Self-healing behaviour in man-made engineering materials: bioinspired but taking into account their intrinsic character

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Man-made engineering materials generally demonstrate excellent mechanical properties, which often far exceed those of natural materials. However, all such engineering materials lack the ability of self-healing, i.e. the ability to remove or neutralize microcracks without (much) intentional human interaction. This inability is the unintentional consequence of the damage prevention paradigm underlying all current engineering material optimization strategies. The damage management paradigm observed in nature can be reproduced successfully in man-made engineering materials, provided the intrinsic character of the various types of engineering materials is taken into account.

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1. Introduction

Engineering materials form the oldest class of man-made materials. They were and are being developed for mechanical purposes, such as to provide strength and stiffness. The properties of such materials depend on the class of materials to which they belong. In the case of metals, the final properties are ultimately determined by the strong, essentially non-directional metallic bond between the atoms, which gives them their valuable combination of strength and formability by plastic deformation, but also a more or less fixed value for their stiffness. Ceramic materials, on the other hand, are based on strong directional ionic–covalent-like bonds, which impart to ceramics not only their high stiffness and high temperature resistance but also their intrinsic brittleness. Polymers are based on an interesting interplay between strong covalent bonds along the polymer chain and much weaker secondary bonds perpendicular to the chain. Unlike the case of metals and ceramics, for polymers, the stiffness can be changed easily (by prior adjustment of the alignment of the molecules to the final loading direction). Finally, in composite materials, at least two materials from different classes are used to obtain a set of properties not easily obtained when using one

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class of materials alone. The intrinsic differences between the various material classes have necessarily led to quite different and non-transferable routes to tailor and improve material properties.

Notwithstanding these differences, all engineering materials ultimately have been developed along a common design paradigm: the damage prevention principle (van der Zwaag 2007). For each material class, appropriate microstructures have been developed that most effectively delay the formation of damage, i.e. the internal separation of a material into two material segments separated by a crack. Given this design strategy, all current man-made engineering materials have in common that during their lifetime the amount of damage can only increase or at best stay constant.

This observation is in sharp contrast to the design concept underlying living ‘natural’ materials, which can be classified as the damage management principle. The key notion of this concept is that the formation of damage is not problematic as long as it is counteracted by a subsequent autonomous process of removing or ‘healing’ the damage.

A common feature in all healing materials is the negative rate of damage formation during the healing stage, during which generally milder loading conditions are imposed than during the damage stage.

Let us now turn to what is necessary at an atomic (or molecular) level to make a material potentially self-healing. First of all, as with any structural material, the self-healing material still has to have its desirable mechanical properties. Hence, it is safe to assume that most of the key structural entities in a self-healing material contribute to this property. As a consequence, self-healing material grades will resemble their classical counterparts designed along the damage prevention concept. For example, a self-healing concrete grade will (superficially) look and behave like an existing concrete grade.

Now, to make a material ‘self-healing’, it is necessary to re-engineer the material such that defects disappear more or less spontaneously, i.e. the empty space of the defect is filled by new matter, which also has the ability to locally restore the macroscopic material properties. Hence, in contrast to current engineering materials, in self-healing materials, a fraction of the total number of atoms making up the material has to be mobile. The mobile component, i.e. the healing agent, not only has to move to the damage site, but also, once it has arrived there, it has to bond the two surfaces together permanently and, in doing so, lose its ability to move.

In the following sections, some solutions to obtain a self-healing behaviour for a range of man-made engineering materials are described. In each example, the natural character of the base material determined the mechanism by which the desired self-healing behaviour was obtained.

2. Thermosetting polymers

The first widely appreciated demonstration of an intentional self-healing engineering material is the epoxy-encapsulated liquid adhesive system developed by a multidisciplinary research team at the University of Illinois, USA (White et al. 2001). The thermosetting epoxy was used as the matrix material for two reasons: first, epoxies are versatile engineering polymers with excellent
mechanical and chemical properties and, second, they are synthesized via a low-temperature cross-linking reaction starting with two low-viscosity ingredients. The low processing temperature and the low viscosity in the starting phase make it easy to introduce discrete healing agents. Realizing that liquids are intrinsically mobile and therefore meet one key requirement for the healing concept, the Illinois team has chosen a reactive liquid resin stored within thin-walled inert poly(urea-formaldehyde) brittle capsules. Upon fracture, the liquid healing agent flows over the fracture surface due to surface tension and comes into contact with crushed catalyst particles also mixed into the epoxy before cross-linking. The catalyst triggers a cross-linking reaction of the healing agent and, provided enough liquid healing agent is available to bridge the gap between the two crack surfaces, a mechanical bond is restored after which the original material can be considered to be healed. In a number of elegant papers (Brown et al. 2002, 2004, 2005a, b, 2006), the Illinois team has demonstrated a high healing efficiency (reaching values of up to 90%) after single fracture due to monotonic loading, as well as a very significant increase in lifetime in the case of fatigue loading (more than 100 times increase at low $K/K_{1c}$ ratios).

