Akademia Górniczo-Hutnicza im. Stanisława Staszica w Krakowie

AGH University of Science and Technology

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PROBLEMS OF THE NIOBIUM ORE PROCESSING INDUSTRY CAUSED BY FLUORINE, AIR AND WATER VAPOR-CONTAINING ATMOSPHERE

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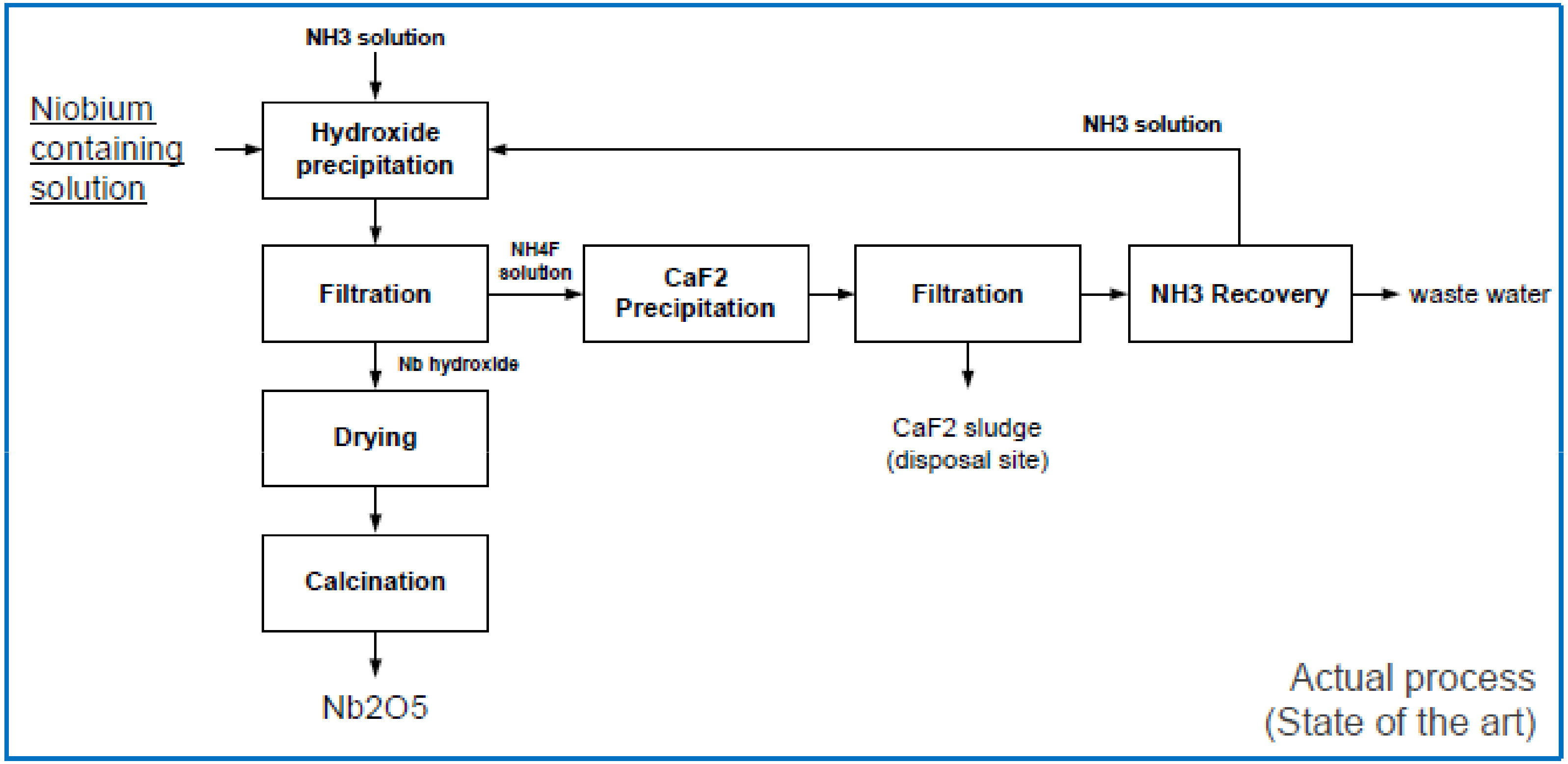
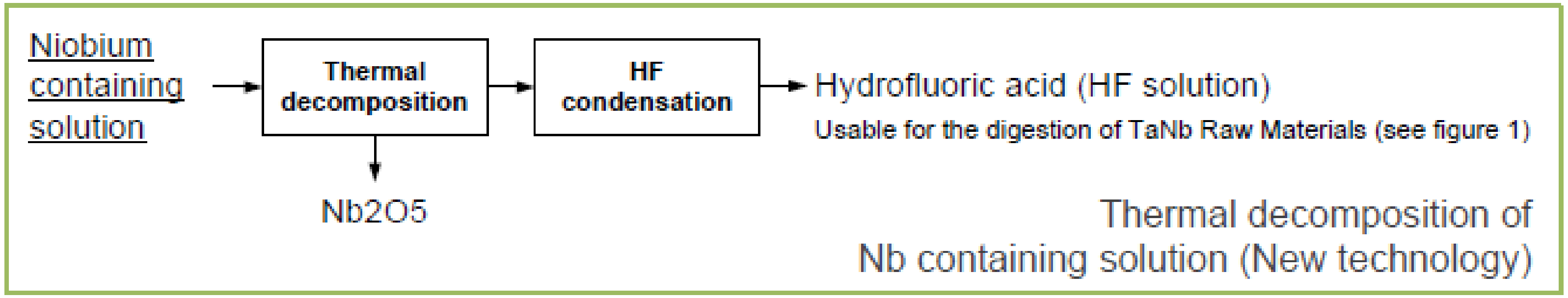
Corrosion in an atmosphere containing fluorine, air and water vapor

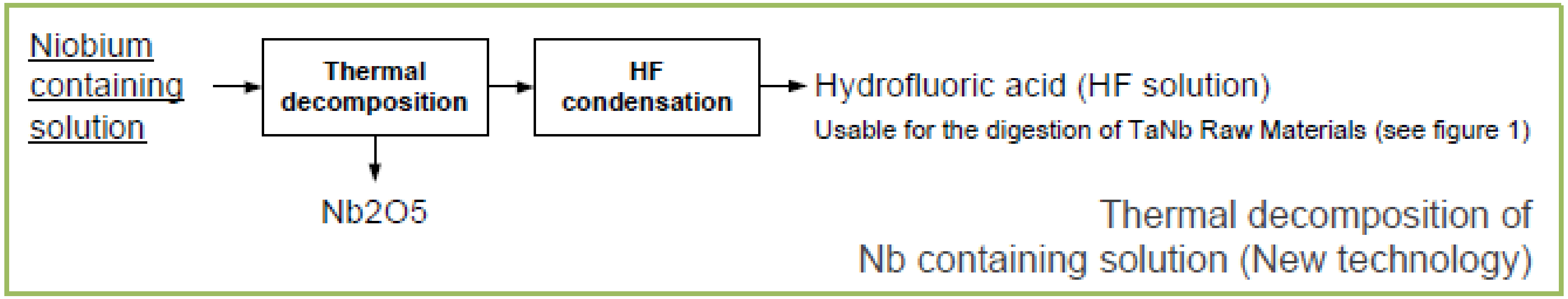
Limiting high-temperature corrosion is particularly difficult when starting new technologies that require the use of extremely aggressive reaction atmospheres, in which the heat-resistance of metallic materials has never been tested before. An example of such a situation is the raw material processing industry for the production of niobium oxide, Nb_2O_5, in which a new process is applied that ensures high purity of the obtained product and at the same time greater efficiency compared to the previously used conventional methods.

The process of decomposition by thermal spraying





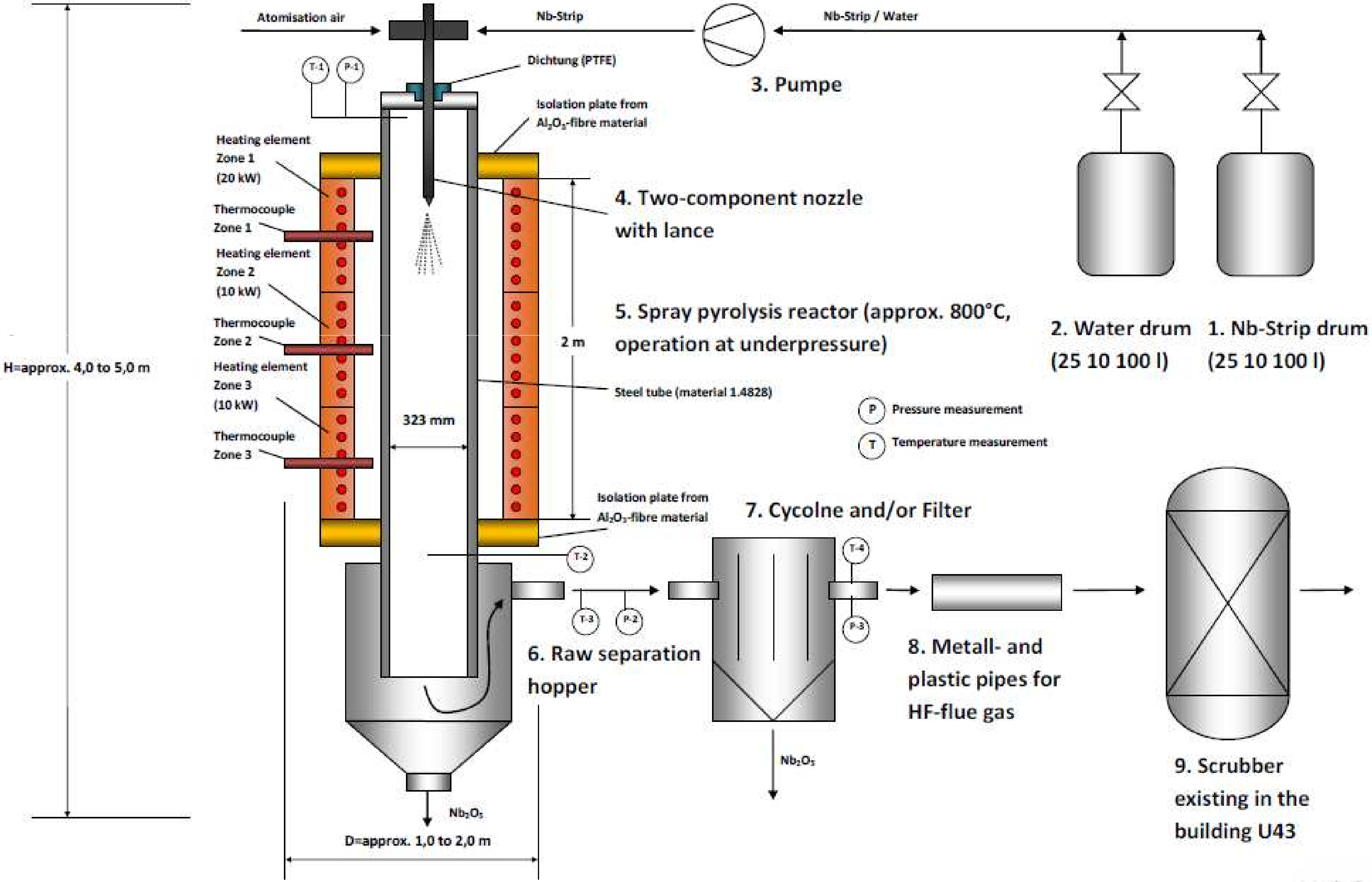
The process of decomposition by thermal spraying



Advantages of the new process:

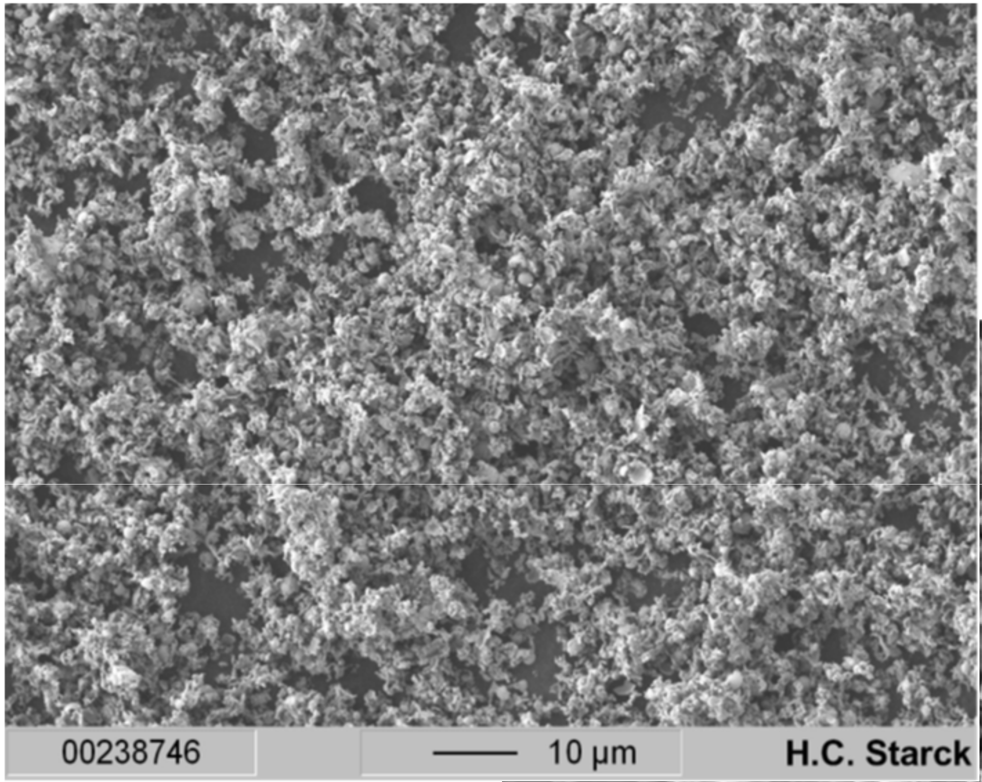
- possibility of HF recycling
- less sewage/sewage sludge due to a lack of hydroxide sediment sludge
- obtaining a new oxide product with the desired characteristics

