Self-Healing Engineering Ceramics with Oxidation-Induced Crack Repair

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Engineering ceramics capable of restoring damage-induced surface cracking may achieve enhanced reliability and longer lifetime at high temperature applications compared with nonhealing ceramics. Selection of healing agents dispersed in ceramic matrix composites which upon oxidation with environmental oxygen may rapidly fill the volume of a surface crack and recover compromised strength are reviewed. Novel approaches envisage acceleration of crack healing to reduce healing period as well as healing temperature. Potential fields of application for self-healing ceramics operating at elevated service temperatures are presented.

1. Introduction

Recovery of structure integrity compromised by crack initiation and growth has become an attractive paradigm for the development of advanced engineering ceramics with improved performance, reliability, and lifetime. Surface cracks are particularly harmful because of the concentration of tensile stress on the surface of a ceramic component applied under load. Healing of surface cracks produced by machining, particle impact, frictional wear, or thermal shock and thermal fatigue by heat treatment in an oxidizing gas atmosphere (stimulated healing), therefore, will have a strong impact on prolongation of lifetime at a given loading stress level (Figure 1).[1,2] The oxidation of dispersed healing agent particles triggers filling the crack with a solid oxide and restoration of load bearing contact between disrupted crack surfaces may cause partial or full recovery of compromised strength. If the service conditions correspond to the state under which oxidation controlled crack regression rate equals stress intensity controlled crack growth rate instantaneous healing may occur and a decline of strength over time can be largely avoided (autonomous or self-healing).[1]

Crack healing in engineering ceramics may be induced by thermally activated perturbation of a crack followed by sintering, crack closure by particle rearrangement, viscous flow of a glass melt into the crack, or by reaction with an environmental atmosphere filling the crack with solid reaction products.[3] While the temperatures for solid-state crack healing within a reasonable time period (<10 h) were found to be as high as the sintering temperatures (e.g., Al$_2$O$_3$ > 1400 °C[5]) significantly lower healing temperatures were reported for oxidation healing of surface cracks (e.g., silicon carbide [SiC] < 870 °C[6] or Ti$_2$SnC < 500 °C[7]). Since Lange’s pioneering work on oxidation-induced healing of surface cracks in SiC by annealing in air at 1400 °C,[8] a variety of other monolithic nonoxide ceramics were demonstrated to exhibit self-healing capability such as but not limited to Si$_3$N$_4$,[9] various M$_{n+1}$AX$_n$ with n = 1 to 3, where M is a transition metal, A is an A group element, and X is either carbon or nitrogen (MAX)-phase carbides[10] including Ti$_3$SiC$_2$, Ti$_3$AlC$_2$, Ti$_3$AlC, Ti$_2$SnC, Cr$_3$AlC, Ta$_2$AlC,[11-13] or other ternary carbides like Zr$_2$Al$_4$C$_5$.[14] Dispersion of a healing agent with a volume fraction of 5–30%, which is capable to undergo a controlled oxidation reaction on or near the interface of a surface crack was successfully demonstrated to extend healing ability even to ceramics that are inert to oxidative healing. For example, SiC particle-loaded Al$_2$O$_3$ matrix composites as well as numerous other ceramic matrices including 3Al$_2$O$_3$·2SiO$_2$, Si$_3$N$_4$, AlN, ZrB$_2$, and ZrO$_2$[17-21] were reported to achieve healing of surface cracks by annealing in air at temperatures >1000–1200 °C even under constant or cyclic stress loading[22,23] and at low oxygen partial pressure.[24] Compared with the base material the self-healing composites even showed enhanced high temperature resistance,[25,26] constant stress, and cyclic fatigue resistance.[25]

Over the past few decades, the number of healing agents that have been investigated for oxidation crack filling has increased enormously by including nonoxide compounds, ternary MAX phases, binary intermetallic phases, and transition metal elements.[27-31] In the following, thermochemical and thermokinetic aspects of crack filling and strength recovery by the oxidation of a healing agent are reviewed. The development of novel ceramic composite systems with enhanced crack-healing ability at lower temperatures and shorter healing periods are discussed and potential applications are presented.
Recovery of strength after stress-induced crack growth during service by stimulated or autonomous crack healing.