In a very recent study, Mookhoek et al. (submitted), using a different polymer system but the same encapsulation approach, provided direct quantitative evidence of the depletion of the liquid-containing capsules in a thin layer surrounding the crack by conducting three-dimensional microtomographic studies involving phase-contrast imaging techniques. A typical example of such a depleted layer surrounding a healed crack is shown in figure 1.
This illustrative figure also points directly at one intrinsic problem of the encapsulated healing agent approach; locally, healing can take place only once. Once the healing agent has flowed out and has cross-linked, healing agent is locally no longer available. Owing to the nature of the barrier wall of the capsules, long-range transport of the healing agent from capsules at distances larger than the microcapsule diameter from the fracture plane is impossible.

In the Illinois approach, the functionalities of the matrix material (providing strength and stiffness) and that of the healing agent (being mobile and reactive) are intrinsically separated. This separation was necessary because, owing to the high cross-linking degree that gives the epoxy (and other thermosetting polymers) their good mechanical stiffness, long-range diffusion of polymer chains or polymer chain segments has become impossible.

An alternative purely solid-state approach to self-healing in a thermosetting system has been developed by Hayes et al. (2007a,b). Their approach focused on dissolving a linear polymer into a thermosetting epoxy. Linear molecules with a solubility parameter carefully tuned to that of the epoxy can meander through the cross-linked network via a reptation mechanism and can restore significant molecular bonding over the interface, provided the two fracture surfaces are brought into intimate contact. The nature of the healing process itself makes it compulsory to heat the material to impart sufficient mobility to the linear molecule and to realize healing on a decent time scale. Furthermore, given the rough nature of the fracture surface, some force has to be applied perpendicular to the fracture surface to bring a sufficient fraction of the fracture surfaces into intimate contact. Using diglycidyl ether of bisphenol A as the matrix polymer and a linear epichlorohydrin-co-bisphenol A polymer as the diffusing agent, more than 60 per cent of the initial strain energy release rate could be recovered using a linear healing agent fraction of only 7.5 wt% following a healing treatment at 140°C. In contrast to the liquid encapsulation approach, the healing process could be repeated a number of times for the same fracture surface, although the degree of recovery decreased per healing cycle.

3. Thermoplastic polymers

Thermoplastics, by their very nature, offer more opportunities to introduce self-healing materials as their molecules are somewhat mobile at temperatures in between the glass transition temperature and the melting temperature. However, molecular mobility generally implies an unwanted loss of mechanical properties, such as stiffness and strength, as well as dimensional stability of the product made thereof.

Four different approaches can be distinguished at this moment.

The first approach is the solvent encapsulation method for thermoplastic polymers patented by Mookhoek et al. (2008). This method resembles the Illinois encapsulation method, but, in this case, a non-reactive solvent is encapsulated. Similarly, as in the thermoset approach, the liquid solvent is locally released once fracture occurs and flows over the fracture surfaces. Provided a solvent with a low vapour pressure is selected, the solvent will not evaporate but will diffuse into the polymer and make it swell locally. Since this process occurs on both sides of the crack, mechanical contact between the two surfaces will be restored. Since the ingress of the solvent leads to a strong reduction of the local glass

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transition temperatures, the macromolecules in the slightly swollen polymer layer become significantly more mobile even though the temperature is not raised. Via polymer reptation, a sufficiently high number of molecular re-entanglements across the former interface are formed. At longer time scales, the local solvent concentration drops to a low level and the original properties of the polymer are, at least partly, restored.