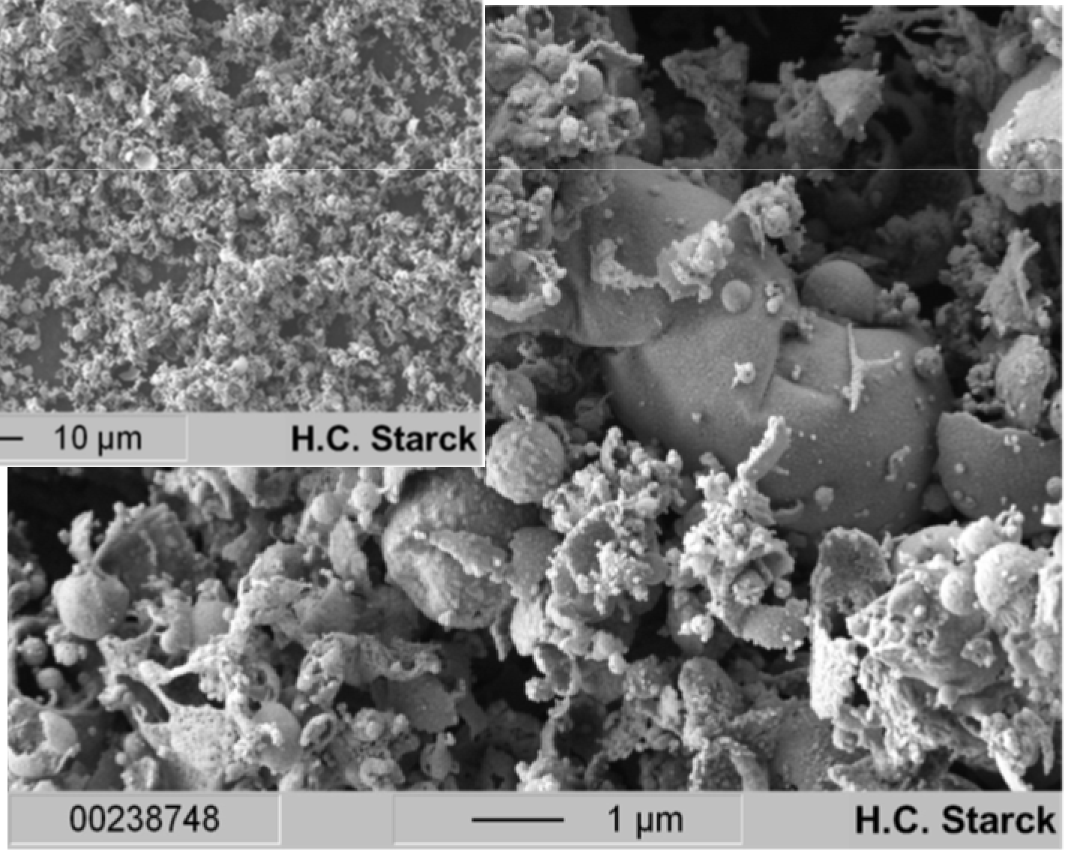
Schematic illustration of an installation for thermal spray decomposition



Photograph of a fragment of the installation for thermal spray decomposition

SEM images of the Nb_2O_5 powder produced by the new process





Material corrosion in atmosphere containing fluorine, air and water vapor

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Reactive atmosphere composition:

8.3 vol. % HF,
53.1 vol. % H_2O
38.5 vol. % air

Problems:

- rapid corrosion procedure
- wide temperature range: 25 – 900 ^{o}C
- toxic atmosphere
- low boiling temperature HF (19.5 ^{o}C)
- HF completely dissolves in water
- presence of an HF-H_2O azeotrope (120 ^{o}C)
- lack of experimental data

Stages of research aiming to reduce corrosion in the thermal spraying process

1. **Thermodynamic analysis:**
   - determining partial pressures of gases in the HF-H_2O-air complex atmosphere
   - determining the phase stability of three-component systems (Fe, Ni, Cr, Al)-O-F in the temperature range of 298-1273 K
   - determining the resilience of volatile metal compounds (Fe, Ni, Cr, Al) in the reactor
2. **Initial selection of alloys intended for the construction of the reactor**
3. **Performing industrial corrosion tests:**
   - determining the corrosion rates of individual alloys
   - research on the morphology of corrosion products
   - chemical and phase composition studies of corrosion products
4. **Indication of one alloy for the construction of the reactor.**

Thermodynamic analysis

The aim of performing thermodynamic calculations was to pre-select metallic materials in terms of their suitability for the construction of an industrial-scale Nb_2O_5 producing reactor. It was assumed that the potential construction materials should be resistant to both the corrosive effects of oxygen and fluorine, as there is no literature data on the basis of which it is possible to assess which of these components of the reaction atmosphere is more aggressive.

It should be emphasized that materials classified as "alumina formers" and "chromia formers" have a very high heat resistance in oxygenates. On the other hand, nickel is very resistant to hydrogen fluoride.

Consequently, four metals were selected for thermodynamic considerations, i.e. aluminum, chromium, nickel and additionally iron, which is the main component of most popular alloys intended for operation at high temperatures.

Determining partial gas pressures in complex HF-H_2O-air atmosphere

$$HF_{(g)} = \frac{1}{2}H_2 + \frac{1}{2}F_2$$

$$HF_{(g)} = \frac{1}{2}H_2 + F$$

$$F_2 = 2F$$

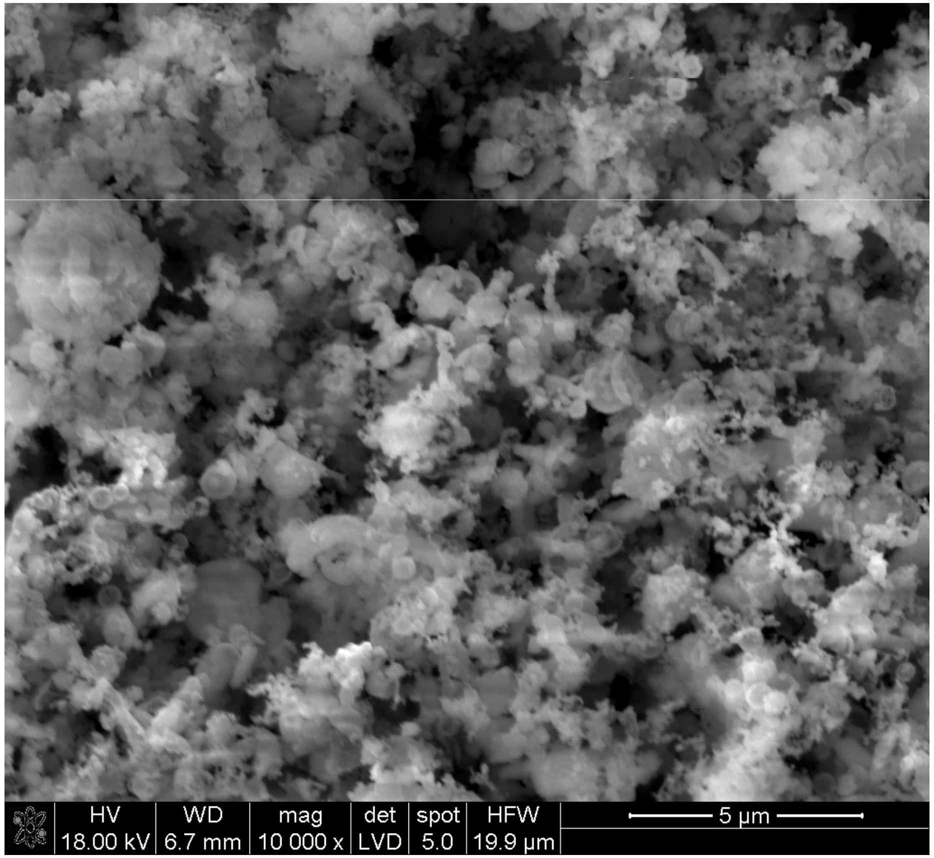
$$\frac{1}{2}O_2 + 2F = F_2O$$

$$2HF + \frac{1}{2}O_2 = H_2O + 2F$$

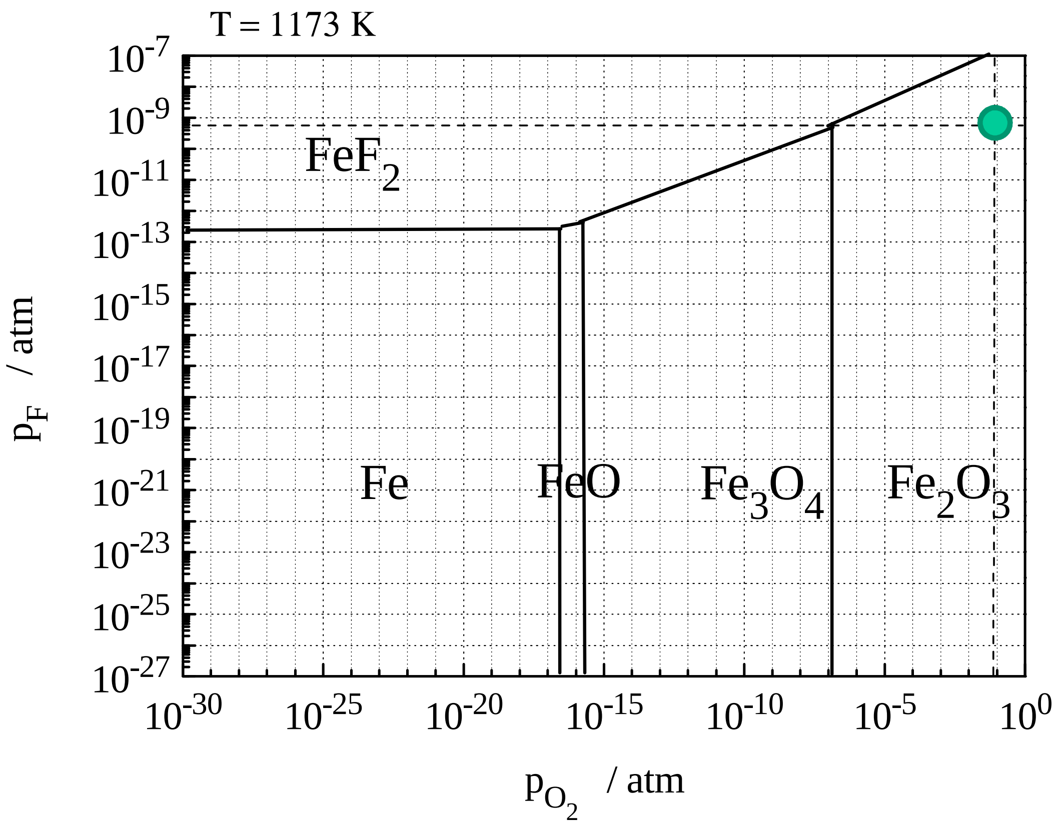
T [K]	p (F) [atm]	p (O_2) [atm]
1273	4.8E-09	0.0798
1173	7.0E-10	0.0798
1073	7.1E-11	0.0798
973	4.6E-12	0.0798
873	1.6E-13	0.0798
773	2.3E-15	0.0798
673	9.7E-18	0.0798
573	6.1E-21	0.0798
473	1.7E-25	0.0798
373	1.9E-32	0.0798
298	1.0E-40	0.0798

Aggressive components in the reaction environment

- atomic fluorine
- molecular oxygen
- liquid HF solution in the reactor (up to 120 ^oC)
- liquid HF solution in Nb_2O_5 pores (up to around 300 ^oC)



Determining phase stability of the Fe-O-F system in the temperature range 298-1273 K



COMMENTS:

