

Self-Healing Materials

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Self-healing materials are able to partially or completely heal damage inflicted on them, e.g., crack formation; it is anticipated that the original functionality can be restored. This article covers the design and generic principles of self-healing materials through a wide range of different material classes including metals, ceramics, concrete, and polymers. Recent key developments and future challenges in the field of self-healing materials are summarised, and generic, fundamental material-independent principles and mechanism are discussed and evaluated.

1. Introduction

Biological materials are evolutionarily optimised functional systems. One of their most outstanding properties is the ability of self-healing and regeneration of function upon the infliction of damage by external mechanical loads. In nature, self-healing can take place either at the level of single molecules (e.g., repair of DNA) or at the macroscopic level: Merging of broken bones, closure and healing of injuries of blood vessels. These processes are familiar, even self-evident (e.g., healing of a small cut in the finger); however, man-made materials generally do not possess this healing ability. Instead, as all current engineering materials they were and are still developed on the basis of the 'damage prevention' paradigm rather than a 'damage management' concept.^[1] It is, however, undisputed that self-healing

materials would offer enormous possibilities, in particular for applications where long-term reliability in poorly accessible areas is important. In addition, self-healing would be ideal for applications which are prone to damage, such as surface coatings. It has to be emphasised that, in general, it is the functionality rather than the exact external or internal micro-structure which is to be repaired.

Different strategies and approaches to devise self-healing materials in the material classes important in engineering have

been investigated, in particular metals, ceramics and polymers. These materials possess different intrinsic properties; nevertheless, for all of them self-healing is based on the same common general principle and uses the same underlying concepts. Prerequisite for a self-healing of a (mechanical) damage is the generation of a mobile phase, which can close this crack (**Figure 1**).

If a damage is inflicted on the material (**a** and **b**), a crack can occur. Self-healing can take place on the microscopic to macroscopic level. The common principle is the subsequent generation of a "mobile phase" (**c**) triggered either by the occurrence of damage (in the ideal case) or by external stimuli. Subsequently, the damage can be removed due to the directed mass transport towards the damage site and the subsequent local mending reaction (**d**). The latter assures the (re)connection of the crack planes by physical interactions and/or chemical bonds. After the healing of the damage the previously mobile material is immobilised again, resulting in the best case in fully restored mechanical properties (**e**). This general principle is not limited to a single material class. However, the required temperature can vary, depending on the materials: Ambient temperature for concrete, low temperatures (<120 °C) for polymers (and their composites), high temperatures for metals (<600 °C) and ceramics (>800 °C), due to their intrinsic properties. Moreover, the size of damage able to be healed can vary substantially according to the size and number of species being transported.

2. Basic Definitions

Self-healing materials have been intensely investigated over the last 10 years, accompanied by a significant increase in the number of scientific publications (from <20 in 2001 to 114 in 2009). As a result of the multitude of different approaches used and materials studied, self-healing materials can be divided into two different classes, depending on the required trigger and the nature of the self-healing process: Non-autonomic and autonomic. Non-autonomic self-healing materials require a modest

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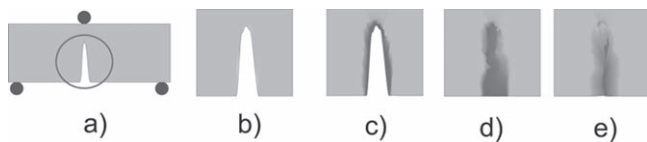


Figure 1. Common basic principle of self-healing materials. a) The mechanical load induces a crack; b) detailed view of the crack; c) a “mobile phase” is induced; d) closure of the crack by the “mobile phase”; e) immobilisation after healing.

external trigger, like heat or light. The (additional) energy for the healing process can be supplied by the prevailing operating conditions as well as by targeted external stimuli (*e.g.*, laser beam, inductive or resistive heating). In the case of polymers, these materials are also denoted as mendable polymers and materials, respectively.^[2] In contrast, autonomic self-healing materials do not require any additional external trigger; the damage itself is the stimulus for the healing. This concept corresponds to an adaptive structure, because the detection of the damage (by a sensor) as well as the repair (by an actuator) proceeds autonomically within the material structure.

