6 Other Materials, Applications and Future Developments

E. Schlangen

Microlab, Delft University of Technology, The Netherlands
`H.E.J.G.Schlangen@tudelft.nl`

6.1 Introduction

This state of the art report discusses self-healing concepts in cement based materials. Cement based materials have a self-healing property by nature. This autogenic self-healing ability of these materials is known for years and also investigated and proven my many authors, as described in the previous chapters. The autonomic self-healing ability, in which the material is designed to be self-healing, is rather new. This area of research received a strong boost after the paper on 'autonomic self-healing of polymer composites' by White *et al.* [6.1] in Nature in 2001. This paper was the motivation for a lot of research teams to start investigating and developing self-healing concepts for various engineering materials. Several of these concepts are discussed in the next section.

It also initiated an international conference series on self-healing materials, which was organized already three times: in Noordwijk, The Netherlands in 2007, in Chicago, USA in 2009 and in Bath, UK in 2011. The fourth conference will be held in Ghent, Belgium in 2013. Conference proceedings of these events are available with many different ideas and suggestions how to approach the self-healing phenomenon and improve the solutions [6.2-6.4]. Also various smaller workshops and special sessions at general material conferences were organised in the last decade.

Furthermore a number of text-books are published dedicated to the theme of self-healing materials in general [6.5, 6.6], with also special attention for self-healing of cementitious materials. Last but not least, already a number of PhD-theses have come out on the topic. Several of them are referred to throughout this report. Real applications of self-healing materials already exist, also for cementitious materials, but are still limited. Some of them are discussed in section 6.3. In the final section some on-going projects are mentioned and an outlook to the future is given

6.2 Self-Healing in Other Materials

In a publication [6.7] of AgentschapNL in the Netherlands a short overview is given of self-healing techniques applied in different material fields. For further

M. de Rooij et al. (Eds.): *Self-Healing Phenomena in Cement-Based Materials*, RILEM 11, pp. 241–256.
DOI: 10.1007/978-94-007-6624-2_6

references it is better to have a look at the conference proceedings [6.2-6.4]. In the sections below the various material classes are discussed.

6.2.1 Self-Healing in 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 [6.1]. 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 healing agents. Realising that liquids are intrinsically mobile and therefore meet the key requirement for the healing concept, 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 ruptured 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 new approach for autonomous healing of polymer networks is based on cross-linking induced by local stresses. These stresses activate a latent polymerization catalyst – completely unreactive until activated – by removing a polymer-bound ligand, revealing a ruthenium-based or other metal-based catalyst that is ready for polymerization. In the most ideal case, when the local stresses have been removed, the polymer-bound ligand would reconnect to the metal, to form again the latent, ‘sleeping’ catalyst that is ready for a new stress-induced activation.

As a new self-healing concept, plasticity can be introduced in a thermosetting polymer material by a radical-induced redistribution of cross-links. In this way, stresses in the polymer structure can be relieved, and the induced plasticity has the ability to repair the material. A photo-induced initiator decomposition can act as a radical source.

Self-healing is not only of interest for thermosetting polymers to repair the three-dimensional network of cross-links, but also for thermoplastic materials: plastics which are processed by melting them, for example, in extruders. As about 80 per cent of the world’s plastic consumption consists of thermoplastic materials, the importance of healing these materials is self-evident. Self-healing in thermoplastic polymers (like polystyrene or polymethyl methacrylate) with a one-component healing system can be established by embedding microcapsules containing well-selected polymer solvents (such as dichlorobenzene). When a crack proceeds in the thermoplastic, the crack eventually opens embedded microcapsules. Solvent is released into the crack, where it wets the surfaces of the crack. Swelling of the thermoplastic allows a decrease in glass transition temperature, and the increased polymer mobility causes re-entanglement of the polymer chains. The material is healed when the solvent diffuses out or evaporates. Healing of thermoplastics is a physical process, in contrast to chemical healing in thermosetting materials. An improved self-healing mechanism is based on latent solvent storage and in situ release upon damage. To this end, a microporous filler filled with a high boiling solvent encapsulated by a polymer can be used. Advantages of microporous fillers, such as microporous silica, pumice, expanded clay or zeolites, are that they are melt processable – which is crucial for thermoplastic resins – and that better mechanical properties are likely. Although the basic self-healing principle has proven to work for specific thermoplastic materials, applying it to industrially manufactured engineering plastics is another challenge.

6.2.2 Damage-Healing in Fibre-Reinforced Composites

Applications in aerospace and automotive use light, strong and stiff structures made of continuous fibre-reinforced composites. The lifetime of these composites – usually glass or carbon fibres embedded in an epoxy resin matrix - is strongly influenced by delamination of layers that make up the composite material, or by matrix cracks in these layers after impact. Delamination in these composite materials is normally not visible on the outside. Conventional ways to repair thermoplastic matrices in composites are mainly applicable to external and accessible damages, instead of internal and invisible microcracks.

