

Self-Healing Phenomena in Metals

van Dijk, Niels; van der Zwaag, Sybrand

DOI

[10.1002/admi.201800226](https://doi.org/10.1002/admi.201800226)

Publication date

2018

Document Version

Final published version

Published in

Advanced Materials Interfaces

Citation (APA)

van Dijk, N., & van der Zwaag, S. (2018). Self-Healing Phenomena in Metals. *Advanced Materials Interfaces*, 5. <https://doi.org/10.1002/admi.201800226>

Important note

To cite this publication, please use the final published version (if applicable).
Please check the document version above.

Copyright

Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

Takedown policy

Please contact us and provide details if you believe this document breaches copyrights.
We will remove access to the work immediately and investigate your claim.

Green Open Access added to TU Delft Institutional Repository

'You share, we take care!' - Taverne project

<https://www.openaccess.nl/en/you-share-we-take-care>

Otherwise as indicated in the copyright section: the publisher is the copyright holder of this work and the author uses the Dutch legislation to make this work public.

Self-Healing Phenomena in Metals

Niels van Dijk* and Sybrand van der Zwaag

In comparison to other materials, in metals and metallic systems self-healing of cracks and crack-initiating defects is difficult to achieve due to the fact the solute atoms that act as healing agents are relatively small and generally have a relatively low mobility at the prevailing operating temperatures. In this review, the scientifically most interesting and industrially most promising approaches to self-healing metals are presented and discussed. The various approaches are separated in autonomous healing methods based on an intrinsic (solid-state diffusion) mechanism and assisted healing methods that need an external intervention. Some promising routes are identified while in other cases the approach has too many intrinsic limitations. Recently, a number of computational studies using molecular dynamics and finite element modeling have been performed to analyze the self-healing potential of metal systems as a function of the imposed conditions and to guide the further development of this family of self-healing materials.

certainly contributed to their impact on society. Most forms of transport (cars, trains, ships, planes), civil constructions (houses, high rise buildings, bridges, power stations, railway stations, airports), domestic appliances (chairs, cupboards, bed frames, domestic equipment), computers (cell phones, PC's, and supercomputers) would not be possible in their current form without highly developed metallic materials.

Currently all metallic materials are developed along the so-called "damage prevention" paradigm,^[1] i.e., their composition and microstructure are optimized such that the initiation and propagation of mechanical damage (in the form of internal damage such as pores or surface initiated cracks) leading to catastrophic failure of the product is postponed as much and as long as possible.

Such a performance needs a careful tuning of the constituent atoms forming the matrix and its secondary phases, the grain size and the dislocation structure in the "pristine" state. Of course, the word "pristine" state is somewhat a misnomer as engineering metals generally have undergone multiple thermomechanical treatments once casted and are in a far-from-equilibrium state. Yet, in this context "pristine" metallic products are those in the shape and condition at the start of their life in an actual construction. All current metallic engineering materials have in common that once a local crack or defect is generated, either by the preceding plastic deformation or simply by mechanical overload of the material, this damage will remain forever and could be the initiator of the final catastrophic fracture event. In simple mathematical terms

$$d(\text{damage})/dt \geq 0 \text{ (for } 0 < t < \text{product life time)} \quad (1)$$

Typical examples of such an accumulation of microscopic damage leading to macroscopic failure are (low and high cycle) fatigue as well as creep failure. Generally speaking metallic systems perform very well under such conditions due to the high bond strength between the metallic atoms as well as a stable dislocation network, which tend to keep the atoms more or less in place or at least in registry, even in case of severe loading or deformation.

The same positive attributes responsible for the excellent mechanical properties of metals are also the attributes for the modest success (in comparison to the field of self-healing polymers,^[2–4] self-healing composites,^[5] self-healing concrete^{[6])} in developing self-healing metallic materials. For a material to become self-healing local processes leading to "local

1. Introduction

Metals are probably the most successful man-made engineering materials currently available. Due to their strong multidirectional metallic interatomic bonds, their crystalline nature, their complete or partial mutual solubility, their extremely wide range of micro- and nanostructures and the fact that 75% of the atoms in the periodic table are of a metallic nature, the range of mechanical properties that can be obtained is exceptional with moduli ranging from 30 to 450 GPa, tensile strength values ranging from 10 to 3000 MPa, failure strains ranging from 0.2 to 5000%, operating temperatures ranging from -273 °C to over 2500 °C. While not directly relevant for their properties, the fact that metals intrinsically have an excellent recyclability

Dr. N. van Dijk
Fundamental Aspects of Materials and Energy Group
Faculty of Applied Sciences
Delft University of Technology
Mekelweg 15 2629 JB, Delft, The Netherlands
E-mail: n.h.vandijk@tudelft.nl

Prof. S. van der Zwaag
Novel Aerospace Materials Group
Faculty of Aerospace Engineering
Delft University of Technology
Kluyverweg 1 2629 HS, Delft, The Netherlands
Prof. S. van der Zwaag
School of Materials Science and Engineering
Tsinghua University
Beijing 100084, China

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/admi.201800226>.

DOI: 10.1002/admi.201800226

temporary mobility,” or more precisely “local temporary directional mobility,” should be organized. In this case the occurrence of local mechanical damage (i.e., the creation of a defect size with superatomic dimensions separated by free surfaces from its surrounding material) causes atoms to move toward the defect site and fill it, such that it is no longer present or cannot grow further under the prevailing conditions.

So, unlike conventional metals, self-healing metals should have a negative rate of damage formation at one or more stages of the product life time

$$d(\text{damage})/dt < 0 \text{ (for } t_i < t < t_{i+\Delta t, \text{healing}} \text{)} \quad (2)$$

where t_i is the time for the onset of the healing reaction.

For healing to take place noncollective atomic motion is required and atoms should move from their initial position to the damage site, and once arrived there should become immobile again. Due to the relatively high melting point of most metallic system the intrinsic low atomic mobility at room temperature of metallic atoms in their crystal lattices is a serious limitation. Two other major obstacles are present on the route toward self-healing metallic materials: i) the intrinsically small size of a single metallic atom and ii) the fact that the motion of a metallic atom generally leads to the motion in the opposite direction of a vacancy. In the case of self-healing polymers the repositioning of a single molecule, or even the motion of a molecular segment in between physical crosslinks, will have a much stronger volumetric effect than the motion of a single atom in a metal. The same applies to the volume generated by the molecular activity in bacterial concrete.^[6] A general overview of the characteristics and requirements for various self-healing materials classes is given by Hager and co-workers.^[7]

In this review paper, we will focus primarily on the developments of self-healing metallic materials that have a chance of becoming an industrial reality, as they can be made by bulk metallurgical and thermomechanical processes also used for existing non-self-healing equivalents. We will focus in particular on precipitation hardenable aluminum alloys and iron-based alloys being model alloys for future self-healing creep-resistant steels. In these alloys, the self-healing behavior is to be realized by relatively minor adjustments in the alloy composition and the microstructural state at the start of their lifetime cycle. These alloys belong to the category of autonomous intrinsic self-healing systems as the healing will take place at the prevailing combination of temperature and stress state and the actual healing agent (the specific element brought into solid solution) forms an integral part of the material itself.

This paper will also address the more academic demonstrations of self-healing metals based on the inclusion of a low-melting point phase. This route belongs to the field of non-autonomous extrinsic healing systems, as the healing requires a dedicated heat input (and dedicated subsequent cooling) and the actual healing agent can be physically separated from the matrix in which it is embedded. Furthermore, examples of self-healing metals that require other external stimuli such as electrical pulses, plastic deformations or elastic deformations due to shape memory effects, are included.



Niels van Dijk studied solid-state physics at the Delft University of Technology and completed a PhD in experimental physics at the University of Amsterdam. He was a post-doc at the French Atomic Energy Agency (CEA) in Grenoble (France). During this period, he performed neutron scattering experiments at the Institute

Laue-Langevin (ILL). He is currently appointed as associate professor at the Delft University of Technology to investigate phase transitions in structural and magnetic materials with radiation techniques. His main fields of expertise are phase transitions, magnetic materials, structural materials, metallurgy, self-healing materials, neutron scattering, and synchrotron radiation.



Sybrand van der Zwaag has been a full professor at the TU Delft since 1992. In 2003 he joined the faculty of Aerospace Engineering to establish his current group Novel Aerospace Materials. From 2004 to 2017 he was the scientific director of the national Dutch program on self-healing materials and the co-chairman of the German

SPP program on the same topic. He also holds a part-time professorship at Tsinghua University, Beijing China.

It should be mentioned that the field of self-healing of corrosion damage of metallic substrates by organic coatings^[8,9] is kept outside the scope of this paper for a lack of conceptual congruency, as the healing does not involve the corroded metal, but the healing of the barrier function of the polymeric coating. Of course, the field of metal-ion based self-healing polymers^[10,11] is also outside the scope of this review. Earlier (partial) reviews on specific self-healing metal systems can be found elsewhere.^[12–18]

2. Autonomous Healing

Autonomous intrinsic healing in metals does not require the assistance of external (mechanical, thermal, electrical, or other energetic) input or triggers, but may require the lowering or complete removal of the forces responsible for the damage creation. These conditions are not different from those for other autonomous intrinsic healing materials such as polymers^[3,4] and natural bone.^[19,20] Also in these cases healing can take place at ambient temperatures, but the external mechanical

load has to be removed temporarily to allow reformation of chemical and physical bonds across the damage site. In the examples of autonomous intrinsic healing metals the composition of the alloy is generally similar (or even identical) to that of known commercial alloys and the “healing agent” is not discernible as a separate identifiable phase in the microstructure, but is present as an alloying element in supersaturated state. Furthermore, the healing takes place under conditions almost identical (at least as far as temperature is concerned) to those under which the damage was formed.