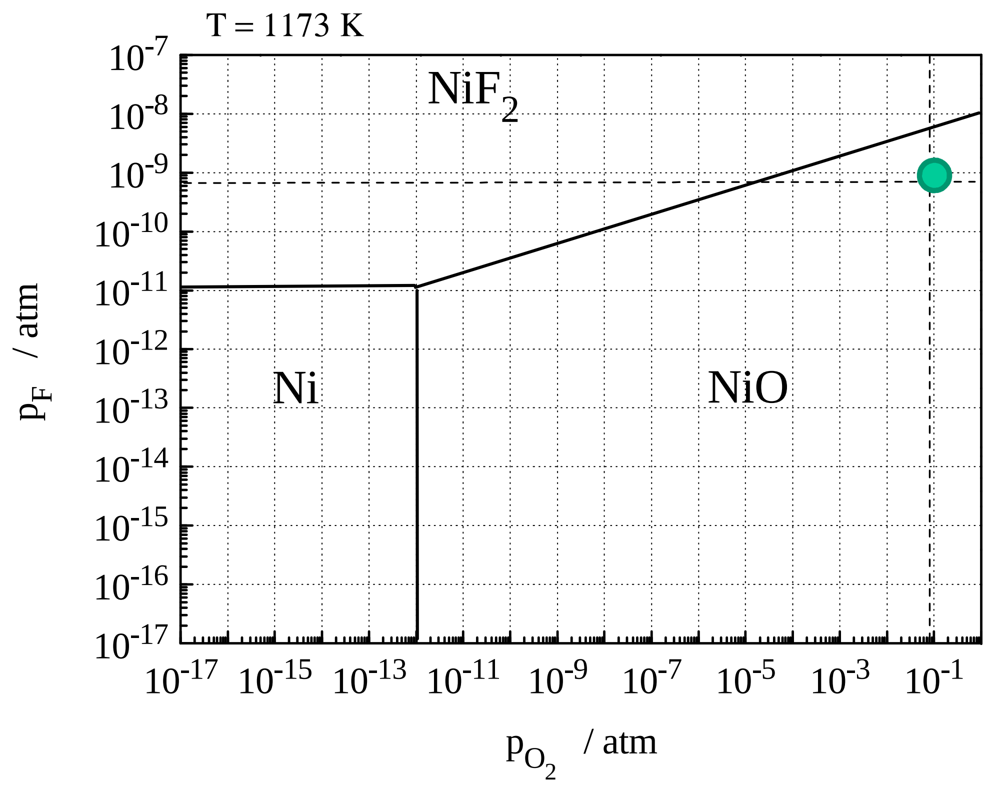
Melting temperature of FeF_2: 972 ^oC

There is no thermodynamic equilibrium state at lower temperatures

The corrosion rate is expected to be very high in oxygen atmosphere and relatively low in F

$$k'_p = \frac{1}{2}\int_{p_F^i}^{p_F^o} (2D_{Fe} + D_F)\, d\ln p_F$$

Determining phase stability of the Ni-O-F system in the temperature range 298-1273 K

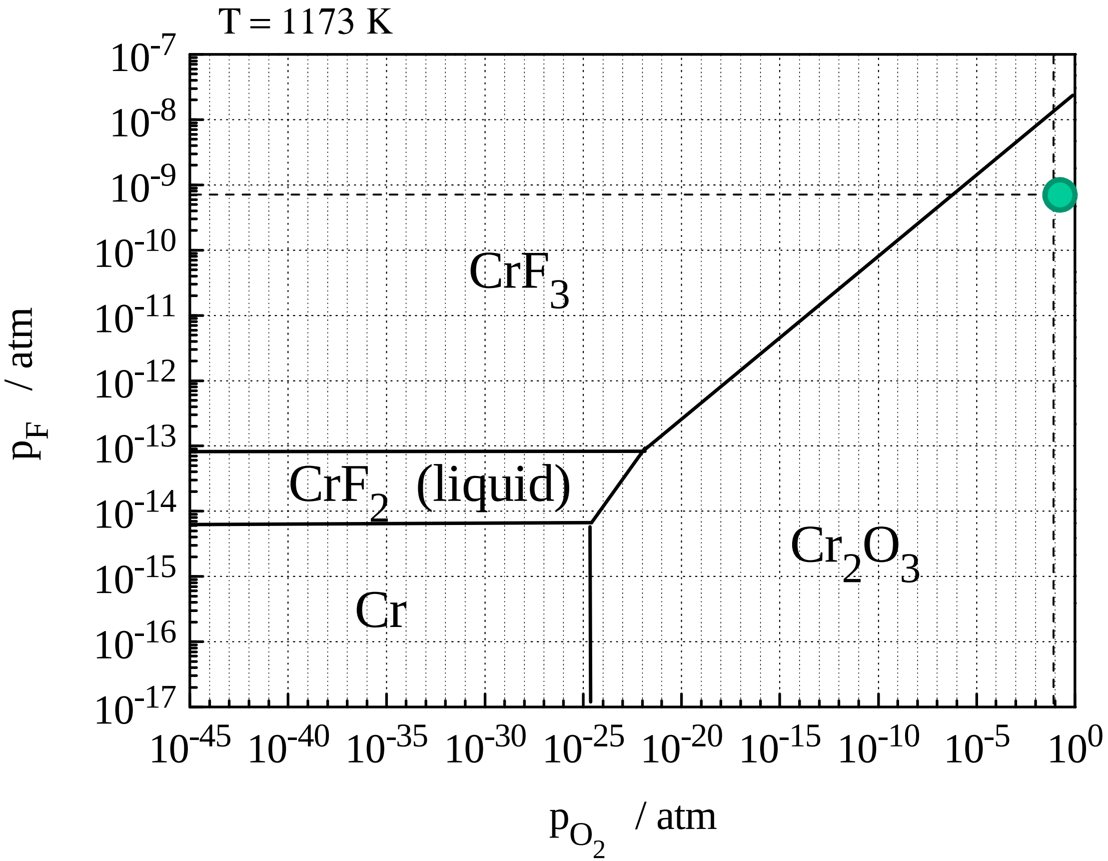


COMMENTS:

There is no thermodynamic equilibrium state at lower temperatures

The corrosion rate is expected to be relatively low in both oxygen and fluorine atmosphere

Determining phase stability of the Cr-O-F system in the temperature range 298-1273 K



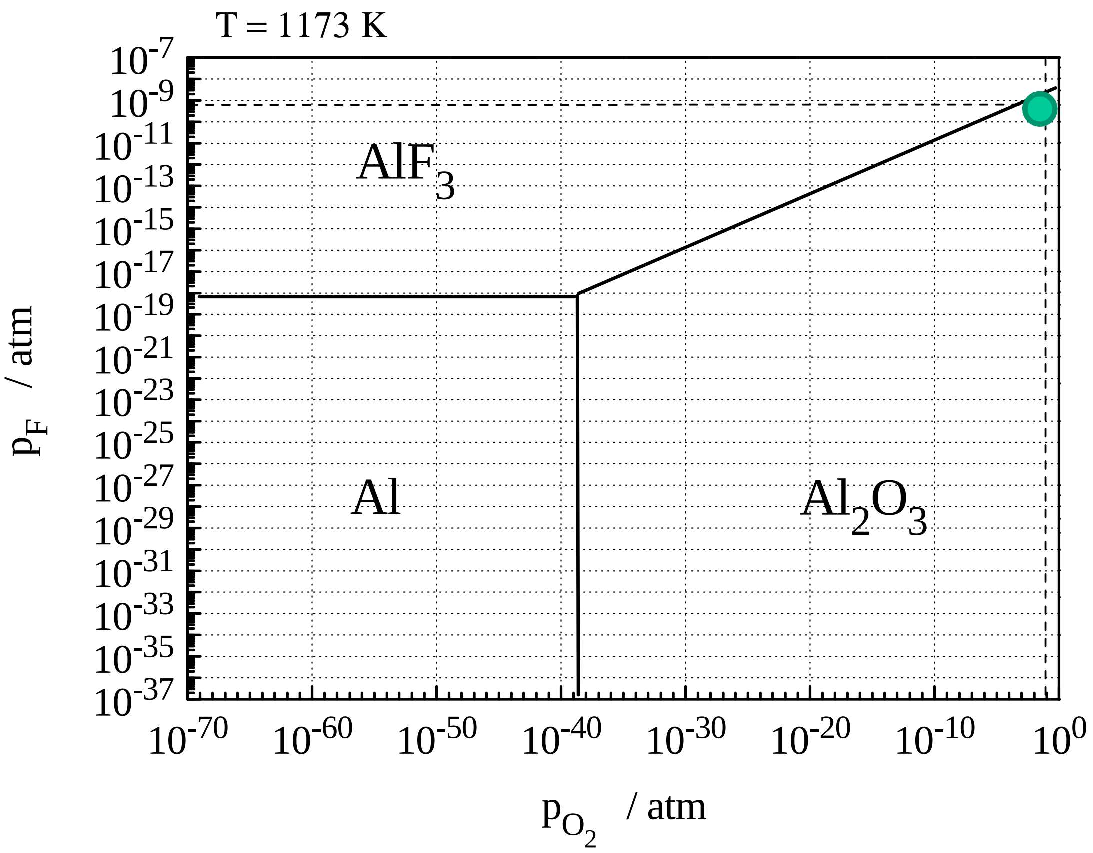
COMMENTS:

Melting temperature of CrF_2: 894 ^oC

There is no thermodynamic equilibrium state at lower temperatures

The corrosion rate is expected to be very low in oxygen and catastrophic in F

Determining phase stability of the Al-O-F system in the temperature range 298-1273 K



COMMENTS:

There is no thermodynamic equilibrium state at lower temperatures

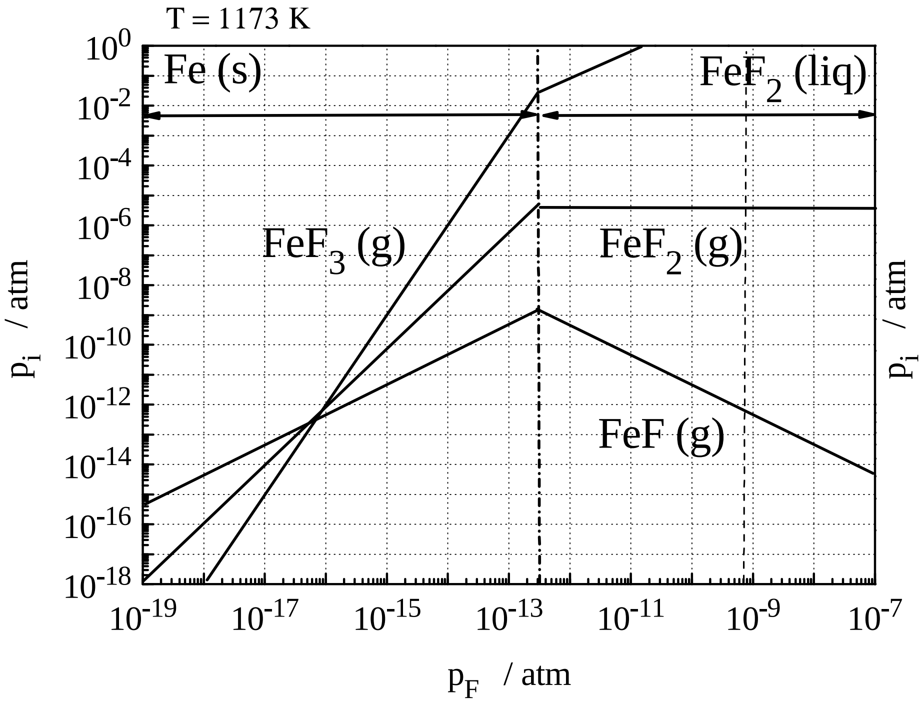
The corrosion rate is expected to be very low in oxygen and high in F

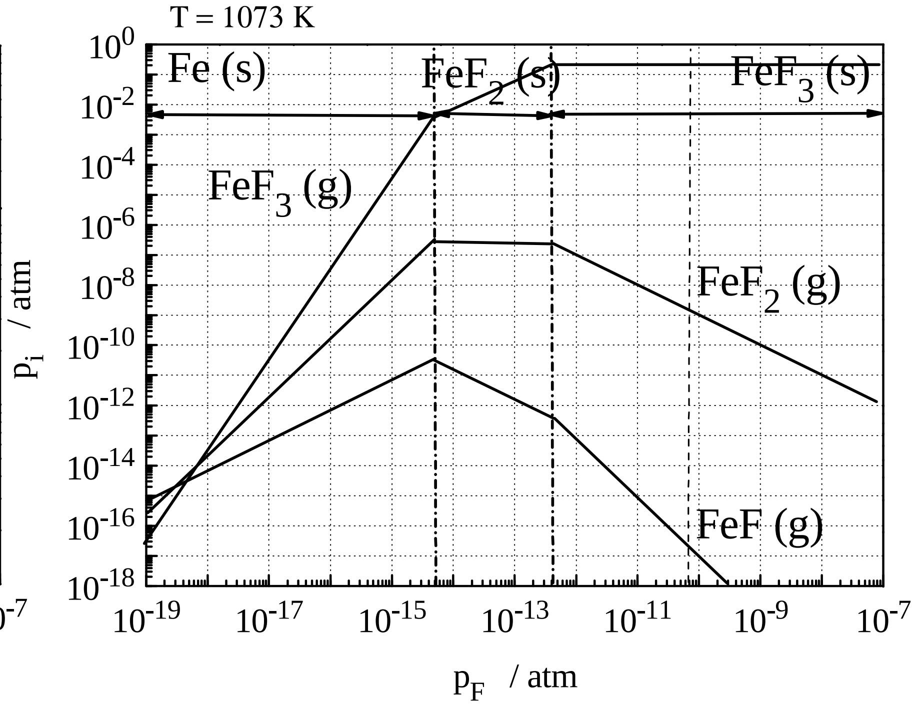
Volatile chromium compounds in the reactor

Due to the high water vapor content in the reactor, the formation of CrOOH, $CrO(OH)_2$, $CrO(OH)_3$, $CrO_2(OH)_2$, etc. should be expected, as opposed to CrO, CrO_2, CrO_3. The rate of chromium evaporation in the form of the above-mentioned compounds is only important at the highest reactor operating temperature.