Internal delamination and matrix cracks need an unconventional solution, and one approach is the autonomous healing of composite materials using supramolecular polymers where fourfold reversible hydrogen bonds are present between ureidopyrimidinone (UPy) dimers. By breaking and restoring the relatively weak hydrogen bonds between the dimers, healing can be established. In a practical way, this is done by developing supramolecular thermoplastic polymer as matrix material, and attaching this matrix to the (glass) fibres of the composite. Somewhat above room temperature the supramolecular polymers are present as long chains. At higher temperatures, but below 100 °C, these chains break at the hydrogen bonds, rendering shorter-chained supramolecular polymers. When a crack is present in the matrix part of the composite, it will be healed by increasing the temperature, as this results in breaking of the hydrogen bonds, leading to shorter polymers, which behave liquid-like and flow to the void of the crack. The crack becomes smaller and vanishes eventually. When the healing is completed, the temperature can be lowered to ‘normal’ conditions. The possibilities and limitations of supramolecular polymers in composite materials will be explored further.

Somewhat related are self-healing supramolecular polymer nanocomposites. They consist of a dynamic physically cross-linked polymer network that is reinforced by inorganic nanoparticles. The polymeric part takes care of self-healing as a result of the high mobility level at a molecular scale, whereas the nanoparticles give the system mechanical strength and stiffness. As the self-healing concept – purely based on polymer dynamics and physical interactions - is built into the material itself, such materials can repair themselves an unlimited number of times. Envisaged applications are the use as the matrix of fibre-reinforced composite panels. In a different approach for self-healing in composite materials, moulded-in shape memory alloy wires are used. The shape memory effect, caused by a thermo-elastic phase transformation, results in contraction of pre-strained wires upon heating. This contraction is used to put a compressive force onto both sides of the delaminated area, while - due to the heating - the thermoplastic matrix material is soft and ductile and, hence, easy to reshape. In this way a pure physical healing occurs. Healing of fibre-reinforced composites can also be performed if a part of the reinforcing fibres is replaced by continuous hollow glass capillaries containing a healing agent. After failure of the matrix and capillaries, the healing agent will be released to do its repairing task. However, as these capillaries are continuous and long reservoirs, they will be drained completely into the damaged region. In case of a future damage, the previously drained healing agent can no longer be used. This issue can be overcome by dividing the continuous hollow capillary in compartments, allowing controlled release of healing agent on a local scale. In this way it would be possible to repair small damages several times. Liquid containing fibres are spun from ortho-dichlorobenzene - H_2O Na^+ alginate emulsions. The alginate forms the solid matrix of the capillary, whereas the compartments are filled with ‘oily’ ortho-dichlorobenzene. Testing of compartmented alginate fibre (diameter ~350 μm) containing 45 weight per cent of ortho-dichlorobenzene embedded in epoxy resin with 30 per cent fibre content shows that the theoretical concept is proven. In future steps, to develop a more practical system, two-component epoxy glues can be used instead of the ortho-dichlorobenzene.

6.2.3 Unravelling of Porous Asphalt Pavements

Due to good water drainage and noise reduction properties, over 60 per cent of the surface of the Dutch highways is covered with porous asphalt concrete: coarse mineral aggregates held together by a bituminous binder, in a porous structure. However, porous asphalt concrete is less durable than its dense counterpart. During its lifetime, the material is exposed to many factors which have a deteriorating influence. Traffic loads, rain, snow, de-icing salts, temperature differences due to day/night cycles, UV radiation. They all age the binder, making it more rigid - more prone to crack - and less acting as a glue between the mineral aggregates.

A phenomenon called ‘ravelling’ causes the main durability problem with porous asphalt concrete. Ravelling comprises the loss of aggregates from the surface layer of an asphalt road, and occurs after a few years of using the porous asphalt concrete. It can increase very fast due to the friction of the tires of passing vehicles. Hence, there is a need for a self-healing mechanism – unravelling the asphalt – with the intention to increase the lifetime of the material. From 12 to at least 15 years for the conventionally used single-layer porous asphalt concrete, and from 8 to at least 12 years for more recently introduced two-layer porous asphalt concrete. Two ways are being explored to make aged asphalt 'softer' and to prevent or close as many (micro)cracks as possible. In the first approach (Fig. 6.1), oil- containing capsules are made. When a microcrack in the bitumen further develops and enters a capsule, the oil flows into the crack and partly fills the crack. The asphalt is rejuvenated by the diffusion of bitumen and oil, decreasing the stiffness of the bituminous binder.

