Routes and mechanisms towards self healing behaviour in engineering materials

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Abstract. Modern man-made engineering materials demonstrate excellent mechanical properties, but the lack of the ability of self healing, i.e. the ability to remove or neutralise microcracks without (much) intentional human interaction, which is typical for most materials as encountered in nature. Such self-healing behaviour requires the presence of mobile species, atoms or molecules, in an otherwise solid material. Upon the occurrence of damage the mobile species directionally flow towards the damage location and once arrived there restores the contact between the two crack faces and the mechanical integrity. This directional flow may occur during regular use conditions (self healing behaviour) or conditions during which the mobility is temporarily increased (stimulated self healing).

In this manuscript a brief overview of the routes and mechanisms which have been used to create self healing behaviour in the principal classes of engineering materials: polymers, metals, ceramics, concrete, asphalt, fibre composites, is presented.

Key words: self healing, damage, design.

1. Introduction

Modern engineering materials are the result of extensive and long term research into the relation between composition and microstructure, on the one hand, and mechanical, physical and chemical properties on the other hand. For a given composition the properties of a material depend on its microstructure, a concept covering features from the smallest length scale (nano-meter level) to the length scale of the product itself (centimeter or meter scale). Good mechanical properties invariably involve a microstructure free of defects and a microstructure which is such that the various components of the microstructure all work together in the prevention of either crack formation or crack extension upon application of mechanical load. While the principle applies to all engineering materials the actual optimal microstructures of course depend on the intrinsic building blocks composing the materials. An optimal microstructure for a polymer composed of linear or branched chainlike molecules of course differs from that for a strong ceramic composed of metallic and non-metallic atoms held together by ionic bonds which itself differs from that of a metal composed of solely metallic atoms held together by metallic bonds. Furthermore, the ideal microstructure of composite materials such as concrete, fibre reinforced composites and fibre metal laminates may yet have another optimal microstructural configuration. However, not withstanding these differences, all current materials have in common that they are optimized on the *damage prevention* paradigm [1], i.e. they are very capable of resisting the formation and growth of cracks, but once the cracks are formed, their size and negative influence will always be present and in time can only become larger and more negative, respectively.

In contrast, natural materials, such as skin, wood, bones and skeletons, grass, etc, often have the special ability that they can, more or less autonomously, heal cracks and other forms of accidental damage. This healing ability is the result of a difference in underlying optimization paradigm for natural materials: *damage management*. To obtain healing it is necessary that atoms or molecules flow from their initial position in the vicinity of the damage site to the actual crack and once arrived there restore physical contact between both crack faces. In time, the material newly deposited in the crack will build up proper load bearing ability. The net result is a restoration of the initial mechanical and other physical properties. To obtain such a self healing behaviour the microstructure of biological materials is much more diverse and complex than that of man-made materials, and it is no longer appropriate to regard the material as a material, but it has to be regarded as a system [2].

2. Routes and mechanisms

While previous reviews on self healing materials [1, 3, 4] have focused on describing the various routes to obtain self healing grouped per material class, in this paper the focus is on the physical or chemical mechanism used to obtain autonomous or stimulated healing.

2.1. Encapsulated liquid adhesives. 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 [5]. Realising that liquids are intrinsically mobile and hence localised fluid flow of a reactive liquid is a straightforward route towards a self healing system, the Illinois team has chosen for a reactive liquid resin stored within brittle thin-walled inert poly(urea-formaldehyde) capsules. Upon fracture the capsules in the crack plane are rup-

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tured and liquid resin flows over the fracture surface due to the surface tension. There it comes into contact with crushed catalyst particles also mixed into the epoxy. The catalyst triggers a crosslinking reaction of the liquid resin and, provided enough liquid is available to bridge the gap between the two crack surfaces, a mechanical bond is restored. The cracked material can now be considered to be healed. A thermosetting epoxy was used as the matrix material for two reasons: epoxies are versatile engineering polymers with excellent mechanical and chemical properties and secondly they are synthesised via a low temperature crosslinking reaction starting with two precursors having a low viscosity. The low processing temperature and the low viscosity in the starting phase made it easy to introduce discrete relatively weak microcapsules without premature capsule failure. In a number of elegant papers [6–9] 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 life time in case of fatigue loading.