In literature, there is a lack of data concerning volatile chromium fluorides.

Volatile iron fluorides in the reactor

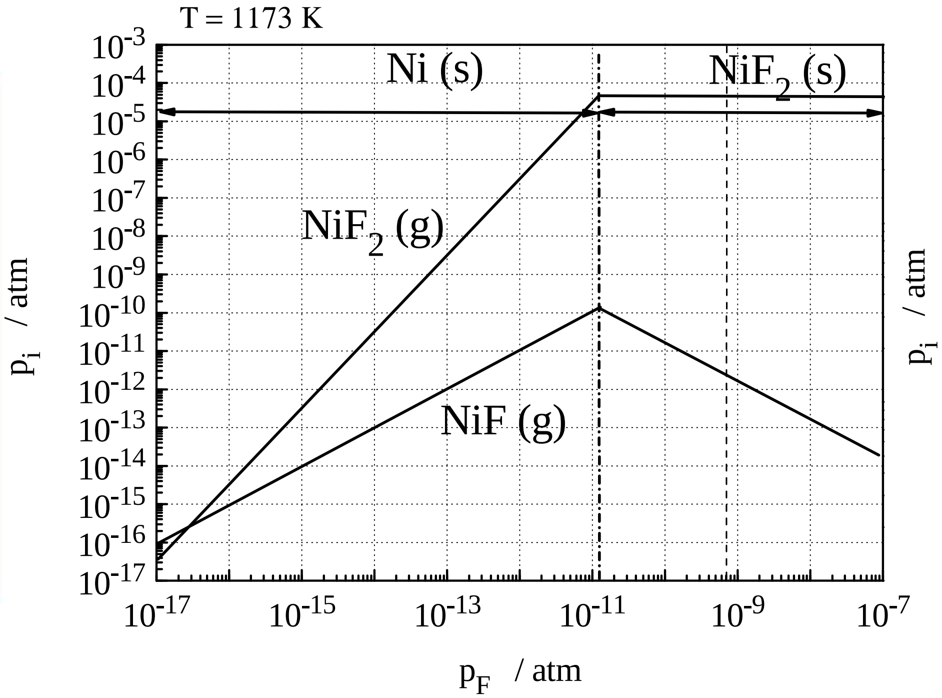


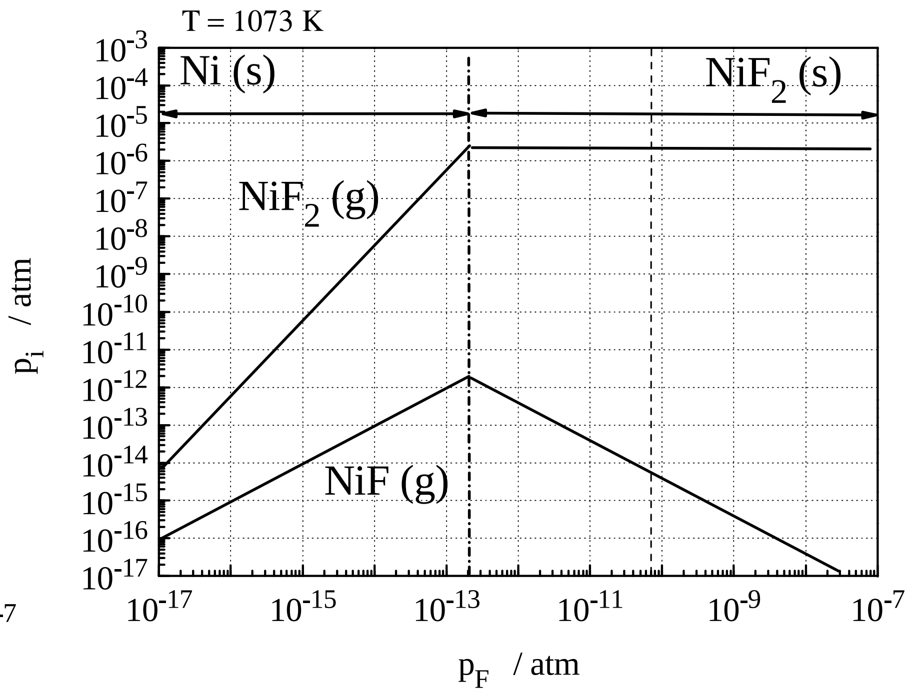


COMMENTS:

A very high evaporation rate of iron fluorides is expected

Volatile nickel fluorides in the reactor

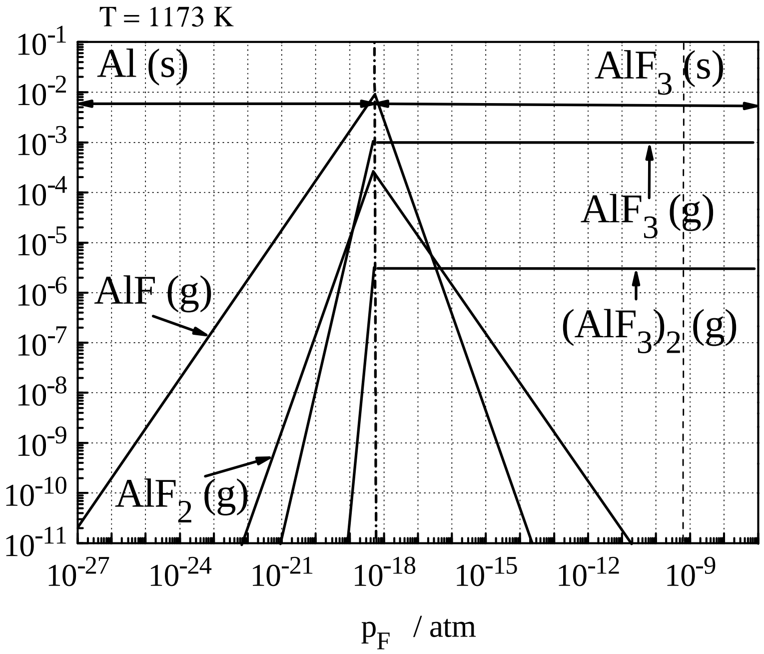


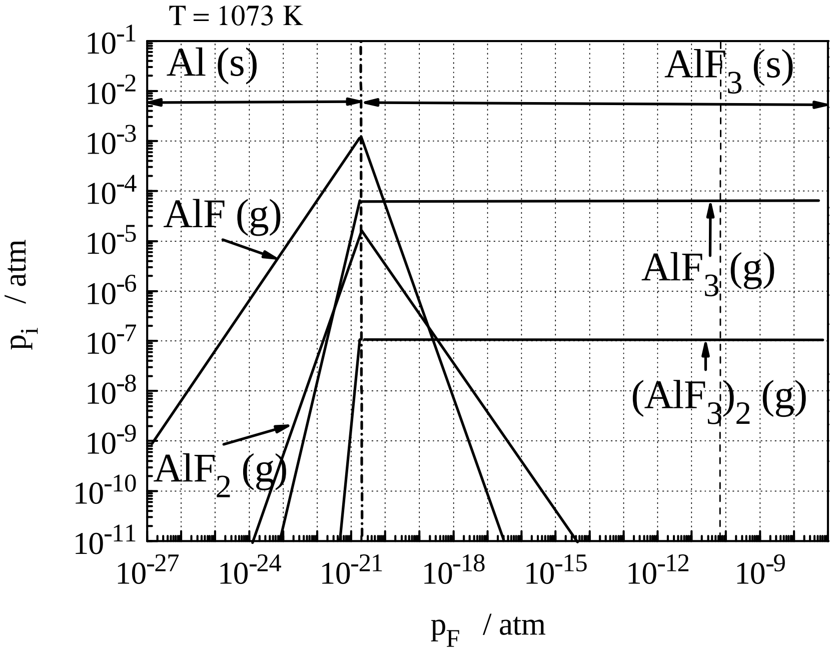


<u>COMMENTS:</u>

A moderate evaporation rate of nickel fluorides is expected

Volatile aluminum fluorides in the reactor





<u>COMMENTS:</u>

A high evaporation rate of aluminum fluorides is expected

Conclusions from thermodynamic calculations

1. Analysis of the phase stability diagrams leads to the conclusion that all considered metals can react with both oxygen and fluorine under the studied conditions.
2. All the compounds presented in the phase stability diagrams can appear in the scales that grow on the surfaces of the considered metals.
3. The results obtained for the Cr-O-F system indicate that chromium, as a component of heat-resistant alloys, should not be used in the construction of the reactor due to the possibility of liquid CrF_2 fluoride formation (melting point: 894^{o}C) and the high resilience of volatile fluorides. This also applies to the presence of iron in the alloys considered as materials for building the reactor, which is undesirable due to the relatively low melting point of FeF_2 (940^{o}C).
4. The performed calculations suggest that nickel is the best material for the construction of the designed reactor among all the considered metals. The presence of residual metals in the potential alloy used in the construction of the reactor seems to be undesirable, although the final decision in this matter depends on their concentrations in the alloy and requires experimental verification.

Initial selection of steel grades intended for the construction of the reactor

1. If fluorination in the reactor is the predominant process, high purity nickel or nickel based materials should be chosen for reactor fabrication.

2. If oxidation in the reactor is the predominant process, materials covered during oxidation by a highly protective chromium oxide scale should be chosen for reactor fabrication. Alumina formers are not recommended for reactor construction due to their poor mechanical properties. However, they can be used as coatings in the future.

Initial selection of steel grades intended for the construction of the reactor

1. Alloys resistant to fluorination:

   2.4066; 2.4068; 2.4360; 1.3917

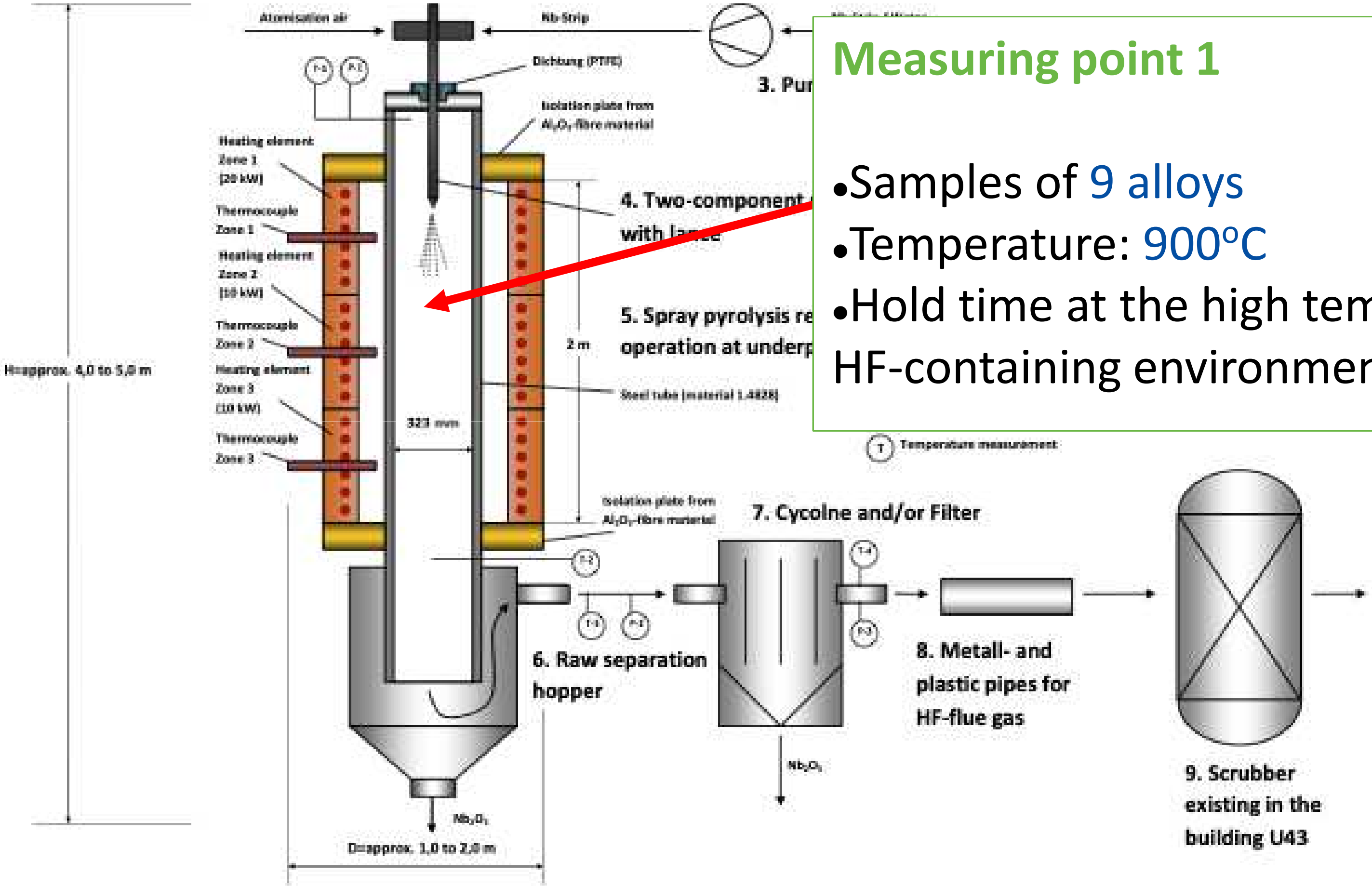
2. Alloys resistant to oxidation:

   Alloy 75; Alloy 625; Inconel HX; 2.4660; 1.4828

Initial selection of alloys intended for the construction of the reactor

Alloy	Ni	Cr	Fe	Mo	Nb+Ta	C	Mn	Si	P	S	Al	Ti	Co	Cu	B	W	Pb	Mg	N
2.4066	99.2 min.	-	0.40 max.	-	-	0.10 max.	0.35	0.25	-	0.005	-	0.10	-	0.25	-	-	-	0.15 max.	-
2.4068	99.0 min.	-	0.40 max.	-	-	0.02 max.	0.35	0.25	-	0.005	-	0.10	-	0.25 max.	-	-	-	0.15 max.	-
Alloy 75	Rest	18.0 - 21.0	5.00 max.	-	-	0.08 - 0.15	<= 1.00	1.00	0.03	0.02		0.20 - 0.60	5.00 max.	0.50 max.	-	-	0.005	-	-
2.4360	63.0 min.	-	1.00 - 2.50	-	-	0.15 max.	2.00	0.50	-	0.02	0.50 max.	0.30	-	28.0 - 34.0	-	-	-	-	-
Alloy 625	58.0 min.	20.0 - 23.0	5.0 max.	8.0-10.0	3.15-4.15	0.10 max.	0.50 max.	0.50 max.	0.015 max.	0.015 max.	0.40 max.	0.40 max.	1.0 max	-	-	-	-	-	-
Inconel HX	Rest	20.5 - 23.0	17.0 - 20.0	8.00 - 10.0	-	0.05 - 0.15	1.00	1.00	0.02	0.015	0.50 max.	-	0.50 - 2.50	0.50 max.	0.01 max.	0.20 - 1.00	-	-	-
2.4660	32.0 - 38.0	19.0 - 21.0	Balance	2.00 - 3.00	(8xC) Nb	0.07 max.	2.00	1.00	0.025	0.015	-	-	1.50 max.	3.00 - 4.00	-	-	-	-	-
1.4828	11.0 - 13.0	19.0 - 21.0	Balance	-	-	0.20 max.	2.00	1.50 - 2.50	0.045	0.015	-	-	-	-	-	-	-	-	0.11 max.
1.3917	41.0 - 43.0	-	Balance	-	-	0.12 max.	1.00	0.30	-	-	-	-	-	-	-	-	-	-	-

Location of samples in the reactor



Measuring point 1

- Samples of 9 alloys
- Temperature: 900°C
- Hold time at the high temperature, HF-containing environment: 105 h

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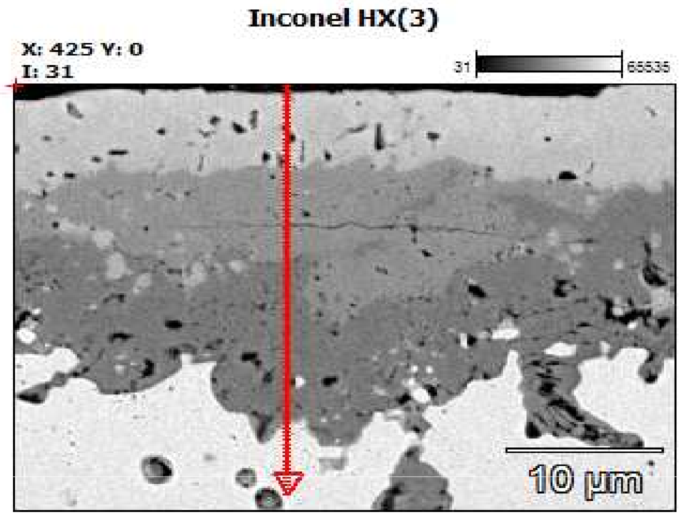
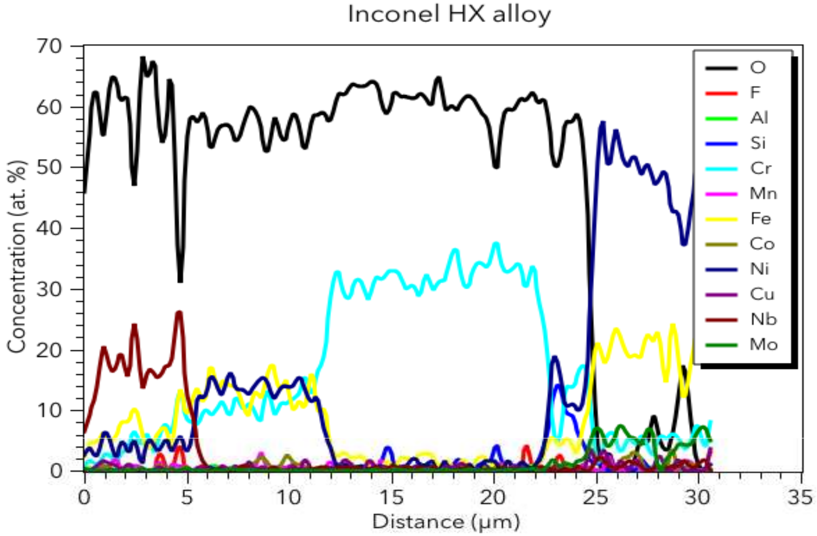
Methods used to determine the corrosion kinetics of individual samples with different steel grades

1. Discontinuous gravimetric method.
2. Scale thickness measurement.
3. Metallic core thickness measurement.

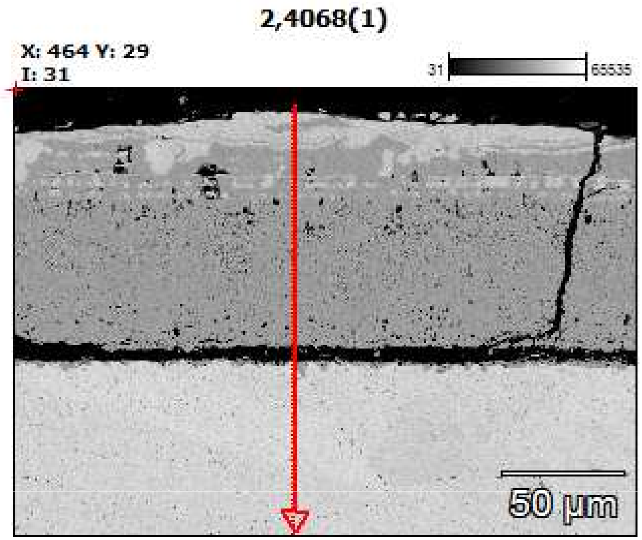
Methods used to determine the corrosion kinetics of individual samples with different steel grades

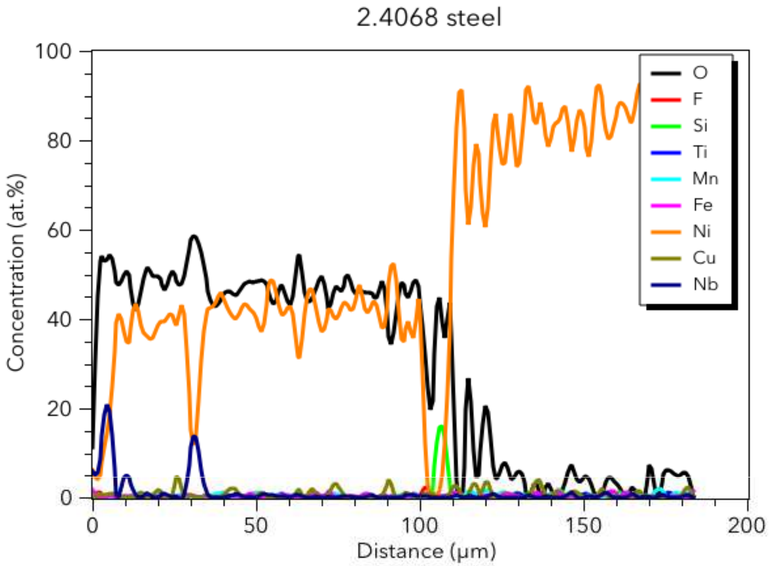


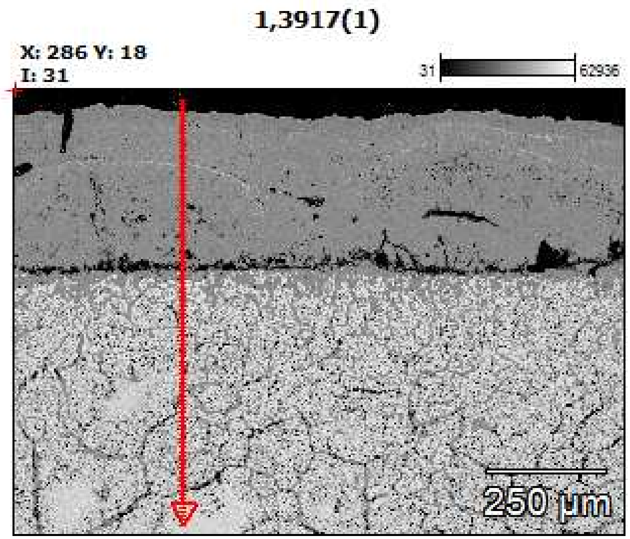


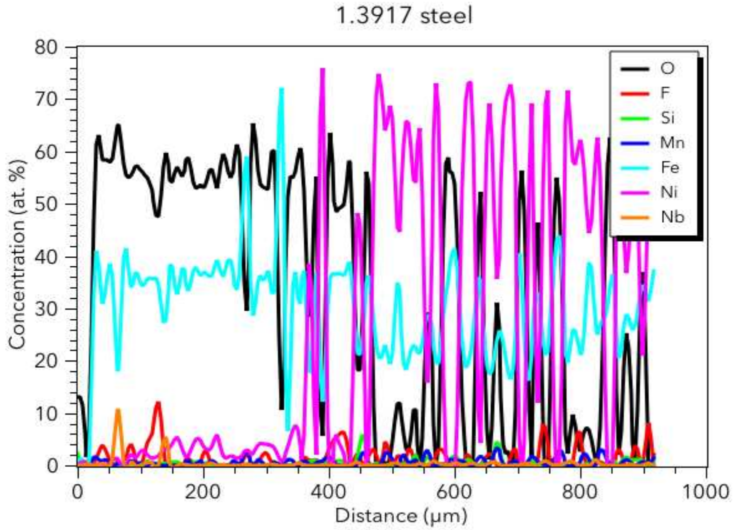
~~Discontinuous gravimetric method~~

Methods used to determine the corrosion kinetics of individual samples with different steel grades



