material should be investigated before comparison to other potential candidates that have higher corrosion resistance and sufficient strength at elevated temperatures. Thus corrosion testing in a High Temperature and High Pressure (HTHP) autoclave at the University of Iceland was performed to investigate the performance of the API L80 carbon steel well casing steel material. The L80 Type 1 carbon steel specimens were tested in a simulated superhot geothermal well environment at 400 °C in H_2S and CO_2 containing steam for 168 hrs with silica compounds. The structure of the corrosion film resulting from the exposure to this simulated environment is investigated and the results from the microstructural and chemical composition analysis with SEM and EDS equipment are reported. Based on this and weight loss analysis the corrosion behavior is described for the L80 type 1 carbon steel samples tested in the simulated superhot geothermal well environment.

Methodologies to evaluate the influence of mineral scales on uniform and stress corrosion cracking of steels in artificial geothermal waters

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Corrosion and scaling are one of the most common challenges in geothermal applications due to the complex brine chemistry combined with the high temperatures and pressures, and the gaseous components. To study mineral scaling at metallic surfaces, appropriate corrosion tests representing the real geothermal reservoir and operating conditions must be selected. In relation with the water composition and reservoir conditions, the thermal gradients between the geothermal fluids and the steel walls of wells and heat exchanger tubes, are major promoters of mineral scaling. These conditions are simulated in laboratory to study the uniform and stress corrosion mechanisms. The implementation of an electrochemical measurement device makes it possible to monitor changes to the electrochemical behaviour of steel subjected to thermal gradients in these environments and so the corrosion response and *in situ* evolution of scales. For the stress corrosion studies, specific low strain rate tensile experiments have been developed. Results from carbon steels (K55 and P110) and stainless steel (13Cr) in artificial geothermal brines representative of Dogger and Soultz geothermal wells in France will be presented.

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Materials and scaling study for geothermal plant

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The use of geothermal fluids is an established method to produce energy with plant efficiency dependent on geothermal fluid temperature and reinjection temperature. Further efficiency gains could be made to the geothermal power production process if heat were extracted from the geothermal fluids down to lower reinjection temperatures. However, lower temperatures could lead to more scaling. Modifications to a high enthalpy power plant were envisaged, including a scaling reactor and retention tank to permit the removal of silica from the fluid before reinjection. To assess the scaling tendency of the geothermal fluids on the likely materials of construction, the performance of a selection of commercially available alloys was evaluated in a simulated geothermal brine. Some 2-part epoxy coatings and thermally-sprayed aluminium were also tested, having been selected either for their hydrophobicity (ie ‘anti-scaling’ properties) or their scale-promoting properties.

Tests were performed in flowing fluid in the laboratory under conditions calculated to simulate the likely fluid flow conditions in the scaling reactor in the field. Testing was performed to evaluate scaling. Short-term electrochemical testing was also performed. Materials tested included bare and coated materials based on SA516 Grade 60 carbon steel, 304L austenitic stainless steel, lean duplex stainless steel, three types of proprietary 2-part epoxy coatings and thermally-sprayed aluminium. Test temperatures were up to 50°C, and relevant to the scaling reactor’s intended operating and design temperatures. The simulated geothermal brine was adjusted to test at different pH. Detailed post-test evaluation was conducted by visual observations, light and scanning electron microscopy (SEM), energy dispersive X-ray (EDX) spectroscopy, metallographic sectioning, and optical profilometry.

Comparative samples have been placed in an operational geothermal plant to demonstrate and assess their scaling and corrosion performance.

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Modeling Localized Corrosion for CRAs in Geothermal Systems

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The aggressive nature of geothermal fluids can lead to corrosion issues due to high temperatures, high flow rates, high amounts of dissolved solids, acid gases (H_2S and CO_2), high chloride concentrations, oxidizing species (O_2), and heavy metals. Although carbon steel is a reliable choice for handling fluids in conventional geothermal energy systems, it is susceptible to high corrosion rates. To mitigate corrosion problems related to carbon steel, corrosion-resistant alloys (CRAs) have been substituted in many geothermal energy systems, particularly in applications undergoing severe corrosive conditions.

Localized corrosion is recognized as the main cause of failure of CRA materials in geothermal energy systems. The ability to predict the occurrence of localized corrosion is essential to prevent catastrophic failure and increase asset integrity and safety. To establish a reliable predictive methodology, it is necessary to quantitatively characterize corrosion and relate it to the properties of the corrosive environment. This is a multi-faceted problem which requires the simultaneous modeling of solution thermodynamics, hydrodynamic conditions, and electrochemical surface reactions.

In this work, a previously developed localized corrosion model has been extended to complex, both aqueous and mixed-solvent, solution chemistries. The model predicts the occurrence of localized corrosion by calculating two characteristic parameters as a function of solution chemistry: 1) the corrosion potential (E_{corr}) and 2) the repassivation potential (E_{rp}), also referred to as the protection potential. The computation of E_{corr} and E_{rp} uses mechanistic approaches that consider the electrochemical reactions and competitive adsorption of aggressive and inhibitive species at the metal/solution interface.

The new repassivation potential model relies on the thermodynamic properties obtained from the Mixed Solvent Electrolyte (MSE) model, which has been previously proven to accurately represent the behavior of the occluded site solutions, including solubility limits, pH, and transport properties.

The model predicts the occurrence of localized corrosion over a wide range of operating conditions and has been verified for CRAs in systems containing corrosive species present in geothermal media containing Cl^-, dissolved O_2, CO_2, and H_2S for a wide range of temperatures.

Effect of oxygen contamination on the corrosion of carbon and stainless steels in CO_2/H_2S-containing media. Comparison between short term electrochemical measurements and 3-month exposures

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This study focuses on experimentally evaluating the corrosion response of 2 carbon steel, 1 CrMo steel and 1 stainless steel tubing materials exposed to CO_2 and CO_2/H_2S-saturated brines under varying oxygen gas concentrations. The experimental matrix is designed to evaluate the impact of oxygen contamination on uniform corrosion and whether localized corrosion is a risk over longer timescales. The first part of the study focused on short term electrochemical measurements using open circuit potentiometry, electrochemical impedance spectroscopy and cyclic potentiodynamic polarization. In the second part of the work, longer-term exposures over 3 months were carried out at 50°C in CO_2 or CO_2+H_2S brines, with or without continuous O_2 contamination. Regular monitoring with electrochemical impedance spectroscopy and open circuit potentiometry, as well as solution chemistry, sample weight-loss and ex situ surface characterization help provide a more complete picture with regards the long-term corrosion performance of these selected grades. A clear aggravation of corrosion by continuous ingress of O_2 is evidenced.

Mitigating Interconnect Corrosion in Solid Oxide Fuel Cells through the Application of a Sliver Coating

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Abstract

Solid oxide fuel cells (SOFCs) efficiently utilize hydrogen as an energy source, with ferritic stainless steel being a prime choice for SOFC interconnects. However, high-temperature challenges such as reduced electronic conductivity, volatile chromium oxide scales, and cathode material compatibility must be addressed. This study investigates the protective oxidation behavior of silver coatings on SUS430 stainless steel in conjunction with the cathode material $LaSrCoFeO_{5+\delta}$ (LSFC). Silver films (approximately 20 µm thick) were applied via screen printing. Four sample types were examined: SUS430, SUS430+Ag (formed by 2-hour, 900 °C air annealing), SUS430+LSFC (formed similarly), and a composite coating of SUS430+Ag+LSFC. Electrochemical tests were conducted from 500-800 °C, resulting in a remarkable reduction in area-specific resistance (ASR) from 13.03 Ω cm^2 (for SUS430+LSFC) to 2.07 Ω cm^2 (for SUS430+Ag+LSFC) at 750 °C. After 100 hours in a dual environment (air+3%H_2O/3%H_2 in argon+3%H_2O), scanning electron microscopy (SEM) analysis demonstrated significantly reduced oxide layer thickness compared to direct cathode contact samples.

Innovative methodology for the use of electrochemistry in corrosion research at increased pressure and temperature

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Abstract:

The methodology for in-situ electrochemistry inside an autoclave system is developed to study the corrosion resistance as a function of temperature (70 °C – 400 °C), pressure ($\leq$ 40 bar), exposure time and environmental composition. For the latter, pure water was initially used and different additives were added in a later stage. Depending on the additive, this is relevant to different industries:

1) salt is added to mimic geothermal brine, relevant to the geothermal power industry,
2) ammonia is added to mimic future coolants, relevant to the heat pump industry; and
3) CO_2 is added, which is relevant for the oil and gas industry.

This study considers 4 different materials: 1) AISI 316 SS, 2) AISI 304 SS, 3) duplex stainless steel, and 4) S235 carbon steel. Their corrosion behavior is studied in-situ (Linear Polarization Resistance (LPR), Electrochemical Impedance Spectroscopy (EIS), Potentiodynamic Scan (PDS)), and ex-situ via post-exposure characterization techniques (Light Optical Microscopy (LOM), Scanning Electron Microscopy (SEM), Low Angle X-Ray Diffraction (XRD), Energy Dispersive X-ray Spectroscopy (EDX)).

Corrosion control and stability of Mg anode / electrolyte interface for aqueous Mg-Air batteries

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The aqueous magnesium-air batteries face limitations with pronounced hydrogen evolution and lower anodic utilization efficiency of Mg anodes in conventional sodium chloride (NaCl) electrolytes. Nitrate-based electrolytes have been noted to elevate anodic utilization efficiency and extend discharge time. However, the reduction reactions from NO_3^- to NO_2^- and the resulting formation of a thicker surface layer can lead to a reduction in discharge voltage. To enhance battery performance and address this issue, it is necessary to identify a suitable additive when using KNO_3.

This study explores the corrosion behaviour, surface composition, and discharge performance of pure Mg anodes in various electrolytes, including NaCl, KNO_3 without and with additive of sodium 5-sulfosalicylate (5-S-Sal). The results reveal that 5-S-Sal effectively inhibits H_2 evolution, enhancing anodic utilization efficiency and specific capacity, compared to NaCl at applied current density from 0.5 to 10 mA/cm^2. Furthermore, the chelating ability of 5-S-Sal can significantly improve the dissolution kinetics of the surface of Mg anode and re-deposition rate of discharge products at the metal / electrolyte interface. This results in the formation of thinner corrosion layer, as confirmed by time-of-flight secondary ion mass spectrometry and X-ray photoelectron spectroscopy results, which show shorter sputtering time and lower binding energy of Mg 2p, respectively. The discharge potential is increased from 1.35 (in pure KNO_3) to 1.60 V (after addition of 5-S-Sal) at the applied current density of 0.5 mA/cm^2. However, higher 5-S-Sal concentrations accelerate Mg anode dissolution, impeding the improvement of utilization efficiency, specific capacity, and energy density.

Hence, it is important to identify a suitable concentration of 5-S-Sal and applied current density, as it must strike a harmonious balance between performance enhancement and mitigation of excessive Mg dissolution. Overall, this research highlights the potential of 5-S-Sal as an additive to improve the corrosion behaviour of Mg anode and performance of Mg-air batteries in chloride-free electrolytes.

Aluminum corrosion prevention in high-voltage electrolyte for Li-Ion batteries

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Aluminum corrosion prevention in high-voltage electrolyte for Li-Ion batteries

Aluminum foils serve as widely utilized cathode current collectors in lithium-ion batteries. However, they encounter several challenges, including localized corrosion by electrolytes during prolonged cycling. These issues ultimately result in the degradation of electrochemical performance. In this study, we investigated the electrochemical behavior of aluminum current collectors produced through additive manufacturing and compared them with counterparts utilizing graphene and chromium conversion as protective coatings in high-voltage electrolytes.

To create a protective film on the aluminum current collector, a spin-coating process and chromium conversion were employed to respectively coat graphene oxide and chromium onto the aluminum surface. Raman spectra and SEM images were recorded to demonstrate the presence and quality of the graphene oxide coating and chromium conversion. Electrochemical characterizations were performed using linear sweep voltammetry, Tafel plots, and chrono-coulometry.

The results revealed a significant oxidation current for the aluminum foil in carbonate solutions, whereas aluminum with graphene oxide coating and chromium conversion exhibited a substantially reduced current, indicating a gradual decrease. Consequently, both graphene oxide coating and chromium conversion demonstrated the ability to inhibit the corrosion of the current collector. These findings collectively suggest that the use of graphene coating and chromium conversion can greatly enhance the electrochemical stability of aluminum foil as a current collector in high-voltage lithium-ion batteries.

Organic/Inorganic Hybrid Electrolyte for Enhancing Performance of Mg-air Batteries

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This work aimed to introduce an organic/inorganic hybrid electrolyte for application to Mg-air batteries with the objective of enhancing their electrochemical performance and mitigating corrosion of pure magnesium anode.

Mg-air batteries attract significant attention due to their natural abundance, lightness, high energy, and high power. Nevertheless, the self-corrosion of the Mg anode in aqueous electrolytes results in the hydrogen generation and severe degradation of the Mg metal. To hinder the Mg anode degradation, an organic/inorganic hybrid electrolyte was used by application of different volume concentration ratio of ethanol and water agents (0 vol%, 20 vol% and 60 vol% ethanol). To better understand its working mechanism, the composition of Mg anode surface corrosion products after immersion in 0.6 M NaCl with different volume concentration ratios of ethanol and water agents was characterized by surface sensitive techniques such as X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). ToF-SIMS and XPS results showed a decrease of the oxide/hydroxide thickness with increase of ethanol concentration, confirming a lower corrosion rate of Mg anode.

Furthermore, by varying the ethanol-to-water fraction in the electrolyte in full batteries, it is shown that a small ethanol content (<< 5 vol%) could greatly enhance the electrochemical performance of a pure Mg anode. Among several ethanol contents, 0.5 vol% showed the best performance with a limited corrosion rate. The lifetime of full Mg-air batteries is drastically prolonged (to more than 40 hours in modified electrolyte compared to only ~11 hours in NaCl electrolyte). The application of a hybrid ethanol-water solvent is a promising way to improve the performance of Mg-air batteries by controlling and tuning the surface reactivity of Mg anodes.

A novel insight into the significantly enhanced discharge performance of Mg-air battery through a mixture of additives

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The systematic investigation of the synergistic effect of ethanol and 3,4-dihydroxybenzoic acid as a complexing agent on the discharge performance of a pure Mg anode is reported. For the first time, the mixture of 30% ethanol and 0.1 M complexing agent is used in Mg-air batteries. The 0.1 M complexing agent significantly chelates with generated Mg^{2+}, causing a strong hydrogen evolution reaction (HER) during discharge. However, the addition of 30% ethanol leads to the formation of a dense inner MgO layer and hinders the deposition of $Mg(OH)_2$ on surface, resulting in a reduced self-corrosion rate of the anode during discharge. Surface analysis performed by time-of-flight secondary ion mass spectrometry (ToF-SIMS) provides evidence of the deposition of S-like species on the Mg surface, acting as precursors for the nucleation of MgO crystals during discharge. Additionally, a formation of $(C_7H_2O_6S)^+$ is also confirmed by thermodynamic calculation. The complexes and MgO together contribute to the formation of a dense inner film layer on the surface, providing superior protection to the Mg substrate. This, in turn, reduces the cathodic sites of HER and inhibits the chunk effect at low current densities. In a solution comprising a mixture of ethanol and dihydroxybenzoic acid, the Mg anode demonstrates a relatively high utilization efficiency of 85.7%, representing a 32% increase compared to its performance in NaCl solution.

AESEC applied to study real-time degradation of Ti-6Al-4V under simulated inflammation

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Ti-6Al-4V demonstrates advantageous combination of high mechanical strength, relatively low stiffness, biocompatibility and high corrosion resistance which is governed by the presence of air-formed, nanometric titanium oxide layer on its surface. However, orthopedic implants, including those made from Ti-6Al-4V, have been documented in literature to experience corrosion *in vivo*. This phenomenon is not purely related to the wear process and could be associated with the presence of reactive oxygen species (ROS) such as hydrogen peroxide (H_2O_2) that are released during post-operative inflammation. H_2O_2-induced degradation is usually described based on *in situ* corrosion studies and further *ex situ* surface analysis. It is still unexplored how Ti-6Al-4V dissolves in H_2O_2-enriched solution directly during corrosion process. Thereby the objective of this study was to analyse the real-time degradation of Ti-6Al-4V under simulated inflammatory conditions using atomic emission spectroelectrochemistry (AESEC). We were focused especially on analyzing dissolution rate under cathodic polarization as it was found that fretting process at biomaterials‘ interfaces can induce potential drop up to -1V. Suprisngly we found that during cathodic polarization, dissolution rate was not proportional to the values of applied potentials. The highest dissolution of both titanium and vanadium (beta-phase) was observed under -0.5V vs. SCE. Findings derived from AESEC measurements, were supported by the oxide layer observations with Transmission Electron Microscopy (TEM) performed on the samples cross-sections. This work increases our understanding of Ti-6Al-4V corrosion in the clinically relevant conditions that can occur for the currently used hip implants.

Effect of different Additive Manufacturing techniques on the microstructure and corrosion resistance of Ti-6Al-4V alloy

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Metal additive manufacturing (AM) technologies are rapidly revolutionizing several industrial fields, due to the possibility to generate complex shaped parts. Biomedical sector is one of the most promising field of application of such technologies, that grant a unique surface roughness that can promote osseointegration. However, AM-produced implants can provide a wide range of properties, strictly dependent on several process factors. Therefore, a full understanding of the impact of these parameters is a matter of primary interest. Thus, the purpose of this work is to examine the effect that the adopted AM technologies, heat treatments and surface finishing provide on the microstructure and the corrosion resistance of Ti-6Al-4V alloy specimens. Three distinct additive technologies have been investigated: electron beam melting (EBM), laser powder bed fusion (LPBF) and material extrusion (MEX). A material science-based approach was adopted to investigate the typical microstructures and phases generated by the manufacturing processes and subsequent heat treatments. The corrosion behavior in a physiologic solution at body temperature was assessed via electrochemical tests. Additionally, an estimation of the total ions release over time was calculated. It was highlighted that surface finishing processes were significantly more impacting on the corrosion performance of the Ti-6Al-4V alloys than the microstructure. The pickled and polished specimens proved to have comparable oxide formation kinetics. However, the former seemed to achieve lower asymptotic current density values, hence ions release rates, proving that the pickled condition is advantageous both in terms of reducing health hazards and increasing osseointegration.

Effect of proteins on static/fretting crevice corrosion of artificial joint materials

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In an ageing society, arthroplasty is considered an effective option for the treatment of osteoarthritis. Fretting corrosion and crevice corrosion occur at the fixation interface of the artificial hip joint, which reduce the service life of the joint. Clinical studies have shown that crevice corrosion at fixed interfaces is relation to fretting wear. Joint synovial fluid and body fluids contain a large number of protein molecules and it is necessary to consider protein effects. Our study shows that the distribution of proteins inside and outside the crevices has a significant effect on the process of static crevice corrosion and fretting-initiated crevice corrosion.

For static crevice corrosion[1], wire beam electrode with different crevice widths were immersed separately in saline with/without protein. The potential and current inside and outside the crevice was tested in situ and the currents were statistically analysed. The results showed that the corrosion current density inside the crevice was significantly reduced when the solution contained proteins. Proteins migrated towards the crevice mouth, causing blockage and changing the width of the crevice, which affected the emergence and expansion of corrosion inside the crevice.

For fretting crevice corrosion[2], based on a special pin specimen design, the fretting were occured in the centre of the artificial crevice. The effect of proteins on the process of fretting-initiated crevice corrosion was investigated in solutions with/without bovine serum albumin, respectively. The results showed that fretting initiated significant crevice corrosion without proteins and corrosion of large areas was observed in the non-contact area inside the crevice. In the presence of proteins, proteins can smigrate into the crevice and block the crevice mouth. The enriched proteins had a lubricating effect and inhibited the occurrence of crevice corrosion.

[1] Heng Liu, et al. CORROS SCI. 215 (2023), 111028.
[2] Heng Liu, et al. CORROS SCI. 225 (2023), 111586.

Fatigue-corrosion behaviour of Ti6Al4V alloys in H_2O_2-containing physiological solution

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Titanium and its alloys stand out as widely employed non-biodegradable materials for medical implants. Among these alloys, Ti6Al4V is the prevalent biomedical implant material. However this materials suffers from degradation when exposed to reactive oxygen species, including oxygen peroxide (H_2O_2), especially during acute or chronic inflammation phases. This degradation process can lead to the deterioration of the implant device and the subsequent release of its constituents into the surrounding tissues, potentially giving rise to health issues. Moreover, for duplex α/β microstructures, selective dissolution of the β phase has been observed under such conditions[1], leading to sharp corrosion damage at the grain boundaries of α grains. These damages stand as initiation sites for fatigue mechanism.

This study, conducted within the context of the French-Swiss project LoCoMecha, investigates the fatigue-corrosion properties of Ti6Al4V with different microstructures when exposed to an H_2O_2-containing solution. To gain deeper insights into the underlying damaging mechanisms, the research involves not only comprehensive in situ electrochemical measurements but also ex-situ characterization of the crack path (e.g. 2D BIB-SEM and 3D FIB-SEM). The results are discussed, focusing on the initiation of corrosion defects at the surface, particularly in the β phase, and the subsequent fatigue propagation within the microstructure.

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Corrosion Mechanism of pure Zinc in different physiological solutions

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Nowadays, biodegradable metal alloys are proposed to replace permanent biomaterials in case of implants that are required to stay in the human body only for the time of tissue healing, avoiding secondary surgery. Among them, Zn alloys are considered highly promising thanks to their corrosion rate which is intermediate between Mg (too fast biodegradation) and Fe (too slow biodegradation) (Huang et al., Corrosion Science 182, 109278, 2021). In the last decades, several papers dealing with the corrosion mechanisms of pure Zn in physiological solutions have been published, but there is still lack of information about the effect on zinc corrosion of different simulated physiological solutions without and with amino acids and proteins, and about the behaviour of zinc at long immersion time (i.e. up to 1 month) in such environments (Dong et al., Corrosion Science 178, 109071, 2021) . Therefore, this work studies the corrosion mechanism of zinc in different simulated body fluids with a specific interest in assessing the role of amino acid and proteins on its corrosion rate. To achieve this goal, zinc coupons were immersed at 37°C in Hanks' solution (HS), Dulbecco's modified eagles' medium (DMEM) and DMEM with 10% of fetal bovine serum (FBS), and their corrosion potential was measured as function of immersion time, while impedance spectra were recorded to estimate the polarization resistance. Corrosion products composition and morphologies were characterised by Raman spectroscopy, XRD, and FEG-SEM equipped with an EDS analyser. Polarization curves were also recorded to get more insight on both the half-cell cathodic and anodic reactions responsible for the overall corrosion process. Direct measurements of Zn ion release rate were carried out using ICP–OES analyses, while the hydrogen evolution rate was estimated by measuring the concentration of H_2 (if any) by chromatography. The experimental results show that generalized corrosion with the precipitation of corrosion products on the surface occurs on pure Zn in Hanks' solution, while localised corrosion and high Zn ion release are observed in DMEM and DMEM+FBS electrolytes due to a complexation action of amino acid and proteins.

Microstructural, mechanical and corrosion analysis of Mg and Zn alloys manufactured by laser powder bed fusion

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3D printed Magnesium (Mg) and Zinc (Zn)-based alloys offer great potential to develop personalised bioabsorbable implants in load bearing applications. For this, the materials must offer enough mechanical integrity, an acceptable degradation rate and no cytotoxicity to replace the healing tissue until its full absorption. To assess this, WE43 and Zn1Mg test probes were manufactured using laser powder bed fusion (LPBF) technology and their mechanical and corrosion behaviour were determined during their in vitro degradation process in simulated body fluid (SFB).

The Zn1Mg printed samples exhibited higher stiffness (E = 94-100 GPa), strength (UTS = 382-409 GPa), and strain to failure (ε_f = 5.2-6.5%) than the WE43 printed samples (E = 47-55 GPa, UTS = 136-233 GPa, ε_f = 3.3-4.7%). Additionally, the WE43 specimens exhibited substantially higher corrosion rates (3-9 mm per year) than Zn1Mg (0.1-0.25 mm/year). Moreover, the corrosion mechanisms differed substantially, with WE43 resulting in H_2 gas production and a bigger tendency to suffer pitting corrosion and Zn1Mg developing complex corrosion products on the surface. The potential of surface treatments, like plasma electrolytic oxidation (PEO) to tune the corrosion behaviour and enhance durability was also assessed. Mechanical tests performed after long term immersion in SBF highlighted that the mechanical integrity of WE43 decreased severely after 7 days of immersion in SBF, whereas Zn1Mg specimens retained their UTS and strain to failure evenafter 2 months of immersion.

Overall, the findings underscore the importance of alloy selection and post-processing treatments in influencing material performance and degradation under in vitro conditions.

Toward a mechanistic understanding of trace-element influence on corrosion at the magnesium-biology interface

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Biodegradable magnesium (Mg) implants are a promising alternative to permanent metallic implants in biomedical applications. Yet, their effectiveness is hampered by unpredictable corrosion in the physiological environment, resulting in premature implant failure and potential toxicity [1]. A key parameter influencing this phenomenon is the behavior of trace noble elements (Fe, Zn, Cu) present in the peri-implant microenvironment and as impurities in Mg. These elements are known to impact Mg dissolution by creating active cathodic sites, though their behavior in physiological conditions is still unknown.

Conventional chemical analysis methods, such as SEM/EDS or XPS, lack the necessary elemental sensitivity and spatial resolution to understand the chemical nature of the interfacial layer forming on corroding implants. In this study, laser ablation coupled with inductively coupled plasma mass spectrometry (LA-ICP-MS) was employed for trace-element analysis of corrosion products [2].

Through the optimization of lateral probing and trace-element analysis on Mg model systems of varying trace element purity exposed to Simulated Body Fluids (SBF), the study achieved sufficient sensitivity (3.6 ppm) to distinguish purity levels based on the Fe content in the Mg Matrix. This data correlates with the dissolved Fe content quantified by ICP-MS liquid-phase analysis (SBF composition) following contact of SBF with Mg. The interplay of Fe with complex electrolytes is further studied by electrochemical quartz crystal microbalance (eQCM) at potentials establishing on Mg surfaces, which revealed insights into Fe-redeposition kinetics and trace-element quantification, particularly in the electrochemical potential range where strong hydrogen reduction dominates the current signal.

This comprehensive approach sheds light on the intricacies of Mg implant corrosion, offering valuable insights for the development of more robust and reliable biodegradable implants in biomedical applications.

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Effect of Flow Rate of Simulated Human Physiological Fluid in Corrosion of a Magnesium Alloy

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Abstract

Magnesium (Mg) is a highly electrochemically active metal (-2.37 V (vs SHE)) that undergoes anodic metallic dissolution and cathodic hydrogen evolution (HE) and hydroxide precipitation ($Mg(OH)_2$), causing localised alkalinisation. Mg alloy ZK60 (Mg-5.5 Zn-0.4 Zr) possess improved mechanical properties, making it suitable for temporary orthopaedic implant application. In an attempt to study electrochemical corrosion of the alloy under appropriate physiological conditions, the conventional modified simulated body fluid (m-SBF) was used in the present study at pH=7.4 at 37 ºC under static and dynamic human blood circulatory conditions (~4 ml/ min). For this purpose, electrochemical impedance spectroscopy (EIS) was carried out at different immersion times (0 h and 12 h). Nyquist plot showed the presence of high-frequency interfacial capacitive, mid-frequency diffuse layer capacitive loops and low-frequency inductive loops in the static (0 h, 12h) and dynamic (12 h) conditions corroborating with the time constants from the Bode plot. As the immersion time increased, the static condition showed ~4.5 times increase in the total resistance (R_t = charge transfer resistance (R_{ct})+ diffuse layer resistance (R_{po})) from its 0 h. In contrast, the dynamic conditions retained their cumulative resistance over the immersion. The combinatorial increase in R_{po} and mid-frequency phase angle in static (12 h) indicate the partial resistance offered by the passive film, which is minimised in the dynamic as the immersion time required to attain the interfacial capacitance is higher due to the electrolyte circulatory effects.

Evaluation of PLA-coated ZnMg alloys as biodegradable materials: pitfalls and proof-of-concept

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A biodegradable material should maintain most of its mechanical properties during the healing process, and then rapidly degrades without toxic effect for the body. Zinc and magnesium, being required for metabolic function, are good candidates. Alloying both into a porous structure is expected to be a good compromise for corrosion rate, hydrogen evolution and weight. Besides, polylactic acid (PLA), as biodegradable polymer, may be used as barrier to delay alloy corrosion. The aim of the present study is to evaluate the behaviour of such material in biological medium.

ZnMg1.5 alloys were prepared by salt leaching into bulk or scaffold rods. As a first trial, PLA layer was prepared by dip-coating process. Corrosion susceptibility was evaluated by polarization and weight-loss measurements. PLA sustainability was monitored by electrochemical impedance spectroscopy (EIS). *Post-mortem* cross section and surface analysis were used to evaluate degradation mode.

First, the importance of experimental conditions on the study of biomaterials has been demonstrated. Parameters such as applied potential range or biological medium may lead to significantly different results, and partially explain the wide distribution of reported corrosion rates.

In this study, ZnMg corrosion rates reach less than 30 µm/year after several days in deaerated physiological saline solution. Alloy microstructure is a critical factor for implant lifetime, with the selective corrosion of eutectic phases in both bulk and scaffold samples, which should affect the mechanical properties.

Once coated with PLA, the initial corrosion rate of ZnMg alloy is significantly decreased, demonstrating the protective role of PLA. The scaffold structure can maintain this effect for a longer time than the bulk morphology. The aim of the future work is to achieve to have a lasting protection with appropriate bonds between PLA and alloy.

Electrochemical Impedance Spectroscopy of Mg stents covered with different stacks of coatings

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Different inorganic and organic layers deposited on stents of Mg-Nd-Zn-Zr alloy were studied by electrochemical techniques in Simulated Body Fluid (SBF) to investigate corrosion behavior. As a novelty this work reported the comparision between plasma-pretreated stents and samples with organic coatings which showed greater corrosion resistance. Additionally in this work, a methodology of EIS data treatment is proposed based both on the use of the Measurement Model and power law model to fit the resistivity distribution of the layers which is rarely reported in the literature. The EIS experimental data were well in agreement with the fitted data calculated with the proposed model. Power law model were used to describe the layers from native oxide layers to organic coatings.

Biocorrosion resistance of a Mg-3Zn-0.4Ca alloy subjected to different thermal and thermomechanical treatments

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Magnesium (Mg) is a very promising material for biomedical applications, including temporary orthopaedic implants. However, the use of Mg alloys as an orthopaedic material is limited due to its fast degradation rate in physiological environment. In this work, the ability of homogenisation, heat treatment to different ageing conditions and hot rolling to improve the suitability of a cast Mg-3wt.% Zn-0.4wt.% Ca (ZX30) alloy for biodegradable implants is investigated. For this purpose, microstructure, hardness and biocorrosion behaviour of the ZX30 alloy in the as-cast and different thermal and thermomechanical conditions were evaluated. Microstructural characterisation was conducted by means of optical microscopy, scanning electron microscopy, electron backscatter diffraction and X-ray diffraction, while the biocorrosion behaviour was assessed by immersion tests and electrochemical measurements of open circuit potential, anodic-cathodic polarisation and impedance in Hank's solution. The results revealed that heat treatment, especially to the peak-aged condition, leads to the best combination of hardness and corrosion resistance in biological environment. The effect of the different thermal and thermomechanical treatments on the mechanical and biocorrosion behaviour of the ZX30 alloy is discussed mainly in terms of grain structure, dislocation density, solute atoms, and second-phase particle distribution.

A study on the degradation behavior of pure magnesium in physiological environment and its surface corrosion product film layer

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Pure magnesium exhibits a lower corrosion rate, making it a potential biodegradable implant material. However, its degradation behavior differs in complex physiological environments and is not fully understood at present. This study conducted immersion corrosion experiments on pure magnesium and found that its degradation rate in simulated body fluid (SBF) was faster (2.29 mm/y) compared to saline (0.60 mm/y). This difference is attributed to the accelerating effect of buffering ions $HPO_4^{2-}/H_2PO_4^-$ on the corrosion of pure magnesium in physiological environments. Hydrogen evolution experiments showed that the degradation rate of pure magnesium in SBF rapidly decreasing within the first 12 h and then stabilizing. Surface and cross-section characterization of corrosion products after 7 days of immersion, using SEM, XRD, and XPS revealed a layered structure of the corrosion product film in SBF. The film consisted of a dense layer of calcium phosphate on top and a porous layer of magnesium hydroxide below. Results from electrochemical impedance spectroscopy (EIS) showed that the capacitance arc radius of pure magnesium in SBF gradually increased, with low-frequency impedance increasing from 126.53 $\Omega\cdot cm^2$ at 1 h to 1318.76 $\Omega\cdot cm^2$ at a later time. Additionally, the resistance of the corrosion product film increased from 86 $\Omega\cdot cm^2$ at 1 h to 789.8 $\Omega\cdot cm^2$ at 168 h, indicating enhanced corrosion resistance during the degradation process. Early corrosion analysis revealed that a protective barrier of insoluble calcium phosphate quickly formed on the pure magnesium in SBF, effectively increasing the substrate's corrosion resistance and gradually reducing the degradation rate. Furthermore, a 4-week implantation experiment in mouse femoral medullary cavities showed the formation of a layered structure rich in calcium phosphate on the pure magnesium, consistent with the degradation behavior observed in SBF. This study provides valuable insights into the degradation behavior of pure magnesium in physiological environments and its potential as an orthopedic implant material.

A comparison of spark and soft PEO regimes in terms of corrosion and wear performance on AZ31 alloy

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Abstract

Plasma electrolytic oxidation (PEO) is an excellent technique for the surface modification of Mg alloys for biodegradable implants due to it improves the corrosion resistance of the alloys and promotes cell adhesion and proliferation. However, PEO coatings have a high internal porosity that can affect their functionality in a short period of time. To reduce this porosity, the soft regime is used, which employs lower current densities and a controlled and less intense arc or spark; in contrast to the spark regime, which requires higher current density and spark intensity to form the coatings with high porosity and less compactness. In this work, the soft regime was explored in comparison to the spark regime to produce dense PEO coatings with good corrosion and wear properties. The coatings were carried out on AZ31 alloy in an alkaline electrolyte containing silicate and a low fluoride content. The influence of frequency, duty cycle and current density in the soft regime was investigated, while the effect of voltage, current density, process time and ramp time in the spark regime was determined. These parameters were examined in terms of morphology/composition, thickness, corrosion and wear resistance. The composition and morphology of the coatings were analyzed by SEM and XRD. The corrosion behaviour the coatings was evaluated in SBF by EIS and H_2 evolution test at 37°C. The wear behaviour was carried out by dry alternating sliding at room temperature. The influence of the studied PEO parameters in the soft regime is discussed in terms of alloy degradation mechanisms and wear behaviour in comparison with the coatings obtained in the spark regime.

Keywords*: Mg, soft and spark regime, corrosion and wear resistance.*

Geopolymer coatings mixed with 'green' additives: effect on magnesium biocorrosion

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Abstract

The rise of magnesium alloy-based bioresorbable materials has become significant in recent years due to their properties. Their bone-like elastic modulus and antibacterial and osseointegrative properties have made these materials ideal candidates in the bone regeneration field.

