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Recent Advancements in Self-Healing Metallic Materials and Self-Healing Metal Matrix Composites

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Engineered self-healing materials inspired by natural biological organisms that can repair damage are receiving increasing interest in recent years. Most studies have been focused on self-healing polymers, concretes, and ceramics. Self-healing metallic materials pose challenges due to the high temperatures used in manufacturing and the chemistries involved. This article summarizes and evaluates the self-healing mechanisms used in metallic materials and reviews recent studies into self-healing in aluminum, zinc, and Sn-Bi alloys. Generalizations about the various classifications are drawn from the review highlighting major hurdles in the widespread practical application of metallic self-healing materials, as well as the potential directions for future studies.

INTRODUCTION

Engineering materials degrade due to wear, fatigue, creep, and environmental conditions that limit their life and can result in catastrophic failures. To improve safety and efficiency of engineered systems, new materials need to be developed that overcome these issues for use in automotive, aerospace, civil structures, and biomedical sectors. *Self-healing materials* have the ability to recover from or repair damage providing an attractive solution.[1] Engineered self-healing materials are inspired by natural biological organisms that can recover from injures.[1–3]

In the last decade, significant research has been performed on self-healing materials, particularly polymers, concrete, and ceramics. Most of this research has been on self-healing polymers because of the relative ease of processing.[4–12] Very few publications are available on self-healing metallic materials or self-healing metal-matrix composites (MMCs).[13–16] The largest challenges to self-healing in metallic structures arise from the high temperatures involved in forming metals, precise chemistries for alloys, and oxidation of surfaces exposed to air. These challenges combined with fundamental material differences often require the use of alternative mechanisms in self-healing metallic structures compared with polymeric and other ones. This article critically reviews the recent investigations of self-healing metallic materials, and future challenges in the field of self-healing metallic materials are summarized.

CLASSIFICATION OF SELF-HEALING METALLIC STRUCTURES

Classification of current metallic self-healing materials focuses on the mechanisms of self-healing, based on material structure or autonomy (Fig. 1). Nonautonomous self-healing materials require external actuation such as the application of heat or an electrical current. Autonomous self-healing materials do not require external actuation, but at this point in time, autonomous metallic self-healing structures are mainly theoretical without significant experimental validation.

Self-healing MMCs have a macroscopic inhomogenious structure and often including shape memory alloy (SMA) fibers and/or encapsulated healing agents dispersed in a matrix. Long or short SMA wires have been embedded as reinforcements in

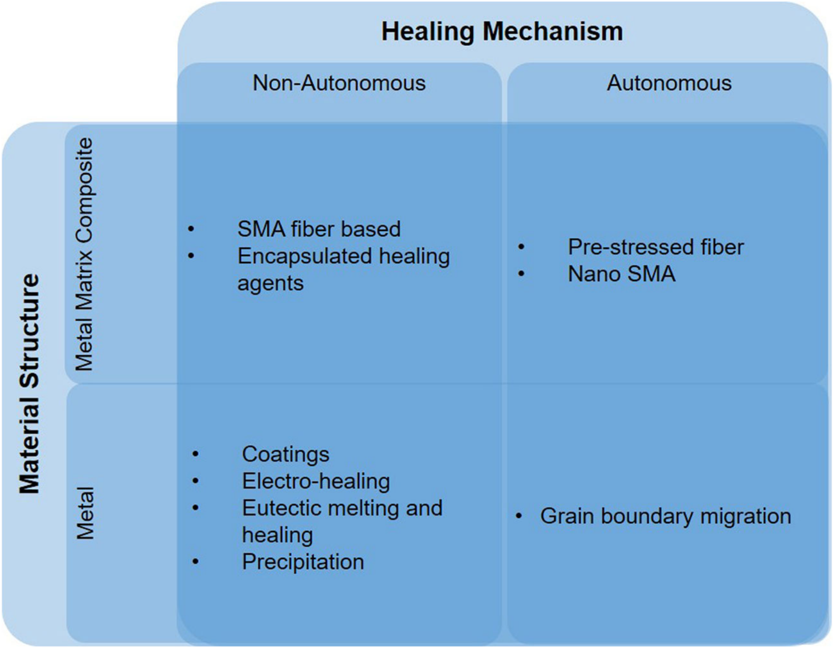

Fig. 1. Classification of the investigated metallic self-healing materials (Color figure online).

metal matrixes (Al, Zn, Sn, or Sn-Bi alloy) to synthesize SMA-based self-healing materials.[17–22] Self-healing materials based on encapsulated healing agents have been synthesized through the addition of capsules or tubes containing a healing agent like a solder.[3,23–28]

