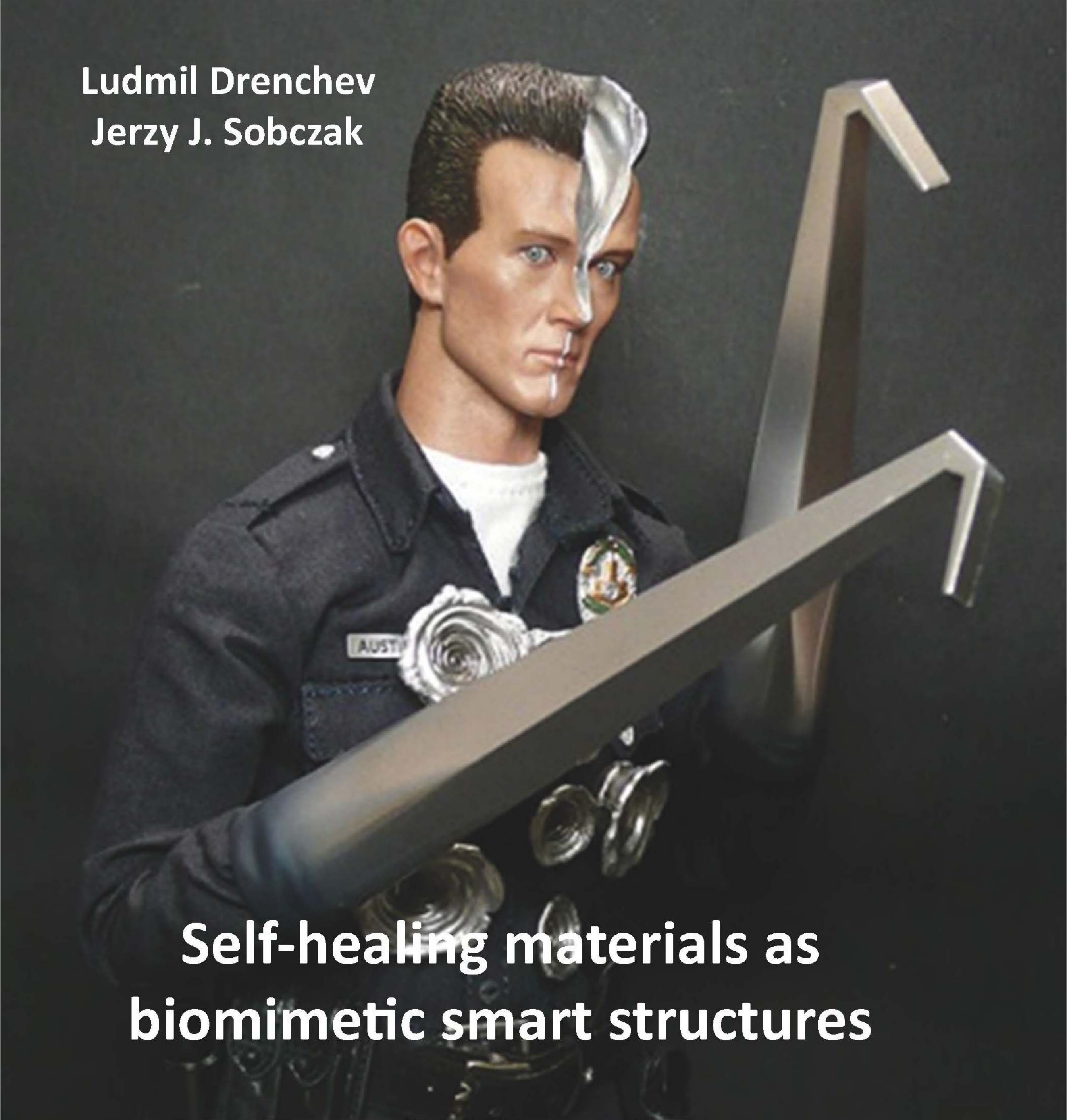
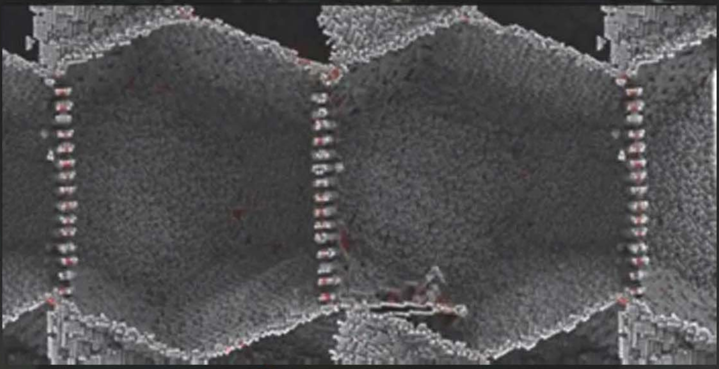
Ludmil Drenchev
Jerzy J. Sobczak



Self-healing materials as biomimetic smart structures



Instytut Odlewnictwa
Foundry Research Institute

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Photo courtesy www.toyhaven.blogspot.com. Image below title taken from the computer simulation of the molecular structure of a metal alloy. A small crack (dark horizontal bar just right of bottom center) mends itself as the alloy is put under stress (*Guoqiang Xu and Michael Demkowicz)* – www.sciencedaily.com/releases.

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Materiały samoleczące się jako biomimetyczne inteligentne struktury

Ludmil Drenchev

Jerzy J. Sobczak

Instytut Odlewnictwa

Kraków 2014

Wydawnictwo pod egidą Komisji Kompozytów Odlewanych
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Fotografia udostępniona przez www.toyhaven.blogspot.com. Obraz pod tytułem pracy przedstawia symulację komputerową struktury molekularnej stopu. Małe pęknięcie (ciemny poziomy pasek u dołu „sześcianu”) ulega samoistnemu „zaszyciu”, gdy stop znajduje się pod obciążeniem (dzięki uprzejmości *Guoqiang Xu* i *Michaela Demkowicza*)
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Spis treści

Resume

This paper is devoted to theoretical and practical aspects of self-healing materials, treated as a result of inspiration with biological intelligent structures (biomimetics). It describes the foundations and development of this material group, proposes their classification and theoretical assumptions for the description of the phenomenon of self-healing based on non-equilibrium thermodynamics. The presented analysis of self-healing materials draws from a wide range of scientific sources, and covers organic, metal and ceramic materials, as well as concrete and asphalt. This monograph is one of the few attempts in the country to describe the birth of the new direction of development in materials science and engineering.

Streszczenie

Opracowanie poświęcone jest teoretycznym i praktycznym aspektom materiałów samoleczących się, traktowanych jako wynik inspiracji biologicznymi strukturami inteligentnymi (biomimetycznymi). Przedstawiono stanowienie i rozwój tej nowej grupy materiałowej, zaproponowano ich klasyfikację, a także założenia teoretyczne do opisu zjawiska samoleczenia w oparciu o termodynamikę nierównowagową. W oparciu o liczne źródła literaturowe zaprezentowano analizę samoleczących się materiałów organicznych, metalowych, ceramicznych oraz betonu i asfaltu. Monografia stanowi jedną z nielicznych w kraju prób kompleksowego ujęcia fenomenu narodzin nowego kierunku rozwoju inżynierii materiałowej.

Preface

Polish Academy of Sciences, acting through the Scientific Committees, due to the intellectual potential and material base must actively engage in carrying out the transformations in the sphere of research in Poland and abroad. Scientific Committees, bringing together the most prominent domestic experts in a given field, should constitute a basis to achieve a "critical mass", resulting in acceleration and development of new research directions. This applies to “self-healing materials”. There is very little information in Polish literature regarding this perspective subject thus the initiative of Professor Jerzy J. Sobczak from Cracow and Professor Ludmil Drenchev from Sofia is very valuable.

One recurring goal of material development has been to emulate materials of nature. Among these, the most elusive is that of self-repair. In approaching this, it is well to be aware of the nature of the differences that separate structural materials created by man and those of natural origins. They appear in chemical composition, mode of synthesis, structure, and above all, in the ability of continuous natural adaptation to environmental conditions as well as replacement, damage-sensing and repair. Self-healing has been receiving an increasing amount of interest worldwide as a method to autonomously repair damages in materials.

This bio-inspired concept offers a designer an ability to re-incorporate functional materials capable of counteracting service degradation to operation whilst still meeting the primary, usually structural, requirements. Most materials present in nature are self-healing composite materials. The most recent studies on self-healing have attempted to mimic natural healing. A perspective on current and future self-healing approaches is offered. The intention is to stimulate debate and reinforce the significance of a multidisciplinary approach in this exciting field.

Namely, press-and-sinter powder metallurgy, is an example of an industrial processing technique that relies entirely on natural “healing” behavior to bond particles and provide mechanical strength. During sintering of a porous body in proximity to the melting point of an alloy, mass transfer occurs producing the liquid phase or solid state bonding across material interfaces. With some aluminum alloys, it has now been shown that significant densification can also occur at lower temperatures by inducing precipitation in pores through controlled cooling from the sintering temperatures.

The development of nanostructured self-healing materials has the potential to significantly impact current research and development of self-healing technologies and presents several new applications. The extension to the nanoscale also enables precise, localized control over the distribution of the self-healing functionality, resulting in a material that has the self-healing capability. One potential means of introducing self-repair in synthetic systems is to embed artificial circulatory networks into materials.

The role of the Committee of Materials Science of the Polish Academy of Sciences can be very important in achieving a "critical mass" in terms of materials covering the scientific, technological, and educational potential and use of advanced diagnostic equipment in order to enter the domestic market of advanced materials and technologies.

Professor Boguslaw Major

Chairman on the Committee of
Materials Science
Polish Academy of Sciences
Corresponding Member of
The Polish Academy of Sciences

Przedmowa

Polska Akademia Nauk, działając przez Komitety Naukowe, ze względu na potencjał intelektualny oraz bazę materialną musi aktywnie włączać się w dokonujące się przeobrażenia w sferze badawczej w kraju i poza jego granicami. Komitety Naukowe, zrzeszające najwybitniejszych krajowych specjalistów w danej dziedzinie, powinny stanowić podstawę do uzyskania „masy krytycznej”, dającej w efekcie przyspieszenie i rozwój nowych kierunków badań. Występuje to w przypadku ***materiałów samoleczących się***. W polskiej literaturze jest bardzo mało informacji dotyczących tego perspektywicznego zagadnienia, zatem inicjatywa prof. Jerzego J. Sobczaka z Krakowa i prof. Ludmila Drencheva z Sofii jest bardzo cenna.

Jednym z powtarzających się celów związanych z rozwojem materiałów jest naśladowanie natury, spośród których najbardziej nieuchwytnym jest „samoleczenie”.

W podejściu do zagadnienia dobrze jest zdawać sobie sprawę z charakteru różnic, które występują pomiędzy materiałami strukturalnymi wytworzonymi przez człowieka a materiałami pochodzenia naturalnego. Ujawniają się one w składzie chemicznym, w sposobie otrzymywania, w strukturze, a przede wszystkim w zdolności do naturalnej ciągłej adaptacji do warunków otoczenia i zastępowania oraz wykrywania uszkodzeń i ich naprawy. Zagadnienie samoleczenia wzbudza coraz większe światowe zainteresowanie jako metoda adresowana do samodzielnej likwidacji uszkodzeń w materiałach.

Koncepcja inspirowana jest biologicznie i oferuje projektantowi zdolność do ponownego włączenia materiałów funkcjonalnych do pracy przez ich zdolność do przeciwdziałania degradacji podczas użytkowania, przy jednoczesnym utrzymaniu podstawowych wymagań. Większość materiałów występujących w przyrodzie to samoleczące się materiały kompozytowe. Najnowsze prace dotyczące samoleczenia ukierunkowane są na próbę naśladowania naturalnego procesu leczenia. Przedstawiane są obecne możliwości i perspektywy. Celem jest stymulowanie dyskusji i wzmocnienie znaczenia multidyscyplinarnego podejścia do zagadnienia w tej ekscytującej dziedziny wiedzy.

Prasowanie i spiekanie stosowane w metalurgii proszków jest przykładem techniki przetwórstwa przemysłowego, które opiera się wykorzystaniu naturalnego „leczenia” do łączenia cząstek w celu uzyskania wytrzymałości mechanicznej. Podczas spiekania porowatej wypraski, w pobliżu punktu topnienia stopu, zachodzi transport masy z wytworzeniem fazy ciekłej lub stałej, prowadząc do związania tworzywa poprzez granice fazowe. W niektórych stopach aluminium wykazano, że znaczący wzrost zagęszczania materiału może również występować przy niższych temperaturach, przez indukowanie wydzielania w porach, co kontrolowane jest chłodzeniem od temperatury spiekania. Rozwój nanostrukturalnych samoleczących się materiałów posiada potencjał mogący znacząco wpłynąć na aktualne badania i rozwój technologii samoleczenia oraz otwiera możliwości różnych nowych zastosowań. Rozszerzenie na nanoskalę umożliwia także precyzyjne sterowanie zlokalizowaną kontrolą odnośnie dystrybucji funkcjonalności samoleczenia w materiale posiadającym zdolność do samoleczenia. Potencjalnym sposobem samodzielnej naprawy może być przykładowo wprowadzenie cyrkulacji sztucznych sieci do materiałów.

Rola **Komitetu Nauki o Materiałach PAN** może być bardzo istotna w osiągnięciu „masy krytycznej” w aspekcie materiałowym, obejmując: potencjał naukowy, technologiczny i edukacyjny oraz wykorzystanie naukowej zaawansowanej aparatury diagnostycznej, mając na celu wprowadzenie na rynek krajowy zaawansowanych materiałów i nowoczesnych technologii.

Profesor Bogusław Major

Przewodniczący
Komitetu Nauki o Materiałach
Polskiej Akademii Nauk
Członek Korespondent PAN

Introduction

The idea of self-healing materials and the possibility of their synthesis has recently attracted the attention of specialists working in various branches of materials science. The scientific pursuits in the area of construction materials with such a unique complex of properties stem from the originality and creativity of those who do not put limits on their imagination. On the other, more practical, hand, there is a great demand for new classes materials with increased safety, long-term durability and minimized amount of repairs, which at the same time would be economically reasonable. Obviously, self-healing materials are still in their infancy and they are designed and produced using the trial-and-error approach. However, they will undoubtedly focus the attention of researchers and engineers and be one of the key challenges of materials science in the 21th century.

In the past century, we experienced a great advancement in the field of materials science, which led to creation of high performance advanced materials, also known as smart materials. They include organic, ceramic and metal composite materials, shape-memory alloys, metallic glasses, functional materials (such as functionally graded structures), high porosity media (especially with directed porosity, such as gasars or lotus structures), and nanomaterials. These impressive results were possible thanks to the rapid advancement in chemistry and physics, as well as and spectacular instruments for observation, measurements and analysis of obtained structures and properties. All these factors resulted in an unprecedented acceleration of material development and achievement of such a level of their characteristics that had seemed unachievable, or even unrealistic. It should be mentioned that the base idea underlying the progress in self-healing materials is the paradigm of damage prevention (first defined by *Sybrand van der Zwaag* from Delft University of Technology). In brief, this way of perception of reality assumes such a manner of material design and synthesis that the formation and evolution of damage as a function of load and/or time is postponed as much as possible. It is obvious that micro- or macroscopic cracks are absent at the beginning of the process and the level of material damage is steadily increasing, never decreasing spontaneously. Now this concept should be changed or at least supplemented with an alternative strategy of damage management. This strategy presumes that materials have a built-in capability to repair the damage incurred during use. Cracks may form, but the material itself is capable of repairing the cracks and restoring its functionality. Such damage management can be seen in natural materials. It gives them ability to repair or heal damage, which results in a "lifelong" performance. Putting the new strategy into practice can be considered as the most serious challenge for material scientists in this century.

Self-healing materials are usually classified generally as advanced materials, especially composite ones, and as biomimetic materials (from *bios* – life, and *mimesis* – imitate). There is no comprehensive theory of the self-healing materials, which is one of the major barriers limiting their design, evolution and practical application. Development of a general theoretical (which means mathematically-based) approach to creation of self-organising systems is another challenge which needs to be faced in the next decades, not only by material scientists but also by physicists and mathematicians. The works in this direction began in the middle of the previous century. *Ilya Romanovich Prigogine*, who was awarded Nobel Prize in 1997, can be considered the father of theoretical description of self-healing substances. With his co-workers, he applied the instruments of non-equilibrium thermodynamics to the investigation of the nature and principles of self-healing. He showed that the so-called dissipative systems may lead to increasing orderliness, i.e. self-organisation. These systems are thermodynamically open and they are characterised by spontaneous breaking of symmetry and formation of complex structures in which interacting elements exhibit long-range correlations. Such systems were already known before, but the universality and generality of the processes involved in these systems was directly shown only in the works of *Prigogine*. In spite of the fact that some of the *Prigogine*'s ideas were subjected to criticism by several authors, they should be considered as pioneering works in this field. It should be mentioned that the general principles of self-organisation and non-equilibrium thermodynamics in substances have not been applied to the study of self-healing materials.

The content of this book is divided into 7 chapters, each devoted to various aspects related to these smart materials. Chapter 1 describes the philosophy of development of self-healing materials and Chapter 2 proposes a classification of these materials. The theoretical basis of thermodynamic processes involved in self-healing is discussed in Chapter 3. The remaining four chapters are devoted to self-healing abilities in organic materials, metallic materials, ceramics, and concrete and asphalt, respectively.

The aim of this review is to provide up-to-date information and deliberations in the field of theory and practice of self-healing materials, as well as to discuss the fundamental theoretical principles underlying their synthesis.

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Wstęp

Sam zamysł zaistnienia, a więc i możliwości syntezy materiałów „samoleczących się” (*self-healing materials*) przyciąga w ostatnich latach uwagę specjalistów pracujących w różnych dziedzinach inżynierii materiałowej. Osiągnięcia naukowe w dziedzinie tworzyw konstrukcyjnych o unikatowym kompleksie właściwości wynikają z oryginalności i kreatywności samego procesu poznania szczególnie tych, którzy w poszukiwaniu nowych rozwiązań materiałowych nie uznają granic fantazji. Z drugiej strony – tej o zabarwieniu praktycznym – istnieje duże zapotrzebowanie na nowe grupy materiałów, zapewniających jeszcze wyższy stopień bezpieczeństwa eksploatacji, długoterminowej trwałości, jak i zminimalizowanej ilości ewentualnych napraw wyrobów z nich wykonanych z zachowaniem racjonalności ekonomicznej samego procesu użytkowania. Proces stanowienia samoleczących się materiałów znajduje się póki co w początkowym stadium rozwoju, a ich projektowanie i wytwarzanie odbywa się najczęściej przy użyciu metody prób i błędów. Bez wątpienia będą one skupiać uwagę naukowców, badaczy i inżynierów w najbliższym okresie i stanowić jedno z wyzwań inżynierii materiałowej XXI wieku.

W Polsce materiały samoleczące się są praktycznie nieznane, a nieliczne prace im poświęcone dotyczą głównie materiałów polimerowych. Samo nazewnictwo tej nowej klasy materiałowej nie jest do końca sformułowane, przyjęte i akceptowane, stąd też w specjalistycznej literaturze krajowej pojawiają się takie określenia, jak materiały „samouzdrawiające” czy „samoregenerujące” i to tylko, o czym już wspomniano, w odniesieniu do tworzyw na bazie materiałów organicznych. Bogactwo języka polskiego pozwala na zaproponowanie także innych terminów przymiotnikowych: materiały „samouleczalne”, „samogojące”, „samozdrowiejące”, „samozabliźniające się”, „samoregenerowalne” („samoregenerujące”), „samonaprawialne”, „samoporządkowalne” („samoporządkujące się”) czy – chyba najbardziej udanie, uogólniająco – „samoodnawialne”. Podobnie „środek/agent gojący”, „leczniczy”, „zabliźniający”, „naprawczy” etc.

Miniony wiek XX wniósł ogromny postęp w ewolucji inżynierii materiałowej, co doprowadziło do wykreowania wielu nowych tworzyw zaawansowanych (*high performance advanced materials*), zwanych także materiałami inteligentnymi *(smart materials).* Należą do nich organiczne, ceramiczne i metalowe tworzywa kompozytowe, materiały z pamięcią kształtu, szkła metaliczne, materiały funkcjonalne (w tym funkcjonalne gradialnie – *functional gradied structures*), media wysokoporowate (w szczególności o ukierunkowanej porowatości – gazary i struktury typu „lotus") czy wreszcie nanomateriały. Te imponujące osiągnięcia były możliwe dzięki szybkiemu rozwojowi chemii i fizyki oraz zastosowaniu spektakularnych instrumentów obserwacyjnych, techniki pomiarowej i profesjonalnej analizy otrzymywanych struktur/właściwości wytwarzanych materiałów. Wszystkie te czynniki doprowadziły do niespotykanego wcześniej przyspieszenia tempa rozwoju nowych materiałów, a zatem i takiego poziomu ich charakterystyk, który wydawał się być nieosiągalny, a niekiedy wręcz nierealny.

Należy zauważyć, że u podstaw rozwoju materiałów samoleczących się leży paradygmat zapobiegania uszkodzeniom (*paradigm of damage prevention*), po raz pierwszy zdefiniowany przez *Sybranda van der Zwaaga* z *Delft University of Technology*. Zaproponowany sposób postrzegania rzeczywistości zakłada, w wielkim skrócie, taki sposób projektowania i syntezy materiałów, iż powstanie i rozwój uszkodzenia wraz z czasem i/lub obciążeniem jest czasowo tak oddalony, jak tylko jest to możliwe. Jest rzeczą zrozumiałą, że mikro- czy makropęknięcia (uszkodzenia) są nieobecne w początkowym stadium procesu a poziom uszkodzenia materiału będzie stały i wzrastający, ale nigdy niezmniejszający się samoistnie. Tak zarysowana filozofia zjawiska powinna być zatem zmieniona lub przynajmniej uzupełniona o alternatywne założenia strategii kontroli „zarządzania uszkodzeniami". Nowa strategia zakłada, że materiały mają wbudowaną możliwość naprawy uszkodzeń szkód zaistniałych w czasie użytkowania. Pęknięcia mogą zaistnieć, ale sam materiał ma zdolność do ich naprawy i przywracania funkcjonalności. Takie „zarządzanie uszkodzeniami" występuje w materiałach naturalnych i skutkuje zdolnością do leczenia i/lub naprawy uszkodzeń, zapewniając funkcjonalność materiału przez cały okres użytkowania. Realizacja tej nowej strategii jest aktualnie najpoważniejszym wyzwaniem dla specjalistów w zakresie inżynierii materiałowej.

Materiały samoleczące się bywają odnoszone do ogółu materiałów zaawansowanych, w szczególności kompozytowych, oraz materiałów biomimetycznych (od gr. *bios* – życie i *mimesis* – naśladować). Systemowa teoria samoleczenia materiałów nie istnieje, co stanowi jedną z głównych barier ograniczających ich kompleksowe opracowanie, ewolucję i wreszcie aplikację praktyczną. Rozwój ogólnego podejścia teoretycznego (opartego o modele matematyczne) do tworzenia systemów samoorganizujących się jest kolejnym wyzwaniem na najbliższe dziesięciolecia nie tylko dla specjalistów, pracujących w obszarze nauki o materiałach, ale także dla fizyków i matematyków. Prace w tym kierunku rozpoczęły się w połowie ubiegłego wieku, a za ojca teoretycznego opisu procesu samoleczenia materii może być uważany *Ilya Romanovich Prigogine*, laureat Nagrody Nobla z roku 1997. Wraz ze współpracownikami zastosował on instrumenty termodynamiki nierównowagowej do badania charakteru i podstaw procesu samoleczenia. Wykazał, że tak zwane systemy rozproszone (*dissipative systems)* mogą prowadzić do zwiększenia stopnia uporządkowania, czyli do samoorganizowania się. Systemy te są termodynamicznie otwarte i charakteryzują się spontanicznym załamaniem symetrii i naruszeniem samego procesu tworzenia się złożonych struktur, w których elementy oddziaływujące wykazują korelacje dalekiego zasięgu. Takie systemy były znane już od dawna, ale uniwersalność i powszechność procesów z nimi związanych bezpośrednio wynikała z prac *Prigogine*'a. Pomimo faktu, że niektóre twierdzenia *Prigogine*'a poddawane były krytyce przez wielu autorów, powinny być uważane za prace pionierskie w danej dziedzinie. Należy wspomnieć, że ogólne zasady samoorganizacji i podstawy nierównowagowej termodynamiki materii nie znalazły póki co zastosowania w badaniach materiałów samoleczących się.