The key parameter for autonomous intrinsic healing metals is the atomic mobility of the solute atoms (and that of the matrix atoms as the transport of the solute atoms through the crystal lattice also requires the diffusional displacement of the matrix atoms in the opposite direction). As the atomic mobility strongly depends on temperature we can define a lower and an upper temperature that confine the temperature window in which appealing combinations of self-healing behavior and adequate mechanical properties can be obtained. For the lowest temperature (T_{\min}) at which a measurable atomic transport can be observed in long yet realistic time scales, we use the generally accepted lower temperature limit at which creep deformation takes place: $T_{\min}/T_m \approx 0.40$, where T_m is the melting temperature (both temperatures are defined in kelvin units). Application of this rule to the two most relevant industrial metallic systems, yields for the minimum temperatures at which autonomous healing can take place values of $T_{\min} \approx 100$ °C for aluminum alloys and $T_{\min} \approx 450$ °C for steels ($T_m = 660$ °C for pure Al and 1538 °C for pure Fe). Of course, at high temperatures close to the melting point the atomic mobility reaches high values and we should have a good potential to achieve self-healing. However, at these temperatures the mechanical properties drop to rather low values, making the material less suitable for real applications. So, more or less arbitrarily we define the maximum operation temperature (T_{\max}) at which we can benefit from self-healing behavior as: $T_{\max}/T_m \approx 0.65$. This limit is again in line with the first-order estimate for the upper operation temperature for creep-loaded metals. For aluminum alloys and steels, these maximum temperatures are about $T_{\max} \approx 330$ °C for aluminum alloys and $T_{\max} \approx 900$ °C for steels. Based on these guidelines it should be possible to design self-healing aluminum grades repairing damage autonomously near room temperature, while in the case of steels, autonomous healing of damage can take place at temperatures at which creep-resistant steels are designed to function.

With the temperature window for healing in metal alloys being defined, it is illustrative to make an estimate of the size of the defects that can be healed via diffusional processes. To this aim we take 10^5 s (≈ 1 d) as an acceptable healing time and use the diffusion coefficient $D = D_0 e^{-Q/RT}$ of Cu in aluminum (with $D_0 = 6.5 \times 10^{-5}$ m² s⁻¹ and $Q = 136$ kJ mol⁻¹)^[21] and the diffusion coefficient of Au in iron (with $D_0 = 7.0 \times 10^{-5}$ m² s⁻¹ and $Q = 227$ kJ mol⁻¹)^[22] (see the next sections why these elements were selected). Such a first-order estimate is informative as it shows that the only very small scale damage, smaller than the characteristic diffusion length $2\sqrt{Dt}$, can be healed. For Cu-containing aluminum alloys the healable damage size ranges from 1.5 nm to 7 μm for the lowest and highest healing temperature, respectively. For Au-containing steels the healable

damage sizes range from 35 nm to 50 μm, respectively. We will now look in more detail into the reported studies on the healing of aluminum alloys and creep steels (and model alloys thereof) and compare the results obtained with the conceptual expectations.

2.1. Aluminum

As stated in the introduction, any intrinsic self-healing reaction in a metallic system requires sufficient mobility of the atoms involved, irrespective whether they are the matrix atoms or the solute atoms dissolved therein. So, if this reaction is to take place at or near room temperature, an alloy with a base metal that has a relatively low melting point such as aluminum offers the highest chance of success.

A high diffusivity is however not the only requirement for self-healing. To heal the damage, i.e., to remove the cavity, one needs a solid-state reaction leading to the formation of a new phase with a significantly larger average atomic volume than that of the constituent atoms. This solid-state reaction at the damage site turns the mobile healing species into an immobile species in accordance with the general conceptual rules for self-healing materials defined in the introduction. A precipitation reaction leading to an increase in the average atomic volume stimulates the precipitation of the new phase in the empty cavity as this is energetically favorable over the precipitation in the matrix because less strain energy is involved. Another requirement for autonomous (intrinsic) healing to take place is that the healing solute atoms are ready available and in an energetically raised state. Such a state can easily be obtained by bringing the solute atoms in a (full or partial) supersaturated state. The fully supersaturated (homogenized) state offers of course the largest potential for self-healing, but leads to relatively low yield strength values, while the underaged state may yield a more attractive combination of a decent yield strength and some remaining self-healing capability.

Probably the first studies into the self-healing behavior of aluminum alloys are those by Lumley and co-workers who studied self-healing in the context of both creep^[12,23] and fatigue.^[12,24] They focused on the supersaturated state as the starting condition and on alloys that show dynamic precipitation reactions leading to a local volume expansion.^[25] Once local creep or fatigue damage occurs precipitation at the defect sites can take place and the nanocrack is effectively removed. This process should lead to an increase in the (high-cycle) fatigue life time, as well as the creep life time. The concept is elegantly visualized in **Figure 1** and shows how a nanod defect would be filled by solute transport along a dislocation intersecting the nanod defect. The acceleration of mass transport by pipe diffusion along dislocations trapped at the nanod defect is crucial to obtain an adequate directional mass transport at temperatures where volumetric diffusion through the undisturbed lattice would be too slow.

Lumley and co-workers^[24] observed a small improvement in the high-cycle fatigue life in an underaged Al–Cu–Mg–Ag alloy tested at room temperature and at maximal stress levels ranging from 140 to 240 MPa for an R value of -1 . The R value expresses the amplitude ratio of the minimum peak stress

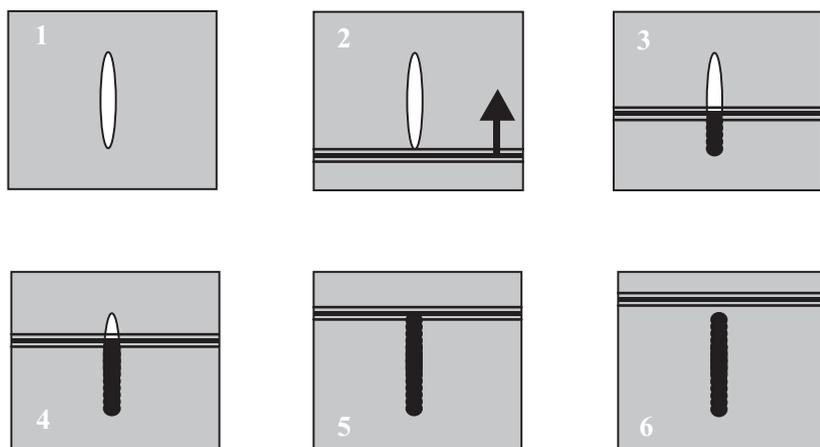


Figure 1. Schematic representation of nanodamage healing via solute transport along a dislocation and subsequent precipitation. Stage 1: initial damage. Stage 2–5 successive healing stages. Stage 6: healed nanodamage. Reproduced with permission.^[24] Copyright 2005, R.N. Lumley.

divided by the maximum peak stress ($R = \sigma_{\min}/\sigma_{\max}$) in the fatigue test. As shown in **Figure 2a**, a more substantial improvement in the fatigue life time, in particular at lower stress levels, has been observed in an aircraft-grade Al–Cu–Mg AA2024 alloy when the fatigue life of the underaged (UA) material was compared with that of the same material in its peak-aged T3 state.^[26,27] For the lowest examined stress value of 260 MPa, the number of cycles to failure for the T3 condition was 3×10^5 cycles, while that for the UA condition was more than 10 times higher. However, such an improvement in fatigue life could only be demonstrated for $R = -0.4$. No improvement was observed when the materials were tested at $R = +0.1$, where all samples tested at a stress range of 260 MPa failed at about 2×10^5 cycles.

A Doppler broadening analysis of the positron annihilation photons in the ($R = -0.4$) fatigue-loaded underaged samples has been performed to determine if dynamic precipitation had taken place.^[26] Positron annihilation provides ideal techniques (in the form of Doppler broadening and lifetime spectroscopy) to monitor the occurrence of nanoscale damage generated by plastic deformation of aluminum alloys and its disappearance upon unloading and subsequent ageing.^[28,29] In particular the Doppler broadening analysis can reveal changes in the local chemical environment of the damage site. It has been demonstrated that changes in the S parameter reflect changes in the degree of clustering of Cu atoms at the defect sites. However, the positron Doppler broadening data on the fatigue-loaded underaged samples as a function of the fractional life time did not show any change in the S parameter until the very last stage of the sample life time, where substantial plastic deformation had taken place near the crack (see **Figure 2b**). Although an improvement in fatigue life time was observed, it could not be connected to the formation of Cu-rich precipitates at early-stage damage sites. While a disappointing outcome, it would be in line with the results from extensive studies on crack initiation in aluminum aircraft alloys,^[30] which showed that for perfectly produced and processed samples the crack initiation primarily takes place at the brittle interface between the larger constituent particles (of 10–20 μm). Crack initiation sites of such dimensions would be too large to be healed by delayed

dynamic precipitation. Furthermore, as argued by Wanhill,^[31] fatigue cracks generally nucleate at or near the sample surface, where precipitation is hindered by the presence of the natural oxide layer. So, although there are indications that intentional supersaturation in precipitation hardenable aluminum alloys can lead to higher fatigue life times, the rigid evidence is yet to be provided.