A key factor in the use of these materials, however, is the bioresorption rate, a phenomenon intrinsically linked to the corrosive behavior of magnesium alloys. Body fluids, in fact, contain non-negligible amounts of chlorides that can trigger widespread corrosive phenomena and induce undesirable consequences such as abrupt loss of mechanical properties (long before the bone tissue is fully healed) and hydrogen accumulation in the tissue itself.

The purpose of this work is to create geopolymer coatings that are admixed with ‘green’ biocompatible substances (such as PEG or folic acid) and test whether they can modulate the corrosion rate of magnesium alloys in a simulated biological environment. The geopolymer coating, due to its micro- and nano-porous nature and with the help of such additives, can regulate the amount of electrolyte reaching the substrate and consequently the corrosion rate without halting the resorption altogether.

The coatings were first produced by dip-coating deposition and were analyzed by SEM/EDXS analysis to study their morphological and chemical characteristics. Corrosion behavior was evaluated by placing the coated samples in contact with saline, phosphate buffer solution (PBS) and Hanks' Balanced Salt Solution (HBSS) in order to simulate the biological environment in a gradually more accurate manner.

Open circuit potential, potentiodynamic polarization tests and electrochemical impedance spectroscopy (EIS) measurements were then performed on both coated and uncoated samples to verify their different behavior.

Electrochemical Corrosion Monitoring of Neural Implant Electrodes

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Platinum electrodes are crucial components of neural implants, serving as the interface between the electric circuit and the nerve tissue. Electrical neurostimulation involves microsecond scale constant current pulses applied over long implantation times (>years). The electrochemistry of the stimulation is not fully understood, and electrode degradation has been observed. This work focuses on the electrochemical investigation of the processes occurring during stimulation that lead to degradation, as well as their correlation with the electrodes' surface state measured *in situ*. The degradation is monitored for thin film and wire platinum electrodes over up to 1.75 billion current pulses with pulse widths in the microsecond range.

A measurement framework was developed that combines the application of current pulses via a neurostimulator and seamless monitoring of the electrode performance utilizing a potentiostat. The framework is capable of fully automated measurements and stimulation over several weeks. A custom-built printed circuit board enables switching between the devices and contains a set of high impedance amplifiers to allow potential tracking of the platinum electrode during stimulation.

Results

The shape of the recorded CVs changes, losing typical platinum features, as the total number of applied neurostimulation pulses increases. The life cycle of the thin-film electrodes can be divided into three distinct phases: a roughening phase, a degradation phase, and a complete dissolution phase. The phases can clearly be separated by analyzing the electrochemical measurements, as well as by interpreting the potential traces recorded during stimulation. Optical and scanning electron microscopy images of the electrodes at the end of the experiment show severe corrosion. The degradation of the electrodes strongly depends on the used stimulation protocol. Only protocols that polarize the electrode sufficiently to reach potentials that lead to surface oxide formation and surface oxide reduction cause severe degradation, whereas protocols that cause only one of these processes don't show changes in the electrodes surface state. This indicates that the driving force of platinum degradation is cyclic platinum oxidation and reduction of the formed platinum oxide.

Anticipating Gold Nanoparticle Size Influence in Acidic Environments: An Electrochemical Perspective

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Gold nanoparticles (Au NPs) have traditionally been considered bio-inert and safe in medical applications; however, recent research has challenged this notion. Also, our previous research showed that the reactivity of Au NPs in biological environments, including cysteine amino acid, is size-dependent, specially under 10 nm. This study aimed at understanding the behaviour of differently sized (5, 10, 20 and 50 nm) Au NPs in L-cysteine solutions of different pH (2, 3, 4, 5 and 6) by using cyclic voltammetry (CV). We have determined that the size influenced oxidation processes of gold and cysteine. Nanoparticles ranging in size from 5 to 10 nm exhibit more intense reactivity with cysteine, whereas particles sized between 20 and 50 nm react less intensely. Less surface reactions led to the oxidation of free cysteine, which subsequently underwent dimerization to form cystine via S-S linkage. The oxidation of the gold-cysteine system includes many electron transitions, peak overlaps, and is complicated. The size dependence of Au NP-cysteine interactions was also confirmed by ToF-SIMS measurements. Also, variations in the pH of the environment also impacted the reactivity of Au NPs with cysteine, although the size dependence occurred at all pH values.

Exploring new and sustainably manufactured *Hybrid* steel as joint replacement biomaterials

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Steel manufacturers Ovako recently produced two types of hybrid steels, Hybrid 55 steel and Hybrid 60 steel, which offer exceptional corrosion resistance in H_2SO_4 and NaCl solutions while containing only 5% Cr elements. The hybrid steels also show higher strength compared to the standard bearing steel with hardness of 55-60 HRC. The hybrid steels are promising to replace austenitic stainless steels and Co-Cr alloys as load-bearing biomaterials.

In this paper, the feasibility of using hybrid steels in joint replacement is investigated by testing their corrosion behaviours in a simulated body fluid (SBF) and biocompatibility at the first time. Electrochemical testing of Hybrid steel samples, including open-circuit potential (OCPs), electrochemical impedance spectroscopy (EIS), and cyclic polarization curves, are performed in simulated body fluid. Preliminary results demonstrated that corrosion resistance, especially pitting corrosion performance, of hybrid steels are comparable to commonly used CoCrMo and Orthinox alloys. Microstructure characterisation and surface chemistry analysis will also be presented to elucidate corrosion mechanism of hybrid steels in simulated body fluids.

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Corrosion behaviour of titanium bactericidal surfaces based on silver and copper ion implantation

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Titanium (Ti) is a widely used material in biomedical applications due to its excellent biocompatibility and mechanical properties. In addition, the surface implantation of metal ions with bactericidal behaviour has been shown to be effective in preventing bacterial colonisation in biomedical titanium implants. This work investigates the corrosion resistance and stability of a series of Ti substrates implanted with silver (Ag) and copper (Cu) ions, as well as a combination of both, by means of Metal Vapor Vacuum Arc (MEVVA) ion implantation. The surfaces of the treated metals were characterized using Scanning Electron Microscopy (SEM), Energy-Dispersive X-ray spectroscopy (EDX), and X-ray Photoelectron Spectroscopy (XPS). Furthermore, the Ag and Cu co-implanted materials were evaluated for their stability in a Hank's solution. The study demonstrates that implanting Ag and/or Cu ions does not lead to a deterioration of the corrosion resistance and stability of Ti in simulated physiological conditions. Specifically, Ag, Cu and Ag+Cu implanted samples present more noble corrosion potential and slightly higher corrosion current in Hank's solution than pure titanium due to the release of Ag and Cu ions.

Cations release from TiNb25Ta4Sn8 based 3D printed gyroid structure

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Beta titanium alloy TiNb25Ta4Sn8 was studied by means of electrochemical techniques (free corrosion potential and potentiodynamic curves) in MEM solution and dental solution (+ 200 ppm F^- / pH 4.2). The solutions were purged by oxygen, air or nitrogen to simulate different oxygen saturation in a body fluid. Thereafter, an exposures up to 6 months in the same media with subsequent released cations analyses were carried out. The dissolution kinetics model was proposed. A transport parameters of gyroid structure were estimated using polymeric (PLA) structure in the simplified diffusion experiment with fluorides in physiological saline. Finally, numeric simulation of the dissolution process in the real implant geometry, and including fluid flow as well, was done using COMSOL Multiphysics software.

Improving understanding of orthopedic implant degradation: Impact of phospholipid vesicles on the corrosion rate of CoCrMo alloy by electrochemical analysis

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Corrosion research on metallic orthopedic biomaterials has traditionally focused on simulated body fluids, aiming to reveal corrosion mechanisms, identify key influencing factors, and predict degradation rates. In the case of Cobalt-Chromium-Molybdenum (CoCrMo) alloys, passive dissolution stands as the primary corrosion mechanism, highly influenced by the chemistry of synovial fluids. However, their composition varies widely due to patient-specific factors (inflammation, joint disease) and includes components (inorganic salts, organic molecules and proteins) which play intricate roles in joint mechanics and implant corrosion. Phospholipids (PLs) serve as effective boundary lubricants, while hyaluronic acid (HA) primarily governs viscosity and lubrication. Post-test examinations have revealed the deposition of thick, insoluble "gel-like" films on implant surfaces in vivo, improving surface protection and reducing wear. However, these lubricating films remain unexplored in terms of chemical reactivity and impact on implant dissolution.

This study investigated the role of HA-phospholipids vesicles on passivation and metal ion release of CoCrMo. Open circuit potential (OCP) variations were monitored over 1 to 168 hours of exposure to cell culture medium, with or without PLs vesicles. Electrochemical impedance spectroscopy (EIS) measurements and polarization curve were employed to assess phospholipid vesicle adsorption and the rate of metal ion release, respectively. CoCrMo's OCP fluctuated around -280 mV/Ref, irrespective of time or solution. Higher dissolution was recorded at 1 hour (1.1 um/year) and then declining with time immersion and in absence of PLs. At 24h, the corrosion current density Jcorr is significantly higher in PLs than in DMEM ($p=0.003$), i.e. accelerating the anodic reactions (Figure 1). EIS measurements revealed decreased resistance in presence of PLs, suggesting their involvement in the electron transfer at the interface. Those insights offer valuable information regarding the kinetics degradation of CoCrMo as the PLs vesicles adsorb onto the metal surface, accelerating its dissolution. Combined with lubrication properties, the effect of phospholipids on the dissolution of CoCrMo orthopedic implants will help to better predict their degradation and ensure application that is more reliable.

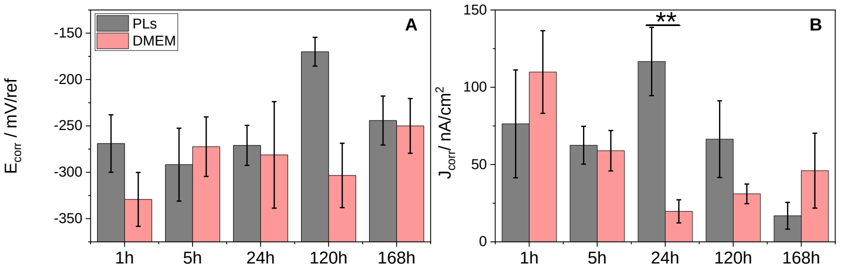

Figure 1 Values of the parameters obtained from the Tafel extrapolation of the anodic polarization of CoCrMo in DMEM with and without HA-PLs vesicles. (A) Corrosion current density J_{corr}, (B) Corrosion potential E_{corr}.

Corrosion Susceptibility of LPBF SS316L

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From a sustainability perspective, there is a drive to make materials with longer operational lifetimes thus reducing environmental impacts associated with continual replacement due to failure. This is viewed as highly important for alternative energy production such as infrastructure for offshore wind turbines or tidal power. This drive extends to stainless steels (SS) even though they have good corrosion resistance. Fortunately, it has been found that the additive manufacturing (AM) technique of laser powder bed fusion (LPBF) produces SS316 with considerably better corrosion resistance than conventionally manufactured (CM) SS316. Here we report on microstructural features that lead to improved performance. The high cooling rates of LPBF leads to a microstructure that is quite different to CMSS. For example, rapid cooling leads to extensive networks of dislocation cell structures which form to accommodate residual stress during cooling. We demonstrate that this is due to the trapping of Mn and S in these structures thereby preventing them from forming MnS particles - a major cause of localized corrosion in CMSS316. Additionally, we observed significant formation of corrosion resistant ∑3 boundaries within the LBPF-SS316 and Mo-enrichment at meltpool boundaries (Mo-MPB). We present EBSD data on statistical aspects of the ∑3 boundaries as well as electron microscopy charactisation of their structure. The Mo-MPBs have a Mo-depleted region just below them which appears to be susceptible to corrosion. There may also be an interplay between the ∑3 boundaries and the Mo-MPBs since many ∑3 boundaries either begin or terminate at the Mo-MPB. We explore possible explanations. In summary, LPBF-SS316 has quite different microstructural features to CM-SS316 and these have different corrosion susceptibilities. The importance of understanding these characteristics will lead to improved protocols for making more corrosion resistant materials.

Effect of chemical etching on surface chemistry, passivity, and corrosion resistance of additively manufactured 316L stainless steel

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Metal additive manufacturing (MAM), a process by which complex multifunctional metal parts are produced in a layer-by-layer fashion, is characterized by highly localized melting and rapid solidification, which promotes the formation of a very fine microstructure with unique directional growth features. 316L-type stainless steel (SS) fabricated by laser-based additive manufacturing (AM), one of the most studied AM alloys to date, is characterized by a fine and interconnected network of sub-granular cells with an etch-resistant border. These cells have a cross-sectional honeycomb-like shape and grow/elongate along the direction of the thermal gradient. This cellular structure is formed due to solute rejection from the solid phase into the solid-liquid interface during solidification, which occurs in a cellular/dendritic fashion because of the fast cooling-rates associated with MAM, forming a micro-segregation structure. The cellular structure in AM 316L SS has been suggested to play a significant role in the enhanced mechanical properties (yield strength and hardness) and corrosion resistance (passivity and pitting resistance) of AM 316L SS compared to conventional wrought material. The enrichment of Cr and Mo at the cells borders increases locally the pitting resistance equivalent number (PREN) of these regions, making the cellular network a physical barrier that partially contains the corrosion attack from further propagating into the material. This study analyses the effect that chemical etching has on the surface chemistry, passivity, and, in general, corrosion resistance of 316L stainless steel parts fabricated by MAM. It explores/reveals the role that this etch-resistant cellular network plays in combination with etching treatment on the surface performance of the material. Electrochemical polarization tests in NaCl solution were complemented with secondary electron microscopy and x-ray photoelectron spectroscopy analyses to gain insights on the role of etching and microstructural features on the passivity and corrosion behavior of these materials. The study followed a comparative scheme between etched specimens and specimens before etching treatment (unetched).

Co-operative enhancement of mechanical properties and pitting corrosion performance for additively manufactured type 420 stainless steel with spherical tungsten carbides

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Our study combines type 420 stainless steel enhanced with spherical cast tungsten carbide (WC/W_2C) powder to produce laser powder bed (LPBF) fusion processed metal matrix composites (MMCs). The size of utilized raw powders for the additive manufacturing process was controlled, with the resulting LPBF Type 420 + 5 wt% WC/W_2C microstructure consisting of austenite, martensitic, and W-rich carbides (WC/W_2C, FeW_3C, M_6C, and M_7C_3) ranging from nm- to μm- length-scales. The spherical cast WC/W_2C demonstrated exceptional compressive strength and wear resistance. The incorporation of W and C from reinforced particles enhanced the resistance to pitting corrosion, resulting in WO_3 and austenite phase formation. The underlying mechanisms contributing to the enhanced mechanical properties and corrosion resistance are discussed, offering valuable insights to advance the application of MMCs through LPBF additive manufacturing routes.

Microstructural features controlling localized corrosion resistance of Fe and Ni-based 3D printed corrosion-resistant alloys

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Abstract

There is a considerable interest among corrosion scientists around Fe and Ni-based alloys processed by laser powder-based additive manufacturing (AM), due to several reports on remarkable resistance of AM alloys to localized corrosion relative to their conventionally processed counterparts. The superior resistance of AM alloys is often attributed to the refined pit-initiating microstructural features. However, there is only a limited understanding with regards to the interplay between the unique AM microstructural features and distinct stages of localized corrosion (pit initiation vs. pit propagation). In this work, we investigate localized corrosion of two workhorse corrosion resistant alloys (CRAs), namely, stainless steel 316L (SS316L) and the Ni-based alloy Inconel® 625 (IN625) fabricated by AM. The rationale behind our investigation is that the AM-SS316L is a low-grade CRA whose localized corrosion resistance is controlled by pit stabilization while the alloy IN625 is a high-grade CRA whose localized corrosion resistance is controlled by pit initiation.

While the pitting potential, E_{pit}, of the AM-SS316L in neutral chloride environments is known to be remarkably high in comparison to wrought alloys based on extensive evidence in literature, the repassivation potential, E_{rp}, of the AM-SS316L is lower than that of wrought, which presents as a large positive hysteresis during cyclic polarization experiments. The E_{rp} and pit stability are especially important for AM 316L because considerable metastable pitting occurs well below E_{pit}, meaning the overall pitting resistance of AM 316L is controlled by pit stability. Based on morphological characterization of artificial pit electrodes, Cr,Mo-depleted melt pool

boundaries (MPBs) in AM SS316L lead to partial repassivation, as MPBs remain active even when the rest of the microstructure is repassivated, serving as preferential pit propagation pathways below the nominal E_{rp}. A potential practical implication is that an AM 316L component may undergo unexpected localized corrosion, crippling its structural integrity. This shows that MPBs, a nanoscale chemical heterogeneity, severely diminish the localized corrosion resistance of AM-SS316L, despite refinement of pit initiating features in the alloy.

On the other hand, AM-IN625 outperforms the wrought alloy in an aggressive concentrated chloride environment even though the AM alloy possesses extensive chemical heterogeneities. IN625 manufactured by the directed energy deposition AM process resists localized corrosion in 7.6 M LiCl at 50 ^{o}C, where the wrought alloy 625 is known to be susceptible. The likely underlying cause is the size refinement during the AM process of (Nb,Ti)-rich nitride inclusions, which are the pit-initiating features in wrought 625. AM-IN625 shows little to no metastable pitting activity, confirming that pit initiation is rate-limiting. The key insight obtained from the above two studies taken together is that AM process-induced chemical heterogeneities play a pivotal role in the case of pit stability-limited low-grade CRA such as 316L stainless steel, while the impact of microstructural refinement is high in pit initiation-limited high-grade CRA such as Ni-based alloy 625. However, it must be emphasized that the rate-limiting step of localized corrosion is not only dependent on the alloy chemistry and the microstructure but also on the environment.

Influence of LP-DED speed (LMD vs EHLA) on corrosion behavior of single layer CRA overlays in marine environments.

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Corrosion Resistant Alloys (CRA) are high-cost materials but very useful in aggressive environments because of their excellent corrosion resistance, thanks to passivity. Nowadays, surface modification technology is very useful for the designing of specific surfaces and get multifunctional material in competitiveness price. A growing technology for this application is Laser based Powder Direct Energy Deposition (LP-DED) -also known as laser cladding or Laser Metal Deposition (LMD)-. This technology offers a welding speed similar to that of arc welding, leading to dilution of the substrate. Extreme High Speed Laser application (EHLA) is a novel type of LP-DED and is applied at speeds 10 to 100 times faster than LMD. The aim of this research is to assess the impact on corrosion behavior in 3,5 wt% NaCl of the EHLA speed increase from LMD, when CRA overlays are applied with graded Pitting Resistance Equivalent Number (PREN).The results obtained are the followings: the chemical composition of coating is more similar to cladding powder with EHLA than with LMD, in terms of the microstructure the grain size is bigger with EHLA, induced by thick monolayer welding strategy. From the corrosion point of view and despite harmful phases like iron oxides, laves phases, carbides, etc. There are few interesting things to point out: firstly, corrosion potential has presented different results for each alloy, 316L powder has a more positive value with EHLA technology but with Inconel 625 the corrosion potential is more negative with EHLA. Regarding Pitting potential, in case of 316L there is an improvement comparing with LMD but in case of INCONEL 625 a contradictory effect is observed. The EIS measurements in layers manufactured with EHLA has showed that the 316L capacitive behavior and passive resistance is better than INCONEL 625, affected by the process parameters.

The main conclusion is that EHLA is beneficial for 316L. However, the corrosion resistance of the INCONEL 625 superalloy has worsened.

Microstructural and Corrosion Assessment of Directed Energy Deposited 316L Stainless Steel Layers on Conventional Material: Implications for Additively Manufactured-based Repair

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ABSTRACT

Nowadays, metal additive manufacturing (MAM) has been targeted as a promising tool for repair applications of damaged parts, among others. This approach may result in extended material lifespan and lower energy, time, and materials consumption. Nevertheless, despite this potential application, the corrosion behaviour and performance of repaired materials through MAM still need to be addressed. Herein, the corrosion behaviour of different layers of 316L stainless steel (SS) printed by Directed Energy Deposition (DED) on its conventionally processed counterpart, a relevant system for repair applications is studied. To this end, the MAM-conventional 316L SS system was immersed in a highly corrosive environment (3.5% NaCl solution at pH 2) for 7 days. The microstructure and chemical composition of the conventional-MAM system were studied before and after immersion by SEM-EDS. The results indicated that MAM layers showed significantly less corrosion damage than the conventionally manufactured part as we can see it in Fig 1. Interestingly, the corrosion attack on the DED layers correlated with their thermal history, indicating heat-affected zones (which were characterized by a depletion of noble alloying elements such as Cr) and un-melted particles as initiation sites. The results obtained in this study contribute to our understanding and future use of MAM for metal part repair, coating, and protection.

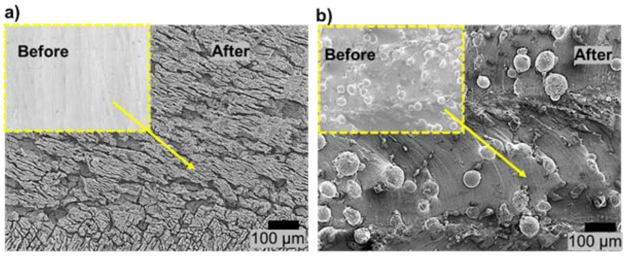

Fig1: SEM image of conventional (a), MAM (b) before and after immersed to corrosive media.

Alloy design approach to inhibiting cracking and improving corrosion resistance in laser additive manufactured Hastelloy X alloy

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Avoiding laser-printing-induced defects like keyholes or cracks to obtain higher mechanical properties and good corrosion resistance is crucial in the additive manufacturing of nickel-based alloys. In this work, we have made various experimental efforts to integrate with the results from Thermo-calc calculation. More specifically, carbon (C) and silicon (Si) were added into the Hastelloy X nickel-based superalloy to reduce incomplete interdendritic liquid filling during the laser powder bed fusion (LPBF) process. It was found that the front region of the crack tip exhibited obvious lattice distortion, numerous dislocation dipoles, and occasional twin boundaries. After optimizing the composition of C and Si, the solidification temperature range is significantly narrowed, the crack sensitivity has decreased by approximately 40%, while the crack density almost reduced by 89%. Moreover, the grain size of the modified Hastelloy X alloy is significantly refined. The high-temperature mechanical strength and corrosion resistance in chloride solution are simultaneously improved accordingly. These results provide a feasible alloy design route for the laser additive manufacturing of defect-free nickel-based superalloys with excellent anti-corrosive and mechanical properties.

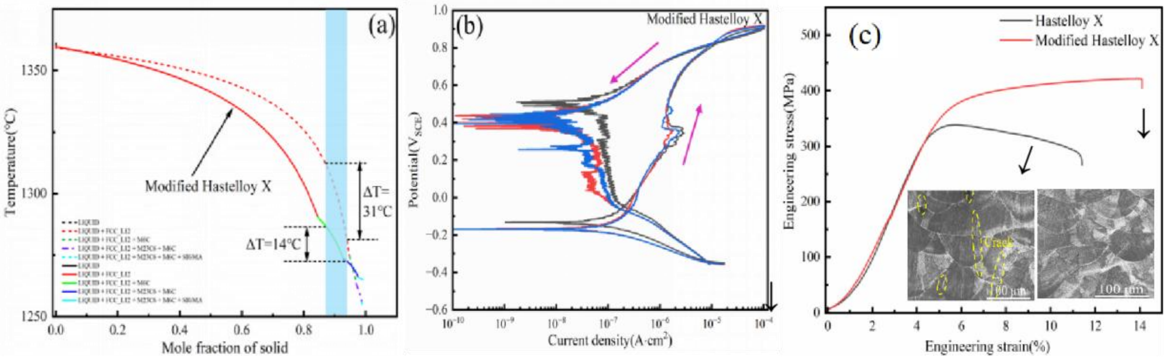

Figure 1. Hastelloy X alloy with addition of C and Si: (a) Calculated solidification curve; (b) Cyclic potentiodynamic polarization curves in chloride solution; (c) Tension strain and stress curves at 750°C.

The influence of robot kinematics on corrosion behavior of cold sprayed Inconel®625 deposits

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ABSTRACT

Due to high Chromium content, Inconel®625 is widely used as protective coating to withstand corrosion at high temperatures and harsh and aggressive environments. So far, Inconel®625 deposits are typically produced by means of thermal process routes such as surface deposition welding or thermal spraying, which both result in the formation of oxides as well as possibly metastable phases in the deposit. To prevent the oxidation, solid state deposition by cold spraying (CS) can offer advantages for building-up deposits in thickness of up to several millimeters. However, CS of nickel-based superalloys like Inconel®625 is still challenging due to their high strength. Thus, the current study explores the influences of robot kinematics (stand-off distance (SoD) and travers gun speed ($V_{trav.}$)) on porosity and corrosion performance of sprayed deposits. Inconel®625 powder was cold sprayed on structural carbon steel substrates using N_2 as propellant gas. The corrosion behavior was then examined by salt spray test in accordance with DIN EN ISO 9227 and open circuit potential analysis. The quality of as-sprayed deposits was characterized in terms of microstructure, porosity, cohesive strength and the corrosion behavior. The results demonstrate that the corrosion resistance can be improved by decreasing the SoD as well as running the CS process with moderate and lower values of $V_{trav,}$ respectively. The findings show that reference deposit with minimum thickness of 200 µm is essential to ensure the noble behavior. Microstructural analyses reveal that the local corrosion attack takes place via the larger pores and non-bonded interfaces as penetration path, which leads to break the passive film and further penetrating the corrosive medium towards interior layers.

Influencing effect of surface roughness on the oxidation and carburization behaviour of LPBF Alloy 625 in a simulated high temperature Allam cycle environment.

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Failing to promptly address the dependence of power production on fossil fuel combustion could lead to increased rates of climate change. The Allam cycle, a climate-friendly novel power generation cycle, utilises CO_2 as its working fluid whilst minimising emissions thus contributing to net-zero goals. The Allam cycle operates at temperatures up to 1100ºC and pressures up to 300 bar. These extreme operating conditions poses challenges to materials' selection for turbomachinery. Additive manufacturing (AM) is a promising technique that can improve time on component production runs and reduce material waste and cost. Laser powder bed fusion (LPBF) an AM technique which offers opportunities in manufacturing nickel-based superalloys.

LPBF is notable for producing high surface roughness as-manufactured, although this can be minimised through design or, for external features, by later post-processing. Thus, adjusting roughness is important for improving performance due to LPBF notability in high surface roughness. This paper investigates the effect of surface roughness on cyclic oxidation and carburization behaviour LBPF Alloy 625. Testing was carried out at 800^0C for 1000 hours in CO_2 + 2.7mol% H_2O + 1.43mol% N_2 + 0.17mol% O_2 + 300ppm SO_2, simulating conditions relevant to an Allam cycle.

Cylindrical coupons of AM Alloy 625 were prepared with different degrees of surface roughness: 600 UK grit size, 6 µm polished, and as-received. The oxidized samples were analysed using scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDX) to characterize the extent of oxide scale growth, depth of carburization (electrochemical etching), and evolution of surface morphology. Electron backscatter diffraction (EBSD) provided grain orientation and boundary character information to elucidate diffusion pathways activated.

Findings show surface roughness plays a significant role in influencing oxidation kinetics, with the polished samples having lower oxidation kinetics, thinner Cr oxide scales, and internal Al oxide. In addition, the LPBF process resulted in the formation of a Nb-rich needle precipitate phase which was observed below the Cr oxide.

Keywords: CO_2, oxidation, carburization, Allam cycle, additive manufacturing, LPBF, surface roughness, Alloy 625.

Investigation on corrosion behavior of laser powder bed fusion 70/30 copper-nickel alloy

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70/30 copper-nickel alloy was manufactured by laser powder bed fusion (LPBF), followed by the comprehensive investigation on the relationship between its microstructures and mechanical properties as well as corrosion behavior. The results show that dislocation tangles at cellular boundaries can greatly contribute to its superior tensile properties than the commercial counterpart. In addition, the combination of dislocation tangles and nanoscale copper enrichment/nickel depletion directly leads to the heterogeneous film formation process during immersion in corrosive media. Moreover, experimental and computation results both suggest that exposed facet is another important role to determine the corrosion behavior of LPBF 70/30 copper-nickel alloy.

Keywords: 70/30 Copper-Nickel Alloy; Laser Powder Bed Fusion (LPBF); Dislocation Tangles; Cu segregation/Ni depletion; Corrosion Behavior.

Corrosion behavior of Al10SiMg alloy manufactured by laser powder bed fusion

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Abstract

This work investigates the corrosion behavior of Al10SiMg aluminum alloy produced by laser powder bed fusion (L-PBF). In particular, the behavior of the as printed surface is compared to that of the nearly defect-free polished surfaces (bulk).

The L-PBF specimens investigated in this work were manufactured with a Concept Laser M2 Cusing machine, equipped with a 400 W single-mode CW ytterbium-doped fiber laser with emission wavelength of 1070 nm. Process parameters were optimized in order to obtain samples with very low porosity. Contouring tracks were scanned to improve the quality of the as-built surface. Besides, part of the samples was produced without contouring in order to investigate the effect of surface roughness on the corrosion behavior of the as printed specimens.

A detailed characterization of the microstructure and electrochemical behavior of the L-PBF Al10SiMg aluminum alloy was carried out by FE-SEM and electrochemical methods (potentiodynamic polarization). The morphology of the attack was evaluated after immersion tests and galvanostatic polarization measurements. This experimental approach was employed to highlight the effect of typical defects and microstructure on the initiation of localized corrosion in L-PBF Al10SiMg aluminum alloy.
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Effect of surface treatment on the anodizing of SLM-produced AlSi10Mg alloy

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In recent years, additive manufacturing (AM), e.g. selective laser melting (SLM), has offered new opportunities to produce Al alloy. In vacuum technologies, AM AlSi10Mg has attracted increasing attention to replace conventional 6xxx alloys due to its excellent properties, such as good thermal conductivity, good weldability and high strength and stiffness to weight ratio associated to the great design flexibility and mass reduction of SLM parts. Identified challenges for their vacuum compatibility remain surface quality, porosity and limited hardness. Part of those can be overcome by using hard anodizing as a surface finish.

This study focuses on the effect of surface treatment on the hard anodizing behavior of AM AlSi10Mg alloy. Three industrially relevant surface pre-treatments, namely as-built, sandblasted, and machined, were investigated to determine to which extend they affect the growth of porous anodic Al oxide layers and the related oxide properties.

Electrochemical measurements, e.g. electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curve, showed, as expected, that machined surfaces are drastically less active than the as-built or sandblasted ones. Interestingly, sandblasting does not fully remove the defective surface layer. This is expected to play a determining role in the properties of anodic barrier-like Al oxides as well as the subsequent porous oxide growth rates.

A comprehensive microstructural analysis combined to structural and electrochemical characterization was conducted to evaluate the performance of the hard anodic coating as a function of anodizing parameters, e.g. surface pre-treatment, electrolyte, temperature and galvanostatic vs potentiostatic growth.

Moreover, the coatings grown in the lab will be compared to industrially grown anodic Al oxides to assess the scalability of the process.

Functional Layered Double Hydroxides coatings on Additively Manufactured Al-Mg alloy for active corrosion protection

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Abstract:

The demand for complex-shaped metallic components with high-cost efficiency, environmental sustainability, and minimal energy impact has triggered research in Metal Additive Manufacturing (AM) or 3D printing. This study focuses on two main challenges: (i) microstructural characterization of a 5356 alloy (Al-Mg alloy) produced by wire arc additive manufacturing (WAAM), and (ii) its surface modification by the formation of Mg-Al-layered double hydroxides (Mg-Al-LDH) to enhance its corrosion resistance in aggressive environments.

The microstructural characterization of the 5356 alloy (OM, SEM, TEM, AFM) reveals a unique microstructure and distribution of secondary phases (e.g., Al3Mg2) compared to their conventionally processed 5XXX alloys in literature.

The synthesis of LDH coating on the 5356 AM alloy surface and the additional intercalation/deposition of 8-hydroxyquinoline as a corrosion inhibitor (8-HQ; LDH-8HQ coating) in the LDH coating were successfully addressed. The characterization (SEM, FTIR, and XRD) and electrochemical assessments (EIS) of the LDH and LDH-8HQ coatings reveal (i) a successful intercalation/adsorption of 8-HQ on the LDH coating, (ii) a corrosion resistance improvement of the 5356 AM alloy after the formation of LDH/LDH-8HQ coatings, and (iii) 8-HQ release in saline media and active protection.

Effect of heat treatment on corrosion behaviour of AlSi10Mg alloy fabricated by LPBF

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Abstract

The AlSi10Mg, is an aluminium alloy that combines good mechanical properties, very good castability and heat-treatable capability as well as low density. For these reasons, it is frequently used in the automotive, aerospace and automation sectors to fabricate, by traditional die-casting procedure, many large structural components and thin parts, such as outboard automotive parts, instrument cases and cover plates, particularly when a certain corrosion resistance is also required. Because of its low hot cracking susceptibility, the AlSi10Mg can be additively manufactured allowing the fabrications of complex near-net shape parts by melting an alloy powder bed layer by layer.

In this paper we assess the effects of different post-processing traditional and modified T5 and T6 heat treatments on the corrosion behaviour of an AlSi10Mg fabricated by laser powder bed fusion (LPBF).

The corrosion behaviour of the as-built and heat-treated specimens was evaluated by electrochemical impedance spectroscopy and potentiodynamic polarization tests during 7 days of immersion in chloride containing solutions (0.1M or 0.6 M) at 30°C.

The evolution of the microstructure after heat treatment and the morphology of the corrosive attack were studied by scanning electron microscopy (SEM) coupled with energy dispersive x-ray (EDX) and by X-ray diffraction (XRD) analyses.

The results showed that the heat treatments significatively modify the specimen microstructures and have a beneficial effect on the corrosion behaviour, reducing the corrosion rates in the tested environments.

Effect of heat treatments on the corrosion behaviour of additively manufactured aluminium alloys with copper

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Additive manufactured aluminium alloys with copper are recently receiving increasing attention as they are expected to exhibit outstanding tensile strength after age hardening. However, the fast-cooling rates promoted by additive manufacturing processes cause the modification of both the microstructure and the distribution of second phases and precipitates and the tensile strength is strongly affected by the heat treatments temperature and time. The corrosion performances of this alloy series are generally considered poor due to the presence of copper, which strongly promotes general as well as local corrosion phenomena. Additive processing of materials promotes alpha aluminium matrix oversaturation in alloying elements giving rise to brand new materials with unique corrosion morphologies promoted by the uneven distribution of alloying elements especially at melt pool boundaries. In this work, the corrosion behaviour of laser powder bed fusion-processed alloy Al2139 AM and a AlSi9Cu3 is investigated, and the corrosion performances are compared to AlSi10Mg alloy, as benchmark. Microstructures were assessed by optical digital microscopy, scanning electron microscopy equipped with x-ray electron dispersive spectroscopy and atomic force microscopy to assess second phases redistribution. Intergranular corrosion tests were also performed to highlight the unique corrosion behaviour occurring at melt pool boundaries. The effect of surface finishing and heat treatments was also studied. Alloy 2139 exhibited penetrating selective corrosion attack of aluminium matrix at the melt pool boundaries as well as AlSi9Cu3 due to the presence of very finely distributed copper-rich second phase. However, the corrosion process and its morphology are strictly dependent upon the microstructure and the ally composition. The effect of heat treatments appears to be effective in certain cases to mitigate the extent of the penetrating attack due to the different re-distribution of copper rich phases and precipitates.