Treść tej książki podzieliliśmy na siedem rozdziałów, w których zawarto różne aspekty dotyczące omawianych materiałów inteligentnych. Rozdział 1 opisuje filozofię stanowienia i rozwoju materiałów samoleczących się; rozdział 2 przedstawia propozycję klasyfikacji analizowanych materiałów. Podstawy teoretyczne procesów termodynamicznych zjawiska samoleczenia omówiono w rozdziale 3. Pozostałe cztery rozdziały poświęcone są fenomenowi samoleczenia materiałów odpowiednio: organicznych, metalowych, ceramicznych oraz betonu i asfaltu. Celem danego kompendium wiedzy jest podzielenie się z Czytelnikiem aktualnymi danymi i przemyśleniami z zakresu teorii i praktyki materiałów samoleczących się wraz z omówieniem podstawowych założeń teoretycznych ich syntezy.

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Chapter 1

The concept of self-healing materials

It seems to be a dream the cracks in buildings to close on their own, or the scratches on car bodies to recover their original shiny appearance by itself, or the damages on asphalt to repair without any external activity. And what do you think your favourite motorcycle to be independent of any corrosion, cracks and surface damages? No doubt, this looks as impossible, sometime even stupid, dreams. But whether to fly to the Sun was a feasible dream for *Icarus*? The theme of tragically failed ambition can be discussed in various aspects but here it is important to mention that *Icarus* of today flays extremely closer to the Sun compared with the ancient *Icarus*. And to have 'long-range' pursuits is the most valuable thing for human civilization, especially when they are feasible.

Imagine yourself standing 1m from a window holding a loaded firearm. Upon pulling the trigger, one might expect the glass to shatter, perhaps showering the ground with a multitude of glass shards. However, when you fire, the bullet goes through and you are surprised to see the results. In fact, upon approaching the window, you find that the hole once there has healed itself leaving only a small scar indicating the point of bullet penetration. Such a feat would seem like a magic trick or the realm of science fiction; however, it is exactly what would happen if the window were fabricated from specific ionomer materials. This unique self-healing response has been recently observed in a certain class of thermoplastic poly(ethylene-co-methacrylic acid) (EMAA) ionomers as an automatic and instantaneous self-repair following ballistic puncture. The repair of damage is complete and fully sealed to leakage even under significant pressure.

Materials science is in the basis of the human civilisation. Men-designed materials determine the pace of breakthrough developments in our daily life. All modern devices we use become better and better mainly because of the elaboration of new materials. Our communication systems became reality only because of new battery materials, novel light-sensitive detector materials and new developments in silicon integrated circuit technology. New ideas impose new requirements to materials scientists try and step-by-step they to satisfy them. Currently, the idea for quantum computing would lead to a quantum jump in computing power, but is still away due to the fact that materials with the required properties and stability have not been created yet. Another example in this direction is the transport of electrical currents in the national grid system which still leads to large energy losses because materials scientists have not been able to create materials having superconductivity at room temperature. From another hand, it is no accident that in last decades the men-designed materials are named ‘knowledge-based’ because their development is only due to the progress in physics, chemistry, engineering, biology, medicine and other scientific branches.

Materials present in all physical devices which are created to satisfy our needs and wishes, and hence cover a tremendous range of properties and functionalities. Here we will focus on structural or engineering materials only, i.e. materials which have been made to perform predominantly a mechanical function in addition to any other function they have to perform. In what follows, structural materials are judged critically on their strength, stiffness, extendibility, and fracture behaviour. This sets them apart from the functional materials, in which properties other than mechanical properties determine their usefulness.

The concept that more ‘compacted’ materials are stronger is induced by century-old experience and observation. It could be explained by the chemical bonds into the materials. A given material is stiff and strong if it consists of as many atoms with high bond strength to neighbouring atoms in as small a volume as possible. For example, diamond, comprised of densely packed small carbon atoms each having a high-covalent bond strength, is the stiffest and possibly strongest material of all. Carbon nanotubes and graphene have almost the same stiffness as diamond since the arrangement of the carbon atoms and the spatial density is very comparable to that of diamond. In graphite, the same carbon atoms are present but they are arranged in a more free configuration in which the cohesion between the atomic planes is much weaker, making graphite soft and even plastically deformable.

All external forces applied to material can destroy some bonds which lead to more or less deterioration of its mechanical characteristics. It is clear that the presence of such defects during the material production or service phases will have an effect on the strength of the material and can lead to the fracture of the product. The correct description and prediction of the extension of micro defects into larger non-fatal or fatal cracks as a function of applied loading conditions and material microstructure is of such importance that it became a special discipline in the field of materials science, the field of fracture mechanics.

Based on the above listed reasons, it can be concluded that the current design philosophy to synthesize a stronger material is based on creating microstructures which contain and oppose the formation and extension of microcracks. In the design of strong materials the following basic guidelines apply:

1. To put as much atoms as possible at the "right" place during the material production cycle (including thermo- and thermo-mechanical post-processing treatments) which means to arrange the atoms in configurations where they find it hard to move.
2. To elaborate material production process in which production defects are avoided.

Obviously, today, the men-designed strong materials are progressing along the *paradigm of damage prevention* which is well identified in [1]. The idea is to reduce as much as possible the defects accruing (during production and/or service) and their propagation. The compromise is always between needed properties and total expenditure for particular material production. Looking around us, we see that principle works very fruitful.

The wise nature acts in a different way mainly in case of animated nature. For example, the nature prefers porous structures instead of thick materials especially in heavy-loaded systems. The aim is not to avoid defects but to control their appearance and propagation. Here the *paradigm of damage prevention* is replaced by the *damage management concept* [1]. In fact, all biological materials possess different inherent mechanisms for self-healing. Most striking example is the complete regrowth of lost limbs in salamanders [2]. The aim of materials science to design and produce self-healing materials causes increasing interest how Nature realizes and controls actual healing responses.

Many new beneficial concepts can be realized in engineering systems which become more sophisticated applying ideas from various biological systems [3,4]. But to follow the nature in man-designed materials and to try to mimic entirely the biologic systems is not good idea and very often it can be impossible to be realized because the biological mechanisms of healing are very complex and often involve many factors acting concurrently. Material scientists understand that the biological mechanisms of healing cannot be directly borrowed for artificial materials. The nature demonstrates a great diversity in micro- and macrostructures, intersystem relations and mechanisms for their realizations ensuring a wide diversity of healing mechanisms. Engineered materials have their own characteristics far from biological ones and because of this, incorporating self-healing functions in such materials, their artificial nature should be taken into account. Due to that reasons, the term "bio-inspired" seems to be more adequate compared to "bio-mimetic".

Realization of self-healing concept imposes some basic requirements. The self-healing process itself consists of three stages. First of all, before healing, the damage should be identified and localised. This is the stage when the self-healing is triggered. Second stage concerns transport and/or releasing of healing agent(s) to 'ill' region. It means that if a material possesses self-healing ability, it has to contain moving phase(s) and mechanisms to convey the substance(s) to the right place. Usually these substances are fixed into void capsules or microtubes homogeneously distributed into the material. Third stage consists of very recovery process. In most cases it needs introduction of additional energy to stimulate reaction between healing agents and also between them and matrix material. This is the case of non-autonomic healing. There is other group of the men-designed materials, usually organic ones, in which autonomic self-healing system is incorporated and they do not need any additional intervention.

Self-healing is triggered by crack-induced rupture of the embedded capsules or microtubes. Healing agent can be released not only by fracture but also by heating or melting. Obviously, once a localized region is depleted of healing agent, further repair is precluded. Re-mendable ability can be incorporated but it seems that till now multiple healing cycles are achieved only in polymers [5,6]. In such a case external intervention in the form of heat treatment and applied pressure are required.

There are four important 'How?' related to design of self-healing materials:

1. How to introduce healing agents?
2. How to trigger healing process?
3. How to supply healing agents to right place?
4. How to provoke healing reactions?

All this questions are interconnected and no one of them can be solved independently. Every particular solution should be conformed to matrix material, operating conditions of the final product, technology implemented and so on.

The first question is related to technologies for introduction of healing agent and the answers vary depending on matrix material and its technological specificity. For example, if the matrix is polymer, the synthesis of the self-healing material will take place at or slightly above room temperature. Thus, the agent in the form of chemically reactive liquids can be introduced by sealed capsules or microtubes [7–16]. In case of metallic materials such approach is extremely difficult to be realised. The healing agent like pure metal and low-temperature solders can be introduced by specific kinds of liquid phase technologies, for example, taking into account immiscibility gap in relative phase diagram. Other possibility to introduce healing substance is by eutectic structures formed in hypo- or hypereutectic alloys. This self-healing concept is based on using the eutectic liquid formed with the solid itself, as a healing phase, and the solid dendritic phase to maintain the structural integrity [17,18]. Use of shape memory alloys is also a promising approach [18–20]. A specific mechanism for damage prevention in metal materials is discussed in [1]. The idea is to prevent the formation of voids by the diffusion of the atoms to form precipitate from an oversaturated but under aged solid–solid solution (alloy). In this case the atoms present into matrix and they become healing agent only when microscopic voids and cracks appear into material. The driving force for the diffusion here is the excess surface energy of these voids and cracks.

The question for triggering of healing process seems to be simpler because options are lucid. In organic materials this is appearance of cracks but in metallic materials, besides cracking, introduced heat energy also could be triggering instrument.

Mechanisms for supplying of healing agents to right place are of crucial importance. Most often these agents in the forms of sealed microcapsules and microtubes are homogeneously distributed into matrix. More smart idea is to build three-dimensional vascular network across multiple-length scales. While the level of vascular interconnectivity and complexity in natural systems is formidable, simplified networks have recently been fabricated and tested [21,22]. Preliminary results indicate that resupply of the healing agent is feasible and extended life of polymers can be achieved in response to repeated damage [22]. The biggest disadvantage of these applying systems is that they reduce mechanical characteristics of the matrix. Design of self-healing materials always should be a compromise between incorporation of healing ability and inherent mechanical resistivity of matrix.

Self-healing reactions can be spontaneous (autonomic) and induced (non-autonomic). Autonomic reactions do not need to be provoked and they take place as a rule in organic materials. The two components of the healing agent come to contact after ruptures of capsules or microtubes which is enough to start chemical reaction and to form specific substance usually polymer. This substance fill void and healing process completes. Induced reactions are typical for metallic materials. To provoke such reactions heat energy should be introduced into the system. Sometimes, when the healing becomes because of atomic diffusion, introduction of heat energy is not necessary.

In order to outline the definition of self-healing materials S. van der Zwaag lists the important properties for self-healing materials to be technologically and economically attractive. In the Table below (Tab. 1.1) these properties are defined for both an “ideal” self-healing material and a “minimal” self-healing material [1].

Table 1.1
Properties of "ideal" and "minimal" self-healing materials [1]

Tabela 1.1
„Idealne" i „minimalne" właściwości materiałów samoleczących się [1]

An "ideal" self-healing material:	A "minimal" self-healing material:
Can heal the damage many times	Can heal the damage only once
Can heal the damage completely	Can heal the damage partially
Can heal defects of any size	Can heal small defects only
Performs the healing autonomously	Needs external assistance to heal
Has equal or superior properties to current materials	Has inferior properties to current materials
Is cheaper than current materials	Is terribly expensive

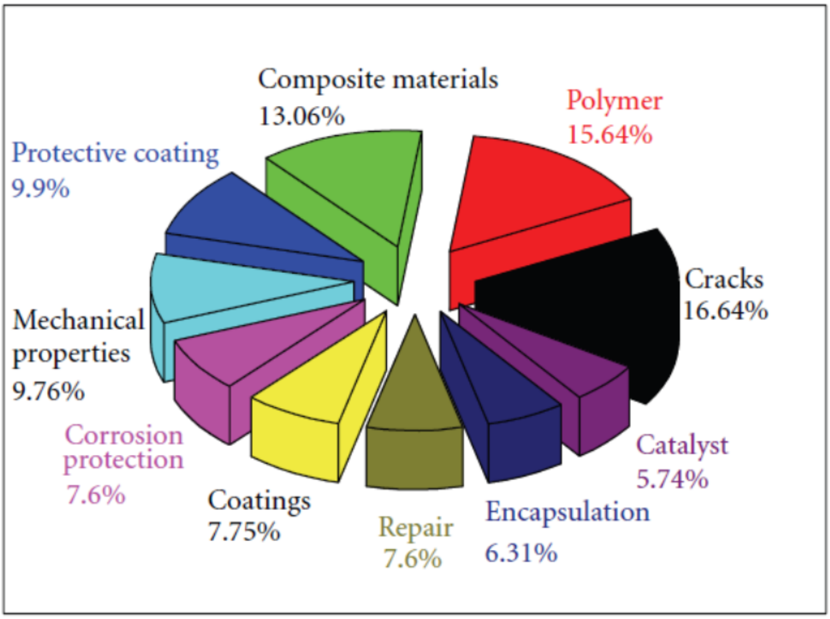


Fig. 1.1. Distribution of publications related to the field of self-healing materials for 2013. All document types, including journal and conference articles, report paper, conference proceeding, and monograph published chapters are recorded according to the Engineering Village web-based information service [23]

Rys. 1.1. Podział tematyczny publikacji związanych z dziedziną materiałów samoleczących się w 2013 roku. Uwzględniono wszystkie typy publikacji, włączając artykuły w czasopismach, opracowaniach specjalistycznych, wydawnictwach konferencyjnych oraz rozdziały w monografiach (opracowany przez serwis informacyjny *Engineering Village* w oparciu o źródła internetowe) [23]

Of course, current experimental self-healing materials are likely to have characteristics that are close to those of “minimal” self-healing materials. The development of “ideal” self-healing materials, if it is possible at all, will take a very long time, but this is not the most important thing. We know that the human civilization evaluates not because reaches his aims but because moves to them.

The number of publications dealing with various aspects of self-healing materials has increased markedly in recent years and in 2013 the publications are almost 10 times more than in 2001. Figure 1.1 presents how the number of refereed various articles in the self-healing field has steadily increased since 2001, based on data collected from the Engineering Village web-based information service [23].

In the end it should be mentioned that self-healing materials for structural applications offer considerable practical benefits because they would allow overcoming the difficulties connected to damage diagnosis and repair. A new self-healing strategy to be created materials with layered or gradually structured self-healing regions seems to be very promising. Gradually designed vascular system or gradually distributed healing agents offer new possibilities to improve mechanical properties of materials elaborated.

Chapter 2

Classification of self-healing materials

Self-healing materials can be classified according to various criteria. The most general partition is based on matrix material, i.e. organic and inorganic

Organic matrix could be epoxy resins and other polymers. Self-healing abilities are incorporated in inorganic materials like metals, ceramics, concrete and asphalt.

Self-healing materials are specified in respect to need stimulation of healing reaction:

a) autonomic,
b) non-autonomic.

If a material needs additional energy, usually introduced by heating, for realization of healing, it is non-autonomic. There exist also systems which do not need any extra intervention and healing process runs autonomically.

Other possible classification of the materials could be on basis of healing agent nature:

1. Monomers and chemical catalysts.
2. Metals and alloys with low melting temperature.
3. Shape memory alloys.
4. Diffusing atoms of different inclusions.
5. Bacteria.

Reasonably, complementary monomers, mixtures of various monomers and chemical catalysts are typical healing agents in organic materials while metal materials prefer metallic healing instruments. Metals, alloys (especially eutectic ones) and solders with low melting temperature and shape memory alloys are successfully tested as healing agents for metallic materials. In this case healing agent could be also atoms with relatively high diffusion coefficient in matrix material. An exotic idea is realized in polymers as well as concrete [24,25]. The authors use bacteria as healing agent. The principle mechanism of bacterial crack healing is that the spore-forming bacteria themselves act largely as the catalyst and can transform a precursor compound into a suitable filler material.

Fashions in which healing substances are stored and supplied into matrix define the followed three groups:

1. Sealed capsules and microtubes.
2. Interconnected channels in vascular network.
3. Sites with well-defined diffusion barriers.

The last type comprises regions of eutectic embedded into alloy matrixes.

Ability for multiple self-healing materials divided them into two classes:

a) materials that repair damage only ones,
b) materials that repair damage many times.

Chapter 3

Thermodynamic basis of self-healing processes

Processes in self-organization systems in general and processes in self-healing materials in particular can be understood only on thermodynamics basis. Below we will introduce some basic thermodynamic concepts in a simple way. The aim is only to outline the thermodynamic frame of the self-healing processes without any dipper look. Well-presented thermodynamic principles can be found in [26] and some particular aspects are discussed in [18].

3.1. Main concepts in classical thermodynamics

Every system is associated with energy and entropy. When a matter undergoes transformation from one state to another, the total amount of energy in the system and its exterior is conserved; total entropy, however, can only increase or, in idealized cases, remain unchanged. These two simple-sounding statements are on the basis of thermodynamics and have far-reaching consequences.

Thermodynamic systems are classified into three types [26]: isolated, closed and open systems according to the way they interact with the exterior.

Isolated systems do not exchange energy or matter with the exterior. Such systems are generally considered for pedagogical reasons, while systems with extremely slow exchange of energy and matter can be realized in a laboratory. Except for the universe as a whole, truly isolated systems do not exist in nature.

Closed systems exchange energy but not matter with their exterior. It is obvious that such systems can easily be realized in a laboratory: A closed flask of reacting chemicals which is maintained at a fixed temperature is a closed system. The Earth, on a time-scale of years, during which it exchanges negligible amounts matter with its exterior, may be considered a closed system; it only absorbs radiation from the sun and emits it back into space.

Open systems exchange both energy and matter with their exterior. All living and ecological systems are open systems. The complex organization in open systems is a result of exchange of matter and energy and the entropy generating irreversible processes that occur within.

It is our experience that if a physical system is isolated, its state – specified by macroscopic variables such as pressure, temperature and chemical composition – evolves irreversibly towards a time-invariant state in which we see no further physical or chemical change. This is the state of thermodynamic equilibrium. It is a state characterized by a uniform temperature throughout the system. The state of thermal equilibrium is a special state towards which all isolated systems will inexorably evolve.

In thermodynamics, the state of a system is specified in terms of macroscopic state variables, such as volume V, pressure P, temperature T, and moles N_k of chemical constituent k, which are self-evident. These variables are enough for the description of equilibrium systems. When a system is not in thermodynamic equilibrium, more variables, such as rate of convective flow or of metabolism, may be needed to describe it. In the state of thermal equilibrium, the values of total internal energy U and entropy S are functions of state variables, i.e.

$$U = U(T, V, N_k) \text{ or } S = S(T, V, N_k) \tag{3.1}$$

It is convenient to classify thermodynamic variables into two categories. Variables such as volume and amount of a substance (moles), which indicate the size of the system, are called extensive variables. Variables such as temperature T and pressure P, which specify a local property, which do not indicate the system's size, are called intensive variables. The values of an extensive variable, such as total internal energy U or entropy S, can also be specified by other extensive variables:

$$U = U(S, V, N_k) \text{ or } S = S(U, V, N_k) \tag{3.2}$$

Intensive variables can be expressed as derivatives of one extensive variable with respect to another [26]. For example, it can be shown that the temperature $T = (\partial U/\partial S)_{V,Nk}$ and $P = (-\partial U/\partial V)_{S,Nk}$. The laws of thermodynamics and the calculus of many-variable functions give us a rich understanding of many phenomena we observe in nature.

The change of the total energy is the given by

$$\mathrm{d}U = \mathrm{Td}S - P\mathrm{d}V + \sum \mu_k \mathrm{d}N_k \tag{3.3}$$

The quantities S, V, and N_k are generalized coordinates that characterize the state of the system in a unique way, while T, P, and μ_k are corresponding generalized forces, namely, the temperature, pressure, and chemical potential.

The First law of thermodynamic is the law of energy conservation, and it states that in an isolated system the internal energy does not change,

$$\mathrm{d}U = \mathrm{T}\mathrm{d}S - P\mathrm{d}V + \sum \mu_k \mathrm{d}N_k = 0 \tag{3.4}$$

The Second law of thermodynamics states that entropy of an isolated system can only increase (in the case of an irreversible process) or remain constant (in the case of a reversible process) so that

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}U + \frac{P}{T}\mathrm{d}V - \frac{1}{T}\sum \mu_k \mathrm{d}N_k = 0 \tag{3.5}$$

3.2. Basic principles in non-equilibrium thermodynamics

Classical thermodynamics studies systems at equilibrium while nonequilibrium thermodynamics deals with dependencies of thermodynamic parameters on time and spatial coordinates. All intensive parameters can depend on time and coordinates $T(x,y,z,t)$, $P(x,y,z,t)$, and $\mu(x,y,z,t)$. For extensive parameters, their volume densities are considered $u(x,y,z,t)$, $s(x,y,z,t)$, and $c(x,y,z,t)$, where u is the energy density, s is the entropy density, and c is the concentration (number of particles per unit volume). Furthermore, flow vectors of thermodynamic quantities are introduced, so that the law of mass conservation is now given by

$$\frac{\partial c}{\partial t} + \nabla J^c = 0 \tag{3.6}$$

where J^c is the mass flow. The First law of thermodynamics is given by

$$\frac{\partial u}{\partial t} + \nabla J^e = 0 \tag{3.7}$$

where $J^e = q$ is the heat flow. Finally, the Second law of thermodynamics is given by

$$\frac{\partial s}{\partial t} + \nabla J^S \geq 0, \tag{3.8}$$

where J^S is the entropy flow.

According to the approach developed by *Lars Onsager*, generalized thermodynamic forces Y_i and thermodynamic flows J_i are associated with every generalized coordinate q_i, so that the rate of entropy density production is given by

$$\frac{\mathrm{d}s}{\mathrm{d}t} = \frac{1}{T}\sum Y_i J_i, \tag{3.9}$$

For example, for the heat flow the force is $Y_T = \nabla\frac{1}{T} = -\frac{1}{T^2}\nabla T$, for the mass flow is $Y_T = -\nabla\frac{\mu_i}{T}$, thus when entropy is produced due to heat and mass flows, using (3.6) and (3.7) it can be written

$$\frac{\mathrm{d}s}{\mathrm{d}t} = \frac{q}{T^2}\nabla T + \frac{J^C}{\left(\frac{T}{\mu_i}\right)^2}\nabla\left(\frac{T}{\mu_i}\right) = \frac{K}{T}(\nabla T)^2 + D\frac{\mu_i}{T}\left(\nabla\frac{T}{\mu_i}\right)^2 \tag{3.10}$$

where $q = -K\nabla T$ (Fourier law of heat transfer) and $J^C = -D\nabla\left(\frac{T}{\mu_i}\right)^2$ (Fick's law of diffusion). Note that entropy rate is always positive. The generalized forces must have the same tensor rank as the flows, e.g., both should be vectors (or scalars, or tensors of the 2nd rank, etc).