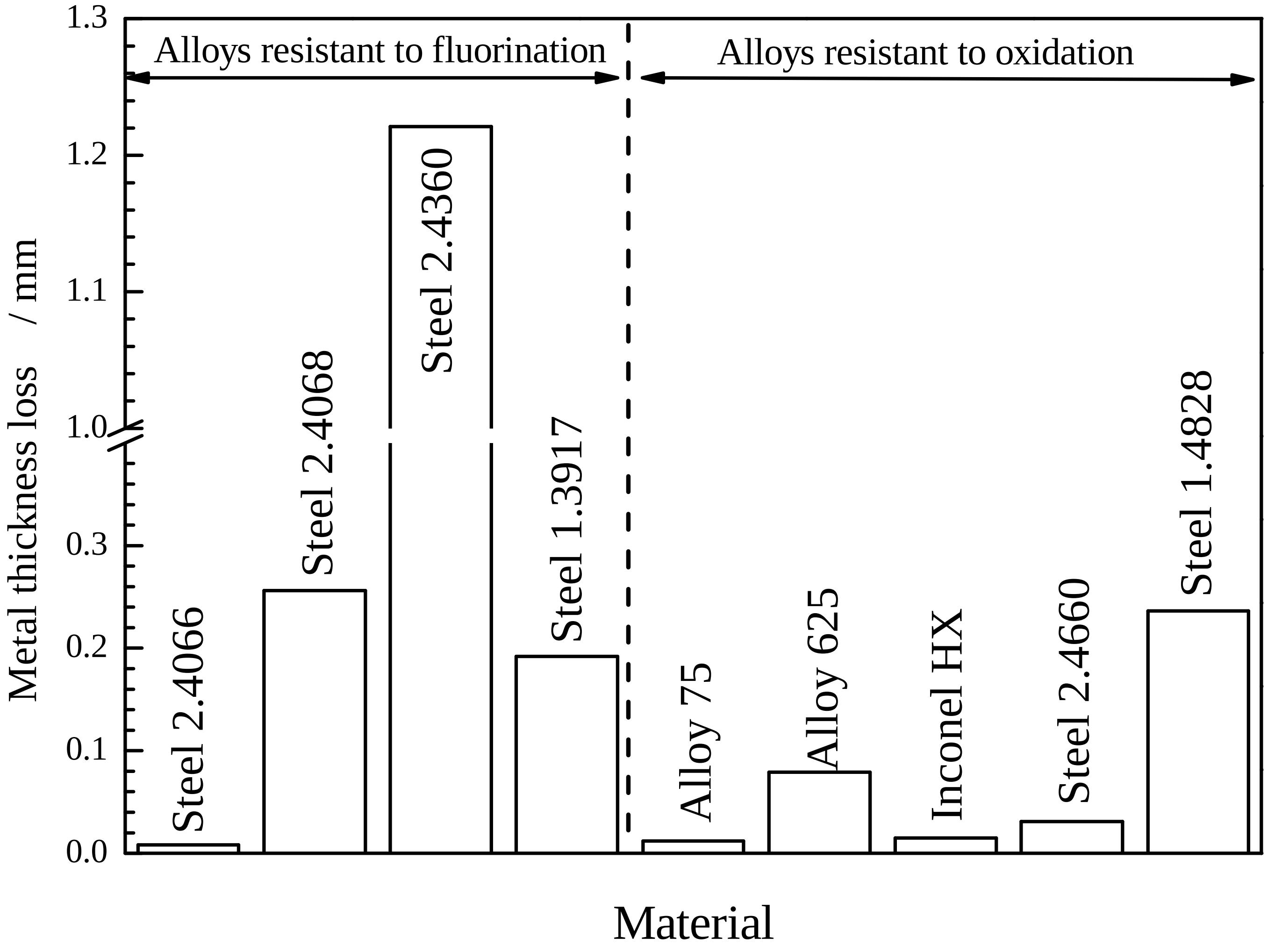






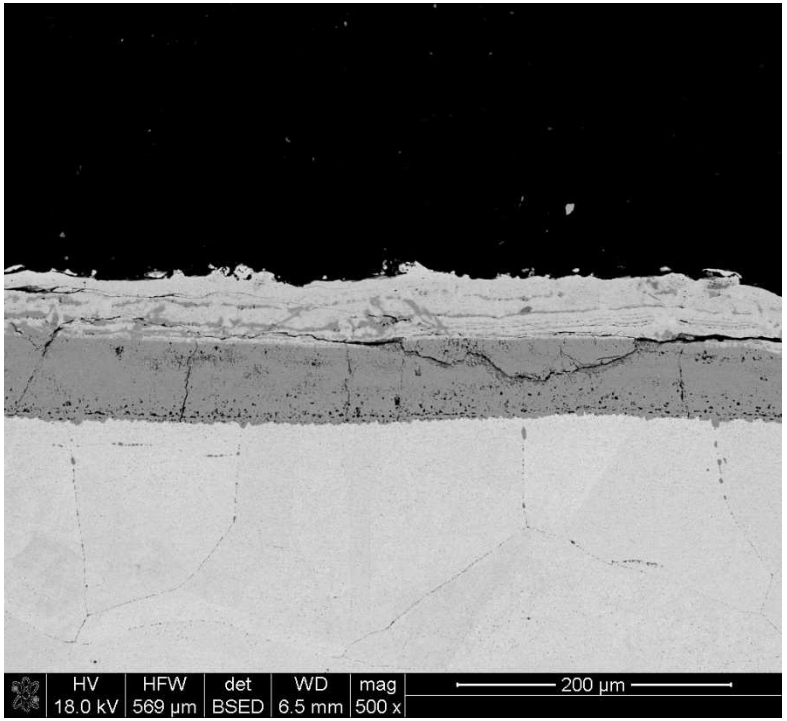
~~Scale thickness measurement~~

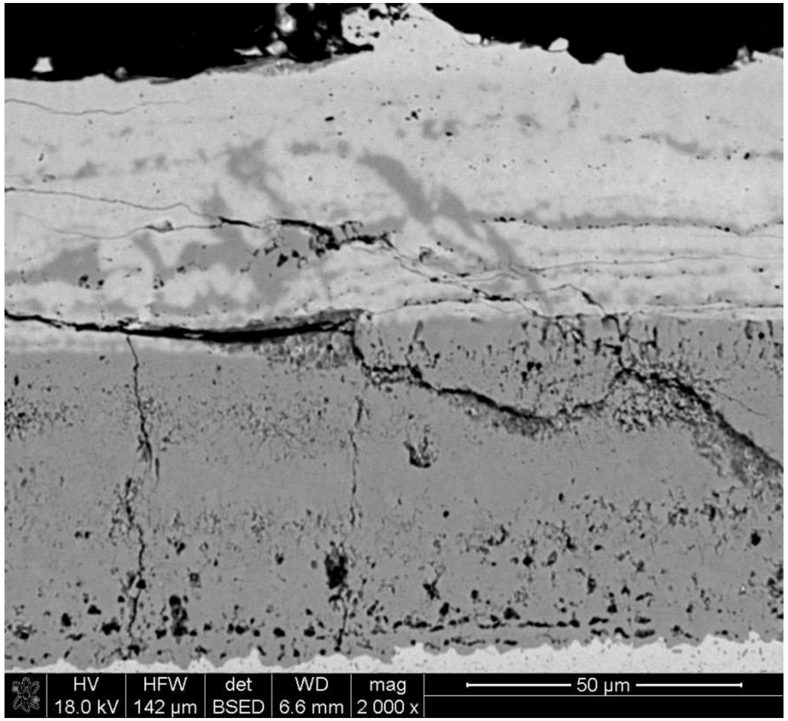
Results obtained from measurements of the samples' metallic core loss



Selected results research on the morphology, chemical and phase composition of corrosion products of individual alloys – 2.4066

2.4066 – the best alloy in the group of nickel-based materials





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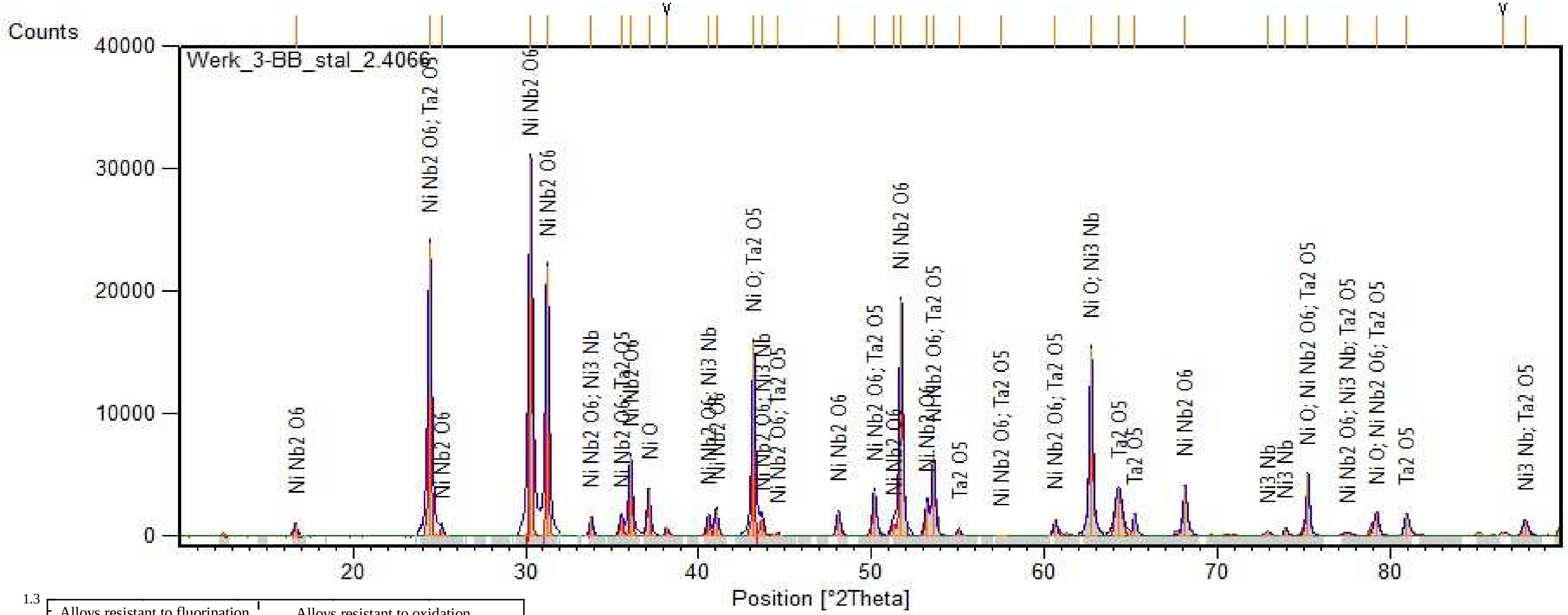
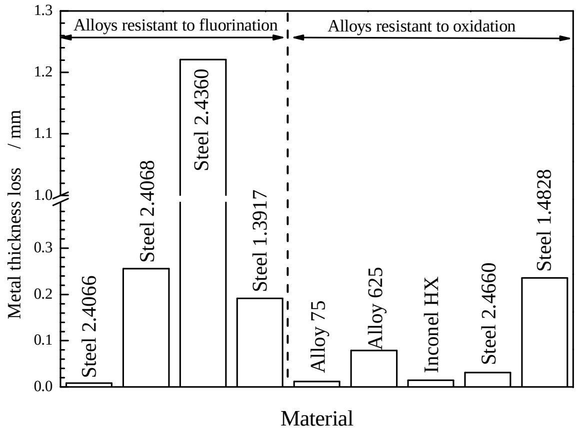
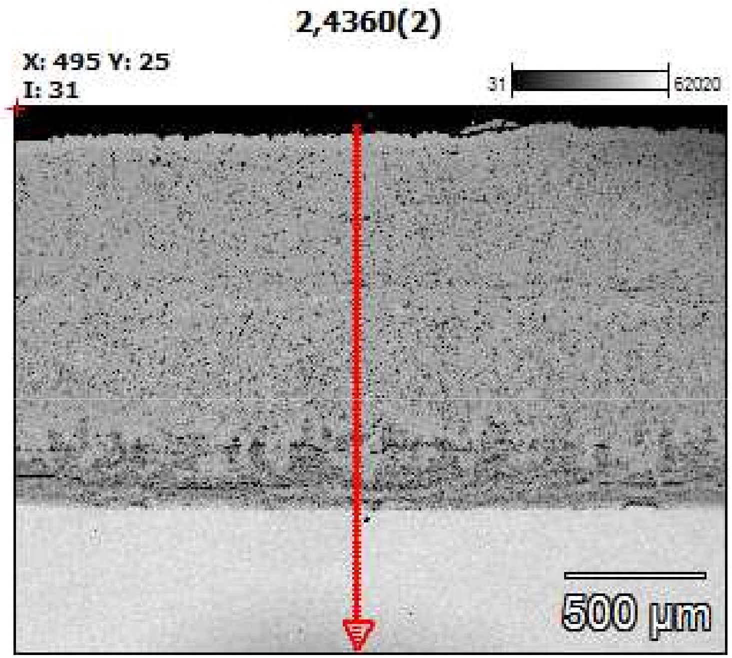
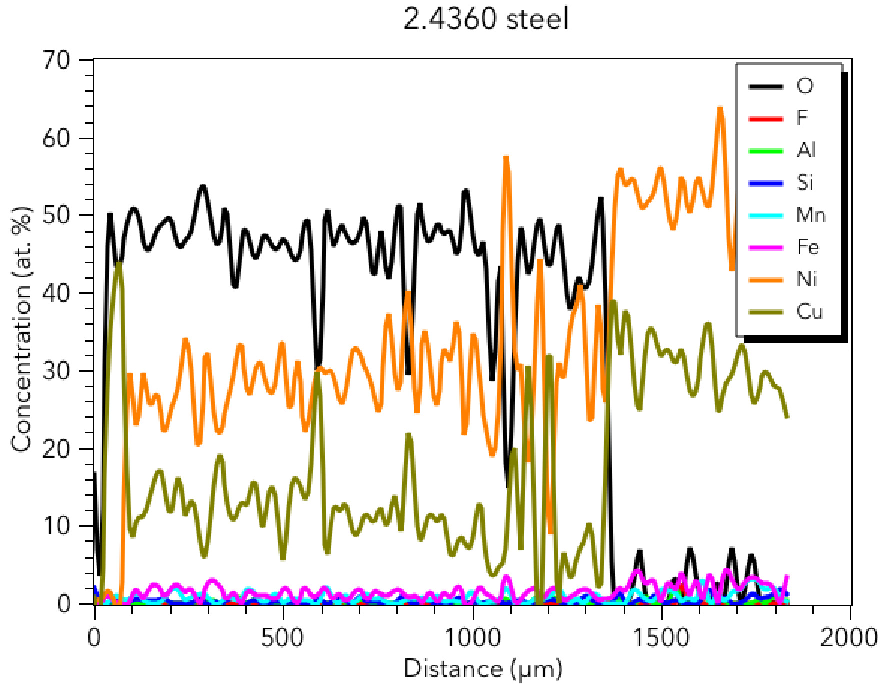
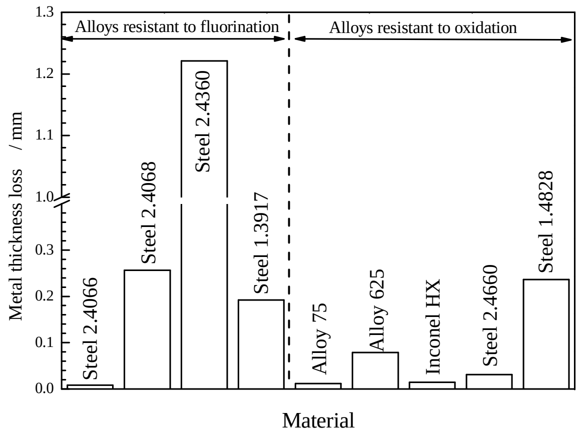