As qualitatively predicted, there is indeed experimental evidence that the creep life time of an underaged AA2024 alloy tested at 150 °C and at a load of 300 MPa exceeds that of the same alloy in its T6 aged state.^[12,23] The effect of supersaturation on the creep life time in aluminum alloys has however not been studied extensively since these reports. So far there is no direct metallographic evidence that that creep life time extension is due to the healing of early-stage

creep damage. In contrast to the case of fatigue damage, in the case of creep failure most of the early stage damage would form internally in the sample and the envisaged precipitation

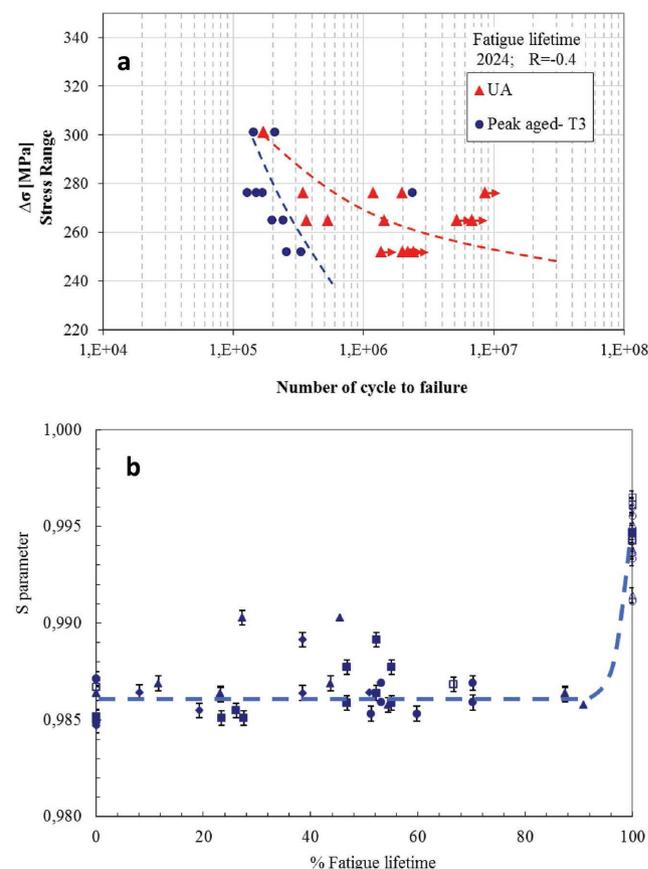


Figure 2. a) Fatigue life time of peak aged and underaged (UA) 2024 aluminum alloys. b) Changes in the S parameter for the Doppler broadening in positron annihilation experiments for the fatigue loaded UA samples as a function of their fractional lifetime. Reproduced with permission.^[26] Copyright 2015, IOS.

reactions would therefore not be affected by side reactions with the environment. It is interesting to note that the temperature at which the life time extension is observed experimentally ($T/T_m \approx 0.45$) fits well within the temperature window for autonomous healing in aluminum predicted in the introduction of this subchapter.

2.2. Steel

When a steel component is placed under a quasi-constant load at elevated temperatures ($T/T_m > 0.4$) for a long period of time creep damage may take place. Creep damage starts with the formation of cavities preferentially formed on the grain boundaries oriented perpendicular to the applied stress. Over time the size and density of these creep cavities will increase slowly. When neighboring cavities coalesce the resulting cavity shows a much more rapid growth. This process will eventually result in a macroscopic crack and fatal damage of the steel component. Creep-resistant steels are extensively applied in power plants, in which the turbines and steam pipes operate at temperatures of 500–700 °C (773–973 K). Considering the melting temperature of pure iron ($T_m = 1538$ °C) as reference temperature, the relative temperature is about $T/T_m \approx 0.5$.

The basic concept to potentially achieve autonomous repair of creep damage in steels was first proposed by Shinya and co-workers^[32] and later refined by Zhang and co-workers.^[33] The idea is to interrupt the creep cavity growth by site-selective precipitation on the free cavity surface to avoid the coalescence of these cavities, which ultimately leads to the development of macroscopic damage. In **Figure 3**, a schematic overview of the self-healing mechanism is presented. In its initial loading state the material consists of an alloy with a supersaturated solute element that wants to segregate, but experiences a significant energy barrier for precipitate the nucleation within the bulk

of the material. Under an applied stress a number of creep cavities nucleate on the grain boundaries oriented perpendicular to the load. These creep cavities then grow in size by a continuous flow of vacancies along the grain boundary. Some of the supersaturated solute atoms now precipitate at the free creep cavity surface, as the barrier for precipitate nucleation is significantly reduced compared to its bulk value. The flux of supersaturated solute along the grain boundary reduces and potentially stops the creep cavity growth. The precipitation continues until the creep cavity is completely filled. This process will restart each time a new creep cavity is formed.

The earliest experimental observations on the (unintended) self-healing of creep damage by site-selective precipitation in compositionally modified stainless steels were reported by Laha and co-workers^[34–38] and reviewed by Shinya.^[13] By adding small amounts of B and N,^[34,35] the creep lifetime was significantly enhanced and at the same time a pronounced BN precipitation inside the creep cavities was observed at a temperature of 750 °C. A detailed analysis of the mechanism^[32,36] indicated that the segregation of B and the precipitation of BN on the creep cavity surface both retard the growth of the creep cavity, and thereby lead to an increase in the creep life time. In a subsequent study it was shown that the addition of Cu in stainless steel resulted in a further enhancement of the creep lifetime.^[37] A more extensive study however revealed that although the short-term creep rupture strength was improved by the addition of copper in stainless steel, the long-term strength was inferior.^[38] The self-healing process of creep damage in fcc Fe by site-selective BN precipitation at the creep cavity surface was also modeled in a multiscale computational study by Karpov and co-workers.^[39]

Inspired by the work on self-healing of creep damage in Cu-containing stainless steels, the self-healing potential of binary Fe-based model alloys designed to show self-healing behavior (rather than good mechanical properties) has been

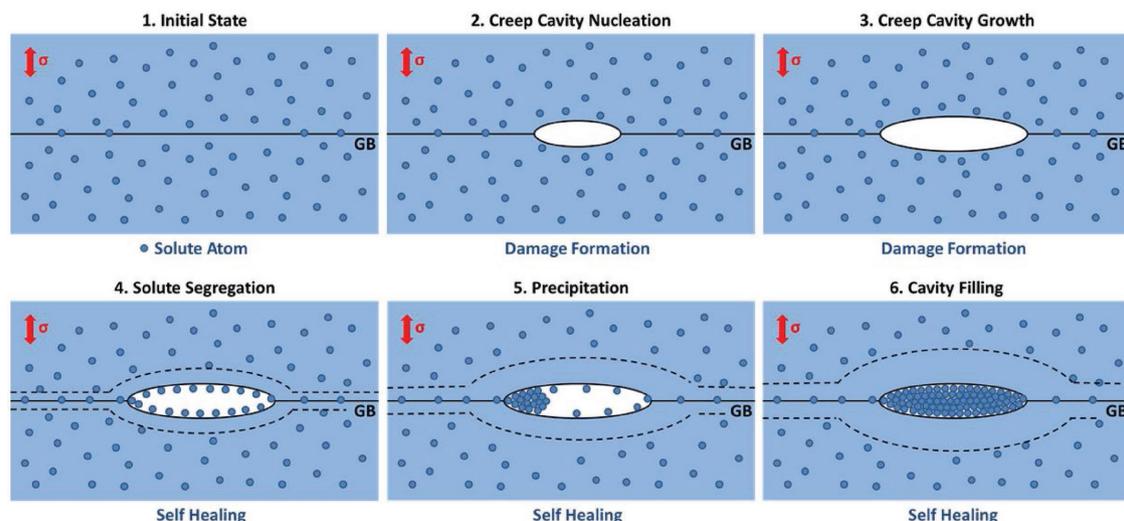


Figure 3. Schematics of the self-healing principle of creep damage in metal alloys: damage formation is followed by self-healing. A metal alloy matrix with a supersaturation of mobile solute atoms is placed under an applied load (σ) perpendicular to the grain boundary (GB) (1). Nucleation of a creep cavity at the GB (2), is followed by growth (3). The added solute favors segregation at the free cavity surface (4), this initiates volume and GB diffusion of solute from the matrix towards the open volume of the creep cavity (5) until the cavity is completely filled (6). The nearby matrix is solute depleted by the diffusion, as indicated by the dashed line. Reproduced with permission.^[33]

investigated systematically by our research team. To this aim we designed a number of (binary) Fe-X alloys for a selected creep temperature of 550 °C in which the following criteria are met: i) the system can be brought into a supersaturated state, with an intended level of supersaturation of about 1 at%, ii) the solute atoms have a larger atomic radius than that of Fe, such that when the solutes precipitate in the creep induced cavities there is a net volumetric filling process, iii) the precipitation of the reaction phase will not occur in the grain interior under the prevailing conditions, iv) the solute atoms diffuse faster than the self-diffusion of Fe and v) in their passage from the grain interior to the damage site, the solute atoms do not interact with each other atoms to form an immobile intermetallic. In support of our program the diffusion coefficients of 28 alloying elements in pure bcc iron have been calculated using ab initio DFT modeling.^[22] As can be seen in **Figure 4**, it is found that the activation energy for the diffusion Q_{FM} is of similar magnitude

for all (substitutionally dissolved) elements investigated and with only minor variations in the preexponential factor D_0 .

Given the success of using Cu as the healing agent in austenitic (fcc) stainless steel, early research focused on Fe–Cu alloys with and without added B and N.^[40–43] The precipitation of supersaturated Cu was clearly accelerated by the presence of dislocations and free surfaces. The nucleation of precipitates however only showed a weak preference for the free surfaces compared to the dislocation network within the matrix and at grain boundaries.^[16] This was ascribed to the relatively small strain energy associated with the precipitation supersaturated copper within the matrix, as a result of the comparable atomic size of Cu and Fe. The precipitation of copper within the grain interior instead of at the creep cavity surface implies a rather inefficient use of the healing agent and potential depletion of the source of healings before the onset of extensive creep cavity formation. For the Fe–C–B–N model alloys (with a bcc lattice structure) no significant defect-induced precipitation of BN precipitates was observed at creep loading conditions.

Clear evidence that self-healing of creep damage could be achieved in (bcc) Fe-based model alloys was found when the creep behavior of Fe–Au (1 at%) and Fe–Cu (1 at%) alloys was compared.^[33] As shown in **Figure 5a**, the creep life time as is significantly enhanced for solutionized Fe–Cu compared to solution-depleted Fe–Cu alloys. In the solutionized samples all Cu was homogeneously dissolved in the matrix at high temperatures, retained in the matrix by quenching and the brought in a supersaturated state at the intermediate operating temperature during creep. In the solution-depleted samples all supersaturated solute was precipitated at the start of the creep test. The solutionized samples are therefore in a metastable state that provides a significant amount of mobile solute potentially available to self-heal creep damage. This is reflected in the increase in creep lifetime. When the solutionized Cu is replaced by solutionized Au, then the creep lifetime was found to be enhanced even further.