Still another property of the respective self-healing process could be used to distinguish material subclasses, leading to the terms ‘extrinsic’ and ‘intrinsic’ self-healing.^[1,3,4] Extrinsic self-healing materials themselves do not owe a hidden intrinsic capability for self-healing; rather, the healing process is based on external healing components, such as micro- or nanocapsules, intentionally embedded into the matrix materials to make them self-healing. The content of these capsules becomes the mobile phase upon damage. On the other hand, intrinsic self-healing requires no separate healing agents, which is to be preferred but, depending on the material class and healing mechanism, not always feasible. Formation of (secondary or primary) chemical bonds as well as physical interactions between the interfaces of the crack (adhesion, wetting) are successful examples to achieve the self-healing *via* this route, provided that the crack width is below a certain limit.

3. Key Developments Concerning Self-Healing Materials

The intense research during the last decade has led to the development of several different concepts for self-healing materials, covering different material classes (*e.g.*, polymers, polymer composites, ceramics, concrete materials, and metals). The key developments regarding general concepts and principles will be discussed in the following short overview.

3.1. Self-Healing Polymers

Currently, polymers (and composites) are by far the most studied material class in the context of self-healing behaviour. This may be due to the ease by which functionalisation and modification of polymeric systems can be achieved, the rather low temperatures required to induce mobility and the large volume of mobile molecules in comparison to the volume of mobile atoms. Initially, research was focused on extrinsic

self-healing by embedded liquid healing agents: Microcapsules filled with a monomer release their content after mechanical damage; afterwards the monomer polymerises in the crack plane with the help of a catalyst, which results in a rebinding of the crack faces (**Figure 2**).^[5] The concept, though undoubtedly working very well,^[5–9] has the intrinsic drawback that locally the regeneration of function can only happen once. Due to the straightforward principle, many other healing agents have been proposed and studied, for instance, pure solvents (*e.g.*, chlorobenzene^[10]) as well as combinations of reactive monomers,^[11] linseed oil,^[12] isocyanates,^[13] polydimethylsiloxane and polydiethoxysiloxane (tin catalysed polycondensation^[14]) or epoxy resins.^[15,16] Moreover, binary systems have been developed which contain additional Pickering stabilisers.^[17]

Semi-commercial microcapsule systems for polymer coatings^[18,19] and bulk polymers are already available.^[20] The healing agent can also be embedded in hollow (glass) fibres enabling the long-range transport of the agent (however, often the macroscopic material properties are negatively influenced).^[21–24] A subsequent biomimetic development is represented by microvascular networks.^[25–26] The systems described can also be used for the simultaneous transport of two healing agents.^[27] A recent numerical study indicated that neither the spherical capsule nor the hollow fibre geometry are ideal for obtaining a good healing efficiency, and much better healing efficiencies can be obtained using elongated capsules with aspect ratios up to a value of 10.^[28] Finally, a recent example of filled microcapsules extended the biomimetic approach: White blood cells are mimicked. A healing agent can be released from microcapsules, which work as a microcarrier (“repair-and-go” system).^[29] The target specificity was increased and a high level of control is achieved. A further extension of the concept might be feasible by linking the generic healing capabilities to specific

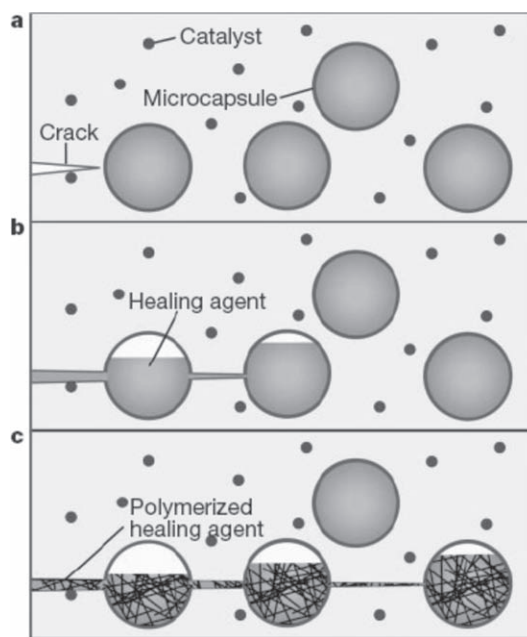


Figure 2. Self-healing with the help of microcapsules. Reproduced with permission.^[5] Copyright 2001, Nature Publishing Group.