2. Thermochemical Aspects of Crack Filling Reaction

2.1. Healing Agent Oxidation

The oxidation of a healing agent to solid reaction products under the operating conditions of a ceramic component is a key requirement for crack healing to occur. For a healing agent A dispersed in an oxide matrix ceramic $M^{x+}O_{y/2}$ stability criteria requires that A does not undergo oxidation to $A^3+O_{y/2}$ by reducing the matrix oxide during manufacturing

$$A + M^{x+}O_{y/2} \leftrightarrow A^{x+}O_{y/2} + M$$  \hspace{1cm} (1)

This condition is fulfilled when the standard free energy of reaction (1)

$$\Delta_f G^0(T) = \Delta_f G^0_{(AOy/2)} - \Delta_f G^0_{(MOy/2)}$$  \hspace{1cm} (2)

is highly positive $\Delta_f G^0(T) > 0$ and hence $\Delta_f G^0_{(AOy/2)} > \Delta_f G^0_{(MOy/2)}$. Suitable combinations of matrix and healing agent dispersion can be identified from Ellingham diagrams. Once a surface crack has formed healing agent particles exposed to the penetrating oxygen will react

$$\frac{2}{y}A + O_2 \rightarrow A^{y+}O_{y/2}$$  \hspace{1cm} (3)

A high exothermic reaction enthalpy of the healing agent oxidation $\Delta_f H^0$ given by the free energy of formation $\Delta_f G^0$ and the formation entropy $\Delta_f S^0$

$$\Delta_f H^0 = \Delta_f G^0_{(AOy/2)} + T \Delta_f S^0$$  \hspace{1cm} (4)

was supposed to be favorable to form a strong bonding between the crack surface and the formed oxide.$^{[5]}$ Furthermore, the formation of an interface reaction phase between the crack filling oxide and the matrix is likely to promote a high bonding strength. For example, ZrSiO$_4$ can form at the interface between ZrO$_2$-matrix and SiO$_2$ crack filling.$^{[32]}$ Al$_2$Si$_3$O$_{13}$ (mullite) at

Al$_2$O$_3$-matrix/SiO$_2$-filling interface,$^{[19]}$ or Nb$_5$Zr$_6$O$_{17}$ at ZrO$_2$-matrix/Nb$_2$O$_5$-NbAlO$_4$ crack filling interface.$^{[33]}$ respectively.

Since a healing agent that has a high oxidation activity gives rise to a large chemical potential gradient in the matrix, slow oxygen diffusion in the matrix is favorable to avoid extended surface oxidation at elevated temperature.$^{[14]}$ In analogy to encapsulated healing catalysts developed for self-healing polymer systems$^{[33]}$ coating of the healing agent particles with an oxygen diffusion barrier layer such as Al$_2$O$_3$ on MoSi$_2$ particles or SiO$_2$ on nano-SiC particles is an option to reduce uncontrolled reaction particularly in matrix ceramics of higher permeability for oxygen like ZrO$_2$.$^{[36,37]}

Filling of the crack gap with the solid oxidation product requires an increase in the volume of the condensed phases before $V_A$ and after oxidation $V_{AOy/2}$. Hence, a volume expansion factor $\varphi$

$$\varphi = \frac{\Delta V_{ox}}{V_A} = \frac{V_{AOy/2} - V_A}{V_A}$$  \hspace{1cm} (5)

greater than 0 is another important criteria. Figure 2 shows the heat of oxidation reaction versus the specific volume change of a number of potential healing agent systems.