An extensive microstructure evolution by various electron microscopy techniques (SEM, EPMA, EBSD, TEM) and atom probe tomography (APT)^[33,44] revealed that in binary Fe–Au alloy the supersaturated solute Au shows a strong tendency to segregate at the free surface of the formed creep cavities. In the absence of creep cavities nanosized precipitates only formed when a high dislocation density was present.^[45–47] As a result of the large difference in atomic size between the Au and Fe atoms precipitate nucleation inside the matrix is strongly suppressed by the large strain energy involved in the heterogeneous nucleation. This strong preference for precipitation at (internal) free surfaces makes the Fe–Au system an excellent example for autonomous repair of creep damage. In **Figure 5b**, a SEM image of the creep cavity filling by gold precipitation is shown as illustration. The efficiency of the healing process was quantified by quantitative image analysis of the SEM images of creep failed Fe–Au alloy samples. As indicated in **Figure 5c**, a healing efficiency of 80% was obtained for low applied stresses, which decreases for higher stresses. This reduction was explained by a simple model^[33,44] that compares the creep cavity growth rate and the filling rate by precipitation. Where the creep rate strongly depends on the applied stress the solute diffusion is mainly controlled by temperature. This suggests that beyond

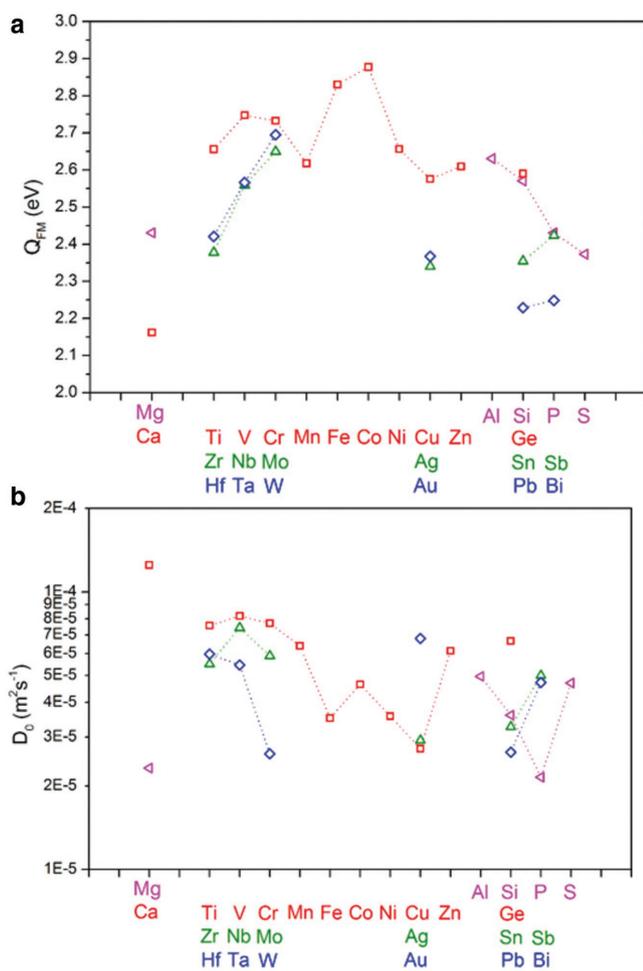


Figure 4. a) Total activation energy Q_{FM} for impurity diffusion in the ferromagnetic state, arranged by row and column of the periodic system: row 3 of the periodic system (purple triangles), row 4 of the periodic system (red squares), row 5 of the periodic system (green triangles), and row 6 of the periodic system (blue diamonds). b) Corresponding prefactor for impurity diffusion D_0 . The dashed lines are a guide to the eye. Reproduced with permission.^[22] Copyright 2017, American Physical Society.

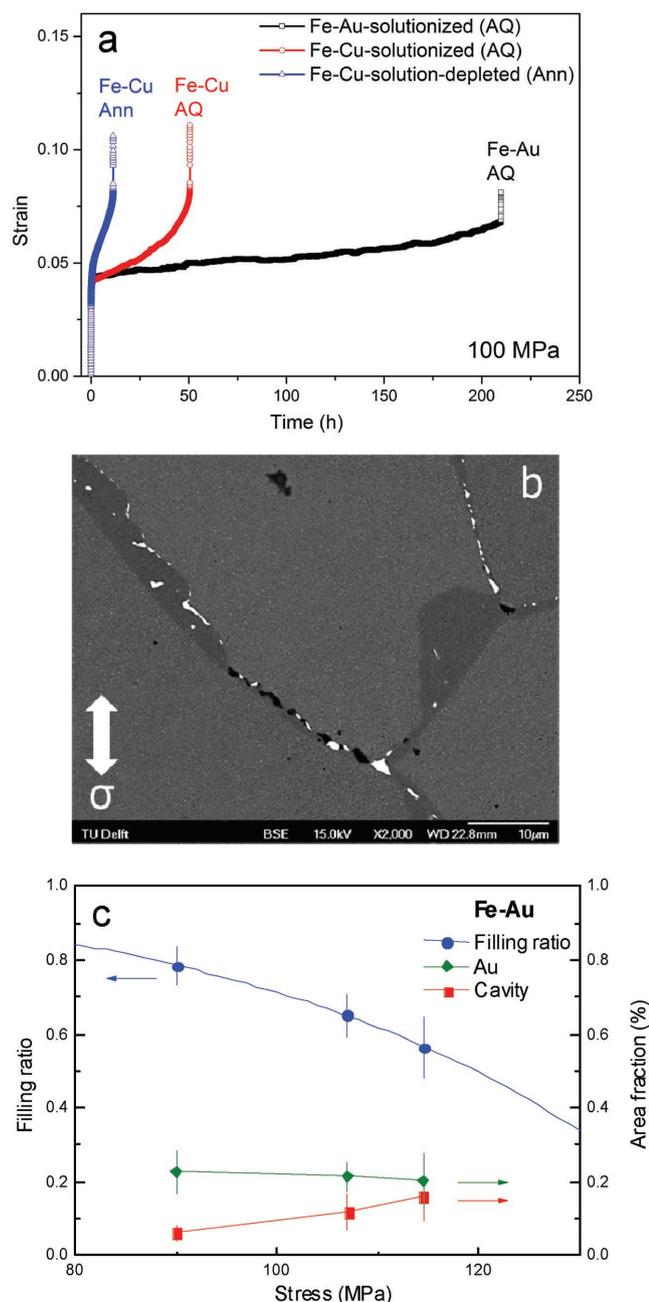


Figure 5. a) Creep curves for the Fe–Au (solutionized) and Fe–Cu (solutionized and solution-depleted) alloys at an applied stress of 100 MPa and a temperature of 550 °C. b) Micrograph of filled and partially filled cavities and microcracks along grain boundaries. c) Experimentally determined areal fraction of unfilled creep cavities, areal fraction of Au precipitates and the resulting fraction of precipitate-filled creep cavities (filling ratio) at different applied stress levels for the Fe–Au alloy. Reproduced with permission.^[33]

a critical stress the precipitation rate inside the creep cavity is insufficient to catch up with the creep cavity growth.

In order to study this self-healing process in full detail 3D studies of the partially filled creep cavities are required. As the creep cavities nucleate in the nanometer size range and reach a size of about a micron by the time the filling is complete a high-resolution tomography technique is required. In **Figure 6**,

experimental nanobeam X-ray tomography data are shown for creep-failed samples of the solutionized Fe–Au alloy.^[48]

With this advanced synchrotron technique a spatial resolution down to 25 nm can be reached. As shown in **Figure 6**, the large difference in electron density allows for a clear discrimination between the creep cavities, the gold precipitates and the matrix. The creep damage is clearly concentrated at the grain boundaries, while at creep fracture the creep damage is partly healed by the gold precipitation. Most informative for the healing process are the partly filled cavities. In **Figure 7**, a series of examples of the partly filled cavities is shown at different levels of filling (indicated by the filling ratio FR). The high spatial resolution provides a detailed view on the complex cavity shapes that are formed during creep. The precipitation is found to form at one or more specific nucleation sites on the free creep cavity surface and then grows into the free volume until the cavity is fully filled. It should be pointed out that the supply of Au atoms to the pores will proceed by an as-yet unestablished ratio of bulk diffusion and grain boundary diffusion, so the actual rate of growth may be higher than that predicted on bulk diffusion coefficient values only. As gold precipitation on the free surface of a creep cavity has been demonstrated convincingly, it would be a logical assumption that gold precipitation also takes place at the outer surface. In a subsequent SEM experiment,^[49] gold precipitation and island formation were indeed observed on the outer surface after in-situ aging at high temperatures. As this outer surface is more accessible it provides direct insight in the precipitation mechanism responsible for the creep cavity filling.

Although the Fe–Au alloy system was found to be an excellent example for autonomous repair of creep damage in Fe-based alloys, the addition of gold has limited practical applications due to its scarcity. The key ingredients identified from the Fe–Au system where a supersaturation of mobile solute with a strong chemical driving force for precipitation combined with a strong preference for precipitation at a free surface compared to the matrix. In order to maintain a high energy barrier for nucleation in the matrix it is logical to search for other elements with an atom size that is significantly larger than iron, which are abundantly available. Recently, it was found that self-healing of creep damage can indeed also be achieved in binary Fe–Mo alloys.^[50] In this system, the solubility of Mo is higher than Au at a temperature of 550 °C. The supersaturated Mo now forms the Fe₂Mo Laves phase precipitate. The healing of creep cavities by Fe₂Mo precipitation in Fe–Mo alloys is illustrated in **Figure 8**. The Fe–Mo system provides a second example for autonomous repair of creep damage, which is still less effective as the Fe–Au system due to a slower healing response. Work is ongoing to study the creep damage healing phenomena in high-purity binary Fe–W model alloys with a similar degree of supersaturation and promising results are obtained.

3. Assisted Healing

3.1. Temperature, Below the Melting Point

The creation of structural damage generally creates additional internal surface when cracks or cavities are generated.