Self-healing metals are more homogenous, employing healing mechanisms including coating-based healing,[29] electro-healing,[30] eutectic-based self-healing,[18] and precipitation-based healing,[31–36] which are described in detail in the following sections. Autonomous self-healing metals are currently under theoretical development based on nano-scale mechanisms including nano-SMA-dispersoid-based self-healing and grain boundary migration.[37,38]

SELF-HEALING MECHANISMS IN METALS AND METAL-MATRIX COMPOSITES

Precipitation-Based Healing

Microcracks or voids in the material serve as nucleation zones for precipitation of supersaturated, or underaged, alloy in precipitation-based healing. In underaged alloys, solute atoms migrate to defects and voids, in effect “healing” them. Van der Zwaag et al.[34] investigated this method, which demonstrated self- healing of voids as a result of their being filled by migrating atoms. However, this “healing” occurs on a nanometer scale similar to the natural process of age-hardening, and it does not have the ability to heal large cracks. To accelerate this process, an alloy can be heated to a certain aging temperature to actuate healing, and the precipitation occurs near the microcracks that are in the localized highly stress region forming precipitates.[1,2] When the alloy cools from a high temperature, it becomes supersaturated, or metastable, and then during aging, a return to equilibrium occurs by precipitation of supersaturated solutes in the cracks or voids.

It was found that[39] the creep resistance of the underaged Al-Cu-Mg-Ag alloy was significantly increased if it was heat-treated at an elevated temperature to an underaged condition rather than the fully hardened, e.g., to T6 temper. Dynamic precipitation of an underaged Al-Cu-Mg-Ag alloy following 500 h creep at 300 MPa and 150°C occurred, often associated with dislocations. Further aging heat treatments resulted in healing of the crack.

Djugum et al.[40] have also investigated the effect of precipitation heat treatment on the crack healing behavior in Al-Cu AA2001 alloy under underaged conditions. Figure 2 shows the microstructures of the alloy that were in an underaged condition, and then after 10 h aging treatment, the crack healed.

Shinya et al.[41] investigated precipitation of boron nitride (BN) as a mechanism of self-healing in 304 stainless steel modified with boron (B), cerium (Ce), and titanium (Ti). The modification of this alloy with B, Ce, and Ti resulted in the preferential precipitation of BN at the creep cavity sites, which was stable at a high temperature in the creep cavity surface, leading to improved creep resistance of the 304 stainless steel. This process has been performed to achieve self-healing at heterogeneous sites such as voids, cracks, and other free surfaces, which could serve as nucleation sites od cracks.

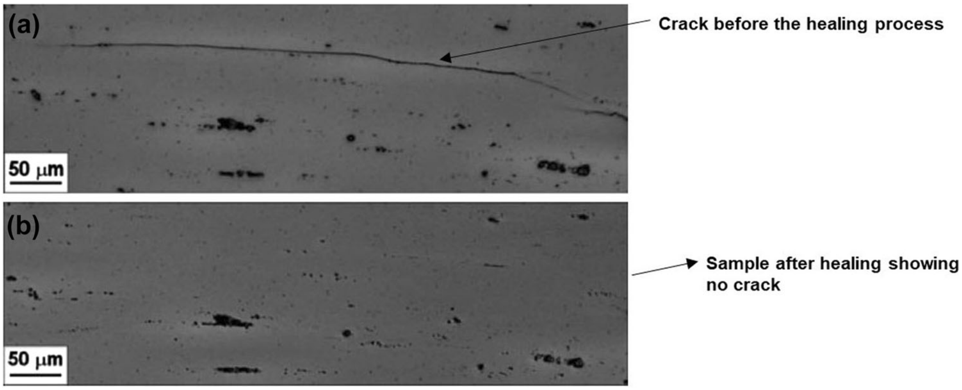

Fig. 2. Micrographs of an Al-Cu AA2001 alloy specimen underaged at 180°C for 5 h and tested. (a) Hairline crack present and (b) crack has been healed by aging for an additional 10 h. Reprinted with permission from Ref. [40].