recognition capabilities given by nature (e.g., enzyme/substrate, antibody/antigen).^[30]

The examples of extrinsic self-healing described up to now concern only materials which show autonomic self-healing: The damage itself initiates the healing process.^[3]

Intrinsic self-healing in most cases still requires a targeted external trigger (mostly heat). But also other stimuli^[31] can be applied for the healing of polymers (besides the well-known mechanical stimulus also electrical, electromagnetic, magnetic^[32] ballistic, and photo stimuli^[33]). In the simplest case, intrinsic self-healing is achieved by physical interactions, i.e. heating of the materials results in diffusion of the polymer chains followed by formation of new entanglements, resulting in the closure of the crack.^[34–37] In case of a ballistic damage, sufficient heat is generated to allow self-healing processes, via the formation of secondary chemical bonds (DuPont, Surlyn® und Nucrel®; already used at shooting-stands).^[38–42] For damage involving the cleavage of the (covalent) polymer chains, self-healing can be achieved by the formation of new chemical bonds. Polycarbonates, for instance, possess reactive endgroups^[43] which can be used for the reconnection of polymer chains. In addition, functional sidegroups of polymers can be utilised for reversible thermal crosslinking by Diels-Alder reactions^[44–48] and Michael additions,^[49] respectively. However, frequently higher temperatures (>100 °C) are required for the self-healing process. Constitutional dynamic polymers (dynamers,^[50]) which consist of monomeric components that are linked through reversible connections, revealed interesting potential for self-healing materials (e.g., in polymer networks),^[51] hitherto not yet properly explored.

As compared to covalent bonds, weaker interactions, like hydrogen bonding,^[52–56] seem to offer promising chances for the development of potential intrinsic self-healing materials, provided the spatial density of the bonds is high enough. A prominent current example of an autonomic intrinsic self-healing polymer, which may lead to a large-scale application (started production by ARKEMA),^[57,58] was developed recently by Leibler *et al.*: An oligomeric, thermoplastic elastomer consisting of fatty acids and diethylene diamine functionalised with urea.^[59,60] During a damage event, mainly hydrogen bonds will break which, since being reversible, are able to rebuild after pressing the surfaces of the cut together (**Figure 3**).^[61] The material properties can be influenced by changing the ratio of the monomers.^[62] The same mechanism has now been used by AkzoNobel coatings to create commercial self-healing automotive repair coatings, which are capable of smoothening surface cracks under the influence of a modest temperature rise. Besides the above described hydrogen bonds, mainly metal complexes or metal-ligand-interactions (e.g., terpyridine metal complexes),^[63–66,67] ionic interactions^[40] and π - π -interactions^[68,69] are auspicious non-covalent interactions for potential self-healing behaviour. The resulting materials behave like a molecular hook-and-loop fastener: Chemical bonds (covalent and non-covalent) will break during a damage event, but the non-covalent ones can form again, similar to the macroscopic analogue. Another new field in self-healing materials is “mechanochemistry”: Mechanical stress can activate for instance a catalyst inducing a chemical reaction.^[70,71] Furthermore, mechanophores are capable of visualization of the mechanical stress

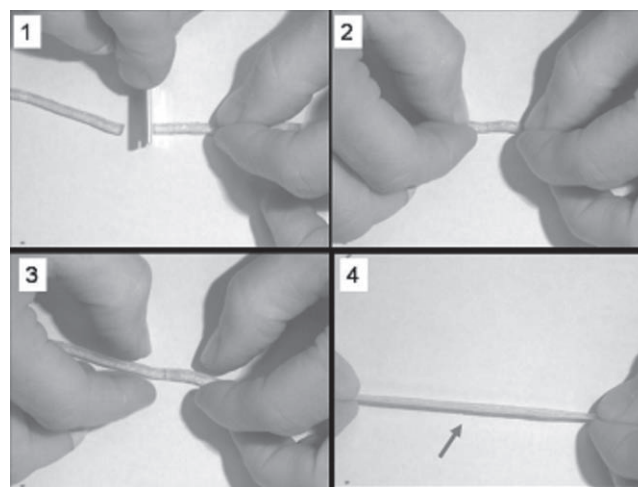


Figure 3. Self-healing properties of a supramolecular polymer by Leibler and coworkers. Reproduced with permission.^[61] Copyright 2008, Ludvig Leibler, CNRS.