In general, flows can be complicated functions of the generalized forces, $J_i = J_i\ (Y_1, Y_2, \ldots, Y_n)$ but in linear approximation, the flows are related to the forces by a linear equation

$$J_k = \sum_i L_{ki} Y_i, \tag{3.11}$$

where L_{ki} are called the *Onsager* (phenomenological) coefficients. Many physical linear empirical laws, such as the *Ohm's* law of electrical resistance, the *Fourier* law of heat conduction, and *Fick's* law of diffusion can be interpreted as linear relationships between generalized forces and flows. Note that (3.11) provides the possibility of coupling of various irreversible processes inside the system, or their interaction with each other in the case when nondiagonal *Onsager* coefficients are different from zero. Due to coupling, a process can occur without its primary driving force or it may move the process in a direction opposite to the one imposed by its own driving force. For example, in thermodiffusion a species diffuses not because of a concentration gradient but because of a temperature gradient. When a species flows from a low to a high concentration region, it must be coupled with a compensating process. The principles of thermodynamics allow the progress of a process without or against its primary driving force only if it is coupled with another process. However, one cannot simply assume that any two phenomena are coupled. Phenomenological coupling, if it exists, must be observed in nature. Below, will be discussed self-healing, which is observed in specially prepared materials with an embedded healing mechanism, as a result of coupling between deterioration and a force which affects healing.

3.3. Self-healing and thermodynamics

According to the thermodynamic principles, healing is possible when the system is shifted away from the thermodynamic equilibrium, which causes a restoring thermodynamic force (e.g., thermal and/or mass diffusion) to drive the system back to equilibrium. The restoring force also drives the healing process that is characterized by a local decrease of entropy [27–30]. Shifting the system away from equilibrium can be achieved by placing it in a metastable state (e.g., creating an oversaturated solution), so that the rupture breaks the fragile metastable equilibrium, and the system drives to the new most stable state, Fig. 3.1. The metastability can also be achieved by heating that causes a phase transition [18] (e.g., melting, the martensite-austenite transition in metals).

Classical thermodynamics does not give direct relationship between natural processes, such as chemical reactions and conduction of heat, and the rate at which entropy changed. Scientists as *Lars Onsager*, *Ilya R. Prigogine* and others developed new ideas on the basis of classical thermodynamics and related rate of entropy change to rates of processes, such as chemical reactions and heat conduction. Their works transform known thermodynamics from a theory of equilibrium states to a theory of irreversibility processes. *Ilya R. Prigogine*, which was well-deservedly called by *Dilip Kondepudi* [31] poet of thermodynamics, used the methods of non-equilibrium thermodynamics to investigate self-healing. He and his co-workers showed that so-called dissipative systems may lead to increasing orderliness and self-organization in general [32]. Such systems should be open (exchange energy, matter, and entropy with the environment), nonlinear and operate for from thermodynamic equilibrium [33]. The dissipative systems are characterized by spontaneous symmetry breaking and formation of complex structures, where interacting particles exhibit long-range correlations [34,35]. Many of these systems were known a long time ago but the universality and generality of the processes involved in these systems was understood only with the works by *Prigogine*. He enunciated principle of minimum entropy production, which states that a non-equilibrium system tends to reach a stationary state of minimum entropy production. It is believed that this ability for self-organization of physical systems led to the formation of complex hierarchical chemical and biological systems. Non-equilibrium dissipative systems may lead to the hierarchy, and their investigation involves the study of instability and loss of symmetry. Self-organization is related to an enormous reduction of degrees of freedom and entropy of the macroscopic system, consisting of many nonlinearly interacting subsystems, which macroscopically reveals an increase of order.

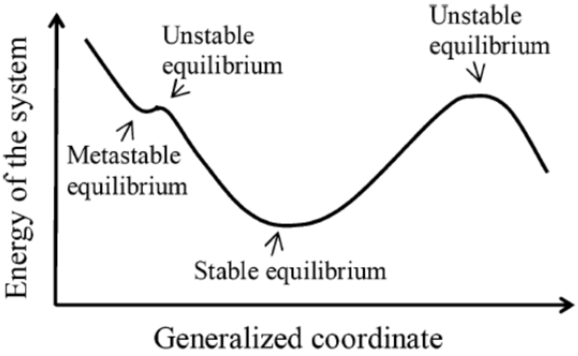


Fig. 3.1. Schematic presentation of system energy as function of generalized system coordinate. A fragile metastable equilibrium is separated by a small energy barrier. When deterioration (e.g., cracking) occurs, the system leaves the metastable state [18]

Rys. 3.1. Schemat ilustrujący zmianę energii układu w funkcji uogólnionego układu współrzędnych. Zakres niestabilnej równowagi nietrwałej (*metastable*) jest oddzielony niewielką barierą energetyczną. Gdy pojawia się zniszczenie (np. pęknięcie), układ wychodzi ze stanu równowagi nietrwałej [18]

The self-healing materials should be considered as a special case of self-organising systems which are away from equilibrium and tend to restore the equilibrium state. The healing is driven by the same thermodynamic force, which tends to restore equilibrium in the system. For example, in the case of the precipitation mechanism, material transport to the voids is caused by the non-equilibrium state of the system, and it is the same mechanism that heals the voids. In the case of a healing agent embedded into the matrix, the transport of the agent is caused by the non-equilibrium and it also heals the crack. For shape memory alloys-fibre reinforced materials, non-equilibrium causes the fibres to attain their original shape and thus to close the crack. Therefore, by relating quantitatively these processes to material microstructure, one can obtain desired structure–property relationships for the design of these materials.

Chapter 4

Organic self-healing materials

Polymeric materials have specific mechanical and chemical characteristics suitable for many structural and functional applications and because of this, incorporation of self-healing abilities into them attracts more and more research interests. I addition, most of them are low-cost high-performance materials which stimulates their application in great number of industrial branches.

Structural polymers and composites are widely used in a variety of applications. However, these materials are susceptible to damage induced by mechanical, chemical, thermal, UV radiation, or a combination of these factors [36]. Structural polymers are susceptible to damage in the form of cracks often formed deep within the structure where detection is difficult and repair is in practice impossible. Damage in polymeric coatings, adhesives, microelectronic components, and structural composites can span many length scales. Structural composites subject to impact loading can sustain significant damage on centimeter length scales, which in turn can lead to subsurface millimeter-scale delaminations and micron-scale matrix cracking [1]. Coatings and microelectronic packaging components have cracks that initiate one even smaller scales. Regardless of the application, once cracks have formed within polymeric materials, the integrity of the structure is significantly compromised.

Polymers can be separated into two different groups depending on their behavior when heated, that is thermoplastics and thermosets. For thermoplastic polymers, however, self-healing of microcracks has not yet been successful. The approaches applicable to thermosetting polymers are not suitable for thermoplastics due to the limitation of the material’s nature. Nevertheless, some pilot studies have been conducted in this direction. With the assistance of artificial measures (such as using solvent and heating), for example, cracks can be healed (or welded).

The achievements in making self-healing thermosetting materials are comparatively more significant. Self-healing processes of thermosetting polymers and their composites fall into two categories: self-healing with and without the aid of healing agent. A new line in synthesis of self-healing thermosetting polymers is formed in last few years. In the focus of the interest is not only the degree of mechanical properties recovery but also the speed of its realization. Usually researcher's efforts are directed to development of extrinsic and intrinsic strategies for rebonding cracks and extension of mechanical properties restoration rather than the speed [37–39]. In fact, crack propagates very quickly (approximately at the velocity of sound or higher in rigid materials) [40,41]. Because of this, the materials should start to heal immediately following crack generation. Establishment of instant self-healing technique is necessary to avoid catastrophic failure in practical application, especially for the components in operation (like wings of flying aircrafts or pipelines conveying fluids).

Self-healing polymer systems can be divided in two groups depending on chemical nature of healing processes. First one comprises polymers in which healing agents are incorporated by means of various technologies; they are named simply self-healing or "smart" materials. Second group consists of polymers that exploit the reversible nature of the covalent bonds and they, for convenience, are labeled "re-mendable".

4.1. "Smart" thermosetting polymers

The achievements in making self-healing thermosetting materials are comparatively more significant. Self-healing of thermosetting polymers and their composites fall into two categories: self-healing with and without the aid of healing agent. The works by Chen *et al.* [5,6] are related with the former class. The authors synthesize highly cross-linked polymeric materials using multifuran and multimaleimide via Diels–Alder reaction. At temperatures above 120ºC, the "intermonomer" linkages disconnect, but then reconnect upon cooling. This process is fully reversible and can be used to restore fractured parts of the polymers.

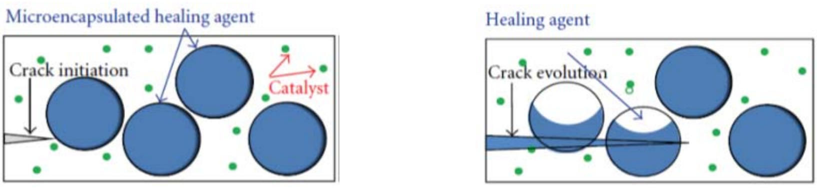
The most common approaches for autonomic self-healing of thermosetting-based materials involve incorporation of self-healing agents within a brittle vessel prior to addition of the vessels into the polymeric matrix. These vessels fracture upon loading of the polymer, releasing the low-viscosity self-healing agents to the damaged sites for subsequent curing and filling of the microcracks.

Healing agent, which aids self-healing, should be in liquid form at least at the healing temperature. It is generally encapsulated and embedded into composite matrix. As soon as the cracks destroy the capsules, the healing agent will be released into the crack planes due to capillary effect and heal the cracks. According to the compositions, the healing agents can be classified as single- and two-component ones. The single-component healants, such as cyanoacrylate [42,43] and polyvinyl acetate [44], are characterized by low viscosity, wide adaptability, and fast consolidation even at lower temperatures. They are cured under the induction of air, and hence not suitable for healing damages deep in the composites. The two-component system consists of polymerizable resin and hardener. When they meet, polymerization is activated so that the cracked parts can be bonded.

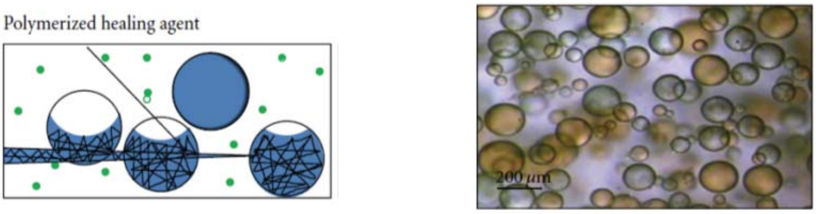
4.1.1. Systems with microencapsulated healing agents

The idea in these systems is upon damage induced cracking in the matrix, microcapsules to release their encapsulated liquid healing agent into the crack planes as schematically shown in Fig. 4.1 [23]. In such a case all the involved materials should be carefully engineered. For examples, encapsulation procedure should be chemically compatible with the reactive healing agent, and the liquid healing agent should not diffuse out of the capsule shell during its potentially long shelf-life. At the same time, the microcapsule walls should be resistant enough to processing conditions of the host composite, while maintaining excellent adhesion with the cured polymer matrix to ensure that the capsules rupture upon composite fracture.

Polymeric microcapsules are most often prepared via a miniemulsion polymerization technique, as described in [46]. The procedure involves the well-known oil-in-water dispersions mechanism of the polymeric material. In the majority of self-healing systems, the microcapsules are made by a ureaformaldehyde polymer, encapsulating dicyclopentadiene (DCPD) as the liquid healing agent [8–10,47] and/or epoxy resin [48–52]. In the case of DCPD, during the *in situ* polymerization process, urea and formaldehyde react in the water phase to form a low-molecular-weight prepolymer; when the weight of this prepolymer increased, it deposited at the DCPD-water interface. This urea-formaldehyde polymer becomes highly cross-linked and forms the microcapsule shell wall. The ureaformaldehyde prepolymer particles are then deposited on the surface of the microcapsules, providing a rough surface morphology that aids in the adhesion of the microcapsules with the polymer matrix during composite processing [53]. Moreover, materials using DCPD-filled ureaformaldehyde microcapsules have shown concrete healing ability in monotonic fracture and fatigue [8–10,47].



a) b)



c) d)

Fig. 4.1. Autonomic healing concept incorporating encapsulated healing agent and embedded catalyst particles in a polymer matrix: a) damage event causes crack formation in the matrix; b) crack ruptures the microcapsules, releasing liquid healing agent into crack plane; c) healing agent polymerizes upon contact with embedded catalyst, bonding crack closed; d) typical SEM image of the urea-formaldehyde microcapsules containing dicyclopentadiene prepared by emulsion *in situ* microencapsulation (adapted from [45])

Rys. 4.1. Schemat autonomicznej koncepcji samoleczenia, uwzględniający obecność środka gojącego (leczniczego) i cząsteczek katalizatora, rozmieszczonych w osnowie polimerowej: a) uszkodzenie powoduje powstanie pęknięć w osnowie; b) pęknięcia powodują rozerwanie mikrokapsułek, z których uwalnia się środek gojący, podążając ku płaszczyźnie pęknięcia; c) środek gojący polimeryzuje w kontakcie z cząsteczkami katalizatora, spajając pęknięcie; d) typowy obraz SEM mikrokapsułek z mocznikiem formaldehydowym, zawierającym dicyklopentadien, wytworzonych *in situ* przez mikrohermetyzowanie (według [45])

Some of the self-healing systems possess unwished side reactions with the polymer materials and air which has negative effect in many specific practical applications. Chemically stable self-healing materials system based on the tin-catalyzed polycondensation of phase-separated droplets containing hydroxyend-functionalized polydimethylsiloxane (HOPDMS) and polydiethoxysiloxane (PDES) is presented in [16]. The catalyst, di-*n*-butyltin dilaurate (DBTL), is contained within polyurethane microcapsules embedded in a vinyl ester matrix and is released when the capsules are broken by mechanical damage. This system possesses a number of important advantages in respect to many others, including:

a) the healing chemistry remains stable in humid or wet environments,
b) the chemistry is stable to an elevated temperature greater than 100°C, enabling healing in higher-temperature thermoset systems,
c) the applied components are widely available and comparatively low in cost,
d) the concept of phase separation of the healing agent greatly simplifies processing, as the healing agent can now be simply mixed into the polymer matrix.

In this system the siloxane-based healing agent mixture is not encapsulated and is phase-separated in the matrix while the catalyst is encapsulated. The low solubility of siloxane-based polymers enables the HOPDMS-PDES mixture and catalyst containing microcapsules to be directly blended with the vinyl ester prepolymer, forming a distribution of stable phase-separated droplets and protected catalyst. When the matrix cracks, a mixture of catalyst released from microcapsules and the healing agent wets the entire crackplane. Addition of an adhesion promoter to the matrix optimizes wetting and bonding of the crack faces. After the healing agent mixture cures, the crack is self-healed (Figs. 4.2a–c). The polycondensation of HOPDMS with PDES occurs rapidly at room temperature in the presence of amine and carboxy licacid organotin catalysts [54]. Because side reactions are limited, organotin catalysts are highly desirable for curing PDMS-based systems, even in open air [54,55]. This stability to water and air is of critical importance for practical realization of self-healing and is a prime motivation for this catalyst system.

An *in situ* encapsulation method demonstrating over an order of magnitude size reduction for the preparation of urea-formaldehyde (UF) capsules filled with a healing agent, dicyclopentadiene (DCPD), is reported in [56]. Capsules with diameters as small as 220 nm are achieved using sonication techniques and an ultrahydrophobe to stabilize the DCPD droplets. The prepared capsules had a smooth outer surface as opposed to the rough, debris covered UF capsules prepared by mechanical agitation. The capsules possess a uniform UF shell wall (77 nm average thickness) and display good thermal stability to 150ºC. The capsules are uniformly dispersed in an epoxy matrix and shown to cleave rather than debond upon fracture of the matrix. The sonication process described in this study provides an efficient method for the production of nanocapsules that meet the requirements for self-healing materials, see Fig. 4.3. These smaller capsules will make self-healing materials responsive to damage initiated at nanoscale and are compatible with composites where the reinforcement spacing requires smaller capsules for applications such as self-healing thin films, coatings, and adhesives. Mechanical properties of the epoxy/capsule composite, including fracture toughness, elastic modulus, and ultimate tensile strength are measured. The values of these moduli are shown in Table 4.1 and are compared to the data for larger capsules size of 180 μm [56].

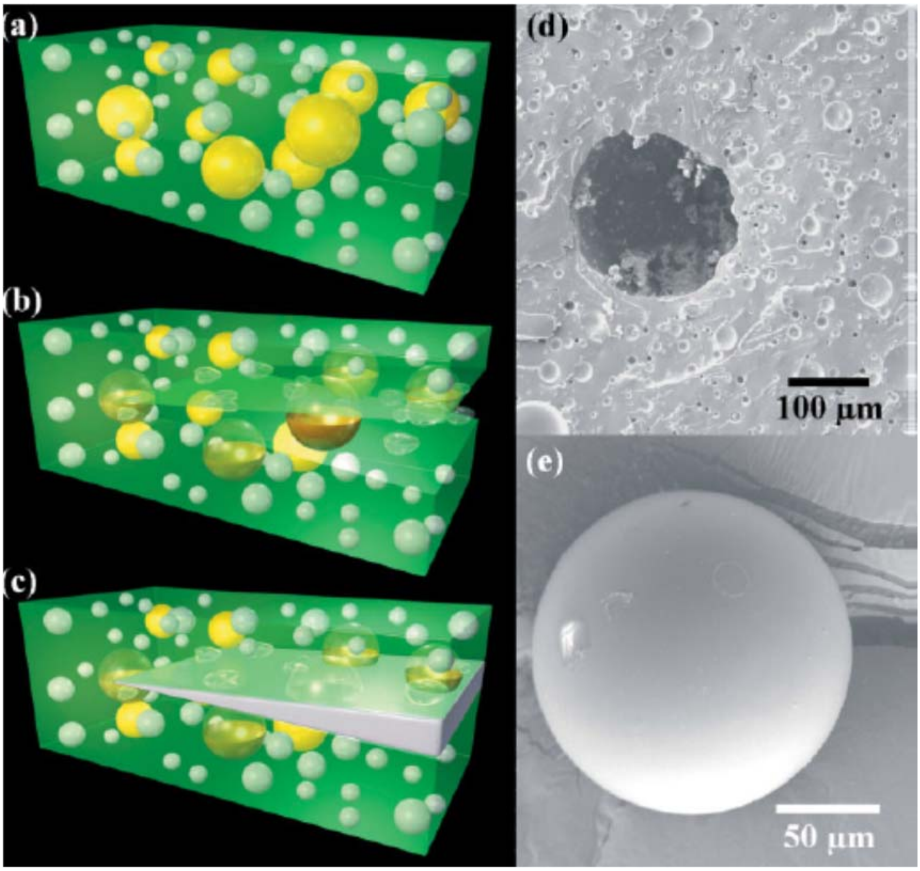
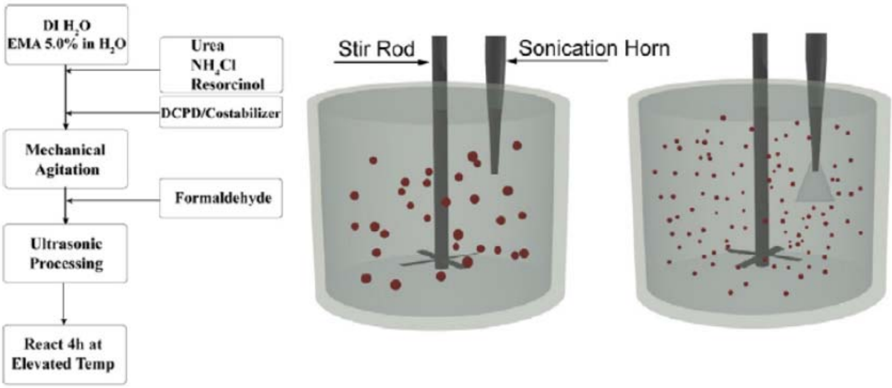


Fig. 4.2. Stages of self-healing process in vinyl ester polymer: a) self-healing composite consisting of microencapsulated catalyst (yellow) and phase-separated healing-agent droplets (white) dispersed in a matrix (green); b) crack propagating into the matrix releasing catalyst and healing agent into the crack plane; c) a crack healed by polymerized PDMS (crack width exaggerated). Scanning electron microscopy (SEM) images of d) the fracture surface, showing an empty microcapsule and voids left by the phase-separated healing agent, and e) a representative microcapsule showing its smooth, uniform surface [54]

Rys. 4.2. Kolejne etapy procesu samoleczenia w polimerze estru winylowego: a) samoleczący się kompozyt zawierający mikrohermetyzowany katalizator (oznaczony żółtym kolorem) oraz krople środka gojącego w postaci oddzielnej fazy (oznaczone na biało), rozmieszczone w osnowie (kolor zielony); b) propagacja pęknięcia osnowy uwalniająca katalizator i środek gojący w płaszczyźnie pęknięcia; c) pęknięcie uzdrowione za pomocą polidimetylosiloksanu (PDMS) (szerokość pęknięcia została pokazana z przesadą). Obraz z elektronowego mikroskopu skaningowego (SEM) d) ilustrujący topografię przełomu z pustą mikrokapsułką i pustkami pozostałymi po środku gojącym oraz e) typowa mikrokapsułka, charakteryzująca się gładką, jednorodną powierzchnią [54]



a) b) c)

Fig. 4.3. Encapsulation method for preparing UF capsules containing DCPD using sonication: a) process flow chart; b) schematic showing the emulsion prior to sonication and c) during sonication [56]

Rys. 4.3. Schemat metody mikrohermetryzowania w odniesieniu do wykonywania kapsułek z mocznika formaldehydu (UD) zawierającego dicyklopentadien (DCPD) z wykorzystaniem ultradźwięków (sonifikacji): a) schemat blokowy procesu; b) szkic ilustrujący stan emulsji przed (b) i w trakcie (c) obróbki ultradźwiękami [56]

Table 4.1. Epoxy/capsules composite characterization [56]

Tabela 4.1. Charakterystyki kompozytu żywica/kapsułki [56]

Volume fraction of capsules	Elastic modulus, E (GPa)	Tensile strength, σ (MPa)	Fracture toughness, K_{IC} (MPa·m$^{1/2}$)
0 – virgin material	2.88 ±0.27	37.9 ±3.4	2.88 ±0.27
0.005	-	-	1.20 ±0.15
0.01	2.91 ±0.23	31.9 ±4.74	1.29 ±0.16
0.02	2.90 ±0.17	26.2 ±2.45	1.52 ±0.02

For the purpose of reducing self-weight, friction noise and cost, improving shock absorption, enhancing corrosion and wear resistance, brake pads made of composite materials with self-healing function are prepared to substitute metal ones by designing ingredients and applying optimized production technology. An original technology for obtaining of dicyclopentadiene (DCPD) microcapsules coated with poly (urea-formaldehyde) is presented in [57]. In this work, polymer matrix composite brake pads with 6 prescriptions are prepared and studied. Three-point bending tests are carried out according to standards in GB/T 3356-1999 and the elastic constants of these polymer matrix composites are experimentally obtained. In accordance with the law of the continuous fibre composite, elastic constants of the short-fibre composite can be calculated by proportions of each ingredient. It is found that the theoretical obtained results are in consistent with the experimental ones. It is shown that self-healing microcapsules used in composite brake pads is feasible.