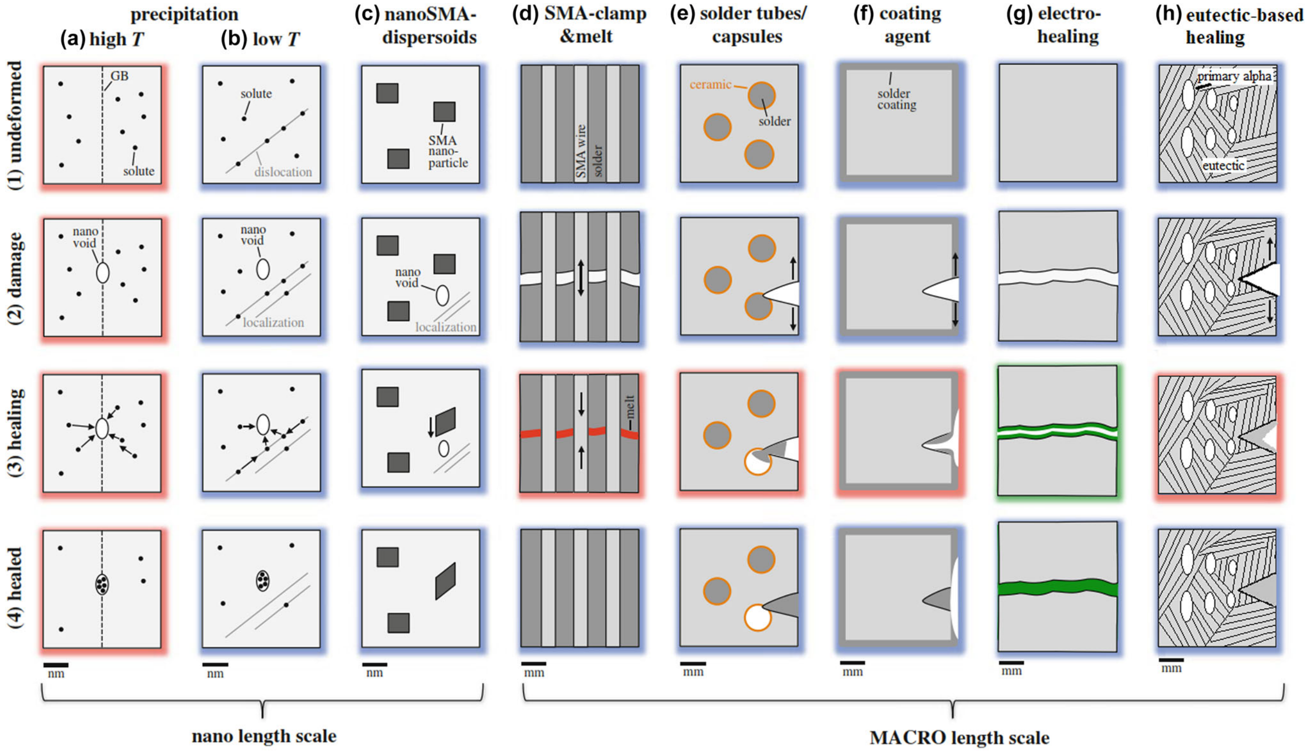

Fig. 3. Schematic representation of the self-healing mechanisms in metallic materials: (a) high-temperature precipitation-based healing, (b) low-temperature precipitation-based healing, (c) nano-SMA-dispersoids-based healing, (d) SMA-based healing, (e) microencapsulation-based (microballoons/microcapsules/microtubes) healing, (f) coating-based healing, (g) electro-healing, and (h) eutectic-based healing. Background shading indicates the conditions required: red = high temperature, blue = low temperature, and green = applied voltage. Reprinted with permission from Ref. [38] (Color figure online).

Researchers[38] reviewed the precipitation healing in two parts. High-temperature (575–750°C) precipitation healing (Fig. 3a) was studied mostly on stainless steel and Cr-Mo-V alloys,[38,41] and low-temperature (120–185°C) precipitation healing (Fig. 3b) was studied mostly on Al alloys.[31,33,36,39,40] Time and temperature are needed to accelerate diffusion, which is the rate controlling sites to provide movement of solid atoms into the matrix, as well as into voids and cracks in the matrix.

Work to date on precipitation-based healing has shown that it is limited to healing small-scale damage. This has the potential to eliminate fatigue crack initiation points over long time periods, but it limits its usefulness to early damage states. Once a crack begins to grow, precipitation-based healing will have a limited effect.

Nano-SMA-Dispersoids-Based Healing

Development of self-healing metallic materials using nano shape memory alloy (nano-SMA) dispersoids was proposed by Grabowski and Tasan.[38] This concept (Fig. 3c) belongs to the group of nanometer-scale healing mechanisms, and nanovoids are closed by phase transformation of SMA nanoparticles.[37] The concept is currently in the modeling stage, and the self-healing ability has yet to be experimentally demonstrated.[38]

The original microstructure consists of a host matrix with embedded coherent SMA nanoparticles (Fig. 3c, line 1) stabilized by the host matrix in its austenite phase (i.e., high-temperature phase). When damage is initiated in the form of dislocation localization and nanovoid formation (Fig. 3c, line 2), the nanoparticles are activated. The stress field of the nanovoid is thought to trigger phase transformation of the SMA nanoparticle from the austenite into the martensite. Phase transformation is accompanied by a strong change in the shape of the particle (Fig. 3c, line 3) that induces local strain fields in the host matrix and eventually leads to crack closure (Fig. 3c, line 4).[38]

Nanodispersoids show a theoretical potential to close small-scale voids and induce residual stresses that may be functional in changing the fatigue properties of a material structure. However, a lack of bonding capabilities in this system could be a limitation in its effectiveness.