Aluminum alloys produced by additive manufacturing: the effect of the native oxide

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The use of additive manufacturing technologies allows many industries to obtain components directly in their final shape, eliminating the need of tooling or final machining. When using a net-shape process, it is of paramount importance to assess the properties of the native oxide layer that forms on the material during printing.

In this study, two materials were analysed: A20X, and Scalmalloy. They were both produced by laser powder bed fusion, using an EOS M270 printer, in an inert atmosphere (Argon) with an oxygen level below 1000 ppm. After production, some of the samples were heat treated, in order to assess the effect of quenching and tempering on the structure of the superficial oxide layers. The electrochemical behaviour of the materials (both in as-built and heat-treated conditions) was characterised by means of Electrochemical Impedance Spectroscopy (EIS) and potentiodynamic polarization, acquiring the measurements in a solution containing 50 vol% of ethylene glycol in water. After electrochemical tests, the morphology of the samples was analysed by electron microscopy and its chemical composition was assessed by EDS and ToF-SIMS analyses.

Results showed that, in as-built conditions, A20X alloy is characterised by a protective oxide layer, having a structure composed of two layers. After heat treatment, both EIS and potentiodynamic polarization highlight a higher corrosion current and a less protective oxide layer.

A different behaviour was found for the Scalmalloy: in this case, the native oxide layer in as-built conditions was less protective, but it was not affected by the heat treatment.

The conclusions of this study are of great relevance to develop and optimise net-shape processes by means of additive manufacturing technologies.

Correlating microstructure and corrosion modes of AA2024 alloy prepared by laser additive manufacturing: a comparative approach

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Modern metal manufacturing has seen a transformation due to the development of additive manufacturing (AM), often termed as 3D printing. This technique has lately become popular for creating metallic components out of a range of metallic alloys and has experienced exponential growth in terms of technologies and applications. The main advantages are the low carbon fingerprint, net shape manufacturing, effective material utilization, adaptability to small-scale (prototyping), and the capacity of exploring alloy compositions not previously achievable through traditional ways. In this sense the aeronautical sector has a big interest on AM of light and mechanically resistant aluminum alloys that are widely used in aeronautics. However, corrosion is a major concern in this kind of aluminum alloys. The AM produces a different microstructure that comprises distinct porosity, dislocation networks, grain shapes, residual stress, and surface roughness and this kind of differences could be correlated with the corrosion resistance. In this study, the corrosion resistance of additive manufactured (AMed) AA7075 was evaluated and compared with the conventional alloy by immersion tests in sodium chloride solution, monitored by electrochemical impedance spectroscopy (EIS). The localized corrosion susceptibility was studied by immersion in three test solutions, specifically sodium chloride solution (3.5% NaCl), EXCO solution, according to ASTM G34-18, and a solution for intergranular corrosion (IGC) test recommended by ASTM G110-15. The results present the correlation between corrosion resistance, microstructure and surface finishing.

Keywords: Additive manufacturing, SLM, Corrosion, AA7075 alloy.

Acknowledgments: This study was performed in the framework of programme Win^{2}Wal financed by SPW- Economie Emploi recherche (Wallonie) - project OptiSurFAM- convention 2310020

Improvement of the Pitting Corrosion Resistance of AA7075 by Mg_2Si Addition and Cerium Conversion Coatings

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AA7075 is a high-strength aluminum alloy. Although AA7075 has attracted attention in the field of additive manufacturing, this alloy is known for its high susceptibility to pitting corrosion [1]. In this study, AA7075 containing Mg_2Si particles was fabricated by spark plasma sintering. In addition, cerium conversion treatments were performed on the specimen, resulting in the formation of cerium-based coatings. The dip-and-dry test indicated that Mg_2Si addition and the conversion coatings improved the pitting corrosion resistance.

Objective

To evaluate the pitting corrosion resistance of AA7075 containing Mg_2Si particles with and without cerium conversion coatings

Experimental

Gas-atomized AA7075 powder and Mg_2Si powder were mixed, and sintering was performed by spark plasma sintering. As conversion treatments, the specimens were immersed in Ce^{3+}-containing solutions. To evaluate the pitting corrosion resistance, dip-and-dry tests were conducted. During the tests, the specimens were dipped in 0.1 M NaCl for 20 min and dried at 298 K and 50%RH for 60 min as one cycle.

Results

In 20 cycles of dip-and-dry, mass loss was reduced by Mg_2Si addition. In addition, conversion coatings were formed on the surface of the specimens containing Mg_2Si particles by the conversion treatments, and the corrosion resistance was improved.

Conclusions

The Mg_2Si addition to AA7075 improved the pitting corrosion resistance and enabled effective and efficient conversion treatments with Ce^{3+}-containing solutions.

Reference

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Corrosion Behaviour of Plasma-Nitrided Metallic Materials Produced by Additive Manufacturing

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Objective:

Additive manufacturing (AM) techniques, including laser powder bed fusion (LPBF), produce metallic materials featuring distinct microstructural characteristics and surface finishes. This study focuses on improving the surface properties of various AM-produced metallic materials through surface hardening treatments like plasma nitriding. Additionally, it seeks to draw comparisons with materials produced via conventional manufacturing methods, aiming to establish a correlation between the enhanced surface characteristics and their manufacturing processes.

Results:

This presentation explores how additive manufacturing (AM) influences the corrosion, mechanical, and tribological properties of metals like stainless, maraging, and tool steels, plus nickel alloys, before and after plasma nitriding. It will discuss how AM's finer grains could improve corrosion resistance by better passive layer formation. AM reduces non-metallic inclusions and avoids macro segregations, aiding corrosion resistance. However, AM's porosity may increase pitting and crevice corrosion risks, and its rapid thermal cycles could heighten stress corrosion cracking due to residual stresses. While plasma nitriding is generally beneficial in enhancing wear and corrosion resistance, the specific microstructures of AM materials can, in some cases, introduce defects that negatively impact corrosion resistance.

Conclusions:

Plasma nitriding significantly improves the corrosion resistance of materials produced via AM, in some instances outperforming those manufactured traditionally. Nonetheless, the distinctive microstructures produced by AM can necessitate further heat treatments to mitigate cracks and other defects.

Corrosion resistant alloys assessment in concentrated MEA and PZ aqueous solutions

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Corrosion resistance of seven stainless steel grades (316L, 304L, 2304 DSS, 2205 DSS, 2507 DSS, E-Brite 26-1, 254 SMO) and one nickel-base alloy (Alloy 625) have been assessed in two CO_2 loaded concentrated amine aqueous solutions, namely with monoethanolamine (MEA) and piperazine (PZ), simulating CO_2 stripping processes of CCUS techniques.

Corrosion has been evaluated on laboratory scale, applying more severe conditions than the operative ones for pressure and temperature to accelerate the corrosion process. Material coupons have been exposed in autoclaves for up to twelve weeks. Weight loss determination, scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS) of exposed surfaces, and residual solvent analytics per inductively coupled plasma (ICP) have been performed.

In the CO_2 loaded MEA aq. solution, three behaviors have been found. Some steel grades performed in a comparable way. Nickel-base alloy, lean duplex (2304 DSS) and superferritic (E-Brite 26-1) grades outperformed the previous one. 316L experienced significant uniform corrosion of at least one order of magnitude higher compared to the other alloys. This result, that is not unexpected based on literature, which shows that 316L may present borderline behavior in high concentrated MEA solution at enough high temperatures. The results also highlight sensitivity of 316L to the test conditions, which needs to be considered when designing the process conditions of CO_2 capture plants.

In CO_2 loaded PZ aq. solvent, all material grades show comparable behavior, confirming a lower aggressiveness of solutions containing this secondary amine.

Droplet corrosion behavior of Low alloy steel under impure CO_2 environment

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Abstract

Carbon capture and storage (CCS) has emerged as a key technology in the global efforts to reduce CO_2 emissions and combat climate change. However, corrosion of CCS infrastructure presents new concerns. Corrosion in CCS system can occur at different stages, including capture, transportation, and storage. This study focuses on the challenges associated with transporting and storing CO_2 due to water drop-out as a result of lower solubility. Water once dropped out of CO_2 gas stream is detrimental to the corrosion resistance of steel pipelines since CO_2 dissolves in the condensed water to form carbonic acid (H_2CO_3) with a low pH of <3. The droplet/drop-out corrosion is further exacerbated by the presence of impurities such as H_2O, SO_x, NO_x, H_2S, O_2 and amines in the CO_2 stream.

In this study, the corrosion behavior of L80 1Cr pipeline steel, under simulated condensation-prone CO_2 environment, was investigated using a combination of electrochemical and in-situ surface monitoring. Moreover, surface analysis techniques such as optical microscopy (OM), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), x-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), etc. were employed to observe the corroded surface morphologies and understand the corrosion products developed across varying exposure times. Corroded surface analysis revealed a general corrosion pattern with severe localized corrosion. The corrosion rate values at different exposure times were found to decrease with time, and this was attributed to formation of oxide film on the metal surface. Iron carbonate, oxides and hydroxides were detected as main constituents of the thin film formed on the corroded steel surface. The variation in temperature and humidity level on the steel surface and the test environment played significant roles in the corrosion process. This work explores how environmental variables and material response can impact material selection and corrosion control measures in CCS applications.

Corrosion of carbon steel exposed in water and dense phase CO_2

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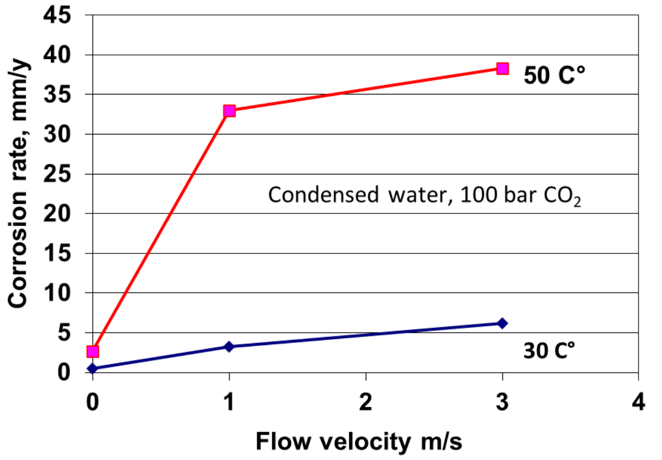
Dense phase (liquid and supercritical) CO_2 is usually transported under dry conditions (no separate aqueous phase) in carbon steel pipelines or tanks. A water phase can be present in pipelines after commissioning (due to pressure testing/hydrotesting), because of accidental ingress of water or due to off- spec. CO_2. The combination of water and CO_2 can be very corrosive and corrosion rates up to 40 mm/y have been measured in laboratory experiments where carbon steel has been exposed under conditions not giving protective corrosion product films or inhibitor films on the steel surface. Much lower corrosion rates (1-2 order of magnitude) are observed when protective corrosion product films precipitate and cover the steel surface. Published experimental results and in-hose data show that protective film formation depends very much on temperature, flow velocity, concentration of dissolved corrosion products, the water volume to the steel surface ratio and the presence of certain impurities (O_2, H_2S, NO_2, SO_2) and their reaction products.



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The present work discusses the effect of the corrosion rate controlling parameters and focuses particularly on how the corrosive environment and the corrosion rate change when the concentration of dissolved corrosion product increases.

Corrosion concerns in Carbon Capture and Sequestration projects – A call for action

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Carbon Capture and Storage (CCS) is an essential part of the Energy Transition, lowering the CO_2 emissions at industrial plants. Many CCS projects are being developed, however they tend to under-estimate corrosion risks. Although CO_2 itself is not corrosive, even low levels of impurities in liquid or dense phase CO_2 will result in drop out of a separate, acidic liquid. The risks related to this so-called 'acid dropout' are currently addressed via the CO_2 specification which strongly restrictions impurity levels. However, this is not considered a fully solid barrier and requires additional mitigation measures to prevent earlier corrosion failures. In addition, because CO_2 is not flammable nor highly toxic, the HSSE risks related to a potential release of liquid or dense phase CO_2 are often considered limited. This is a misconception, which further underlines the necessity of robust corrosion control in CCS projects.

Key words: Carbon Capture and Storage, CCS, Acid Corrosion, Impurities, Corrosion Barrier Management

TX22 duplex and TX25NP superduplex 125ksi corrosion performance under simulated CO2 injection well conditions

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Nowadays, carbon capture and underground storage (CCUS) rises like one of the technologies for mitigating climate change and meeting one of the most challenging targets of the Paris agreement: 14% of the total emissions reductions by 2060 must come from CCUS. In this context, material selection for the CO2 injection wells depends on the presence and type of impurities related to the CO_2 source and the capture technology used. In this work, particular environmental conditions in CCUS Kasawari project offshore Sarawak in Malaysia were considered to test the corrosion resistance of cold hardened grade 125ksi, TX22 S31803 duplex and TX25NP S32750 superduplex seamless tubes. Two different environments containing different type and level of impurities simulating the in-service conditions in the CCS injection wells were selected. To study the stress corrosion cracking (SCC) and crevice corrosion (CC) of both materials four-point bend (4PB) test according to NACE TM0316 and ASTM G48 method E were used respectively. The first environment consisted in 1650 mg/l NaCl and 410 mg/l of CH_3COONa in the liquid solution (pH around 2,9) and 2,32 psi of H_2S and 2900 psi of CO_2 at 194ºF (90ºC) in the gaseous phase. The second environment introduced different type and content of impurities NaCl, CH_3COOH, KCl, $CaCl_2$, $MgCl_2.6H_2O$, $NaHCO_3$ and Na_2SO_4 (pH around 3,7) and maintain the same gaseous phase and testing temperature. The test duration was 720 hours in both experiments. In addition, to find out if there was an effect of the crevice former material on the results, both PVC and metal crevice formers of the same superduplex material were used to test the TX25NP. The TX22 did not show any SCC in any case, but CC was observed in one of the tested specimens of each environment. The TX25NP did not show any SCC or CC in any case and the effect of the type of crevice former was negligible in this grade. The characterization of the TX22 corroded specimens was performed by means of optical and scanning electron microscopy. Although the simulated PREN of ferrite was higher, pits were clearly spread over this phase. Finally, based on these results the selected material for the Kasawari project was grade TX25NP 125ksi.

Hydrogen Embrittlement of 13Cr Martensitic Stainless Steel in Simulated Downhole CCS Environments

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Carbon Capture and Storage (CCS), in which CO_2 emissions into the atmosphere are reduced by underground injection of generated CO_2, is attracting strong attention as one means of achieving carbon neutrality. In CCS, the impurity gas contained in the CO_2 differs depending on the CO_2 source. CO_2 captured from the blue hydrogen production process is contaminated with H_2 as an impurity gas.

Since existing oil and gas production technology is used for CCS, downhole tubing and casing are used as the CCS injection pipe. Regarding carbon steel, hydrogen adsorption and fracture behaviour in high-pressure hydrogen gas has been reported [1]. In that report, the amount of adsorbed hydrogen in carbon steels such as L80 and P110 in 20 to 100 bar H_2 was measured at 25 °C or 80 °C , and was found to be 90 % lower than that in a sour environment (Solution A specified in NACE TM-0177). It was also reported that hydrogen embrittlement (HE) did not occur in either L80 or P110 in a constant load test in high-pressure hydrogen gas.

In CCS, high corrosion resistance is required in the tubing materials because CO_2 gas is dissolved in geological formation water, resulting in a lower pH. Therefore, 13Cr is a candidate material for CCS injection tubes, but there is little data on HE in high-pressure hydrogen gas environments.

In this study, the hydrogen adsorption of 5 types of 13Cr martensitic stainless steel in high-pressure hydrogen gas was measured to collect systematic data on HE in CCS applications. The HE susceptibility of each steel was determined by a constant displacement test in which various amounts of hydrogen were introduced under cathodic charging. As a result, it was found that no HE occurred in any of the investigated martensitic 13Cr stainless steels at hydrogen contents corresponding to the hydrogen partial pressure assumed in CCS.

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Evaluating Performances of Cement-Metal Interface in CO_2 Storage

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Using non-producing oil wells for CO2 storage is one of vital strategy of Carbon Capture, Utilization and Storage (CCUS) applications to migrate climate change. In this process, captured CO_2 is injected in supercritical form, mixing with certain unwanted impurity such as H_2O, H_2S, SO_x, NO_x. Subsequently, specific cement slurry is pumped down the wellbore and cured at high temperature to form cement plugs to prevent CO_2 from emission and immigration into adjacent fluid-bearing formations. However, the unavoidable microporous and micro-annuli structure of cement can act as potential conduits for the transport of corrosive agents to the interface of cement and metal of casing materials, thus leading to metal corrosion issues and cement degradation, which become a safety threaten to the long-term CO_2 storage.

This study aims to understand the corrosion/degradation behaviour of the abandoned pipelines/casing used for CCUS initially focusing on evaluating the performances of cement-metal interface and furthermore placing particular emphasis on the impact of various CO2 conditions and impurities. Galvanostatic electrochemical technique combined with abundant characterization techniques, such as Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX), X-ray tomography (CT), X-ray diffraction (XRD), transmission electron microscopy (TEM) is employed for qualitative and quantitative insights into the intricate details of reaction products at interface and identify instances of phase debonding. To further explore the mechanism of metal corrosion and cement degradation, Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES) analysis and Thermogravimetric (TG) analysis are applied to investigate material dissolution and cement carbonation, respectively.

The laboratory-scale findings providing a basic understanding of performances of cement-metal interface, will be used to define testing parameters for a flow loop test facility, simulating real-world well conditions to ensure the long-term reliability and integrity of infrastructure in CO_2 storage.

Multi-method characterisation of the thermal ageing of winding insulation for electric machine lifetime evaluation

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With the profound and continuous growth in electric mobility as one of the drivers, the use of electric machines is become more widespread. These machines are comprised of machine windings (stators, rotors, generators…) that must be well insulated to prevent the flow of unwanted current between conductors, and thus short-circuits. The rising demands of these electric machines, namely through increasing the operational voltages, requires re-evaluation with regards to their long-term reliability. The expected lifetime of an electric motor can be improved with machine design and materials selection as a function of the operating conditions, wherein health monitoring is also considered a key aspect in technological evolution.

Current understanding is that electric machines usually fail through mechanical or electrical faults. The electric modes of failure are often linked to the premature cracking or delamination of polymeric winding insulations exposed to the severe electrical, thermal, mechanical, and environmental stresses encountered within modern electric machines. In this study, we present the basics of electrical insulation systems, their function and the materials used, followed by primary ageing mechanisms, and associated stresses. The focus will be given to thermal ageing. Overheating within machines encourages insulator faults leaving the risk of partial discharges – which themselves exacerbate insulated winding degradation. We share progress on the *in situ* and *ex situ* methods employed to evaluate this ageing phenomenon. Differential scanning calorimetry is shown to be advantageous in characterising the temperature resistance of different insulators and indicating thresholds to not exceed. Whereas *ex situ* X-ray computed tomography sheds light on the extent of the damage encountered by thin polymeric films, the development of a bespoke microfluidic electrochemical cell permits probing the dielectric properties of damaged and undamaged winding insulations.

The influence of hydrogen permeation on the protection performance of the Cu coating of nuclear waste containers

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Hydrogen permeation and corrosion behaviour of Cu-coated carbon steel under simulated nuclear waste disposal conditions of the Beishan area have been investigated. The permeation current (with −500 μA cm^{-2} charging current) decreased from 3778 to 141 and 47 nA cm^{-2} respectively when 5 and 10 μm thick Cu coatings were electrodeposited on the steel. The XRD analysis suggests the formation of CuH during the hydrogen charging treatment, and its subsequent decomposition formed a protective CuOH/Cu_2O layer on the charging surface when exposed to simulated groundwater for 44 h. No damage to the Cu coating-steel interface was observed in the cross-section analysis.

Mapping hydrogen activity at high local resolution by scanning Kelvin probe techniques

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Knowledge on hydrogen distribution in materials is of crucial importance on meeting the challenges met in energy and transport systems. The Scanning Kelvin Probe (SKP) technique has been used for many years to map and monitor hydrogen in materials. It is a non-destructive technique, unlike Secondary Ion Mass Spectroscopy (SIMS) or Atom Probe Tomography (APT), and can provide high-resolution temporal and spatial measurements of local activity. This information can be used to understand the interaction of the material with hydrogen. Although successful results have been reported, there are still challenges to be addressed. To accurately measure the amount of hydrogen present, a suitable layer is required. However, this layer can quickly become saturated at high activities. Additionally, in very small microstructures, hydrogen from behind can obscure the observation of the local interaction of the hydrogen we want to study locally. These problems and strategies to overcome them will be presented.

Comparison of methods for measuring hydrogen content in metallic materials

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The presence of hydrogen in a metal can significantly alter its mechanical properties. In the development and processing of many alloys, hydrogen is the cause of porosity, cracks, and significant embrittlement. Moreover, the diffusion of hydrogen into metallic materials can lead to delayed or sudden rupture processes. Given its consequences, the measurement of hydrogen in materials is of great interest. One of the techniques used to address this demand is TDS (Thermal Desorption Spectroscopy) which measures the hydrogen content, and the information obtained is therefore not local but global. However, hydrogen is not distributed homogeneously in materials. Microstructural defects such as grain boundaries, precipitates, dislocations, vacancies and oxide layers or metallic coatings are all parameters which will influence the hydrogen distribution.

Therefore, it is interesting to couple TDS with techniques for local observation of hydrogen, which would provide more precise information on the locations where hydrogen segregates. Hydrogen measurements using TDS are carried out in AISI316L alloys and compared to, electrochemical permeation, Time-of-Flight Secondary Ion Mass Spectrometry (ToF SIMS) and Laser Induced Breakdown Spectroscopy (LIBS). An analysis of the advantages and complementarity of the techniques was then conducted.

Towards durable Ni-based catalysts for HER in acidic medium: synthesis and performance of macroporous Ni-P coatings

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Hydrogen is playing a crucial role in clean energy transition opening new possibilities to low-emission transportation, energy generation and storage. Nevertheless, its production still predominately relies on the fossil fuels. The commercial success of H_2 production through electrolytic water splitting is hindered by the use of noble metal-based electrocatalysts which offer superior performance but have high cost and scarcity. The exploration of alternative, affordable, and earth-abundant electrode materials with outstanding durability and electrocatalytic properties is a challenge.

In this work, Ni-P alloys with two different P contents (2 wt.% and 12 wt.%) were fabricated via electroless deposition onto macroporous polyurethane foam and carbon cloth templates to obtain electrodes with enhanced activity towards hydrogen evolution reaction (HER) in acidic medium. The structural transformations caused by heat treatment and their effect on resulting HER activity of the catalysts was investigated. The stability of the electrodes was studied by combining the chronopotentiometry and electrochemical impedance spectroscopy, keeping the catalysts under working conditions for up to 168 h (7 days). The performance of the macroporous catalysts was compared to dense counterparts and conventional Pt/C catalyst. Furthermore, the insights into the possible catalysts' degradation mechanisms are gained based on the samples and electrolyte characterization after the testing. The obtained results demonstrate that macroporous Ni-P alloys possess the required characteristics of a promising electrocatalyst: low overpotential for HER, low Tafel slope, and excellent stability in acidic medium.

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The investigation of hydrogen embrittlement behaviours of X65 pipeline steel and its weldment

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Hydrogen is becoming an increasingly utilized clean and renewable energy source in various industries, necessitating the development of safe and efficient infrastructure for its transport and storage. While high-strength steel pipelines offer a cost-effective solution, the challenge of hydrogen embrittlement (HE) arises. HE occurs when hydrogen absorption and permeation in metals degrade local mechanical properties, rendering the material susceptible to hydrogen-induced cracking (HIC) at stresses lower than the yield stress. Understanding the behaviour and underlying mechanisms of HE and HIC is crucial for predicting the performance of hydrogen industry infrastructures. This research firstly investigated the HE susceptibility of X65 pipeline steel under the impact of various electrochemical hydrogen charging conditions (different pH levels, charging current densities, and charging periods). Subsequently, the HE and HIC behaviour in the weldment of X65 steel pipeline were assessed using 'optimized' electrochemical hydrogen charging conditions. Results indicate that HE susceptibility of X65 steel varies significantly with hydrogen-charging electrolytes, and to a lesser extent, with electrochemical charging variables. Charging in low pH electrolytes, higher current densities, and longer periods leads to increased susceptibility. Within the weldment, the weld metal is the most susceptible zone to HE and HIC, attributed to the differences in microstructural features such as Ti-rich inclusions, martensite/austenite constituents, and prior austenite grain boundaries, as key crack initiation sites under hydrogen influence.

Evolvement of the passive layer of 316L stainless steel employed for bipolar plates in hydrogen fuel cells

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Thin 316L stainless steel (SS) sheets are being implemented as bipolar plates (BPP) for proton exchange membrane fuel cells (PEMFCs). Besides the performances, the long term durability of a PEMFC is critical for heavy duty applications and it is essential to gain a deeper understanding of the contribution of the bipolar plate on the whole degradation of the PEMFC performances over time. Therefore, changes in the passive layer, the main source of corrosion protection, need to be characterized comprehensively, starting from the SS sheets material, along the various steps of the industrial manufacturing process towards to the final BPP product, as well as the subsequent changes occurring during PEMFC operation.
We implemented a tool box including X-ray photoelectron spectroscopy and time of flight – secondary ion mass spectrometry to characterize the surface chemical composition and the chemical depth profile of the passive layer, respectively. These were combined with results from electrochemical investigations in conditions simulating the PEMFCs environment, tracking the open circuit potential and the corrosion current, and characterizing the passive layer with electrochemical impedance spectroscopy (EIS). The power law model was used to extract the passive layer thickness, and a Mott-Schottky analysis was conducted to extract the charge carrier densities of the chromium oxide and the iron oxide layers[1]. We quantified severe changes in the structural and chemical characteristics of the passive layer at all the steps experienced by the 316L SS with, furthermore, the EIS enabling the analysis of the passive layer not only as a whole, but also a disentangling of the respective changes in the iron oxide and chromium oxide layers.

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Study of the degradation of proton exchange membranes (PEMFC) by FIB / FEG / SEM.

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Fuel cells based on proton exchange membranes (PEMFC) are characterized by their high energy density, demonstrating high performance in different applications both in transportation (automotive, aircraft, trains, and ships), stationary (buildings, industries) and portable. Their use with hydrogen energy contributes to cleaner and safer energy production. However, PEMFCs have limitations in terms of cost, reliability, and durability. For this reason, fuel cells continue to be the subject of intense basic and applied research in developed countries around the world.

The core of a PEMFC consists of a membrane electrode array (MEA), the MEA components must have sufficient stability under fuel cell operating conditions. In this work, the membrane electrodes prepared by FIB in cross section are analyzed by FEG/TEM. The MEA preparation has been specially designed and optimized to allow the observation of all components in cross section, including the membrane and gas diffusion electrodes. The characterization of the MEAs has been carried out before and after long-term operation of fuel cells under portable power conditions and has been verified by electrochemical tests

Effect of Native Oxide Layer on Hydrogen Entry into Iron Using Deuterium Isotope

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In the fight against the climate change, the use of hydrogen as energy medium can significantly contribute reducing CO_2 emissions. However, hydrogen gas, in contact with steel pressure vessels for storage or steel pipelines during transport, may adsorb and penetrate in steel, possibly causing its embrittlement and lead to failures. Although it is believed that the native iron oxide serves as a barrier to hydrogen uptake [1], the exact mechanism of hydrogen penetration through oxidized surfaces remains unclear. Therefore, it is crucial to investigate the process of hydrogen adsorption and transport through iron oxide layers into bulk metal. This study aims to better understand the role of iron oxide films against hydrogen uptake.

We propose a novel approach, based on Time-of-Flight Secondary Ions Mass Spectrometry (ToF-SIMS) and isotopic markers (D_2) to investigate the penetration of hydrogen in low carbon iron samples. Owing to the capabilities of ToF-SIMS (high sensitivity, isotopic detection, and in-depth profiling), this method enables us to study nanometric layers, in particular the hydroxide/oxide native layers and their modification during the initial stages of hydrogen adsorption/diffusion at low D_2 gas pressure (on the order of 10^{-6}mbar). In addition to ToF-SIMS measurements, a detailed chemical characterization of the native oxide film was conducted using X-ray Photoelectron Spectroscopy (XPS) to determine its nature (composition/thickness) and its alteration after exposure to D_2. The deuterium concentration profile obtained by ToF-SIMS on an oxide-free iron surface after D_2 exposure indicates that deuterium is present at the first few nanometers of the metal surface. In contrast, deuterium penetration was not observed through the native iron oxide. No modification of the oxide layer was observed after 1 hour exposure to D_2. This confirms that the native oxide layer limits the entry of D_2 into iron.

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Mechanical Roughening of Fe-Cr single crystal alloy Decreases Hydrogen Uptake

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Abstract

The growing utilization of hydrogen underscores the imperative to ensure the mechanical integrity of systems exposed to this element. While extensive research has focused on hydrogen's interaction with bulk materials, investigations into its interaction with surfaces are relatively scarce. However, neglecting this surface interaction is unwarranted, as surface acts as a critical barrier between the hydrogenated environment and the bulk material. This study addresses this gap by examining the influence of various surface finishes on hydrogen/surface interactions in a single crystal Fe-24.8Cr-1Mo alloy. Mechanical roughening's impact on hydrogen absorption was assessed by comparing specimens with different surface finishes achieved through standard preparation and polishing methods.

Electrochemical permeation tests and thermal desorption spectroscopy unveiled notable differences in hydrogen uptake, diffusion, and trapping between coarse-polished and fine-polished specimens. These variations were attributed to surface alterations induced by mechanical roughening. Microstructural observations indicated substantial modifications to both surface topography and subsurface microstructure. Diverse surface preparations, combining mechanical roughening and heat treatments, were proposed to isolate the effects of surface topography and subsurface microstructure modifications. Subsurface observations aimed to evaluate the impact of these surface modifications when in contact with hydrogen. This study elucidates the intricate interplay between surface characteristics and hydrogen absorption in iron, providing valuable insights for material design and engineering applications.

Influence of corrosion products on hydrogen entry into pipeline steel

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The repurposing and retrofitting of existing natural gas infrastructure for gaseous hydrogen presents a critical challenge due to the potential risk of hydrogen embrittlement of steel components. While numerous studies have explored environmental and material parameters associated with this risk, the role of the actual surface state, a fundamental factor in hydrogen entry into steel, is often neglected in the gas industry's HE investigations. This oversight limits the practical applicability of scientific findings.

This study aims to address this gap by focusing on the influence of relevant corrosion product (CP) layers on hydrogen entry into steel under conditions relevant for the gas infrastructure. Initially, CP layers on the surface of pipelines within underground gas storage facilities were characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD), and infrared spectroscopy methods (FTIR and Raman). Subsequently, model samples with varying CP layer compositions and morphologies were prepared to investigate the impact of these layers on hydrogen entry.

The effect of CPs on hydrogen entry was studied using thermal desorption spectroscopy after gaseous and electrochemical hydrogen charging. The efficiency and kinetics of hydrogen entry, based on surface state, were further examined using electrochemical permeation tests and scanning Kelvin probe analysis.

The results obtained from this comprehensive study are crucial for estimating absorbed hydrogen concentrations in steel under field conditions. These data are pivotal for accurately assessing the risk of hydrogen embrittlement in gas networks, providing valuable insights for the safe repurposing of the natural gas infrastructure for gaseous hydrogen.

Applicability of L360 Natural Gas Pipelines for 100 % Hydrogen Transport

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To achieve the carbon neutrality strategy in Europe by 2050, clean and renewable energy sources are highly demanded. Compared to other renewable and clean energy sources, hydrogen offers the most reliable solution as an efficient energy carrier. Therefore, the expansion of hydrogen production and applications shows a significant increase nowadays. Nevertheless, hydrogen transport still faces challenges in terms of cost and hydrogen embrittlement. In this frame, the HyGrid2 project funded by the Austrian Research Promotion Agency (FFG), is the first project in Austria to repurpose an existing natural gas pipeline for 100% hydrogen transport.

L360 pipeline that served for natural gas transport is evaluated using constant load tests for the base metal and the weld. The L360 material was loaded to 80, 100 and 120 % of yield strength and exposed to different environments, including dry hydrogen and hydrogen plus H_2S mixtures, wet conditions with distilled water, and NaCl solution, under a hydrogen partial pressure of 120 bar. Using thermal desorption spectroscopy (TDS), the hydrogen uptake under the different conditions was measured. The welded material showed higher hydrogen content under all conditions compared to the base material. In addition, the presence of a wet environment enhances hydrogen uptake, especially in the presence of H_2S. Based on the delivered results, the L360 material shows high applicability for hydrogen transport. Further tests are planned to study the applicability under dynamic operating conditions.

Comparison between Degassing and Desorption for Estimate the Concentration of Diffusible Hydrogen in carbon steel

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The goal of achieving carbon neutrality by 2050 is a significant topic today. The cornerstone of this process, called energy transition, is the use of new energy vectors, such as hydrogen, that seems to be the best strategy to convert and storage the energy surplus arising from renewable sources. Therefore, introducing hydrogen gas into actual gas grids across Europe would be a possible pioneering approach. Knowing the compatibility of metals with hydrogen gas and the issue of pipeline integrity is essential. Various approaches are used to evaluate the behaviour and hydrogen embrittlement susceptibility of traditional pipeline steels through extensive experimental research today. Consequently, it is crucial to know the hydrogen uptake inside the metal, particularly diffusible hydrogen that has a primary role in these phenomena.

In this work, a methodology is proposed to study hydrogen uptake in traditional API 5L grade X65 steel using the cathodic charging method. The influence of environment is investigated, it is studied different solutions having representative pH values of waters present in the soils. After charging, the diffusible hydrogen content is measured via two different methods: the first one by employing Leco analyser to evaluate gaseous thermal desorption and the second one, using an electrochemical method, by anodic polarization in an alkaline solution, to measure circulating electrical charge. The results of thermal desorption measurement and electrochemical desorption measurement are compared in order to estimate diffusible hydrogen solubility and repeatability of the measurement process.

Rapid asessment of hydrogen pressure resulting from electrochemical charging

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In the shift towards a sustainable energy future, hydrogen is key to achieving a climate-neutral, zero-pollution economy. Adapting steel pipelines for hydrogen transport, however, confronts the challenge of hydrogen embrittlement (HE), where hydrogen absorption into steel undermines pipeline integrity. To address this issue and study the uptake and diffusive behaviour of hydrogen atoms into steel, researchers prefer electrochemical hydrogen charging over gaseous charging due to its safety and controlled environment. However, matching the hydrogen activity (fugacity) in electrochemical charging with that in gaseous charging is crucial for accurate HE studies, as this correlation significantly affects the extent of hydrogen embrittlement (HE). Our study develops a simple method to optimally charge hydrogen into pipeline steel. We engineered a specific electrochemical setup, finding that charging at -1050 mV vs. Ag/AgCl in 3.5wt% NaCl simulates a hydrogen pressure of 15-20 bar, and can can be increased either by amplifying the cathodic charging conditions or with hydrogen recombination poisons, hence aligning with the ideal pressure for pipeline transportation of hydrogen gas at 200 bars or higher. These results were corroborated by collaborative research using hydrogen permeation and thermal desorption spectroscopy (TDS) to analyze hydrogen diffusion in steel, establishing a relationship between hydrogen fugacity and overpotential. Additionally, we validated these findings with a computational model simulating hydrogen generation and migration in steel, accounting for pressure variations under various conditions. The model's accuracy was confirmed by aligning its predictions with our experimental pressure measurements.