![Figure 2. Oxidation reaction enthalpy $\Delta H_{ox}$ (1000 °C) and volume expansion factor $\varphi$ for stoichiometric oxidation of tentative healing agents.](image-url)
SiC is the most common healing agent applied in a large number of oxide as well as nonoxide matrix ceramic composites.  The high stability of SiC facilitates manufacturing of nanocomposites which offer accelerated crack-healing capability combined with superior mechanical properties. Ternary MAX phases provide a good compromise between sufficient stability during manufacturing and high oxidation activity at temperatures <1230 °C and even <1000 °C. Furthermore, the nanolaminate crystal structure of MAX phases may enhance the toughness of healing agent loaded ceramic composite.

Transition metals exhibit larger values of $\varphi$ and $\Delta_t H^0$ compared with carbides and nitrides but their high oxidation reactivity makes manufacturing more complicated. Crack healing was demonstrated for various ceramic matrix composites (CMCs) loaded with only 5–10 vol.% of nanosized Ni, Co, and Ti, respectively. Intermetallic aluminides like NiAl were successfully applied for oxidative self-healing even though crystalline alumina or aluminate formation limits their volume expansion factor.

Borides and silicides reveal large volume expansion factors and a high crack filling activity. Amorphous or liquid silicate or boride oxidation products of low viscosity can form that are able to fill crack space by enhanced wetting and viscous flow at lower temperatures. For example, mullite filled with TiSi$_2$ and alumina loaded with TiB$_2$ + TiSi$_2$ were demonstrated to achieve crack healing at temperatures <587 or <770 °C, respectively.

Additional selection criteria for healing agent dispersed in various matrix systems were derived from analysis of self-healing phenomena and from the requested characteristics of the oxide filling the crack space. Bonding of elastic properties as well as formation of a strong interface bonding is required to achieve a high strength of the healed zone. Another favorable condition is that the thermal expansion mismatch between the healing oxide and the matrix generates a residual stress in the crack filling oxide after cooling lower than the matrix room-temperature strength (tensile or compression). The experimental-based approaches for healing agent selection were supported by coupling fracture mechanics with continuum mechanical approaches and numerical simulation finite element method to connect damage evolution with crack-healing process and to predict the lifetime of CMCs. Reactive molecular dynamics simulations were applied to study atomistic mechanisms associated with crack advance and simultaneous crack healing by local healing agent oxidation reaction.

### 2.2. Healing Agent Loading Fraction

Complete filling of the crack gap with a solid oxidation product of a healing agent dispersed in the matrix ceramic is considered as an essential requirement to obtain full strength recovery. The fraction of crack filling $\psi(T, t)$ in a representative volume element containing uniformly distributed spherical healing agent particles of equal size $d_{\text{ha}}$ sectioned by a planar crack of crack opening width $w$ was derived from the volume of oxide formed $V_{\text{ox}}$ to the volume of the crack gap $V_{\text{cr}}$ by

$$
\psi(T, t) = \frac{V_{\text{ox}}}{V_{\text{cr}}} = \left( \frac{d_{\text{ha}}}{w} \right)^3 \varphi_{\text{ox}} \varphi_{\text{al}} \alpha(T, t)
$$

$\alpha(T, t)$ is the healing temperature $T$ and time period $t$-dependent conversion ratio of a healing particle to its oxide (reaction degree variable defined as the weight ratio of converted oxide to unreacted particle) given by the particle oxidation kinetics. If each particle sectioned by the crack is fully oxidized $\alpha = 1$ and a minimum threshold volume loading fraction $\varphi_{\text{ha}}^*$ is obtained

$$
\varphi_{\text{ha}}^* = \left[ \varphi \left( \frac{d_{\text{ha}}}{w} \right) \right]^{-1}
$$

that is necessary to achieve complete crack filling ($\psi = 1$). Figure 3 shows the variation of $\varphi_{\text{ha}}^*$ versus the oxide expansion factor $\varphi$ for different healing agent particle sizes normalized to the crack opening width $d_{\text{ha}}/w$.