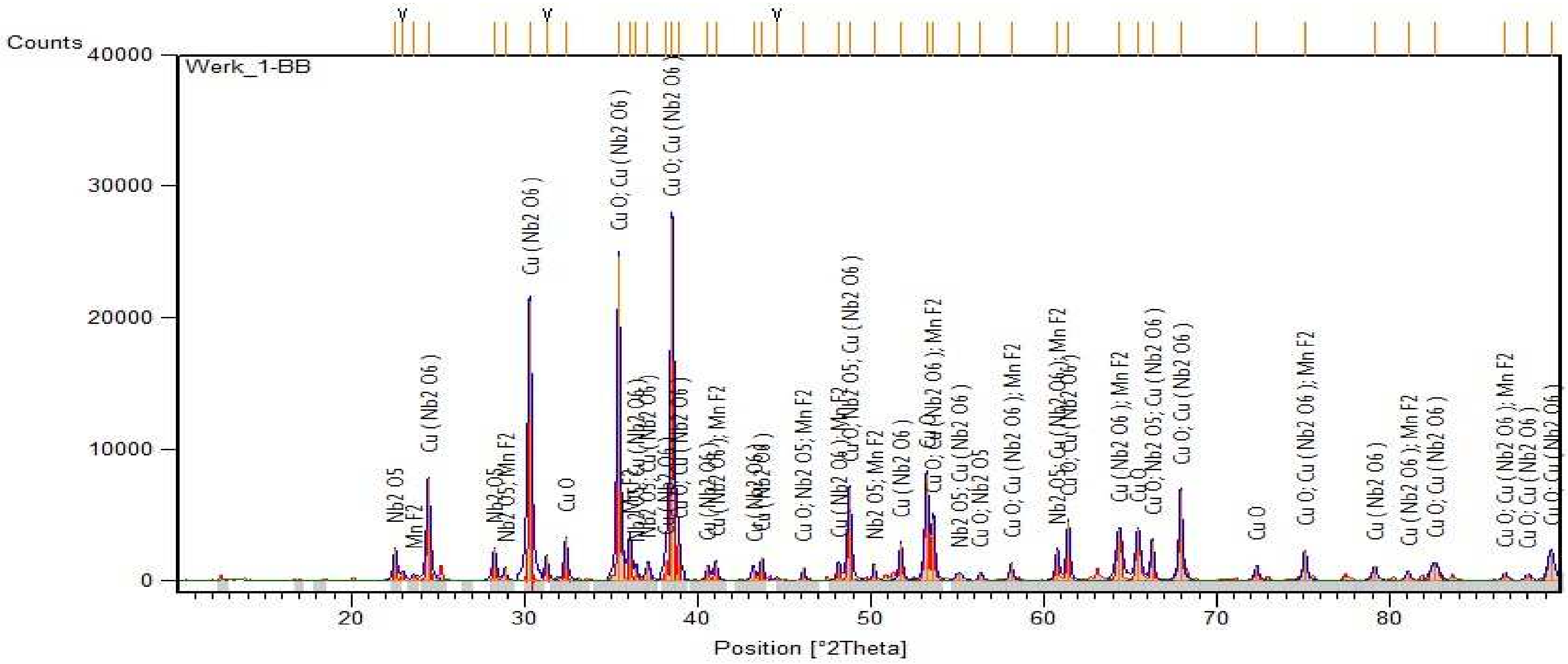
Selected results research on the morphology, chemical and phase composition of corrosion products of individual alloys – 2.4360



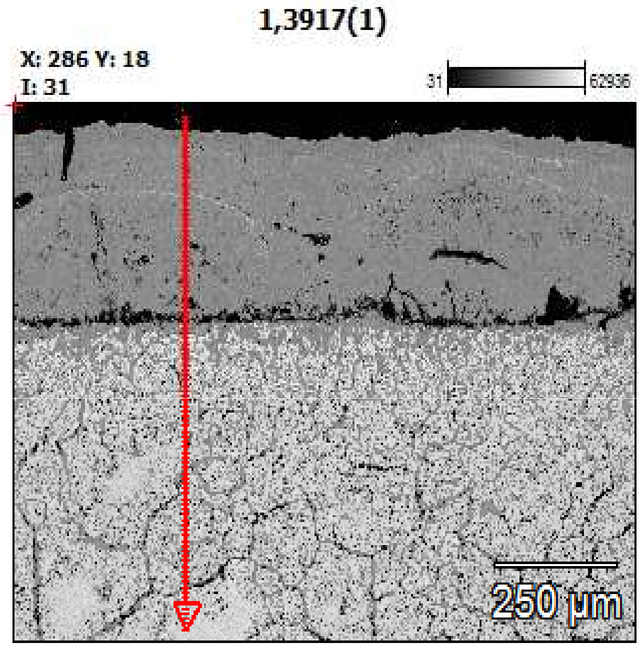


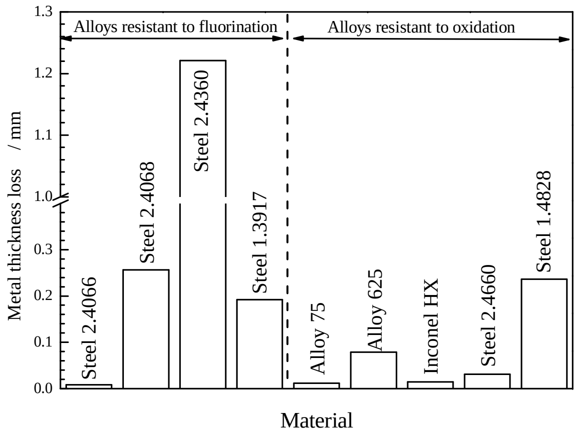


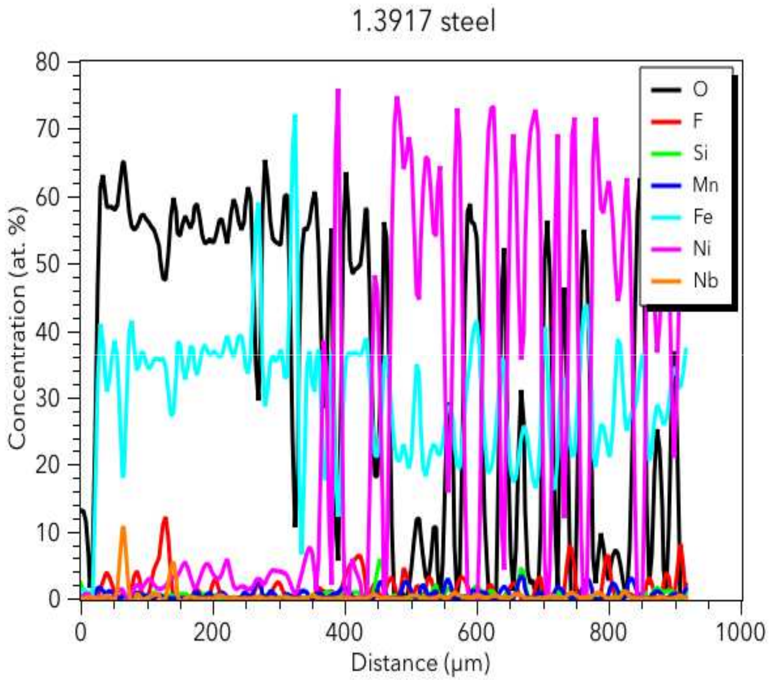
Selected results research on the morphology, chemical and phase composition of corrosion products of individual alloys – 2.4360



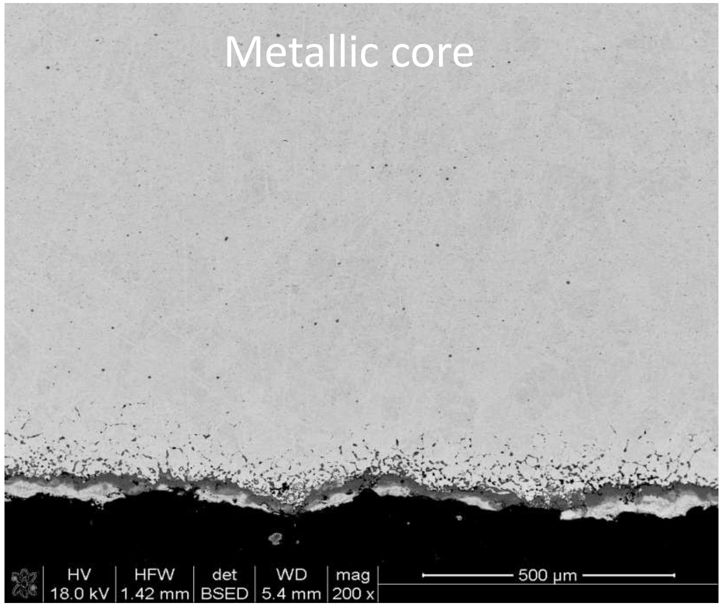
Selected results research on the morphology, chemical and phase composition of corrosion products of individual alloys – 1.3917