Development of an equivalent approach in terms of hydrogen embrittlement between cathodic and gaseous hydrogen charging

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The aim of this study is to establish equivalence models in terms of damage between cathodic charging and the gas environment and to validate them on H_2 storage and transport steels. In this way, the mechanical strength and damage of pipelines under gaseous charging can be estimated. However, certain factors such as the characteristics of the electrochemical environment (nature, pH, temperature, etc.) or the surface oxide layer are decisive in establishing this equivalence. This work is divided in three parts: solubility of hydrogen within the material after several hours of loading; trapping and diffusion processes; and finally, mechanical behaviour of the material under a hydrogen charging. Three materials are studied: a ferrito-pearlitic steel (L485-MB), a martensitic one (QTM) and the Armco® iron as a reference.

Cathodic polarization in NaCl 3.5% and sulfuric acid were performed in order to identify the different potential and current ranges which show a predomination of the Volmer (adsorption) mechanism on the Heyrovsky and Tafel ones (recombination). Afterwards, the optimal charging conditions were applied for various durations in order to establish solubility curves. Electrochemical permeation tests were carried out in the two different environments under the same conditions. In-situ mechanical tests were performed in a non-aggressive environment (NaCl 3.5%) under different cathodic potentials (showing a brittle fracture due to hydrogen) and different stress concentration factors (with or without a notch). Decreasing the imposed potential decreases the reduction of the area, which implies an embrittlement of the steel. The difference of behaviour between each studied material in those three parts in an electrochemical environment will be discussed. Furthermore, a comparison between the latter and results obtained in a gaseous environment (H_2) will be made.

Towards a *Virtual Hydrogen Lab*: computational predictions of hydrogen-assisted fractures

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Virtual Testing can be a game-changer in the deployment of a hydrogen energy infrastructure, enabling efficient and optimal component design, providing mechanistic predictions of material behaviour and fitness-for-service assessment, and preventing catastrophic failures. However, this highly sought ambition has long remained elusive due to the challenges associated with the complex multi-scale and multi-physics nature of hydrogen embrittlement. This work shows how those challenges can be overcome by improving our understanding of the physical phenomena at play, and by developing robust computational electro-chemo-mechanical schemes that can resolve the underlying physical processes. A comprehensive finite element framework has been developed that can: (i) quantify hydrogen uptake from both gaseous and aqueous electrolyte environments, (ii) simulate the diffusion and trapping of dissolved hydrogen, and (iii) predict the nucleation and growth of cracks, assisted by hydrogen. This has been largely facilitated by the development of two computational technologies: coupled multi-physics models and phase field modelling. Predictions can be obtained for problems of arbitrary complexity (3D, multiple cracks, etc.), at both laboratory and component scale levels. Importantly, these predictions are obtained based purely on physical parameters that can be independently measured. The potential of the framework developed will be demonstrated by addressing two case studies of significant technological interest: (1) quantifying the critical pressure at which hydrogen can be transported in natural gas pipelines without leading to structural integrity issues in welds, and (2) conducting reliable virtual hydrogen-assisted fatigue crack growth experiments for arbitrary choices of loading frequency, material, load ratio, pre-charging condition, and hydrogen pressure.

Hydrogen permeation in pure iron containing porosities: the 'double rise' shape explained

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As the world shifts towards carbon-free energy sources, hydrogen has emerged as a potential key player in adressing the growing demand for sustainable energy. Hydrogen dissolved in metals can lead to detrimental effects on their mechanical properties and increase their susceptibility to hydrogen embrittlement. The study of hydrogen-metal interactions remains an active area of research to understand the complex interplay between hydrogen and materials for the development of safe and reliable hydrogen-based technologies.

As hydrogen diffuses through the lattice, it interacts with traps such as porosities, blisters, dislocations, etc. Porosities can trap hydrogen [1], leading to the formation of hydrogen-induced defects that can compromise the material's mechanical properties. Understanding the mechanisms of hydrogen interaction with defects such as porosities is then essential. The study, in particular, investigates the impact of porosities in electrochemical permeation experiments. It appears that an atypical 'double rise' shape is observed in hydrogen permeation rising transients on pure iron containing porosities. The unusual shape comprises a fast initial rise, a short pseudo-plateau, and a slow second rise. Similar patterns emerge in the decaying transients. An FEM model has been developped recently [2] to simulate hydrogen transport in porous metal (non-equilibrium model). The 3D numerical model effectively replicates the 'double rise' behavior, attributed to limited recombination/dissociation kinetics at bulk-porosity interfaces. Overall, porosity is identified as the primary factor behind this unique permeation curve shape.

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[2] Yaktiti A, Dreano A, Gass R, Yvert T, Carton JF, Christien F., Int J Hydrogen Energy 2023

Influence of retained austenite and carbon content in hydrogen diffusion in 3rd generation advanced high-strength steels

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The importance of hydrogen in the energy industry and steelmaking is constantly growing with new fossil-free technologies being developed and adapted. To facilitate sufficient performance levels for this large-scale green transition, novel hydrogen-resistant high-strength steels are needed. Here, we focus on hydrogen diffusion in 3rd generation advanced high-strength steels (AHSS) with 0.2–0.4 wt.% C and varying amounts of retained austenite (RA). The goal was to gain insight into hydrogen diffusion behaviour in these martensitic-austenitic microstructures, and how carbon and RA content and properties affect hydrogen diffusion. While these steels can have exceptional mechanical properties, they are also susceptible to hydrogen embrittlement due to their high strength and predominantly bcc microstructures.

Hydrogen permeation experiments were carried out at room temperature with an in-house Devanathan-Stachurski cell with 0.1M NaOH electrolyte used for both cells. Samples were electroplated with 1μm thick palladium on the detecting side. Hydrogen diffusion coefficients (D), subsurface hydrogen contents (C_H), and reversible trapping site densities (N_T) were calculated from the permeation data using Permeator, the in-house mathematical curve-fitting GUI tool. These results, accompanied with mechanical properties and extensive microstructural characterisation utilising SEM, TEM, and XRD, are compared regarding RA vol.%, alloying, processing routes, and microstructural features for different AHSS.

This research is expected to help in recognising key factors and their effects on hydrogen diffusion in 3rd generation AHSS. Quantifying key factors affecting hydrogen diffusion facilitates further development of AHSS by giving means to mitigate their susceptibility to hydrogen embrittlement and its' deleterious effects.

Modelling of hydrogen diffusion and trapping in 2¼CrMo low alloy steel

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Multiple institutional and industrial organizations are pushing towards using hydrogen as a storage medium and energy vector. For this reason, the components currently employed in the energy sector, such as piping and storage components or compressors, require a redesign process to account for the interactions with hydrogen, especially concerning the effects of hydrogen embrittlement. Hydrogen does interact with metallic materials degrading their mechanical properties, and the detrimental effects are strictly related to its concentration, which can vary over time due to the ability of hydrogen to diffuse and be trapped. Determining the hydrogen distribution inside of a component is further complicated by the poor knowledge of hydrogen adsorption and absorption mechanisms when a given surface is exposed to gaseous hydrogen, which complicates the evaluation of the surface hydrogen flux. This research aims to develop a diffusion and trapping model of a low alloy stainless steel (namely 2¼CrMo), which is considered a promising alloy in the hydrogen transport sector due to its high strength at temperatures up to 400-600 C°. For this purpose, an experimental campaign consisting of Thermal Desorption Spectroscopy (TDS) and permeation testing was performed on a set of samples in a range of temperatures of interest for the typical material in-service applications. Trapping typology was first determined and verified for the selected material through an in-depth microstructural analysis, also employing TEM microscopy. Permeation testing in an electrochemical and gaseous environment in the temperature range of interest allowed for the characterization of diffusion and trapping. Finally, all the data was collectively interpreted to obtain a diffusivity and trapping model suitable for simulating the evolution of hydrogen concentration in industrial components.

In-Situ Measurement of Diffusible Hydrogen in Ferritic and Austenitic Stainless Steels using Laser-Induced Breakdown Spectroscopy

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Hydrogen is playing an ever more intimate role in the design of materials in modern infrastructure. The embrittlement of alloys from diffusible hydrogen is a safety and economic concern, with more drive towards its usage in supplementing global energy demand, and as a formation product from corrosion processes. Therefore, there is a necessity to establish in-situ detection routines for material lifetime assessment and corrosion monitoring. Laser-Induced Breakdown Spectroscopy (LIBS) is a “quasi non-destructive” elemental analysis technique which employs a high-power laser to ablate and ionise a small region of the sample surface (typically > µm). The resultant plasma then quenches, releasing photons characteristic of the elements that make up the plasma. Emitted photons are subsequently captured by a CCD to produce an atomic spectrum plot. In this study, type 316L austenitic, type 420 ferritic stainless steel, and mild steel samples were cathodically charged in a modified Devanathan-cell. The cell was coupled with LIBS to obtain information about hydrogen diffusion and effusion over time. Emission spectra were analysed, with time-resolved LIBS measurements providing instantaneous information about local hydrogen concentration on sub-mm length-scale. Advantages and disadvantages of using LIBS for local hydrogen analysis are discussed.

Effect of lattice misfit on hydrogen trapping in γ/γ' nickel alloys

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The objective of this study is to characterize the impact of lattice misfit in γ/γ' nickel alloys on hydrogen trapping. Two Ni-Cr-Al-Ti alloys containing only the γ matrix and the γ' precipitates were designed and fabricated from ultra-pure metals using vacuum induction melting. The alloy compositions were adjusted to have significantly different lattice misfits between the γ and γ' phases. The phases present and lattice misfits were verified using X-ray Diffraction and Transmission Electron Microscopy. These alloys, along with pure Ni, were studied in the precipitated state and the annealed state. Electrochemical permeation, Thermal Desorption Spectroscopy (TDS), and Glow Discharge Optical Emission Spectroscopy (GD-OES) were performed to understand the hydrogen diffusion and trapping behavior. Very slow hydrogen apparent diffusion and very high hydrogen apparent solubility were found in any γ/γ' alloy compared to nickel. On the other hand, slower hydrogen diffusion as well as slightly lower hydrogen solubility was found in the low-misfit alloy than in the high misfit one. Comparison of the TDS peak shapes suggests a large amount of shallowly trapped hydrogen in the high misfit alloy, presumably because of high stress fields around the γ' precipitates. On the other hand, slightly less hydrogen, more deeply trapped, is observed in the low misfit alloy. It is suggested that the lattice misfit is not the only parameter governing hydrogen trapping.

Hydrogen permeation through ferritic steel under high pressure gaseous charging: Theoretical and experimental considerations

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With the increase in the use of hydrogen in the global energy mix, the introduction of hydrogen into natural gas storage and distribution networks on a large scale is underway. Safety issues linked to the compatibility of existing pipeline and storage ferritic steels with hydrogen gas are central. It is well known that hydrogen diffuses into steel, weakens it mechanical properties, and leads to hydrogen embrittlement. A second risk facing high pressure installations arises from hydrogen permeation across the through thickness – resulting in permanent leaks. Although rather well evaluated for aqueous media and high temperature systems, the labile kinetics of hydrogen absorption in steels are relatively less known for high pressure hydrogen gas at near-ambient temperatures. Furthermore, the presence of trace impurities such as water, oxygen and H_2S in the transported/stored high pressure hydrogen, may impact the surface state and uptake of hydrogen to varying extents.

The objective of this paper is to present our experimental developments and hydrogen permeation results across ferritic steel, that have included studies at pressures ranging from 5 – 80 bar H_2 and temperatures from ambient to 140°C. Amongst notable results, we reproducibly find that a native iron oxide film on polished surfaces is highly resistant towards hydrogen uptake across a typical experiment timescale of several days which highlights the relevance of surface state. Strategies to overcome this natural oxide barrier to measure generalized hydrogen uptake are demonstrated, along with insight on the care needed to successfully conduct such experiments under high pressure.

Influence of Corrosion-Induced Hydrogen Entry on Mechanical Properties of Galvanized Press-Hardened Steel

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Application of galvanized press-hardened steel (PHS GI) for manufacturing of passive safety components of cars is conditioned by their long-term resistance in corrosive conditions. A possible reason for their failure may be the entry of a critical amount of atomic hydrogen into their structure caused by atmospheric corrosion. Recent studies showed that in the initial stages of atmospheric corrosion of PHS GI, a significant amount of hydrogen is produced by the cathodic hydrogen evolution reaction (HER), but only a small fraction of hydrogen atoms enter the steel structure. However, the effect of processes such as corrosion product formation, cyclical contamination by corrosion agents and formation of through-coating defects on the mechanical properties of this material is still little known.

This work describes the relationship between formed and absorbed hydrogen and its influence on mechanical properties of PHS GI in later stages of atmospheric corrosion. Samples pre-corroded for different time under controlled atmospheric conditions to simulate various stages of PHS GI lifetime were investigated by scanning Kelvin probe, respirometry, thermal desorption analysis and slow strain rate test.

Two times less hydrogen was produced on pre-corroded PHS GI recontaminated with chlorides with more than three times lower corrosion rate in comparison with fresh PHS GI. In the same time, the HER ratio in the overall cathodic process was two times higher. Slight deterioration of tensile strength was observed, but corrosion was identified as the main cause. Both corrosion and hydrogen absorption contributed to a significant deterioration of elongation by approximately 50%. The main hydrogen entry spots were cracks in the coating. The interface between corrosion products and coating also played a role.

Corrosion behaviour of aluminium alloy 2024 in atmospheric conditions

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Aluminium alloys, e.g. aluminium alloy 2024, are widely used in the aerospace industry although they are susceptible to intergranular corrosion under certain conditions. The mechanisms and morphology of intergranular corrosion are strongly dependent on the exposure conditions. The objective of the present work is to evaluate the contribution of corrosion-induced hydrogen on the initiation and propagation steps of intergranular corrosion for an aluminium alloy 2024 in simulated atmospheric conditions.

The experimental approach combined corrosion tests with EBSD, SKPFM and TDS measurements, all performed on samples extracted from a 60 mm thick sheet of aluminium alloy 2024 in the T351 state. Corrosion tests were cyclic tests alternating immersion periods in a chloride-containing solution and emersion periods to simulate atmospheric corrosion conditions. Before corrosion tests, the samples were analysed by EDSB to identify, in selected areas, all interfaces i.e. low-angle grain boundaries (LAGBs), coincidence site lattice grains boundaries (HAGBs CSL) and random high-angle grain boundaries (HAGBs). Then, the corroded interfaces in the previously selected areas were all identified, which made it possible to quantify the susceptibility to initiation and propagation of corrosion of the various GBs. The tests were complemented by measurements of the global hydrogen content, thermo-desorption spectroscopy and scanning kelvin probe force microscopy experiments so as to analyse the influence of corrosion-induced hydrogen on the reactivity of the GBs, and determine its contribution to the extent of the intergranular corrosion damage.

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Simultaneous observations of hydrogen entry and pH distribution in a NaCl droplet on an Fe sheet using polyaniline

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Abstract

Hydrogen entry is known to be promoted due to the corrosion reactions, but the detailed mechanism of corrosion-induced hydrogen entry is still unclear. To elucidate the hydrogen entry mechanism, real-time analysis of hydrogen entry into steels is required. In this study, the hydrogen entry behavior and pH distribution in a NaCl droplet on an Fe sheet was visualized in situ using polyaniline, which is known to visualize the hydrogen distribution in a metal with high spatial and time resolutions.1)

A Ni layer was electrically plated on one side of an Fe sheet at $-30\ \mathrm{A\,m^{-2}}$ in Watts bath (333 K) for 180 s. A thin polyaniline layer was electrically polymerized on the Ni layer at 1 V in a 0.5 M H_2SO_4-0.5 M aniline solution for 200 s using a Pt wire as a counter electrode. A droplet of 0.1 M NaCl-50 mM thymol blue was placed on the other side of the Fe sheet. The droplet and polyaniline layer were observed using digital cameras.

A large crystallographic pit was generated at the initial stage of corrosion in the NaCl droplet, but the hydrogen entry was barely promoted by pitting. Subsequently, island-like rust formation was confirmed, enhancing hydrogen entry. The acidification under the rust-formed area was found to promote hydrogen entry. Near the periphery of the area where rust-formed, alkalization proceeded. It seemed that the alkalization thickened the rust-formed area. After the disappearance of the droplet due to drying, hydrogen entry was found to be promoted under the thick rust layer.

Reference:

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Hydrogen embrittlement inhibition of pipeline steel by environmentally friendly carboxylate compounds

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To minimize greenhouse gas emissions, hydrogen is considered a potential alternative to fossil fuels. Existing high-strength steel pipelines, currently used for gas and oil, are proposed to be used for hydrogen transport, which could significantly reduce delivery costs. However, hydrogen embrittlement (HE) poses a challenge for these pipelines, as hydrogen can permeate steel, degrade its mechanical properties, and potentially cause premature failure. For underground steel pipelines, hydrogen can be generated from cathodic reactions under cathodic protection potentials on the external surface of the pipeline and/or from internal hydrogen fuels. HE mitigation using chemical inhibitors is a practical approach to protecting pipelines. Unfortunately, existing HE inhibitors are either environmentally unfriendly or not sufficiently effective. This paper reports a research effort to explore more efficient and environmentally friendly HE inhibitors. In this work, the nontoxic carboxylate anion, trans-4-hydroxy-cinnamate, has been combined with different cations and used as HE inhibitors. Various rare earth elements, such as lanthanum and cerium, have been combined with trans-4-hydroxy-cinnamate for their ability to accelerate hydrogen recombination. The experimental results indicate that the addition of synthesized rare earth carboxylate compounds, $La(4OHcin)_3$ and $Ce(4OHcin)_3$, to a NaCl solution can significantly reduce hydrogen permeation currents in X65 steel under electrochemical hydrogen charging. The SEM images reveal that some precipitates containing rare earth elements form on the steel surface during hydrogen charging, which blocks the steel surface sites and reduces hydrogen absorption. These findings suggest that trans-4-hydroxy-cinnamate-based compounds have the ability to act as HE inhibitors. This research points toward an approach for developing effective, environmentally friendly HE inhibitors by combining functional cations with trans-4-hydroxy-cinnamate, enhancing the inhibitor film formation ability on steel surfaces and improving HE inhibition efficiency.

Effect of hydrogen at cryogenic temperatures on tensile properties of various 316L stainless steel

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Austenitic stainless steels are known to achieve high strength and maintain their high ductility at cryogenic temperatures. Therefore, they are good candidate materials for storage and transportation applications at cryogenic temperatures. In the hydrogen economy context, cryogenic hydrogen transport and storage is one of the solutions being studied to ensure its deployment. Nevertheless, some material challenges with storing and transporting of liquid hydrogen (boiling point at atmospheric pressure -253°C) and cryo-compressed gas (slightly higher cryogenic temperatures) have been detected. In particular, the observation of hydrogen embrittlement at low temperatures and high H_2 pressures is most of the times associated to α'- martensite transformation.

In this work, the resistance to hydrogen embrittlement at temperatures down to -150°C at 100bar H_2 has been evaluated for 316L stainless steels with different chemical compositions. The rather new hollow specimen technique has been used for the characterization. This technique has been validated by: 1- modelling and 2- by comparing the results with standard tensile specimens tested at the same environment conditions. The temperature screening down to -150°C shows premature failure of the samples tested at 100bar H2 compared to the ones tested at 100bar He for temperatures between 0 and -100°C. The loss of ultimate tensile strength, elongation, and reduction of area is maximized at around -100°C. No or minor H effect on the mechanical properties is observed at -150°C, the mechanical properties obtained under H_2 and He are about the same. In addition, secondary cracking was observed on all the samples tested under H_2 which is indicative of hydrogen embrittlement. A clear effect of the meta-stable austenite on the properties and on the resistance to Hydrogen Embrittlement was observed. Finally, the effect of the chemical composition and internal cleanliness is discussed.

Fracture toughness evaluation under H2 pressure : techniques available, limitations and cases of study

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Hydrogen is known as a possible green energy alternative to the fossile sources in a near future. Producing and using hydrogen will require the development of a full industrial sector, from the production using native gas or electrolyzers, transportation in existing or new pipeline networks, storage in salt caverns or depleted oilfield and development of adapted engines for cars or turbines for aircrafts. This molecule is however well known as a possible embrittling agent if it is absorbed by metals and is also flammable and explosive with a very low activation energy needed for ignition.

To ensure the safe transportation in pipelines or the storage in metallic containers or facilities, one must ensure the safety making the qualification through facture mechanics tests consisting generally in fracture toughness and fatigue crack growth rate evaluations. Regarding fracture toughness, the main standard documents applicable to the use of the metals in hydrogen atmosphere are ASME B31.12 / ASME BPVC. The standard recommends the use of compact tension specimen (CT) loaded under constant strain using bolts and exposed in the pressurized hydrogen atmosphere for a standardized period of time. This standard suffers however from large limitations due to the very high ductility of the steels to be tested and experience shows that it cannot be used to fine-tune the behavior of materials when the environment is changed (e.g. if the pressure is varied, if the hydrogen contains impurities…). A research work is therefore ongoing at the French Corrosion Institute (FCI) and other institutions in Europe to find a better technique. Through cases of study, different techniques will be discussed and some insights in the behavior of steels when operated in degraded environments will be given.

Electrochemical charging and hydrogen embrittlement of a low alloy steel

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Hydrogen is considered as a versatile energy vector, and the possibility to reuse part of the existing natural gas (NG) transport and distribution network to convey high pressure hydrogen (or mixtures with NG) is currently explored. To this aim, it is necessary to characterise the compatibility with gaseous hydrogen of the materials present in the gas network, in particular the resistance to hydrogen embrittlement (HE).

The susceptibility of steels and other metallic materials to HE is usually evaluated performing mechanical tests in situ with high pressure hydrogen, as several standards suggest (ISO 11114-4, ASME VIII Div 3, ANSI/CSA CHMC 1 …). These tests are expensive and time consuming, mostly due to the dangers related to proper high pressure hydrogen handling and the required equipment. Non-standardized tests have been proposed: one of the most common methods is the electrochemical charging.

The present study is focused on the behaviour of low alloy steel (T95 according to API specification). The specimens are pre-charged in sulphuric acid 0.1 N containing arsenic trioxide, with different cathodic current densities (0.5 to 5 mA/cm^2) and test duration (1 to 3 days). After hydrogen charging, the material is mechanically characterized through J-integral and tensile tests in air and the fracture surface is observed by means of Scanning Electron Microscopy (SEM).

The fracture toughness of the material charged with hydrogen is always reduced vs the values measured for not charged specimens, and the effect is enhanced by the increase of hydrogen content.

The comparison with literature results, obtained with high pressure hydrogen on similar alloys, show the suitability of the electrochemical charging to simulate different values of hydrogen pressure. The advantages and the limitations of the method employed in this study are critically discussed.

Effect of hydrogen on fracture micromechanism of an X70 pipeline steel

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As the transition towards green energy and a low carbon economy continues, the demand for hydrogen gas is expected to rise. Accordingly, robust infrastructure for storage and transport of gaseous hydrogen is needed: repurposing part of the natural gas pipeline grid for hydrogen service is an economical solution for managing this energy transition. However, the problem of hydrogen assisted degradation of a steel's mechanical properties is well known, and the current net should be assessed for its compatibility with hydrogen gas to ensure its structural integrity. Smooth and notched round bar tensile tests as well as single edge notched tension (SENT) fracture toughness tests are performed with and without electrochemical hydrogen charging to investigate the hydrogen embrittlement susceptibility of an API 5L pipeline steel. Different notch radii allow tensile tests to capture a range of positive initial stress triaxialities, in addition to SENT fracture toughness testing representing a small notch radius. Hydrogen effect on fracture micromechanism is assessed through fractographic analysis. X-ray micro computed tomography (CT) scans are used to qualify void formation in uncharged and hydrogen-charged case. Hydrogen charging caused a reduction in ductility through a partial shift from ductile fracture to quasi-cleavage, observed as fisheyes on the fracture surface, and enhanced void formation. Additionally, hydrogen promoted splitting along the banded microstructure, which could have a significant influence on SENT fracture toughness tests.

Assessment of hydrogen effect on failure mechanisms of low alloy carbon steel for pipeline

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The expected increase of clean hydrogen production will be a great challenge for transport infrastructures and the conversion of existing gas pipelines to hydrogen is a promising and cost saving solution. To assess the suitability of pipelines repurposing, a study has been conducted aiming at providing a better understanding of the failure mechanisms of low alloy carbon steel under gaseous hydrogen environment (30 bar). To this end, an original approach based on post-mortem advanced characterization on laboratory tested samples has been performed.

First, statistical fractography is used to evaluate the local damage parameters and to calculate the fracture toughness. To check the accuracy of the model, the calculated fracture toughness is compared with the experimentally measured values. In order to characterize the interactions between the crack and the microstructure in the presence of hydrogen, Electron Backscatter Diffraction (EBSD) mapping is performed. The objective is to discern the nature of cleavage planes susceptible to failure under the influence of hydrogen. Lastly, nanoindentation tests are performed to assess the localization of plastic deformation associated with hydrogen-induced embrittlement. These tests have also permitted the evaluation of plastic zone size near the crack tip.

Effects of temperature and hydrogen on fatigue properties of austenitic stainless steel 304L

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To design liquid hydrogen tanks, it is crucial to have a comprehensive understanding of the factors that affect fatigue crack initiation and propagation in materials used in hydrogen environments at cryogenic temperatures. For austenitic stainless steels, it is well-known that hydrogen embrittlement (HE) results in a loss of ductility in tension. The maximum embrittlement occurs at around -83°C, and this effect disappears at very low temperatures. The aim of this work is to assess the high-cycle fatigue resistance of austenitic stainless steels in a hydrogen environment within the temperature range of -120°C to 100°C. A special attention will be paid to the separation of the respective effect of hydrogen diffusion and trapping and temperature-induced phase transformation on the other hand. The austenitic stainless steel grade selected for this study is 304L. Fatigue resistance of the steel was tested at various temperatures in air, revealing significant ratcheting deformation during fatigue loading. The tests were conducted at R = 0.1 and F = 10Hz. Furthermore, the analysis of fatigue life shows that the lower the temperature, the higher the fatigue life for a given stress amplitude. Meanwhile, the rate of the martensitic transformation with respect to temperature has been estimated. A significant increase in the fraction of martensite formed has been observed that at low temperatures (-83°C) in air. The influence of hydrogen gas on fatigue strength has been investigated at different temperatures. The results suggest that hydrogen may not have any effect on ratcheting deformation, but it does impact the fatigue life at higher stress levels when exposed to a hydrogen pressure of 1.5 MPa at room temperature. Moreover, fracture surface analysis shows no significant difference between specimens tested in air and those tested in a hydrogen environment. Finally, the influence of internal (ex-situ charging) and external (in-situ charging) hydrogen will be discussed.

Fatigue Lifetime Assessment of Seamless Pipes for Hydrogen Gas Storage and Transport

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To insure the integrity of assets for the storage and the transport of hydrogen gas is key for the adoption of hydrogen as a reliable and safe source of energy. Fracture mechanics approach is well adapted to predict the lifetime of these structures in service, much more than in sour gas environments where, yet, the embrittlement is also due to hydrogen. Basics arguments of this assertion will be reminded. Process for the determination of the fatigue lifetime of seamless pipes for hydrogen gas transport or storage will be described, combining non destructive assessment of surface imperfections and resistance of the material to hydrogen stress cracking and hydrogen enhanced fatigue. Several cases study have been investigated, highlighting the strong impact on the fatigue lifetime of the ratio outer diameter on wall thickness but also the working pressure, the initial flaw size and shape, the fatigue crack growth rate and load ratio. It is discussed for which configurations hydrogen enhanced fatigue can be disregarded and for which configurations an infinite longitudinal crack can be considered instead of a semi-elliptical crack for assessing fatigue lifetime.

The behaviour of N80Q Steel and its weld in underground hydrogen storage conditions under constant loads

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Abstract

Most of the energy sectors worldwide are actively looking for systems suitable for hydrogen use. Oil and gas companies explore the possibility of using existing underground storage facilities for hydrogen storage. Among the materials in the API 5CT steel family, N80Q is extensively used for tubing and casing. Its martensitic microstructure makes it particularly interesting for an in-depth investigation regarding its behaviour in a hydrogen environment. This research focuses on inspection of N80Q steel and its welds. Constant load testing was performed with mini-tensile specimens across various media. In the underground section, the presence of Hydrogen Sulphide (H_2S) was anticipated due to Sulphate-reducing bacteria (SRB), while CO_2 was expected from Cushion gas. Therefore, Tests were conducted in different media, including pure hydrogen (H_2) and a mixed gas (H_2+H_2S+CO_2). The tests were conducted in dry and wet conditions by using an artificial brine solution. The constant load testing involved three different loads - 80%, 100%, and 120% of the material's yield strength. For welds, additional characterisation tests were carried out, like hardness mappings. The hydrogen uptake in the stressed specimens was measured by using an ELTRA's H-500 analyser with a heat extraction technique. In case of a fracture, the post-fracture analysis was conducted with high-resolution SEM. All tests were conducted under a pressure of 288 bar. This study contributes to the oil and gas industry to use the current tubing and casing materials that are used for underground natural gas systems for hydrogen storage facilities.

Keywords – Hydrogen, carbon steel, Martensitic, welds, storage.

Influence of hydrogen uptake on additively manufactured and conventional austenitic stainless steels 316L

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With increased energy demand in the present-day world, a strong driving force prevails in the transition from an existing fossil fuel-based economy to a circular and sustainable renewable energy-based economy. Hydrogen is regarded to play one of the most significant roles in achieving a carbon-neutral society. However, this also poses several major challenges raised by hydrogen-induced metal/alloy degradation (hydrogen embrittlement) during the generation, separation, transportation, and storage of hydrogen.

Additive manufacturing (AM) is a promising means of production of corrosion resistant alloys for hydrogen service. The hydrogen embrittlement resistance of SS 316L parts by conventionally manufactured and directed energy deposition (DED) was examined in this study. We investigated the effect of hydrogen on additively manufactured (AM) 316L stainless steel and compared it with conventionally manufactured (CM) 316L sample. Therefore, electrochemical hydrogen charging was performed on both AM and CM 316L samples to achieve a comparable hydrogen content in the samples, which were further measured by TDS and GDOES.

Identically samples were **in-situ / ex-situ charged** for tensile test to quantitatively correlate the mechanical degradation by introducing different contents of hydrogen into the sample. A combination of surface characterization techniques; SEM, EBSD, XRD, and EBSD are deployed to accurately characterize and gain an improved understanding of the hydrogen embrittlement mechanism in CM and AM (as-built and heat treated) stainless steel. The higher presence of hydrogen reduced ductility in the as-built AM sample but did not significantly influence the response in CM materials. Hydrogen-charged samples exhibited a large area of brittle fracture mode, while hydrogen-free samples showed ductile fracture morphology.

Hydrogen-assisted degradation of 3rd generation of martensitic advanced high-strength steels

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Hydrogen delayed fracture is one of the major problems for the industrial application of advanced high-strength sheet metal steels, whose employment is rapidly increasing beyond the original automotive sector. Hydrogen is especially dangerous for ultra high-strength martensitic grades since relatively low hydrogen concentrations may severely reduce their ductility, and its accumulation at local geometric features may cause premature unexpected failure. To properly manage this phenomenon many interlinked factors have to be considered like diffusion, trapping and the mechanism of hydrogen-assisted damage. To this purpose, three grades of martensitic advanced high strength steels (1300, 1500 and 1700) were firstly characterized by permeation and desorption testing to understand their hydrogen diffusion, trapping and room temperature outgassing behaviour, followed by slow strain rate tensile testing on specimens with different hydrogen concentrations. Fractographic analysis of the failed specimens was finally performed in order to understand the underlying failure mechanism, aided by modelling of the hydrogen diffusion in the material during the mechanical test. The results and methodologies of this investigation will provide a more detailed insight of the relevant interactions for delayed fracture in those materials for manufacturers and designers.

Investigation of a high-pressure hydrogen pipeline made of 1.4462 duplex stainless steel after 12 years in service

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To achieve climate targets in the transport sector, a transition from fossil-based fuels to renewable energy-based technologies is essential. In addition to battery-electric vehicles, transportation concepts based on renewable hydrogen such as fuel cells or hydrogen combustion engines are also being utilized or developed.

These concepts typically require gaseous hydrogen under high pressure, thus peripheral structures such as fueling stations operate with pressures of up to 1000 bar. The materials used under these conditions are required to ensure long-term safety and should therefore show negligible signs of fatigue under operation. A segment of a high-pressure hydrogen pipeline from a fueling station was replaced during a routine inspection after 12 years of operation under real-life conditions and could thus be examined in detail.

The tube segment is made of duplex stainless steel 1.4462. It was examined regarding the occurrence of possible hydrogen embrittlement effects. Therefore, various investigations have been carried out on material properties including notched impact strength, hardness, fatigue, trapped hydrogen content, as well as slow strain rate tensile tests, hydrogen permeation measurements, and microstructural analysis. Due to the availability of some material characteristics obtained before installation, the effects of long-term H2 operation on the material can be shown.

Effect of residual ferrite content on hydrogen embrittlement at low temperature of austenitic stainless steels

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Austenitic stainless steels (ASS) are widely used for cryogenic thanks to their good ductility properties. Nevertheless, these grades can be affected by hydrogen embrittlement (HE) at low temperature. According to literature, ASS are mainly sensitive to HE in the temperature range of -150°C to 0°C.

In this study, HE of two ASS (304L and 316L) has been evaluated with slow strain rate traction (SSRT) tests with pre-charged specimens. First, several pressures and durations of pre-charging conditions have been studied to highlight optimal conditions to exhibit HE susceptibility with SSRT. Second, SSRT tests have been performed with hollow specimens. This method allows hydrogen charging during mechanical solicitation. Then, a comparison of SSRT results with pre-charged specimens and hollow specimens provides insights on the methodology to determine HE susceptibility of the material. Finally, metallurgical parameters, such as residual ferrite content, have been studied to quantify their effect on the HE susceptibility. Ferrite phase is clearly more sensitive to HE than austenite phase. Specimen examination after SSRT exhibits failure initiation at ferrite/austenite interface.

The effect of austenite stabilization on the high-pressure hydrogen embrittlement resistivity

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Green gaseous hydrogen is one of the most promising energy carriers in near future. In order to distribute large volumes, compression or liquification of the gas is required. For that purpose, hydrogen resistant austenitic stainless steels are necessary for containers and valves in the automotive or aerospace industry and for tubes for long-distance hydrogen transmission.

Subject of the present work is the hydrogen embrittlement (HE) effect in austenitic stainless steels. The chemical composition affecting interatomic bonds (cohesion) and stacking fault energy (SFE) is considered to rank the different materials. In literature, several studies on hydrogen-charged low stable austenitic steels confirmed a hydrogen-induced ε- and α-martensite phase formation. The main reason for this transformation is the decreasing effect of hydrogen on the SFE and extensive plastic deformation accompanied by hydrogen charging. To confirm the hydrogen-caused effects on the austenite phase stability, slow strain rate tests (SSRT) of A286 (S66286) and Nitronic 50 (S20910) were performed under high-pressure gaseous atmospheres and with in-situ electrochemical charging. In addition, low temperature testing is performed to characterize the role of temperature decreased SFE on the HE resistivity. The SSRT are accompanied by fracture surface analysis, x-ray diffraction (XRD) and microstructural characterization.