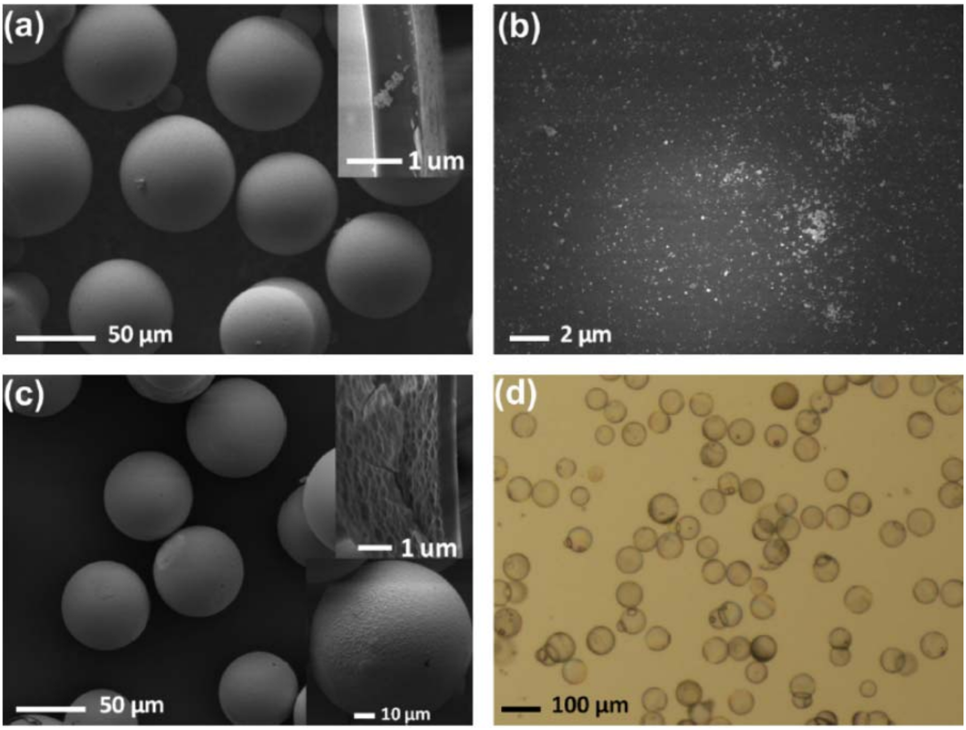


Fig. 4.4. a) Overview with the cross-section of the original HGBs; b) surface morphology of the original HGBs; c) overview with the cross-section (inset at top right) and a typical enlarged etched HGB (inset at bottom right) and d) microscopic image of the etched HGBs [58]

Rys. 4.4. a) Wygląd zewnętrzny wyjściowych mikrosfer szklanych (HBS); b) morfologia powierzchni HGBs; c) wygląd mikrosfer w przekroju poprzecznym (wstawka w prawym górnym roku) i typowa mikrosfera po trawieniu (wstawka w prawym dolnym rogu) oraz d) obrazy strukturalne trawionych HBS [58]

Etched hollow glass bubbles (HGBs) with through-holes at micron level are used as micro-containers for epoxy and amine solution to realize the self-healing functionality in epoxy matrix [58], see Fig 4.4. The average diameter (66.9 ±8.2 µm), the average shell thickness (0.79 ±0.41 µm), as well as the cavity inside the shell are investigated. In order to check the mechanical robustness and the rupturability of the HGBs, micro-compression tests of single

HGB are conducted to measure their mechanical responses, which reveal the relatively high compressive strength and brittle feature. A new type of self-healing epoxy is developed based on the dual HGB carriers and the self-healing performance is optimized systematically to obtain better healing behaviour. It is found that the highest healing efficiency of about 62% is achieved at 50ºC for 24 h when 12.5–15.0 wt. % healing agent carriers is incorporated at the optimized ratio of 4 : 1 for epoxy loaded HGBs (HGB-E) to amine loaded HGBs (HGB-A). It is also found that the healing efficiency increased with increased healing duration at 50ºC. In addition, the fracture toughness is improved and the tensile modulus keeps constant while the tensile strength is deteriorated by the incorporation of the carriers.

Self-healing materials should take effect immediately following crack generation in principle, but the speed of autonomic recovery of mechanical properties through either extrinsic or intrinsic healing strategy reported is not that fast. Mostly, a couple of hours are taken for reaching steady state or maximum healing. To accelerate the healing process, Xiao Ji Ye *et al.* [59] make use of antimony pentafluoride as instant hardener of epoxy and successfully encapsulate the highly active antimony pentafluoride-ethanol complex in terms of hollow silica spheres. Accordingly, self-healing agent based on microencapsulated antimony pentafluoride-ethanol complex and epoxy monomer is developed. Epoxy material with the embedded healant capsules can thus be healed within a few seconds, see Fig. 4.5, as demonstrated by impact and fatigue tests. It is believed that the outcome presented here might help to move the self-healing technique closer to practical application, especially when the engineering significance of epoxy material is concerned.

Microcapsules containing a solvent and reactive epoxy resin are a critical component for the development of cost-effective, low toxicity, and low flammability self-healing materials. A robust *in situ* encapsulation method for protection of a variety of oil soluble solvents and reactive epoxy resins surrounded by a thin, polymeric, urea-formaldehyde (UF) shell is reported in [52]. Resin-solvent capsules are produced in high yield with diameters ranging from 10 μm to 300 μm by controlling agitation rates. These capsules have a continuous inner shell wall and a rough exterior wall that promotes bonding to a polymer matrix, see Fig. 4.6. Capsules as small as 300 μm in diameter are achieved through sonication and stabilization procedures. The presence of both the epoxy resin and solvent core components is confirmed by differential scanning calorimetry (DSC) measurements, and the relative amount of epoxy and solvent in the liquid core is determined by thermogravimetric analysis (TGA). The capsules are shown to satisfy the requirements for use in self-healing materials including processing survivability, thermal stability, and efficient *in situ* rupture for delivery of healing agent.

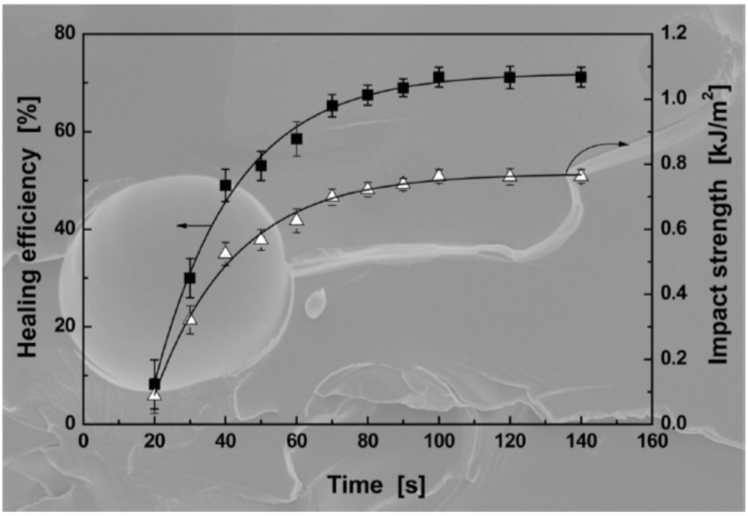
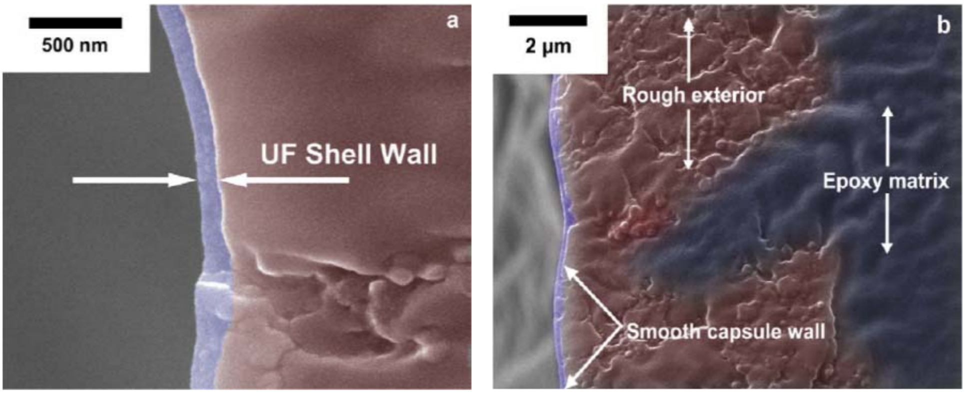


Fig. 4.5. Healing efficiency versus healing time of self-healing specimens determined by impact test. Impact strength of the virgin self-healing specimen is 1.070 ±0.025 kJ/m^2 [59]

Rys. 4.5. Zależność efektywności leczenia od czasu leczenia samoleczącej się próbki, wyznaczona w próbie udarności. Udarność próbki wyjściowej (przed uszkodzeniem) wynosiła 1,070 ±0,025 kJ/m^2 [59]



a) b)

Fig. 4.6. SEM images of Epon 828–EPA microcapsules in false color showing (a) the shell wall (light blue) of a ruptured microcapsule and (b) the three-part interphase region comprised of smooth shell wall (light blue), rough exterior (red), and epoxy matrix (dark blue) [52]

Rys. 4.6. Sztucznie podkolorowany obraz SEM mikrokapsułek Epon 828-EPA, ilustrujący (a) grubość ścianki pękniętej mikrokapsułki (kolor jasnoniebieski), b) trójfazowy obszar zawierający gładką ściankę (kolor jasnoniebieski), szorstką składową (kolor ceglasty) oraz osnowę epoksydową (kolor ciemnoniebieski) [52]

A novel method for making of nanocapsules used as self-healing materials is prepared by interfacial polymerisation method using modified aliphatic amine (HB-1618) and UF resin as core and shell materials respectively is presented in [60]. Silane coupling agent KH560 is used to modify the surface of UF nanocapsules. Fourier transform infrared spectra results indicate the core materials has been successfully encapsulated in UF shell; moreover, physical or chemical combinations are observed between the surface of nanocapsules and KH560. The analyses of thermal stability and mechanical properties reveal that addition of KH560 significantly improved the thermal stability, tensile strength and elastic property. Scanning electron microscope results indicate that the addition of KH560 leads to an excellent interfacial adhesion between the surface of nanocapsules and resin matrix, thus improving the ability of self-healing, beneficial for high levels of healing efficiency in the matrix materials.

A process active at very low temperature (-50ºC) for the repair of damaged structural material is developed and discussed in [61]. The self-repair function is based on the metathesis polymerization of ENB activated by Hoveyda–Grubbs' first generation catalyst. The self-healing epoxy mixture, containing the catalyst powder allows a cure temperature up to 180ºC. Dynamic mechanical analysis is used to determine mechanical parameters. The autorepair composite shows a high modulus in a wide temperature range, a glass transition temperature at about 100ºC and a self-healing efficiency of about 95%.

Theoretical investigation on healing of epoxy resins with embedded ethyl phenylacetate solvent loaded capsules and shape memory alloy (SMA) wires under fatigue loading in tapered double cantilever beam mode is presented in [62]. It is concluded that in an under-cured epoxy matrix with solvent-filled microcapsules, there exists a threshold stress intensity below which crack progression eventually stops while above, the diffusion rate cannot compete with the crack progression and a more classical behaviour is observed. It is also shown that SMA wires do help restore the fatigue life of a fully broken sample.

A self-healing fibre-reinforced structural polymer matrix composite material is demonstrated in [47]. In the composite, a microencapsulated healing agent and a solid chemical catalyst are dispersed within the polymer matrix phase. Healing is triggered by crack propagation through the microcapsules, which then release the healing agent into the crack plane. Subsequent exposure of the healing agent to the chemical catalyst initiates polymerization and bonding of the crack faces. Self-healing (autonomic healing) is demonstrated on width-tapered double cantilever beam fracture specimens in which a mid-plane delamination is introduced and then allowed to heal. Autonomic healing at room temperature yields as much as 45% recovery of virgin interlaminar fracture toughness, while healing at 80ºC increases the recovery to over 80%. The *in situ* kinetics of healing in structural composites is investigated in comparison to that of neat epoxy resin.

Various aspects of technology and functionality of thermosetting polymers with microencapsulated healing agents can be found in [1,63–68].

4.1.2 Systems with healing agents in hollow fibers

The original idea of hollow spheres is extended for hollow reinforcement fibers, used in fiber reinforced plastic, embedding a liquid resin. Various self-healing systems are developed, such as self-validating adhesives [69] and self-healing epoxy composites [10,51]. It is demonstrated that hollow glass fibers are able to improve structural performance of materials without creating sites of weakness within the composite [70–72]. These hollow fibers offer increased flexural rigidity and allow for greater custom tailoring of performance, by adjusting, for example, both the thickness of the walls and degree of hollowness [73,74]. By using hollow glass fibers in these composites – alone or in conjunction with other reinforcing fibers – it would be possible not only to gain the desired structural and performance improvements, but also to introduce a reservoir suitable for the containment of a healing agent [72–75]. Upon mechanical stimulus (damage inducing fracture of the fibers), this healing agent would pour into the damage site to initiate repair [76,77].

The first systems that have been investigated in 1996 and 1998 by C. Dry [43] has validated that the proposed architecture for releasing chemical substances from repair fibres is totally possible. One of the initial challenges encountered when creating this type of self-healing systems is the development of a practical technique for filling the hollow glass fibers with repair agent. When one tries to solve this problem, the dimensions of the glass fiber itself must be considered, including diameter, wall thickness, as well as the viscosity, wetting phenomena and healing kinetics of the repair agent. Bleay *et al.* [78] are among the first to develop and implement a fiber filling method involving “capillary action” that is assisted by vacuum, which is now the main commonly used process. The chosen glass fiber should be also evaluated for its capacity to survive to the composite manufacturing process without breakage, while still possessing its ability to rupture during a damage event in order to release the required healing agent. It is shown to restore mechanical strength of damaged specimens but also causes significant problems by curing upon contact with the opening of the fiber, which prevented the healing agent from reaching the site of damage in the sample. Motuku *et al.* [79] have clearly determined that hollow glass fibers are best suited for this kind of application, as opposed to polymer tubes or those made of metal, which often do not provide controlled fracture upon impact damage.

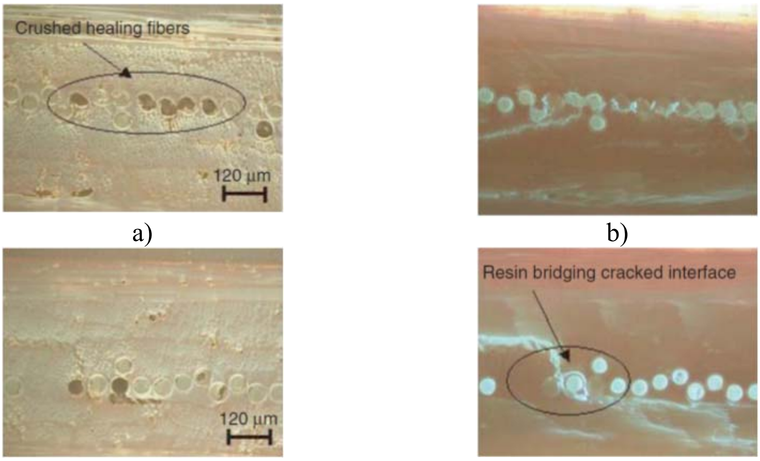
In 2003, Hucker *et al.* [74] have shown that hollow glass fibers of a larger diameter offered an increased compressive strength, while giving larger volume of healing agent to be stored. The second important parameter to investigate is the capacity of the healing agent to adequately reach the site of damage and subsequently undergo healing. This mechanism will obviously depend upon the viscosity of the healing material, as well as the kinetics of the repair process. Various authors [72,76,77,79] have then used liquid dyes inside the composites in order to serve as a damage detection mechanism, providing hence a visible indication of the damage site and also a clear information for the flow of healing agents to those sites.

Finally, the third parameter to optimize is the concentration of healing fibers within the matrix, their spatial distribution, and the final dimensions of the specimen, which is directly related with the mechanical properties of the final self-healing material. As early demonstrated by Jang *et al.* [80], the stacking sequence of the fibers within the material plays a role in inhibiting plastic deformation and delamination and will also affect the response to an impact damage event. In order to maintain high mechanical properties, repair fibers need to be adequately spaced within the material. Motuku *et al.* [79] have shown that thicker materials have shown better performances in healing studies. These parameters, however, will depend upon the dimension choice of fiber and chemical choice of the healing agent employed, and so optimization will depend on the specificities of the system being studied.

The majority of the works done on self-healing hollow fiber materials have focused on demonstrating the feasibility of such concept for self-repair and have reported qualitatively on the healing capacity of the studied systems. Recently, numerous works have reported quantitatively on mechanical properties associated with healing of the materials. The inclusion of hollow glass fibers into a composite system is shown by Jang *et al.* [80] and Trask and Bond [81] to give an initial reduction in the strength of the material, either by 16% in glass fiber reinforced polymer (GFRP) composites and by 8% in carbon-fiber reinforced polymer (CFRP) composites. These “self-repairing” composites are shown to recover 100% of the virgin strength for GFRP and 97% of the virgin strength for CFRP, but in both cases the composite materials are subjected to a heat treatment to aid in delivery of the resin to the damaged area as well as in curing of the healing agent. More recently, in work of Williams *et al.* [82] is developed autonomic self-healing a carbon fiber-reinforced polymer (CFRP), and has demonstrated the significant strength recovery (>90%), which is possible when a resin filled hollow glass fiber system is distributed at specific interfaces within a laminate, minimizing thereby the reduction in mechanical properties whilst maximizing the efficiency of the healing event.

A method for dry filling of glass pipette tubes with cyanoacrylate and epoxy adhesive in the 1 : 2 ratio is reported in [44], which is similar to the approach presented in [43]. Because the hollow glass capillaries have diameters (on millimeter scale) much larger than those of the reinforcing fibers in composites, they have to act as initiators for composites failure [78]. To minimize the detrimental effect associated with the large diameter fibers, it is employed hollow glass fiber with an external diameter of 15 μm and an internal diameter of 5 μm [78], but filling of healing agents into such fine tubes becomes rather difficult because of very high values of capillary pressure. Other authors [72] consider the placement of self-healing hollow glass fiber layers within both glass fiber/epoxy together with carbon fiber/epoxy composite laminates to mitigate damage and restore mechanical strength. The study reveals that after the laminates are subjected to quasi-static impact damage, a significant fraction of flexural strength can be restored by the self-repairing effect of a healing resin stored within hollow fibers. The hollow glass fibers ranging in diameter from 30 μm to 100 μm and hollowness up to 65% can be filled with uncured resin systems that bleed into a damage site upon fiber fracture, as shown in Fig. 4.7. After being cured they provide a method of crack blocking and recovery of mechanical integrity. More details of such healing system can be found in [75–77,81].

In order to simplify the healing techniques based on either resin-filled hollow fibers or microcapsules, Jones *et al.* developed a solid-state healable system, which employs a conventional thermosetting epoxy resin, into which a thermoplastic (i.e. polybisphenol-A-*co*-epichlorohydrin) is dissolved [83,84]. Upon curing, the thermoplastic material remains dissolved in the thermosetting matrix, in contrast to the conventional thermoplastically toughened matrices. It is hypothesized that upon heating a fractured resin system, the thermoplastic material would mobilize and diffuse through the thermosetting matrix, with some chains bridging close cracks and thereby facilitating healing. Considering that most self-healing polymers are inherently electrically insulating, which limits their ultimate responsivities and precludes their use in related analytical applications, Williams *et al.* study a class of organometallic polymers comprising *N*-heterocyclic carbenes and transition metals as an electrically conductive, self-healing material [85]. These polymers are found to exhibit conductivities of the order of 10^{-3} $S{\cdot}cm^{-1}$ and showed structurally dynamic characteristics in the solid state. Thermal treatment enabled the material to flow and to refill the cracks via a unique depolymerization process.



a) b)

c) d)

Fig. 4.7. Crushed-healing fibres located under the impact site viewed under normal a) and UV b) illumination. Healing resin bridging cracked interface viewed under normal c) and UV d) illumination [85]

Rys. 4.7. Wypełnione środkiem leczniczym puste włókna szklane (w przekroju, częściowo uszkodzone) rozłożone poniżej płaszczyzny pękania, widoczne w świetle a) normalnym oraz b) ultrafiolecie (UV). Środek gojący (żywica) spaja pęknięte powierzchnie, co uwidoczniono w świetle c) normalnym oraz d) ultrafioletowym [85]

Intrinsic and extrinsic self-healing strategies can be employed to mitigate the effects of local damage in order to (partially) restore a lost property or functionality and to avoid premature catastrophic failure of the whole system. It is well known that polymer architecture has a crucial influence on mechanical, physical and thermal properties. However, the effect of polymer architecture on the healing capabilities of self-healing polymers has not yet been studied in detail. The effect of polymer architecture on the intrinsic healing character of polymeric materials using different reversible chemistries is analysed in [86]. On-going and future developments in the field suggest it will be possible to use traditional polymer architecture and multilayer concepts to obtain an intrinsic healing polymer with high mechanical properties that acts as a fully dynamic system.

4.1.3. Remendable thermoplastics and ionomers

Thermoplastics are plastics which become pliable or moldable above a specific temperature and returns to a solid state upon cooling. Most thermoplastics have a high molecular weight. The polymolecules chains associate through intermolecular forces, which permit thermoplastics to be remolded because the intermolecular interactions increase upon cooling and restore the bulk properties.

In this way, thermoplastics differ from thermosetting polymers, which form irreversible chemical bonds during the curing process. Ionomers are thermoplastic ionic polymers that comprise repeat units of both electrically neutral repeating units and a fraction of ionized units (usually no more than 15 mole percent) covalently bonded to the polymer backbone as pendant moieties. This means that most ionomers are copolymers of the neutral segments and the ionized units, which usually consist of carboxylic acid groups. Both polymeric materials possess "built in" abilities for self-healing because of their chemical nature and there is no need to introduce this property to such materials.

Crack healing of thermoplastic polymers has been subject of extensive research in the 1980s. The polymers investigated cover amorphous, semicrystalline, block copolymers, and fiber-reinforced composites. It has been discovered that when two pieces of the same polymer are brought into contact at a temperature above its glass transition (Tg), the interface gradually disappears and the mechanical strength at the polymer-polymer interface increases as the crack heals due to molecular diffusion across the interface. For example, by using thermoplastics chain mobility with a minimal application of heat, Lin *et al.* [87] have studied crack healing in PMMA (poly(methyl methacrylate)) by methanol treatment from 40ºC to 60ºC. The authors have found that the tensile strength of PMMA treated by methanol can be fully recovered to that of the virgin material. On the other hand, another example of photo-induced self-healing in PMMA is reported by Chung *et al.* [88]. Mixture of photo linkable TCE (1,1,1-tris-(cinnamoyloxymethyl)ethane) with UDME- (urethane-dimethacrylate-) and TEGDMA- (triethyleneglycol-dimethacrylate-) based monomers, blended with visible light photo-initiator CQ (camphorquinone), is polymerized into a hard and transparent film after its irradiation for 10 min with a 280 nm light source. The healing is shown to only occur upon exposure to the light of the correct wavelength, proving that the healing is light initiated. Healing efficiencies in flexural strength up to 14% and 26% are reported using light or a combination of light and heat (100ºC). However, healing was limited to the surfaces being exposed to light, meaning that internal cracks or thick substrates are unlikely to heal. In summary, self-healing of thermoplastic polymers can be achieved via a number of different mechanisms, including (*i*) recombination of chain ends, (*ii*) self-healing via reversible bond formation, (*iii*) living polymer approach, and (*iv*) self-healing by nanoparticles, in addition to the (*v*) molecular interdiffusion and (*vi*) photo-induced healing reported here. The processes are well known and have been well reported. A detailed description of these approaches can be found in [1,63,89].

Jud and Kausch [90] tested crack healing behavior in a series of poly(methyl methacrylate) (PMMA) samples of different molecular weights and degrees of copolymerization. They induced crack healing by heating the samples above the glass transition temperature under slight pressure. It is found that full resistance is regained during short-term loading experiments. The establishment of mechanical strength should result from interdiffusion of chains and formation of entanglements for the glassy polymer [91].