SMA-Based Healing

Integration of shape memory components into self-healing materials enables bulk geometry restoration after a fracture, a capability not present with other forms of self-healing. This is critical to returning a structure to its original functionality after incurring major damage. The core of this approach is to embed SMA reinforcements into selected self-healing metal matrices (Fig. 3d). SMAs have two unique properties: shape memory effect and pseudoelasticity.[42] The former refers to the ability of an SMA to undergo deformation in the martensitic state and then recover its original, undeformed shape upon heating above its austenite transformation temperature. The latter is associated with an SMA being able to recover high applied strain upon unloading of the material while in its austenitic phase. Substantial recovery stresses can be generated if shape recovery is constrained during heating in the high-temperature state and these can actuate geometric restoration, closing cracks in self-healing materials. SMA-reinforced self-healing materials are inherently nonautonomous, requiring external actuation (typically heating) to initiate the healing process.

Critical challenges for SMA-reinforced self-healing materials include (I) ensuring bonding between the SMA and the matrix. (II) compatibility between SMA and the metal matrix during synthesis, (III) understanding the mechanics of the SMA-reinforced matrix and kinetics of recovery, (IV) knowledge of damage location to activate the healing mechanism.

Self-healing of SMA wire-reinforced metal-matrix composites has been explored by several researchers.[17,43,44] Manuel and Olson[17,45] fabricated a Sn-based self-healing proof-of-concept composite using a Sn-21Bi (wt.%) matrix alloy reinforced with 1% equiatomic NiTi SMA wires. After a complete matrix fracture in a tensile test, the composite was healed at 169°C for 24 h in an oven, cooled to room temperature, and tensile tested again. It was found that the crack was closed and the healed specimens demonstrated a recovery of 95% of its original tensile strength. Heating both activated the SMA to restore geometry and softened the matrix solders sufficiently to bond the fracture back together. During heating, NiTi wires began to apply forces on the matrix while trying to return to the original geometry (shorter lengths), corresponding to the trained shape of the SMA.

Other alloys also have been investigated as matrix materials for self-healing components.[17,21,22,44,46] Manuel's work[43] on healing in a magnesium-based matrix revealed that partial healing would occur at a given temperature. Rohatgi[21] studied incorporating NiTi SMA wires in an Al-A380 matrix. It was found that the SMA wires by themselves would be unable to pull the damage faces back together because of poor bonding between the wire and the matrix. This was

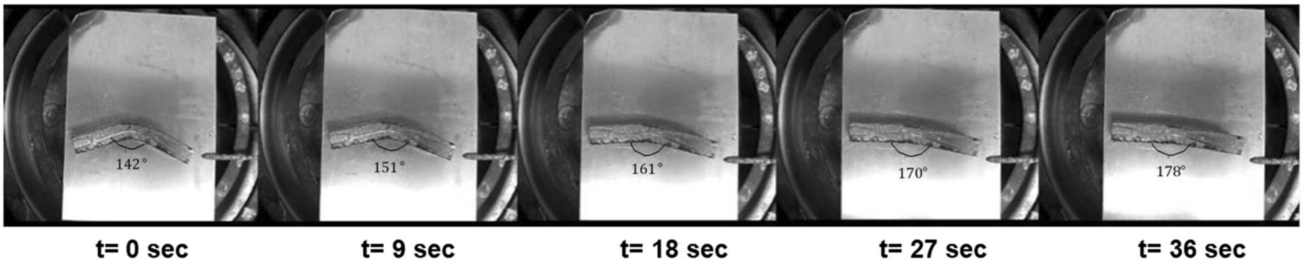

Fig. 4. Snapshots of healing of bended Sn-20%Bi/NiTi bar at equal intervals of time starting at $t = 0$ s. Reprinted with permission from Ref. 19.