Results show that the chemical composition and thus austenite phase stability has a significant influence on the HE resistivity. A threshold of the nickel-equivalent exists, above which austenitic stainless steels seem to be resistant against HE. Electrochemical and gaseous charging lead to comparable results at room temperature. The results of the present work support the development and improvement of hydrogen resistant austenitic steels with increased strength and toughness under hydrogen atmospheres.

Hydrogen Embrittlement of Martensitic Steel Grades with Different Strength Levels

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Understanding hydrogen embrittlement plays a key role for safely deploy materials in services related to energy transition. Turbomachinery for hydrogen applications needs, among others, the class of martensitic steels, which are a valuable selection for their convenient strength to cost ratio. This material class has been largely characterized in hydrogen environment, but there is room for further studies, particularly for high strength levels needed in turbomachinery and energy applications and by considering the actual engineering failure modes.

The goal of this work is to show embrittlement measurement of three selected martensitic steels (two low alloy steels and one precipitation hardening) obtained by Slow Strain Rate (SSR) method at typical operating conditions. The steels have different strength levels. Two grades are within the typical API yield strength upper limit, i.e. 827 MPa, while one is over this limit. This test measures the embrittlement as a ratio of ductility and strength characteristics, in both inert and hydrogen environments. Outcomes have been compared with a proposed acceptable limit.

SSR Tests have been carried out on smooth specimens, as well as on notched specimens, whose notch replicates the same geometrical criticalities of actual components, to replicate the in-service stress conditions.

Test results, show how embrittlement is not only correlated to the strength of the selected grades (which is largely know on existing literature), but can have a noticeable correlation with other factors, like microstructure and cleanliness features of the materials, which should be carefully considered for any material selection. It is also shown how the combination of smooth and notched specimens can provide a more accurate evaluation in case of low embrittling ratios.

Fracture surface analysis as well as microstructure characterization is reported showing different fracture morphologies (e.g. intergranular or transgranular) and microstructural features of the three grades.

Wireless UT Sensors For Structural Health Monitoring & Remote Operations In A Post COVID19 World

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ABSTRACT

Nothing like a crisis to force people think and act differently. The concept for deployment of installed ultrasonic sensors to either replace or augment manual inspections to improve operational efficiencies and outcomes is by no means a newfangled idea. As with all technology, components get smaller and sensors become more deployable and affordable. The same with wireless UT sensors. Over the last decade the O&G industry has been marked by falling oil prices, reductions in new builds/expansions, declines in CAPEX budgets, and corporate reorganization in efforts to cut costs. Then COVID19 arrived, and the world changed in a matter of weeks. Instead of trying to cut costs, many refining and chemical plants shifted their thinking to working smart versus hard. This presentation will detail how wireless UT sensors combined with new ways of thinking has transformed the industry to save millions of dollars in asset integrity and operating efficiencies.

Key words: Corrosion, Ultrasound, UT Sensors, PIMS (Permanently Installed Monitoring Systems), Downstream, Refining, Chemical, Wired UT (Ultrasonic Thickness), Wireless UT (Ultrasonic Thickness), Monitoring, Asset Integrity

INTRODUCTION

For decades, many asset owner/operators across the O&G value chain (and other critical industry segments) of upstream, midstream, & downstream have struggled to identify the root cause of fluctuating corrosion/erosion rates due to unreliable or infrequent data during various operating intervals on their most valuable of assets. This key missing data point has forced mechanical integrity teams, corrosion engineers, inspectors, and operations to, in many cases, make the best guess or hypothesize how to operate with a limited data set of information. In almost all cases, a time-based inspection or maintenance interval is used to gauge the useful lifetime of assets based on this limited data simply because these assets couldn't give their owners a real-time health diagnostic of how they were doing … until now. This paper will detail how COVID-19 offered a much needed reset button of opportunity for asset owners across many segments to rethink their decision making process by using technology to their favor. Many of these asset owners have now been able to take the next leap into strategic asset integrity planning by utilizing sensors and real-time data to not only safely and more efficiently operate assets but in some cases, achieve the financial holy grail of life-extension services for their most critical assets and components.

Creation of corrosion forms in representative scale samples for acoustic emission clustering

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The corrosion of 316L stainless steel poses a significant challenge in the industry. For example, in the marine industry, the corrosion of 316L stainless steel can lead to structural integrity issues in offshore structures and vessels. To detect corrosion in 316L, the use of acoustic emission is a notable method, particularly for detecting localized corrosion. Although corrosion is frequently studied through acoustic emission, the used methods are generally to accelerate corrosion processes using electrochemical means, which affects the acoustic emission signals. The aim of this study is to create and monitor different forms under more industry-representative conditions, and to identify corrosion processes using machine-learning based clustering algorithms.

In particular, as acoustic emission detects the signature of the evolving defects, it should be possible to identify the nature of the source if the characteristics of the signals differ. Indeed, there are several potential sources of acoustic events during a corrosion process, including passive film rupture, metal tearing but also the formation, evolution and explosion of hydrogen bubbles.

To study different forms of corrosion (uniform and pitting corrosion), 316L sheets are exposed to HCl solutions of different concentrations in multiples experimental configurations. Standard acoustic emission features such as temporal or frequency features are then extracted from signals and clustering can be applied to the data.

The main results of our study are the determination of experimental procedures capable of producing representative acoustic data sets. The application of clustering algorithms allows demonstrating the presence and identification of multiple clusters in the different forms of corrosion. Furthermore, our results show the possibility to isolate specific corrosion forms, like pitting corrosion.

Detection and monitoring of electrochemically generated and controlled corrosion pit by ultrasonic lamb wave technique.

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Corrosion is a major issue for fleets maintenance in aeronautical industry. It is often underestimated until it is it too late despite the fact that assets life span can be preserved and maintenance costs can drastically be reduced [1] if corrosion is detected and attended soon enough. Nondestructive Testing (NDT) methods have been developed to monitor such damages and widely used by aeronautical industry [2] to investigate and detect structural damage on aircrafts but it still need human intervention to be done. Recent ultrasonic techniques using piezo electric transducers (PZT) networks offer new options to achieve this goal.

In this exploratory work we make use of ultrasonic lamb wave to detect and follow in-situ electrochemically generated and controlled localized corrosion. Ultrasonic lamb waves are ultrasonic waves classically around a hundred kHz that propagate in the material thickness. In our application ultrasonic lamb waves are generated by four PZT discs bonded at the back of the material. An impulse burst centered around 200 kHz is emitted by one of the PZT disc and the response of the structure is recorded by the three other ones. Then the process is repeated by rotating the configuration between all four PZT elements. We demonstrate here that we were able to detect and monitor in-situ the growing of a single localized controlled corrosion damage.

The aim of this work is to provide a new method to detect and monitor corrosion damage. In the future PZT could be directly embedded in the structure to provide continuous monitoring. That means limited human intervention and more data to reliably train machine learning algorithm to provide predictive maintenance plan.

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Corrosion source location on a plate of magnesium alloy WZ73 analyzing Lamb-wave propagation

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Abstract

The acoustic emission technique was used for localizing corrosion on a plate of alloy WZ73 in contact with a NaCl solution. At a distance d = 1.66 m, the Lamb wave characteristics of corrosion induced AE events were examined and compared to a pencil lead break reference signal and a simulated corrosion event signal, that was analyzed by a scanning laser Doppler vibrometer. The correlation of corrosion and reference signals allowed wave path reconstruction and ultimately corrosion source localization.

Interactions Between Grounding and Cathodic Protection Systems in Reinforced Concrete Structures: Experimental and Numerical Investigation

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Abstract

This paper elucidates the interplay involved in grounding a reinforced concrete structure, wherein the steel reinforcement is protected from corrosion by means of an Impressed Current Cathodic Protection System (ICCP).

In electrical installations, metallic masses susceptible to accidental energization, such as a cathodic protection cabinet, are systematically connected to the earth. This grounding connection involves a buried metal electrode in the soil, facilitating the flow of leakage currents. This precaution is primarily implemented to ensure the safety of individuals and equipment through a differential switch. Various standards govern grounding requirements, including specifications for maximum resistance.

Several concrete structures have their reinforcement electrically connected to the ground to reduce the electrical resistance of the grounding electrode. In this article, the study focuses on the influence of the connection of the reinforcement to the ground on the effectiveness of the cathodic protection system.

In addition to leakage currents resulting from an insulation fault, concrete structures may also be exposed to stray currents affecting the ground, originating from external sources. This article also explores the impact of parasitic phenomena on cathodic protection.

To comprehend these intricate physical phenomena, a fully instrumented, real-size mock-up of reinforced concrete was set-up. A network of reference electrodes and metallic coupons facilitated the monitoring of the potential of the steel reinforcement and the distribution of protective current. Additionally, artificial stray currents were induced in the ground surrounding the mock-up.

A 3D numerical model was also developed to interpret the monitoring data. This study, integrating experimental and numerical approaches, draws conclusions regarding the compatibility between the reinforcement grounding and cathodic protection.

Prediction of atmospheric corrosion through corrosion monitoring sensors and machine learning algorithms

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Atmospheric corrosion may significantly reduce the load resistance of zinc-coated structural steel members in buildings [1]. Accurately predicting corrosion rates is critical for selecting materials and designing effective corrosion protection strategies. However, conventional methods such as corrosion coupons are time-consuming, and only generate limited data. In contrast, recent advancements in galvanic corrosion monitoring sensors offer a more efficient solution. However, the accuracy of these sensors remains uncertain due to a limited understanding of their response under diverse environmental conditions. Although previous research has explored the response of Fe-Cu type corrosion sensors [2], comprehensive investigations into other corrosion monitoring sensors are still lacking.

This study aimed to investigate the response of both Fe-Ag and Zn-Ag type corrosion sensors. Corrosion coupons and monitoring sensors were exposed at five air quality monitoring stations in Hong Kong for twelve months. Real-time corrosion monitoring data and environmental data were collected once per hour. After the exposure test, the results revealed a strong correlation between the mass loss of the exposed coupons and the monitoring data, confirming the effectiveness of the monitoring sensors in predicting corrosion rates. Through statistical analysis, several environmental parameters were identified as key factors influencing the sensor responses. Furthermore, the performance of machine learning models in predicting sensor responses was also compared.

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Predicting Atmospheric Corrosion Through Knowledge Sharing Strategies in Machine Learning

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Atmospheric corrosion sensors, essential in assessing corrosion rates and environmental corrosiveness, have consistently demonstrated their utility in predicting metal performance. Nonetheless, the data generated by these sensors is complex, and it is challenging to determine interpretable correlations between the different variables measured using only analytical corrosion expertise. Recently, studies[1,2] have shown that machine learning models are able to unravel unexplored patterns between the environment and the current output, thereby unlocking the potential to develop predictive atmospheric corrosion models. However, one limiting factor is the large amount of data from long testing times required to make proper predictions in the environment where the sensor was placed. Our research argues that the specific subdomain of machine learning called transfer learning (TL) can solve this issue. In essence, TL attempts to transfer knowledge from a previously developed machine learning model (the source) to another similar task (the target). As such, it provides a way to improve the modeling performance in domains where data is scarce. Building upon the findings of our initial study[3], which demonstrated the effectiveness of TL in extrapolating data from a salt spray test to an outdoor environment we are now extending our model to include more diverse types of corrosion. Additionally, we are incorporating a broader range of accelerated tests and expanding our datasets to cover more varied outdoor environments. This expansion is aimed at not only enhancing the generalizability of our TL models but also at gaining a deeper understanding of the scenarios where TL is most applicable.

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Automated Processing of Corrosion Data through Unsupervised Analysis of Impedance Spectroscopy Spectra

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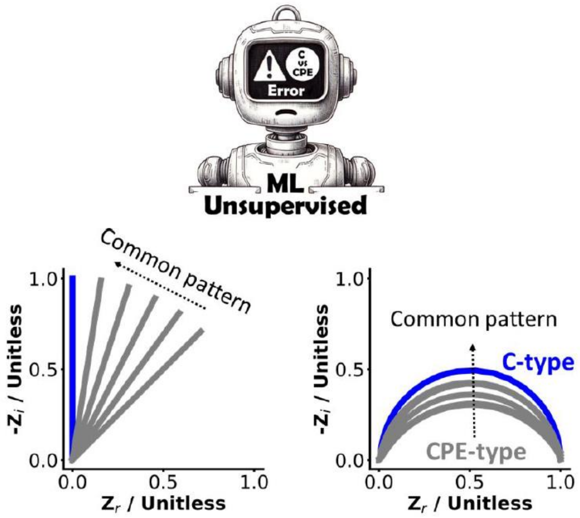
The increasing feasibility and prevalence of corrosion monitoring and sensing through electrochemical impedance spectroscopy (EIS) registration lead to the generation of massive EIS databases. This proliferation of data presents significant challenges in processing and interpretation, tasks traditionally managed manually by fitting individual impedance spectra, which have now become untenable on such large scales. This work delves into the adequacy of unsupervised machine learning (ML) in addressing this issue, examining its strengths, limitations, and potential optimization pathways. As we navigated the intricacies of non-linear dimensionality reduction, particularly focusing on t-distributed stochastic neighbor embedding (t-SNE) and uniform manifold approximation and projection (UMAP) algorithms, a pattern emerged: these techniques excel at categorizing divergent impedance spectra but exhibit limitations when dealing with analogous circuit configurations, especially those substituting a capacitor with a constant phase element. This observation not only underscores a limitation but also highlights that unsupervised ML approaches, alone, might not fully unravel the nuances of EIS spectra. In the final part, we discuss the implications of this finding from a practical standpoint, especially for corrosionists seeking to apply these methods in their work.



Demonstrating the performance of a fluorine detector in nitric acid media

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Objectives

To assess the actual corrosiveness of a nitrofluoric acid solution to zirconium it is important to distinguish bound fluorine from free fluorine. However, measurement methods that are currently used only quantify the total amount of fluorine and without informing on the chemical form of fluorine. Detecting free fluorine in these media is of great interest for monitoring equipment. The aim of this project is therefore to manufacture a prototype of such a probe and to test its laboratory performances.

Results

Tests are carried out using a prototype probe immersed in HNO_3 2N, with a 10mg/L, 50 mg/L and 150 mg/L content of fluorine F^-. Protoype's response is compared to gravimetric results obtained on samples that are corroded in the same conditions. The kinetics of both methods are in very good agreement. The performance of the prototype enabled a thickness variation of about 1 µm to be detected in the 50 mg/L and 150 mg/L solutions and about 0.5 µm in the 10 mg/L solution, with times that depend on the corrosivity of the medium.

An extended critical pitting potential dataset assembled by meta-analytic principles - Data descriptor

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The critical pitting potential is a widely applied technique for fast electrochemical assessment of pitting corrosion resistance of stainless steels. This work presents an elaborate pitting potential data set on stainless steel alloys, assembled by meta-analytical principles. It intends to summarize the reported literature in a systematic and quantitative manner, by expanding significantly a previously reported CRA electrochemical measures database[1]. A systematic review on Web of Science and the data from two European RFCS projects served as additional sources. In its current state, the data set consists of more than 6500 entries from roughly 350 publications.

Next to identifiers for the individual measurement and its source publication, the data set consists of four groups of parameters: (1) surface treatment and metallurgical state, (2) test medium and conditions, (3) the alloy composition and (4) electrochemical test parameters including the critical pitting potential.

New to this data set in comparison to previously described data sets is the quantification of test parameters. Descriptions of surface treatment, metallurgical state and test medium have been quantified to allow for optimal application of regression or machine learning routines. In addition, test medium parameters include not only halides (Cl^- and Br^-), temperature and pH, but also aeration, agitation and several other anions that are known to influence the pitting potential. Some examples are SO_4^{2}, NO_3^- or $(H)CO_3^{(2)-}$, but also MoO_4^{2-} and CrO_4^{2-}. Alloy composition comprises all elements typically reported in stainless steel standards. An additional highlight is the event indicator, which clarifies whether the pitting potential corresponds to an actual pitting event or to transpassive dissolution.

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[1] Nyby *et al* "Electrochemical metrics for corrosion resistant alloys" *Scientific Data* **8**(58) **2021**

An embedded potentiostat and automated data analysis for corrosion monitoring in remote places

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University of Freiburg/Germany, IMTEK – Department of Microsystems

Corrosion is a massive factor in the durability, safety, and profitability of many installations in remote locations, such as offshore facilities. While the corrosion cannot be avoided, protection and maintenance are possible when timely information about changing conditions is available. Electrochemical methods allow for precise corrosion rate and mechanism analyses in the lab. A similar analysis could be applied continuously on-site, preventing expensive, repetitive inspections.

Therefore, we developed Freiburg's Potentiostat (FreiStat) [1], an embedded potentiostat based on the AD5940 integrated circuit (Analog Devices) and a microcontroller platform in the Feather format (Adafruit), which features USB, WiFi, or LoRa connectivity. The key is our sophisticated open-source software framework comprising the firmware, a Python library, and an optional graphical user interface. All essential voltammetric and amperometric methods are implemented, resulting in analytical performance comparable to expensive bench-top devices. The software framework, the schematic, and the board layout are publicly available on GitHub [2].

In this study, we focus on an improved FreiStat hardware to enhance the OCP reading accuracy and the software framework application for automated Tafel analysis. The hardware modification includes an instrumentation amplifier stage at the reference electrode input, reducing the leakage current below 10 fA. Our results compare different steel samples (C1018 and 1.1274/C100S) in aqueous salt solutions around neutral pH with different concentrations of chloride ions and in substitute ocean water. The automated Tafel analysis was implemented both as an edge method and in the cloud to compare the two evaluation schemes.

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2. https://github.com/IMTEK-FreiStat, last accessed: 2024-01-30

High-Temperature Electrochemical Analysis of Chloride-Containing Molten Salts: Cell Design and Quasi-Reference Electrode Selection for Corrosion Studies

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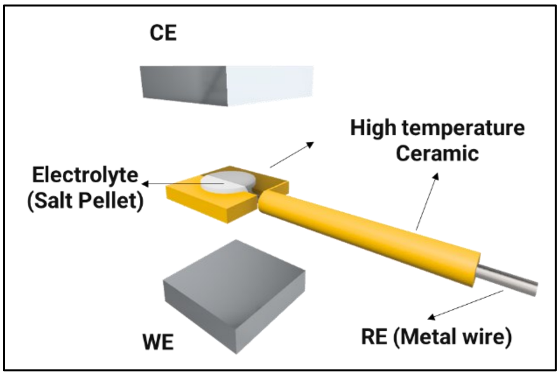
Abstract

This research aims to identify an optimal reference electrode for analyzing chloride-containing multicomponent salt mixtures at high temperatures, particularly in partially molten states. The selection is challenging due to the corrosive nature of molten salts and the complexity of maintaining connections between electrodes and salt at elevated temperatures. A novel cell configuration with a solid electrolyte (pre-pressed salt pellet) and 625 alloy plates as working and counter electrodes is proposed. Various metals, including nickel, silver, platinum, and tungsten, are tested as quasi-reference electrodes. The focus is on ensuring electrode stability, crucial for reliable and reproducible electrochemical measurements. Cyclic Voltammetry and Open Circuit Potential experiments are conducted to systematically assess and select the most stable reference electrode for high-temperature electrochemical analysis in chloride-containing partially molten salts. Additionally, the study explores the development of an oxide layer on reference electrode surfaces and its impact on stability at high temperatures. This research contributes to a better understanding of corrosion control in extreme environments, pertinent to combustion-based processes involving partially molten salts.



An illustration indicating the positioning of the working (WE), counter (CE), and reference electrodes (RE) within the cell.

Investigating corrosion under insulation (CUI) using a novel sensor-based approach, supported by ORP-EIS data

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Corrosion under insulation (CUI) is a form of localized corrosion that occurs due to moisture and ions penetration through the insulation. CUI is a serious concern for petroleum and chemical industries since it is the significant cause of hazardous failures [1-2]. Several on-line techniques can be used to investigate CUI, but monitoring CUI with these techniques is a complicated and time consuming process since some methods require the removal of insulation and cladding or cannot give a direct and reliable indication of the corrosion [3]. In this research we are using a newly developed sensor for monitoring corrosion under a thick layer of insulation. This technique, which is developed by iSensPro, is used as a non-destructive and in-situ method for detecting CUI. To understand and validate the results of the sensor, experiments have been conducted by odd random phase electrochemical impedance spectroscopy (ORP-EIS) [4]. With these two methods, we investigate corrosion under insulation from the top surface of the pipes (cladding) without insulation removal. The primary objective of this research is to investigate the correlation between ORP-EIS data and sensor data for the purpose of analysing electrochemical reactions and monitoring electrolyte uptake within insulation materials. In our previous research, we successfully demonstrated that sensor data can be correlated to the electrochemical characteristics of organic coated metals, including water uptake, transport properties, and corrosion [5].

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[2]. Q. Cao et al. Corrosion engineering, science and technology. 1743-2782 (2020).
[3]. Y.Hou et al. Material degradation. 39 (2020).
[4]. T.Breugelmans et al. Electrochemistry communications. 12 (2010).
[5]. Z.Jiryaeisharahi et al. Progress in organic coatings. (2024), under review

Electromagnetic quantification of moisture in insulation for improved safety, mitigation of energy losses and corrosion under insulation

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Moisture in thermal insulation causes corrosion under insulation, presents a safety hazard for personnel, impacts on process stability and increases energy consumption. Historically, process plant operators have had no satisfactory techniques available to detect and measure those regions of insulation that are being degraded by unwanted liquid ingress.

In this work we describe a novel, minimally-intrusive approach for detecting and quantifying unwanted liquid ingress using electromagnetic waves transmitted over long distances through pipes' thermal insulations. The interaction between known quantities of moisture and the electromagnetic excitations are described and a satisfying relationship between moisture content distributed throughout insulation and electromagnetic signal transmissions is demonstrated.

This work shows that for the first time, process plant operators can intermittently or permanently monitor and quantify moisture content over large portions of process plant and can estimate the degradation and damage being caused. With this knowledge, operators can then promptly identify those regions of process plant requiring most urgent maintenance or repair.

Modelling of Longitudinal and Torsional Waves on Viscoelastic Coated Pipelines

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Abstract

The deployment of long-range guided wave devices at critical locations on ultra-deepwater pipelines, where high failure probability is anticipated, may justify deferred or reduced frequency of initial in-line inspections (ILI) without compromising pipeline integrity. This could reduce ILI costs and production disruptions. However, determining appropriate ILI deferral requires understanding the resolution, sensitivity, and probability of detection (PoD) of the non-destructive technique compared to conventional ILI methods like magnetic flux leakage. These parameters depend on pipeline wall thickness, geometry, and surface conditions (e.g. bare, coated, corroded). Therefore, investigating how these factors impact guided wave testing (GWT) performance is critical. This study aims to design a finite element model simulating 24 m long, neoprene-coated, welded steel pipes. The model is used to evaluate coverage, resolution, and accuracy of long-range ultrasonic inspection for internal corrosion detection. Additionally, PoD as a function of defect size is characterized to determine the 90% detection likelihood with 95% confidence threshold.

Keywords: Guided Wave Ultrasonics, Corrosion Monitoring, Viscoelastic coating, Probability of Detection, Defects.

Comparative Analysis of CMI and DCVG in Corrosion Protection for Buried Pipelines

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This presentation offers a detailed analysis of Current Magnetometry Inspection (CMI) versus Direct Current Voltage Gradient (DCVG) for evaluating corrosion protection in buried pipelines. The ability of CMI to detect a wider range of coating defects, including smaller ones, is crucial for accurately assessing the state of steel at a pipeline under Cathodic Protection (CP). The analysis reveals the comprehensive detection capabilities of CMI in identifying and assessing defect severity and corrosion status. In contrast, DCVG, while effective, shows limitations in such detailed assessments. The data suggests CMI's enhanced effectiveness in providing insights into the integrity and efficacy of CP, particularly in complex scenarios.

Identification, Characterization and Prioritization of Pipeline Integrity Threat Anomalies with Non-Contact Magnetic Gradient Tomography Method (MTM-G)

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Abstract

To prevent pipeline failures on buried metallic pipelines, a corrosion and pipeline integrity management plan must be implemented. On piggable buried pipelines, inline inspection is the most used pipeline integrity assessment tool for identifying and quantifying corrosion defects before prevention and remediation actions are implemented. For difficult to pig pipelines the Association for Materials Protection and Performance (AMPP) direct assessment (DA) methodologies are used to address external corrosion, internal corrosion, and external stress corrosion cracking issues.

One of the biggest advantages of inline inspection is the ability to identify and quantify defects on buried piggable pipelines. On difficult to pig pipelines, there is no direct assessment (DA) indirect inspection tools that can identify metal loss from aboveground without exposing the buried pipeline for ultrasonic thickness measurements. This deficiency has led to the advancement of Non-Contact Magnetic Gradient Tomography Method (MTM-G). This technology can locate stress concentration areas and help prioritize areas of concern on a pipeline by measuring the magnetic field strength. With the magnetic field strength, metal loss can be measured and quantified on all buried pipelines (including unpiggable pipelines). MTM-G can be effective in detection of anomalies associated with the mechanical stresses, directly measured by natural magnetic response from the pipeline material and without necessity direct assess to the size of each individual defect. For pipeline integrity management programs, the local stresses are registered directly and conventional safety parameters (like Psafe, Tsafe, SCF, ERF) are assessed through direct magnetic response measurements.

This paper presents proven identification, characterization, and prioritization of pipeline integrity and geohazard anomalies on buried pipelines. The results from this case studies are good news for unpiggable pipeline operators that have been looking for ways to identify and prioritize anomalies to ensure effective pipeline integrity management.

Corrosion Inhibitors Residual Measurements Economics Opportunity

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Abstract

Electrochemical biosensors are advantageous analytical devices or tools that convert a bio-signal by biorecognition elements into a significant electrical response.
The complexity chemistry of corrosion inhibitors and proprietary of the active ingredients present a second dimensional challenge in determining their concentrations. The involved advanced analytical technologies are colorimetry, chromatography, and spectroscopy. The major drawbacks of these technologies include their limited portability, detection limitation, and rather expensive instrumentation, which hinder their deployment and use in the field. While the main technology gaps are lacking of reliable, sensitive, and selective analytical methods to detect low concentrations of these chemicals in complex solution and in presence of other chemicals. The Corrosion inhibitor detection technology market and opportunities will be detailed in this paper which are driven by global demand on crude and aged facilities.

Key words: Corrosion inhibitors, residual, analytical method, detection technologies, Corrosion monitoring, Corrosion control,, Corrosion Inhibitor Residual,
.

An updated Pitting Resistance Equivalent Number by proportional hazard regression of reported pitting potentials

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KU Leuven - Ghent, Ghent/Belgium
2) Orstat, Faculty of Economics and Business, KU Leuven, Leuven/Belgium

The pitting resistance equivalent number (PREN) is a simple calculation tool to compare pitting corrosion resistance of stainless steels in chloride environments. Its formulation takes the elemental composition into account, with a focus on Cr, Mo and N. For other alloying elements or impurities, such as W Mn and S, the influence is known qualitatively but their specific importance is less broadly supported.

Besides alloy composition, the test medium directly influences the corrosivity of a fluid and so the observed corrosion resistance. Chlorides contribute mostly to corrosivity, but its action is inhibited by other anions, such as OH^-, SO_4^{2}, NO_3^- or $(H)CO_3^{(2)-}$ [1, 2]. Furthermore, surface pretreatments (grinding, passivation) and metallurgical state (quenched, sensitized, work hardened) influence corrosion resistance but quantification remains limited. There would be a high added value to know how a change in alloy composition compares to differences in conditions (chlorides, temperature, anions), surface treatments and metallurgical state.

A pitting potential data set was constructed by meta-analytical principles to include all forementioned parameters as covariates. Statistical techniques were applied to correct for missing data, source dependence and the competition between actual pitting and transpassive dissolution. Because the pitting potential has been explicitly linked with Weibull statistics, the current study explores how the parametric Weibull model quantifies the impact of surface treatment, test medium and alloy composition on pitting potential. This regression analysis allows us to update the PREN formulation, and not only to include alloy composition, but also surface treatments, test medium composition and test conditions.

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[2] McDonald, Zhu *et al.*" Corrosion of rebar in concrete. Part I – IV" *Corrosion Science* (2020 - 2021)

Corrosion monitoring and vapor-phase protection study of mild steel in simulated storage and transportation atmospheres

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Abstract - Corrosion monitoring can provide a direct basis for early risk warning of infrastructure with technologies such as electrochemical sensors (EIS), quartz crystal microbalance (QCM), electrical resistance probes (ER), and others. In this report, the corrosion behavior of carbon steel was investigated when contaminated by lone and mixed NaCl-$(NH_4)_2SO_4$ particles during cyclic wetting and drying test, aiming at understanding the atmospheric corrosion mechanisms of carbon steel in coastal industrial environments. In contrast to the deposition of NaCl particles, the corrosion of $(NH_4)_2SO_4$ deposition on carbon steel is unique, where the thickness loss of NaCl-contaminated metal presents an “up-ramp” increase, but that of $(NH_4)_2SO_4$-contaminated shows a sharp increase in the first period but a “plateau” increases in the subsequent test regardless of the $(NH_4)_2SO_4$ loading density. Moreover, mixed NaCl and $(NH_4)_2SO_4$ deposit could synergistically accelerate the corrosion of mild steel more than any single kind of NaCl or $(NH_4)_2SO_4$ deposit under the same deposition density. With increasing NaCl proportion in the mixed deposition, the main growth mode of corrosion products is also gradually transformed from horizontal to perpendicular direction. Besides, the interfacial interaction of microdroplets in anti-rust oil was investigated by quartz crystal microbalance, and the evolution of localized corrosion was mapped by wire beam electrode in a simulated atmospheric environment, hoping to understand the emulsion and demulsification process of water /oil interface and the corrosion kinetics of mild steel under oil film.

Performance of MoO_x pH sensor prepared by thermal oxidation for the long term monitoring of nuclear waste disposals

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"Cigeo" is the name of a future deep geological disposal facility for high-level and intermediate-level long-lived radioactive waste, to be built in France, at 500 m depth within the Callovo-Oxfordian formation (Cox). The Cox is a 130 m thick clay-rich rock, dating back to 160 million years ago and lying at a depth of 400 to 600 m. It is a water-saturated environment with extremely low permeability, porosity and hydraulic conductivity. In order to monitor the evolution of the near-field around radioactive waste, the implementation of reliable sensors turn out to be useful to support storage safety and reversibility. pH is one of the important parameters characterizing physical, chemical, and electrochemical transformations to be monitored.

This study aims to develop pH innovative all-solid-state electrodes based on molybdenum Oxide (Mo_xO_y)/ molybdenum (Mo). Understanding the electrochemical behavior of such metallic coatings is the key point of our research, as provides the tools for constructing and exploiting the Potential-pH abacuses, which are necessary for developing robust and reliable pH sensors. The sensors were prepared by thermal oxidation at 370, 400, 500 and 600°C. The sensibility of electrodes was then evaluated by potentiometric measurements during electrode immersion in pH buffers solutions, at 25°C, under both oxic (at atmospheric pressure) and anoxic conditions (in a glove box, $pN_2 = 1$ atm; $pO_2 = 10^{-6}$ atm) and in the presence and the absence of sulfides.

MoO_x films seem to be robust and steady on adherence and exhibit a good and increasing sensitivity with the heat treatment temperature. After thermal oxidation, the immersion of the electrodes in milliQ water for 70 days allows the hydration of the MoO_x layer, which is responsible for another increase of sensitivity. XPS analyses were carried out before and after hydration, to determine the main redox couples responsible for electrode response to pH variations. Finally, the performance of MoO_x - pH sensors show their utility and ability for long-term pH monitoring.

Effect of alloy composition on cathodic current density for cathodic protection of aluminium

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4. Norwegian University of Science and Technology NTNU, Trondheim, Norway

Objectives. Cathodic protection (CP) design codes are focused on steel and do not provide the necessary information about how to design with Al. The objective of this work was to investigate CP design criteria for aluminium in seawater, i.e. effect of alloy composition on cathodic current density.

Results. Various 6000 series model alloys, and commercial 6082 and 5083 were studied. Cathodic current density depended on their contents of Cu, Fe and Si. An initial peak in current density after about 40 days exposure with CP correlated strongly with Cu content. A TEM and GDOES investigation showed that a Cu rich film had been formed at the interface between the alloy and a layer of Al_2O_3. The current density then decreased over a period of about 100 days, and the Cu film was shown to disappear. The current density stabilized at a lower level that correlated with the Fe/Si ratio in the alloy, and a simple mathematical relationship was found. Si is known to reduce the cathodic activity of Fe rich intermetallic particles, which was verified by cathodic polarization of synthesized Fe rich particles with varying Si content. The design current density for CP of aluminium in DNV RP-B-401 is 10 mA/m², while the current density in this work stabilized on values between 0 and 20 mA/m², depending on alloy composition.

Conclusions and significance of the work. The current demand for CP of aluminium alloys depends on the alloy composition, i.e. the contents of Cu, Fe and Si. The current demand for some alloys is higher than the design value in DNV RP-B-401, i.e. non-conservative.

Hydriding of titanium tubes under cathodic protection: Study of the influence on the mechanical properties and application of the case main condenser in French nuclear plants

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[*]***Keywords: condenser, mechanical properties, cathodic protection, hydrides, titanium***

Introduction

Titanium, due to its good corrosion resistance in seawater, has been selected for material of condenser tubes on seaside PWRs. However, other condenser parts are made of less noble materials: copper-aluminium alloy or unalloyed steel. The use of these different materials, electrically connected and immerged in seawater, may lead to galvanic corrosion of the less noble components. That is why cathodic protection (CP) is used to protect those against this particular corrosion. Impressed current cathodic protection system is installed on seaside condensers of nuclear plants and potential values of structure are set. If this potential is adjusted at too highly negative values, hydrogen may be produced in titanium tubes. Due to high affinity between Ti and H, they combine to form Ti-hydrides, which may induce an embrittlement of the tubes. This embrittlement may lead to the apparition of cracks and so to the pollution of the secondary circuit by the cooling water. The understanding of the damage mechanism is expected to help finding solution to limit its consequences on the performance of the plant.

Objectives

In order to study the impact of such hydriding phenomena, tensile strength tests and metallographic examinations have been performed. This presentation will speak about the results and the interpretation of this expertise. A focus will be made on the following points:

- To determine the impact at room-temperature of hydride layer on Yield Strength (YS), Ultimate Tensile Strength (UTS) Elongation at break and fatigue related to its thickness.
- To increase the understanding of the hydriding phenomenon with the study of degradation in relation to multiple factors as the position of the tubes, the distance to the tube sheet or the strain hardening due to the tube expansion during the manufacturing.
- To characterize the degradations observed in operation and establish a possible link with hydriding.

Implementation of a Cathodic Protection solution on corroded FPSO mooring chains

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Mooring lines for permanently moored Floating Production and/or Storage and Offloading Units (FPSO) are critical components to ensure that the floating units remains on station at all to times and therefore are a key contributor to their integrity. The mooring line of a floating unit moored in deep water environment is usually consisting of a top chain - synthetic wire rope – bottom chain assemblies, attached to piles at the bottom and connected at the top to the FPSO. Mooring chains are made of carbon steel (CS) and exposed to harsh seawater environment and high corrosion risks. Corrosion control of the mooring chains is then essentially based on corrosion allowance (CA) when uniform or generalized corrosion is the expected type of corrosion for CS exposed in seawater. However, under specific conditions, localized corrosion with higher corrosion rates have been experienced on mooring chains in submerged near-surface zone. This paper will focus on severe localized corrosion observed on the top chain links of FPSOs operating in Gulf of Guinea and the measures implemented to limit such active corrosion.