In a very recent study Mookhoek et al. [10] provided direct quantitative evidence of the depletion of the liquid containing capsules in a thin layer surrounding the crack by conducting 3D microtomographic studies on a cracked and healed sample. A typical example of such a depleted layer surrounding a healed crack is shown in Fig. 1.
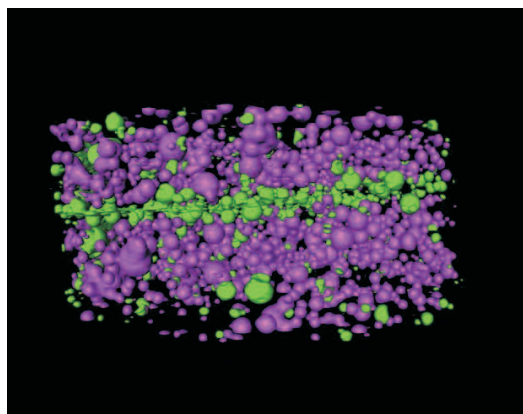

Fig. 1. 3DX-ray microtomographic reconstruction of the depletion of the capsules in the immediate vicinity of the crack. Purple coloured capsules still contain the original liquid healing agent. Green coloured capsules are depleted (see text, colour online)

This illustrative figure immediately points at the intrinsic problem of the encapsulated healing agent approach: locally healing can take place only once. Once the liquid resin has flowed out and has crosslinked, locally it is no longer available to heal new cracks at the same location.

Already at the early stages of development of the field it has been realised that the spherical shape of urea-formaldehyde capsules in the Illinois approach, which is a direct consequence of the interfacial polymerisation reaction used to make the microcapsules, does not allow long distance transport of the healing agent towards the crack and to provide large volumes of healing agent to the damaged site. Long hollow fibres offer unique opportunities for transport-

ing liquid healing agents over long distances. Fibre reinforced composites based on the hollow fibre concept offer the closest approximation in self healing man-made materials to natural materials with a vascular system. The concept was originally introduced by Dry et al. [11–13] for concrete using hollow glass fibres filled with a liquid epoxy resin. The concept was later implemented by Trask and Bond [14–16] for high performance carbon fibre – epoxy composites. In their composites they replaced some of the regular 10 μm diameter carbon fibres by hollow glass fibres filled with a liquid resin system. The glass fibres were intermingled with the carbon fibres in the prepreg production. The resulting quasi-isotropic laminate was then laterally loaded using ball indentation to simulate impact loading. The results showed that a very good healing efficiency could be obtained and that for modest damage levels even full restoration of the initial buckling strength of the composite panel could be obtained. However, given the complexity of describing both the architecture of such a composite, the damage invoked by perpendicular indentation or impact, and the relation between buckling strength and damage in an anisotropic material, there is still a lot to do before the healing efficiency can be quantified in approximate equations enabling actual component design.

While liquid-filled long hollow fibres have attractive features their production is very complex and costly. Hence it could be attractive to explore the route of elongated capsules rather than spherical capsules, to embed the healing agent in the matrix in order to have improved healing at a reduced cost. In a recent numerical study [17] it was shown that an aspect ratio of only 10 is enough to double the healing efficiency per unit area of crack surface. In this study it was also demonstrated explicitly for the first time that the crack opening spacing plays an important role in the degree of healing to be obtained, as the crack opening determines the amount of liquid healing agent to be made available at the crack surface in order to establish contact between both opposite crack faces and to restore load bearing contact across the original crack faces. Some partially successful routes towards the production of elongated capsules can be found in [18].

As a final remark, it should be pointed out once more that in the liquid encapsulation approach, the functionalities of the matrix material (providing strength and stiffness) and that of the healing agent (being mobile and reactive) are intrinsically separated. So, in the liquid encapsulation concept the matrix material itself is non-self healing, and the healing action comes from a distinct liquid healing agent.

2.2. Encapsulated solvents and rejuvenators. A potentially interesting new alternative for the healing of thermoplastic polymers is the encapsulation of a solvent, rather than a liquid adhesive. While in the case of a liquid adhesive the healing agent has all the healing potential and the matrix material essentially is inert, in the case of solvent encapsulation the solvent plays a different role. In solvent based healing the solvent dissolves into the matrix polymer and in doing so, reduces its glass transition temperature. For the right polymer system and a sufficiently high solvent concentration the glass

transition temperature is brought to a value below room temperature. Provided the two faces of the crack are brought into physical contact due to swelling or due to an external force, polymer interdiffusion across the interface can occur and over time the mechanical strength is partially restored. The first set of experiments in this field by Mookhoek [18] yielded a strength recovery of $> 60\%$ after a relatively long contact time of 14 days. An important advantage of this approach over that of encapsulated liquid adhesives is that in time the solvent in time evaporates and a homogeneous polymer sample is retained. For thermoplastic polymer samples produced via a solvent evaporation route or samples produced via injection moulding the method has already shown promising results. To make this approach industrially attractive, it will be necessary to develop capsules which will be able to withstand the heating and deformation processes in a polymer extruder, yet break when fracture in the final sample occurs.