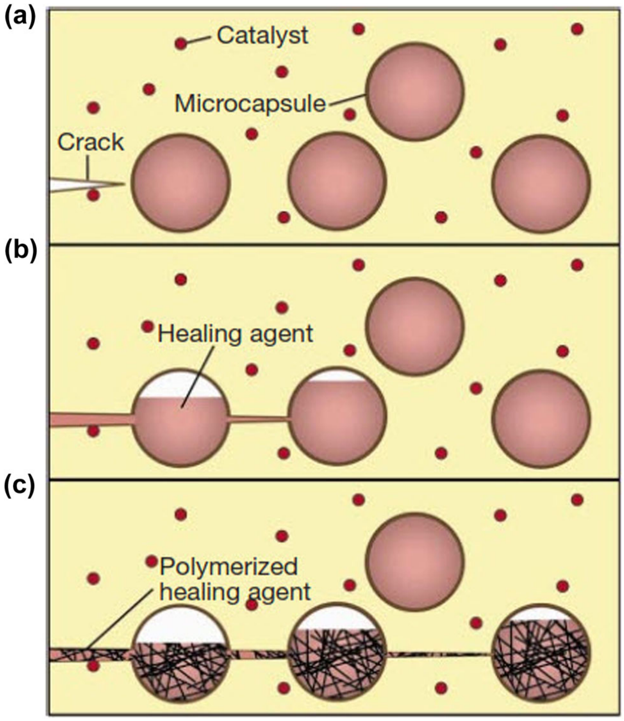

Fig. 5. Schematic representation of the self-healing by microencapsulation. A microencapsulated healing agent is embedded in a structural composite matrix containing a catalyst capable of polymerizing the healing agent. (a) Cracks form in the matrix wherever damage occurs. (b) The crack ruptures the microcapsules, releasing the healing agent into the crack plane through capillary action. (c) The healing agent contacts the catalyst, triggering polymerization, which bonds the crack faces. Reprinted with permission from Ref. 51 (Color figure online).

overcome by wrapping SMA wire around a threaded stainless steel rod and casting Al-A380 around the rod/wire preform. This rod served as a mechanical anchor in the material, which the SMA could pull against even if the entire wire disbonded from the matrix. It was found that the reinforced component had nearly double the strength and ductility of the unreinforced sample. Due to the absence of rebonding or residual compressive loads between the damaged surfaces, there was no significant recovered strength, only significant reduction in the width of the crack.[47]

Ferguson et al.[22] investigated incorporating NiTi SMA wires in a Zinc ZA-8 die casting alloy. Different frames and preforms were used in the synthesis of ZA-8/SMA specimens to test the effect of providing a mechanical anchor for the NiTi to react against. This design was intended to both restore bulk geometry and bond across fractures. It was found that the specimens with mechanical anchors recovered a greater portion of their pristine strength (about 30%) than samples that relied on direct load transfer between the matrix and reinforcement.

Recently, Misra[19] fabricated a self-healing MMC composed of a Sn-20Bi (wt.%) matrix with 20% volume fraction NiTi wire reinforcement. Bonding between the NiTi and the matrix was improved by etching the native titanium oxide layer off of the NiTi in an inert environment and then encasing it in flux before casting it in the matrix. The assessment of healing was done by observing and measuring the recovery of plastic strains produced by a three-point bending test. The bent sample was put on a hot-plate and its shape recorded as it returned to its original shape. Snapshots from the footage of straightening of the bent sample were taken at uniform time intervals while healing was done at 165°C, as shown in Fig. 4. The kinetics of shape restoration and extent self-healing need to be quantified.

He also performed one of the few studies on the temporal performance of self-heling materials, even nonmetallic systems. NASA researchers[46] have developed a self-healing, aluminum-based composite system using a liquid-assisted healing in conjunction with SMA wire reinforcements with the focus on fatigue cracks propagating through the matrix. It was found that more than 90% ultimate tensile strength was recovered after self-healing. In another study, vacuum hot pressing (VHP) was used to improve bonding between SMA wires and matrix while fabricating the composites.

Mechanics of Self-Healing

Integration of SMA into self-healing has created an opportunity to use constrained recovery to generate residual compressive loads across fractures upon healing. This residual load leaves the structure capable of withstanding externally applied loads without bonding as reported by Salowitz et al.,[47] similar to post-tensioned concrete structures. Ongoing efforts seek to characterize this capability such that healed structures can be designed to be able to resist external axial and bending loads. This capability is envisioned to advance self-healing with bonding because adhesive bond strength is known to increase with applied pressure.[48] Additionally, generation of compressive loads across fracture faces has the potential to advance the utilization of other forms of bonding, like diffusion bonding, in self-healing metals.[49,50]

Significant studies are still necessary to characterize the temporal response of self-healing materials in general, and this is especially important for NiTi-reinforced ones capable of macro-scale deformations. Understanding of the time scales involved in healing mechanisms will enable sequenced recovery of large-scale damage and deformation like setting a bone. Additionally, designed residual stresses created through constrained recovery mechanisms can potentially improve the static and fatigue strengths of self-healing materials.