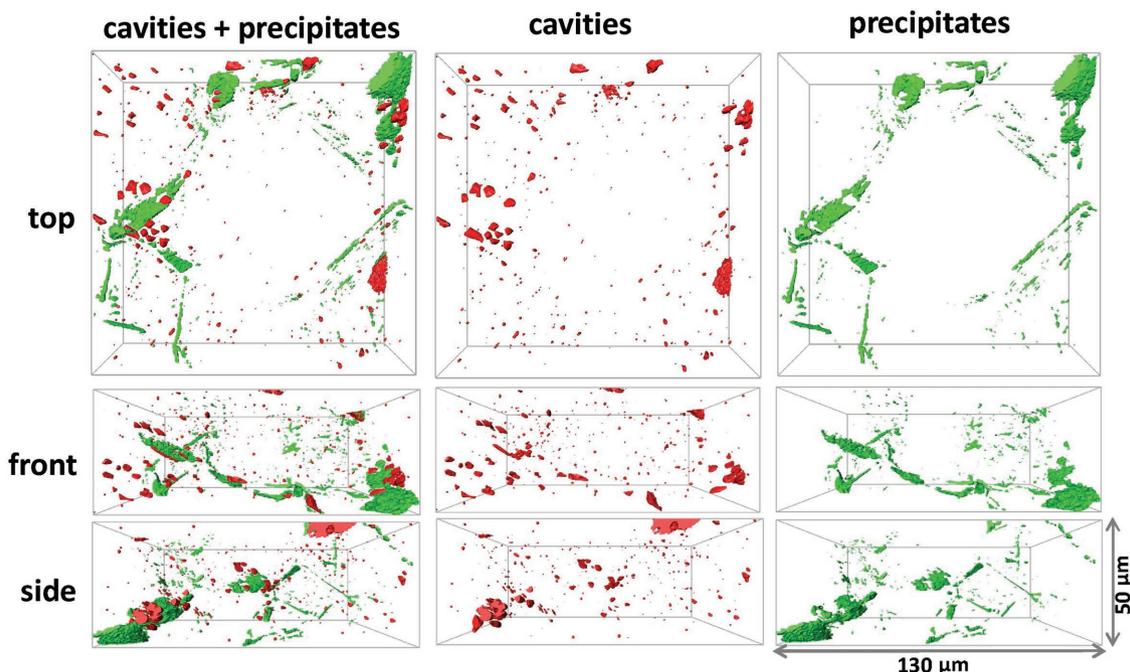


Figure 6. Region of interest ($130 \times 130 \times 50 \mu\text{m}^3$) revealing the microstructure of the Fe–Au alloy after creep failure at a temperature of $550 \text{ }^\circ\text{C}$ and an applied stress of 80 MPa . The applied stress is normal to the top view. Reproduced with permission.^[48] Copyright 2016, Elsevier.

In the absence of an external force to stabilize this added free surface of the cracks the system is in a metastable state with an excess surface energy. When the atom mobility is limited at the operating temperature this metastable state is maintained on the time scale relevant for its life time. Enhancing the temperature for a limited period of time will now temporarily enhance the atom mobility, which tends to drive the system towards a reduction of the excess surface energy. When the preferred structure of the material is

well defined the original structure may be repaired by the temporal increase in temperature.

An elegant demonstration of this effect was provided by Kovalenko and co-workers.^[51] They considered a system of single crystalline gold particles on a sapphire substrate, in which the particles were plastically deformed by indentation with an atomic force microscopy (AFM) tip. Annealing to a temperature of $660 \text{ }^\circ\text{C}$ ($T/T_m = 0.65$) for 10 min resulted in a full recovery of the original shape of the particle. A comparable demonstration of low temperature sintering effects leading to crack healing has been given by Chen and co-workers^[52] for porous silver interlayers in power electronic devices. In pure iron crack healing was demonstrated by in situ TEM when the temperature was raised to $700\text{--}750 \text{ }^\circ\text{C}$ ($T/T_m \approx 0.55$) with a migration rate of 0.3 nm s^{-1} .^[53] To heal sizeable cracks within a reasonable time scale the temperature needs to be raised significantly. This process can be considered as sintering and generally the component dimensions cannot be controlled without an additional confinement of the outer shape. The temperature assisted crack and pore healing was elegantly analyzed in the computational study by Wang and co-workers.^[54]

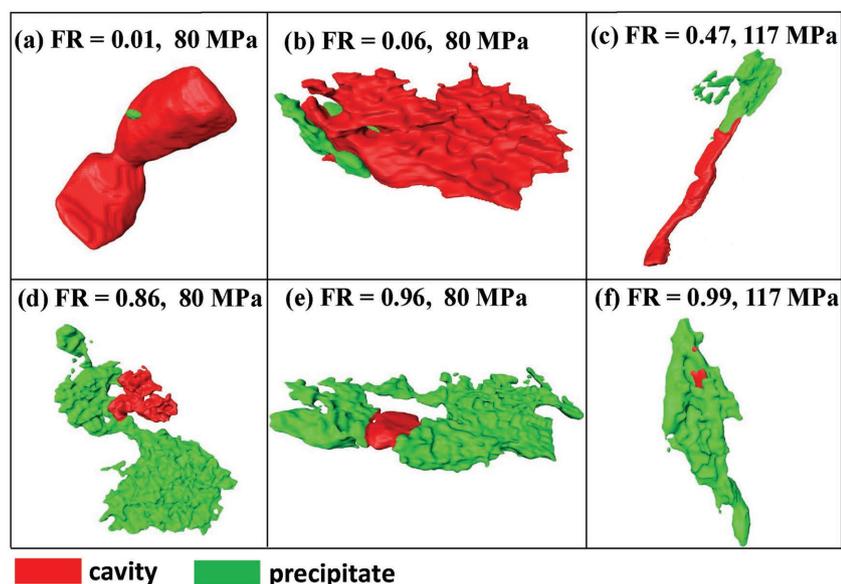


Figure 7. Examples (top view) showing cavities (a–f) with different filling ratios (FR). The applied stress is normal to the top view. Reproduced with permission.^[48] Copyright 2016, Elsevier.

This process can be considered as sintering and generally the component dimensions cannot be controlled without an additional confinement of the outer shape. The temperature assisted crack and pore healing was elegantly analyzed in the computational study by Wang and co-workers.^[54]

3.2. Temperature, Above the Melting Point

As stated in the introduction, atomic mobility is the key phenomenon to be taken into account in the design of self-healing

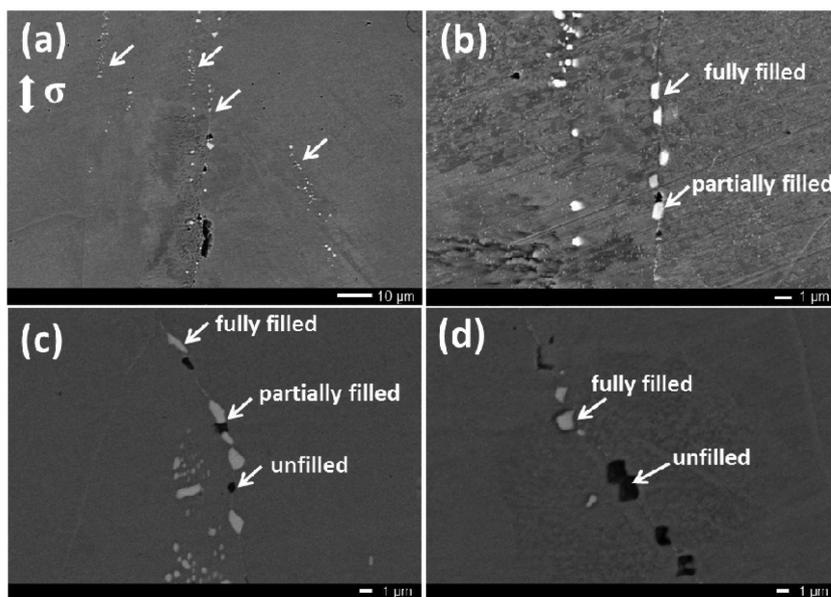


Figure 8. Micrographs (a–d) of the Fe–Mo alloy after creep for a stress of 160 MPa at a temperature of 565 °C demonstrating cavities and precipitation at grain boundaries parallel to the loading direction. Reproduced with permission.^[50] Copyright 2016, The Authors, published by Springer.

for other materials such as asphalt^[60] and high-temperature ceramics,^[61–64] albeit that in this case the system is non-autonomous and requires thermal activation. When the original approach from White and co-workers is followed, there would be the additional technical complexity that a ceramic shell surrounding the solder droplet is required, analogous to the alumina coating around the Mo₂Si healing particles used in novel self-healing thermal barrier coating systems.^[65] Recently, Kim and co-workers designed a (Al, Cu, Si)_{100-x}(Sn, Bi)_x alloy system with a microstructure consisting of spherical particles of a Sn–Bi phase with a low melting point (137 °C) embedded without a shell in a Al–Cu–Si matrix phase with a high melting point (517 °C).^[66] They demonstrated that alloys processed to this microstructure showed the desirable ability to heal internal cracks (up to a width of 28 μm) induced by hot rolling at a temperature of 150 °C.

metals. Hence it is not surprising that research has been directed to approaches in which local melting of one of the phases present in the material plays an important role. This approach has been explored first by Manuel^[14,55] who designed a composite material consisting of shape–memory alloy (SMA) wires embedded in a low melting point matrix metal. In case of fracture, the crack is assumed to run through the relatively weak brittle matrix and to leave the SMA wires intact, due to a low interfacial bond strength and a superior tensile strength. Upon heating of the composite, the SMA wires contract, thereby close the crack gap and ascertain physical contact between the opposite crack faces. Upon further heating the matrix (partially) melts and the crack is filled completely by the liquid fraction. Upon subsequent cooling to the starting temperature well below the melting temperature a mechanically recovered sample should be obtained. The process has been demonstrated to work using a Sn-21Bi (wt%) low-temperature solder as matrix and 1 vol% NiTi SMA wires. A 95% strength recovery was obtained upon healing for 24 h at 169 °C (at this temperature 20 vol% of liquid is present). More recent studies along the same line are performed by Rohatgi and co-workers,^[56,57] who used a zinc-based alloy as matrix material. Of course, one can question the practical relevance of this approach as the presence of a semiliquid matrix during the healing process requires additional measures to maintain the shape of the sample and prevent liquid leakage from the matrix. The only potential application field we could identify is that of solder alloys (optionally reinforced with SMA nanowires) for electronic applications.