An alternative approach 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 (Kalista & Ward 2007). 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 ionomic material are capable of fully covering the hole created by the passage of supersonic bullets of up to 9 mm (figure 2). Similar experiments on non-ionomeric polymers of comparable properties invariably left a sizeable hole upon ballistic impact. In a number of quasi-static pull-through studies at various temperatures, Varley et al. (2008a,b) unravelled the various processes involved in healing in ionomeric polymers.

A more 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

![Figure 2. SEM of the impact site of a 7 mm ballistic projectile on an ionomer plate.](0023 15kV ×12 1mm WD 44)

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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 remendable polymers (Chen et al. 2002, 2003). Multifunctional furan- and 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 120°C. Samples of this polymer were stressed to complete failure and subsequently healed by heating to approximately 90–120°C, followed by cooling to room temperature. The healed polymer exhibited approximately 57 per cent 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 remendable polymers, which can go through repeated cycles of cracking and remending at the same site. The limitations of this system are the working temperature of the materials, which is too low (below 120°C) for many applications, and the lengthy and costly synthesis of the monomers, which is problematic for large-scale production. However, new DA–RDA polymer systems based on cheap monomers are currently under construction.

Meijer and co-workers (Sijbesma et al. 1997) have introduced supramolecular polymers that use the cooperative effect and directionality of quadruple hydrogen bond units for mechanical and self-healing purposes. These polymers were fabricated by employing 2-ureido-4-pyrimidone (UPy) end groups, which form dimers held together by self-complementary DDAA (donor–donor–acceptor–acceptor) hydrogen bonds. Monomers containing two and three binding sites led to the formation of linear and cross-linked polymers, respectively. The high dimerization constant leads to a high degree of polymerization. The polymeric networks generated by this method dissociate and melt above approximately 90°C, and behave much as thermoplastic elastomers. Recently, Cordier et al. (2008) reported the development of a self-healing rubber, based on a similar approach.

4. Composite materials

Fibre-reinforced composites are a particularly promising field of self-healing materials because of their fibre content and polymer matrix. When hollow, long fibres offer unique opportunities for transporting liquid healing agents over long distances and providing large volumes of healing agent to the damaged site. In this sense, a fibre-reinforced composite is the closest approximation in self-healing man-made materials to natural materials with a vascular system. The concept was originally introduced by Dry (1994, 1996, 2000) for concrete using hollow glass fibres filled with a liquid epoxy resin. The concept was later implemented by Trask & Bond (2006; Trask et al. 2007a, b) for high-performance carbon fibre–epoxy composites. In their composites, they replace part of the regular 10 μm diameter carbon fibres by hollow glass fibres with an outer diameter of 60 μm and a hollowness fraction of approximately 50 per cent. The glass fibres were intermingled with the carbon fibres in the prepreg production.

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Using a combination of regular all-carbon fibre prepregs and carbon fibre–glass fibre prepregs, a quasi-isotropic laminate with the glass fibres at the $45^\circ$ interlayers was produced, which was then laterally loaded using ball indentation to simulate impact loading. The flexural strength of this composite was measured without indentation damage, after indentation damage and after healing the indentation damage, and the results are shown in table 1. The corresponding data for the ‘carbon-fibre-only’ control composite are also included in table 1.

The data in table 1 show some characteristic trends for self-healing engineering materials.

(i) The initial strength level of the self-healing grade is lower than that of the regular grade. This is not surprising since part of the volume of the material is taken up by the liquid agent, which does not contribute to the strength (and via local stress intensity factors lowers the strength even further). As pointed out by van der Zwaag (2007), this drop in initial strength values is quite acceptable as long as the reduction factor is smaller than the safety factor, which effectively takes into account strength reduction due to unforeseen damage during use, employed in calculating the dimensions of real constructions.

(ii) The strength difference after the impact between the self-healing grade and the control regular grade is significantly less than that for the initial undamaged strength. This trend is not surprising as the inclusion of a weaker phase can also lead to crack ‘blunting’ or beneficial crack branching.

(iii) The post-impact strength of the (thermally stimulated) self-healing grade returns to a high level, while the post-impact strength of the control composite remains at its low value.

It is clear that the field of self-healing composites needs significantly more development, but the combination of tailorable of the healing agent deposition and the generally higher added value of fibre composites over other engineering materials will undoubtedly give self-healing composites a better chance of early commercial introduction.