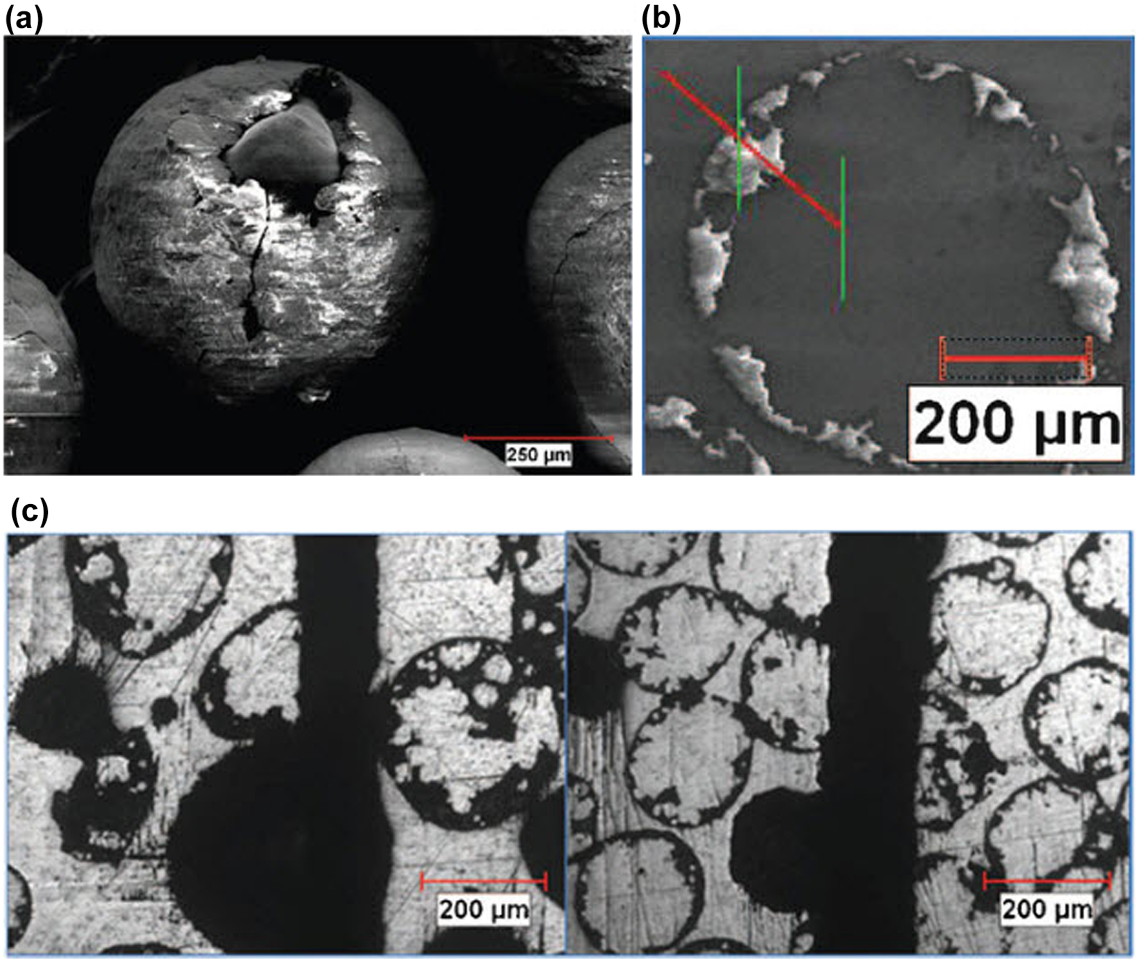

Fig. 6. (a) SEM image of an Al_2O_3 microballoon filled with Sn-Bi eutectic. Note the crack and hole in the microballoon that allows the Sn-Bi eutectic to fill the microballoon during infiltration and the Sn-Bi eutectic is visible inside of the microballoon. (b) SEM cross section of an Al_2O_3 microballoon filled with Sn-Bi eutectic composition dispersed in a Sn-0.7% Cu matrix. The line in the upper left is the path of the EDX line scan with two markers. (c) The optical microstructure of the large and small Al_2O_3 microballoons encapsulating Sn-Bi eutectic in a Sn-0.7% Cu matrix after healing heat treatment. Both images are of ×50 magnification. Reprinted with permission from Ref. [18].