Though the volumetric crack filling model neither considers the complex nonplanar crack morphology nor the oxidation of nonsectioned particles in a reaction zone around the crack, it is evident that $\varphi_{\text{ha}}^*$ decreases with increasing values of $\varphi$ and $d_{\text{ha}}/w$. Thus, for SiC healing agent, SiC$_{35}$ particles ($\varphi = 1.13$, see Figure 3) and realistic values of $d_{\text{ha}}/w = 10–5$ for indent surface cracks a threshold healing agent fraction of $\varphi_{\text{ha}}^* \approx 0.09–0.18$ is predicted which coincides well with experimentally observed values ranging from 0.072 to 0.2. However, if the healing agent particle size becomes very small complete crack filling either requires high volume fractions or crack filling will be limited to cracks with very small opening width only. For example, for SiC$_{35}$ of $d_{\text{ha}} < 100$ nm and $\varphi_{\text{ha}} = 0.18$, e.g., $d_{\text{ha}}/w \approx 5$ (see Figure 3), only cracks with an opening width $w < 20$ nm are supposed to be completely filled with SiO$_2$. In contrast, accelerated oxidation kinetics of nanosized particles promotes crack filling in the early state of crack growth when the crack opening is still very small. That is why nanosized healing agent systems have a high potential for self-healing at elevated service temperatures of engineering ceramics. It also follows that stimulated healing of a ceramic component containing cracks of large opening width requires significantly larger healing agent particle size. For example, taking typical values of $w < 0.5–5$ μm near the surface, a minimum SiC$_{35}$ particle size of $d_{\text{ha}} > 2.5–25$ μm is supposed to be necessary for crack filling.

![Figure 3. Threshold volume fraction of healing agent required for complete crack filling as a function of volume expansion factor and normalized particle size.](image-url)
3. Thermokinetic Aspects of Strength Recovery

3.1. Crack Filling and Strength Recovery

Analysis of strength recovery after crack healing involves preparation of a specimen with an artificial surface crack by wedge cutting or indentation (Vickers), annealing in air at a constant temperature, and measurement of fracture strength after a healing period of time. Instead of preparing a single crack of defined geometry crack patterns were formed by quenching the specimens (thermal shock).\(^{[58]}\) Since crack healing during service at high temperatures may proceed under a simultaneous loading stress a cyclic or constant load was applied on the standard bar specimens during healing.\(^{[23]}\) Repeated crack healing was revealed by a high resolution in situ 4D synchrotron X-ray tomography coupled to a loading stage.\(^{[41]}\) The method was able to quantify the rate and local position dependence of crack repair upon multiple healing cycles.

Fracture strength of brittle ceramics scales with fracture toughness \(K\) and the effective crack length \(c\) according to Griffith’s relation

\[
\sigma_c = \frac{K_c}{Y\sqrt{c}} \tag{8}
\]

where \(Y\) is a geometrical constant depending on the loading and crack geometry. Since the crack size \(c\) differs for the virgin, the damaged and the healed specimen a strength recovery factor \(\eta\) is expressed by the ratio of the rupture strength values \(\sigma\) measured on virgin (v), damaged (d), and healed (h) specimen, respectively

\[
\eta(t) = \frac{\sigma_{h(t)} - \sigma_d}{\sigma_v - \sigma_d} \tag{9}
\]

No healing occurred when \(\eta = 0\), whereas for \(\eta > 0\), damage-induced strength loss recovered partially and may attain the value of the virgin material for \(\eta = 1\) when \(\sigma_h \rightarrow \sigma_v\).