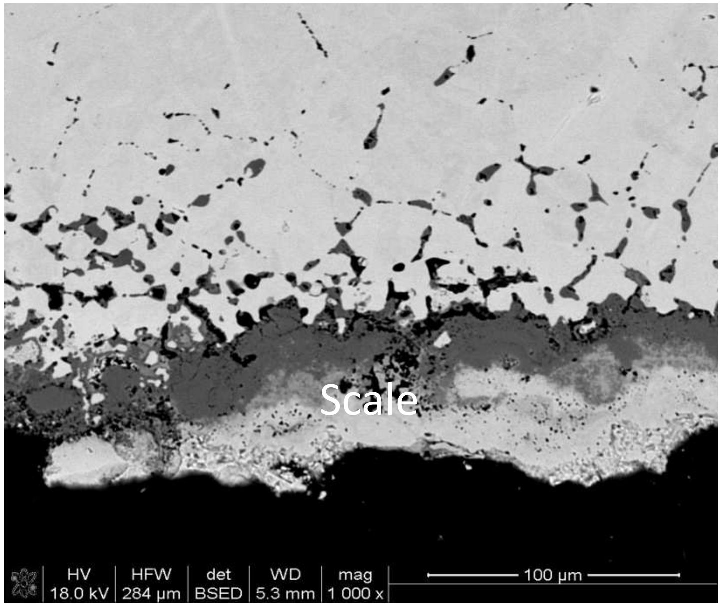


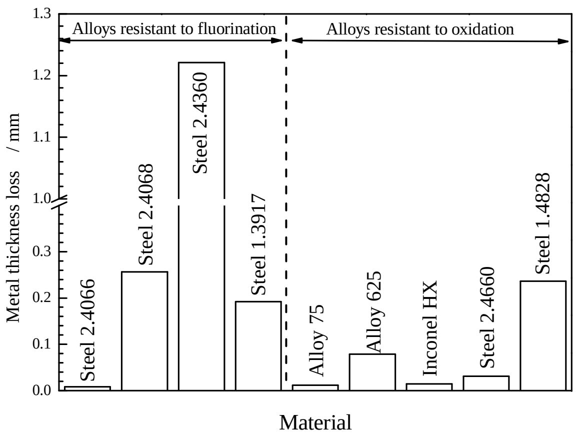




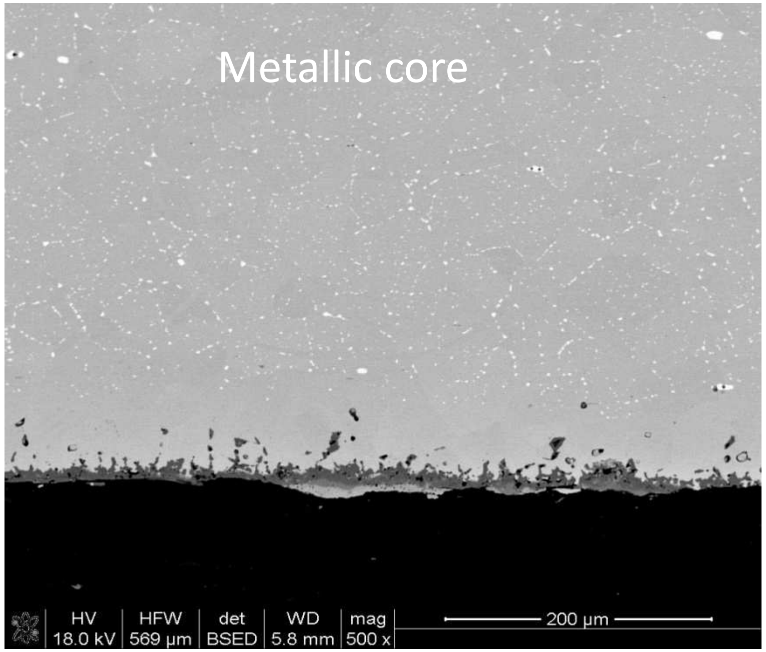
Selected results research on the morphology, chemical and phase composition of corrosion products of individual alloys – Alloy 75

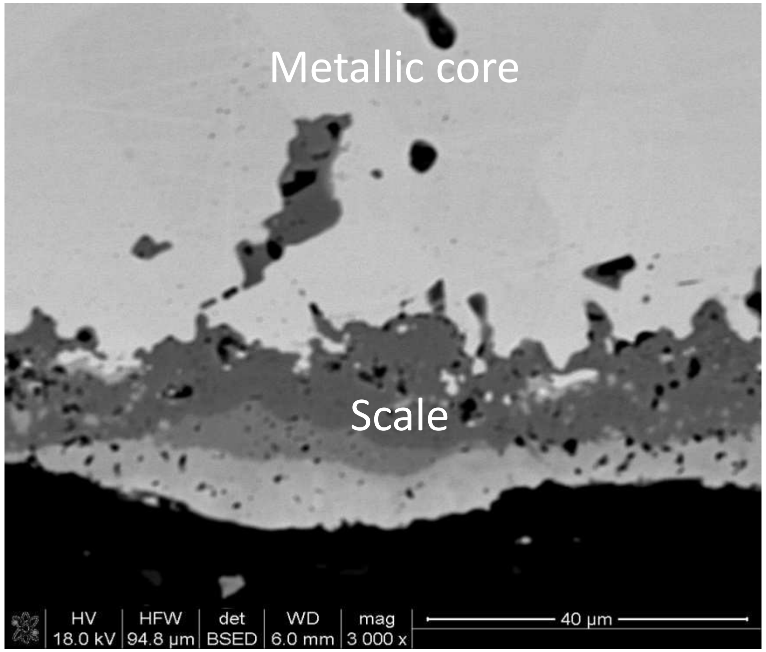


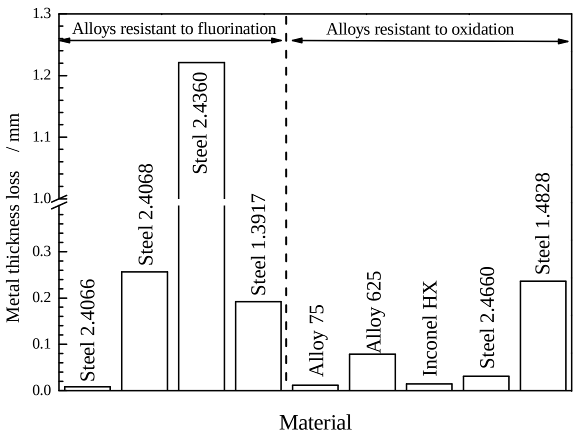




Selected results research on the morphology, chemical and phase composition of corrosion products of individual alloys – Inconel HX







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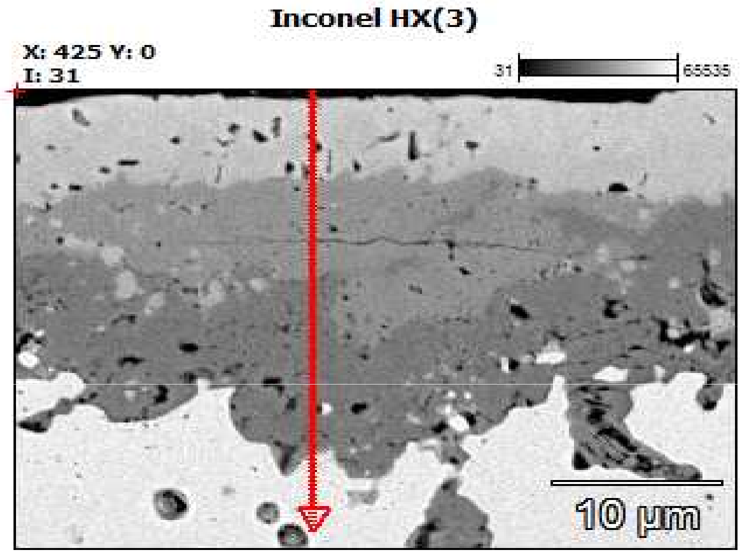

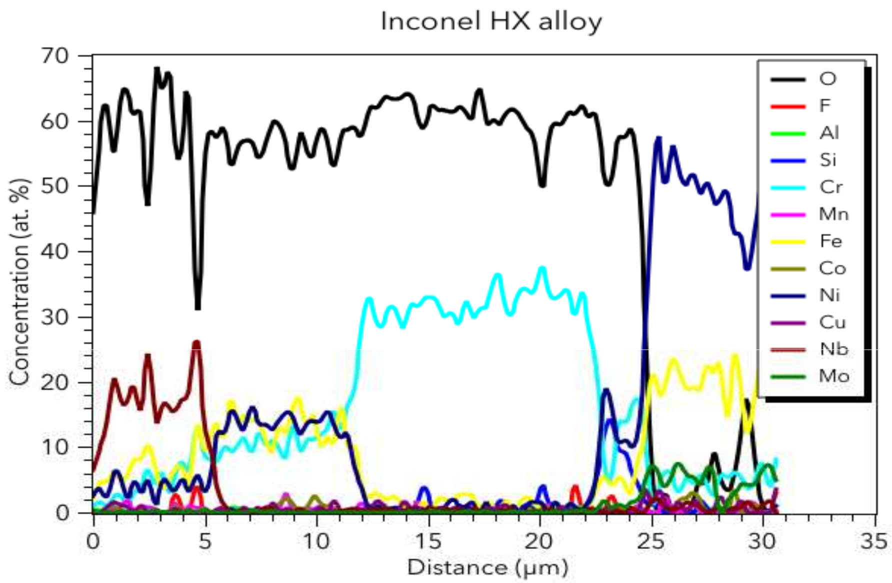

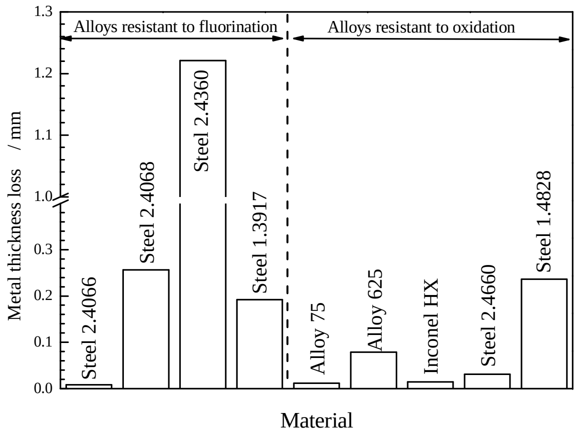

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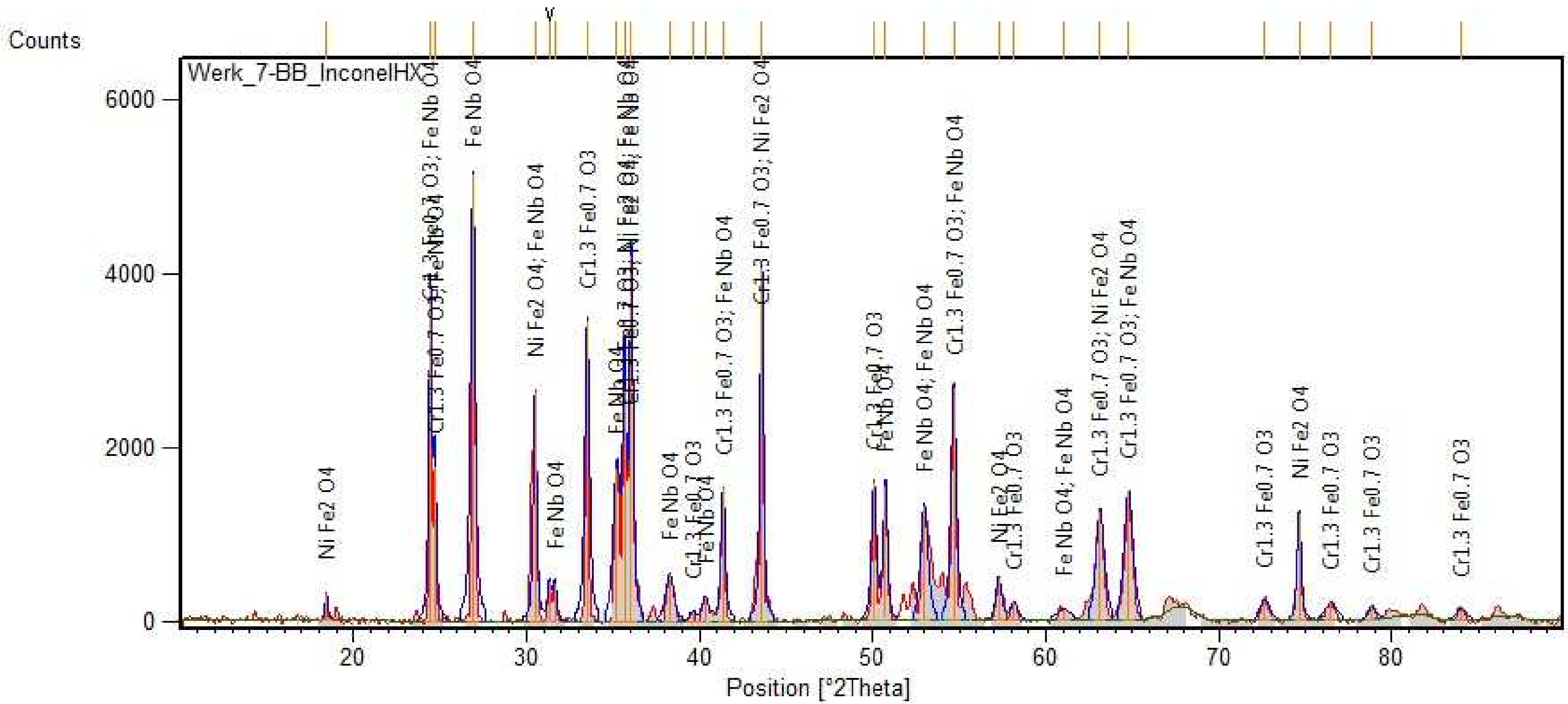

Summary of research results

- Nickel-based materials, potentialy resistant to fluorination, definitely corrode faster than oxidation-resistant alloys with high chromium content (chromia formers).
- The corrosion rates of tested chromia formers are comparable. Among these materials, Inconel HX seems to be slightly better than all the others. However, this should be verified during longer experiments.
- In future experiments, it is reasonable to check the corrosion resistance of chromia formers containing small amounts of reactive elements, such as Ce, Y, Hf (e.g. Nikrothal 40), or up to 2 wt. % aluminium (Incoloy RA 602 CA), because such materials could be more suitable for fabricating the new reactor. Alumina formers (e.g. Kanthal APM) are other possible corrosion-resistant materials, which may be used as coatings or cover elements.

THE END