The alternative approach to that of a low melting point matrix reinforced by high melting point fibers is that of a high melting point matrix containing capsules of a low melting point metal.^[58] This concept closely resembles the original White concept^[59] and the many derivatives thereof

3.3. Plastic Deformation

The combined effect of high temperature and compressive stress is a rather invasive operation, but can result in an effective healing of internal cracks in the metal microstructure. Yu and co-workers^[67] demonstrated that self-healing of internal cracks could be achieved in a low-carbon steel when hot plastic deformation was applied at temperatures ranging from 900 to 1200 °C ($T/T_m = 0.65–80$). During the deformation the sample thickness was reduced to values between 90% and 50% of its original value. It was found that the degree of crack healing increases with increasing heating temperature, reduction ratio, and holding time.

Xin and co-workers^[68] adopted a similar crack healing procedure on a different low-carbon steel. By applying a fixed reduction at different temperatures ranging from 900 to 1200 °C, a significant crack healing and recovery of the tensile strength could be achieved within 2 h for the highest operation temperatures. From a microstructure analysis it was concluded that the crack healing is by atomic diffusion at the lowest temperature of 900 °C ($T/T_m = 0.65$), while at higher temperatures of 1000 °C and beyond ($T/T_m > 0.70$) it mainly occurs more rapidly in the form of recrystallization and grain growth. The evolution of crack healing can be divided into four stages: i) the formation of bulging particles on the crack surface, ii) bridging of the crack by the particles resulting in crack segmentation, iii) spheroidization of the crack segments, and iv) diminishing of the spherical voids and vanishing of the crack healing zone.

In a subsequent study, the same authors also investigated the recovery of the impact properties after the described assisted healing operation.^[69] It was found that the degree of recovery of the impact properties after the crack healing treatment increases with increasing healing temperature and

holding time in the temperature range from 900 to 1100 °C, while the impact properties deteriorate at 1200 °C. When the cracks have disappeared completely the tensile properties of the crack-healed samples were fully recovered, while their impact properties were only partially restored.

While the combination of pressure and high temperature certainly works to reduce the amount of internal defects in metallic products, as the extensive industrial application of hot isostatic pressing illustrates, one can question whether the expression “self-healing” applies to this route. It certainly is not an in situ or autonomous healing route.

3.4. Electric Field

One form of assisted healing of metals that is currently investigated is the use of an electric field to generate a higher atomic mobility near a defect site and in doing so promote the repair of internal cracks. Zheng and co-workers^[70] developed a novel crack-healing approach, called electrohealing, by means of an electrochemical process in which metallic ions in electrolyte are used as a healing agent. Pure Ni sheets with a through-thickness crack were taken as an example. Cracks with sizes in the micrometer range or larger are successfully healed. Healing efficiencies up to 96% were achieved.

An alternative approach to use electric field was adopted by Song and co-workers,^[71] who demonstrated that internal cracks in a titanium alloy could be healed by electropulsing using the discharge of a capacitor to generate a current through the metal specimen. Around cracks the current is locally enhanced as the flow is concentrated, which leads to a resistive heating at the edges of the open-volume defect. The inhomogeneous temperature rise will induce a thermal compressive stress inside the material. This stress field is highly localized. As a result, the pulse current which is automatically concentrated at the damage site generates a temperature gradient and compressive stresses at these sites that directly heal the internal defects in the metal.

4. Modeling

Modeling studies on (intrinsic) self-healing of structural damage in metals have up to recently been small in number. Computational investigations generally either focus on microscopic cracks using continuum models by employing finite element model (FEM) calculations^[54,72,73] or on the time evolution of nanoscale cuts or voids using atomistic models by employing molecular dynamics (MD) calculations.^[74–79] In some cases multiscale modeling is used to incorporate atomistic properties in the microscopic description of the damage repair.^[39]

The general characteristics of the crack evolution in a self-healing metal have first been evaluated by Wang and co-workers^[54] using FEM calculations. The void healing process was analyzed, which resulted in some analytical solutions for idealized cases. From the numerical and analytical calculations the parameters that control the rate of the self-healing process were derived. While their model did not include any metal specific properties and regarded the metals as an isotropic continuum, the analysis gave some interesting indications that the healing rates of pores via diffusion fluxes at high temperatures should be strongly dependent on the inter-pore spacing.

In a recent paper by Pan and co-workers^[72] a phase field model was proposed for continuum damage healing based on nonequilibrium thermodynamics. The healing was motivated by the diffusion of healing agents released by capsules of solute atoms and described by a diffusion equation with a chemical reaction. It is found that the mechanical loading, the accumulation of damage and the diffusion of healing agents work together to govern the damage healing.

Karpov and co-workers analyzed the self-healing process of creep damage in fcc Fe by site-selective BN precipitation at the creep cavity surface with a dedicated multiscale computational model,^[39] as illustrated in **Figure 9**. The time required to fill a creep cavity by BN precipitation was analyzed as a function of the creep cavity size, the applied stress and the aspect ratio of the cavity. The diffusional flux of supersaturated solute responsible for the filling of creep cavities in the self-healing

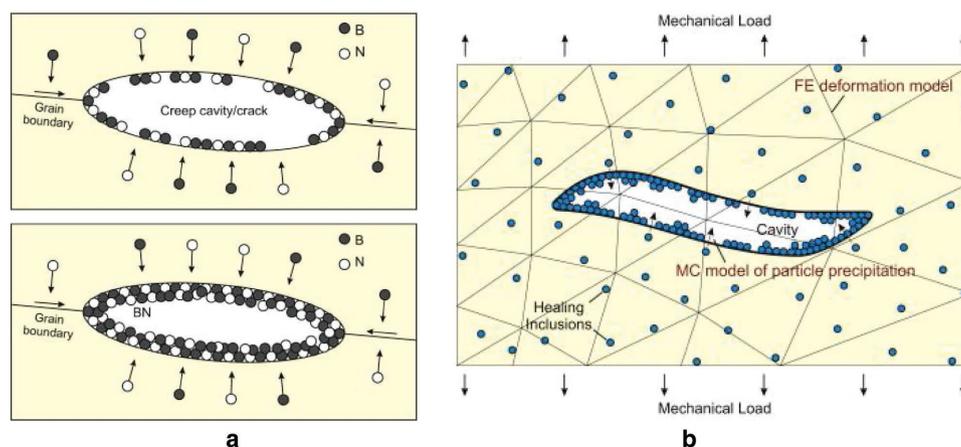


Figure 9. a) Illustration of boron nitride precipitation on creep cavity surface in stainless steel and b) Multiscale physical model of a self-healing material sample featuring the corresponding precipitative mechanism. The finite-element model requires a dynamic update due to kinetic processes in finite elements overlapping the cavity and the parameters of the kinetic Monte-Carlo model depend on the sample deformation. Reproduced with permission.^[39] Copyright 2012, Elsevier.

$\Sigma 29(370)$, $T=500$ K

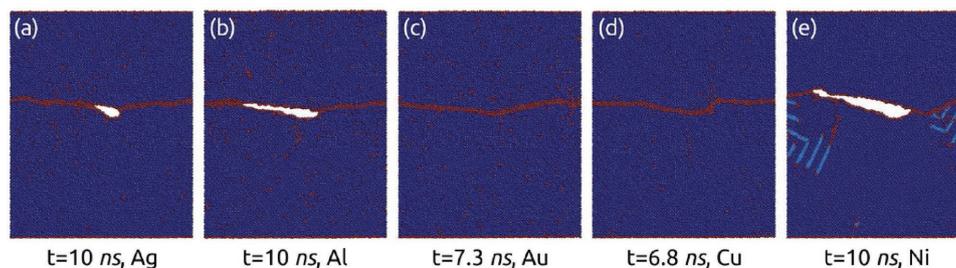


Figure 10. Influence of material type on the interaction between a nanocrack and shear-coupled grain-boundary motion. Bicrystal models containing a $\Sigma 29(370)$ grain boundary deformed at 500 K in a) Ag, b) Al, c) Au, d) Cu, and e) Ni. Self-healing is only observed for Au and Cu. Reproduced with permission.^[78] Copyright 2016, AIP Publishing.

process was analyzed by Versteylet et al.^[73] for bcc Fe alloys by FEM modeling of creep cavities located on a grain boundary. It was found that the effective dimensionality of the solute flux strongly depends on the spacing of the creep cavities with respect to the cavity size and on the ratio between the grain-boundary diffusivity and the bulk diffusivity.

MD studies on self-healing in metals generally focus on the recovery of nanoscale damage at relatively short time scales. A nice example is the computational study by Xu and Demkowicz,^[74] that demonstrated a complete healing of nanocracks by the generation of crystal defects known as disclinations in nanocrystalline nickel. In a subsequent study the self-healing of nanocracks in nanoscale palladium was investigated by MD calculations.^[75] Similarly, Li et al.^[76] investigated the healing of nanocracks in a copper plate subjected to shear stress. The results show that the process of crack healing is actualized through the emission of dislocations at the crack tip and the dislocation annihilation at the free surface. In a subsequent study,^[77] the MD calculations were generalized to include

compression. The crack healing of nanovoids during stress-driven grain-boundary motion was analyzed by Aramfard and Deng.^[78] As shown in **Figure 10**, to examine the influence of metal type on the healing of nanocracks during grain-boundary motion under shear five types of fcc metals were examined. Depending on the metal type, the crack could heal, grow, or show a combination of both. Al and Ni showed significant crack growth and propagation along the grain boundary (Figure 10b,e), while Cu and Au showed complete crack healing (Figure 10c,d) and Ag showed a partial crack healing at the beginning, followed by crack growth later on (Figure 10a).