Filling the space between disrupted crack interfaces with solid oxidation reaction product causes the compromised strength to recover, and it is reasonable to correlate the reduction of crack opening width \(w\) with a regression of crack length \(c\). Taking to a first approximation Irwin’s elasticity relationship for crack opening profile \(w(r)\) varying with distance \(r\) from the crack tip\(^{[59]}\)

\[
w(r) = \frac{K_c(1 - 2\nu)}{E} \sqrt{\frac{8r}{\pi}} \tag{10}
\]

where \(\nu\) and \(E\) are the Poisson ratio and the Young’s modulus, respectively, crack opening width on the surface correlates with the crack length by \(w(r = c) \propto \sqrt{c}\). It also follows that a maximum crack length exists which is confirmed by experimental observations of maximum crack lengths able to be healed of 250–500 \(\mu\)m.\(^{[19,60,61]}\) It has to be noted that common length of relaxed (unloaded) indent cracks extending on the surface and not into the depth was measured. Since recovered strength will be limited by the inherent flaw population as given by the crack length \(c_f\), which corresponds to a crack opening \(w_c\), in the virgin material, Figure 4, correlation of fracture mechanics with the volumetric crack filling model\(^{[46]}\) yields

\[
\eta(T, t) = \psi(T, t) \tag{11}
\]

The normalization factor \(\psi\) is given by fractional reduction of opening width, crack length, or strength, respectively, upon crack extension

\[
\psi = 1 - \left(\frac{w_t}{w_d}\right) = 1 - \left(\frac{c_t}{c_d}\right)^{1/2} = 1 - \left(\frac{\sigma_t}{\sigma_d}\right) \tag{12}
\]

Thus, for \(\eta \rightarrow 1\) it follows that \(\psi \rightarrow 1/\epsilon\) and complete volumetric crack filling is not required to achieve strength recovery to the level of the virgin material, Figure 4. If small inherent surface flaws are filled strength recovery may attain values of \(\eta > 1\) and strength after healing can be even higher than in the as processed virgin material.

3.1.1. Healing Temperature and Time

Evolution of crack filling with the condensed oxidation reaction products was analyzed to derive crack healing kinetics.\(^{[62,63]}\) Adapting the volumetric crack filling model,\(^{[46]}\) the minimum healing time period to achieve full strength recovery with \(\eta \rightarrow 1\) (and \(\psi = 1/\epsilon\)) by isothermal annealing derives from Equation (6) as

\[
\epsilon \left(\frac{d\eta}{dt}\right) \varphi_{ox} h_{env}(T, t) = 1 \tag{13}
\]

Diffusion limited reaction proceeding in spherical particles was described by rate expressions which combine 1D diffusion relation \(a(T,t) = \left[k(T)t\right]^{1/2}\) with 3D contracting volume equation \(a(T,t) = 1 - \left[1 - (k(T)t)\right]^{1/2}\).\(^{[64]}\) \(k(T)\) is a rate constant expressed in Arrhenius form \(k(T) = Q_o \exp(-Q_a/RT)\) with \(Q_o\) a pre-exponential or frequency factor and \(Q^a\) the activation energy of the rate controlling diffusion process. For example, thermal analysis of the oxidation kinetics of Ti particles was found to follow 3D contracting volume equation at least in the early stage of oxidation healing.\(^{[46]}\) Though oxidation of healing
particles dispersed in a ceramic matrix sectioned by a surface crack may involve complex selective oxidation phenomena, a transport limited rate term of the form \( a(T,t) = (k(T))^{1/n} \) is a reasonable approximation at least for the intermediate state of oxidation.\(^{[65]}\) Experimentally values for \( n \) were found to range from \( n \approx 1.5 \) to \( n > 3 \) (SiC: \( n \approx 1.8 \)^{[24]} Ti\(_2\)AlC: \( n \approx 3 \)^{[66]} Ti\(_2\)Al\(_0.5\)Sn\(_0.5\)C: \( n \approx 1.5 \) to \( 2.2 \)^{[39]} and Ni: \( n \approx 2 \)^{[67]}). Rearranging Equation (13) yields a generalized integral relationship for the isothermal strength recovery rate \( v_h = (1/t_h) \) given as the inverse of the shortest time period \( t_h \) which can heal a crack completely^{[24]}

\[
v_h = \frac{1}{t_h} = A_h \exp \left( -\frac{Q^*}{RT_h} \right) \left( \frac{p_{02}}{p_0} \right)^n \tag{14}\]