in a polymeric material; mechanical forces induce a conversion between a colourless and a coloured structure.^[72]

3.2. Self-Healing Ceramics and Concrete

Recently, the autogenous self-healing of hydraulic concrete materials has been the object of intensive scientific and application oriented research. In damaged concrete, water permeates through the cracks and induces the local formation of hydrates which lead, depending on water pressure, pH-value, crack morphology and crack width, to a detectable crack healing.^[73] As with all materials of interest here, crack width plays an important role in the self-healing process. For this reason, Engineered Cementitious Composites (ECC) have been developed that control the crack width to values below 60 μm even for very high strains well in excess of the strain leading to the first observable crack.^[74] In addition, a bio-inspired approach to self-healing concrete is being investigated: Bacteria are immobilised in the concrete and will be activated if water permeates into fresh cracks, where they start to precipitate minerals.^[75] In contrast, little is known on the regeneration processes in cracked engineered ceramic materials. Thus, the maximum crack length and, more importantly, the width of the mendable cracks, the optimal conditions (preferably low temperatures) as well as the local heat transport properties which change with crack growth and shrinkage, still remain as open questions. With most current ceramics, very high local temperatures are required for repair, due to the high activation energies of the diffusive mass transport in the covalent or ionic structures of ceramics (e.g., SiC/ $\text{Al}_6\text{Si}_2\text{O}_{13}$ -composite: 1300 °C).^[76] On the other hand, it could be shown that Al_2O_3 - and $\text{Al}_6\text{Si}_2\text{O}_{13}$ -ceramics reinforced by SiC-whiskers are able to completely heal cracks up to a length > 100 μm .^[77] The extensive regeneration of the original strength could be demonstrated in SiC- and Al_2O_3 -ceramics (sintering temperature >1400 to 1600 °C).^[78] Considerably lower reaction temperatures can be expected if the grain boundary is wetted by an intergranular glass phase. Depending on the glass transition

temperature T_g (Na-Ca silicate glass 500 °C, and SiO_2 1100 °C), stress relaxation processes, viscoelastic flow processes and diffusion can be initiated at considerably lower activation temperatures. The healing reaction starts by grain boundary and surface diffusion at contact points in the region of crack faces.^[78] Further energy supply results in the formation of spherical and cylindrical pores that can collapse at high temperatures provided they have small radii. The driving force is the reduction in surface energy (*Rayleigh instability*). Model calculations taking into account the surface diffusion-controlled collapse in Al_2O_3 have shown that a pore radius smaller than 10 to 25 nm offers the possibility for closing the pore.^[79] In addition, the oxidation of non-oxidic phases in oxidising atmosphere (air) was shown to be another effective healing mechanism.^[80,81] Furthermore, in multi-component and multi-phase ceramic materials the formation of an eutectic melt as well as the local particle rearrangement induced by a phase transition ($\text{ZrO}_{2, \text{mkl}} \rightarrow \text{ZrO}_{2, \text{tetr}}$) are considered as promising healing mechanisms.^[80]

While most of the work in the field of ceramics focuses on crack healing processes at temperatures above the working temperature, few efforts have been made on healing below these working conditions. As an example, a glass phase containing $\text{Si}_3\text{N}_4/\text{SiC}$ -composite already features a significant healing already at 1000 °C (also under cyclic stress), which leads to a distinct increase in the static and the dynamic fatigue strength.^[82] Further investigations on this material have demonstrated a significant influence of the stress frequency.^[83] Other examples are self-healing oxidation and corrosion protection coatings on SiC-ceramics (burner nozzle), where the combustion heat initiates the healing reaction. A reactive filler (MoSi_2) embedded in a SiOC-matrix is oxidised by permeating oxygen, whereby the formed SiO_2 closes the crack completely (Figure 4).^[84]