These localized corrosions are thought to be due to microbiologically induced corrosion (MIC) that developed underneath the heavy marine growth. Checks of the Cathodic Protection (CP) potential along the chain concluded on the absence of current drainage from the FPSO CP system that could have help to protect the chain top section against corrosion. To limit such active corrosion on the chains, several solutions have been envisaged like for instance, forcing current drainage from the FPSO cathodic protection system to the chain. Finally, the selected remedial action has consisted in the implementation of a dedicated galvanic anode CP system installed on the chain stoppers and electrically connected to the mooring chains top section. To design the retrofit system, several key parameters were studied such as the interlink resistance but also the attenuation of the cathodic protection potential along the chains using CP modelling software to confirm the section of chain exposed to MIC threat can be adequately protected by CP over the concerned length.

Impressed Current Cathodic Protection (ICCP) of a submarine museum in Saint Nazaire (France)

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The submarine Espadon is now converted into a museum located in Saint-Nazaire (France) within the ecomuseum. Manufactured in the 1950s, it is located in the airlock of the old port lock, and maintained in partial immersion. It is the only submarine that can be visited afloat in France.

Saint Nazaire Agglomeration Tourism decided in 2021 to launch a complete rehabilitation of the submarine.

In this context a new cathodic protection system has been designed and implemented. This project was divided into two stages. First, we realized in-situ tests. We injected current through stabilized current supply and followed the potential to estimate the real current requirement of the structure.

In a second time we proceeded to the design and installation of cathodic protection system of the outer hull of the submarine. An impressed current cathodic protection has been selected. It was constituted of 3 transformer rectifier, 6 Ti-MMO anodes and 3 zinc reference electrodes. In order not to modify the structure of the submarine, the anodes were fixed on the concrete walls of the area. Reference electrodes are suspended near the hull.

We have done its commissioning and adjust current on a three-month period. We have calibrated the permanent reference electrodes prior to perform measurements. We used portable silver/silver chloride sea water reference electrode for calibration and measurements.

Optimization and performance improvement of photoelectrochemical cathodic protection materials in marine environments

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In recent years, the position of the ocean in national strategic development has become increasingly prominent. However, metal materials that serve in harsh marine environments are facing extremely serious corrosion problems, which seriously hinders the rapid development of marine technology. Photoelectrochemical cathodic protection technology (PECCP) is a newly green and environmental-friendly corrosion protection technology, which can use the abundant solar energy in the ocean to "treat corrosion with light" - utilizing the photoelectric conversion effect of semiconductor materials to generate electrons, and then transfer them to marine metals to provide a protective effect similar to the impressed current cathodic protection technology. Here, we summarize some research progress of our research group in the application of TiO_2-based ordered structured materials in PECCP in recent years, and provide some new ideas for corrosion protection of metal materials in marine atmospheric zone.

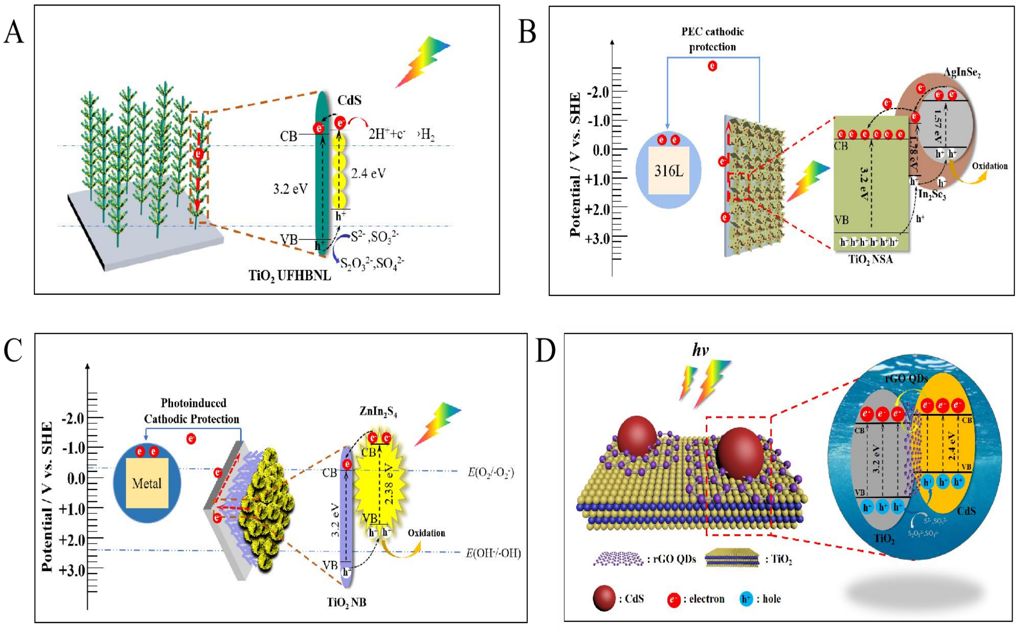

Figure 1. The constructed PECCP photoanodes and schematic illustration of the mechanism.

Optimization of Cathodic Protection Retrofitting Solutions for Offshore Jackets

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1) TotalEnergies, Pau/France

When comes the need for extending the lifetime of offshore conventional production facilities, Cathodic Protection (CP) retrofitting for jackets shall be studied to propose the most optimized and cost-effective solution. Whatever the cathodic protection system (Impressed Current or Galvanic Anodes), real needs in terms of CP current and relevant anodes to reach the new service life must be accurately evaluated. In some cases, Oil & Gas Companies deal with CP specialized Contractors to provide such CP design and to define the need for galvanic anodes sled or other retrofit solutions for jackets. However, it can happen that the proposed CP design and relevant retrofitting equipment to be installed appear as very excessive, leading to very high costs. Actual CP current demand and the need for new anodes shall be driven by the initial cathodic protection design, the last CP potentials measured on the jacket, the last inspection results assessing the anode mass consumption but also taking reference of international standards to provide an optimized design for the future years of operation. Such assessments often show that necessary conservatism in original design can result in a relatively reduced need for retrofit anode mass. Timing of retrofit is important and will be discussed. There, the experience of senior CP specialists is required to challenge the proposal from CP contractors, define the most adapted CP design retrofitting solution with respect to the extended service life, and really limit CP retrofitting and relevant costs to the minimum required.

SEAGA Project: Presentation of a multidisciplinary research programme about environmental impact of Al-Zn-In galvanic anode dissolution

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Metallic structures immerged in seawater are subject to corrosion. To prevent it, cathodic protection is one of the most common solutions. Cathodic protection is an electrochemical method which involves providing electrons to the structure to be protected. Two types of cathodic protection system are available: Impressed Current Cathodic Protection system (ICCP) or Galvanic Anode Cathodic Protection system (GACP). GACP is based on the corrosion of a sacrificial material instead of structure to be protected. This dissolution leads to the transfer of metallic elements in the marine environment. The environmental impact of such cathodic protection is not well documented and there is no consensus in the scientific community. That is why EDF carries a research program called SEAGA (Suivi Environnemental des produits de degradation des Anodes Galvaniques Aluminium-zinc-indium – Environmental study of Aluminium-Zinc-Indium galvanic anodes corrosion products). It is a collaborative project bringing together scientific and technical partners with solid experience in different fields: ecotoxicology, seawater chemistry, analytical chemistry, material characterisation, material degradation, …

The sheet piling of a gabionade of EDF installation was chosen because it has the largest quantity of installed anodes: around one hundred and fifty-five tons.

This study focuses on three objectives:

- Evaluate the influence of cathodic protection by Al-Zn-In galvanic anodes on the chemical characteristics of the different targeted compartments (water, fauna, sediment).
- Contribute to the knowledge of the chemical composition of the oxide deposits formed on the surface of the anodes when they dissolve and the destination of released metallic elements in the environment.
- Evaluate the potential impact on marine environment, especially on fauna, close to the structure to be protected.

This project will begin at the second semester of 2024th and finish at the first semester of end of 2027.

INTERNAL CATHODIC PROTECTION DIGITAL SIMULATION

OBJECTIVES :

Many factors impact the design of internal cathodic protection such as conductivity, chemical parameters, geometrical discontinuities like flanges, internal pipes, nozzles as well as metal differences which can create galvanic corrosion.
These protections are currently carried out mainly by feedback on existing installations and can lead to miscalculation and bad results.
The purpose of 3D modeling, will be:

- to optimize anode geometries for homogeneous distribution of wall's potential and currents
- to estimate and optimize cost prior to installation (number and power of DC generators, anodes' quantity...)
- to select the best location to put the reference electrodes.
- to monitor anode lifetime

RESULTS :

With some iterations, solutions can be found to protect non-obvious geometries. The method to follow (from first hypothesis to the way to mesh will be explained) and examples will be showed of a perfect match between modeling and what is found regarding corrosion when internal inspections are led.

CONCLUSION :

Digital modeling should be used whenever a Cathodic Protection (either with impressed current or galvanic anodes) is planned to be used inside tanks or capacities.

High accuracy Marine contact less Cathodic Protection Measurements and analysis

Autonomous vehicles have been introduced as efficient tools for subsea pipeline inspections. It has also been demonstrated that AUVs can be used to perform contactless and continuous electric field measurements of the Cathodic Protection (CP) systems along pipelines. In this lecture we present some improvements over other systems where the electrodes are in flush with the AUV's hull, and the system is fully integrated with the AUV. The system provides highly reliable and calibrated electric field measurements, with excellent signal-to-noise ratio. The in-flush integration of the electrodes significantly reduces the risk of damages during launch and recovery of the AUV.

A working CP-system generates electric currents in the seawater which can be measured as a 3D electric field in the vicinity of the pipeline or underwater structure. In particular, electric current is going out from each anode and returns into the structure at dedicated drain points or at places where the coating has been removed or damaged into bare metal. The CP-system works as a galvanic element.

An AUV equipped with an electrode sensor system can continuously measure the 3D electric field at a height of 5-10 m above a pipeline in a speed of 3-4 knots. The electric currents going out from each anode into the seawater, are obtained from a linear system of equations with the measured electric field. Once, the electric currents going out and into the pipeline, the anode material consumption rate can be estimated. In fact, the anode output current is proportional to the material loss rate. With this information together with camera pictures, the status of the CP system can be determined. Damages are revealed and the amount of consumed anode material are determined.

The AUV integrated electrode sensor system has successfully been tested on a pipeline section partly on the seafloor and partly buried. The AUV was flying 5-6 m above the pipeline section in 3 knots. Multiple runs back and forth were conducted to check for repeatability and consistency in the acquired data. The vertical component of the electric field from two of the runs is shown in the left plot of figure 1.

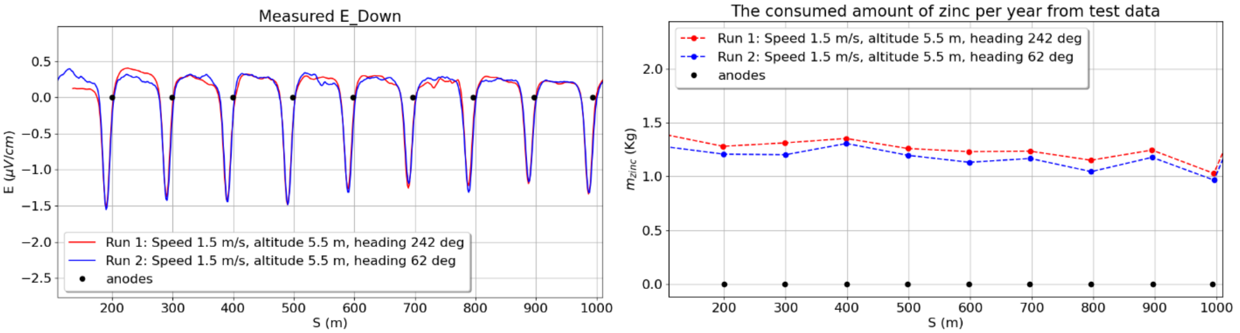

Figure 1. Vertical electric field data (left) and estimated anode material consumption rate (right).

The signal to noise ratio in the signal peaks above the anodes is high (about 30 dB). The repeatability between the runs are good with low noise in the data between the peaks. This data accuracy makes it possible to determine the anode output currents with high precision and then enabling good estimations of the consumption rate shown in the right plot of figure 1. It can be concluded that the AUV with the implemented electrode system and accurate navigation facilities efficient and accurate investigations of pipeline CP-systems on or below the seafloor.

Coatings for marine propeller: experimental investigation of antifouling performance and impact on cathodic protection current demand

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Marine propeller work in a severe environment with high rotational speed in corrosive seawater and biofouling development. An uncoated propeller is the primary source of ship's cathodic protection current demand. For military ships, this high current demand will decrease their electric discretion. Furthermore, the uncoated propeller promotes the development of biofouling on its surface and leads to the increase of fuel consumption.

In this study, the impact of three coating systems on cathodic protection current demand and theirs antifouling performance were investigated thanks to a specific multichannel electrochemical rotating system.

Cathodic protection modeling and installation of a steel pipeline embedded in masonry

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Christophe BAETE, ELSYCA, Leuven/Belgium
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The subject of this study pertains an aboveground 1000 mm steel pipe settled by anchoring blocks at discrete intervals along the slope of the mountain. Due to the remote location and limited construction techniques at time of installation (70 years old pipeline), the anchoring blocks consist of masonry with heterogeneous composition.

A field test was performed to assess the condition of the steel pipe in contact with the masonry and to perform some preliminary on-site testing for defining the current demand of the structure. The data was used to calibrate a finite element (FEM) based computer model that was use for designing an effective cathodic protection system. The system was installed in august 2023 and some results will be presented after close one year of operation.

Advancing Cathodic Protection Depth: Integrating Discrete Anodes with Electroconductive Coating for Enhanced Performance in Reinforced Concrete

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Abstract

Reinforced concrete structures encounter formidable challenges stemming from the corrosion of embedded rebars, jeopardizing their long-term durability. This study delves into cathodic protection as a sustainable remedy, with a specific emphasis on contrasting single anodic device utilization with a dual anodic device approach. In scenarios where reinforced concrete structures confront chloride exposure on an inaccessible surface, the reinforcement in need of protection is distantly positioned from the exterior that is reachable. Consequently, employing discrete anodes deeply embedded in the concrete may prove insufficient to furnish adequate protection to the rebars near the surface exposed to chlorides.

This manuscript addresses the implementation of a dual anodic device system: an electroconductive device synergized with discrete anodes. Devising such a dual impressed current cathodic protection system entails addressing various challenges, including the optimization of current distribution between the two anodic devices. Striking the optimal balance for overall performance while averting rebar over-polarization and anode acidification constitutes pivotal considerations.

Confronted with these challenges, the amalgamation of multiple anodic systems on a singular structural element may yield intriguing performances. This article spotlights the innovative integration of discrete anodes within the concrete matrix and an electroconductive coating on the exterior. The objective is to showcase the advantages of this combined approach in achieving a sufficiently profound level of cathodic protection.

The presented combinatorial strategy furnishes the capability to effectively polarize rebars situated deep within the concrete, a challenge unaddressed by the deployment of a lone system. This methodology opens avenues for more efficient cathodic protection solutions, fortifying the endurance of reinforced concrete structures.

In conclusion, the paper underscores the imperative for an efficient monitoring system to govern the distribution of current protection between the two anodic systems. A solution incorporating AI Technology is consequently delineated.

Analyzing the Risk of Brittle Failure in Prestressed Concrete Structures: Interplay between Corrosion and Cathodic Protection

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2) Bluespine, Champfleury/France

Abstract

This paper delves into the potential risk of brittle failure in prestressed concrete structures, examining scenarios involving corrosion and/or cathodic protection. Firstly, the risk of brittle failure attributed to the corrosion of prestressed wires is addressed. Non-uniform corrosion of steel in concrete structures leads to local notches in prestressed wires, resulting in stress concentration. This stress concentration diminishes the plasticity reserve in the corroded area, potentially surpassing the ultimate stress locally and leading to brittle failure. The study demonstrates that, in the context of prestressed reinforced concrete structures, the brittle failure of a wire does not necessarily induce a collapse of the overall structure.

Secondly, the paper explores the risk of brittle failure caused by hydrogen embrittlement. Hydrogen evolution in concrete structures under cathodic protection may occur as a cathodic electrochemical reaction due to high polarization. The limit potential for this evolution depends on the local pH, as discussed in the paper concerning the macrocell process of steel corrosion in concrete. The paper scrutinizes both the effects of hydrogen on the behavior of reinforcing steel and its impact on the bond at the steel-concrete interface.

Thirdly, the discussion extends to the concept of safe potential in cathodic protection, following the specifications of the EN ISO 12696:2022 standard. Evaluating the risk of brittle failure in concrete structures, the paper demonstrates that corrosion poses a more significant risk compared to hydrogen embrittlement. Consequently, the paper proposes a new examination of the safe potential to suggest a unified value applicable to both reinforced and prestressed concrete structures.

Impressed current cathodic protection of prestressed concrete structures: safe potential limit and approach of risk management

Elie SASSINE [1], *Chantal CHALHOUB* [1], *Arnaud DUBOSC* [1], *Erwan COLOMB* [1],
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Abstract

Impressed Current Cathodic Protection (ICCP) is one of the electrochemical techniques used to reduce or stop corrosion in reinforced and prestressed concrete structures. To guarantee the performance of ICCP, some risks need to be controlled, such as acidification of the anodic zone and the insufficient protection of steels. These two risks can be controlled by following the specifications mentioned in the ISO 12696:2022 standard. This standard also manages the risk of excessive protection for plain reinforcing steel by avoiding potentials more negative than -1100 mV vs Ag/AgCl/0,5M KCl. As a reminder, a safe potential limit for prestressing steel was set at -900 mV vs Ag/AgCl/0,5M KCl before 2022. The existence of this limit relies on the risk of hydrogen embrittlement of prestressing high-yield steel tendons under ICCP. However, this former safe potential limit is no longer considered in last version of the standard (2022). Today, the standard states that the safe potential limit for prestressing high-yield steel shall be determined for each structure, but does not clearly explain how to do it properly. Moreover, the standard mentioned the safe potential limit may not exist in case of pre-corroded tendons. In this context, the aim of this article is to present a general 3-step approach to control the risk of hydrogen embrittlement in prestressed concrete structures:

- Step 1: Determination of a safe potential limit based on water's stability domain (Pourbaix diagram) and by considering the available scientific literature.
- Step 2: Management of the risk of overpolarization by defining an optimal network of embedded reference electrode.
- Step 3: Additional acoustic monitoring

Application of a galvanic anode on an historical building

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Olivier LESIEUTRE, Resmaibe, Fleurieu sur Saône/France
Myriam Bouichou, Laboratoire de Recherche des Monuments Historiques
, Champs-sur-Marne/France
Elisabeth Marie-Victoire, Laboratoire de Recherche des Monuments Historiques, Champs-sur-Marne/France

The renovation of a French building classified as a historic monument must meet specific requirements, in particular very precise rules within the framework of the scientific and technical control. This presentation reports the development of a galvanic anode for the cathodic protection of steel I-shaped metal frame made up of riveted angles and plates embedded in concrete.

Depth analysis of gradient formation and degradation in wrinkled coil coatings by XPS and FPA-FTIR

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Coil coating represents a highly efficient method to produce high-quality finishes, which are specifically tailored to enhance the corrosion resistance and aesthetics of metallic sheets. For desired low-gloss appearance in, *e.g.*, roofings, wrinkle coatings with a certain degree of surface corrugation are commonly applied. However, despite various mechanical and chemical mechanisms contributing to wrinkle formation have been extensively discussed in in the past, a profound understanding of textured finishes based on comprehensive and in-depth experimental analysis is yet to be acquired.

Here, the interior chemistry of wrinkled polyester-melamine based coil coatings was thoroughly examined by combining advanced surface analysis techniques with cryo-ultra-low-angle microtomy (cryo-ULAM), which was recently determined to provide effective means for the assessment of the internal structure of organic coatings [1]. The presence of a thin corrugated skin with specific mechanical and structural properties at the coating surface and chemical gradients inside of such wrinkled coil coatings were consistently detected by X-ray photoelectron spectroscopy (XPS) mappings and focal-plane-array Fourier-transform infrared (FPA-FTIR) spectroscopy in attenuated total reflectance mode recorded along extended cryo-ULAM sections. Furthermore, correlative depth-resolved analysis allowed to investigate degradation processes inside the organic coating matrix after accelerated weathering in QUV testing chambers, which consequently enabled to quantify the loss of the melamine triazene functionality within the coating material.

References

[1] D. Leidlmair, J. Duchoslav, G. Mayr, M. Arndt, H. Gsaller, B. Strauß, D. Stifter, Elemental and chemical depth profiling of high-build single-component (1K) polyester-polyurethane coil coatings, Progress in Organic Coatings 179 (2023) 107490, doi: https://doi.org/10.1016/j.porgcoat.2023.107490.

Four-electrode experiments for impedance analysis of polymer-based coatings

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Barrier effect of organic coatings, although encompassing numerous inherent mechanisms of the polymer system (water uptake, ion and gas permeability, substrate adhesion, or chemical stability), remains poorly defined, and its implication in corrosion protection is not well understood[1]. Understanding the barrier effect and more precisely the water/macromolecule interactions and the behavior of the macromolecule in a hydrated environment is crucial in the durability of corrosion protection.

In recent years, we have demonstrated, that Electrochemical Impedance Spectroscopy (EIS) is a powerful tool for probing the molecular mobility of organic coatings during immersion in an aqueous electrolyte in the temperature range [25 °C; 80 °C][2,3]. From the impedance spectra analysis, the response of the substrate and particularly the appearance of corrosion was also identified[3].

The present work aims first, to compare the impedance response obtained with a three and a four-electrode experimental cells to highlight the role of the metal/polymer interface, at room temperature. Then, a four-electrode thermostatic measurement cell was developed to study a polymer system, the polyamide 11, in the form of a free-standing film (unsupported on metal). Diffusion of water and chloride ions into the polymer film were analyzed in relation to the molecular mobility and charge transport phenomena. Finally, differential calorimetry analyses (DSC) in immersion complemented the understanding of water/polymer interactions.

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2- *A. Roggero et al.,* Thermal activation of impedance measurements on an epoxy coating for the corrosion protection: 2. electrochemical impedance spectroscopy study, *Electrochim. Acta 303 (2019), 116-124.*
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Characterizing the surfactant distribution and its effect on the water transport in a model waterborne anticorrosion coating

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In response to the prevailing environmental concerns of our time, government agencies have made significant efforts to restrict the release of volatile organic compounds (VOCs). As a result, waterborne coatings have emerged as a promising alternative to solvent-based coatings in various applications due to their inherently low VOC emissions. However, it is worth noting that waterborne coatings may exhibit inferior properties and durability compared to advanced solvent-based solutions, thus limiting their applicability in diverse markets. One of the key challenges in further enhancing waterborne coatings lies in the limited understanding of the intricate relationships between the heterogeneous architecture of the polymer film, its chemical composition, and crucial performance parameters such as water uptake, adhesion, and mechanical properties. This study aimed to establish a connection between the architecture of the polymer film and its water absorption characteristics. By tuning both the particle size and interparticle cohesion through annealing and surfactant content, one can control the polymer film's architecture. Rheology was employed to characterize the architecture and concentration of heterogeneities within the film. Gravimetric and Electrochemical Impedance Spectroscopy measurements were utilized to investigate the water absorption properties. Additionally, a water-soluble fluorescent compound was introduced to illuminate the preferred routes of water absorption within the film's microstructure. These routes were expected to contain higher concentrations of surfactant, given the compound's polar nature. This approach enabled the visualization of surfactant distribution throughout the films, as well as its variation in relation to the aforementioned architectural parameters. Notably, the distribution of surfactant was found to be strongly correlated with both the anticorrosion properties and mechanical properties of the coatings. The precise determination of architectural parameters, achieved through the deconvolution protocol of the relaxation spectrum combined with imaging of surfactant concentration, has resulted in a deeper understanding of the mechanisms governing film formation and water absorption in these coatings.

In-Situ Analysis of Waterborne Coatings: Combining Reflective Microscopy and Electrochemistry to Explore Adhesion and Corrosion Dynamics

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With European directives mandating reduced volatile organic compound (VOC) emissions, alternatives to solvent borne coating systems are gaining relevance – such as water-reduced and waterborne colloidal coating systems. In the past couple of decades, there has been substantial progress in waterborne coatings; nevertheless, the more advanced solvent-based equivalents are still fundamentally better understood, highlighting the need for further research to bridge this knowledge gap. This study focuses on waterborne colloidal coating systems, where film formation is complex and its relation to protection is not fully understood. Waterborne colloidal coatings can develop various defects during their formation – such as nanoscopic holes, interfaces, cracks, adhesion loss, etc – facilitating the penetration of water, oxygen, and ions to the metal substrate. At the moment, there is not much known about the specific effect of these defects on adhesion and corrosion behaviour. In this work we used an in-situ optical-electrochemical technique to investigate the impact of colloidal particle size on film defects and its relation to water/ion penetration, adhesion and corrosion properties. Model waterborne coating systems were used, with film heterogeneity primarily introduced by varying colloid particle size and surfactant concentration. The systems under study were optically monitored at high spatial and temporal resolution at their Open Circuit Potential (OCP) or while being catholically polarized to induce film failure at the metal/coating interface—cathodic delamination and, in some cases, blister formation. Image correlation combined with electrochemistry allowed revealing fundamental processes taking place at the coating/metal interface. The study also tries to make correlations between the radii of metal ions in the electrolyte and defect dimensions in the coating. Real-time monitoring and analysis of optical and electrochemical data provided insights into water/ion interaction at the metal/coating interface and its movement through the coating—factors critical to understanding and predicting corrosion and coating failure.

The charge-transfer mechanisms of ‘D and I-type’ conductions in detached and attached films: What do we know so far?

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Abstract

The coating heterogeneity is caused by the variation in the polymer structure that affected the coating resistance and charge-transfer mechanisms which is linked to the diffusion process. In this work, Direct and Inverse conduction (D-type and I-type) behaviours have been investigated by electrochemical impedance spectroscopy (EIS). The epoxy-amine (Bisphenol A diglycidyl ether and m-xylenediamine) films were exposed to 0.5M and 3.5M NaCl solutions. It has been found that the diffusion process in a single-layer film developed faster than in double-layer films. All of the single-layer samples exhibited D-type behaviour with fairly low coating resistance in the range of MΩ/cm^2 compared to double-layer at a similar thickness. The double-layer films provided resistance up to GΩ/cm^2 and there is more possibility to find the I-type behaviour as the diffusion pathway was disconnected by the interface between the two films. The switching behaviour from I to D-type has been identified in the double-layer films when the diffusion process was fully presented and some samples maintained the coating resistance at the same values even when the electrolytic concentration was changed. The switching behaviour was also found in the attached coating in a similar manner. Nevertheless, the resistance in the attached coating of the same coating system provided much higher coating resistance compared to free films, roughly, 2 – 3 orders of magnitude. These results suggest that the interface between metal and coating has an important role in coating resistance as well as any changes in D and I-type behaviours.

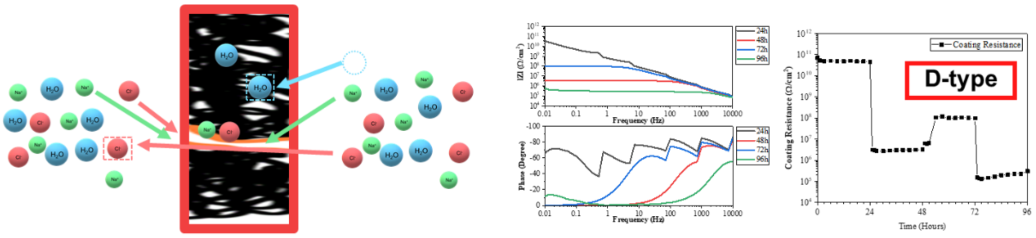

Figure 1: Schematic illustrations of D-type behaviour in a single-layer film.

The Location of Adsorbed Water in Pigmented Epoxy-Amine Coatings

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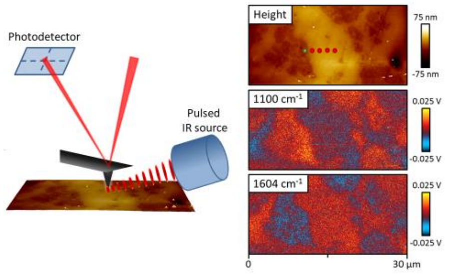
Pigmentation can exacerbate problematic water uptake into protective paints, leading to detrimental effects such delamination, swelling and plasticization. Potential underlying mechanisms include poor adhesion between the pigment and binder, the formation of hygroscopic interphase regions close to the pigment particles, and internal stress. Here, we demonstrate the use of nanoscale chemical mapping using AFM-IR and nanothermal analysis to investigate the contribution of these mechanisms directly for model coatings based on diglycidyl ether of bisphenol-A (DGEBA) cross-linked with triethylenetetraamine (TETA). Whilst moisture uptake increases in the presence of a microscale silica matting agent, no chemical interphase could be detected close to the wax-coated particles. Instead, nanothermal analysis reveals attenuated thermal expansion of the polymeric binder and raised Tg values, supporting favourable polymer-pigment interaction and an increase in internal stress in the polymeric network. This is confirmed by mapping water distributions directly using AFM-IR, where no accumulation at the intact pigment-polymer interface/interphase is detected. Finally, further evidence is provided by bulk thermal analysis, where increased plasticization and desorption enthalpies demonstrate that water sorption into the bulk polymer binder increases as a function of added pigment volume concentrations.



The AFM-IR experiment and images highlighting the height, location of pigments and binder.

Reference

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Relationship between corrosion resistance of heat shrinkable sleeves (HSS) and different degrees of polyethylene's electron beam crosslinking-A case study

Heat shrinkable sleeves (HSS) mostly used for corrosion protection of steel pipeline's field joints operating at high temperature or sever mechanical stresses and electron beam radiation is used to achieve PE crosslinking which this one step process in comparing to chemical crosslinking is a rapid, popular, reliable, clean and efficient use of energy technique for modifying and promoting of physical, mechanical and chemical properties of HSS and can take place without any additives, Although because of high capital cost it would be expensive and needs more safety precaution.in the view of the many process that can take place during the aging of polymers, the possibility must always be considered that some degree of linking-up can occur between the initially un-linked chains. Definitely the extent of crosslinking and finding the optimum parameters for achieving of that such as electron beam dose and conveyer speed would be effective on the HSS application and reaching to optimum properties.

In this investigating and after producing backing layer(PE) ; irradiation was carried out at radiation processing center using an electron beam accelerator RHHDOTRON TT200 with different electron beam energy and the phenomenon of the PE crosslinking was studied on the basis of gel content measurement, according to ASTM D2765.after stretching the cross-linked sleeves at a first temperature close to or above it's softening or melting point and subsequently cooling to a second temperature below it softening or melting ,to thereby freeze the crosslinkred material in it's stretched form ,and meanwhile after laminating to hot melt adhesive ; 1000 field joints of a 20" gas pipeline (about 10 Km)was applied by these HSSs which were produced in different conditions , and uniformity and easily of applying was studied and field mechanical testing such as peel test was performed.

According to results and investigating on the relations between the gel content - irradiation dose - peel strength uniformity and easily of application,10 Mev electron beam determined as an optimum dose and it was summarized that the gel fraction increased with the irradiation dose up and a significant increase with draw ratio but at higher doses remained without considerable change .meanwhile for reaching to the best quality and application uniformity of HSS shrinking, the degree of crosslinking was determined about 68 up to 70 %.

How long can you store a 3LPE coated pipeline outside in a temperate climate?

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GRTgaz operates a network of gas transportation pipelines of 32 000 km protected against corrosion by cathodic protection and a variety of organic coatings. Among these coatings the 3-layered polyethylene coatings (3LPE) are applied on a significant and growing part of the network since the mid 90's. The study of its ageing is thus of foremost importance for GRTgaz and most European pipeline operators.

Prior to their operational life, 3LPE coated pipes can be stored outdoor for an extended amount of time during which various ageing phenomena take place, including antioxidants loss, photo and thermo-oxidation and cracking of the external polyethylene layer leading to an increased mass transfer and a decreasing coating resistance. Thus, there should be a maximum storage time - not to be exceeded - before which 3LPE lose their anticorrosive properties.

In order to validate sound operational practices, antioxidants loss was modelled, both in laboratory and natural conditions at the storage facility of Chateauroux (1). In the meantime, chemical and physical ageing of polyethylene was followed using FTIR spectroscopy and Scanning Electrochemical Microscopy. Finally anticorrosive properties of stored 3LPE coatings were investigated through Electrochemical Impedance Spectroscopy thanks to the CQM probe provided by C-CUBE, a company specialized in the production of coating degradation sensors with over 15 years of experience in EIS data interpretation and the development of coating lifetime models (Figure 1).

Figure 1: Artificial (left) and natural (middle) ageing of polyethylene. EIS measurement with the CQM probe (right).

Keywords: oxidation; polyethylene; modelization; storage; 3LPE; microcracking ; FTIR ; EIS ; OIT ;

1. **Gueugnaut, D. Teygeman, C. et Rousselot, D.** *Modellization of the antioxydants loss from the surface of medium density polyethylene gas pipes aged under natural or artificial environmental conditions.* s.l. : 17th Annual Conference on Advances in the stabilization and Degradation of Polymers, 1995.

Degradation of marine coatings during hygrothermal cyclic corrosion tests

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Abstract

Water ballast tanks inside heavy duty marine cargo tankers usually employ barrier type organic coatings with epoxy based polymer binders. Understanding critical factors influencing the performance of barrier type organic coatings is very important to provide guidance to formulators and shorten the formulation cycles. Degradation of barrier type organic coatings pigmented with flaky aluminium pigments and mineral oxide extender pigments under hygrothermal cyclic corrosion tests were investigated by scanning/transmission electron microscopies and nanoscale X-ray tomography as well as Fourier transform infrared (FTIR) spectroscopy and differential scanning calorimetry (DSC). By comparing the physical and chemical status of individual coating elements before and after hygrothermal cyclic corrosion tests, it was found that coating degradation is indicated by three critical factors. These factors are the stability of the binder, glass transition temperature (Tg) of the coating, and the stability and structural weakness of pigments. It is demonstrated that differences in these factors can have significant impact on the coating integrity and subsequent corrosion protection attributes.

Failure Analysis of Fusion-Bonded and Liquid Epoxy Coatings in Gas Transporting Pipelines

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This paper focuses on an investigation conducted on failed liquid and fusion-bonded epoxy coatings used internally for sour gas transportation. Different analytical techniques have been utilized, such as Fourier Transform Infrared Spectroscopy, Thermogravimetric Analyzer as well as Differential Scanning Calorimetry. The experimental evaluation of different coating systems elucidates the mechanisms leading to premature failure. The improper curing of powder coating materials was found to be the root cause of the failure as deduced by the obtained glass transition temperatures.