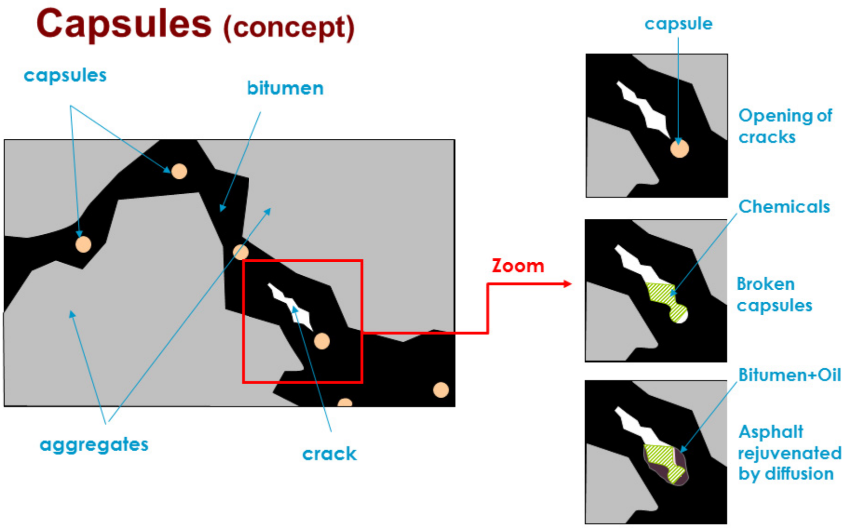

Fig. 6.1 Self-healing asphalt with encapsulated rejuvenator

In the second approach (Fig. 6.2), conductive fibres like steel wool are incorporated into the bitumen. Bitumen melts by the heat generated by electric currents in these fibres, induced by an alternating magnetic field by a coil placed above the asphalt, resulting in crack closure and restoring the material properties. The principle of the induction heating approach has already been proven. To increase the conductivity, electrically conducting fibres appear to be much more efficient than non-fibrous fillers. A practical test has been conducted successfully on a highway in the Netherlands [6.8]. This method is ready to be applied commercially (see also section 6.3).

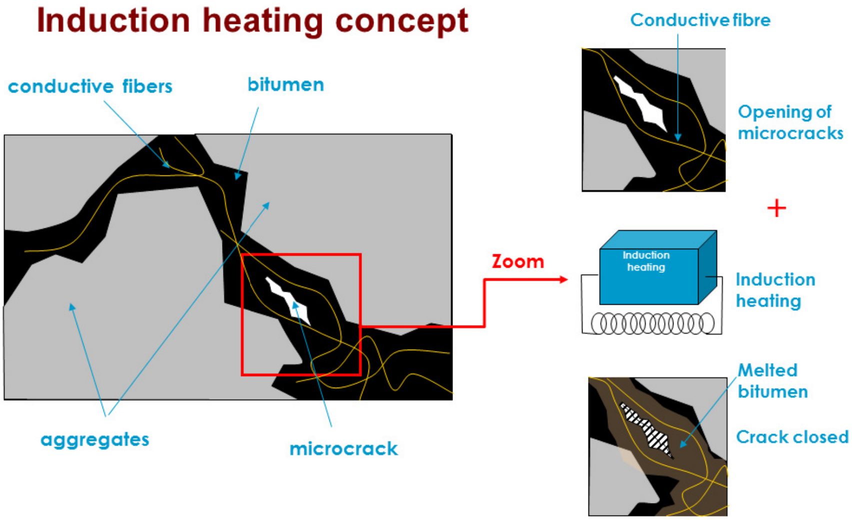

Fig. 6.2 Self-healing asphalt with induction heating approach

6.2.4 Metals and Ceramics

Ti_2AlC: is it a metal or a ceramic? Its lattice structure and resistance to high temperatures are ceramic characteristics, whereas its machinability and toughness are typical for metals. Another remarkable feature of this metal-ceramic is its self-healing ability when used at high temperature, as can be demonstrated by the bending strength recovery after heat treatment. The initial flexural strength of more than 200 MPa drops to about 150 MPa after damage has been introduced. However, heat treatment at 1200 °C in air for only two hours reveals a strength of more than 200 MPa. This remarkable recovery is attributed to the formation of α-Al_2O_3 and TiO_2 by thermal oxidation, which heals cracks, pores or other damaged micro-areas. Cracks of typically 4-10 micron width have been healed. However, the maximum dimensions of crack widths to be filled have not been determined yet. The quantification of the processing window for thermal healing of these materials in relation to the dimensions of the damage is on-going.