A variant of this solvent based encapsulated route has been used by Garcia Hernandez who has explored the effect of capsules containing a so called re-juvenating oil on the fracture and healing behaviour of asphalt and bitumen [19]. Also in this case, the liquid medium encapsulated serves to depress the glass transition temperature near the crack surface to enable local interdiffusion of the material present.

2.3. Polymer diffusion. An alternative approach to self healing in a thermoset system, in which the matrix and healing agent are not microscopically separated, has been developed by Hayes and Jones [20, 21]. Their approach was based on dissolving a well-chosen linear polymer into a thermosetting epoxy. Linear molecules with a solubility parameter carefully tuned to that of the epoxy can meander through the crosslinked network via a reptation mechanism and can restore significant molecular bonding over the interface provided the two fracture surfaces are brought in 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 realise 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 in intimate contact. Using a diglycidyl ether of bisphenol A (DEGBA) as the matrix polymer and a linear epicholorohydrin-co-bisphenol A polymer as the diffusing agent, more than 60% of the initial strain energy release rate could be recovered using a linear healing agent fraction of only 7.5 wt%. 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.

In the Hayes and Jones approach, as well as in the solvent based healing approach discussed earlier, self healing is based on the reptation of molecules below its glass transition temperature. This concept of self healing based on polymer reptation has been take one step further by Picken et al. [22], who demonstrated that the combination of an amorphous polymer well above its glass transition temperature and nanoparticle reinforcements leads to a polymer with both good healing ability and adequate mechanical properties due to the nano-reinforcements.

2.4. Thermoreversible chemistry. A more chemical approach to induce self healing in thermoplastic materials is the incorporation of thermally reversible cross-link groups in or on the polymer backbone. These thermally reversible crosslinks will break during mechanical loading of the polymer, but can be restored using a modest temperature raise. Unlike the routes involving encapsulation of a liquid, the thermo-reversible route allows multiple healing at the same location as no ingredients are being consumed in the healing process and depletion of healing agent does not occur. Although the route via thermo-reversible bonds require a more drastic re-design of the polymer to make it self healing, the route is seen as very promising.

Two types of reversible chemical crosslinks need special attention as they have been used in self healing systems: the polymer systems based on the Diels-Alder (DA) and Retro Diels Alder (RDA) reaction and the polymers containing quadruple hydrogen bonds.

Wudl and co-workers were the first to employ the DA-RDA strategy to prepare thermally re-mendable polymers [23, 24]. Multifunctional furan- and maleimide-based monomers were used to form highly cross-linked polymeric networks. The schematics a polymer with DA bonds connecting via side chains is shown in Fig. 2.
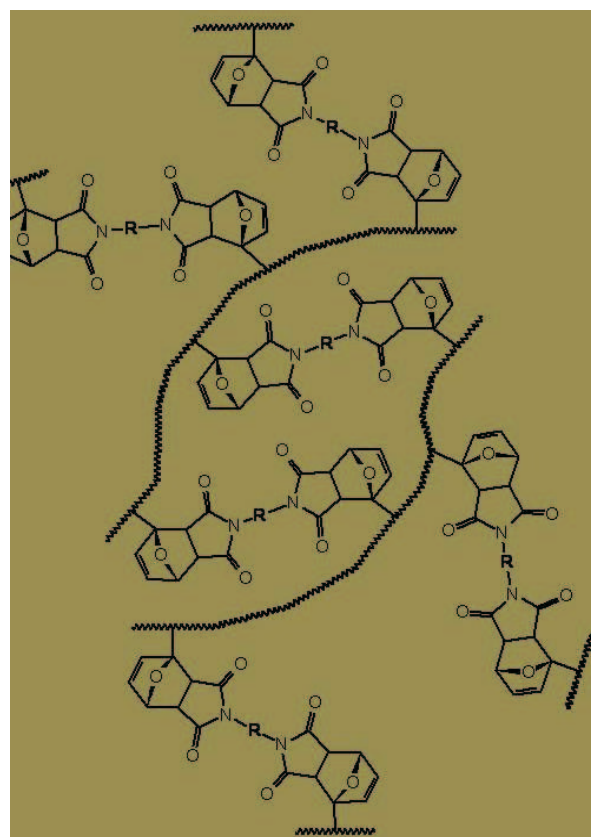