\( p_{02}/p_0 \) denotes the local oxygen partial pressure (in the crack) compared with the ambient pressure.\(^{[24]}\) It is evident from the definition of constant \( A_h = \frac{Q_o}{\rho d_{hA} w_d \phi \phi_h} \) that the minimum healing time is not only dependent on the maximum healing time and oxygen activity but also strongly depends on the loading fraction of healing agent \( \phi_h \) as discussed earlier. For a crack annealed for periods of \( t_h = 1 \) to \( 300 \) h values for the activation energy \( Q^* \) of SiC and Si\(_2\)N\(_4\) dispersed in various matrix systems were experimentally measured ranging from 150 to 413 kJ mol\(^{-1}\).\(^{[11]}\) Correlation with activation energies observed on SiO\(_2\) growth on SiC of \( Q = 397 \) kJ mol\(^{-1}\) suggest that the rate-controlling step for oxidation is the diffusion of O\(_2\) ions in the SiO\(_2\) layer formed on the SiC and Si\(_2\)N\(_4\) healing particles.\(^{[68]}\) Oxidation layer growth kinetics of single phase MAX-phase materials was reported to be governed by the inward diffusion of oxygen through the oxide reaction layer (primarily A-oxide).\(^{[66]}\) Figure 5 shows experimentally measured healing rates of a variety of healing agent-filled ceramic composite systems.

### 3.2. Accelerated Strength Recovery

Instantaneous self-healing during service implicates that the crack regression rate due to oxidation filling the crack space equals the crack progression rate driven by the loading stress intensity. Novel design criteria envisage acceleration of crack healing rate to achieve full strength recovery within a few minutes instead of hours at lower temperatures than 1000 °C. The Arrhenius law predicts that the rate constant \( k(T) \) will be governed by the activation energy barrier \( Q^o \). Following thermodynamic arguments for solid-state reaction kinetics, chemical or mechanical activation of the repair filler triggers an increase in Gibbs free energy, \( \Delta G \), which gives rise to a reduction of the activation energy barrier, \( (Q^o - \Delta G) \) at least in the early stage of healing reaction. It is evident that a reduction of activation energy barrier corresponds to an equivalent decrease in healing temperature \( T_h = T_h/T \propto (1 - \Delta G) \).\(^{[6]}\) Since Gibbs energy scaling laws for solid-state activated processes predict \( \Delta G \) to scale inversely with the particle size \( d_{hA} \)\(^{[70]}\) acceleration of crack healing kinetics mainly envisages reduction of the particle size down to nanometer scale. While theoretical calculations suggest that the grain size effect requires very small particle size \( d_{hA} < 100 \) nm, experimental results yield activation energy reduction at much larger particle sizes <10 μm which was attributed to surface defects on the powder particles.\(^{[71]}\) For example, reduction of particle size of SiC healing agent dispersed in Al\(_2\)O\(_3\) ceramic from 268 to 10 nm caused the activation energy \( Q^o \) to decrease from 380 to 197 kJ mol\(^{-1}\) and the healing temperature \( T_h \) (10 h) from 1300 to 920 °C, respectively.\(^{[6]}\) A reduction of TiC particle size from 3 μm to 50 nm reduced the activation energy from 244 to 122 kJ mol\(^{-1}\) with the healing temperature of TiC-loaded oxide ceramic composite materials falling from 1000 down to 400 °C.\(^{[72]}\)