Zako and Takano [92] introduce a method of impregnating small particles (50 μm) of thermoplastic adhesive in a glass/epoxy composite laminate. The cure temperature of the epoxy matrix is 110ºC. The embedded thermoplastic particles melted when damaged composites are subsequently heated to 120ºC for 10 min on a hot plate. In subsequent three point bend testing, the load-displacement curve indicates that stiffness is recovered in the repaired specimen.

Huber and Hinkley [93] offer a polyurethane thermoplastic elastomer which is able to demonstrate self-healing capacity. This shows that ionic crosslinks or clusters are not the only morphology or structure that can facilitate self-healing and that other types of reversible crosslinked morphologies such as the hydrogen bonding in urethane systems may facilitate the process.

Comparison of thermoplastics with other types of polymers again highlights that the unique properties are based on the combination of the chemical structure and morphology. A non-ionic thermoplastic, although exhibiting higher levels of viscous healing compared to the ionomer, has negligible elastic healing and therefore displays little capacity to self-heal when the two mechanisms are considered together. Similarly, a covalently bonded low-crosslink density thermoset network, displayed no healing at all despite having been moved well into its elastomeric or rubbery phase above its glass transition temperature. Clearly, the covalent bonds prevent sufficient molecular mobility of the polymer chains across the interfacial region to enable healing to occur. Thus it can be seen that the ionomer systems can exhibit behaviour consistent with both thermoplastic and thermosetting behaviour which facilitate the self-healing process. The thermoplastic behaviour promotes molecular mobility and chain entanglement, while the physical crosslinking through the ionic domains ensure that there is a high level of structural integrity of the polymer even at above the melting point and thus preventing wholesale melting of the polymer.

Hayes and colleagues [83] have developed a two-phase, solid-state repairable polymer by mixing a thermoplastic healing agent into a thermosetting epoxy matrix to produce a homogeneous matrix which contrasts with the discrete particles of uncured epoxy reported by Zako and Takano [92]. These systems offer the capacity for self-healing, but are not autonomous. They require damage sensing, some form of higher decision-making via a feedback loop and heating requirements that would pose significant practical challenges in application.

Synthesis of crosslinked self-healing polyurethane/urea based on a Diels–Alder reaction (C-PMPU–DA) from a multiple-furan monomer and a commercial bismaleimide is discussed in [94]. The multiple-furan monomer (PMPU–furan) is obtained from a functionalized prepolymer (polymeric MDI: PBA-200052:1) by furfuryl amine. The structures of both the PMPU–furan and C-PMPU–DA are characterized by attenuated total reflectance (ATR)–Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry, thermogravimetric analysis, and 1H-NMR. The self-healing properties of C-PMPU–DA are also investigated by the recovery of the mechanical properties. The results showed that C-PMPU–DA exhibited good thermal reversibility and self-healing properties. C-PMPU–DA exhibited thermosetting properties at room temperature, although it exhibited thermoplastic properties at higher temperatures and may find applications in self-healing materials, recyclable materials, or removable materials.

The inherent mending properties (in the sense of repair requiring external intervention) of poly(acrylic acid) (PAA)/poly(allylamine hydrochloride) (PAH) CoPECs and how these are facilitated by salt and result in actual self-healing (i.e., entirely autonomous repair) is investigated in [95]. It is demonstrated that working with PAA/PAH CoPECs samples cut for imaging purposes and conditioned in high concentrations of salt, the materials tended to stick together without a change in temperature and that they sometimes became very difficult or even impossible to separate again. Two parameters influencing the strength with which pieces stuck together (Fig. 4.8) are the time the samples are in contact and the NaCl concentration under which this occurred. It is concluded that these properties are of particular importance in view of the high potential of these materials for biomedical applications, as they could not only allow for their auto-repair *in situ*, but also lead to the assembly of complex materials through the combination of CoPECs containing different types of cells or biomolecules. Because it is based on the interdiffusion of polyelectrolytes, self-healing in CoPECs does not require any polymer modification or additional chemical compound, in contrast to many other self-healing polymeric materials.

Host-guest assemblies are a powerful approach to create supramolecular materials with versatile functions. A new mode of radical polymerization is demonstrated in [96]. The polymerization is achieved via magnetocaloric effect to fabricate novel host-guest supramolecular gels within 5 min. The resulting gels can repair themselves spontaneously when damaged, without the assistance of any external stimuli, and possess great mechanical strength. Moreover, the Fe_3O_4-doped supramolecular gels show accelerated self-healing (from 24 h to 3 h) under an applied magnetic field, which is attributed to the synergy between host-guest healing and a magnetocaloric effect. The interesting development of method and materials in this work provides a new insight into the rapid fabrication of novel bio-inspired materials for extensive applications. This strategy might open a promising avenue for accelerating the use of host-guest assemblies to rapidly build robust materials.

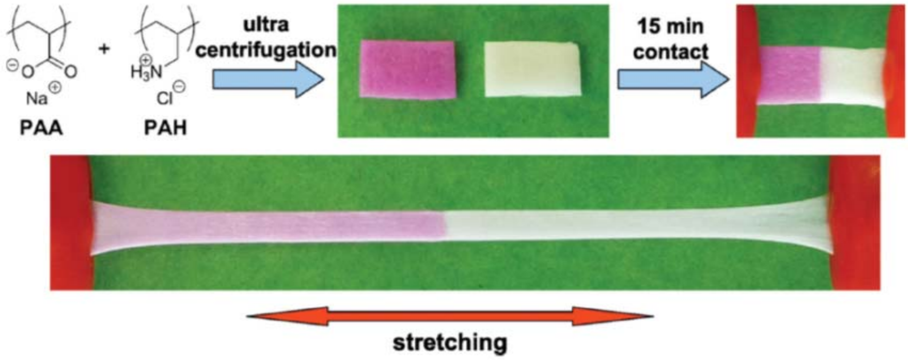


Fig. 4.8. General procedure of making, cutting, mending, and stretching of the compact polyelectrolyte complexes (all at room temperature): CoPECs are made by mixing solutions of PAA and PAH then compacting by ultracentrifugation in the presence of salt. CoPECs are compressed to obtain thin sheets and cut into the desired shapes (here, the PAH in the left-hand piece of complex is labeled with rhodamine). For mending they are brought into contact for the desired time period (here 15 min) in a specific salt concentration (here 2.5 M NaCl). After reconditioning the samples are stretched until they broke [95]

Rys. 4.8. Schemat ogólny procedury wytwarzania, cięcia, kompletowania oraz rozciągania kompleksów polielektrolitowych (CoPECs) o zwartej strukturze (w temperaturze pokojowej): kompleksy CoPECs są wytwarzane przez zmieszanie roztworów polikwasu akrylowego (PAA) i polichlorowodorku alliloaminy) (PAH) z zagęszczaniem przez odwirowywanie w obecności soli. Następnie CoPECs są walcowane (bądź kształtowane pod różnego rodzaju naciskami zewnętrznymi) do postaci cienkich arkuszy, a zatem cięte do postaci wymaganych kształtów (w danym przypadku PAH umieszczony jest po lewej stronie kompleksu w połączeniu z rodaminą). Proces klejenia przebiega zwykle w czasie kilkunastu minut (w danym przypadku 15 min) przy zadanym stężeniu soli (tutaj 2,5 M NaCl). Po skompletowaniu próbki poddawane są próbie rozciągania aż do zerwania [95]

An effective approach for development of self-healing polymers is that of using in-built electrostatic attractive forces in combination with a temperature increase to heal the polymer. This approach has been shown to work successfully in the case of ballistic impact on certain ionomers, such as Surlyn 8920 [97]. Ionomers are thermoplastic polymers that typically contain 20–30 mol. % of ionic species, often due to partial acid neutralization during polymer synthesis, which are incorporated into the structure of the polymer. These ionic side groups give rise to the formation of electrically bound physical clusters. These clusters make an important contribution to the high-temperature elasticity of the material and the restoration of mechanical properties at lower temperatures. In the case of ballistic impact, the impact energy itself is responsible for a local temperature increase of the order of 160–200°C. As a result, 4 mm thick sheets of ionomeric material are capable of fully covering the hole created by the passage of supersonic bullets of up to 9 mm, see Fig. 4.9. Similar experiments on nonionomeric polymers of comparable properties invariably left a sizeable hole upon ballistic impact. In a number of quasi-static pull-through studies at various temperatures, [98,99] unravelled the various processes involved in healing in ionomeric polymers.

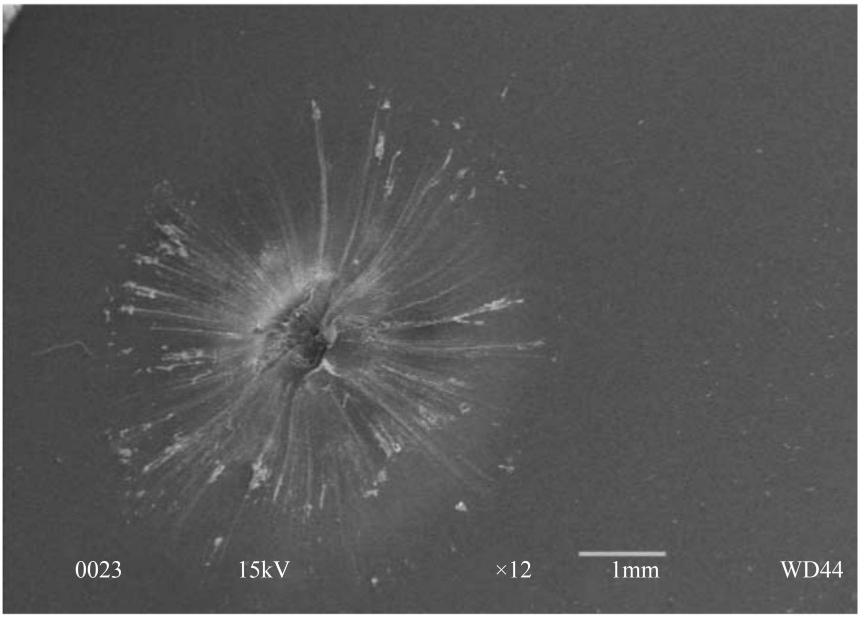


Fig. 4.9. SEM of the impact site of a 7 mm ballistic projectile on an ionomer plate [100]

Fig. 4.9. Obraz z mikroskopu elektronowego (SEM) miejsca uderzenia 7-milimetrowego pocisku balistycznego w płytkę jonomerową [100]

Another chemical approach to induce self-healing in thermoplastics is the incorporation of thermally reversible cross-link groups in or on the polymer backbone. These thermally reversible cross-links will break during mechanical loading of the polymer, but can be restored by raising the temperature. Two types of reversible chemical cross-links need special mention as they have been used in self-healing systems: polymer systems based on the Diels–Alder (DA) and retro Diels–Alder (RDA) reaction, and polymers containing quadruple hydrogen bonds.

Wudl and co-workers were the first to employ the DA–RDA strategy to prepare thermally re-mendable polymers [5,6]. Multifunctional furanand maleimide-based monomers were used to form highly cross-linked polymeric networks. The polymers were submitted to heating/cooling cycles and their structural changes were followed by solid-state ^{13}C NMR spectroscopy. These measurements clearly demonstrated the occurrence of the RDA reaction at approximately 120ºC. Samples of this polymer were stressed to complete failure and subsequently healed by heating to approximately 90–120ºC, followed by cooling to room temperature. The healed polymer exhibited approximately 57% of the original polymer strength, but, for later modification of the polymer, higher healing efficiencies and base properties were obtained. Thus, it was shown that the DA–RDA principle provides a simple and efficient way to prepare re-mendable polymers, which can go through repeated cycles of cracking and re-mending at the same site. The limitations of this system are the working temperature of the materials, which is too low (below 120ºC) for many applications, and the lengthy and costly synthesis of the monomers, which is problematic for large-scale production. It should be mentioned that these new DA–RDA polymer systems based on cheap monomers are currently under construction.

A comprehensive and informative model of the ionomeric self-healing process has been presented in [101] where the macroscopic recovery process and the microscopic model of healing are discussed. The macroscopic recovery process confirms the conclusions that the healing process should be considered as a combination of the elastic response “closing the hole”, followed by the localised viscous flow “sealing the hole”. The actual recovery mechanism by which the polymer is able to close the hole, assuming satisfactory elastic rebound is illustrated by the model. Examination of the cross section of a theoretical puncture zone highlights that during impact, the length of the polymer is stretched and increased, so that when the bullet exits the other side and removes some polymer, there is sufficient quantity to cover the hole during the rebound.

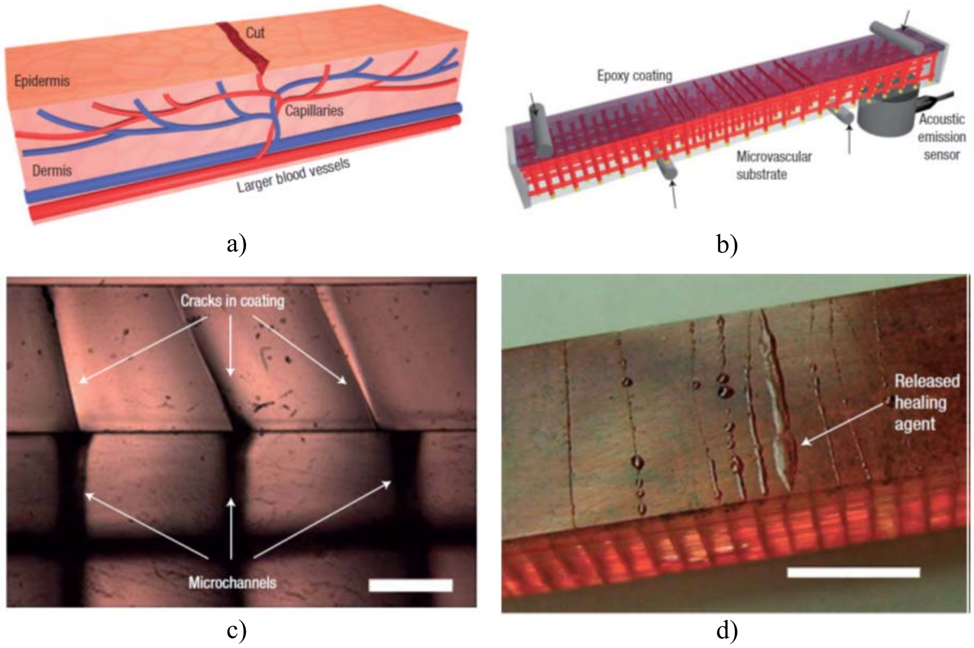
The first applications of ionomers as self-healing polymer systems are focused upon military applications in the areas of reducing the vulnerability of fuel tanks to combustion [102]. The application of ionomers as light weight and low cost alternatives to current methods of reducing fuel tank vulnerability to combustion has been investigated in [103]. It is found that the instantaneous healing of a fuel tank to impact by 12.7 mm armour-piercing bullets is a major improvement over the current self-sealing systems, which are specified to heal within 2 min. This enormously reduced the level of fuel spray such that there is minimal fuel leakage, offering significant improvements over existing technologies.

To summarise the self-healing mechanism of ionomers is controlled by the inherent chemical structure and morphology of the polymer itself. Due to the fact that it is controlled by the chemical structure, it would be expected to be repeatable many times being dependent primarily upon the degradation of the polymer. It is not an autonomic process but is activated when thermal energy is transferred to the polymer. During impact, energy is absorbed which is elastically stored and dissipated as heat. This increases the local temperature of the impacted polymer to above the melting point (disrupting the physical crosslinks) while having little effect upon the temperature of the surrounding polymer. However, the ionic domains persist in the melt so that the polymer is able to be elongated to high levels of strain and rebound elastically when the stored energy is released at failure.

Finally, it is critical for the success of healing that there is sufficient balance of elastic strength to rebound, and at the same time, the polymer must be molten enough to be able to melt and chemically diffuse across interfacial boundaries.

4.2. Self-healing materials with microvascular networks

To overcome the difficulty of short supply of a healing agent in microcapsule-based self-healing concept, another approach similar to biological vascular system of many plants and animals is explored by White *et al.* [21,22]. This approach relies on a centralized network (that is microvascular network) for distribution of healing agents into polymeric systems in a continuous pathway. The fabrication process is complex and it is very difficult to achieve synthetic materials with such networks for practical applications. In this process, organic inks are deposited following a 3D array and the interstitial pores between the printed lines are infiltrated with an epoxy resin. Once the polymer is cured, the fugitive ink is removed leaving behind a 3D microvascular channel with well-defined connectivity. Polymeric systems with microvascular networks are prepared by incorporating chemical catalysts in the polymer used to infiltrate the organic ink scaffold, see Fig. 4.10. Upon curing the polymer and removing the scaffold, the healing agent is wicked into the microvascular channels. Several researchers reported such fabrication processes and related self-healing capabilities [104–107]. However, this approach cannot be used in the case of corrosion protective coatings since a microvascular network cannot be created in a metallic substrate.



a) b)

c) d)

Fig. 4.10. Self-healing materials with 3D microvascular networks: a) schematic diagram of a capillary network in the dermis layer of skin with a cut in the epidermis layer; b) schematic diagram of the self-healing structure composed of a microvascular substrate and a brittle epoxy coating containing embedded catalyst in a four-point bending configuration monitored with an acoustic-emission sensor; c) High-magnification cross-sectional image of the coating showing that cracks, which initiate at the surface, propagate towards the microchannel openings at the interface (scale bar = 0.5 mm); d) optical image of self-healing structure after cracks are formed in the coating (with 2.5 wt. % catalyst), revealing the presence of excess healing fluid on the coating surface (scale bar = 5 mm) [22]

Rys. 4.10. Materiały samoleczące się z przestrzennymi (3D) sieciami mikronaczyń: a) schemat sieci kapilar w warstwie skóry właściwej wraz z warstwą naskórka; b) schemat struktury samoleczącej składającej się z podłoża mikronaczyń i kruchej powłoki epoksydowej, zawierającej katalizator osadzony w czteropunktowej konfiguracji, pozwalającej na monitorowanie procesu zginania za pomocą czujnika emisji akustycznej; c) struktura przekroju powłoki (podziałka wynosi 0,5 mm) ilustrująca pęknięcia, zainicjowane na powierzchni i propagujące w kierunku otwartych mikrokanałów w pobliżu powierzchni rozdziału; d) obraz z mikroskopu świetlnego struktury samoleczącej się po inicjacji pęknięć powłoki (zawierającej 2,5% wag. katalizatora), na powierzchni której uwidoczniony jest nadmiar środka gojącego (podziałka wynosi 5 mm) [22]

A bio-inspired vascule approach [87] to self-healing in high performance thermoset composite materials has been extensively researched by Bond, Trask and co-workers over the past 10 years, primarily due to the integration challenges and volume limitations of microcapsule-based systems. Hollow glass fibres (HGFs) [83,88–93] and microvascular channels [52,58–60] have successfully demonstrated reliable methods for self-healing agents (SHAs) delivery to damaged areas through multiple mixed-mode testing. Norris *et al.* have further developed this concept with the stimuli triggered delivery of a pre-mixed commercial epoxy SHA into an aerospace grade composite material, when subject to low energy impact damage, to recover compression after impact (CAI) strength [61,62,108].

A demonstration of a self-healing fibre reinforced polymer (FRP) composite material using a double cantilever beam (DCB) coupon specimen geometry, facilitated by the delivery of novel epoxy-metal triflate self-healing agents (SHAs) via embedded microvascular channels is presented in [109]. Thermal cure analysis and mechanical testing is employed to characterise the self-healed polymer. A bio-inspired series of vascules incorporated into an FRP composite material facilitates the delivery of SHAs to exposed fractured crack planes. Healing is effected by ring-opening polymerisation (ROP) of an epoxy resin using novel metal triflate catalysts injected after Mode I crack opening displacement. The focus of this research is a ‘proof of concept’ study for fracture repair in FRP test specimens using conventional industrial composite material manufacturing techniques and the aforementioned novel SHAs. The results reported have shown a significant recovery of fracture toughness (>99%) that matches the initial fracture mechanism of the host FRP material and an ability to create a repair with superior toughness than the original host polymer matrix material.

4.3. Self-healing coatings

Application of organic coatings is the most common and cost-effective method of improving the corrosion protection and, thereby, the durability of metallic structures. A wide range of engineering structures, from cars to aircrafts, from chemical factories to household equipment, is effectively protected by the coating systems. The main role of an organic polymer coating in corrosion protection is to provide a dense barrier against corrosive species. Along with these barrier properties, resistance to a flow of charge, electronic and ionic, is also important since the corrosion processes have electrochemical nature and the transfer of charge is involved. However, defects appear in the organic protective coatings during exploitation of the coated structures opening a direct access for corrosive agents to the metallic surface. Also, exposure of these coatings to aqueous electrolyte solutions causes many coatings to swell and develop conductive pathways not present in the coating before the exposure. The corrosion processes develop faster after disruption of the protective barrier. Therefore, an active self-healing of defects in coatings is necessary in order to provide long-term protection effect.

Self-healing coatings investigated so far are based on nanocontainer or fibre systems that store self-healing agents. In most of the systems the release of the self-healing agent occurs as a result of mechanical damage [16]. However, not all mechanical damage leads to corrosion and corrosion is not necessarily initiated at mechanical cracks. Ideally, the release of self-healing agents should only take place when corrosion is initiated. Triggers for sensing the corrosion of a metal system that have been investigated in depth are the change of pH or change of ionic strength [110–112]. But the most reliable and case selective trigger is the change of the electrochemical potential, as it always and only decreases when corrosion occurs. For instance, conducting polymers (CPs) can store active anions as counter-charge to the oxidized polymer backbone, which can be released upon onset of corrosion and subsequent reduction of CP [113–120]. Considerable research has been conducted on CP for corrosion protection, however there are three crucial points which must be taken into consideration:

1) The efficiency of release of anionic inhibitors is based on their ionic mobility and has to compete with cation incorporation in the CP, which is usually the preferred situation.

2) Due to fast cation incorporation, electropolymerized CP films with continuous ionic networks may even enhance corrosion and can lead to a fast breakdown of the coating system.

3) CPs applied on non-noble metals such as zinc tend to react with the metal. Consequently metal and CP are usually electronically decoupled (Fermi-level misalignment) and the CP loses its capability to sense the potential changes of the metal, due to the formation of an insulating layer [121,122].

A comprehensive overview of different approaches for self-healing anticorrosion coatings is presented in [123]. Two completely different concepts of self-healing are suggested for protective coating systems. The first one is closer to the classical understanding of self-healing and is based on the mechanisms that allow the recovery of mechanical integrity of damaged coatings. The different approaches, which are based on the active suppression of corrosion processes in defected areas, are also considered there as another self-healing concept.

To address the drawbacks of the present CP-based coatings Vimalanandan *et al.* [124] propose a CP-based nanocapsule system for redox-triggered release of self-healing agents, which comprises a redox-sensitive polyaniline (PANI) shell and a self-healing agent encapsulated in the core, see Fig. 4.11, synthesized by the miniemulsion technique [125]. The PANI capsules with remarkable switchable permeability for the stored agents encapsulated into them have been prepared and successfully applied with a model polymer matrix onto a zinc substrate. This composite coating is capable of corrosion triggered release of active agents that can stop the corrosion and related delamination. The trigger signal is the change of potential concurrent with the progress of delamination along the interface.