As an alternative for this high-temperature oxidative healing, electrochemical healing is a new approach. Here, the desired crack-filling product is obtained by controlled electrochemical reactions at room temperature. Furthermore, this concept would open up interesting opportunities for surface crack healing in tribological applications - as these metalceramics are very sensitive to surface defects - and healing of anti-corrosive coatings.

6.2.4.1 High-Temperature Lubricants

Other self-healing developments in the field of ceramics occur by introducing soft surfaces on the originally hard ceramics. Softening of hard ceramics is especially important when two ceramic surfaces come into contact with each other - and possibly damage each other - as is the case in the contact between ceramic valves and valve seats in car engines. Ceramic materials in car engines allow for higher combustion temperatures, resulting in a better efficiency. Introducing a soft phase on one surface can reduce friction between two ceramic surfaces. By doping yttria-stabilized tetragonal zirconia with 5 weight per cent of the solid lubricant copper oxide and sliding it along alumina, the ‘soft phase’ copper oxide is squeezed out mechanically, forming a thin surface layer and restoring the damaged surface. At high temperatures, above 500 °C, first there is an increase in friction followed by a reduction. At room temperature, the friction is reduced somewhat more due to the fact that a ‘soft’ aluminum hydroxide surface layer forms between the two ceramics.

6.2.4.2 Self-Healing of Nanocracks in Alloys by Nanosized Precipitation

Aluminium is the second most commonly used industrial metal – only to iron. Precipitation hardened aluminium alloys are of great interest in applications where a combination of low weight and high mechanical strength is necessary, such as in airplanes, cars and buildings. Plastic deformation of this type of alloys, due to forces applied to the material, ultimately leads to its failure. Plastic deformation first leads to the displacement of dislocations – linear lattice defects in a crystal structure – through the material, which in turn leads to the formation of defects. When the level of deformation increases, the defects get connected to each other to form voids. These voids initiate cracks on a nanoscale, which subsequently grow and ultimately lead to the material’s failure. How to prevent such a degradation process of metals? As substantial mobility of atoms in metals is only limited to high temperatures, self-healing at room temperature seems to be difficult. However, recent investigations have shown that treatments at temperatures lower than usual or interrupted treatments lead to improved resistance to creep – deformation due to long term exposure to levels of stress below the yield strength – and extend the fatigue lifetime of aluminium alloys. These heat treatments appear to leave a substantial amount of alloying atoms as copper and magnesium in a super-saturated solid solution. During static loading (creep) or varying loading (fatigue), these atoms may become available to precipitate at dislocations and nanoscale voids. Here, they decrease the dislocation mobility and void growth rate, a process which can be considered as self-healing.

A similar approach is used for self-healing of deformation damage in steel. Since its mechanical properties can be tailored to get the desired combination of strength and formability, steel is a popular construction material. However, in demanding applications varying loads and temperatures cause the formation of nanoscale cracks, which grow and ultimately lead to failure of the steel components. In the same way as with aluminium alloys, self-healing of nanocracks in steel can be achieved by the formation of nanosized precipitates to fill these cracks. Again, the presence of super-saturated mobile solute atoms in the steel is required here. In boron steels, boron and nitrogen atoms migrate to the nanocrack to form boron nitride. The same holds for copper added steels, where copper atoms migrate to the nanodefect to form a precipitate, either as spherical copper particles or as a network of copper along dislocations or interfaces. In addition to the aluminium alloys and iron-based model alloys mentioned above, steels of higher technological importance for industrial applications are investigated – such as alloyed austenitic and martensitic steels. In both systems, mobile elements should form precipitates at the initial creep damage, and immobilise further crack growth.

6.2.5 Organic Coatings

Polymeric coatings can add functionalities like protection against corrosion or UV radiation to a product. The highly crosslinked network structure of these coatings gives them high resistance to mechanical stress and solvents. Coatings with low surface energy groups at the surface – such as fluorinated groups - have an additional feature: they display weak interactions with anything that is in contact with the surface. Hence, it is difficult for dirt and other substances to stick to these coatings, and these coatings are easy to clean. When such coatings get damaged during use, it is desirable to retain the coating functionalities. Preferably in a self-healing way using self-replenishing materials, where the underlying cross-linked polymeric network should act as a reservoir of low surface energy groups. After the damage has occurred in the upper 5 to 10 nm of the coating, there is a driving force for groups with lower surface energy to move towards newly created interfaces of the damaged surface, while still connected to the network. The level of the low surface energy groups in the bulk of the coating, as well as their homogeneous distribution throughout the coating depth, should be adequate to have a sufficient amount of these groups available at the newly created interface during replenishment.