5. Metallic systems

By its very nature, self-healing of defects in metals is a slow process, as metallic atoms, i.e. the healing agents, are strongly bonded and have a small volume. Generally, defects in metals can be healed by the formation of precipitates at the...
defect sites that immobilize further growth until failure. The healing agents, supersaturated solute atoms dissolved in the matrix or accumulated at the interfaces, tend to have a limited mobility. Even at temperatures close to the melting point, the characteristic diffusion rates result in very small volumes of the transported healing agents. For this reason, self-healing in metals is often restricted to systems operating at relatively high temperatures and for moderate defect formation rates. The self-healing process is most effective for nanoscale defects, as larger defects require a rapidly increasing volume of healing agents. Two particular metallic systems are, however, worth discussing in more detail: underaged aluminium alloys and creep-resistant steels.

Only recently, it was recognized that underaged aluminium alloys can demonstrate superior mechanical properties compared with the fully aged alloys, when free solute atoms can be activated to self-heal nanoscale defects by the formation of precipitates in the open volumes (Lumley et al. 2003; Lumley 2007). When an age-hardenable aluminium alloy is solution treated at high temperatures, quenched and annealed for a relatively short period at elevated temperatures, an underaged microstructure is produced that still retains a substantial amount of solute in solid solution. These solute atoms can diffuse into the open-volume defects created by plastic deformation during creep or fatigue. Self-healing of nanoscale defects in underaged aluminium alloys can be achieved by applying either an additional ageing step after deformation or deformation at elevated temperatures. In creep tests on Al–Cu–Mg–Ag alloys, it was found that dynamic precipitation, in which the movement of dislocations under load promotes the nucleation of precipitates at the defect sites, is a strong self-healing mechanism in underaged alloys. For stainless steels, a similar improvement in creep lifetime was observed at high temperatures (750°C) when the matrix was supersaturated with boron and nitrogen or with copper atoms. The growth of open-volume defects at the interfaces was found to be immobilized by the formation of BN and Cu precipitates at the crack opening (Shinya et al. 2006; Laha et al. 2007).

In recent positron annihilation spectroscopy studies, we have monitored the time-dependent precipitation process responsible for self-healing in underaged Al–Cu–Mg alloys in situ during deformation and annealing (Hautakangas et al. 2007, 2008). Positrons are uniquely suited for these in situ studies as they have a strong affinity for open-volume defects when they are implanted in a material. During their lifetime of 100–500 ps, they are generally trapped at defect sites until they annihilate with an electron, generating two 511 keV gamma particles. Simultaneous measurements of the positron lifetime, characteristic for the defect concentration, and the Doppler broadening, reflecting the momentum distribution of the electrons involved in the annihilation, give a detailed insight into the concentration and chemical composition of the defect sites. The Doppler broadening gives a fingerprint of the chemical environment at the annihilation site. In its simplest form, two parameters $S$ and $W$ are derived from the Doppler-broadened 511 keV gamma particles, where parameter $S$ reflects the spectral weight of the low-momentum electrons and $W$ for the high-momentum electrons.

In figure 3, the Doppler-broadening data for low and high electron momenta are shown in an $(S,W)$ plot. The positron data measured in the underaged (UA) alloy indicate the existence of positron-trapping sites with high local Cu content. Immediately after plastic deformation, the concentration of open-volume defects
is high in both the fully precipitated and UA material. During ageing, the character of the positron traps is observed to change depending on the thermal pretreatment of the sample. In contrast to the fully precipitated T3 material, in the UA alloy, the rapid initial diffusion of retained solute atoms to the deformation-induced open-volume defects yields final positron parameters close to those of the undeformed alloys. This shows that, by interrupting the conventional heat treatment, a significant number of solute atoms remain in solution and that these can be driven to and associated with the deformation-induced open-volume defects, a requirement for the successful implementation of self-healing in age-hardenable alloys.

6. Ceramics and ceramic coatings

As indicated in §1, 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

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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.

Self-healing of ceramic oxide scales, such as Al$_2$O$_3$, SiO$_2$ and Cr$_2$O$_3$, which offer protection against corrosion of an underlying metallic component, is well known (Sloof 2007). In particular, for applications at elevated or high temperature, damage in terms of cracking or delamination of the protective oxide scale occurs due to stresses generated by mismatch of the coefficients of thermal expansion between the oxide scale and the metallic component upon thermal cycling. This damage can be repaired by selective oxidation of the metallic alloy if the component operates in an oxidizing environment, the alloy contains sufficient healing agent (i.e. the selectively oxidized element) and the diffusion of this element in the alloy is fast enough. Apart from sintering, the ability of self-healing monolithic oxide ceramics is limited.