The healing mechanism of nanocracks in nanocrystalline metals during creep was analyzed by Meraj and Pal.^[79] An example of the relatively fast crack healing in nanocrystalline nickel is shown in **Figure 11**. For very small nanoscale defects, a high temperature was found to be sufficient in MD calculations to show healing in bcc Fe.^[80] In line with the nucleation of grain-boundary cavities during creep, it is expected that below a certain critical size a generated crystalline defect is unstable as a

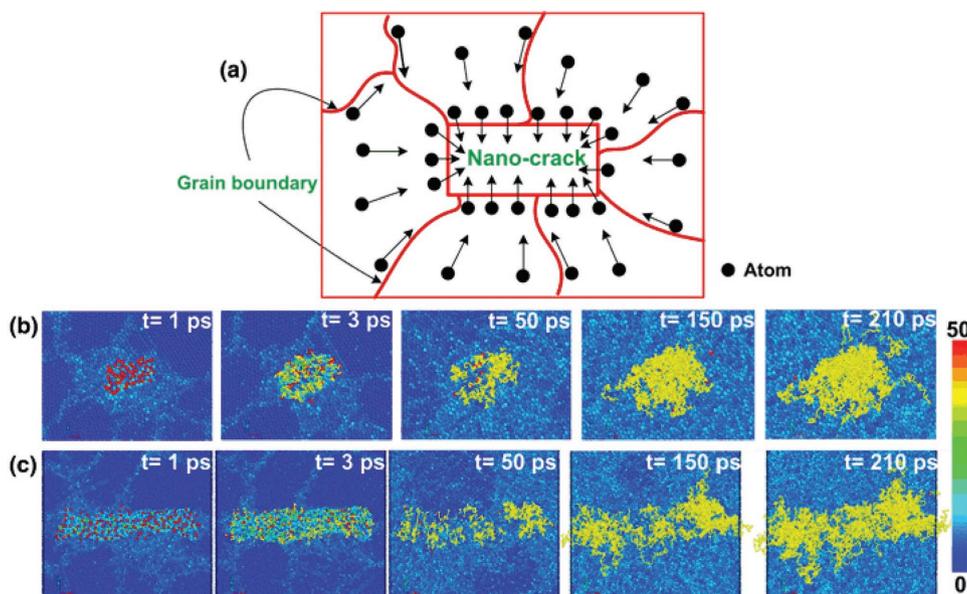


Figure 11. a) Schematic pictorial representation of nanocrack healing mechanism and simulated atomic trajectory snapshots of nanocrystalline Ni having b) a $(4 \times 3 \times 3)$ nm³ and c) $(12 \times 3 \times 3)$ nm³ nanocrack at different time steps (red color represents the selected atoms and yellow color represents the atomic trajectory). Reproduced with permission.^[79] Copyright 2017, Springer.

result of the increase in surface energy.^[81] It would be useful if the relative stability of the damage considered in the MD model calculations would be analyzed in more detail. The more stable the structural damage, the bigger the achievement is to build in a self-healing mechanism.

5. Prospects

In this review, we have tried to address the most promising and scientifically interesting approaches to self-healing in metals. The analysis shows that intrinsic healing in metallic alloys should be possible by a clever use of supersaturation of alloying elements likely to have a preference for more “space.” For this potential to be realized it is important to conduct the experiments in the right temperature range and to focus on damage modes that have a tendency to form within the material itself. Healing of surface defects (other than restoration of the natural oxide layer) remains a less promising route, although it cannot be excluded. Current experiments on self-healing of fatigue damage have led to mixed results, but the analysis as presented here suggests that the fatigue-healing experiments may have been conducted at the lower side of the recommended temperature range. As to the self-healing of creep damage the outlook seems more promising, as the studies on model alloys clearly demonstrate that filling of pores can occur and does have a positive effect on the life time. In coming years research should focus on combining the insight gained from the self-healing model alloys and from the research on computational (re)design of creep-resistant alloys^[82,83] to incorporate self-healing capabilities. While autonomous healing so far only seems to have been studied experimentally for aluminum alloys and steels, there may be many interesting, but as yet unexplored options for self-healing in other metals like, e.g., nickel-based alloys for high-temperature applications. Similarly, the self-healing of Ag and Au alloys for electronic applications, where the reliable behavior at relatively high temperatures (at low mechanical loads) is crucial, seems a field worth exploring systematically.

While multiphase microstructures (each phase having a different chemical composition due to a clever use of element partitioning in the solid state) are the most promising routes forward in the realization of high-performance steels, it is unlikely that the local differences in chemical composition can be tailored to such a degree that they result in significant difference in average atomic mobility and can be used towards the creation of quasi-extrinsic self-healing metals.

The reported experiments on extrinsic self-healing metallic composites certainly lived up to their conceptual and scientific expectations, and more work can be done to monitor and quantify the healing under a wider spectrum of damage and healing conditions. However, realistic application areas for such systems have not yet been identified.

Finally, while some modeling work on the self-healing behavior of metals has been done, there is ample scope for further work in this field, as the current models are generally descriptive and lack predictive power. The next generation predictive models should be of a multiscale nature where i) the actual healing mechanism takes place at an atomic length scale,

ii) the damage to be healed is generally at a micron or submicron scale, and iii) the products to benefit from the healing action are generally of macroscopic dimensions.

Acknowledgements

It is our pleasure to acknowledge the financial support for our research on self-healing metals from the Delft Centre for Materials, the IOP Self-Healing Materials program (IOP-SHM), and the Chinese Science Council (CSC). The authors thank their collaborators Shangming He, Sami Hautakangas, Maria Luisa Ripoll, Meysam Mahdavi Shahri, Gijs Langelaan, Sasha Zhang, Casper Versteyley, Haixing Fang, Henk Schut, René Alderliesten, and Ekkes Brück.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

creep damage, fatigue damage, metals, precipitation, self-healing

Received: February 9, 2018

Revised: February 28, 2018

Published online: May 10, 2018

- [1] S. van der Zwaag, *Self Healing Materials: An Alternative Approach to 20 Centuries of Materials Science*, Springer Series in Materials Science, Vol. 100 (Ed: S. van der Zwaag), Springer, Dordrecht, The Netherlands **2007**, pp. 1–18.
- [2] M. Hager, S. van der Zwaag, U. Schubert, *Self Healing Materials*, Advances in Polymer Science, Vol. 273 (Eds: M. D. Hager, S. van der Zwaag, U. S. Schubert), Springer, Basel, Switzerland **2016**.
- [3] J. Dahlke, S. Zechel, M. D. Hager, U. S. Schubert, *Adv. Mater. Interfaces* **2018**, 5, 1800051.
- [4] Y. Yang, M. W. Urban, *Adv. Mater. Interfaces* **2018**, 5, 1800384.
- [5] N. Zhong, W. Post, *Composites, Part A* **2015**, 69, 226.
- [6] N. de Belie, E. Gruyaert, A. Al-Tabbaa, P. Antonaci, C. Baera, D. Bajare, A. Darquennes, R. Davies, L. Ferrara, T. Jefferson, C. Litina, B. Miljevic, A. Otlewska, J. Ranogajec, M. Roig, K. Paine, P. Lukowski, P. Serna, J.-M. Tulliani, S. Vucetic, J. Wang, H. M. Jonkers, *Adv. Mater. Interfaces* **2018**, 5, 1800074.
- [7] M. D. Hager, P. Greil, C. Leyens, S. van der Zwaag, U. S. Schubert, *Adv. Mater.* **2010**, 22, 5424.
- [8] S. J. Garcia, H. Fischer, S. van der Zwaag, *Prog. Org. Coat.* **2011**, 72, 211.
- [9] H. C. Soo, S. R. White, P. V. Brown, *Adv. Mater.* **2009**, 21, 645.
- [10] G. R. Whittell, I. Manners, *Adv. Mater.* **2007**, 19, 3439.
- [11] R. K. Bose, N. Hohlbein, S. J. Garcia, A. M. Schmitt, S. van der Zwaag, *Phys. Chem. Chem. Phys.* **2015**, 17, 1697.
- [12] R. Lumley, *Self-Healing Materials: An Alternative Approach to 20 Centuries of Materials Science*, Springer Series in Materials Science, Vol. 100 (Ed: S. van der Zwaag), Springer, Dordrecht, The Netherlands **2007**, pp. 219–254.
- [13] N. Shinya, *Self-Healing Materials: Fundamentals, Design Strategies, and Applications* (Ed: S. K. Ghosh), Wiley, Weinheim, Germany **2009**, pp. 219–250.
- [14] M. V. Manuel, *Self-healing Materials: Fundamentals, Design Strategies, and Applications* (Ed: S. K. Ghosh), Wiley, Weinheim, Germany **2009**, pp. 251–265.