In an investigated model system, a polycaprolactone based precursor combined with a tri-isocyanate cross-linker forms a polyurethane cross-linked network. This network is expected to have adequate flexibility so that movement of the low surface energy groups to the surface is possible within an acceptable timeframe. The low surface energy groups are based on perfluoro-alkyl groups connected to the tri-isocyanate cross-linker of the coating network via dangling chains.

A next step is to introduce inorganic nanoparticles into the polymer matrix that contains self-replenishing functional groups with low surface energy. Using this hybrid organic/inorganic material it will be possible to achieve self-healing and retain the surface structure at the same time. Both experimental and modelling investigations have to be performed to understand the competing factors that affect the segregation of the functional groups to the air/coating interface.

Existing paint coatings for inhibiting corrosion of metals (especially aluminium alloys used in aerospace) are made of three layers: conversion coating, primer layer and topcoat. The primer layer acts as a reservoir for the corrosion inhibitor, which is released whenever the coating system gets damaged. The inhibitor reacts with the surface and forms a passivating layer, thereby inhibiting corrosion. So the coating is really a self-healing paint system. However, these coatings are toxic as both the primer and the conversion coating contain the toxic and carcinogenic compound chromate Cr(VI). So there is a need for alternatives – in particular new and safe inhibitors - to be incorporated in the organic coating. Ideally, for self-healing of defects in coating systems, it is desirable to have a component to inhibit corrosion of the underlying metal and also to repair the polymer coating. Since rare earth metal ions are known to be effective corrosion reducers for metals, they form the basis for a new coating system. In this respect cerium dibutylphosphate is a multifunctional inhibitor. It displays both cathodic inhibition via the cerium ion, as well as anionic inhibition via the dibutylphosphate anion.

Alternatively, pH changes can trigger self-healing. Currently available coatings to protect metals from corrosion are fully hydrolysed and polymerised into networks of, for example, siloxane bonds. Damage to these layers will allow the corrosion process to proceed. Furthermore, a damage site triggers pH changes and accelerates deterioration of the metal surface. To solve this problem, new multilayer sol-gel coatings are being developed which - thanks to pH changes inherent to the corrosion process - can initiate a self-healing process. Internal stresses in polymer coatings have a negative influence on mechanical performance of the coating and adhesion to the metal substrate. Early cracking of the material when deformed or bent, and self-propagating cracks are the result of these stresses. Normally, the cross-linked polymer chains are hindered to relax these stresses due to the highly cross-linked thermoset nature of the coating. To avoid these detrimental phenomena, internal stresses may be released by replacing a part of the covalent cross-links in the coating with reversible cross-links, for example dimers of quadruple hydrogen-bonding ureidopyrimidinone (UPy) moieties. The reversible character of these supramolecular cross-links stems from the non-covalent hydrogen bond between the dimers. These reversible cross-links cause superior relaxation of stresses and good creep relaxation behaviour, even below the glass transition temperature where the coating normally becomes rigid and brittle.

This type of preventive healing is completely autonomous, as no external stimuli are required for the material to recover from internal stresses. This approach can not only be used inside the polymer coating, but also at the interface between the polymer coating and the metal substrate to repair the adhesion in case of delamination. The use of reversible, supramolecular bonds across the coating/substrate interface offers the possibility of restoring much of the original adhesion force after delamination has occurred. Besides ‘normal’ thermoset coatings, powder coatings are also very well suited to protect metal components against corrosion. Although powder coatings are generally harder than their liquid applied counterparts, cracks in these coatings are ‘hard’ to repair, as the functionality and looks of the coatings are often worse after repair. Self-healing should be ideal for this type of coating. Best results are expected with a two-stage corrosion protective self-healing powder coating using a combination of active and passive corrosion protection. When the coating is damaged in such a way that the metal substrate becomes exposed to the environment, corrosion inhibitors embedded in the coating will be released. They shield the open surface from corrosives in the atmosphere - protect the metal in a passive way - and bridge the period between damage and subsequent active self-healing. From that moment on, active self-healing of the coating commences via a heating/cooling cycle to carry out a thermo-reversible (retro-) Diels-Alder reaction. By increasing the temperature - currently to about 170 °C - the polymeric network originally synthesized by a Diels-Alder reaction at low temperatures reverts into its constituents, furan and maleimide groups - the retro- Diels-Alder reaction. After cooling down, these compounds react with each other again in a Diels-Alder way to the polymeric network, and the self-healing procedure has come full circle. The 'self-healing' retro-Diels-Alder reaction temperature of 170 °C is rather high for a practical application, and can be decreased by introducing electron-accepting groups in the furans and electron-donating groups in the maleimide.