Enhancing the ion mobility is another approach to reduce \( T_h \). A decrease in \( T_h \) was achieved in Al\(_2\)O\(_3\) composite loaded with the MAX-phase healing agent Ti\(_2\)AC (\( A = \) Al or Sn). Distinguished by even lower bonding and migration energies of A-element Sn substituted for Al in the nanolaminate solid solution crystal structure\(^{[73]}\) preferred diertcalation of Sn resulted in a reduction of \( T_h \) from 870 to 677 °C for \( t_h = 3 \) h.\(^{[74]}\) Mobility may also be increased by the formation of melt phase of low viscosity. Si or B containing healing agents can form a transient liquid silicate melt in the initial period of healing agent oxidation which can wet and penetrate easily into the crack and may attain rapid healing at lower temperatures. For example, adding Y\(_2\)O\(_3\) to the Al\(_2\)O\(_3\)/SiC\(_{hA}\) triggers the formation of a metastable eutectic silicate melt from which mullite precipitates at a temperature about 100 °C lower than in the Y\(_2\)O\(_3\) free system.\(^{[19]}\) Y\(_2\)O\(_3\) acts as an activator which decreases melting temperature and viscosity. B\(_2\)C was introduced in SiC-based CMC to generate B\(_2\)O\(_3\), which is liquid >450 °C and is able to flow and to seal matrix cracks efficiently.\(^{[75]}\) B-doped MoSi\(_2\) healing agent dispersed in ZrO\(_2\) thermal barrier layer system was shown to form a low viscous borosilicate melt flowing rapidly into the crack space and subsequently forms ZrSiO\(_4\) at the crack matrix interface.\(^{[26]}\) An Al\(_2\)O\(_3\) composite loaded with 30 vol% SiC healing agent and additionally doped with 0.2 vol% manganese oxide (MnO) was demonstrated to reveal strongly accelerated healing.\(^{[76]}\) The healing activator (MnO) triggers the formation of a low viscous super-cooled liquid able to penetrate rapidly into the crack space and form a strong bonding upon crystallization resulting in an accelerated full strength recovery at 1000 °C within 10 min.

Other forms of healing agent like preceramic polymers applied as surface coatings or interfaces in fiber-reinforced CMCs may extend the concept of oxidation crack healing. High temperature self-healing SiBCN ceramics derived from

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**Figure 5.** Kinetics of oxidative crack healing of various healing agent/matrix ceramic systems.
hyperbranched polyborosilazanes exhibit self-healing functionality by forming low viscous boron oxide and boron silicon oxide melt by annealing in air at 1000 °C which is able to wet crack surface effectively.\[77\] Novel approaches envisage the induction of crack healing even at room temperature (nonthermal activation). Al\(_2\)O\(_3\) composites loaded with 20–30 vol% of Ti powder distinguished by an excellent electrical conductivity were electrochemically anodized at room temperature.\[78\] The oxidized Ti particles formed TiO\(_2\) bridges that healed the crack and full strength recovery was achieved. Overall, research on crack-healing engineering ceramics has achieved pronounced progress as summarized in the example of Al\(_2\)O\(_3\)-based ceramic composites and the reduction of healing temperatures, Table 1.

### 4. Applications

Self-healing ceramics anticipated to apply at elevated temperatures may ensure structural integrity and achieve enhanced reliability and lifetime of components and structures where maintenance is difficult.\[80\] Self-healing coatings are of high relevance for oxidation barrier, thermal barrier, electrical insulation, as well as fiber/matrix interface coatings in light-weight fiber-reinforced CMCs. Since typical service temperatures in the hot section of solid oxide fuel cells (>677 °C) or gas turbine components (>1250 °C) are high enough to trigger oxidation reaction of the healing agent no stimulated healing process is required and crack repair may occur during service (self-healing).\[81,82\]

| Year | Healing temperature [°C] | Example | Healing reaction | Ref. |
|------|--------------------------|---------|-----------------|------|
| 1938 | >1400                    | Al\(_2\)O\(_3\) monolith | Crack disintegration and pore elimination (resintering) | [79] |
| 2005 | > 1200                   | Al\(_2\)O\(_3\) composite loaded with SiC | Passive oxidation of healing agent at elevated temperatures | [22] |
| 2015 | >770                     | Al\(_2\)O\(_3\) composite loaded with MAX phases | Accelerated healing agent oxidation at lower temperatures | [39] |
| 2018 | >587                     | Al\(_2\)O\(_3\) composite loaded with SiC + activator MnO | Activated healing with transient low viscous phase | [76] |
| 2019 | Room temp.               | Al\(_2\)O\(_3\) loaded with >30 vol% Ti | Nonthermal low temperature healing by electrochemical oxidation | [78] |