Fig. 2. Schematic diagram of the use of DA reactions to connect main chain polymers via side chain reversible reactions

The polymers were submitted to heating/cooling cycles and their structural changes followed by solid-state ^{13}C NMR spectroscopy. These measurements clearly demonstrated the occurrence of the RDA reaction at ca. 120°C. Samples of this polymer were stressed to complete failure and subsequently healed by heating to ca. 90–120°C, followed by cooling to room temperature. The healed polymer exhibited ca. 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 (<120°C) for many applications and the lengthy and costly synthesis of the monomers that is problematic for large scale production. However, new DA-RDA polymer systems based on cheap monomers are currently under construction.

Meijer and co-workers [25] have introduced supramolecular polymers that utilize the cooperative effect and directionality of quadruple hydrogen bond unit for mechanical and self healing purposes. These polymers were fabricated by employing 2-ureido-4-pyrimidone (UPy) end groups that 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 polymeric networks generated by this method, dissociate and melt at or above 90°C, and behave much like thermoplastic elastomers. Polymers with such a quadrupole hydrogen bond cross-linking are being produced on a semi-industrial scale and offer promising behaviour for self healing coatings and small plastic components. Recently, Cordier et al. [26] have reported the development of a self-healing rubber, based on a similar approach but changing the nature of the reversible chemical bond and taking good care in preventing local crystallization as this would reduce the molecular mobility. This product is now to be developed on an industrial scale too.

Finally, recent work at the TU Eindhoven has shown that sulphur bonds can also be used to create reversible chemical bonds in polymers leading to interesting results.

2.5. Reversible physical crosslinking. An alternative approach to the use of reversible chemical bonds 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 ionomers, such as Surlyn 8920 [27] Ionomers are thermoplastic polymers which typically contain 20–30 mol% of ionic species, often due to a partial acid neutralisation during the polymer synthesis, that are incorporated into the structure of the polymer. These ionic side groups give rise to the formation of electrically bound physical clusters. The clusters have 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 in the

order of 160–200°C. Due to the combined effect of increased elasticity above the melting temperature and the self healing behaviour due to cluster formation, the passage of a 9 mm bullet through a 4 mm thick sheets of ionomeric material leads to full closure of the hole (Fig. 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. [28, 29] unravelled the various processes involved in healing of ionomeric polymers.
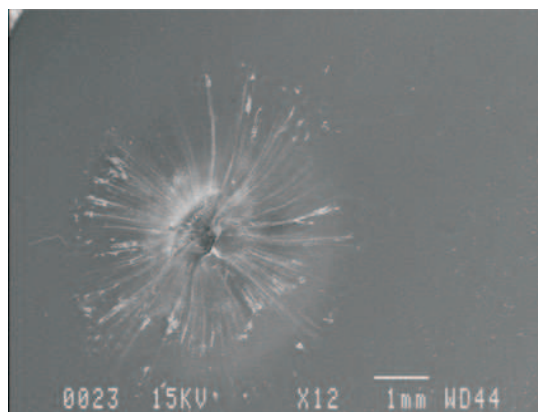

Fig. 3. SEM micrograph of the impact site of a 7 mm ballistic projectile on an ionomer plate

In more recent work, the role of the physical network in self healing behaviour has been further elucidated by adding carboxylic acid based modifiers and their analogues to affect the local charge build up and the healing strength [30]. Current work on ionomeric polymers focuses on the healing of surface scratches in order to create self healing floorings or coatings. Interesting preliminary results have been obtained.