- [15] J. B. Ferguson, B. F. Schultz, P. K. Rohatgi, *J. Met.* **2014**, *66*, 866.
- [16] S. M. He, S. Zhang, N. H. van Dijk, *Self-Healing Materials: Pioneering Research in the Netherlands* (Eds: S. van der Zwaag, E. Brinkman), IOS Press, Amsterdam, The Netherlands **2015**, pp. 87–97.
- [17] S. Zhang, N. H. van Dijk, *Self-Healing Materials: Pioneering Research in the Netherlands* (Eds: S. van der Zwaag, E. Brinkman), IOS Press, Amsterdam, The Netherlands **2015**, pp. 99–107.
- [18] B. Grabowski, C. C. Tasan, *Self-Healing Materials. Advances in Polymer Science, Vol. 273* (Eds: M. D. Hager, S. van der Zwaag, U. S. Schubert), Springer, Basel, Switzerland **2016**, pp. 387–407.
- [19] M. Diba, S. Spaans, K. Ning, B. D. Ippel, F. Yang, B. Loomans, P. Y. W. Dankers, S. C. G. Leeuwenburgh, *Adv. Mater. Interfaces* **2018**, *5*, 1800118.
- [20] C. Dooley, D. Taylor, *Fatigue Fract. Eng. Mater. Struct.* **2017**, *40*, 655.
- [21] *Smithells Metals Reference Book*, 7th ed. (Eds: A. Brandes, G. B. Brook), Butterworth-Heinemann, Oxford, UK **1992**.
- [22] C. D. Versteyle, N. H. van Dijk, M. H. F. Sluiter, *Phys. Rev. B* **2017**, *96*, 094105.
- [23] R. N. Lumley, A. J. Morton, I. J. Polmear, *Acta Mater.* **2002**, *50*, 3597.
- [24] R. N. Lumley, R. G. O' Donnell, I. J. Polmear, J. R. Griffith, *Mater. Forum* **2005**, *29*, 256.
- [25] R. N. Lumley, I. J. Polmear, A. J. Morton, *Mater. Sci. Technol.* **2003**, *19*, 1483.
- [26] M. Mahdavi Shahri, M. L. Ruiz Ripoll, M. Mavrikakis, S. van der Zwaag, R. C. Alderliesten, H. Schut, *Self-Healing Materials: Pioneering Work in the Netherlands* (Eds: S. van der Zwaag, E. Brinkman), IOS, Amsterdam, The Netherlands **2015**, pp. 79–85.
- [27] M. Mahdavi Shahri, R. Alderliesten, S. van der Zwaag, H. Schut, *Adv. Mater. Res.* **2014**, *891–892*, 1577.
- [28] S. Hautakangas, H. Schut, N. H. van Dijk, P. E. J. Rivera Díaz del Castillo, S. van der Zwaag, *Scr. Mater.* **2008**, *58*, 719.
- [29] S. van der Zwaag, N. H. van Dijk, H. M. Jonkers, S. D. Mookhoek, W. G. Sloof, *Philos. Trans. R. Soc., A* **2009**, *367*, 1689.
- [30] S. A. Barter, L. Molent, R. J. H. Wanhill, *Int. J. Fatigue* **2011**, *41*, 11.
- [31] R. Wanhill, *Self-Healing Materials: an Alternative Approach to 20 Centuries of Materials Science*, Springer Series in Materials Science, Vol. 100 (Ed: S. van der Zwaag), Springer, Dordrecht, The Netherlands **2007**.
- [32] N. Shinya, J. Kyono, K. Laha, *J. Intell. Mater. Syst. Struct.* **2006**, *17*, 1127.
- [33] S. Zhang, C. Kwakernaak, W. G. Sloof, E. Brück, S. van der Zwaag, N. H. van Dijk, *Adv. Eng. Mater.* **2015**, *17*, 598.
- [34] K. Laha, J. Kyono, S. Kishimoto, N. Shinya, *Scr. Mater.* **2005**, *52*, 675.
- [35] K. Laha, J. Kyono, T. Sasaki, S. Kishimoto, N. Shinya, *Metall. Mater. Trans. A* **2005**, *36A*, 399.
- [36] K. Laha, J. Kyono, N. Shinya, *Philos. Mag.* **2007**, *87*, 2483.
- [37] K. Laha, J. Kyono, N. Shinya, *Scr. Mater.* **2007**, *56*, 915.
- [38] K. Laha, J. Kyono, N. Shinya, *Metall. Mater. Trans. A* **2012**, *43A*, 1187.
- [39] E. G. Karpov, M. V. Grankin, M. Liu, M. Ariyan, *J. Mech. Phys. Solids* **2012**, *60*, 250.
- [40] S. M. He, N. H. van Dijk, H. Schut, E. R. Peekstok, S. van der Zwaag, *Phys. Rev. B* **2010**, *81*, 094103.
- [41] S. M. He, N. H. van Dijk, M. Paladugu, H. Schut, J. Kohlbrecher, F. D. Tichelaar, S. van der Zwaag, *Phys. Rev. B* **2010**, *82*, 174111.
- [42] S. M. He, P. N. Brandhoff, H. Schut, S. van der Zwaag, N. H. van Dijk, *J. Mater. Sci.* **2013**, *48*, 6150.
- [43] S. Zhang, H. Schut, J. Kohlbrecher, E. Brück, S. van der Zwaag, N. H. van Dijk, *Philos. Mag.* **2013**, *93*, 4182.
- [44] S. Zhang, K. Kwakernaak, F. D. Tichelaar, W. G. Sloof, M. Kuzmina, M. Herbig, D. Raabe, E. Brück, S. van der Zwaag, N. H. van Dijk, *Metall. Mater. Trans. A* **2015**, *46A*, 5656.
- [45] S. Zhang, J. Kohlbrecher, G. Langelaan, F. D. Tichelaar, E. Brück, S. van der Zwaag, N. H. van Dijk, *Acta Mater.* **2013**, *61*, 7009.
- [46] S. Zhang, G. Langelaan, J. C. Brouwer, W. G. Sloof, E. Brück, S. van der Zwaag, N. H. van Dijk, *J. Alloys Compd.* **2014**, *584*, 425.
- [47] S. Zhang, H. Schut, J. Čížek, F. D. Tichelaar, E. Brück, S. van der Zwaag, N. H. van Dijk, *J. Mater. Sci.* **2014**, *49*, 2509.
- [48] H. Fang, C. D. Versteyle, S. Zhang, Y. Yang, P. Cloetens, D. Ngan-Tillard, E. Brück, S. van der Zwaag, N. H. van Dijk, *Acta Mater.* **2016**, *121*, 352.
- [49] W. W. Sun, H. Fang, N. H. van Dijk, S. van der Zwaag, C. R. Hutchinson, *Metall. Mater. Trans. A* **2017**, *48A*, 2109.
- [50] S. Zhang, H. Fang, M. E. Gramsma, C. Kwakernaak, W. G. Sloof, F. D. Tichelaar, M. Kuzmina, M. Herbig, D. Raabe, E. Brück, S. van der Zwaag, N. H. van Dijk, *Metall. Mater. Trans. A* **2016**, *47A*, 4831.
- [51] O. Kovalenko, C. Brandl, L. Klinger, E. Rabkin, *Adv. Sci.* **2017**, *4*, 1700159.
- [52] C. T. Chen, S. Nagao, K. Suganuma, J. T. Jiu, H. Zhang, T. Suguhara, T. Iwashige, K. Sugiura, K. Tsuruta, *Appl. Phys. Lett.* **2016**, *109*, 093503.
- [53] K. W. Gao, L. J. Qiao, W. Y. Chu, *Scr. Mater.* **2001**, *44*, 1055.
- [54] H. Wang, P. Huang, Z. Li, *Self-Healing Materials: An Alternative Approach to 20 Centuries of Materials Science*, Springer Series in Materials Science, Vol. 100 (Ed: S. van der Zwaag), Springer, Dordrecht, The Netherlands **2007**, pp. 255–277.
- [55] M. V. Manuel, *PhD Thesis*, Northwestern University, Chicago, USA **2007**.
- [56] P. K. Rohatgi, *Mater. Sci. Eng. A* **2014**, *619*, 73.
- [57] J. B. Ferguson, B. F. Schulz, P. K. Rohatgi, *Mat. Sci. Eng. A* **2015**, *620*, 85.
- [58] M. Nosonovsky, P. K. Rohatgi, *Biomimetics in Materials Science: Self-Healing, Self-Lubricating and Self-Cleaning Materials*, Springer Series in Materials Science, Vol. 152, New York, USA **2012**, pp. 53–73.
- [59] S. R. White, N. R. Sottos, P. H. Geubelle, J. S. Moore, M. R. Kessler, S. R. Sriman, E. N. Brown, S. Viswanathan, *Nature* **2001**, *409*, 794.
- [60] T. Al-Masoori, R. Micaelo, I. Artamendi, J. Norambuena, A. Garcia, *Constr. Build. Mater.* **2017**, *155*, 1091.
- [61] M. C. Chu, S. Sato, Y. Kobayashi, K. Ando, *Fatigue Fract. Eng. Mater. Struct.* **1995**, *18*, 1019.
- [62] K. Ando, B. S. Kim, M. C. Chu, S. Saito, J. Takahashi, *Fatigue Fract. Eng. Mater. Struct.* **2004**, *27*, 533.
- [63] S. Yoshioka, L. Boatemaa, S. van der Zwaag, W. Nakao, W. G. Sloof, *J. Eur. Ceram. Soc.* **2016**, *36*, 4155.
- [64] L. Boatemaa, C. Kwakernaak, S. van der Zwaag, W. G. Sloof, *J. Eur. Ceram. Soc.* **2016**, *36*, 4141.
- [65] A. L. Carabat, S. van der Zwaag, W. G. Sloof, *J. Am. Ceram. Soc.* **2015**, *98*, 2609.
- [66] J. T. Kim, H. J. Kim, S. H. Hong, H. J. Park, Y. S. Kim, Y. J. Hwang, Y. B. Jeong, J.-Y. Park, J. M. Park, B. Sarac, W.-M. Wang, J. Eckert, K. B. Kim, *Sci. Rep.* **2018**, *8*, 2120.
- [67] H. Yu, X. Liu, X. Li, A. Godbole, *Metall. Mater. Trans. A* **2014**, *45A*, 1001.
- [68] R. Xin, Q. Ma, W. Li, *Mater. Sci. Eng. A* **2016**, *662*, 65.
- [69] R. Xin, Q. Ma, D. Guo, W. Li, *Mater. Sci. Eng. A* **2017**, *682*, 433.
- [70] X. G. Zheng, Y.-N. Shi, K. Lu, *Mater. Sci. Eng. A* **2013**, *561*, 52.
- [71] H. Song, Z.-J. Wang, X.-D. He, J. Duan, *Sci. Rep.* **2017**, *7*, 7097.
- [72] Y. Pan, F. Tian, Z. Zhong, *Int. J. Damage Mech.* **2018**, *27*, 754.
- [73] C. D. Versteyle, N. K. Szymański, M. H. F. Sluiter, N. H. van Dijk, *Philos. Mag.* **2018**, *98*, 864.
- [74] G. Q. Xu, M. J. Demkowicz, *Phys. Rev. Lett.* **2013**, *111*, 145501.
- [75] G. Xu, M. J. Demkowicz, *Extreme Mech. Lett.* **2016**, *8*, 208.
- [76] J. Li, Q. H. Fang, B. Liu, Y. Liu, Y. W. Liu, P. H. Wen, *Acta Mater.* **2015**, *95*, 291.
- [77] Q. Fang, J. Li, H. Luo, J. Du, B. Liu, *J. Alloys Compd.* **2017**, *710*, 281.
- [78] M. Aramfard, C. Deng, *J. Appl. Phys.* **2016**, *119*, 085308.
- [79] M. Meraj, S. Pal, *Appl. Phys. A: Mater. Sci. Process.* **2017**, *123*, 138.
- [80] D. Wei, J. Han, A. Kiet Tieu, Z. Jiang, *Scr. Mater.* **2004**, *51*, 583.
- [81] R. Raj, M. F. Ashby, *Acta Metall.* **1975**, *23*, 653.
- [82] L. Qi, W. Xu, S. van der Zwaag, *Acta Mater.* **2014**, *77*, 310.
- [83] L. Qi, S. van der Zwaag, W. Xu, *J. Mater. Sci. Technol.* **2017**, *33*, 1577.