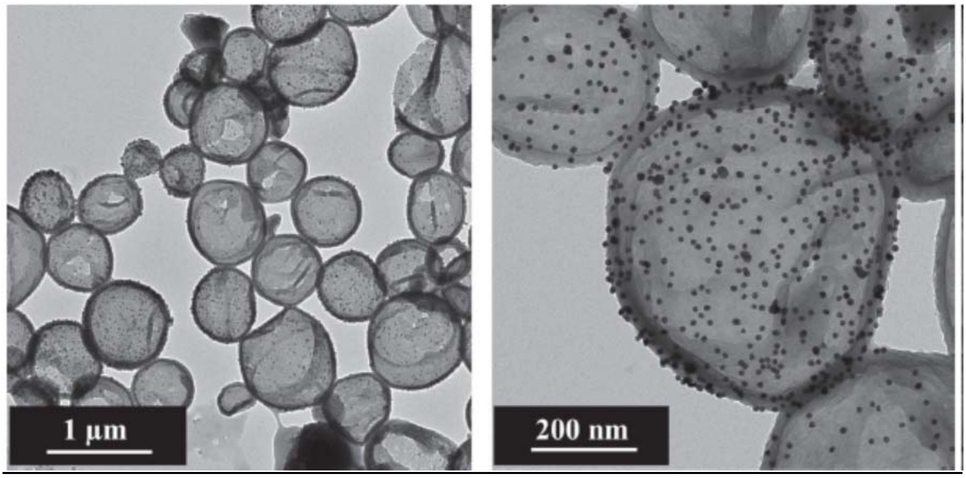


Fig. 4.11. Transmission electron microscopy (TEM) micrographs of PANI capsules decorated with gold nanoparticles [124]

Fig. 4.11. Obraz z elektronowego mikroskopu transmisyjnego (TEM) kapsułek z polianiliny (PANI) z naniesionymi na ich powierzchni nanocząsteczkami złota [124]

Kumar *et al.* attempted to introduce different types of capsules loaded with corrosion inhibitors and coating repair compounds into commercially available paints [126]. The efficacy of self-healing corrosion protection coatings with urea-formaldehyde and gelatin microcapsules (50–150 µm diameter) containing several types of film forming agents has been studied. The microcapsules stay intact for a long time in the dry coatings and are ruptured only by a damage releasing the core constituents to the defect. The chosen microcapsules are stable for more than two weeks even in paint formulations. However, the results of the experiments suggest that they should be mixed with paint preferably at the time of application. Moreover, the best results are obtained when the microcapsules are sprinkled as a discrete layer on top of a thin layer of previously applied primer and then a second layer of primer is deposited followed by a topcoat layer (see Fig. 4.12). The corrosion protection performance in this case is shown to be far superior compared to the mixing of the microcapsules in the primer before being applied. Accelerated corrosion tests of these experimental coatings based on ASTM D 5894 indicate that incorporation of the self-healing microcapsules into commercially available primers can remarkably reduce under film corrosion on steel enclosures for outdoor equipment.

Sauvant-Moynot *et al.* suggested using a self-healing coating together with a cathodic protection system. Specific film formers sensitive to pH and electrical field are introduced to the coatings applied on metal structures and are used under cathodic protection [127]. A dried water soluble and self-curable epoxy electrodepositable adducts as fillers (30 wt. %) are used as organic film formers. A significant reduction in the current needed for cathodic protection is revealed demonstrating the self-healing ability of the coatings under study. The barrier properties are significantly increased in comparison to scratched reference samples. The idea of reflow-healing of protective coatings has already found its commercial realization. Nissan has announced the “Scratch Guard Coat” painting system, which contains a newly developed high- elastic resin providing reflow in artificial scratches [128]. The new coating system is effective for about three years and is five times more resistant to abrasions caused by a car-washing machine compared with a conventional clear paint.

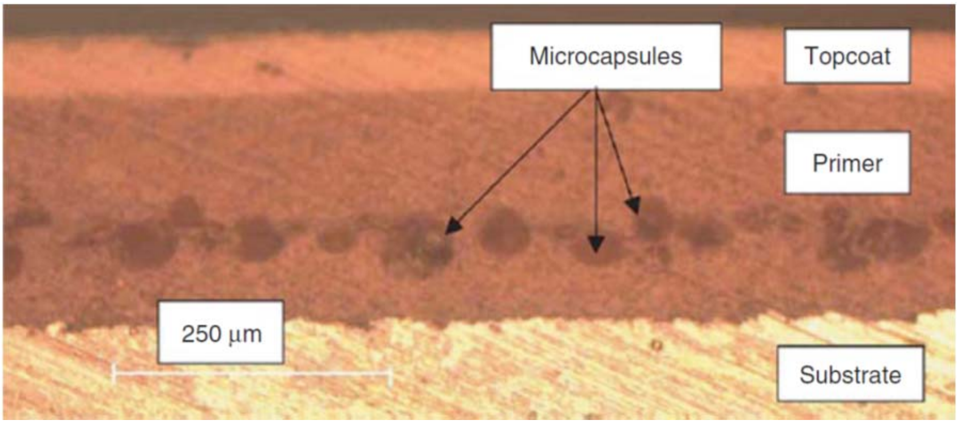


Fig. 4.12. Optical micrograph of cross section of coating with microcapsules [126]

Rys. 4.12. Obraz z mikroskopu świetlnego przekroju powłoki z mikrokapsułkami [126]

Looking to the future of self-healing anticorrosion coatings, an idea of multilevel self-repair response seems to be the most promising. A multilevel self-healing concept would combine in the same coating system the different damage reparation mechanisms that gradually act in response to different environmental impacts [123]. The different active components of the protective system must be able to respond to the different type and levels of impact imposed to the coating. One example of this approach is demonstrated in the work of Kumar *et al.* [126] when a polymerizable healing agent and a corrosion inhibitor were encapsulated together providing the healing of the defect by polymerization and corrosion inhibition at the same time. The synergistic protective effect originating from the combination of the different self-healing mechanisms can be achieved by incorporating different types of nanocontainers in the same coating system. These nanocontainers can be added to the same polymer film or added to different layers such as primer, clear coat, or topcoat depending on their functionality and the target of the active compounds. This approach allows the creation of protective coatings that will adequately respond to the environmental impacts providing effective self-healing and long-term service life of the anticorrosion coating systems. One can expect that the performance of the coating that is constituted by a conversion coating with active anticorrosion component, a primer doped with 'smart' nanocontainers of corrosion inhibitor and a topcoat with capsules of a polymerizable healing agent, will provide outstanding corrosion protection properties and a long-term performance without the necessity of repairs.

One of the most important issues, which limit a wide use of self-healing coatings for different commercial applications, is the high cost of the suggested technologies. Only a more extensive development of these approaches and high investments to the area can lead to lower prices opening the exciting possibilities to see the 'smart' self-healing coatings in our day-to-day life.

Chapter 5

Self-healing metallic materials

Most recent studies have concentrated on polymers and ceramics because it is easier to incorporate self-healing in non-metallic materials than in metallic materials. However, metallic self-healing alloys and composites are of great practical importance. The field of self-healing metals and metal composites has received serious attention only in the last 10 years [20,129–131]. It is much more difficult to heal metallic materials than polymers, because metallic atoms are strongly bonded and have small volumes and low diffusion rates.

A common theme in the research that has been published in the area of self-healing metals is microstructure manipulation and control. Self-healing metals can be broadly classified as per their microstructural characteristics into two categories: liquid-assisted and solid-state healing [63]. These categories describe the mechanism by which the self-healing metal transports matter to the damage site. As for the first category, the design of self-healing metals relying on liquid-assisted healing has focused on metal-matrix composites reinforced with shape memory alloy (SMA) wires in which the matrix partially liquefies at an elevated temperature. The microstructure is designed to maintain structural stability during healing by only allowing the liquid available at the crack surface to participate in damage remediation. The metals in the second category rely on the solid-state healing mechanism to exploit the strong driving force for solute diffusion to high-energy surfaces such as cracks or voids. Work in this area has primarily focused on aluminum alloys and steels. In both categories of self-healing metals, numerical and analytical modelling has been used to further understand the behaviour and explore the mechanisms that give these metals their unique characteristics. This chapter highlights the approaches of several researchers who have developed metals with the ability to self-heal and/or self-repair.

Several strategies of embedding the self-healing properties into engineering materials have been suggested so far (Fig. 5.1). First is to embed healing agent that is stored within thin-walled inert brittle macrocapsules embedded into the matrix. When a crack propagates, the capsules fracture, the healing agent is released and propagates into the crack due to capillarity (Fig. 5.1a).

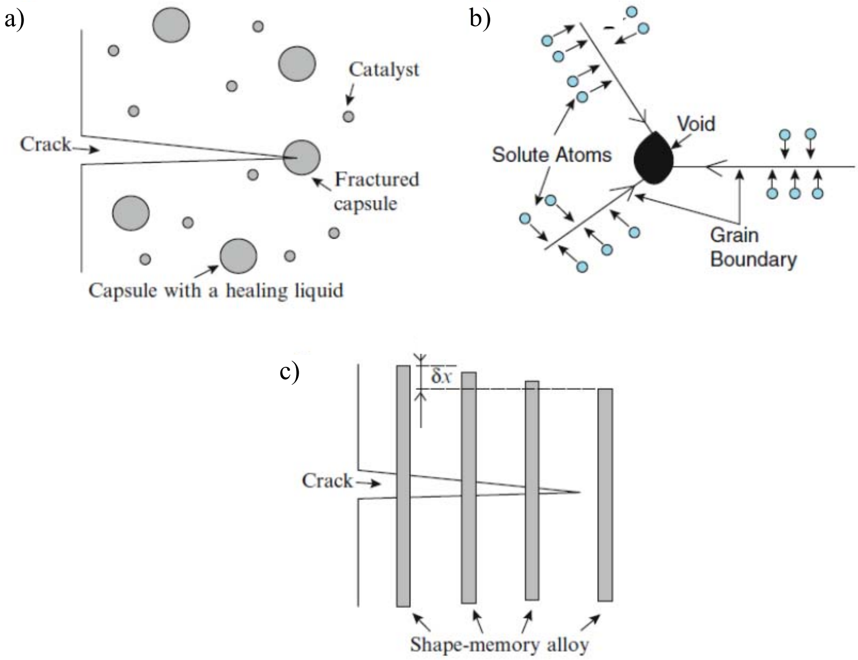


Fig. 5.1. Self-healing in metallic materials by: a) encapsulation of a healing agent; b) precipitation in an over-saturated alloy; c) embedding of shape-memory alloy (SMA) microwires [18]

Rys. 5.1. Schematy samoleczenia w materiałach metalowych: a) kapsułkowanie środka gojącego; b) procesy wydzieleniowe w stopie przesyconym; c) kompozyt zbrojony mikrodrutami z pamięcią kształtu (SMA) [18]

Another strategy is the formation of precipitates at the defect sites that immobilize further growth until failure. Van der Zwaag *et al.* [100] called this mechanisms "damage prevention" because the idea is to prevent the formation of voids by the diffusion of the atoms to form precipitate from an oversaturated but under aged solid-solid solution (alloy). The driving mechanism for the diffusion is the excess surface energy of microscopic voids and cracks that serve as nucleation centres of the precipitate which plays the role of the healing agent (Fig. 5.1b). As a result, the newly formed void is sealed by the deposit of atoms in the form of precipitates before it grows and thus minimizes the creep and fatigue. Manuel and Olson [19] used another approach: reinforcement of an alloy matrix with a microfiber or wires made of a shape-memory alloy, such as nitinol (NiTi). SMA wires have the ability to recover their original shape after some deformation has occurred if they are heated above the phase transformation temperature. If the composite undergoes crack formation, heating from the surface will activate the shape recovery effect of the SMA wires, and close the cracks (Fig. 5.1c). The third approach is to use a healing agent (such as an alloy with a low melting temperature) embedded into a metallic solder matrix, similarly to the way it is done with the polymers. However, encapsulation of a healing agent into a metallic material is a much more difficult task than in the case of polymers. The healing agent should be encapsulated in microcapsules which serve as diffusion barriers and which fracture when a crack propagates.

A research of self-healing metal matrix composites, with the aid of models developed by the authors for the manufacturing processes and self-healing behaviour is presented in [132]. The concept of self-healing described in this work consists of controlling a low temperature melting alloy imbedded within a higher temperature alloy to create a self-healing composite (SHC). When the SHC is damaged or cracked, heat may be applied to the affected area where upon the low melting alloy will melt and flow into the crack healing the damage and scaling the crack. In this study a theoretical analysis, metallurgical design, experimental synthesis and computational fluid dynamics of a self-healing aluminum alloy are discussed. The aluminum alloy matrix is reinforced with microtubes of alumina (Al_2O_3) that are filled with a low melting point solder alloy. The aim of the study is to find the influence and efficiency of the solder in healing an aluminum matrix. To check this effect a crack is created in the metal surface, piercing the microtube(s) filled with solder, and then the SHC is heated above the melting point of the solder alloy. The feasibility of this approach is proved by the results obtained.

There are some certain requirements to healing agents suitable for metallic materials. Most important of them are: to have relatively low melting temperature and to have as better as possible wettability in respect to matrix, i.e. low contact angle between liquid agent and solid matrix. Because of this the results published to date are related to application of metals as Zn, Sn, Bi, In, solder composition 42Sn-58Bi. All of them wet aluminum-based matrix (contact angle smaller than 80º) and melting temperature smaller than 280ºC, except Zn which melting temperature is 419ºC.

Various techniques for obtaining of self-healing materials are tested in University of Wisconsin-Milwaukee and the results are discussed in [18]. The materials under consideration are as follows:

1. Aluminum matrix-bismuth healing alloy. This is a strongly wetting system with the contact angle of 45º. The bismuth coefficient of shrinkage is negative 3.32%; this means that bismuth's volume expands

about 3.32% when it solidifies. Experimental and simulation results show that the liquid metal flows through the crack and fills it if the crack has volume of 10% of the container's volume. Both experimental and simulation results show that the matrix is healed but the bond between aluminum and bismuth is weak and reaction is not observed.

2. Tin matrix-indium healing agent. This system is not strongly wetting with the contact angle of 70º. Another parameter needed to simulate the healing process of the composite is the contact angle between healing agent and capsule, which is assumed to be 125º. Liquid metal must sufficiently expand to overcome the contact resistance of the container walls in order to penetrate into the crack cavity. It is observed that in both cases, the liquid remained inside the container and the crack is not filled, this implies that the matrix is not healed, and self-healing is not observed.
3. Epoxy matrix-dicyclopentadiene healing agent composite. This material is studied for comparison with metallic healing agents. The composite consists of epoxy matrix and dicyclopentadiene healing agent. Healing of 200-μm crack is observed. In general, the results of these tests showed that whether healing takes place or not depends on the orientation of the crack in respect to gravity [133].
4. Several additional specimens are studied, and in particular, a composite made of an aluminum alloy matrix with ceramic microtubes as reinforcements that encapsulated a lower melting point alloy solder (the healing agent). In this case the crack is partially filled but the bond between the aluminum matrix end the solder is poor.
5. Aluminum Al206 as a matrix, hollow quartz tubes as the reinforcement filled with aluminum brazing alloy Al802. The melting point of the brazing alloy Al802 is almost half of that of the matrix, which facilitates selection of healing temperature. The crack is drilled on the aluminum surface and then the composite is heated up to 425°C. The healing agent flows inside the crack and it appears that there has been a reaction between aluminum and healing agent creating a strong bond at the interface. This makes the brazing alloy a potential candidate to heal aluminum matrix.

Some efforts to encapsulate a low melting point metal in hollow microspheres that can act as a barrier between the low melting point metal and a higher melting point alloy during casting are discussed in [134]. Sn-filled fly ash cenosphere embedded in Mg matrix by pressure infiltration, Zn-filled Al_2O_3 hollow spheres embedded in Al-Zn matrix by stir casting and Sn-Bi-eutectic-filled Al_2O_3 hollow spheres embedded in Sn-0.7% Cu matrix by pressure infiltration are tested. A hole has been drilled into the sample to simulate a crack extending through multiple low-melting-point-metal-filled spheres. Heating can cause the Sn-Bi eutectic to melt and flow out into the hole. Preliminary tests with aluminum based composite materials reinforced by two healing agent are also shown in this work. In the first test is used Al-A206 matrix and encapsulated in Al_2O_3 Pb-Sn solder as healing agent and in the second test Sn cased in aluminum is used. The very healing processes are realized high-temperature treatment [135]. Up to now the results of all above techniques do not satisfy practical requirements. Aluminum matrix and Sn or Al-Zn alloy as healing agent. No healing effect is observed.

It could be concluded that at the date the introduction of healing agent by meals of microcapsules or microtubes is not promising method for preparing of self-healing metallic materials.

One of the most often investigated technique for incorporation of self-healing ability to metallic materials is applying of shape memory alloys. This technique employs micron-size SMA wires to pull together a crack and then bonds the damaged surfaces together using a partial melting technique. SMAs are materials that will revert to a “trained” shape upon the application of heat due to phase changes involving two phases known as austenite and martensite. The SMA transforms from the martensite to the austenite phase upon heating, and back to the martensite phase upon cooling. In the martensite state, the SMA can be easily deformed, responding to stress by “twinning” or changing the orientation of its crystal structure [136–137]. In self-healing situations, SMA wires embedded in a metallic system revert from martensite to austenite upon heating to achieve crack closure. If the wires embedded in the sample have been prestrained, then a clamping force is exerted on the damaged material.

Matrix materials used in these types of systems to date have all been off-eutectic alloys. Off-eutectic alloys have markedly different solidus and liquidus temperatures, and between these temperatures, an off-eutectic alloy exists as a semisolid paste of solid particles surrounded by molten liquid above a certain temperature. The amount of molten material can be controlled by heating to a specified temperature. Tin and bismuth form one such binary eutectic with a low melting point of 139°C that has been investigated in SMA-based healing studies by Manuel and Olsen [19,138]. A damaged sample can be healed when the temperature of the system is elevated to a point at which the SMA wires attempt to return to their original configuration, and clamp the damaged surfaces together. As the healing temperature is between the solidus and liquidus temperatures, the material partially melts while leaving enough solid to maintain the structural integrity of the system. The liquid at each surface can then flow or otherwise bridge the gap created by the damage and upon cooling resolidify, thus, healing the system. The overall process is shown in Fig. 5.2.

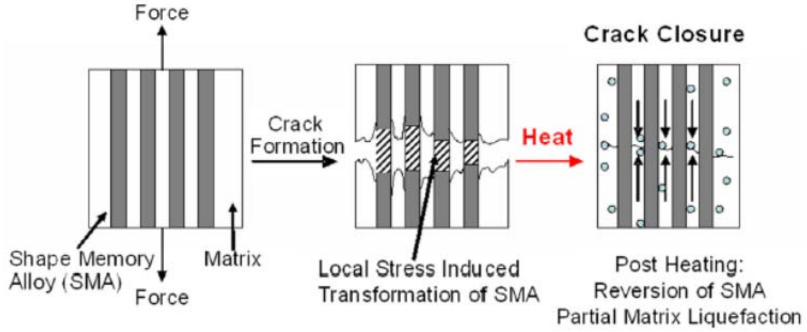


Fig. 5.2. Schematic overview of the self-healing process in metal/SMA composite [20]

Rys. 5.2. Schemat procesu samoleczenia w kompozycie metal/SMA [20]

Manuel and Olson [19] fabricate a Sn-based self-healing proof-of-concept composite using a Sn-13at.%Bi matrix and NiTi SMA wires. The SMA wire reinforcements are continuous and uniaxially oriented with a volume fraction of 1% in the matrix. Prior to casting, the wires are sputter coated with 5 nm of gold to increase the wettability of the wire surface. Tensile tests are performed to assess the mechanical behaviour of the composite and matrix alloys. The composite display 73% increase in uniform ductility in comparison with the unreinforced prototype alloy due to composite toughening: improving from 3.7% to 6.4%, which is attributed to either grain refinement of the alloy due to the presence of the SMA reinforcement or interfacial debonding or crack bridging along the matrix/reinforcement interface. To demonstrate healing efficiency, tensile tests are performed on the composites at room temperature until complete matrix failure. After crack healing, the specimens are again tensile tested to failure to determine the amount of strength recovery, which achieved greater than 95% of the original composite ultimate tensile strength. It is also found [138] that in case of Mg-based alloy the SMA wires pulled the crack closed, the rough crack walls came into contact and prevented full closure. Unlike in the Sn-Bi matrix composite, the force applied by the SMA wires could not overcome the matrix strength of the Mg-based alloy. Poor wetting of the reinforcement and low strength of the interface is also identified as deleterious to the performance of the composite.

Compared with the surface self-healing for corrosion, self-healing of mechanical damage inside metallic materials is very difficult. Main reason is that there is no means for delivery of healing agents in metallic materials. The self-healing methods for polymers and composite materials have been well studied, and excellent methods have been proposed. These methods, however, are difficult to be applied to metallic materials. It seems to ineffective to embed microcapsules or vascular networks filled with healing agents in metallic materials, and the adhesive as a self-healing agent is too weak to bond the cavities and cracks. For the development of self-healing creep cavity and fatigue cavity/crack in metallic materials, new ideas for delivery of healing agents to the damage sites and healing reactions for the fatal damages should be elaborated.

In principle, creep and diffusion processes can contribute to closing micro-cracks and pores at elevated temperatures. Self-healing properties of Al-Cu-Mg alloys are studied in [139–141]. The deformed underaged aluminum alloy AA2024 is aged at room temperature and the influence of the precipitation of fine Guinier-Preston-zones on the mechanical properties is determined. It could be shown by positron annihilation spectroscopy that the deformation-induced defects due to diffusion and clustering of Cu atoms could be healed by secondary precipitations. In the context of metallic composite materials, effects of the yield stress anomaly and the development of oxygen diffusion barriers on the mechanical properties of high-performance materials are being investigated [142].

The work by Lumley and Polmear [143] has revealed a self-healing mechanism in underaged aluminum alloys by dynamic solute precipitation during creep and fatigue loading. In underaged alloys, the residual solute that has yet to undergo precipitation is available to precipitate at open volume defects under applied loading. According to Lumley and Schaffer [140], this mechanism is analogous to the precipitation-induced densification mechanism seen in Al-8Zn-2.5Mg-1Cu (in wt. %) powder alloys. In these alloys, slow cooling from 620°C produces a heterogeneous precipitation of the equilibrium η phase ($MgZn_2$) on open pore surfaces, thereby leading to an 8% reduction in porosity.

Creep studies were performed on a series of aluminum alloys to investigate the performance between an alloy in the underaged and fully hardened (T6) condition. Results from these investigations revealed that the underaged alloy demonstrates a reduction in secondary creep rate. This increase in creep resistance has been attributed to the presence of residual solutes forming solute atmospheres around dislocations (acting as a barrier to dislocation motion) and dynamic precipitation of the θ-phase on defect structures [143].

The precipitation-induced densification mechanism revealed by Lumley and Polmear [143] is further investigated in underaged commercial AA2024 aluminum alloys by Hautakangas *et al.* [144,145] using positron lifetime spectroscopy. This technique uses positrons to evaluate strain-induced defects as a function of aging time. A positron is an electron antiparticle that can be trapped by open volume defects, negative ions, or solute aggregates with a higher positron affinity than the matrix. The work by Hautakangas *et al.* verifies Lumley's observation that dynamic precipitation is occurring on defect structures. They concluded that dynamic precipitation is assisted by strain-induced vacancies and pipe diffusion of solute atoms through the dislocation core. This allows the retained solute atoms to precipitate at internal open volume defects leading to self-healing. In light of the work by Lumley and Polmear [143] on self-healing aluminum alloys, a recent study has highlighted the need to characterize the self-healing behaviour of metals under conditions similar that seen in service. Studies by Wanhill [146] have shown that in aerospace aluminum alloys, fatigue cracks are frequently initiated at external surfaces. These surfaces are continually exposed to corrosive environments reducing the ability for an externally imitated fatigue crack to self-heal. It is also suggested that although there may be experimental evidence of solute migration to free surfaces causing filling of internal cracks and voids, this phenomenon cannot solely explain the change in fatigue behaviour. It is a suggested notion that dislocation drag by solute atmosphere and dislocation pinning by dynamic precipitation are mechanisms that are independent of self-healing and may contribute to the increased fatigue strength of aluminum alloys.