2.6. Opto-chemical reactions. In contrast to other routes in which either temperature or a chemical substance is used to initiate the healing action, a recent study on heterogeneous OXE-CHI-PUR networks has shown that UV radiation can also be used to accomplish the self healing action [31]. The various components are connected with the network which provides different functionalities. The polyurethane network provides desirable heterogeneity through polyurethane and polyurea components, and OXE-CHI provides the cleavage of a constrained four-membered ring (OXE) and ultraviolet (UV) sensitivity through CHI, the latter being a product of deacetylation of chitin, which is the structural element of exoskeletons of crustaceans (e.g. crabs and shrimp) occurring in abundance in nature. The PUR networks were allowed to crosslink under ambient conditions to form solid films and then were mechanically damaged by creating a scratch. Figure 4 illustrates a mechanical damage of OXE-CHI-PUR films. When the damaged area was exposed to a 120 W fluorescent UV lamp at 302 nm wavelength of light for 15 (Fig. 4A2) and 30 (Fig. 4A3) min, the damaged area vanishes. The upper portion of Fig. 4 illustrates IR images of the damaged area, whereas the lower part illustrates optical images.
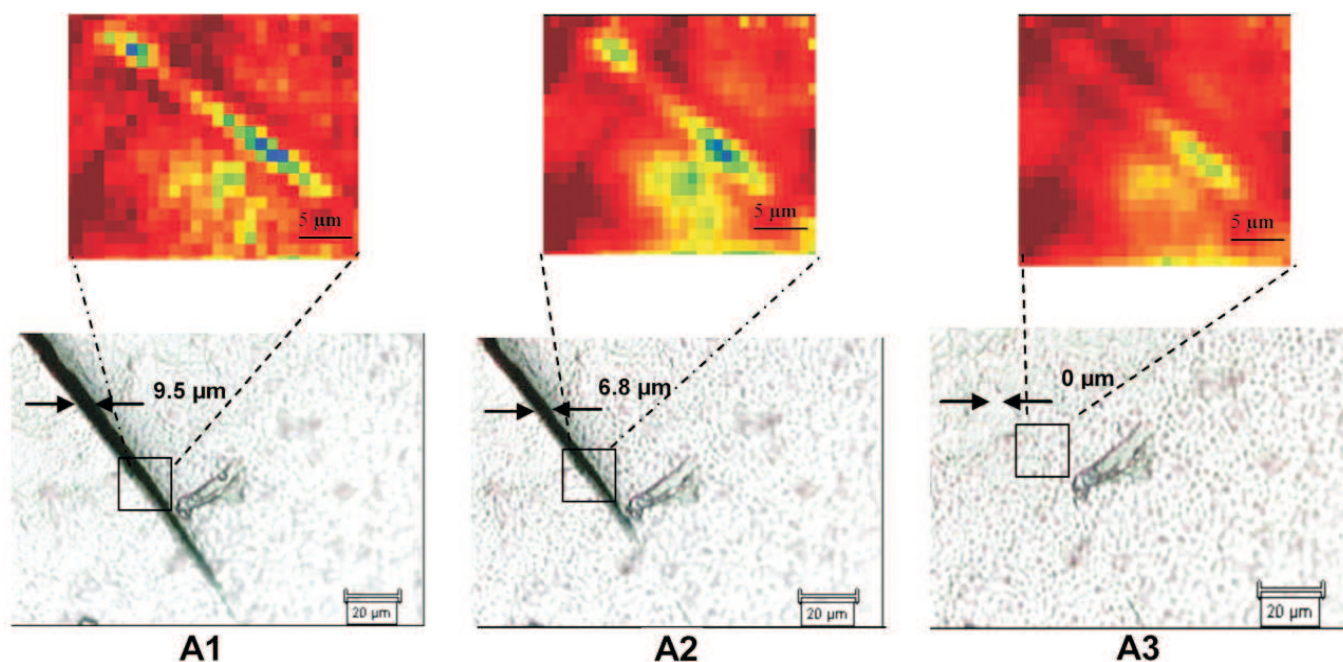
Fig. 4. IR (**upper**) and optical (**lower**) images of OXE-CHI-PUR networks recorded as a UV exposure time. A1 – 0 min; A2 – 15 min; A3 – 30 min. (SOM provides details regarding spectroscopic changes detected by IR imaging.) after Ref. [31] (colour online)

The experiments illustrate that the presence of OXE-CHI precursor is the key factor responsible for remendability of the network. Neither PUR nor CHI-PUR alone is able to repair the mechanical damage, whereas the presence of covalently bonded OXE-CHI entities facilitates the self-healing process. Although the repair action was performed under artificial UV radiation, it has been demonstrated by calculations that the healing reaction would take place in a comparable time in full sun light conditions at mid European latitude. Because crosslinking reactions are not moisture sensitive, dry or humid climate conditions will not affect the repair process. The above networks exhibit the ability to self-repair upon exposure to UV light, but if exactly the same previously repaired spot is damaged again, the ability for further repair may be limited by the thermosetting characteristics of these networks. While this study demonstrated the occurrence of scratch healing upon UV radiation, the actual mechanism of mass transport towards the crack has not been elucidated and more work needs to be performed. Nevertheless the route of healing via optical radiation offers many interesting options for surface healing in coatings at inaccessible applications such as high rise buildings.