Rubber is a special type of organic material. Rubber coatings and liners are widely used in chemical industry – flue gas desulphurization units, as an example – to protect steel structures from corrosion. Due to extreme operating conditions, such as high temperatures and extremely low pH values, they have a tendency to degrade in time. As removing and replacing the rubber liners is a time-consuming and expensive procedure, another solution has to be found. To develop a more sustainable polymer barrier liner for this purpose, the protective coating should be able to repair the barrier function autonomously when it is lost by damage. Hence, an appropriate polymer blend has to be found which exhibits a phase separation when the originally present dense top layer has been damaged. This phase separation should subsequently initiate migration of the most mobile component of the blend to the outer surface of the coating. When this component crystallizes or hardens – possibly by using the reactive environment of the flue gas treatment unit – the damaged part of the barrier liner will be restored.

6.2.6 Self-Healing Thermal Barrier Coatings

To improve engine efficiency and to protect them against high temperatures, vanes and blades in turbine engines of airplanes and power plants need to be coated. These so-called thermal barrier coatings allow a temperature of combustion gases of 1200 to 1300 °C, a much higher temperature than even superalloys normally can withstand. However, due to thermal cycling, delamination of the coating occurs. During heating and cooling, high mechanical and thermal stresses develop due to a mismatch between the thermal expansion coefficients of the metal blades and the different layers in the mainly ceramic coating system. Small cracks and pores, which have been present in the coating since its manufacturing, coalesce into delamination cracks due to the release of these stresses. As the small pores and cracks themselves play a positive role with respect to heat conductivity and creep resistance of the yttria-stabilized zirconia topcoat of the coating system, only the coalescence into delamination cracks should be prevented or healed.

Application of a self-healing thermal barrier coating will extend the coating lifetime and increase the time towards expensive revision of these turbine engines. A self-healing approach of which the principle has been demonstrated is by co-depositing $MoSi_2$-based healing particles to the thermal barrier coating. In case of delamination crack formation in the coating, oxygen from the surroundings flows in these cracks and oxidizes molybdenum disilicide to form SiO_2, which heals the crack, and volatile MoO_3 to compensate for volume increase. Remarkably, damage which has been generated in thermal barrier coatings of airplane turbines upon cooling can be repaired during take-off, when the engine temperature is more than 1200 °C. This implies self-healing 'in the flight'. During cruise flight (800 to 900 °C) the healing particles are inactive. Over the past few years, the proof of principle of this healing mechanism has been demonstrated. However, for a successful application this mechanism has to be developed further. To this end, healing particles will be encapsulated in a shell of alumina to prevent premature oxidation of the healing agent, so that the healing mechanism will become active only when required.

6.2.7 Self-Healing Functional Materials

The possibilities for self-healing materials in functional devices are virtually inexhaustible. An example is the repair of conductivity in (transparent) electrodes or conducting leads because the conducting pathway has interrupted. Or repair of cracks in membranes in fuel cells and batteries. Or healing of surface areas which have to separate two phases and are vulnerable due to differences in thermal expansion coefficients, or sensitive to creep. Other examples are damage caused by fatigue due to alternating loads in microelectromechanical systems (MEMS). Or healing of layers that are 'buried' in a composite device, such as a multilayer that cannot be disassembled, like in OLEDs, solar cells, foil displays, etc.

By measuring the conductivity through a material, it is possible to detect and possibly quantify microcracks in an electrically conducting material, as these cracks (locally) interrupt the conductivity. By incorporating conducting structures in a material that originally is not conducting, it will be possible to determine the structural integrity of this material in real-time. In line with this argument, it will be possible to apply an electrical field (potential difference over the material) or an electrical current to heal the material. This is advantageous on locations which are hard to access, but also in consumer electronics. As an illustration, conducting polymers can make use of such an electrically driven self-healing process. Suitable multifunctional monomers can form a conducting polymer network after polymerization. Suppose a microcrack is formed in the material, for example, by a mechanical load, which interrupts the polymerization-formed bonds. Consequently, the total number of electrically conducting pathways in the material decreases, resulting in an increase in electrical resistance in the material. This increase in resistance – or decrease in conductivity – can be used as a trigger to increase an applied electrical field over the material. As the microcrack is the cause of the increased resistance, this larger electrical field generates heat at the site of the microcrack. When this thermal energy is large enough to make polymerization possible, the cracked material can be healed again to the originally conducting polymer network. American research reveals that complexes between N-heterocyclic carbenes and transition metals are very promising as electrically conducting self-healing materials.

6.3 Applications

6.3.1 Applications in Various Fields

As mentioned before, the applications of self-healing materials are still limited, but will grow in the coming years. A few applications are available, mainly in the coating industry. Several products can be found for car-paints [6.9, 6.10]. (Small) Scratches on cars disappear when the car is placed in the sun if this coating is applied. The coatings are also available for applications in many other areas [6.11].