Encapsulated-Based (Microballoons/Microcapsules/Microtubes) Healing

White et al.[51] developed autonomous self-healing in polymers by embedding microcapsules filled with a monomer healing agent, dicyclopentadiene (DCDP), dispersed throughout a polymeric epoxy matrix that contained a catalyst. Figure 5 schematically shows the mechanism of the microcapsules/microballoons self-healing in polymeric materials where a crack will propagate and rupture the capsules releasing the agent (a monomer), which would flow into the crack and bond in place after polymerizing due to contact with a catalyst dispersed in the matrix.[11]

Self-healing MMCs were developed by using encapsulated healing agents like what was done with polymers (Fig. 3e). Encapsulated solders for self-healing were also proposed by Rohatgi et al.[23] in 2008 to develop new self-healing MMCs.[23,24] In these methods, low melting temperature materials were encapsulated inside ceramic shells, which were then dispersed within a host matrix that had a higher melting temperature. When a crack formed in the host matrix, the ceramic carrier cracked if it was suitably located. Upon heating, the low-temperature solders melted and flowed out of the ceramic capsules into the crack filling the crack via capillary action and bonding under certain conditions (Fig. 3e).

The strength recovery of this healing process is dependent on wettability between the host metallic material and the properties of the low-melting-temperature alloy.[16] Strength restorations of 60% of the original predamaged strength have been achieved.

Martinez-Lucci et al.[23] have investigated the possibility of embedding Al_2O_3 ceramic micro tubes filled with Sn60Pb40 solder inside an Al-206 alloy host matrix. An intentional crack was created such that one of the ceramic (Al_2O_3) tubes was pierced. Although crack filling was achieved by heating above the melting temperature of the solder, the interface between the solder and the Al matrix needed to be improved.

Another study was performed by Ruzek[18] in which Al_2O_3 microballoons were filled with a low melting healing agent (Fig. 6a) and were then incorporated into higher melting metallic matrices to form self-healing composites (Fig. 6b). The higher temperature matrix alloy was Sn-0.7% Cu, which melts congruently at 226°C. The Sn-Bi eutectic alloy (Bi-42% Sn) was chosen as the low-melting-point healing agent encapsulated within the hollow microballoon since it has a low melting temperature of 138°C. Rods of Sn-0.7% Cu were cast, and then a hole was bored down the length of the rod. This cavity was then filled with the Sn-Bi eutectic. A small notch, 350-μm wide, was cut into the side of the sample to simulate a crack. Hollow Al_2O_3 microballoons were used as containers for the low-melting-point Sn-Bi healing agent, and cracks or holes were introduced on the surface of hollow microballoons allowing them to be filled with low melting healing agent using pressure infiltration. Figure 6a shows typical Al_2O_3 microballoons with a crack in the side, to allow it to be filled with low-melting Sn-Bi eutectic.[18] The microstructure of this system was confirmed by SEM and an EDX line scan. Figure 6b and c shows a cross section of an Al_2O_3 microballoon filled with Sn-Bi eutectic in a Sn-0.7% Cu matrix. The line demonstrates the path of the line scan.

Designing the original matrix microstructure is difficult when capsules filled with solders are used.[38] The ceramic capsules need to contain holes of a requisite size and shape for them to be filled with solder during pressure infiltration with molten solder. Additional problems with the solder tubes/capsules concept occur during the damage and healing phases. First, for the solder to have any effect, the crack in the matrix must not only hit a capsule but must also crack the ceramic shell such that the solder can flow out of the fractured capsule into the crack. This condition is not easily fulfilled because cracks can propagate along the interface between the host matrix and the ceramic shell and healing will not occur. Second, even if the first condition is fulfilled, and the solder can be activated to flow into the crack, the solder must wet the crack properly and, more importantly, bond strongly to the crack surface. These issues must be addressed before self-healing metals based on encapsulated metallic healing agents can be widely deployed.[38] In contrast to self-healing polymers, at this point in time, capsule-based heling in metallic structures is not autonomous, requiring heat to melt an encapsulated healing agent. Another challenge in the encapsulated healing agent approach, which appears in many material categories, is that the "healing agent" will bond the structure in its damaged geometry. At small scales, this can solidify with significant residual stress concentrations at (filled) crack tips, and at large geometries, this could affect the function of the structure.