However, healing of cracks in such ceramics may be realized when a component is added that oxidizes if it meets a crack and the reaction products fill up the crack gap. This concept resembles the self-healing concept that has been applied successfully to polymers (cf. §2), where encapsulated liquid adhesive upon fracture is released, fills the crack gap and polymerization is initiated by the catalyst already added to the polymer matrix. Such an approach has been adopted for thermal barrier coatings made of yttria-stabilized zirconia (ZrO$_2$ with 6–8 wt% Y$_2$O$_3$). These coatings are applied to, for example, combustion chambers and the blades and vanes of gas turbine engines to increase the operating temperature and thereby enhance the turbine efficiency. During operation, cracks develop in these coatings, and if these cracks run parallel to the interface, delamination of the coating occurs, which leads to deterioration of the coated component. As an ‘encapsulated’ healing agent, a high-temperature-resistant intermetallic can be added to the coating, which, upon oxidation, forms products that fill the crack gap. To this end, intermetallic compounds based on Mo–Si are being explored (Kochubey & Sloof 2008). Then, a crack gap in the ceramic coating is filled with SiO$_2$ and the associated volume increase is in part compensated by volatile MoO$_3$ species leaving the system.

In contrast to oxide-based ceramics, carbide- or nitride-based ceramics have the ability of autonomous self-healing by oxidation. For example, microcracks in SiC and Si$_3$N$_4$ and their composites can be healed effectively with SiO$_2$ formed upon high-temperature oxidation (Ando et al. 2005). This crack-healing ability makes these ceramics attractive as high-temperature structural components.

A new class of ternary ceramics shows even more promising ability of autonomous self-healing by oxidation. These ceramics are composed of layered compounds denoted by $M_{n+1}AX_n$, with $n = 1–3$, where $M$ is an early transition metal (e.g. Ti, V, Zr, Nb, Hf, Ta), A is an element such as Al or Si, and X is C or N. Recently, oxidation-induced crack healing in Ti$_3$AlC$_2$ has been investigated (Song et al. 2008a, b). In figure 4, it is shown that a 5 µm wide crack in this ceramic is fully repaired due to the formation of mainly Al$_2$O$_3$ and some TiO$_2$ upon high-temperature oxidation. The outward diffusion of the weakly bonded

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Al is much faster than that of the strongly bonded Ti atoms in the Ti$_3$AlC$_2$ structure. The preferential nucleation of Al$_2$O$_3$ occurs mainly at the ledges of the fractured lamellar Ti$_3$AlC$_2$ grains as well as on the hexagonal basal surfaces, thereby ensuring a good adhesion with the parent matrix. Moreover, the properties in terms of hardness, Young’s modulus and coefficient of thermal expansion of the healing product are comparable with those of the Ti$_3$AlC$_2$ matrix. This, in combination with the ultrafine grain size of the reaction product, makes it likely that the mechanical strength is largely restored, but this is still the subject of further study.

7. Concrete

Concrete technically falls within the class of ceramic materials but deserves special mention because of its unexpectedly high self-healing potential. Most traditional types of concrete still contain, even at older age, variable amounts of matrix-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 reaction with crack-ingress water, a process that results in partial or even complete self-sealing of cracks. This form of autogenous self-healing is efficient; however, its functionality has been shown to be largely limited to concrete that has been prepared with mixtures characterized by a low water-to-binder ratio. Moreover, it also appears to be effective only for cracks with a maximum width generally smaller than 100 µm (Li & Yang 2007). The limited effectiveness appears to be largely due to the restricted expansive potential 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, which form the bulk of observed self-healing products (Li & Yang 2007; Nijland et al. 2007).