Electrochemical approaches to assess corrosion protection of battery electric vehicle coolants

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As battery electric vehicles (BEVs) gain prominence in the automotive industry, the development of tailored antifreeze coolants for BEVs becomes increasingly critical [1]. To enhance electrical safety, conventional antifreeze coolants used in ICEs are being transformed into low electrical conductivity coolants for BEVs [2-3]. However, ensuring corrosion protection in these low-conductivity environments is a multifaceted challenge. The selection of corrosion inhibitors and the evaluation of corrosion resistance using established electrochemical techniques are complicated by the contribution of the ohmic drop [4]. Therefore, exploring different electrochemical techniques for assessing corrosion protection in low-conductivity coolants for BEVs is imperative. This research aims to investigate the suitability and effectiveness of various electrochemical methods, such as potentiostatic, galvanostaircase, and potentiodynamic polarization tests, to address the challenges posed by BEV cooling systems. These techniques offer the potential to uncover corrosion mechanisms, optimize corrosion inhibitor selection, and enhance overall corrosion protection in this specialized context. Moreover, the introduction of new materials in BEV cooling systems, especially new Aluminium alloys, asks for a thorough examination of galvanic coupling effects. The novelty of these materials requires an in-depth investigation to assess their compatibility and potential corrosion risks within the cooling system environment. Understanding the galvanic interactions among these materials is crucial to ensure the long-term durability and reliability of BEV cooling systems. The outcomes of this research contribute to a better understanding of corrosion protection of BEV thermal management systems, improving its efficiency and longevity in the rapidly evolving automotive landscape.

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Assessing the Impact of Stress Scenarios on Electrolytic Conductivity of Coolants

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An effective cooling system is mandatory to ensure the safe operation of electric vehicles, to protect vehicle components from damage caused by overheating and to optimize operational efficiency. In contrast to internal combustion engines, the coolants used in electric drives are faced with the additional requirement to comply with a maximum permissible electrolytic conductivity. This necessitates the development of new low-conductive coolants, as conventional coolants exhibit relatively high conductivity due to the presence of ionic additives in high concentration. The coolant development process requires to assess changes in electrolytic conductivity under operational conditions. However, test methods for evaluating the extent of impact factors inducing conductivity changes, such as chemical aging of the coolant or ions released from the materials employed, are still scarce.

This study investigates how various thermal and corrosive stress scenarios affect the alteration processes of an ethylene glycol-based coolant concerning its electrolytic conductivity. The investigation includes thermal stresses based on the glassware corrosion test ASTM D8485 and the influence of electrochemical stress, exemplified by potentiodynamic polarization. Initial results demonstrate that conductivity development depends on both the applied temperature and the aeration rate of atmospheric air introduced into the coolant. Challenges related to electrochemical investigation arise from the high ohmic resistance of low-conductive coolants. These challenges are addressed by optimizing electrode positioning to provide reproducible electric field conditions and stirring the electrolyte to reduce concentration gradients inside the coolant. The experiments are complemented by the characterization of ion concentrations through atomic emission spectroscopy and ion chromatography. In summary, this research aims to enhance understanding of correlations between electrolytic conductivity and stresses imposed on low-conductive coolants, thereby contributing to the development of more resilient cooling systems for electric vehicles.

Stability of Platinum and Platinum Alloy Electrocatalysts in Proton Exchange Membrane Fuel Cells

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The commercialization of low temperature fuel cells is significantly inhibited by high materials costs and poor service life which can largely be attributed to high platinum loading requirements, and degradation/durability issues of the oxygen reduction reaction (ORR) electrocatalysts at the cathode, respectively. These degradation and durability issues can be traced to the corrosive environment and voltages under which the ORR electrocatalysts must operate. To elucidate the mechanisms under which degradation and durability issues occur, platinum and platinum alloy thin films, as well as platinum nanoparticles, were studied using transmission electron microscopy, chemical analysis, and in-situ electrochemical scanning probe microscopy. Results of these studies indicate that the stability of platinum films are directly related the voltage at which the fuel cell is operated. Additionally, the stability of Pt nanoparticles was shown to be directly related to particle size as a function of potential. Studies of platinum alloy thin films suggest that increased stability can be achieved, the degree of which is strongly dependent on the alloying metal.

The dependence of Pt and Pt alloy stability on potential generally indicates that separate degradation mechanisms are operational at different potentials. For higher potentials (~800 mV and above), dissolution-redeposition of Pt from the surface of nanoparticles is observed. For potentials between ~400 to 800 mV, one must also consider surface diffusion transport as a potential degradation mechanism. At low potentials (<400 mV), Pt and Pt alloys are relatively stable. These results will be discussed in general as pertaining to the stability of nanoscale materials in electrochemical systems with an emphasis on the impact to fuel cell operating conditions.

Access to Stray-Current Corrosion Life-time Calculation of Electrification Vehicle due to Corrosion Environment

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Electrification vehicle adapts a high voltage battery to increase a driving mileage. High voltage battery and related control components are subject to corrosion and deterioration when exposed to an environment of corrosive environment and customer usage conditions, which causes total stray-current corrosion in the ground and connector connections due to leakage current.

In order to maintain the electrification performance in the corrosive environment, a basic study was conducted to predict the corrosion life-time of the ground and connector. Galvanic corrosion due to dissimilar materials and surface treatments (Fig.1); A corrosion rate algorithm was developed through a basic study on the corrosion impact of current flow.

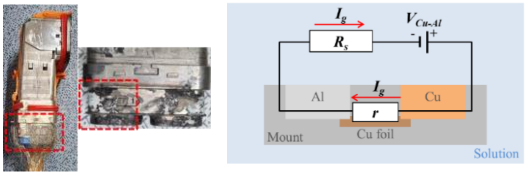

Fig.1. Galvanic corrosion test

Fig.2. Simulation of stray-current corrosion

Wiring was connected to each ground to measure the stray-current (leakage current) and stored on a tablet automatically through a data acquisition system. A simulation tool was developed that can predict the stray-current corrosion lifetime by measuring current while driving on various ground and connectors of electrification vehicles (Fig.2).

Intelligent approaches for corrosion inhibitor screening and coating development

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Abstract

The emergent materials genome engineering research field has spurred development in intelligent methodology that is transforming the corrosion research paradigm. For example, high-throughput and automated experiments are employed to substantially accelerate the screening of corrosion-resistant materials and the evaluation of corrosion behaviors under complex/combinatorial influencing factors. Machine learning tools are revealing their power to predict corrosion rates and rapidly discover optimized materials composition out of large search spaces, thereby reducing the time and cost associated with traditional 'trial-and-error' corrosion evaluation methods. This talk will summarize several latest works from this group on the application of high-throughput experimental evaluation and machine learning prediction on corrosion inhibitor screening and coating development.

Exploring novel corrosion inhibitors: machine learning-driven identification, loading in LDH materials & performance in coatings.

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The VIPCOAT project develops an open innovation platform for the development of active protective coatings. One of the interoperable apps supports the exploration of novel corrosion inhibitors based on a machine learning (ML) model.

In this work, small molecules were short listed as potential novel corrosion inhibitors based on quantitative structure-property relationship (QSPR) ML models. After experimental confirmation of the corrosion inhibition properties, suitable inhibitors were selected on parameters such as inhibition efficiency, toxicity, availability, and cost. Many of the selected corrosion inhibitors are potentially reactive with the coating matrix. Therefore, the corrosion inhibitors were loaded into layered double hydroxides (LDH) before they were incorporated into coatings to assess their performance as a leaching corrosion inhibitor.

The paper presents the first full exploration process using the inhibitor exploration tool from the VIPCOAT platform, from Machine Learning prediction, confirmation of activity, selection of candidates, loading in LDH containers, demonstration of release from the LDH and finally, the validation of corrosion protective properties in a coating system using leaching tests and accelerated corrosion testing. Practical challenges and considerations are discussed of this new tool to explore new corrosion inhibitors for active protective coating systems on AA-2024.

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The Impact of Active Learning on the Data-Driven Discovery of Corrosion Inhibitors for AA2024 Alloys

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The urgent need to replace hexavalent chromium-based treatments with safer and more cost-efficient corrosion inhibitors for aluminium (Al)-based materials has prompted the exploration of small organic molecules as promising alternatives for mitigating corrosion rates in Al alloys [1]. While experimental techniques have made significant progress in screening potential corrosion inhibitors, their scope is limited given the vast chemical space of available compounds (estimated at ~10^{63}). In this context, quantitative structure-property relationship (QSPR) models present a synergistic opportunity to preselect a shortlist of promising candidates for experimental testing and thereby incrementally increasing the pool of available training data for QSPR modelling strategies.

In this study, we present a data-driven model developed for a set of small organic molecules, aiming to predict their corrosion response for the Al alloy AA2024-T3. The model utilizes molecular descriptors that encode the geometric and electronic structure as input features. Supervised machine-learning models, including random forests and artificial neural networks, have been developed to predict the performance of compounds that have not been used for training of the model. Repetition of multiple loops of testing, predicting and retraining enabled the exploration of how active learning affects the robustness and accuracy of predictions. The results demonstrate the potential of the developed QSPR models to predict the corrosion behaviour of small organic molecules by rationally increasing the underlying training database, offering a more efficient and targeted approach to identifying corrosion inhibitors for AA2024-T3.

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Understanding pretreatment for recycled Al alloys using multi-scale modeling

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Metals and alloys hold unique properties such as strength, malleability, recyclability, corrosion as well as temperature resistance, etc., which play an indispensable role in automotive, aerospace & construction industries among others. However, due to the occurrence of inevitable corrosion, various kinds of pretreatment coatings have been introduced to provide long-term protection against the corrosive environments. Furthermore, the recyclability of metals also contributes to sustainability efforts across these industries. Typical pretreatment coatings include both conversion (e.g., chromates, phosphates, titanates, zirconates) and thin organic coatings (silanes, acrylics, epoxies etc.). Here, we focus on conversion coatings, titanates, and zirconates (with and without organic additives). These conversion coatings can improve corrosion resistance, paint adhesion, better film formation, and more complete surface coverage. Despite their widespread use in industry, there is still a lack of accurate atomistic models for TiO_2 and ZrO_2 for MD simulations. This lack of accurate model makes it difficult to predict how these materials will interact with other components such as metals, metal oxides, small molecules, or biomolecules. This uncertainty can lead to inaccurate predictions about material performance or hinder the development of new technologies.

Herein, we report the development of all-atom models of rutile TiO_2 (r-TiO_2), anatase TiO_2 (a-TiO_2), and monoclinic ZrO_2 (m-ZrO_2) using the INTERFACE force field (IFF). The models and parameters are validated for both bulk and interfacial properties with accuracy over 95% with respect to experimental measurements, enabling quantitative simulations and predictions of structural and interfacial properties of complicated chemical and biological systems comparable and superior to density of functional theory (DFT), plus real-temperature dynamics on a scale of 1 to 1000 nm. Moreover, the real surface chemistry is included deriving from experimental measurement, allowing accurate simulations of surface interactions in electrolytes at various pH values. The models can predict the adsorption behavior of different polymers on various metal oxide surfaces, which is crucial in designing effective coatings. The interaction mechanisms between the functional groups of polymers and metal oxide surfaces are also elucidated, providing a deeper understanding of how these coatings work. In addition to corrosion protection, these insights can also be applied to other areas such as catalysis, sensors, and energy storage devices where polymer-metal interactions play a significant role.

Atomistic Models of Epoxy/Amine Coatings at Iron Oxide Interfaces

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Modelling and simulations can provide insight into problems that experiments cannot explore, complementing experimental results. In epoxy-based coatings, the significance and impact of surface-induced segregation of the coating during the cure has proved difficult to investigate through experimental means alone.[1] We have created a robust workflow to model the crosslinking reactions of various precursors in the presence of a surface, overcoming challenges of previous methods related to the implementation of the atomistic reaction and the definition of reacting units.

As a model epoxy-amine system, diglycidyl ether of bisphenol A (DGEBA) and m-xylylenediamine (MXDA) have been used. We find an enrichment of MXDA at the solid interface, resulting in a reduced crosslink density at the interface compared to the bulk. Further, the depletion of MXDA from the film beyond the contact layer leads to the low crosslink density region extending further into the film than the enriched contact layer. This results in distinct regions of excess amine and excess epoxy close to the surface. The consequences in performance of this phenomena require further investigation, but it is possible to envision advantages and disadvantages. On one hand, the low crosslinking at the interface leaves uncoordinated amine groups that can form bonds with the metal oxide surface, providing adhesion. On the other hand, the reduction of crosslinking near the surface and in the film may result in the pathways allowing water, small molecules, and ions to travel through the coating, reducing the corrosion protection performance. The effect on mechanical properties may also be significant.

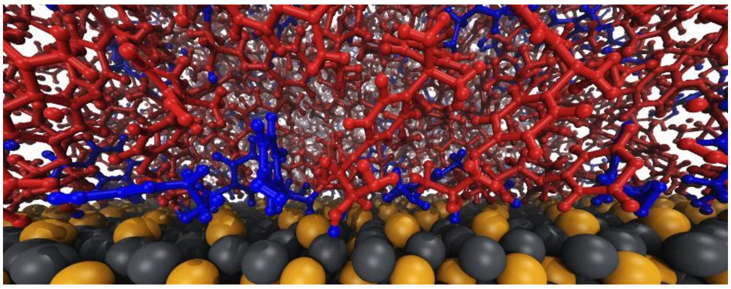

Figure 1. Example DGEBA (red) / MXDA (blue) mixture at a hematite surface.

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Gibbs-Laguerre tessellation cells for geometric modelling of corrosion inhibitor pigments in active protective coatings based on SR-nano-CT images

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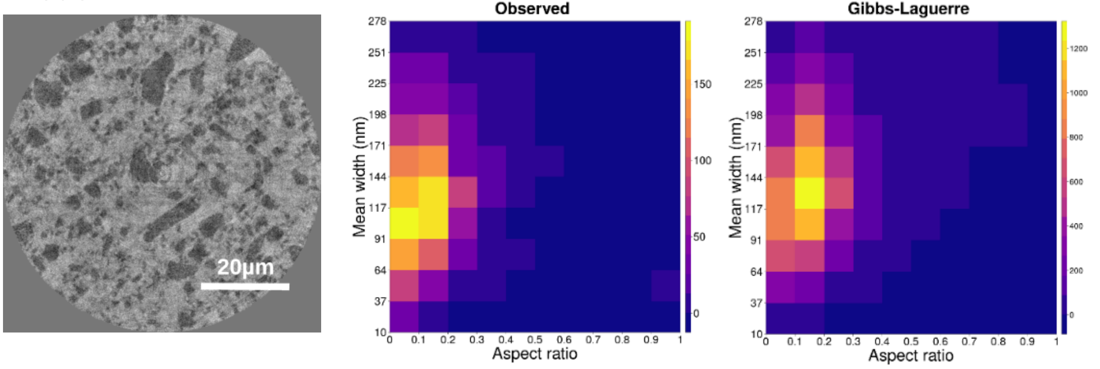
Coatings containing inhibiting pigments effectively protect from corrosion. If a defect occurs, the coating absorbs moisture from the environment, and the pigments dissolve releasing molecules into the defect that renew the corrosion protection. Leaching of corrosion inhibitors depends critically on chemical composition and concentration of the inhibitors. The EU funded VIPCOAT project aims to create and develop an open innovation platform to facilitate a new coating development based on modeling solution. Numerical analysis of the leaching process within 3D models of the coating microstructure is one way to achieve this. We present stochastic geometry models, which enable the creation of virtual corrosion inhibitor particle systems. The two main challenges here are to obtain the size and shape distributions of commonly used inhibitor particle types and to correctly reflect the observed correlations of particle sizes and shapes in the model. To solve the first task, we analyze nano-tomography images obtained by synchrotron radiation. Particles are connected in the 3D images. They are separated by a sophisticated and complex algorithm. Second, we use Gibbs-Laguerre tessellations allowing to incorporate the observed size-shape distributions directly into the model fit.



Left: 2D slice from Zernike phase contrast image of a sample with $LiSO_4$ particles (dark). Center: Joint distribution of size (mean width) and shape (aspect ratio) of the $LiSO_4$ particles. Right: Size-shape distribution of the fit Gibbs-Laguerre tessellation cells.

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Finite element modelling for the prediction of AA2024 corrosion protection through the use of active coatings

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Nowadays, aluminum alloys (AAs) are among the main structural materials in the aeronautical industry due to their favorable properties. However, their microstructural heterogeneity makes them susceptible to local corrosion which imposes the need for corrosion protective coatings. Chromium based corrosion inhibitors have proven to be effective for protection of AA structures. Nonetheless, given their toxicity and carcinogenic nature, their usage is limited due to strict international legislation signifying the need for safe alternatives. Recent studies show promising results for various inhibitors but further studies are essential to understand an inhibitor's efficiency and applicability. While extensive screening experiments would be time consuming, modelling has been considered as a possible faster alternative.

This work presents a 2D finite element model simulating the leaching and protection behavior of active protective coatings. The model geometry used is a defect through an active protective coating exposing the underlying metal surface. The electrolyte varying composition, the expected interactions among the inhibitor and the different species within the electrolyte are considered. The electro-chemical effect of the inhibitor on the alloy is described through kinetic coefficients in the Butler-Volmer equation which are fitted using data obtained from linear sweep voltammetry measurements. The leaching mechanism of the inhibitor within the coating is described. Concentrations of the different species, potential and current changes over the surface, are calculated. A follow up study is conducted to relate the initial inhibitor pigment volume concentration with the obtained pH and concentration of the active protective molecule in the electrolyte.

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FEM to predict corrosion critical conditions in a coating defect under static and dynamic electrolyte conditions

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Corrosion control of aluminum alloys in the aerospace industry is of high importance to prolongate the service life of aircraft structures. Commonly used high-strength aerospace aluminum alloys such as AA2024 are susceptible to localized corrosion (e.g. pitting corrosion) due to the presence of copper-rich intermetallic particles in the alloy matrix. Therefore, a complex coating system consisting of several (organic) coating layers loaded with corrosion inhibitors is usually applied to provide both barrier and active corrosion protection. Dedicated evaluation of these corrosion protective layers is strictly necessary. While laboratory trial procedures and outdoor test programs are personnel and time intensive and accelerated corrosion tests can lead to limited service performance information, predictive modeling of the durability and lifetime of (organic) coated aerospace aluminum alloys under long-term environmental corrosion can provide a promising alternative.

Predictive modeling of (organic) coated aerospace aluminum alloys aims to develop a deterministic modeling and simulation concept that allows to forecast the onset of corrosion on relevant micro-defects of a simplified corrosion protection scheme with or without active corrosion protection. Furthermore, it allows to generate fundamental understanding of corrosion processes, of important parameters and boundary conditions and constitutes an important first step towards more complex and accurate predictive deterministic and/or hybrid models.

In this work, a finite element modeling (FEM) approach is developed and validated to model the corrosion critical conditions in a coating defect for coated aerospace aluminum alloys under atmospheric conditions with and without active corrosion protection under static and dynamic electrolyte film conditions.

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Modelling of Crosslinked Epoxy-Amine coatings: A Coarse-Grained Molecular Dynamics Study

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Computational design of coatings calls for the development of multi-scale modelling methods that can circumvent costly experiments. To make accurate predictions about the highly tunable, macroscopic properties of polymer systems which depend strongly on the degree of cross-linking, one needs a bottom-up approach that accounts for the chemistry specific details present at small length and time scales and an ability to simulate these specific models over macroscopic length and time scales, which is beyond the capability of all atom simulations.

We report a general methodology for deriving a structure based coarse grained molecular dynamics (CGMD) model, of a mixture of both cross-linked and un-crosslinked epoxy (DGEBA) and amine (MXDA) mixture based on an underlying atomistic model. The intra-molecular interactions are derived from the inversion of relevant simulated probability distribution functions computed from particle trajectories of isolated polymers. Owing to complexity of the model, the non-bonded interactions between CG beads have been estimated from the inversion of relevant correlation functions computed from atomistic trajectories. We perform cross-linking reactions between the components and compare the resulting structures obtained from the CG model with those obtained from an independent atomistic simulation. The range of the non-bonded interaction and the equilibrium bond length between the terminal DGEBA and MXDA beads are crucial parameters which dictates this agreement between the CGMD and atomistic models. The reduction in the degrees of freedom of the CG model in comparison to its atomistic counterpart (probed by matching average density and the radial distribution functions) allows us to access significantly larger system sizes ($L_{CG} \approx 10^3 \times L_{atom}$) for longer timescales ($\approx \mu s$). A comparison between cross-linked structures obtained via the CGMD simulations, and those probed via small angle neutron scattering experiments for MXDA-DGEBA mixtures is presented. The approach is general enough to be extended to other polymer-based formulations.

VIPCOAT open innovation platform: Laboratory testing of active corrosion protection in defects of coatings on aluminum AA2024 unclad for validation of modelling and simulation

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Simulation activities in the VIPCOAT project aim at the prediction of active corrosion protection in a defect of a corrosion inhibiting organic coating on an aluminium substrate depending on the environmental conditions, the leaching of the inhibitor and its efficiency at given local conditions. The models are based on industrially relevant testing environments and defect configurations, with the aim of comparing the simulation results to traditional laboratory evaluation methods.

Model coatings with and without corrosion inhibitors (Cr(VI)-free, Cr(VI)-loaded) on aluminium specimens AA2024uc were subjected to artificial damages and exposed to corrosive environments: Stationary conditions (no exchange of electrolyte in the artificial defect and no change of climate conditions), and non-stationary conditions (exchange of the electrolyte in the artificial damage with and without change of climate conditions). The corrosive attack was assessed and analyzed with regard to the leaching properties of the inhibitors and the test conditions. Concepts are discussed to use test evidence for validation of VIPCOAT platform simulations.

VIPCOAT open innovation platform can support the development and selection of corrosion protection schemes for aluminium parts. Results on the impact of different cyclic corrosion test regimes on model coatings and corrosion propagation under the paint layer exemplify future use cases and extension of the models.

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Workflow for documenting data of corrosion experiments

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Models are often only loosely described in textual form. As specified in the CEN Workshop Agreement ModGra (CWA 17960:2022), graphical modelling provides a convenient and handy tool to construct and document material and process models. It also allows us to specify precisely what information is obtained from experiments and sensors and what consecutive information processing is performed. The latter is vital for experimental data. Post-processing often incorporates filters, like noise and data reduction and reconciliation operations.

The **Pro**cess **Mo**delling suite ProMo implements a modelling environment based on ModGra, paired with an ontology approach to generating process models. The basis is an ontology that defines a fundamental data structure, specifically, variable classes for application domains used to construct mathematical models for the basic entities defined in the CWA. The result is a simple or complex mathematical model for a process and a complete documentation of the data flow between the modelled processes. Thus, one obtains complete information on the data flow, which one can map into various common formalisms for knowledge representation. In turn, one can use them to generate application interfaces to interoperable data spaces that store, retrieve and exchange data in a computational environment. The latter may be as simple as performing the post-processing of experimental data or full-blown multi-scale dynamic models of any part of the modelled object.

We demonstrate for corrosion-related use cases (pigment production, leaching, salt spray tests) how this approach enables a user-friendly workflow for documenting experimental data.

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Digitalizing innovative advanced materials to support European Green and Digital Transition: VIPCOAT and DigiPass Projects

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Collaborative innovation and transparency in development and production of innovative advanced materials and products calls for digital environment to ensure interoperability of data sharing and to assists end-users in decision making on components and KPIs of advanced materials. The developed in the frame of the EU funded VIPCOAT project digital environment connects industrial R&D, scientific experimentalists and modellers as well as external data sources, platforms and relevant data bases like REACH and PubChem on a single user-centric platform to support collaborative innovation processes.

We will demonstrate the VIPCOAT open innovation platform. The innovation potential in developing collaboratively new active protective coatings for aeronautics along distributed production chains is considered as a demonstration example. Since VIPCOAT understands that in the end industrial players and their respective ecosystems are responsible for delivering innovations fighting today`s grant challenges, the new project DigiPass CSA built on VIPCOAT to contribute to the twin green-digital transition as a cornerstone of today's European strategy.

This transition should lead to a circular, sustainable, and net-zero-emission European economy that works for people. The DigiPass CSA goal is to coordinate and support activities to create a sustainable digital platform that works for people and simultaneously assists with Digital Materials & Product Passports and collaborative innovation-by-design processes in a circular economy served by advanced materials. This extension will support better the use-phase of products suffering from corrosion and in particular their circularity-by-design along the full materials live cycle.

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Corrosion behaviour in chloride molten salts of different metallic materials employed in $Na/ZnCl_2$ battery

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The rising demand for energy storage is motivating research on innovative batteries. Molten salt batteries like sodium-metal chloride ZEBRA cells, have been studied for over 30 years, but continue to interest researchers who seek further performance gains. Driven by a desire to reduce overall battery costs, exploration of alternative cathode materials, such as the substitution of Ni by less-expensive alternatives like Zn, is ongoing. The $Na/ZnCl_2$ cell comprises a liquid Na negative electrode, a sodium ion-conducting solid electrolyte (beta alumina), and a $ZnCl_2$ positive electrode. A secondary liquid electrolyte, $NaAlCl_4$, functions as a catholyte, operating within a temperature range of 270 to 350 °C [1]. The avoidance of rapid degradation poses a significant challenge for these batteries due to the corrosive nature of molten salts, particularly chlorides, at elevated temperatures. The corrosion of metallic components, especially current collectors, is a critical issue, since it leads to the formation of corrosive product layers that elevate ohmic resistance and impacts electrical conductivity, resulting in cell voltage losses. In this study, Zn, Mo, Cu, and the alloys 201 and 316L underwent corrosion testing in a molten salt mixture at 280 ºC. Following a brief introduction to the $Na/ZnCl_2$ battery concept, the presentation will share preliminary findings on the electrochemical behavior, microstructural changes, and degradation of these metals when exposed to molten salt.

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Optimization of slurry aluminide coating deposition processes on ferritic and austenitic alloys to resist high-temperature molten salts corrosion and mechanical stresses

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Concentrated solar power (CSP) emerged as a reliable technology able to manage sunlight intermittency. However, the use of expensive materials required to withstand corrosive high temperature (HT) molten salts makes it uncompetitive. The EU-funded COMETES project focuses on the development of low-cost slurry aluminide coatings resistant to corrosion and mechanical stresses to allow CSP plants overall cost decrease and more efficient heat storage. A coated ferritic-martensitic T91 was exposed in Solar Salt at 580°C in air and compared with uncoated 347H austenitic steel. Novel slurry aluminides were also produced onto 347H, as alternatives for harsher operating conditions like Li, Na and K molten carbonates at 700ºC. Coated and uncoated 347H were thus exposed in the above-mentioned carbonates. The coating process was optimized according to: (1) surface preparations – grinding, grit blasting, chemical attacks – (2) coating methods – spraying, dipping – and (3) post-treatments – sealing, pre-oxidation. Microstructural characterization showed the formation of a 170 and 70 μm-thick Fe-Al rich multilayer coating with a 23 and 68 at.% of Al on the T91 and the 347H, respectively. Coatings' homogeneity was shown to mainly depend on surface preparation and subsequent diffusion heat treatments which were optimized to limit crack formations. In terms of corrosion resistance, coated T91 behaved as well as bare 347H in Solar Salt after 500h and formed a very thin $NaAlO_2$ oxide. In carbonates, the developed coating was shown to slightly improve 347H performance, reducing the need for maintenance. Post-treatments have also proved effective in improving coating protectiveness. Microhardness measurements allowed to precisely characterize the gradient of mechanical properties from the surface to the specimens' core. The brittleness of the coating was assessed and crack formation was related to applied stress via 3-point bending tests. The most promising solutions for future long-term exposures and stress corrosion cracking testing will be presented.

On the corrosion characteristics of 310N stainless steel in oxide-rich solar salt at 600 °C

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Abstract

Thermal Energy Storage (TES) system plays an important role for the dispatchable electricity generation in the Concentrated Solar Power (CSP) plants. Molten nitrate salt mixture, also known as Solar Salt (60wt.% $NaNO_3$: 40 wt.% KNO_3) is a commonly used storage and heat transfer media in modern CSP plants coupled with the TES system. Currently, the operating temperature range of the CSP plants is 290-565 °C which is set by the freezing temperature on the lower end and thermal decomposition on the upper end. The volumetric storage capacity as well as the heat-to-electric conversion efficiency is mainly depending on the applied hot tank temperature. This means, basically the future developments in the field of TES systems are targeting to operate at higher temperatures (≥600 °C) to enable cost-effective electricity generation in CSPs. At higher temperatures, evidence exists that the nitrate ions in the solar salt decompose into nitrite ions, and subsequently, the nitrite ions decompose into various oxide ion species. Salt decomposition ultimately increase the corrosion susceptibility of the structural materials in CSP's piping, tanks and receiver tubes. To avoid severe damage and operational cost increase of a plant, it's very important to evaluate the corrosion performance of potential structural materials for the CSP applications. Our on-going research is aimed to examine the corrosion behavior of 310N stainless steel (SS) at 600 °C, under condition that simulate the solar salt decomposition over long-term operation in TES systems. Imitating the extreme decomposing process of solar salt in short-term duration and its corrosivity to 310 N SS, is being carried out by adding 0.1 wt.% Na_2O to the nitrate mixture. In this presentation, it will be shown that how an intentionally added oxide impurity in solar salt affect the corrosion resistance of 310N SS by means of XRD, SEM-EDX and/or FIB-EDX characterizations. The impact of an oxide-rich solar salt on the corrosion characteristics of 310N SS will be discussed by comparing with its corrosion tendency in pure solar salt.

Impact of Solar Salt Chemistry on the Corrosion Evolution of Austenitic Stainless Steel

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Efficient energy storage solutions are essential for harnessing solar energy effectively. Thermal energy storage (TES) within Concentrated Solar Power (CSP) plants has emerged as a mature and promising solution for efficiently harnessing intermittent solar energy. Solar Salt (60% $NaNO_3$/40% KNO_3) serves as an economical, low-toxicity and none pressurized heat transfer fluid (HTF) and heat storage medium in the CSP systems. However, there is currently a lack of comprehensive information on the corrosion of metallic components by Solar Salt under controlled salt decomposition. Solar Salt undergoes decomposition at elevated temperatures, generating multiple types of soluble ionic species nitrite (NO_2^-), and oxide (O^{2-}) ions. While earlier studies have primarily focused on the corrosion rate of various metallic alloys in Solar Salt, understanding the role of Solar Salt chemistry on the corrosion process is a vital aspect to mitigate corrosion. This study manipulates salt decomposition by altering the purge gas (nitrogen and synthetic air) over Solar Salt and investigates the evolution of salt chemistry with and without the presence of steel. Furthermore, gold sputtering was performed on the steel samples before exposure to trace the evolution of the corrosion layer. The changes in Solar Salt chemistry were investigated using ion chromatography (IC) for nitrate and nitrite ions and titration for oxide ions, while the corrosion process is concurrently examined through mass loss measurements and SEM-EDX analysis. The aim is to evaluate the influence of varying gas atmospheres and the presence of steel on Solar Salt chemistry and its corrosivity. The results reveal that nitrogen gas purging substantially increases the decomposition of salt into nitrite and oxide ions, intensifying its corrosiveness over time. The presence of steel also influences salt decomposition depending on the purged gas atmosphere. Interestingly, the presence of gold particles within the middle of the corrosion layer in the air purged atmosphere visually illustrates a counter diffusion involving various cations and anions across the corrosion layer. By controlling the Solar Salt decomposition, the corrosivity of the Solar Salt can be decreased to a large extent and the CSP-TES system life span can be improved.

Evidence of redox control by titanium chloride to mitigate the corrosion in molten chloride salt

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Molten salt (MS) systems have many attractive features including nuclear MS reactors, thermal energy storage, solar power plants… Due to a low melting point, a high thermal stability and the low cost of molten chloride salts (MCS), the possibility to develop MS reactors and especially Generation IV nuclear reactors has been studying since decades. However, such an aggressive medium could be responsible for material corrosion. One of the best challenges regarding safety and sustainability is the compatibility between high temperature MCS and materials. Hence, the discovery of corrosion-resistant materials should be considered. However, corrosion mechanisms in MS are not comparable to those in aqueous solution, and no passivation layer is sufficiently protective to limit the corrosion. The aims of the presented research were the development of a fast, *in situ* and reliable method to evaluate the metal behavior in MCS and the definition of a corrosion mitigation way.

Results show that metal behavior in MCS could be predicted by measuring its open circuit potential (OCP) and to compare it to the redox potential of the medium. Besides, addition of an amphoteric species (titanium chloride) in MCS was used to buffer and significantly lower the salt redox potential. Hence the potentials of many metals and alloys were measured in the immunity domain. Corrosion tests of commercial alloys (stainless steel, Inconel 600) performed 1 week in MCS revealed that if the difference between the MCS potential redox and the material potential (ΔE) is positive, the metal was corroded, whereas a ΔE~0 delayed/prevented material degradation (Figure 1).

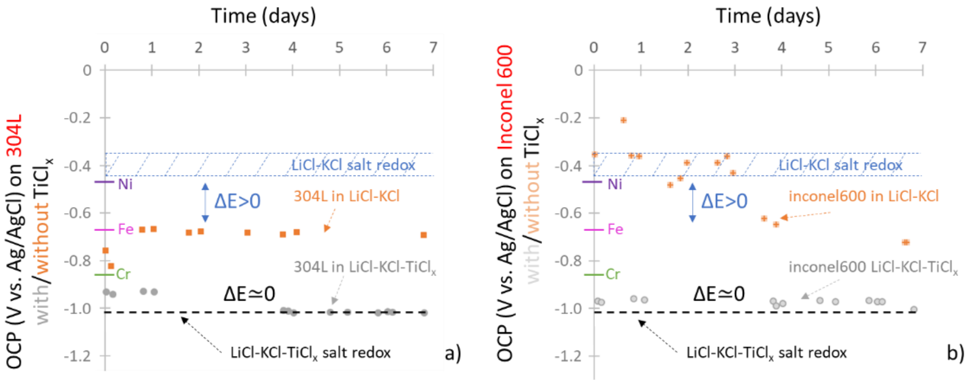

Figure 1: OCP obtained on 304L(a) and inconel600 (b) with/without redox control

Fast-track approach to molten salt-resistant materials

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In the face of climate change, the necessary energy transition involves the development of new technologies and with it an urgent need for structural materials resistant to diverse corrosive environments. In the frame of the French initiative DIADEM (DIscovery Acceleration for the deployment of Emerging Materials), the targeted A-DREAM project aims to accelerate the discovery of materials resistant to corrosive environments thanks to an integrated approach involving digital design, high throughput synthesis and accelerated materials corrosion assessment. It focuses on molten salts environment used as heat-transfer fluid and/or fuel for solar power plants and nuclear reactors. A database will be constructed, containing both corrosion resistance data and thermodynamic and kinetics parameters.

To acquire corrosion data, a wide range of materials (metallic and ceramics) and of manufacturing and coating processes (conventional, additive manufacturing, combinatory PVD, cold spray,…) is tested for a short duration at 450 °C, under argon. A pellet of LiCl-KCl in eutectic proportions is placed on each sample. After testing, the corrosion resistance is assessed by mass variation, corrosion products dissolved in the salt are analysed by ICP and the corroded sample by GDOES.

To determine thermodynamic and kinetic parameters, electrochemical techniques such as square wave voltammetry and cyclic voltammetry are used to determine the diffusion coefficient and the apparent standard potential of pure elements (Fe, Cr, Ni for example) in LiCl-KCl at 450°C. The determination of these parameters will enable us to better understand the corrosion mechanisms and the influence of the material composition on their resistance to the molten salt.

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Corrosion behaviour of candidate MSR structural materials exposed to molten chloride salts

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Abstract

Generation IV nuclear reactors are a promising concept that have gained significant attention in recent years. Among them, the Molten Salt Reactor (MSR) uses molten salts as fuel and coolant. Research efforts into their design has brought a set of intrinsic benefits compared to traditional Light-Water Reactors (LWRs), especially in terms of safety and sustainability. However, a key challenge in the design of these reactors is the corrosive nature of the salts, which combined with the high operation temperature, may cause corrosion in an accelerated manner, thus compromising the integrity of the reactors' structural materials.