2.7. Precipitation reactions. By the very nature of this class of materials, self healing of damage in metals is an unlikely and slow process as metallic atoms, i.e. the healing agents, are a) strongly bonded and b) have a small volume. So the rate of mass transport to fill the damage site is intrinsically low. The self healing process is therefore most effective for nanoscale defects. Two particular metallic systems are worth discussing in more detail: underaged aluminium alloys and creep-resistant steels.

It has been demonstrated that underaged aluminium alloys can show superior mechanical properties compared to 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 [32]. 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 to the open volume defects created by plastic deformation during creep or fatigue. Self healing of nanoscale defects in underaged aluminium alloys can either be achieved by applying an additional aging step after deformation or by applying deformation at elevated temperatures. In creep tests on underaged 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.

For stainless steels a similar improvement in creep life time was observed at high temperatures (750°C) when the matrix was supersaturated with boron and nitrogen or with copper atoms. The open volume defects at the interfaces was found to be immobilised by the formation of BN and Cu precipitates at the crack opening [33–35].

To monitor the time-dependent precipitation process responsible for self healing in underaged Al-Cu-Mg alloys in-situ during deformation and annealing and follow the healing process more closely we performed positron annihilation experiments [36, 37].Positrons are a 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 life time 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 op the positron life time, characteristic for the defect concentration, and the Doppler broadening, reflecting the momentum distribution of the electrons involved in the annihilation gives a detailed insight in the concentration and chemical composition of the defect sites. The Doppler broadening gives a finger print 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 gammas, where parameter S reflects the spectral weight of the low-momentum electrons and W for the high-momentum electrons.

In Fig. 3 the Doppler-broadening data for the low- and high-electron momenta are shown in a (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 remains in solution and that these can be driven to and associate with the deformation-induced open-volume defects, a requirement for the successful implementation of self-healing in age-hardenable alloys.
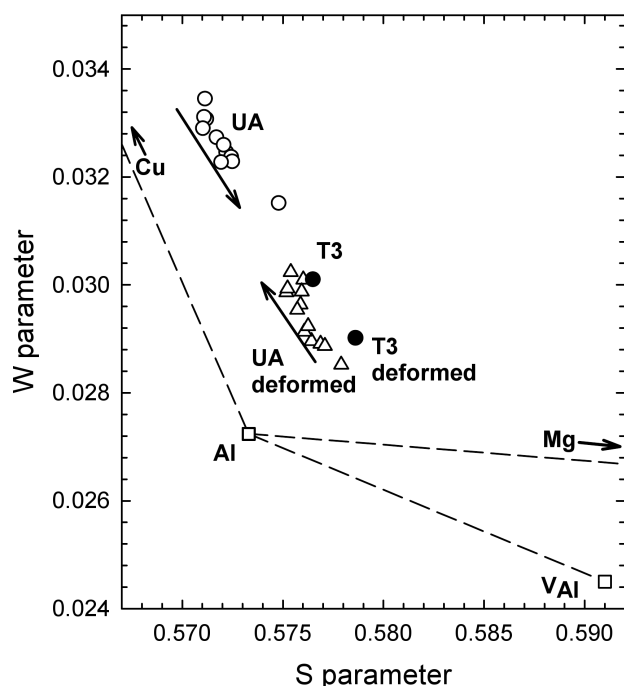

Fig. 5. Plot of the positron annihilation parameters S and W for a self healing aluminium alloy due to a deformation step and due to the healing action (see text)

2.8. Oxidative healing. However, healing of cracks in ceramics may be achieved when a component is added that oxidizes if it meets a crack and the reaction products fill up the crack cap. Such an approach has been adopted for thermal barrier coatings made of yttria stabilized zirconia (ZrO_2 with 6–8 wt.% Y_2O_3). These coatings are applied to for example combustion chambers and blades and vanes of gas turbine engines to increase the operating temperature and thereby enhancing the turbine efficiency. During operation cracks develop in these coatings due to thermal stresses due to a succession of heating and cooling cycles. If these crack 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, compounds based on Mo-Si are being explored [38]. For this system, a crack gap in the ceramic coating will be filled by the SiO_2 formed, while 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_3N_4 and their composites can be healed effectively with SiO_2 formed upon high temperature oxidation [39]. 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 as $M_{n+1}AX_n$ with $n = 1-3$, where M is an early transition metal (e.g. Ti, V, Zr, Nb, Hf, Ta) A is an element of the I (e.g. Al or Si) and X is C or N. Recently, the oxidation-induced crack healing in Ti_3AlC_2 has been investigated [40, 41]. In Fig. 4 it is shown that a 5 μm wide crack in this ceramic is fully repaired due to the formation of mainly Al_2O_3 and some TiO_2 upon high temperature oxidation. The outward diffusion of the weaker bonded Al is much faster than the stronger bonded Ti atoms in the Ti_3AlC_2 structure. The preferential nucleation of Al_2O_3 occurs mainly at the ledges of the fractured lamellar Ti_3AlC_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 modules and coefficient of thermal expansion of the healing product are comparable with those of the Ti_3AlC_2 matrix. This, in combination with the ultra fine grain size of the reaction product makes is likely that the mechanical strength is largely restored.