3.3. Self-Healing Metals

Self-healing (by physical and chemical effects) pursues the objective to recover the function or surface of the metallic material. However, this goal unfortunately is still far from being reached, as self-healing in metals is intrinsically more difficult than in other material classes.^[1] Given the small size of metal atoms and the absence of directionality in the chemical bonds, currently known mechanisms of healing in metals only lead to healing of defects with a rather small volume. Hence, examples of successful work on this class of materials are yet scarce. An effect known and utilised in technology since long is the reaction of metallic surfaces with surrounding material, which

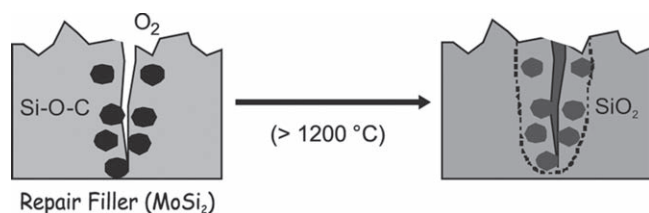


Figure 4. Self-healing of cracks in SiOC/ MoSi_2 oxidation protection coatings on SiC-ceramics.

can lead to surface layers protecting the metal against harmful effects by the atmosphere. In principle, creep and diffusion processes can contribute to closing micro-cracks and pores at elevated temperatures. Recently, the self-healing properties of Al-Cu-Mg alloys were investigated.^[85–87] The deformed under-aged aluminium alloy AA2024 was aged at room temperature and the influence of the precipitation of fine Guinier-Preston-zones on the mechanical properties was 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. In other studies, shape-memory alloys (SMA) were integrated into resins with filled microcapsules.^[88]

Three other examples of self-healing in metal composites or alloys are worth to be mentioned: (1) Ti-Bi-alloys in the form of wires were arranged in parallel to the stress direction, so that a potential crack would proceed vertically to the direction of these wires. The wires perform two tasks: They contribute to crack bridging, and they function as tie rods. As the material is able to undergo a martensitic transformation, the wire can withstand high strains and, thus, enable the bridging of the crack. If the damaged composite material is heated above the martensite finish temperature, the wire will adopt its shorter austenitic form and, consequently, pull the crack planes back. (2) Experimental so-called creep steels have demonstrated the potential for self-healing creep cavities usually caused by nucleation, growth and coalescence, which can lead to creep fracture.^[89–91] Therefore, autonomously self-healing cavities could prevent material failure, for example in high-temperature applications of steel. The precipitation of copper, boron and nitrogen, which are intentional alloying elements in these steels, within the creep cavities improved the long-term stability of steel significantly, provided a heat treatment was applied which would safeguard the mobility of these alloying elements. The heat treatment imposed deviates significantly from that used to give commercial creep steels not having a self-healing capability their optimal properties. (3) Incorporation of capsules filled with liquid into an electroplated coating was recently successfully demonstrated.^[92] The coating was 15 μm thick, while the polymer capsules are a few hundred nanometres in diameters. While the self-healing properties have not yet been proven it is considered a major success to include liquid-filled capsules into an electroplated coating since the electroplating process typically tends to destroy the capsules. In the event of surface damage, the capsules are designed to release a liquid capable of closing cracks or inhibiting corrosion.

Another topic of special interest is the incorporation of intermetallic phases featuring yield stress anomalies into metallic or intermetallic matrices. The research includes theoretical considerations and experimental verification by fabrication of composites, mechanical testing and structure characterisation. However, the quantitative evaluation of the efficiency of self-healing in these materials will have to await a full understanding of the interaction of phase composition, size distribution and topology, matrix (e.g., ductile metal, intermetallic phase or high-performance polymer), fabrication method, microstructure, and mechanical properties.

Table 1. Selected potential mechanisms to give rise to self-healing behaviour for the discussed material classes. The colour code indicates the expected or demonstrated level of success (dark grey – positive; light grey – potential; white – unlikely).