This study, carried out within the European MIMOSA project [1], focuses on the corrosion behaviour of various structural materials, namely ceramics, stainless steels and Ni-based alloys, exposed to molten NaCl-$MgCl_2$-$CeCl_3$ salt, where $CeCl_3$ is used as a surrogate for $PuCl_3$. The aim of the research is to do a fast screening through a comparative study on the corrosion behaviour of several candidate materials exposed to the molten salt at high temperatures under a controlled argon environment by characterizing the alloys, as well as the salts, before and after the exposure experiments.

The research methodology involves the systematic evaluation of corrosion resistance by analytical techniques such as Optical Microscopy (OM), Scanning Electron Microscopy – Energy Dispersive X-ray Spectroscopy (SEM-EDS), X-ray Diffraction (XRD) and Differential Scanning Calorimetry (DSC).

[1] MIMOSA (MultI-recycling strategies of LWR SNF focusing on Molten Salt technology) EURATOM-2021-NRT-01 project, https://www.mimosa-euratom.eu/

Corrosion Resistant Bi-Layer and Tri-Layer Metallic Structures for Molten Salt Nuclear Reactors

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Abstract

The molten salt reactor (MSR) is a type of nuclear reactor in which the primary coolant is a molten salt mixture. These types of reactors operate at near atmospheric pressure while at much higher temperatures (up to 700-750°C) than light water reactors. Identifying corrosion resistant materials that can perform acceptably under these conditions is challenging. Previous research has shown that Ni-based alloys and alloys with dense Ni coatings were effectively inert to corrosion in fluorides. However, the ability of other alloy coatings to resist corrosion in molten salts has not been adequatly explored. The goal of this work was to understand the ability of different bi-layer and tri-layer coatings to resist corrosion attack under a molten salt environment in order to determine the effectiveness of a diffusion barrier in mitigating inter-diffusion between the surface layer and substrate.

High-temperature molten salt exposures over a temperature range of 610 °C to 850 °C showed that the bi-layer coatings provided some corrosion resistance, with the Ni-Alloy 617 structure showing the best corrosion resistance. The W-Alloy 617 and Mo-Alloy 617 coatings had good resistance at temperatures below 750 °C. The Ta-Alloy 617 samples, despite having a predominately intact Ta coating, showed intergranular attack at all temperatures tested.

The tri-layer materials all had some amount of delamination of the outer coating. In the case of the Ni tri-layer system, the Ni outer layer provided protection against intergranular corrosion below 680 °C. The Mo and W tri-layer samples, though delaminated, also provided some protection against intergranular corrosion but at lower temperatures. This research showed that the Ni alloy coatings showed the best corrosion resistance, however there is potential to utilize other corrosion resistant materials as coatings in a molten salt environment.

Design and characterization of new Compositionally Complex Alloys (CCAs) for Molten Salt Reactors

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In recent times, Compositionally Complex Alloys (CCAs) have gained attention in the nuclear industry as potential structural materials for reactors due to their suggested superior irradiation resistance compared to conventional alloys [1]. The broad compositional range of these alloys provides increased flexibility for optimizing various properties, including electrochemical ones [2]. This study focuses on the development of corrosion and irradiation-resistant materials for Gen IV Molten Salt Reactors (MSRs), capable of withstanding chloride-based molten salts at around 550°C.

Following the work of Herschberg et al. [3], both new computationally designed alloys and "reference alloys", obtained from literature, were synthesized through cold crucible induction casting and examined. The alloys, rich in Ni and containing either Al or Mo as the main alloying element along with Cr, underwent microstructural analysis in both as-cast and homogenized states (XRD, SEM, EDS, TEM), along with comparisons to thermodynamic predictions using ThermoCalc software. Mechanical properties were estimated through hardness measurements and the initial assessments of the corrosion behavior of the alloys were conducted via prolonged static immersion tests in chloride-based molten salts, simulating their anticipated in-service environment.

Acknowledgements

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Experimental characterization of complex concentrated alloys for molten salt nuclear reactors

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The pressing energy challenges of today and their expected evolution in the near future have intensified focus on cutting-edge technologies in the nuclear sector. Within this realm, Molten Salt Reactors (MSRs) have captured considerable attention. Yet, the progress of MSRs faces the hurdle of pinpointing and ensuring access to materials that can withstand demanding operational conditions. These conditions include resistance to irradiation, creep, and corrosion at temperatures reaching up to 800°C [1]. The objective of this work is to design and characterize novel alloys that meet these specifications.

The selected design criteria meet several expectations. Enhancement in irradiation resistance is anticipated through the integration of a "high-entropy" matrix [2]. Moreover, a strategic decision was made to avoid the presence of cobalt, thus mitigating the presence of the ^{60}Co isotope during irradiation. Physical and machine learning models have been developed to predict the creep resistance (relying on both precipitation strengthening and diffusion) and corrosion resistance (achieved via the formation of an alumina scale, which is the most effective in a molten salt environment [3]). These models were integrated into a genetic algorithm and several optimal materials were manufactured and subsequently subjected to experimental characterization.

A promising alloy, called “KoR1G” (mainly rich in Ni, Fe, Mn, Cr and Al), has been characterized and optimized in terms of microstructure (SEM-EDX-EBSD, TEM, XRD) and mechanical properties (hardness measurement). Microstructural analyses have generally confirmed the thermodynamic predictions (Thermo-Calc software), although some slight inconsistencies were noted. The confirmation of the presence of ordered γ' nano-precipitates and $M_{23}C_6$ carbides raises expectations for a high creep resistance, in line with predictions from models.

Corrosion protection is expected from the presence of an alumina scale, Thus, oxidation tests, conducted under variable experimental conditions, including exposures to temperatures ranging from 700 to 950°C under different partial pressures of oxygen were conducted in the purpose of characterizing the nature and thickness of the oxide layer (SEM-EDX and XPS). Subsequent corrosion tests in molten salts will serve to validate and quantify the protection imparted by this oxide layer.

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Molten Salt Dealloying Corrosion of Ni-Cr alloys in FLiNaK: Factors Controlling Dealloying

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Molten salts (MS) are used as a very efficient heat transfer medium and as a fuel carrier in fluoride salt-cooled high-temperature reactors (FHRs) and molten salt nuclear reactors (MSRs). Because of their low vapor pressure, wide liquid temperature range (450–1000ºC) under ambient pressure, and high heat capacity, molten fluorides in particular have physical characteristics that enable radically varied designs. In high-temperature Gen IV MSRs, where environmental degradation by corrosion and other processes is crucial, structural materials are required for operation. The most widely used materials for MRSs manufacture are Ni-Cr alloys. Understanding and illuminating features or attributes to describe the corrosion process, such as the effect of microstructure, crystal orientation, environment, and physical characteristics are essential.

The main goal of this study was to understand the factors controlling the morphological evolution of Ni-Cr alloys in molten FLiNaK salts at 600ºC due to selected compositions, plastic deformation, as well as grain size and crystal orientation as driven by applied potential and temperature. The main focus of this work is on Ni-20Cr (wt.%). However, other compositions (Ni-5Cr, Ni-10Cr, and Ni-15Cr (all wt.%)) are discussed as well. Although corrosion attacks can take many different forms, two common types for Ni-20Cr alloys in MS are heterogeneous corrosion and bicontinuous dealloying. Where bicontinuous dealloying is involved, corrosion is marked by both an intragranular uniform corrosion front and deep penetration along grain boundaries and dislocation bands.

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Understanding the effect of surface machining on corrosion behavior of Ni-based alloy GH3535 in molten LiNaKF salt

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Abstract: Ni-based alloy GH3535 is the main structural material for the thorium-based molten salt reactor of China. The reactor components will be in direct contact with the molten salt during operation, therefore surface play a vital role in the early stage corrosion of the components. In addition, machining generally acts as the final stage during components' manufacture.

In this study, GH3535 plates were milled with representative parameters; topography of machined surfaces, elements distributions and microstructure of machining-induced deformation zones were investigated *via* complementary techniques before and after corrosion tests. The corrosion tests were performed in the static high temperature molten LiF–NaF–KF salt at 650°C in argon atmosphere. The results show that a severely plastically deformed zone with gradient microstructure and residual stresses was formed on the machined plates; the deformed zone consists a topmost nano-crystalline layer, a twining intersected layer and a slightly deformed layer near the substrate. After molten salt corrosion, a more severe intergranular Cr element dissolving rate was found at the machined samples in deformation zones than their polished counterparts. Mechanisms of the formation of the deformation region on the alloy, and also relationship between the microstructure and corrosion behavior were discussed based on microstructural features of deformed region as well the the elements dissolution.

Keywords: Nickel-based alloy; Surface machining; Ultrafine-grained layer; Molten salt corrosion; High temperature corrosion.

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Effect of yttrium addition on the corrosion behavior of Ni-based alloy GH3535 in high-temperature molten LiF-NaF-KF salt

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Abstract

Molten salt reactor is a typical fourth generation reactor which has many advantages comparing with the water-cooled reactors. However, the operating environment for the materials is severe than the water-cooled reactors because of the high operating temperature and the use of molten salt as coolant. Corrosion of the structural materials in the molten salt and the resulting components thickness reduction is an important problem to be solved for the development of commercial reactors.

Ni-based alloy GH3535 is now the best candidate material for molten salt reactors because it is superior corrosion resistance to molten salt. However, the corrosion resistance of this alloy is still incompetent in accident conditions. In the present study, the effect of Yitrium addition (0.05%, 0.1%, 0.3% and 0.5%) on the corrosion behavior of alloy GH3535 is molten LiF-NaF-KF salt was studied with complementary techniques, such as electron microscopes, Synchrotron Radiation grazing incident X-ray diffraction. The corrosion tests were performed in the static high temperature molten LiF–NaF–KF salt at 800 °C in high purity argon atomosphere for 1000hrs. We found that the addition of 0.05 wt% Y led to ~40% reduction in weight loss for the alloy, whilst adding more than 0.1 wt.% Y led to opposite effect. Microstructrual and near surface chemistry results indicated that the formation of a YF_3 and Y_2O_3 contained layer in the surface region was the main reason for the beneficial effect of Y. The results are discussed in order to provide a mechanistic interpretation for beneficial effect of Y on the corrosion resistance of the alloy and these findings are important for the development of corrosion resistant alloys.

Keywords: Ni-based alloy, Molten salt corrosion, Yttrium, Active metal dissolution, Gracing incident XRD

Corrosion Investigations of Nickel Alloys and Stainless Steel in Molten NaOH at High Temperature: A Study for Molten Salt Reactors

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With the growing demand for sustainable energy solutions, molten salt reactors (MSRs) have emerged as a promising GenIV technology for safe and efficient nuclear power generation. The successful deployment of MSRs relies on the longevity and reliability of structural materials that can withstand high temperatures and irradiation in highly corrosive environments. This paper evaluates the corrosion characteristics of nickel alloys and stainless steel when exposed to molten sodium hydroxide (NaOH) at 600 ºC, simulating the harsh chemical conditions encountered in MSR environments.

Oxide formation, corrosion products and degradation mechanisms were investigated using electrochemical techniques, SEM/EDS and XRD to provide insights into the durability of nickel-based alloys and stainless steel. Furthermore, investigations were carried out to explore the effects of blanket gases and cathodic protection techniques for corrosion mitigation.

The outcomes of this study provide valuable information for the design and implementation of robust and enduring molten salt reactors contributing to the realization of sustainable, reliable and safe energy solutions.

Influence of oxide concentration on corrosion behaviour of SS316L and its alloying elements in molten LiCl-KCl medium

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Molten chlorides reactors are being studied to reduce the amount of spent nuclear fuel produced by nuclear power plants during electricity production. One of the key issue of this study is the compatibility of the materials involved with this highly corrosive media and its main impurity: oxide ion (O^{2-}).

The aim of this work was to study the influence of O^{2-} concentration on 316L stainless steel and its alloying compounds (Chromium, Iron, Nickel, Molybdenum) in molten LiCl-KCl eutectic (59.2/40.8 %mol) at 550°C. In order to accurately quantify $[O^{2-}]$, a titration method, previously developed in our laboratory [1], was transposed to chloride medium.

The first step in this work was to ensure a high degree of control over the experimental conditions. Additions of Li_2O followed by square wave voltammetries were performed to build a calibration curve for O^{2-} titration. An electrolysis method, using a glassy carbon anode and a nickel cathode, was also developed to decrease O^{2-} content in the bath. These two techniques allowed to accurately study $[O^{2-}]$ influence (in between less than 0.005 mol.kg^{-1} up to 0.150 mol.kg^{-1}) on the behaviour of the pure metals making up SS316L. Linear voltammetry and immersions followed by elemental analysis were performed: Cr and Mo showed reactivity towards O^{2-}, Fe showed dissolution behaviour and Ni showed corrosion resistance. The behaviour of SS316L was finally studied with the same methods, the results obtained on pure metals were consistent with their behaviour in the alloy. A prolonged immersion of SS316L in LiCl-KCl at 550°C, containing O^{2-}, was also carried out to complete the study.

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Comparison of the corrosion resistance of various alloys in molten NaCl-$MgCl_2$

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What is common between a plate of noodles, concentrated solar plant and some of the Gen-IV nuclear reactors? Well, all of them could be improved with salt!

For the solar field, using molten chloride as the heat fluids leads to higher operating temperatures yielding to a better efficiency.

The so-called molten salt reactors (MSR) are basically using molten fluorides or chlorides both as a fuel and heat fluids. The French strategy is to reduce the existing nuclear waste while producing energy using fast neutron spectrum that can transmute actinides such as Pu or Am. A French project gathering the major French stakeholders of the nuclear field (CEA, CNRS, EDF, Framatome, Orano) and funded by the french government through the France 2030 program, is studying the feasibility of a chloride molten salt reactor using NaCl-$MgCl_2$-Pu/$AmCl_3$ as a primary fuel.

The corrosion of materials in this media is one of the main issue. Because of its hygroscopicity, many impurities are present in the salt, making it very aggressive. A lot of data is reported in the literature regarding the corrosion behavior of industrial alloys but the chemistry of the salt is such a key factor that it is very tricky to compare different studies.

The work done here aims at presenting a comparative study of the behavior of several materials in a qualified (*i.e*, with a known and reproducible amount of impurities) NaCl-$MgCl_2$ at 600°C. The protocol of purification and qualification involving electrochemistry is also presented.

Cathodic protection and microbiologically influenced corrosion – Observations from laboratory and field studies

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Cathodic protection (CP) is a well-known and common method used to prevent metallic corrosion in marine environments. While there is anecdotal evidence from the field that CP may be effective in areas where microbiologically influenced corrosion (MIC) is present, there are inconsistencies in the research literature about the ability of CP to prevent MIC.

The present work discusses research undertaken over a 5-year period looking at laboratory and field studies of CP and accelerated low water corrosion (ALWC), a form of MIC. Laboratory studies used microbiological inoculum sourced from locations suspected of ALWC, and examined how testing conditions can affect outcomes. Various parameters including chemical, electrochemical, metallurgical and sessile microbial communities were monitored. The results indicated that test conditions conducive to MIC could be created in the laboratory and that an applied potential of -900 mV (Ag/AgCl/seawater) reduced MIC while making little difference to the sessile microbial communities. A field study was also conducted within the Port of Newcastle (Australia) using a combination of microbial analysis, water quality analysis and laboratory-based corrosion tests. No signs of ALWC were seen on areas within the port where CP was applied, whereas another area without CP showed clear indications of ALWC, suggesting that CP was reducing the likelihood of ALWC and MIC from occurring.

Corrosion Performance of different Corrosion Resistant Alloys for Mechanically Lined Pipes in Seawater During Hibernation Phase

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Abstract

The oil and gas industry mainly transports its production through pipelines, risers and flowlines, also enabling transport between platforms and with onshore terminals. These pipelines are frequently subject to biocorrosion phenomena. This process is aggravated during periods of hibernation, when the pipes can be filled with seawater-based fluids for hydrostatic testing. The present work aims to evaluate the susceptibility of corrosion resistant alloys (CRA), regarding crevice corrosion associated with microbiological corrosion phenomena when exposed in natural seawater under conditions representative of pre-comssioning/hibernation periods. Three alloys were studied on a laboratory scale (UNS N08825, UNS N06625 and UNS S31254), simulating the hibernation period for until 90 days long, at temperatures of 15 and 30ºC. Creviced specimens (torque of 3 N.m) with and without welding were evaluated in systems with and without natural seawater renewal (with biostimulation for closed systems). For a complete analysis of the process, chemical, microbiological, dissolved oxygen and image analyzes were carried out, in addition to monitoring the open circuit potential (OCP). Localized corrosion characterization of the different alloys has been assessed under these conditions as well. The results obtained so far have revealed a high concentration of microorganisms that form biofilms in the alloys studied. Confocal microscopy analyzes show mature biofilms with high cell concentration. OCP monitoring revealed faster ennoblement in seawater renewal experiments and at higher temperature condition. From these results, we can conclude so far that the presence of microorganisms has accelerated the ennobling process,

3D printing technology meets marine biofouling: a study on antifouling resin for protecting marine sensors

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Abstract

Biofouling frequently diminishes the sensitivity and longevity of marine sensors. Addressing this challenge, diverse antifouling strategies have been proposed, considering the structural disparities among sensor types. In this investigation, we utilized acrylic photosensitive resin with controllable hydrolysis as a foundational material to craft a pioneering 3D printing photosensitive resin exhibiting superior dispersion properties of Cu_2O antifouling agents. The surface of the photocured resin remained stable, exhibited minimal linear shrinkage, and facilitated the printing of intricate, high-precision physical components, while maintaining exceptional mechanical properties. Subsequently, a specific antifouling device for the sensing surface of a pH meter composite electrode was designed and 3D printed using the developed resin. This device effectively deterred bacterial and algal growth, ensuring stable monitoring of the pH meter composite electrode for a minimum of one month. Furthermore, the exudation rates of Cu^{2+} and Zn^{2+} from the antifouling tablets under static conditions were found to be reasonable. This study documents the development and assessment of a device that effectively thwarts the adhesion of marine organisms, thereby enhancing the maximum underwater transmittance of glass surfaces in a real sea setting. Our innovative antifouling approach exhibits considerable potential for ameliorating the performance of marine sensors deployed on sensing surfaces. Overall, this work exemplifies a pioneering application of 3D printing technology in the realm of marine antifouling.

Enhancing Corrosion Resistance of Al-Mg Alloys through Biomineralization

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In recent decades, new emerging microbiological technologies have been studied, based on the recognition that microorganisms can inhibit corrosion by different mechanisms, the so-called MICI (microbiologically influenced corrosion inhibition), opening up different lines of research. In this context, biomineralization has been attracting the attention of researchers, with an increasing number of studies showing that different types of mineralized layers formed on metal surfaces can reduce the risk of corrosion.

In this framework, the MICOATEC project aims to study solutions based on mineralization influenced by marine microorganisms. Several AA5083 alloy samples were immersed at the Genoa Outdoor Experimental Marine Station (GEMS) for different periods of time and solar exposure (light and dark sides). Post-test characterization using a range of complementary techniques (SEM/EDX, XPS, ToF-SIMS) provided new insights into modifications of AA5083 surfaces. On the dark side, an Al/Mg oxide/hydroxide layer was formed, allowing Cl^- penetration. Pitting attack was observed after immersion. On the light side, a dual layer structure was formed, in which a hydrated Mg-rich outer layer with extracellular polymeric substances (EPS) on the top has proven to play a role in the corrosion inhibition process as a barrier to the penetration of Cl^-. A first assessment of the corrosion resistance properties was performed by a natural atmospheric exposure test (marine/industrial outdoor test site, Sines-Portugal) allowing to confirm that the dark side showed a more severe localized attack and that the hydrated Mg-rich outer layer naturally formed on the light side showed to improve the corrosion resistance. A comparative study of the corrosion resistance was performed using artificial salt fog test (ISO 9227) to assess the behaviour of hydrated Mg-rich biomineralized layer formed on Al-Mg surfaces versus commercial conversion treatments. After 1000 hours of test, the Al-Mg samples with the biomineralized layer showed no significant degradation.

This work was financially supported by the ANR, in the framework of the MICOATEC project (ANR-19-CE08-0018).

Success in Developing CVD Graphene Coating on Mild Steel: A Disruptive Approach to Remarkable/Durable Corrosion Resistance

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ABSTRACT

The talk will discuss the challenges in developing corrosion resistant graphene coating on most common engineering alloys, such as mild steel, and present recent results demonstrating circumvention of these challenges. In spite of traditional approaches of corrosion mitigation (e.g., use of corrosion resistance alloys such as stainless steels and coatings), loss of infrastructure due to corrosion continues to be a vexing problem. So, it is technologically as well as commercially attractive to explore disruptive approaches for durable corrosion resistance. Graphene has triggered unprecedented research excitement for its exceptional characteristics. The most relevant properties of graphene as corrosion resistance barrier are its remarkable chemical inertness, impermeability and toughness, i.e., the requirements of an ideal surface barrier coating for corrosion resistance. However, the extent of corrosion resistance has been found to vary considerably in different studies. The author's group has demonstrated an ultra-thin graphene coating to improve corrosion resistance of copper by two orders of magnitude in an aggressive chloride solution (i.e., similar to sea-water). In contrast, other reports suggest the graphene coating to actually enhance corrosion rate of copper, particularly during extended exposures. Authors group has investigated the reasons for such contrast in corrosion resistance due to graphene coating as reported by different researchers. On the basis of the findings, author's group has succeeded in demonstration of remarkable and durable corrosion resistance of mild steel as result of development of suitable graphene coating.

Mechanisms of formation and corrosion protection by conversion coatings

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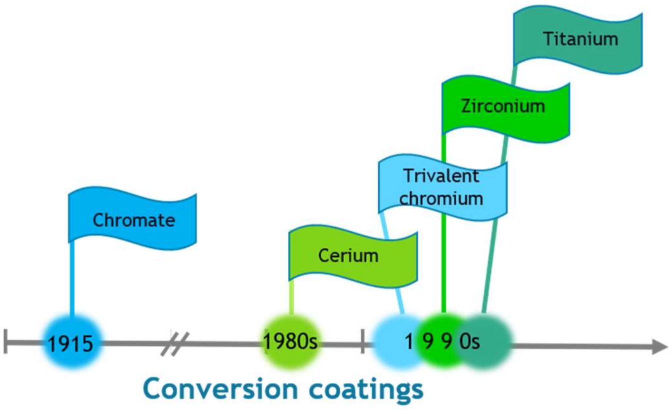
Conversion coatings provide increased interfacial adhesion of the metal substrate to a subsequent organic coating and offer immediate corrosion protection. The development of coatings based on transition elements of the 4th and 6th periods and rare earth elements spanned more than a hundred years and accumulated a vast knowledge of the mechanisms and structure of these coatings. Among them, chromate has the most extended history, being the most essential conversion coating, which is now mostly banned for health and environmental reasons. The focus on other conversion coatings has been in the last thirty years, as illustrated in the scheme. Conversion coatings based on Zr, Cr and Ti are already commercialised, whilst rare earth coatings are still in the research stage, along with, for example, those on molybdate and vanadate.



The formation mechanism of conversion coatings on Al alloys has been vastly investigated but less so on other materials such as cast alloys, steels and zinc substrates. In the lecture, the mechanisms of Ce/Zr/Cr coating formation will be presented, considering various effects such as conversion bath parameters and type of substrate. The composition, thickness, and structure of conversion layers were analysed through SEM/EDS, XPS and ToF-SIMS techniques. The correlation between the aqueous chemistry and the deposition mechanism of coatings will also be discussed.

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Anti-corrosion challenges in the automobile industry linked to the environment : sustainability, weight reduction, management of critical raw materials, etc….

Claire Czechowski, Stellantis, France

Dare forward 2030, slashing our carbon emissions by half by 2030 on the path to achieve carbon net zero in 2038. What are the challenges arising from these objectives for the corrosion protection of our vehicles?

Reliability studies of protective layers for electronic devices by EIS

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Polymers plays a crucial role for various kinds of encapsulation of electronics, e.g. dam and fill encapsulations, potting or mold compounds. Depending on the specific issues the different types of polymers are used in various designs. The encapsulated electronic assemblies are subject to ageing due to the ambient conditions (humidity, temperature) and the operating conditions (e.g. electric fields). The expansion of the application fields is often associated with harsher environmental conditions (e.g. off-shore application). These and the continuously increased application of power electronics requires adapted materials and processes (transfer molds) for the encapsulation considering the specific requirements (power density, miniaturization). As part of a research project, the suitability of (Electrochemical) Impedance Spectroscopy for the characterization of the material, the monitoring of the process quality as well as the state-of-health (SoH) over the lifetime should be evaluated. Several challenges arise in this context. The materials commonly used for the molding are particle-reinforce epoxy mold compounds (EMC) which are characterized by high resistivity (10^{15} -10^{16} Ω cm). In combination with coating thicknesses of a few millimeters, this results in a very high-resistance system (> T$\Omega \cdot$ cm^2). In addition, in-line perspective monitoring of SoH requires the use of miniaturized electrodes for EIS, which necessitates the measurement of very low current densities. Overall, EIS is reaching the limits of what is currently possible with commercially available devices. In this paper, the authors address the challenges and evaluate the possibilities of EIS for the characterization of thermal transfer molds with extremely high resistances as well as suitable accelerated aging tests.

H_2O_2-driven corrosion of Ti6Al4V investigated by electrochemical impedance spectroscopy and quantitative microstructure analysis

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Ti6Al4V, as biomedical implant material, degrades in the presence of reactive oxygen species, such as oxygen peroxide (H_2O_2) during acute or chronic inflammation phases [1]. This leads to the device degradation and the release of its constituents in the surrounding tissues, which may cause health issues (peri-implantitis, osteolysis, neurotoxicity). H_2O_2 is also used as tissue disinfection agent during surgical operation.

In this contribution, within the framework of the French-Swiss project LoCoMecha, the in-vitro corrosion by H_2O_2 is investigated by in situ electrochemical methods like impedance spectroscopy and ex situ characterisation techniques, notably high-resolution imaging and spectroscopy (SEM-SE, SEM-EBSD, SEM-EDX, FIB-SEM and (S)TEM-EDX). The effect of the microstructure of the samples prepared by forging and additive manufacturing on the alloy corrosion will be reported. The extent of β phase dissolution, a key-aspect for the mechanical integrity of the implant is assessed by quantitative microstructure analysis. First insights on the mechanisms of the Ti6Al4V degradation (β phase dissolution and α phase oxidation) will be provided.

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Oxygen Reduction on Magnesium Alloys as Secondary Cathodic Process: Myths, Facts, Cause and Effect

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Oxidation of magnesium exposed to a simple saline electrolyte is accompanied by surface alkalinization due to the hydroxyl ions generated by cathodic reactions. Tracing the amount of released hydrogen was thought to be a reliable measure of magnesium degradation rate. Hydrogen evolution reaction is however not the only cathodic process supporting magnesium oxidation. Recently, experimental evidence obtained by different methods have been presented by several groups that oxygen reduction is an important secondary cathodic reaction during magnesium corrosion. This finding might be especially relevant for the biodegradable implant applications where strong oxygen consumption at the metal/fluid interface *in vivo* could induce hypoxia and cause inflammation or antibiosis. The talk will present on overview of the recent publications [1-4] to demonstrate the contribution of oxygen reduction to the total cathodic process on degrading magnesium and explain the factors influencing the extent of oxygen reduction for different alloys and testing media. The role of transport properties of the surface film in limiting oxygen diffusion will be considered. Unravelling the mechanisms of magnesium corrosion is vital for establishing reliable research methodologies, developing new alloys, and predicting magnesium degradation behavior.

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A corrosion model describing the in-vivo behaviour of biomedical alloys

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Understanding the corrosion behaviour of metals for biomedical applications is a prerequisite for improving and further developing materials and optimising clinical procedures in arthroplasty. A combination of in-vitro and in-vivo electrochemical measurements on titanium and a CoCrMo alloy have been carried out in order to achieve this goal. For the in-vivo measurements, a systematic experimental protocol was designed and validated to perform the electrochemical tests in the synovial fluid extracted from a cohort of 154 patients undergoing primary total knee/hip arthroplasty (TKA/THA), punction with TKA and TKA/THA revision surgery.

The obtained in-vivo results showed that the anodic and the cathodic behavior of the tested materials can significantly change depending on patients. The dominating cathodic reaction at open circuit potential is the oxygen reduction reaction. Moreover, in the cathodic domain the presence of organic species also plays a major role on the electrochemical kinetics. This can be explained by the adsorption of organics limiting the access of oxygen to the surface and thus its reduction. Thus, the electrochemical response is determined by the interaction of organics and oxygen and not simply by one of these factors taken separately. An analytical corrosion model has been proposed to describe the observed behaviour considering the Volmer-Butler equation for the oxygen reduction reaction and a Langmuir isotherm for the adsorption of proteins.

Innovative Solutions for Anti-Corrosion in Battery Casing Top Covers: A Comprehensive Methodology and Evaluation

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As the demand for advanced energy storage systems continues to rise, the longevity and reliability of battery components become critical factors in ensuring overall system performance. This paper delves into the complexity of addressing the anti-corrosion requirements of battery casing top covers, presenting a meticulously designed methodology aimed at identifying and evaluating effective solutions.

The methodology encompasses a multifaceted approach, incorporating specific anti-corrosion testing procedures that simulate real-world corrosion phenomena on the top cover. Electrochemistry studies are conducted to scrutinize potential galvanic coupling risks between various components of the battery casing and the screws used in its assembly. This comprehensive methodology provides a robust framework for assessing and mitigating corrosion risks in battery systems.

The study evaluates three pre-coated steel solutions as potential alternatives to traditional cathodic paint applications. Through rigorous testing and analysis, these solutions demonstrate excellent performance in meeting the stringent anti-corrosion requirements of battery casing top covers. The presented findings showcase the effectiveness of the selected solutions, emphasizing their viability for application as battery casings top covers.

The research not only contributes valuable insights into the corrosion mitigation strategies for battery casings but also lays the groundwork for future advancements in material science and design engineering. By focusing on the intricate details of anti-corrosion solutions and employing a systematic methodology, this paper provides a significant step forward in ensuring the durability and reliability of battery systems in diverse and challenging environments.

Electrochemical investigation of titanium alloy corrosion triggered by electroactive *Desulfovibrio ferrophilus* biofilm in simulated seawater containing exogenous electronic shuttle

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Titanium alloys are widely used in marine engineering due to their excellent overall mechanical properties and corrosion resistance. Excellent biocompatibility of titanium alloy contributes to microbiologically influenced corrosion (MIC) triggered by adhering biofilms. In this work, A series of electrochemical methods, in particular electrochemical impedance spectroscopy (EIS), were used to investigate the MIC behaviour of titanium alloys induced by electroactive *Desulfovibrio ferrophilus* biofilm. The addition of the electron shuttle significantly reduced the impedance and R_{ct} values of the titanium alloy and decreased the phase angle in the low frequency region, indicating that the electron shuttle accelerated the destruction of the protective layer of the titanium alloy surface in the *D. ferrophilus* environment and decreased the energy barrier for the bacteria to obtain electrons. The Hilbert-Huang transforms revealed the formation of corrosion pits. Potentiodynamic polarization curves measurements proved that riboflavin-shuttle increased the anodic dissolution rate.

Reduced-Dimension Modelling and Visualisation of Corrosion Inhibitor Leaching in Coatings

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Industrial coatings often incorporate corrosion inhibitors, which prevent metal corrosion by creating a protective layer in damaged areas. Upon exposure to the environment, these corrosion inhibitors dissolve and diffuse from the coating, creating a void network within the polymer matrix. The precise factors governing the leaching timescale and the impact of the porous structure's topology on mass transport are challenging to inspect directly and remain still not fully understood.

We developed a new experimental method to model the leaching of corrosion inhibitors from coatings at reduced dimensionality (i.e., in 2D) and larger scales, enabling the direct visualisation of the process. Utilising high-precision micromilling techniques, we manufactured complex porous structures that contain geometrical features similar to those found in corrosion protection coatings. The porous structures are filled with a solid crystal of dextrose, chosen as a model solid phase for its high diffusivity and solubility in water. The dissolution and diffusion processes commence as one end of the porous structure is exposed to a water bath and are captured with a high-resolution camera. We obtain the leaching rate by tracking the solid interface as water ingresses into the system. Our approach streamlines the exploration of a broad parameter space, allowing for a comprehensive examination of how quantities such as porosity and tortuosity control the process. This is achieved through the use of a simplified physical system that is more manageable and employs readily accessible experimental techniques.

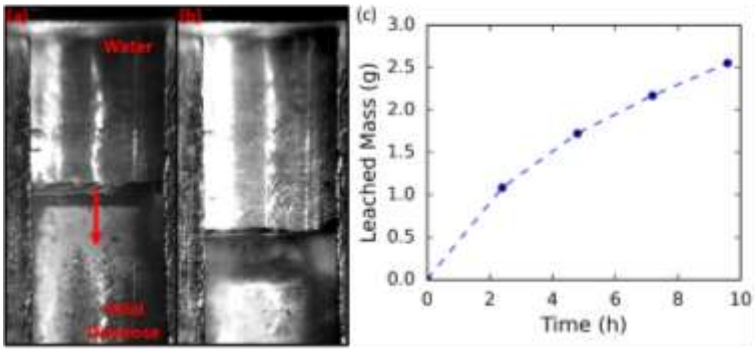

Figure 1. (a-b) Leaching of dextrose in an example geometry over a 9 hour period. (c) Leached mass as a function of time.

Development of new NiMoCrAl alloys resistant to molten chloride salts corrosion

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Molten Salt Reactors (MSR) are a type of nuclear reactor working with molten salts as heat collector with nuclear fuel usually dissolved in the salts. One of the most challenging aspects for future use is to find structural materials that can withstand both corrosion in chloride salts and neutron irradiation at 600-700°C. Ni-Mo-Cr alloys seem to be good candidates to resist to molten chloride corrosion [1] as chromia (Cr_2O_3) or alumina (Al_2O_3) protective layers can improve corrosion resistance [2].

The main objective of our study is to evaluate the influence of Cr substitution by Al in a $Ni_{70}Mo_{10}Cr_{20-x}Al_x$ system on its corrosion resistance. The selection of alloys is based on microstructure, corrosion resistance and mechanical properties. Compositions of interest, produced by arc melting, are identified using CALPHAD method, characterized by SEM/EDS, XRD and hardness measurements and then immersed in $NaCl-MgCl_2$ molten salt at 600°C for one week.

SEM/EDS and XRD analyses show that in molten salt, substitution of Cr for Al promotes formation of different oxide layers composed of element such as Al, Mo, Mg, and O which reduces the mass loss of the alloy. At the same time, substitution of Cr for Al from 10%at up to 20%at triggers the precipitation of Ni_3Al and a BCC phase composed of Mo, which induces a significant increase in hardness.

The best compromise for our application could be composed of Al content between 5 and 10 %at or between 15%at and 20%at in order to limit the mass loss in corrosion and promote formation of a passive oxide layer while having controlled hardness.

[1] J. Busby & al. - technical gap assessment for materials and component integrity issues for molten salt reactors - ORNL/SPR-2019/1089

[2] Zhu & al. Solar Energy Materials & Solar Cells, 2022, 241, 111737