Coating-Based Healing

Leser et al.[29] developed a 60% indium-40% tin (wt.%) self-healing coating with a melting point of 124°C (0.005–0.015 mm thick) on the surface of a titanium alloy with a thickness of 2.03 mm. If a surface crack occurs, the system can be heated above the melting point of the In-Sn alloy and the melted surface alloys fill the crack (Fig. 3f) in the titanium alloy when the specimen is heated about 124°C. Crack healing tests showed that fatigue crack growth with low crack-tip driving force could be arrested after the self-healing process, and about 50% reduction in crack growth rate occurred at a higher crack-tip driving force. The self-healing coating could be activated repeatedly in inert environments, demonstrating the possibility of multicycle heating.[29]

Electro-healing

Zheng et al.[30] have investigated electro-healing in pure nickel sheets in which crack healing is provided by electrodepositing metal ions onto the crack in an electrolytic bath under controlled electric currents (Fig. 3g). The cracks with sizes in the micrometer range up to 100 μm were successfully healed using the electro-healing process. Almost 96% tensile strength was recovered via this process.[30] Although this approach is effective, the need to place a structure in a bath combined with the small scale of healing may be limiting.

Eutectic-Based Healing

Eutectic-based healing was investigated by Ruzek and Rohatgi[18] based on using the eutectic liquid formed within the solid itself as a healing phase while the solid dendritic phase maintained the structural integrity. The preferred way to achieve this is to use a matrix alloy composition that is away from the eutectic composition of a system, resulting in the dendrites of a phase to form at a higher temperature and eutectic. Upon cooling, dendrites of the primary phase would form first from the melt since they have a higher melting point. These dendrites would change the composition of the remaining interdendritic liquid due to solute rejection pushing the composition of the interdendritic liquid to the eutectic composition, which would solidify between the dendrites. To activate this system for self-healing, the temperature of the system had to be elevated to a point where the interdendritic eutectic would melt and flow to a crack in the sample and act as a healing phase, while the solid dendrites maintained the structural integrity of the system. The liquid eutectic is then available to flow between the dendrites and into any cracks or voids present in this system. Upon the cooling of the system, this liquid eutectic in the cracks will solidify, thus, healing the system (Fig. 3h).

CURRENT APPLICATIONS AND FUTURE OPPORTUNITIES FOR SELF-HEALING METALLIC MATERIALS

Despite the attractive advantages of using self-healing in metallic materials including low maintenance cost, long service life, and the prevention of catastrophic failures, the use of self-healing in metallic materials in real-life applications has not been extensive especially for load-bearing applications.[16]

Currently, self-healing MMCs are at a research stage. There are no commercial products based on self-healing metallic materials or self-healing MMCs at this point in time. However, currently, self-healing polymers are commercially available such as a self-healing cutting mat.

Nevertheless there are several potential applications for self-healing metals and self-healing MMCs. The self-healing metallic materials for wing components, structural components, rotating parts, wind turbine blades, and metallic implants can be designed for the aerospace, spacecraft, automobile, renewable energy, and biomedical industries, respectively, since they can result in higher mechanical properties, including strength, and fatigue resistance.

CONCLUSION

Self-healing metallic materials are a new emerging area in materials science and engineering. Inspired by nature, researchers are attempting to impart the ability of self-repair to engineered materials. Specific challenges facing the development of self-healing metallic materials, includes improving wetting, overcoming oxidation, providing sufficient capillary pressure, and healing macroscopic damage, without sacrificing strength or functionality. Critical points are healing macroscopic damage, which, like healing a bone, may require an ordered step in healing-like restoration of the original geometry and keeping the joint geometry interact followed by bonding. More in-depth research and understanding of the mechanics, dynamics, and temporal response of healing processes are necessary to achieve this vision. Structural health monitoring (SHM) can supply information about the damage, like the nervous system of a biological system, providing information about the existence, location, and severity of damage, enabling actuation of appropriate healing mechanisms in order and information about residual capabilities of the system while it is damaged or healed. SHM may also be able to provide information about the quality of healing after it has occurred.

Self-healing can lead to more robust behavior, longer fatigue lifetime, increased safety, lower maintenance costs, and many other desirable attributes required in transportation systems, space structures, biomedical implants, and building structures. Self-healing using shape memory alloy fibers has been demonstrated in low-melting alloys, including Tin-based alloys/solders, aluminum alloys, and zinc-based alloys. It is necessary to develop new self-healing mechanisms for high-temperature alloys. Self-healing using microballoons containing healing agents has been demonstrated in aluminum alloys and solder alloys. Self-healing of nanovoids and microcracks by precipitation healing, precipitation, and diffusion have been shown in aluminum alloys, nickel-based alloys, and steels. It is necessary to develop autonomous healing in metallic alloys since most of the techniques developed to date require external triggers, including thermal or electric. Remote structural health monitoring and autonomous self-healing need to be incorporated into materials and components to improve their performance.

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