Other metallic material that has demonstrated the potential for self-healing creep cavities is steel. High services temperatures can significantly reduce the creep strength and ductility of steel. Creep fracture occurs when cavities nucleate on the grain boundaries, grow, and then coalesce. Studies by Shinya *et al.* and Laha *et al.* [147,148] have shown that creep cavitation is accelerated by the presence of sulphur. It has also been shown that the removal of sulphur promotes the diffusion of boron to the creep cavity to precipitate boron nitride on the creep cavity surface. Studies on type 304 austenitic stainless steels have demonstrated continuous boron nitride precipitation causing self-healing of the microstructure. It has been suggested that the precipitation of boron nitride plays a dual role in the enhancement of creep performance. The first role is the filling of creep cavities and the second role is the suppression of creep cavity growth through the alteration of its surface diffusion characteristics [149]. The suppression of creep cavity formation can be seen in Figure 5.3.

Shinya and co-workers group [148–154] and Lumley and co-workers [143,156] have proposed practical self-healing methods for creep cavity in heat resisting steels and fatigue cavity/crack in Al alloys, respectively. Their self-healing methods resemble each other and make use of solute atoms as healing agents. The solute atoms in heat resisting steels are delivered to surfaces of creep cavity through volume diffusion in the bulk, whereas the solute atoms in Al alloys are delivered to fatigue cavity/crack surfaces through pipe diffusion along dislocations. The delivered solute atoms segregate or precipitate on the cavity and crack surfaces. Main points of both self-healing methods are summarized and compared in Table 5.1 [157].

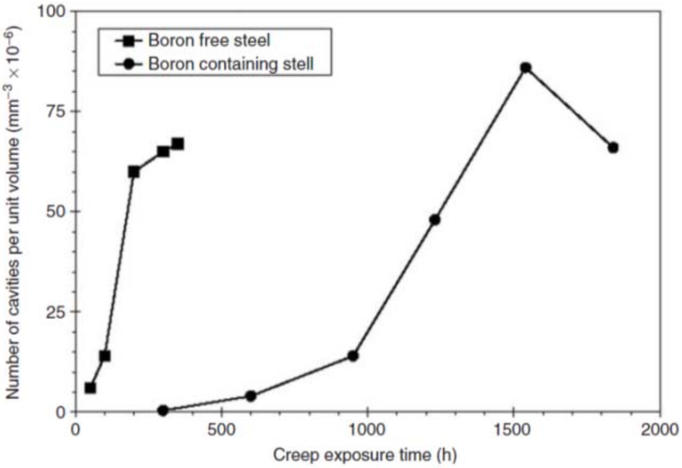


Fig. 5.3. Change in the number of cavities per unit volume in a boron-free and boron-containing 347 type austenitic stainless steels exposed to 78 MPa at 750°C [20]

Rys. 5.3. Zmiana ilości pustek w jednostce objętości w stali typu 347 bezborowej oraz zawierającej bor, poddanej obciążeniu w próbie pełzania wynoszącym 78 MPa w temperaturze 750°C [20]

The steels and the Al alloys with the self-healing of the damages could be produced easily only by additions of traces of B/Ce or small amount of Cu. Heat treatments for the materials are conventional one. Owing to the simple methods and low cost, the self-healing methods would be applied to a lot of materials and contribute to prevention against failures of plants and structures in the near future.

Exploring the mechanism for elimination of vacancies and interstitial defects around grain boundaries is of special significance for nuclear materials. Formation energies and diffusion barriers of point defects at different sites near $\Sigma = 11(113)$ grain boundary in copper have been calculated by first principle in order to investigate the interactions between grain boundaries and defects [158]. The results show that grain boundaries (GBs) facilitate the diffusion of both vacancy and interstitial defects to GBs, and the interstitials are more active than the vacancies in this kind of diffusions. Furthermore, with low energy barrier, interstitials could be emitted from the grain boundary and annihilate bulk vacancies, indicating that grain boundaries can play a role of the sink for both radiation-induced defects and significantly improve the radiation resistance of the material.

Table 5.1. Main points of self-healing methods for creep cavity and fatigue cavity/crack [157]

Tabela 5.1. Główne charakterystyki metod samoleczenia w odniesieniu do pustek pełzania oraz pustek/pęknięć zmęczeniowych [157]

Characteristic	**Shinya's group**	**Lumley's group**
Materials damage	Creep cavities in heat resisting steels	Fatigue cavities/cracks in Al alloys
Healing agents	Solute B and solute N atoms	Solute Cu atoms
Delivery of healing agent	Volume diffusion of solute B and N atoms through bulk	Pipe diffusion of solute Cu atoms through dislocations
Healing reaction	Segregation of B atoms on creep cavity surfaces Precipitation of BN compound on creep cavity surfaces	Precipitation of Cu or Cu-containing phase on fatigue cavity/crack surfaces Segregation of Cu atoms and precipitation of Cu-containing phase on dislocations
Effect of reaction on healing	Suppression of creep cavity growth	Closure of fatigue cavities/cracks Suppression of localized deformation by pinning dislocation

Although the applied research approaches reviewed have obtained marginal success, the development of self-healing metallic systems has the potential to benefit a wide range of industrial applications and thus deserves greater investment in fundamental research.

Chapter 6

Self-healing ceramics

Ceramic materials are generally characterized by strong and directional chemical bonds and, even more so than metals, have a very limited atomic mobility, again making self-healing behaviour very difficult to achieve. However, for these systems, it has been realized that oxidative reactions at high operating temperatures can lead to reaction products that can be used to fill cracks of modest dimensions. If the fine-grained reaction product has sufficient adhesion to the parent ceramic and has decent mechanical properties itself, some interesting restoration of mechanical properties can be obtained. If the reaction product has poor mechanical properties, blocking of the original crack could still be desirable as it will ‘heal’ the protective character of this ceramic material when it is used as an antioxidation coating on top of an underlying metallic substrate [100].

In the case of the structural ceramics, the most severe damage is surface cracks, which is possible to be introduced by crash, fatigue, thermal shock, and corrosion during their service time. Over the past 30 years, ceramics have become the key materials for structural use at high temperature due to their enhanced quality and good processability. Structural ceramics are also expected to be applied in the corrosion environments such as air, because of its chemical stability. Thus, self-healing of surface cracks in the structural ceramics is an important issue to ensure the structural integrity of ceramic components.

Probably, the study on the strengthening behavior of ceramics by heat treatment is reported in 1966 by Heuer and Roberts [159]. Then, Lange and Gupta [160] reported the strengthening of ZnO and MgO by heat treatment, and used the term ‘‘crack healing’’ for the first time in 1970. Now, we can find more than 250 reports on the strengthening effects by heat treatment for cracking ceramics. The crack-healing mechanisms in these reports can be roughly categorized into three groups [63]:

1. Re-sintering.
2. Relaxation of tensile residual stress at the indentation site.
3. Cracks bonding by oxidation.

Re-sintering [161–163], that is, diffusive crack-healing process, is an older crack healing concept and commences with a degradation of the primary crack. This regression generates regular arrays of cylindrical voids in the immediate crack tip vicinity. Also, some studies [164–166] on the model and the kinetics of diffusive crack healing in single crystalline and polycrystalline ceramics have been proposed.

In the field of ceramic nanocomposites, there are many reports also available on crack healing. The original impulsion for research in crack healing of ceramic nanocomposites originates from the works of Niihara and co-workers [167–169]. They observed that the strength of the alumina containing 5 vol. % of submicrometer-sized SiC particles can be enhanced by annealing at 1300°C for 2 h in argon. Various mechanisms have been proposed to explain this phenomenon. Nowadays, this mechanism is confirmed to be driven by the oxidation of SiC particles.

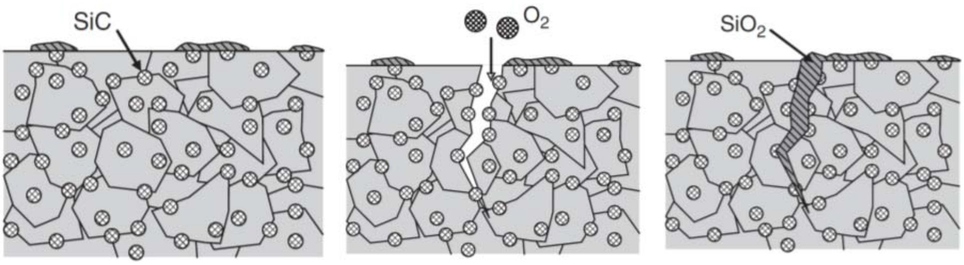
Ando and co-workers observed that the similar crack healing in mullite ($3Al_2O_3$ $2SiO_2$) [170–172], Si_3N_4 [173–176] and alumina [177–180] based composites containing more than 15 vol. % SiC particles can recover the cracked strength completely. They found that the healed zone is mechanically stronger than the base material and proposed the following requirements to obtain a strong healed zone:

1. Mechanically strong products (compared to the base material) should be formed by the crack-healing reaction.
2. The volume between crack walls should be completely filled with the products formed by the crack-healing reaction.
3. The bond between the product and crack wall should be strong enough.

To keep the structural integrity of ceramics, an efficient self-healing should occur. This is possible if healing the surface cracks obeys the following conditions:

1. Healing must be triggered by cracking.
2. Healing must occur at high temperature (as structural ceramics are expected to typically operate at high temperature, about 1000°C, in air) in the corrosion atmosphere, such as air.
3. Strength of the healed zone must be superior to the base material.

Self-crack healing driven by the oxidation of silicon carbide (SiC) can be qualitatively understood to satisfy requirements 1 and 2. Figure 6.1 shows the schematic of the crack healing in the ceramics containing SiC particles heated at high temperature in the presence of air. Cracking allows SiC particles located on the crack walls to react with the oxygen in the atmosphere resulting in healing. Subsequently, the crack is completely healed as oxidation progresses. The details of the valid conditions can be found in [181].



a) b) c)

Fig. 6.1. Schematic illustration of crack-healing mechanism in ceramic containing SiC: a) initial material; b) cracked material; c) materials after healing [63]

Rys. 6.1. Schemat mechanizmu samoleczenia pęknięcia w ceramice zawierającej SiC: a) materiał wyjściowy; b) materiał z zainicjowaną szczeliną pękania; c) materiał po samoleczeniu [63]

The following equation showing oxidation of SiC also supports the above findings:

$$SiC + 3/2\ O_2 = SiO_2 + CO \tag{6.1}$$

There exist two important features in the above mentioned process. One is the increase in the volume of the condensed phase and the other is the generation of the huge exothermic heat. Because mole number of silicon is held constant during the oxidation, the volume increase is found to be 80.1%. As oxidation progresses, the crack walls are covered with the formed oxide. Finally, the space between the crack walls is completely filled with the formed oxide. For the complete infilling of the space between crack walls, it is necessary to contain more than 10 vol. % SiC. Another important parameter for attaining the complete infilling is the size of crack.

Most important factor to decide the self–crack-healing ability is the volume fraction of SiC. It is necessary for achieving strong crack-healed zone that the volume between crack walls is completely filled with the products formed by the crack-healing reaction. Therefore, there is lower limit of SiC volume fraction to endow with adequate self-crack-healing ability. The crack-healed strength varies with SiC volume fraction and shows a maximum at SiC volume fraction of 7.5 vol. % [63]. From the strength difference, the crack-healing ability cannot be estimated by the strength recovery behaviour alone.

However, the fracture surface observations can reveal whether the crack is completely healed.

Ceramics containing SiC whiskers also show self-crack-healing ability, but there are some differences between the crack-healing behaviours driven by oxidations of SiC whiskers and that of SiC particles. This difference arises from the geometric relation between SiC whiskers and the crack wall. The SiC whiskers stick out at the crack wall and bridge between crack walls as illustrated in Figure 6.2. Owing to this geometry, partial bonding between the crack walls can be formed despite the small amount of oxide formation. The partial bonding [180,182] is observed in the crack-healed zone of alumina/20 vol. % SiC whiskers with diameter of 0.8–1.0 µm and length of 30–100 µm).

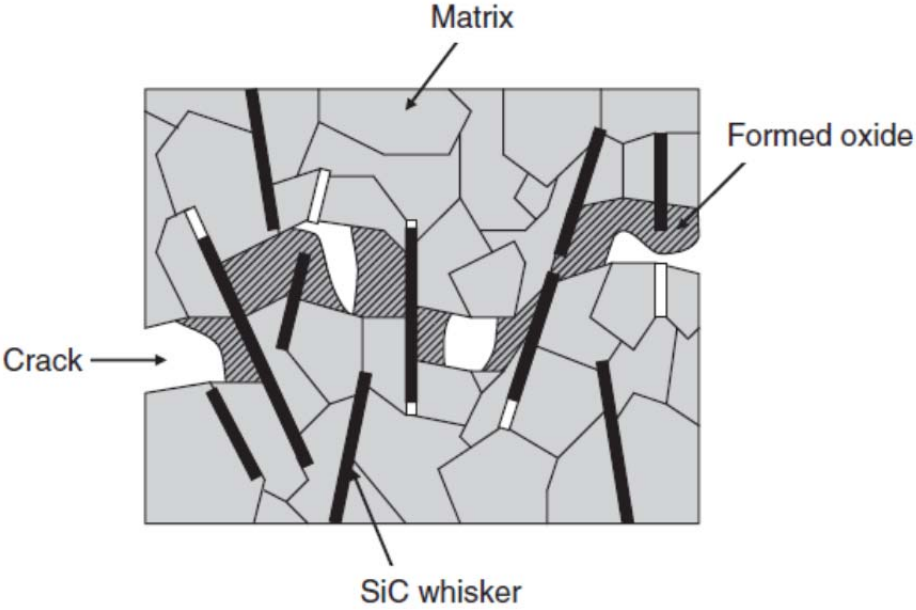


Fig. 6.2. Schematic illustration of crack-healing mechanism by SiC whiskers [63]

Rys. 6.2. Schemat mechanizmu samoleczenia pęknięcia w obecności wiskerów SiC [63]

Also monolithic SiC [183,184] has excellent self-crack-healing ability. These composites can be prepared from commercially available powders using ball mill mixing and hot pressing techniques. Sintering additives does not show any influence on crack-healing ability. Moreover, a further improvement in mechanical properties can be obtained by employing the optimized sintering conditions. For example, entrapped SiC particles [177] presented in the alumina matrix grains, when alumina containing 15 vol. % SiC particles composite is hot pressed at 1600ºC for 4 h. The entrapped SiC particles can inhibit the glide deformation of alumina grains above 1000ºC and this increases the temperature limit for bending strength.

Nanometer-sized SiC fine particles enhance the self-crack-healing rate because it gives large increment in reactive area and makes the surface of SiC particles active. This effect gives large benefit to self-crack healing at relatively low temperatures at which self-crack-healing is completed in more than 100 h.

Reaction synthesis is a promising process for directly fabricating nanocomposites which are difficult to obtain by the normal sintering of nanometer-sized starting powder compacts. Reaction synthesis to fabricate alumina-SiC nanocomposite [185–190] are reported. Using the reaction synthesis according to the formula

$$3(3Al_2O_3 \cdot 2SiO_2) + 8Al + 6C = 13Al_2O_3 + 6SiC \tag{6.2}$$

Zhang *et al.* [191] succeeded in fabricating alumina nanometer-sized SiC particles nanocomposite, in which the formed SiC particles are mainly entrapped inside the alumina grains. Employing the similar process to prepare alumina–SiC nanocomposite, Nakao *et al.* [192] investigated the effect of nanometer-sized SiC particle on the crack-healing behavior.

The result demonstrates that the nanometer-sized SiC with particle size of 20 nm can significantly increases the self-crack healing rate compared to the commercial 270 nm SiC particles. Furthermore, the nano-SiC particles can attain the complete strength recovery within 10 h at 250°C, which is a lower temperature compared to the commercial SiC particles. Although nano-SiC makes crack-healing reaction activated at lower temperatures, it gives same level of refractoriness as the alumina containing commercial SiC particles composite. Therefore, it is noted that the use of SiC nanoparticles is a most valuable route to enhance the valid temperature region of self-crack-healing.

Chapter 7

Self-healing concrete and asphalt

Over the last decade, the concept of concrete infra-structure able to repair itself without human intervention has emerged as a possible cure for overcoming civil infrastructure deterioration. While the idea remains a novelty in practice, it has attracted a significant amount of attention in the research community. Many different approaches to functionalizing concrete to possess self-healing ability have been investigated. Given that damage in concrete is dominated by cracks, much attention has been given to self-repair of cracks. In a few cases, field trials have been launched. These studies hold promise to the feasibility of future civil infrastructure smart enough to detect its own damage and undergo repair by itself. Thus self-healing concrete has significant implications in extending service life, and reducing economic, social and environmental costs of civil infrastructure. That is, self-healing concrete could be a major enabling technology towards sustainable civil infrastructure.

Concrete technically falls within the class of ceramic materials but deserves a special attention because of its unexpectedly high self-healing potential. A concept of self-healing concrete for sustainable infrastructure through reduction of maintenance and repair in the use phase is presented in [193]. According to this concept, self-healing must satisfy at least six robustness criteria – long shelf life, pervasive, quality, reliable, versatile, and repeatable. Self-healing approaches may be broadly grouped into five categories – chemical encapsulation, bacterial encapsulation, mineral admixtures, chemical in glass tubing, and intrinsic self-healing with self-controlled tight crack width. These approaches are schematically illustrated in Fig. 7.1. Related approaches that require human intervention, such as applying heat, are not considered here.

All five self-healing approaches have been demonstrated to be effective to some extent under certain laboratory conditions. However, there are limitations in almost all approaches that will require additional investigation before the vision of truly self-repairing civil infrastructure can be fully realized. In some cases, the limitations are intrinsic to the fundamental nature of the self-healing approach so as to make it impossible to attain robustness. In fact, very little work has been conducted in self-healing under a natural environment. Conditions in the field such as highly variable temperature and precipitation may render self-healing that looks promising under highly controlled conditions in the laboratory meaningless. This is an area of research that should receive much more attention in the future, if the objective is to realize extended service life and to reduce economic, social and environmental life-cycle costs for civil infrastructure. Given the trajectory of research and progress made over the last decade, self-healing sustainable concrete infrastructure appears to be a realistic expectation in the recent future provided that the six self-healing robustness criteria are met with additional research and validated under field conditions.

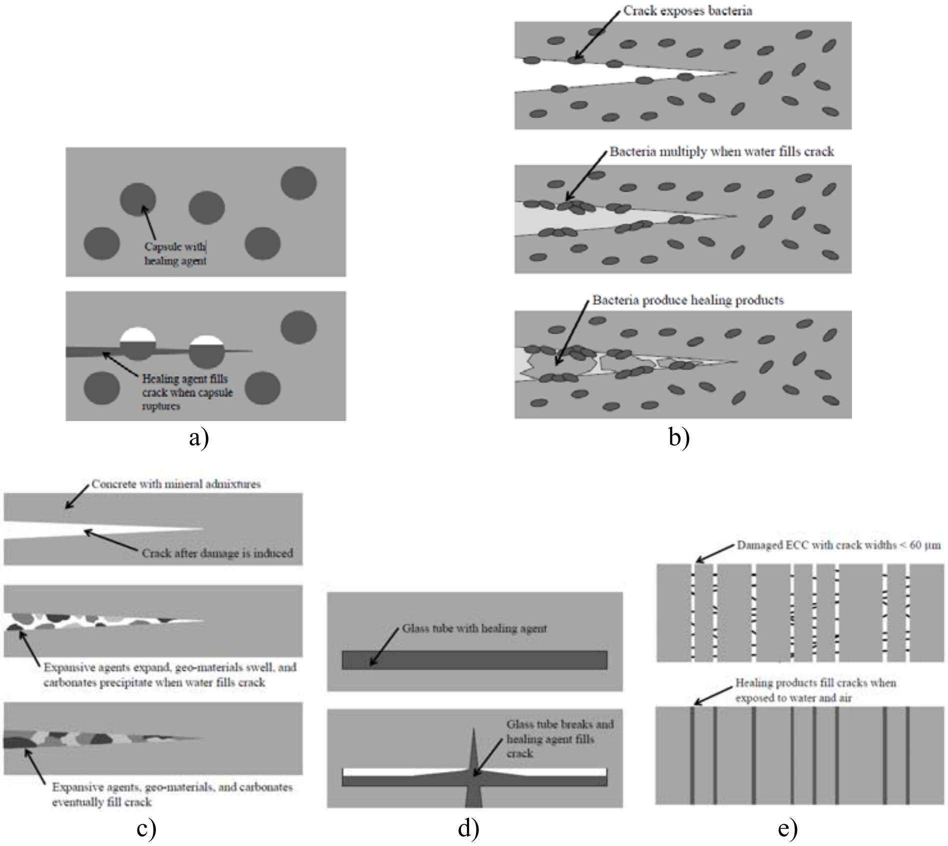


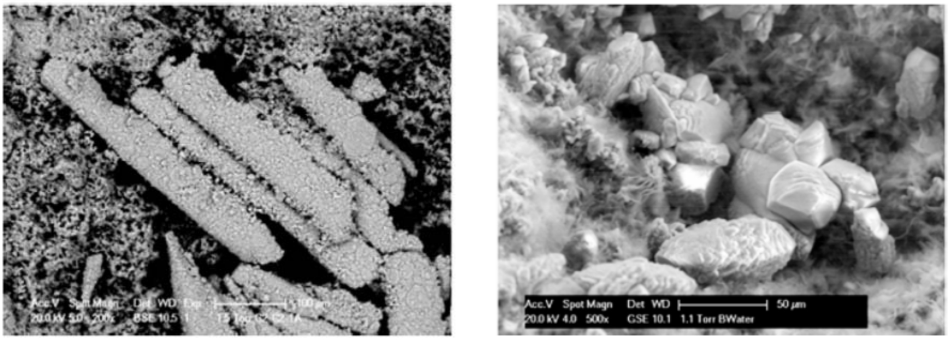
Fig. 7.1. Schematic presentation of: a) chemical encapsulation self-healing approach; b) bacteria additive self-healing approach; c) mineral admixtures self-healing approach; d) glass tubing self-healing approach; e) self-controlled crack width self-healing approach [193]

Rys. 7.1. Schemat ilustrujący poszczególne metody samoleczenia: a) przez chemiczne kapsułkowanie; b) wprowadzanie bakterii; c) wprowadzanie mineralnych domieszek; d) wprowadzanie szklanych rurek; e) kontrola szerokości szczelin pękania [193]

It is concluded that while significant progress has been made over the last decade in laboratory studies, important knowledge gaps must be filled in all categories of self-healing approaches to attain the goal of smart sustainable infrastructures that possess self-repair capability in the field.

Most traditional types of concrete contain variable amounts of embedded unhydrated cement particles. These particles can be considered as homologues of micro-reservoirs filled with healing agent, as they can still undergo hydration upon reactionwith crack-ingress water long after the production of the concrete. This form of autogenous self-healing can be efficient but its functionality has been shown to be largely limited to concrete mixtures prepared with a low water-to-binder ratio. Moreover, it also appears to be effective for cracks with a maximum width generally smaller than 100 μm only [194]. The limited effectiveness appears mainly due to the restricted expansion of exposed unhydrated cement particle surfaces as well as to the limited availability of CO_2 needed for the production of calcium carbonate-based minerals [194,195]. The restricted effectiveness in traditional concretes has led to the development of mixtures purposely designed toyield concrete with superior self-healing properties. In ECC (engineered cementitious composite) the self-healing efficiency could be even further optimized due to the functionality of added PVA fibers to the concrete mixture. The high polymer fiber content in the matrix favors the formation of numerous evenly distributed micro cracks characterized by crack widths of maximally 50 μm upon overloading. The tight crack width in combination with the high binder content results in high self-healing efficiencies as was successfully demonstrated under both lab [194] and field conditions [196]. Although concretes based on low water-to-cement ratio mixtures feature substantial autogenous self-healing capabilities, their application potential for most common constructions is limited for both economic and environmental reasons. Special engineered mixtures are comparatively very expensive, and as cement production accounts worldwide for nearly 10 per cent of anthropogenic CO_2 emissions, current policies strongly advocate future limitation of cement usage [197]. Therefore, alternative self-healing mechanisms, which are not based on the application of non-sustainable cementitious compounds, are currently under investigation.