6.3.2 Applications in Civil Engineering; Asphalt

As presented in section 6.2 the development of self-healing asphalt has led to real applications of the material in the field. A first test section has been made of 400 meter long on a Dutch Highway and after that it has been applied already at three other locations in the Netherlands. Details of the application are described in [6.8]. To make a quantitative prediction of the financial benefits that can be obtained when using self-healing materials the balance between increased material costs and reduced maintenance and user costs are key. Operating costs, disposal costs and environmental costs also contribute to the equation. It is expected that periods between road maintenance will extend when self-healing asphalt is used, resulting in a decrease in user costs. Rijkswaterstaat in the Netherlands made a study of the financial benefits of using self-healing asphalt in the surface layers on highways. This calculation will be used as an example. According to this study, the average annual costs for major repairs of 74 km^2 of standard PAC in the Netherlands are amounted to 180 million euros. By extending the life span of standard Porous Asphalt Concrete (PAC) by 25 percent - so from 12 years on average to 15 years – the annual costs for major repairs can be reduced by 35-50 million euros. At an extension of the life span from 12 years on average to 18 years - so by 50 percent - the annual savings on major repairs could be as much as 60-80 million euro. In this simplified analysis, the additional cost pertaining to the use of enhanced self-healing asphalt are not taken into account.

Besides these ‘direct’ maintenance savings, self-healing asphalt yields indirect advantages, for instance less traffic jams due to road maintenance and hence less social traffic jam costs. Traffic jam costs, expressed as capitalised hours of time loss of waiting people and their alternative routes, amounted in 2008 in the Netherlands to 2.8 billion euros, of which ‘only’ 4 percent or about 110 million euros were caused by road maintenance. It would be reasonable to assume that the number of traffic jams decreases proportionally with the length of the maintenance period. Therefore, a life span extension for self-healing asphalt with 25 percent from 12 years on average to 15 years would render 22 million euros less traffic jam costs. At a life span extension of 50 percent - from 12 years on average to 18 years - the social traffic jam costs would be 37 million euros less. Again, here the additional cost for applying self-healing asphalt is not taken into account.

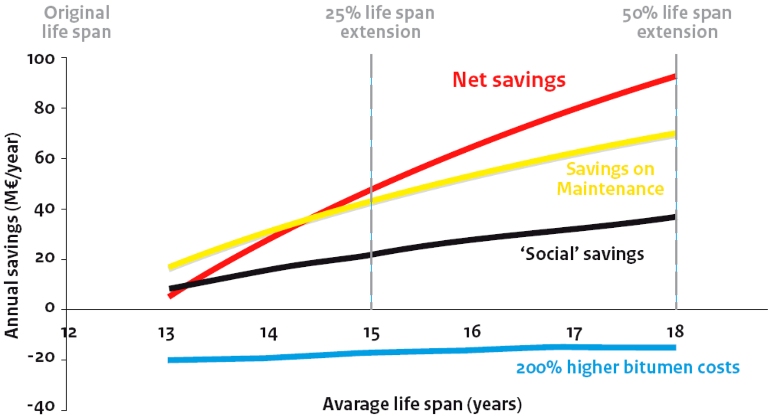

Fig. 6.3 Annual savings that can be achieved using asphalt with extended life span. The net savings are the sum of savings related to maintenance and social costs and higher bitumen costs.

The combined annual savings related to major repairs and social traffic jam costs are approximately 65 million euros at a life span extension of 25 percent and over 100 million euros at a life span extension of 50 percent, for the entire PAC area in The Netherlands. To determine the net savings, the additional costs for self-healing asphalt have to be subtracted. A 100 percent (or 200 percent) higher bitumen price results in approximately 8 million (or 16 million) euros additional annual costs. So even if the price of self-healing bitumen will be twice as high as for standard bitumen, The Netherlands can save approximately 90 million euros annually by investing in self-healing asphalt with a 50 percent extended life span compared to traditional PAC (see Fig. 6.3).

The Netherlands is fairly small. It has only 3% of the European asphalt production and only 1/3 of this (so only 1%) is used in surface layers. If we extend the analyses of savings by using self-healing asphalt from the Netherlands to Europe, the number of 90 million euros has to be multiplied at least by a factor 100. (actually it should be a larger factor since only the highways in the Netherlands have PAC surface layers and not the secondary roads).

According to this analysis the total annual savings for Europe would be 9000 million euros.

Benefits accrue for both ‘society’, as road users, and the road maintenance authorities with the use of self-healing asphalt. Planning of maintenance agreements will be facilitated for road contractors using this new material.