In a very recent study research at the TUDelft has shown that under laboratory conditions the Ti_2AlC MAX phase ceramic is even capable of restoring a large fraction of the initial strength at its operating temperature of 1000°C no less than 8 times, provided the crack opening distance remains below a threshold value of about 10 μm [42].
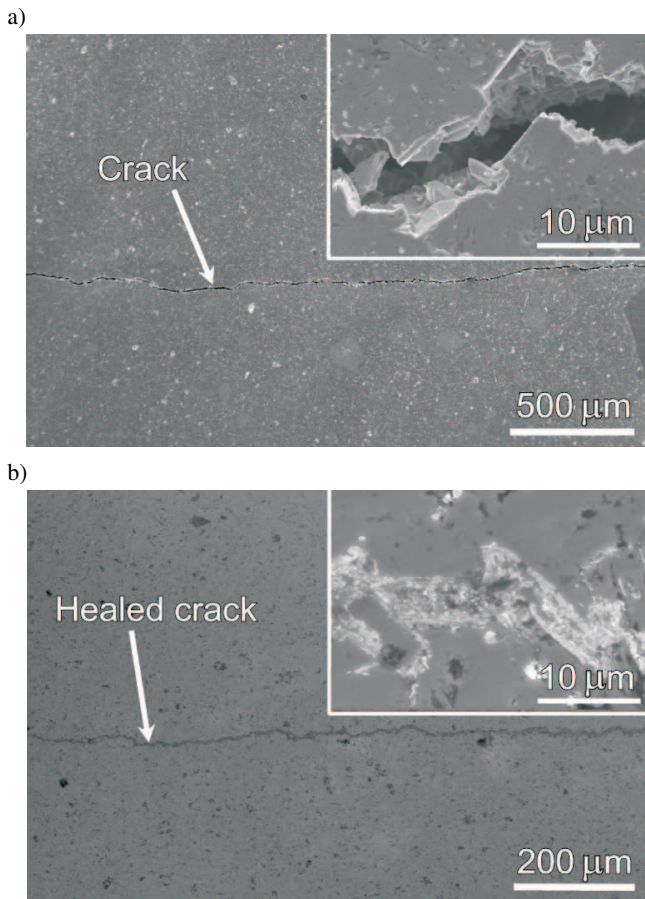
a)

b)

Fig. 6. Oxidation-induced crack healing in Ti3AlC2 ceramic; a) open crack just after fracture and b) the same crack after the healing process (see text)

2.9. Particle jamming. An elegant alternative to the liquid encapsulation route applicable to damaged materials in the presence of an electrolyte is the route proposed by Aksay [43] who utilised colloidal aggregation at surfaces by electrohydrodynamic (EHD) flow. The technology is now being tested with a system consisting of a metal cylinder with a thin layer of insulating ceramic film in the inner wall and a concentric metal wire to apply an electrical field to the system. A colloidal dispersion of polystyrene or silica particles is used to detect and repair defects that occur in the inner wall of the metal tube when the insulating film cracks. When cracks form in the insulating coating, the metal underneath is exposed to create a high electric field and current density at the damaged site. This causes colloidal particles to coagulate around the defect. The aggregation process itself is not sufficient to repair the defect since the voids between the colloidal particles prevent formation of a completely dense surface. One approach to deal with this problem is to use polymeric colloidal particles with low glass transition temperature that can deform to seal the interstitial voids. A second approach is to fill in the interstitial spaces through simultaneous electrodeposition of metal from the anodic (sacrificial) electrode. This produces a coating of a ceramic/metal composite at the site of the initial defect, preventing further material failure.