In the routes described above all healing actions were due to physic-chemical reactions, not involving intermediate agents to control or accelerate the healing reaction. However, in one route the use of calcium carbonate-producing bacteria, as agent to control the healing action in concrete, has been demonstrated successfully. Efficient sealing of surface cracks by mineral precipitation is observed when bacteria-based solutions where externally apply by spraying onto damaged surfaces or by direct injection into cracks. These treatments result in regained material strength and reduction of surface permeability [198,199]. However, in the latter studies bacteria or their derived enzymes are not applied as a truly self-healing system but rather as an alternative, more environmental friendly, repair system. To create autogenous self-healing behavior, at the Technical University Delft the option of using viable bacteria as a matrix-embedded healing agent is explored [200,201]. Major challenge in the latter approach is to identify bacteria and their needed metabolic components which are not only sustainable, but which also do not negatively influence other concrete characteristics. Moreover, this biological system must also feature a long-term self-healing functionality, preferably in agreement with the constructions service life. In the latter studies a specialized group of alkali resistant spore-forming bacteria affiliated to the genus *Bacillus* is identified as an ideal self-healing agent as the spores of these bacteria appear particularly resistant to concrete incorporation and, moreover, feature life spans of over 100 years [202]. Furthermore, once incorporated in concrete, these bacteria appear able to convert various natural organic substances to copious amounts of large, over 100-µm sized, calcium carbonate-based crystalline precipitates, see Fig. 7.2.



a) b)

Fig. 7.2. SEM photographs showing self-healing activity in bacteria-based concrete specimens. Larger (50–500 µm-sized) calcium carbonate-based precipitates produced by concrete incorporated bacteria on the surface of cracks: a) plate-like and b) robust spherical [203]

Rys. 7.2. Struktury SEM ilustrujące proces samoleczenia w próbce z betonu, zawierającego bakterie. Większe (50–500 µm) wydzielenia na bazie węglanu wapnia powstają na powierzchni pęknięć: a) wydzielenia płytkopodobne i b) wydzielenia sferyczne [203]

Such a bacteria-based self-healing mechanism thus appears to be a promising alternative to non-sustainable cement-based healing systems particularly because the formation of large crystalline precipitates potentially enables sealing of larger than 100 µm-wide cracks. The formation of large precipitates can be explained by the high local bacterial CO_2 production rates. Due to conversion of CO_2 into carbonateions under alkaline conditions and subsequent reaction with free calcium ions leached from the concrete matrix calcium carbonate-based precipitates are formed. Furthermore, locally produced CO_2 directly reacts with matrix portlandite (calcium hydroxide) crystals which contributes to calcium carbonate based mineral formation. The intrinsic CO_2-producing capacity with the concomitant production of large-sized precipitates in the bacteria-based self-healing concrete may result in a superior self-healing rate and capacity compared to traditional or engineered non-sustainable self-healing cementitious systems. The beneficial effect of bacterial closure of the deformation induced cracks has been demonstrated in water permeability tests [1]. Even for quite substantial cracking the bacterial self-healing concrete shows no residual permeability after all owing two weeks for crack healing. Such a restoration of water impermeability may be as important as the restoration of mechanical properties, in particular for underground constructions (tunnels, basements and underground garages) in sloppy water carrying soils. While several technical issues yet need to be solved, the route of bacteria supported self-healing concrete seems very promising and is now entering a pre-commercialization stage.

Mechanical properties and self-healing behaviour of Engineered Cementitious Composite (ECC) are investigated in [204]. Three ECC mix proportions with different volume of fly ash are used in this research. The mechanical properties of ECC are revealed via compressive strength, deflection capacity and cracking behaviour. Meanwhile, the self-healing behaviour of ECCs is investigated by sorptivity test and rapid chloride penetration test (RCPT). It is found that both compressive strength and crack width decrease with increasing volume of fly ash, while deflection capacity shows the opposite trend. Micro-cracks produced by pre-loading heal themselves after cured in water, thus decrease sorptivity and charge passed of micro-cracked specimen. The sorptivity test result suggests that ECC mixture with fly ash/cement ratios of 4.0 by weight reveals best self-healing behaviour. Therefore, with excellent capacity of crack width control, deformability and self-healing behaviour, ECC can be an ideal material for durable concrete infrastructure.

In fact, the researches in the area of self-healing concrete and asphalt started in 1994 by pioneering works of C. Dry. He and his co-workers elaborated the concept for application of hollow glass fibers filled with a liquid epoxy resin in order to incorporate self-healing ability in concrete [43,205,206]. Long hollow fibers offer unique opportunities for transporting liquid healing agents over long distances.

Two methods that employ capsules and a vascular system to supply saturated $Ca(OH)_2$ solution for self-healing concrete are discussed in [207]. Self-healing induced by saturated $Ca(OH)_2$ solution is simulated and filling fraction of a crack as a function of healing time is calculated. By combining the calculated filling fraction with the absorption properties and the probability of a crack hitting capsules, the efficiency of self-healing by using capsules to supply saturated $Ca(OH)_2$ solution to cracks is determined. In addition, in the case of using a vascular system, ultrasonic pulse velocity measurements are carried out to evaluate the potential of self-healing. Based on these investigations, conclusions are drawn as follow:

1. When using capsules to supply liquid healing agent to cracks, the liquid healing agent released from capsules increases linearly with the increase of capsule size and dosage.
2. Because the absorption of the bulk matrix, the released saturated $Ca(OH)_2$ solution cannot be held in cracks for a long time for self-healing. The efficiency of self-healing by using capsules to supply saturated $Ca(OH)_2$ solution to cracks is very low. Only a few percentages of a crack (the crack width is 10 lm) can be filled by self-healing reaction products when the capsule dosage is less than 5% (by volume) and the capsule diameter is less 200 μm.
3. The efficiency of self-healing by using a vascular system to transport saturated $Ca(OH)_2$ solution to cracks is high because the saturated $Ca(OH)_2$ solution can be supplied continuously from outside of the specimens. The restoration of ultrasonic pulse velocity through the samples can reach about 80% when saturated $Ca(OH)_2$ solution is supplied continuously for 250 h.

The physico-chemical process of self-healing in blast furnace slag cement paste is investigated in [208]. With a high slag content of 66% in cement paste and saturated $Ca(OH)_2$ solution as activator, it is found that the reaction products formed in cracks are composed of C\S\H, ettringite, hydrogarnet and OH-hydrotalcite. The fraction of C\S\H in the reaction products is much larger than the other minerals. Large amount of ettringite formed in cracks indicates the leaching of SO_4^{2-} ions from the bulk paste and consequently the recrystallization. Self-healing proceeds fast within 50 h and then slows down. According to thermodynamic modelling, when the newly formed reaction products are carbonated, the filling fraction of crack increases first and then decreases. Low solubleminerals such as silica gel, gibbsite and calcite are formed. Compared to Portland cement paste, the potential of self-healing in slag cement paste is higher when the percentage of slag is high.

More details about various self-healing approaches and their chemical nature can be found in [193,207,209].

Another civil engineering material for which self-healing behaviour would be very attractive is asphalt, a semi-porous mixture of bitumen and granular filler materials. Damage in asphalt pavements is affected by the quality of the mastic including its cohesive strength, ability to resist fracture damage, and the ability of microcracks in the mastic to heal during rest periods. The fatigue damage process is influenced by fracture in which crack growth is induced and microcrack healing in which microcrack surfaces, at least partially, rebond. The healing process affects the fatigue process most profoundly when the microcracks are small. Therefore, processes that impede the growth of microcracks, and keep them small, affect the fracture and healing processes and, therefore, the damage process. The interruption of microcrack growth due to dispersed filler that interrupts crack-tip energy is an example of such a process. A large discussion on mechanisms and principles for incorporation of self-healing abilities in asphalt are given in [210].

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Appendix

In all above presented materials and concepts it is assumed that self-healing abilities should be additionally incorporated into base material because man-made structures and especially alloys have generally been designed to be stable and resist change when in service. But, at the moment, there are some valuable researches which demonstrate that this self-healing concept should be modified to allow metals and alloys to undergo controlled microstructural changes so that they can respond to service conditions. This concept will provide challenges both with respect to design principles and in engineering practice.

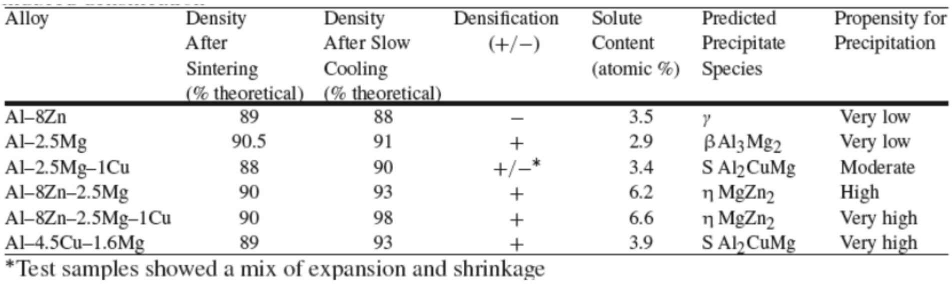
Roger Lumley shows in [A1] how formation of various precipitations in Al-alloys plays role of self-healing mechanism. Formation of such precipitates can be induced by metallurgical processes such as sintering, aging and dynamic precipitation in response to loading conditions. Below we will present briefly some results but more details can be found in [A2–A7].

Self-healing effect in some aluminum based alloys is result of precipitation and densification of the material. Lumley and Schaffer [A2] have shown that substantial pore closure may be initiated by the precipitation of particles of a second phase into the void space of porous materials by slowly cooling from elevated temperature, and this is found to apply to a range of Al alloys as shown in Table A1 [A1]. In particular, the propensity for an alloy to undergo precipitation, and its solute content, are both very important in this process. During slow cooling from an elevated sintering temperature, the alloy behaves according to its phase diagram, in that the decrease in temperature forces the heterogeneous precipitation of a second phase as the alloy moves towards its equilibrium, two-phase state. Figure A1 shows a backscattered SEM image of the surface of an internal pore, demonstrating precipitation into the open pore space.

Age hardening is first reported in a ternary Al-Cu-Mg alloy in 1911 by Alfred Wilm [A3]. This phenomenon is associated with alloy systems in which there is a decreasing solid solubility of solute elements with decreasing temperature. In case of aluminum alloy Al-4Cu the equilibrium precipitate θ(Al_2Cu)is incoherent with the Al lattice and, because it is normally coarsely dispersed, it causes little strengthening. Generally, θ forms when the alloy is averaged at relatively high temperatures, and often appears on grain boundaries. The hardness-time curve for an Al-4Cu alloy aged at 150ºC is shown in Fig. A2, together with the peak aged microstructure which contains both the θ' and θ'' phases as plates viewed edge-on, on the $\{100\}_{\alpha}$ planes.

Table A1. Volume changes in different aluminum alloy systems by the process of precipitation induced densification [A1]

Tabela A1. Zmiana objętości wybranych stopów aluminum wywołana procesami wydzielania, prowadzącymi do zagęszczenia struktury [A1]



Alloy	Density After Sintering (% theoretical)	Density After Slow Cooling (% theoretical)	Densification (+/−)	Solute Content (atomic %)	Predicted Precipitate Species	Propensity for Precipitation
Al–8Zn	89	88	−	3.5	γ	Very low
Al–2.5Mg	90.5	91	+	2.9	βAl_3Mg_2	Very low
Al–2.5Mg–1Cu	88	90	+/−*	3.4	S Al_2CuMg	Moderate
Al–8Zn–2.5Mg	90	93	+	6.2	η $MgZn_2$	High
Al–8Zn–2.5Mg–1Cu	90	98	+	6.6	η $MgZn_2$	Very high
Al–4.5Cu–1.6Mg	89	93	+	3.9	S Al_2CuMg	Very high

*Test samples showed a mix of expansion and shrinkage

Al–8Zn 89 88 − 3.5 γ Very low
Al–2.5Mg 90.5 91 + 2.9 βAl_3Mg_2 Very low
Al–2.5Mg–1Cu 88 90 +/−∗ 3.4 S Al_2CuMg Moderate
Al–8Zn–2.5Mg 90 93 + 6.2 $\eta MgZn_2$ High
Al–8Zn–2.5Mg–1Cu 90 98 + 6.6 $\eta MgZn_2$ Very high
Al–4.5Cu–1.6Mg 89 93 + 3.9 S Al_2CuMg Very high

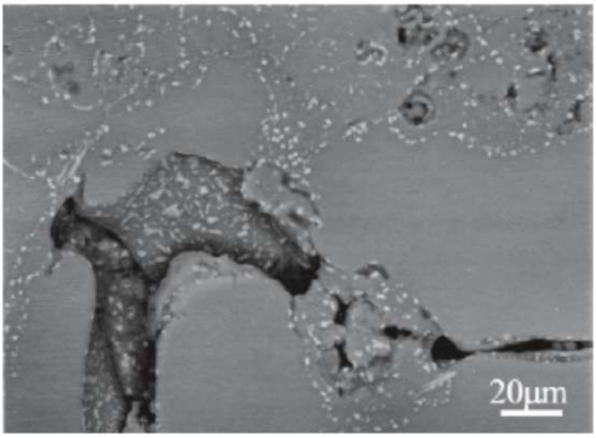


Fig. A1. SEM image showing precipitation onto a pore surface occurring during precipitation induced densification [A2]

Rys. A1. Obraz SEM ilustrujący mechanizm wydzieleniowy przy powierzchni porów, występujący podczas zagęszczania struktury [A2]

Age hardening is first reported in a ternary Al-Cu-Mg alloy in 1911 by Alfred Wilm [A3]. This phenomenon is associated with alloy systems in which there is a decreasing solid solubility of solute elements with decreasing temperature. In case of aluminum alloy Al-4Cu the equilibrium precipitate θ(Al_2Cu) is incoherent with the Al lattice and, because it is normally coarsely dispersed, it causes little strengthening. Generally, θ forms when the alloy is averaged at relatively high temperatures, and often appears on grain boundaries. The hardness-time curve for an Al-4Cu alloy aged at 150ºC is shown in Fig. A2, together with the peak aged microstructure which contains both the θ' and θ'' phases as plates viewed edge-on, on the $\{100\}_\alpha$ planes.

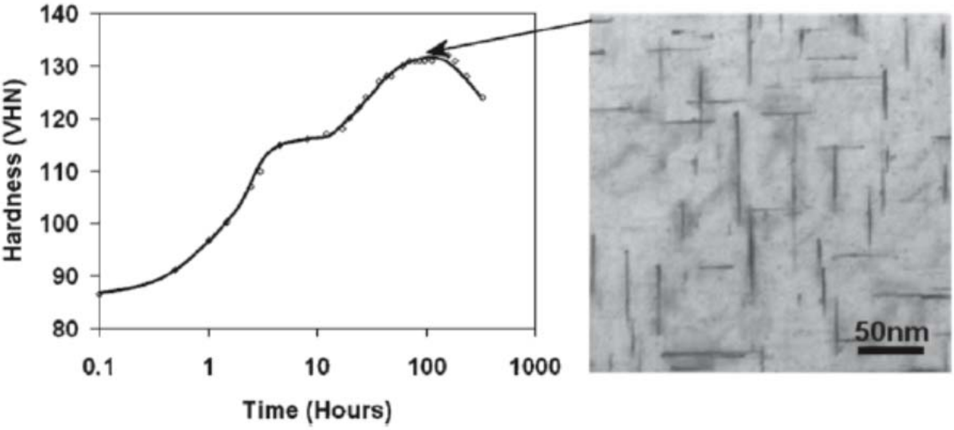


Fig. A2. Transmission electron micrograph showing precipitate structure, and hardening diagram of Al-4Cu aged at 150°C viewed in an $\{100\}_\alpha$ crystallographic orientation [A1]

Rys. A2. Obraz SEM przedstawiający strukturę wydzieleń w orientacji krystalograficznej $\{100\}_\alpha$ w połączeniu ze schematem utwardzania stopu Al-4Cu, starzonego w temperaturze 150°C [A1]

Precipitation into a sharp angle by the process of precipitation induced densification for a geometry that approximates to a crack, is shown in Fig. A3. It is therefore suggested that a process of crack closure or crack modification may also occur during fatigue. What is most important is that enough solute atoms can be rapidly delivered to the crack site, which seems inherently practical by pipe diffusion along dislocation lines.

Fig. A4 shows the volume changes that occur in association with precipitation of θ' in the Al-Cu-Mn-Si alloy 2025 [A4], and it is observed that linear dimensional changes of approximately 0.16% occur to the material during ageing over a range of temperatures. The dimensional changes associated with precipitation however differ with each alloy system. Generally, the growth of Al alloys as a result of precipitation is greatest in alloys containing substantial amounts of Cu, but is reduced progressively with increasing Mg content in alloys such as 2014 and 2024. The Al-Mg-Si alloy 6061 displays effectively no change in dimensions during heat treatment, whereas 7000 series alloys contract (Fig. A4 (b)) [A5].

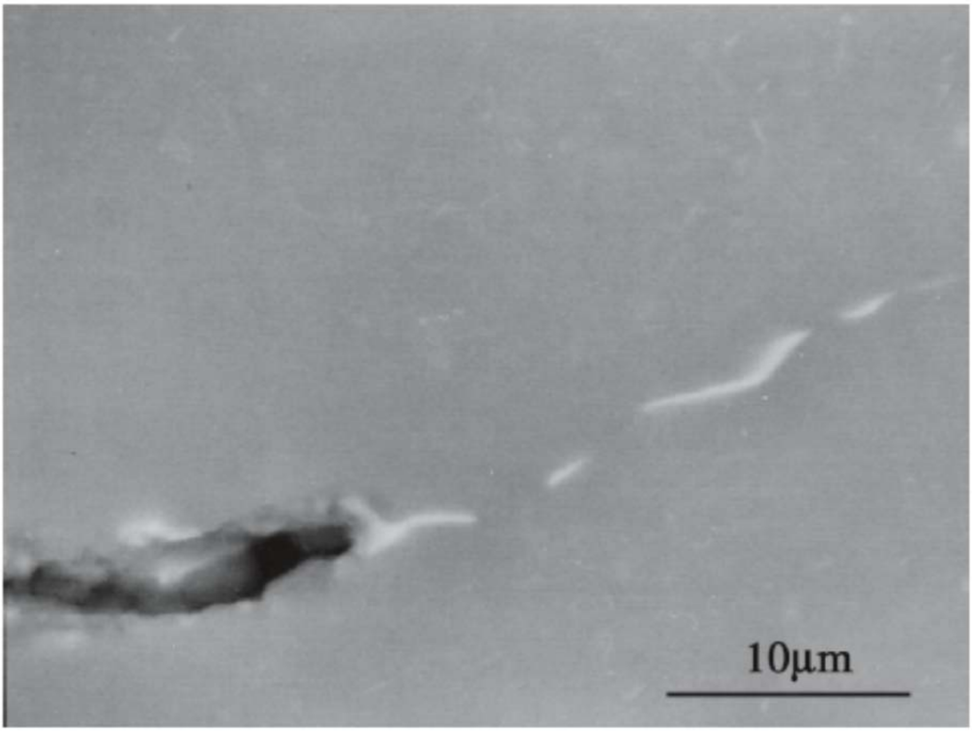


Fig. A3. Backscattered electron micrograph showing a crack-like feature with heterogeneous precipitation at the tip of the defect in an Al-Zn-Mg-Cu alloy. The precipitate phase $MgZn_2$ is observed as the white phase present in the microstructure [A3]

Rys. A3. Obraz w kontraście elektronów wstecznie rozproszonych ilustrujący heterogeniczne wydzielenia szczelinopodobne w końcowym fragmencie wady w stopie Al-Zn-Mg-Cu. Wydzielona faza $AlZn_2$ widoczna jest w strukturze jako faza biała [A3]

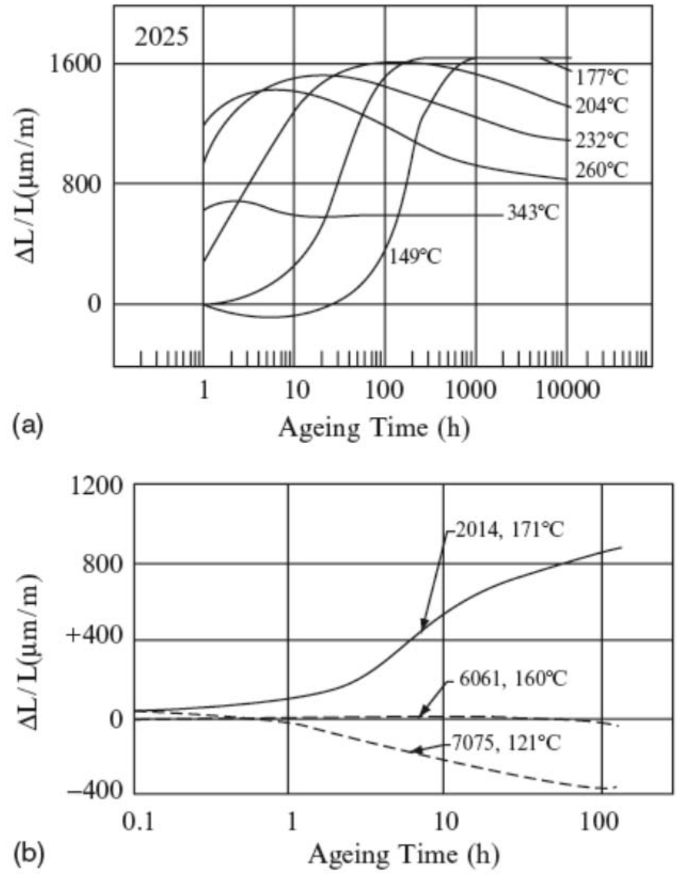


Fig. A4. (a) Dimensional changes occurring during ageing of the Al-Cu-Mn-Si alloy 2025, aged at different temperatures, (b) dimensional changes during ageing of different aluminum alloys during artificial ageing [A5]

Rys. A4. Zmiany wymiarowe występujące w trakcie starzenia stopu 2025 (Al-Cu-Mn-Si) w zależności od temperatury starzenia (a) oraz zmiany wymiarowe w trakcie sztucznego starzenia różnych stopów aluminum [A5]

It is interesting to mention that these processes have parallels with the behavior of natural materials. Certainly, precipitation of crystalline materials into cracks does occur on a wide scale in geological processes (see Fig. A5), but biological processes governing the repair of bone and tissue are more relevant because of their inherent efficiency.


5cm

Fig. A5. Precipitation of crystalline minerals (dendrites) into cracks within rocks. The mineral is a magnesium compound and is a constituent of the parent rock [A1]

Rys. A5. Wydzielenia w krystalicznych minerałach (dendrytach) widoczne w przełomach skał. Minerał zawiera związek magnezu i jest składnikiem skały rodzimej [A1]

In conclusion we would like to site R.N. Lumley [A2]: “Because the studies conducted thus far have been relatively limited, the information contained within this chapter should not be considered exhaustive, and is open to improvement, modification and discussion. However, it does appear clear that self healing in Al alloys in service, and potentially other metals, does seem feasible.” We believe that deeper study of self-healing processes based on precipitation can result in important and useful results not only for aluminum alloys.

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