The restricted effectiveness in traditional concretes has led to the development of mixtures purposely designed to yield concrete with superior self-healing properties. These high-strength and high-performance concretes are based on mixtures with a very low water-to-binder ratio, consequentially resulting in high proportions of unhydrated binder particles present in the material matrix. In engineered cementitious composites, the self-healing efficiency could be
optimized even further due to the functionality of PVA fibres added to the concrete mixture. The high fibre content in the material matrix suppresses localized brittle fracture but, instead, favours the formation of numerous evenly distributed microcracks characterized by crack widths of maximally 50 μm. The tight crack width in combination with the high binder content results in high self-healing efficiencies, as was successfully demonstrated under both laboratory (Li & Yang 2007) and field conditions (Lepech & Li 2006). Although concretes based on low water-to-cement ratio mixtures thus feature substantial autogenous self-healing capabilities, their application potential for most common constructions is limited for both economical and environmental reasons. Special engineered mixtures are comparatively very expensive, and as cement production accounts worldwide for nearly 10 per cent of anthropogenic CO₂ emissions, current policies strongly advocate future limitation of cement usage (Worrel et al. 2001). Therefore, alternative self-healing mechanisms, which are not based on the application of non-sustainable cementitious compounds, are currently under investigation.

One recent and promising development is the application of calcium carbonate-producing bacteria as a healing agent in concrete. Efficient sealing of surface cracks by mineral precipitation was observed when bacteria-based solutions were externally applied by spraying onto damaged surfaces or by direct injection into cracks. These treatments resulted in regained material strength and reduction of surface permeability (Bang et al. 2001; De Muynck et al. 2008). However, in the latter studies, bacteria or their derived enzymes were not applied as a truly self-healing system but rather as an alternative, more environmentally friendly, repair system. Therefore, as, from an economical and practical perspective, autogenous self-healing is most attractive, the possibility to use viable bacteria as a matrix-embedded healing agent to obtain a truly self-healing system was explored (Jonkers 2007; Jonkers & Schlangen 2008). A major challenge in the latter approach was to identify bacteria, and their needed metabolic components, that are not only sustainable, but also do not negatively influence other concrete characteristics. Moreover, this biological system must

**Figure 5. ESEM photographs showing self-healing activity in bacteria-based concrete specimens.** Larger (50–500 μm-sized) calcium carbonate-based precipitates ((a) plate-like and (b) robust spherical) produced by concrete incorporated bacteria on the surface of cracks. Scale bars, (a) 100 μm and (b) 50 μm. (Photographs: Arjan Thijssen, Microlab, TU Delft.)
also feature a long-term self-healing functionality, preferably in agreement with the construction's service life. In the latter studies, a specialized group of alkali-resistant spore-forming bacteria affiliated to the genus *Bacillus* was identified as an ideal self-healing agent, as the spores of these bacteria appeared particularly resistant to concrete incorporation and, moreover, feature lifespans of over 100 years (Jonkers 2007). Furthermore, once incorporated in concrete, these bacteria appeared able to convert various natural organic substances to copious amounts of large, over 100 μm-sized, calcium carbonate-based crystalline precipitates (figure 5).

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 CO₂ production rates. Owing to conversion of CO₂ into carbonate ions under alkaline conditions and subsequent reaction with free calcium ions leached from the concrete matrix, calcium carbonate-based precipitates are formed. Furthermore, locally produced CO₂ directly reacts with matrix portlandite (calcium hydroxide) crystals, which contributes to calcium carbonate-based mineral formation. In contrast to bacteria-based concrete, these CO₂-mediated precipitation reactions are comparatively extremely slow in traditional or chemically engineered concrete (months instead of hours) as local CO₂ delivery here predominantly relies on diffusional transport from a distant source. Particularly, the intrinsic CO₂-producing capacity with the concomitant production of large-sized precipitates of the bacteria-based self-healing concrete that is currently under development may result in a superior self-healing rate and capacity, compared with traditional or engineered non-sustainable self-healing cementitious systems.

### 8. Concluding remarks

While Nature has shown an extreme diversity in microstructures and microstructural systems and, subsequently, has shown a wide diversity in healing mechanisms, it is unwise to try to copy these healing mechanisms in man-made engineering materials in a direct manner. As shown in this paper, engineering materials have their own characteristics and, in designing self-healing behaviour in such materials, their intrinsic or natural character has to be taken into account. Notwithstanding the fact that the field of self-healing engineering materials spans less than a decade, a surprisingly wide range of approaches have already been identified. In the coming years, more routes will be discovered, and it is to be foreseen that some of the concepts may be employed in real commercial material grades very soon.

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