Electroplating is one option for filling the interstitials between colloids and cement the colloidal patches to the sidewalls. In practice, however, in-situ electroplating is problematic as the high ionic strength of commonly used electroplating baths destabilizes the dispersion. Instead, a sacrificial (copper or nickel) metal anode to fill the interstitials was used. As the anodic metal dissolved, the ions moved by electromigration to the defect. Since the charged colloidal particles have higher electrophoretic velocities than the metallic ions, particles migrated into the defects first. The incoming metallic ions were then reduced to form a metallic bond between colloids and cement them together. Colloidal coagulation was avoided since the ionic strength due to dissolved metal ions is low.

While this particle jamming technique is still at its infancy, it may hold interesting promises for healing in membrane materials such as encountered in batteries. The jamming of particles has also been studied for granular materials and some theoretical guidelines may be found there [44].

2.10. Delayed chemical reaction. Concrete technically falls within the class of ceramic materials but deserves a special attention because of its unexpectedly high self healing potential. 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 reaction with 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 appeared to be effective for cracks with a maximum width generally smaller than 100 μm only [45]. The limited effectiveness appears largely 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 [45, 46]. The restricted effectiveness in traditional concretes has led to the development of mixtures purposely designed to yield 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 fibre content in the matrix favours 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 [45] and field conditions [47]. 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 economical and environmental reasons.

2.11. Bacterial action. In the routes described above all healing actions were due to physico 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 was observed when bacteria-based solutions where 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 [48, 49]. 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 environmental friendly, repair system. To create autogenous self healing behaviour, at the Technical University Delft the option of using viable bacteria as a matrix-embedded healing agent was explored [50, 51]. Major challenge in the latter approach was 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 was identified as an ideal self healing agent as the spores of these bacteria appeared particularly resistant to concrete incorporation and, moreover, feature life spans of over 100 years [52]. 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 (see Fig. 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 CO_2 production rates. Due to conversion of CO_2 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 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. Even for quite substantial cracking the bacterial self healing concrete showed no residual permeability after allowing 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-commericalisation stage.
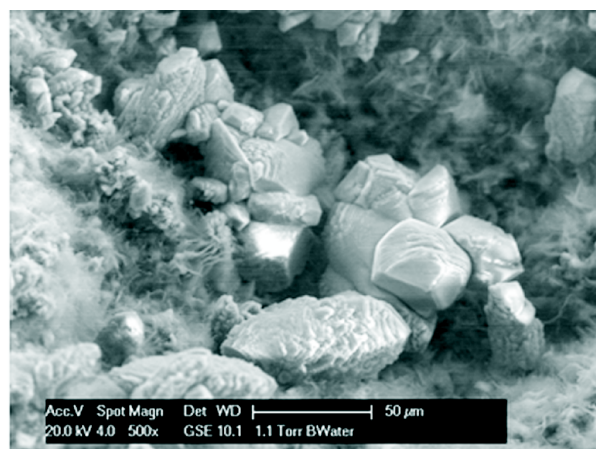
a)
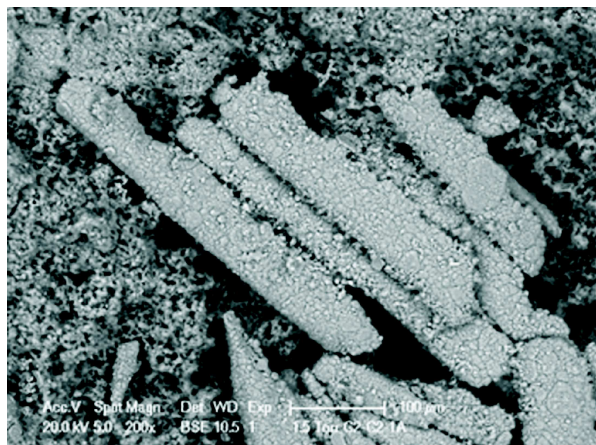
b)

Fig. 7. ESEM photographs showing self-healing activity in bacteria-based concrete specimens. Larger (50–500 μm-sized) calcium carbonate-based precipitates (plate-like, left picture; robust-spherical, right picture) produced by concrete incorporated bacteria on the surface of cracks. Scale bars: left picture 100 μm, right picture 50 μm. (Photographs: ArjanThijssen, Microlab – TU Delft)

3. Conclusions

While the field of autonomous self healing engineering materials started only 10 years ago with only one route and mechanism, that of the encapsulated liquid adhesive route for thermoset polymers, research worldwide for thermosets and other materials has now found a much wider range of alternative routes and mechanisms and undoubtedly more routes will be discovered in the future. To turn these experimental approaches under laboratory conditions into commercially available materials and products, it is necessary to initiate research into the quantification of the healing behaviour as a function of the damage characteristics and the healing mechanisms. Such an extension is now becoming overdue.

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