Mechanism	Encapsulation	Channel transport	Expanding phases	Temperature increase	Phase separation	Reversible crosslinks	Biological processes	Electrochemical process
Polymer & composites	Dark grey	Dark grey	Dark grey	Dark grey	Dark grey	Dark grey	Light grey	White
Ceramics & concrete	Dark grey	Dark grey	Dark grey	Dark grey	Dark grey	White	Dark grey	Dark grey
Metals	Light grey	Light grey	Dark grey	Dark grey	Dark grey	White	White	Dark grey

applications (e.g., LEDs) or of medical implants could contribute significantly to optimise economic efficiency; for example the lifetime of stents could be elongated and, thus, therapy costs could be reduced significantly. Optimised lightweight construction accompanied with a higher structural reliability in aircraft and automotive engineering could reduce energy costs as well as environmental burden. The high potential for applications of these materials is also manifested in the started production of self-healing elastomers by Arkema and by self-healing coatings (e.g., Autonomic MaterialsTM).^[58]

4. Fundamental Principles and Mechanism

The above overview on the self-healing behaviour of three distinctly different material classes described some of the prevailing healing concepts and their potential applicability to each material class (Table 1). The concepts apparently can be applied more easily to polymers than to metals or ceramics, due to the special molecular architecture of the polymers and the temperature range in which they are used. However, the latter material classes also offer good chances, whereby concepts developed either exclusively for them or originally for polymers could be applied. The different lines of research could be expected to profit from synergy effects, despite the lack of such effects up to now.

5. Potential Applications of Self-Healing Materials

During their use, all natural and synthetic materials accumulate damage. If the accumulated damage zone exceeds a critical value, this will result in component failure and, consequently, in loss of the function of the device. In contrast, self-healing materials have the ability to reverse the damage development once, several or even multiple times and hence are able to expand the lifetime and the reliability of the material and thus of the device significantly ('damage management'). Such new levels of performance are of particular relevance to materials that are used without or with only limited access by men, for example in medical applications as well as in civil, aerospace, automotive and power engineering. If self-healing of damage caused by manufacturing or during application can significantly increase the effective lifetime and reliability of future novel materials, costs could be drastically cut down, also by reducing monitoring and controlling measures. In addition, a substantial saving of resources and energy could be anticipated due to the reduction of hitherto necessary safety margins for the constructive geometry of mechanically, thermally and corrosively exposed components in almost all technical areas. Self-healing materials would greatly improve materials' reliability and, thus, revolutionise component construction and design. Moreover, the extension of the lifetime of critical components, for example in constructions for alternative energy production (wind energy, photovoltaic, solar heat), in new lighting

6. Conclusions

Research on self-healing materials has been a topic for almost one decade now and represents a wide interdisciplinary area, showing a large variety of different approaches. The progress achieved also becomes visible in dedicated conferences (Delft 2007, Chicago 2009, Bath 2011). Some of the concepts developed are driven by the direct application of the materials. However, to gain a deeper understanding of the basic mechanisms and principles of self-healing materials is still a challenging aim. If attained, it will undoubtedly lead to the development of a next generation of (tailor-made) self-healing materials.

Up to now, the design of new self-healing materials has mostly been inspired by nature, and nature will definitely stay an important source of inspiration for the development of new concepts. However, in copying the model the intrinsic character of engineered materials has to be taken into account.^[93–95]

Self-healing up to now refers almost exclusively to structural materials: Mechanical damages are being healed or mended, and afterwards the mechanical properties are (partially) restored. However, other challenges exist, e.g., to develop self-healing materials which are capable of restoring other properties (conductivity, colour, fluorescence) after mechanical damage as well as other negative influences (extreme light, heat, and others). The well-established microcapsule concept could be successfully applied for the restoration of conductivity by the release of a charge-transfer salt as 'healing-agent'.^[96] Challenges also exist with respect to nanostructured systems (e.g., photonic nanomaterials/metamaterials). These systems are particularly prone to damage due to their large surface (compared with the volume).^[95]

We expect the next decade of research on self-healing materials to lead to a range of new commercial applications, and that new concepts covering also properties other than mechanical will emerge.

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