Investments for the development of self-healing asphalt in road construction will need to be made now, with long-term performance investigation required to prove a successful investment. Return of this investment will materialise in the form of an extended life span of the asphalt and consequently less maintenance costs. In practice, the financial risk can only be taken by the road manager or by road contractors with a combined construction and maintenance contract. To evaluate this risk it is important to understand the capacity of self-healing asphalt at an early stage, for example through pilot projects with a sufficiently long evaluation time.

6.3.3 Applications in Cement Based Materials

Several applications have been realized in cement based materials. The fibre reinforced materials, which are self-healing by nature, but can also be ‘upgraded’ to become more self-healing, are applied in several projects. An overview of the applications can be found in [6.12].

The self-healing concept in which cementitious composites are produced that incorporate various mineral admixtures is applied in projects in Japan [6.13].

The bacterial concrete is tried out to repair a leaking concrete structure in the Netherlands. Details can be found in [6.14].

6.4 Future Developments and Outlook

In [6.7] it is stated that future applications of self-healing materials are most likely to be applied in places where reliability and/or durability play a key role:

- In places that are difficult to access to perform (expensive) repairs, such as at high altitude (high buildings, wind turbines at sea), underground (piping) or under the water surface (cables and piping).
- Applications where reliability and safety are key issues, even during overload or unforeseen circumstances: storm surge barriers or nuclear reactors or long-term storage of nuclear waste.

- Structures which have to last very long (several decades), such as in large infrastructural applications as dikes, dams and tunnels.
- Applications where large repairs result in a lot of inconvenience in society, such as repairs of roads and in energy supply.
- High-tech equipment for the production of high-quality products; machines which have to be in operation 24/7, where downtime should be minimized.

For cement-based materials various concepts and methods are developed in the laboratory. To apply them on a larger scale, some up-scaling should be done. In real structures large amounts of healing agents should be produced on an industrial scale. This is not always an easy task. Industrial production involves usually a different approach and some more research to obtain equivalent material to the one that is produced in the laboratory. However, projects are under development to realize this. If enough healing agent is available real applications can be made. First this will be done, still, on a relatively small scale, in which monitoring of the self-healing process is performed. If enough experience is gained larger applications will follow.

Another aspect of bridging the gap to real applications is creating more confidence among contractors and owners of structures in the use of self-healing materials. In order to do this it is important to be able to show the long term behaviour of structures build with self-healing materials. This is of course not an easy task. Accelerated tests can help for this, to show that self-healing materials will perform also on the long term. Furthermore, it is necessary to perform Life-Cycle-Analyses to show that in the end structures with self-healing materials will last longer, perform better and are more durable and sustainable in the end. Investing some more when the structure is built, can definitely pay off.

References

6.1. White, S.R., Sottos, N.R., Geubelle, P.H., Moore, J.S., Kessler, M.R., Sriram, S.R., Brown, E.N., Viswanathan, S.: Autonomic healing of polymer composites. Nature 409, 794 (2001)

6.2. Schmets, A.J.M., van der Zwaag, S. (eds.): Proceedings 1st International Conference on Self-healing Materials. Springer, Noordwijk aan Zee (2007)

6.3. White, S.R. (ed.): Proceedings 2nd International Conference on Self-Healing Materials 2009, Chicago (2009)

6.4. Bond, I. (ed.): Proceedings 3rd International Conference on Self-Healing Materials, Bath, UK, June 27-29 (2011)

6.5. van der Zwaag, S.: Self-healing materials, an alternative approach to 20 ceturies of materials science. Springer Series in Materials Science, vol. (100). Springer, Dordrecht (2007)

6.6. Ghosh, S.K. (ed.): Self-healing Materials: Fundamentals, Design Strategies, and Applications. WILEY-VCH Verlag GmbH & Co., Weinheim (2009)

6.7. NL-Agency, Self-healing materials, concept and application, Ministry of Economic affairs, The Netherlands (2011)
6.8. `http://www.selfhealingasphalt.blogspot.com`
6.9. AkzoNobel, `http://www.akzonobel.com/aac/news/pressreleases/2009/new_self_healing_clearcoat_from_akzonobel.aspx`
6.10. Bayer MaterialScience Self-healing Coatings, `http://www.youtube.com/watch?v=FYfhk9ZBxa0`
6.11. Beckman Institute, University Illinois, Autonomic Materials, `http://www.autonomicmaterials.com/applications/`
6.12. `http://ace-mrl.engin.umich.edu/`
6.13. Ahn, T.-H., Kishi, T.: Crack self-healing behaviour of cementitious composites incorporating various mineral admixtures. J-ACT 8(2), 171–186 (2010)
6.14. `http://www.selfhealingconcrete.blogspot.com`