Table 2. Examples for potential applications of crack-healing ceramic composites.

| Field             | Application                      | Example matrix/(healing agent) | Ref. |
|-------------------|----------------------------------|--------------------------------|------|
| Aerospace/aeronautics | Aeroengine vane, liner       | SiC\(_x\)/(SiC/\((CrB_2\_C_3)\)) | [49] |
|                   |                                  | Al\(_2\)O\(_3\)/ (SiC\(_{nano}\)) | [69] |
|                   | Aeroengine turbine blade        | Al\(_2\)O\(_3\)/(SiC\(_{nano}\))\_Al\(_2\)O\(_3\) | [83] |
|                   | Aeroengine combustion chamber   | C\(_x\)/SiC/(B\(_x\)) | [86] |
|                   |                                  | Al\(_2\)O\(_3\)/ (TiC) | [87] |
|                   | Aeroengine exhaust gas cone     | SiC\(_x\)/ (SiC/B) | [88] |
|                   | Oxidation barrier coatings on CMC | MgAl\(_2\)O\(_3\)/ (SiC + \(Y_2\)O\(_3\)) | [89] |
|                   | Hot structure parts             | Zr\(_2\)O\(_2\)/ (Zr\(_2\)B\(_2\)/SiC) | [90] |
| Energy            | TBC on gas turbine metal blades | Zr\(_2\)O\(_2\)/ (MoSi\(_2\))/B) | [28] |
|                   | Coating on SOFC interconnector  | MgAl\(_2\)O\(_3\)/ (SiC + \(Y_2\)O\(_3\)) | [81] |
|                   | Nuclear fuel cladding oxidation barrier | ZrO\(_2\)/ (Zr\(_2\)Al\(_2\)) | [91] |
|                   | High performance bearings      | SiOC/(CrSi\(_x\)) | [92] |
|                   | Coil springs for HT            | Mullite/(SiC\(_{nano}\) + SiC) | [93] |
use of gas separation ceramic membranes operating at high temperatures and gas pressure. Subjected to thermal cycling and thermal shock loading in service self-healing would be highly attractive to extend lifetime of a key component. Ceramic materials in high porosity are applied in concentrated solar power conversion and storage systems. Working above 677 °C in air atmosphere volumetric solar air receiver, solar heat power storage foams, or solar heat reactors suffer from repeating thermal shock and thermal cycling. Instantaneous crack healing during service may provide extension of lifetime. Electrochemical oxidation at low temperatures is of interest for electrical contact applications as, e.g., pantographs of high-speed trains, where healing by electrochemical oxidation in contact with humidity and air might reduce wear at high velocities, or grounding contacts working in high-power off-shore wind mills subjected to corrosion and wear.

5. Conclusions

Healing of surface cracks not only causes a pronounced strength recovery but also has severe beneficial effects on fracture probability, fatigue strength, and lifetime. Increased reliability and load carrying capacity may allow crack-healing engineering ceramics composites to be applied under higher service loading conditions compared with the base materials. Tentative healing agent systems must provide a pronounced volume expansion and release of heat of reaction upon thermally activated oxidation on a crack interface. Among others mainly binary ceramics like SiC and Si3N4, transition metals, binary intermetallic phases including aluminides, silicides, and borides, and ternary MAX phases were demonstrated to be able to restore disrupted crack interfaces by oxide crack filling and achieve recovery of compromised strength to the level of the virgin material. Extending the search field to multicomponent phases M—Si—Al—B with M = transition metals and rare earth metals may have a high potential for tailoring the healing agent oxidation behavior and matching the thermomechanical properties of crack-filling oxide with various matrix materials.

Acceleration of crack filling by reduction of healing agent particle size down to nanometer scale, formation of low viscous multicomponent silicate or borate melt phase and solid solution formation allows lowering of the healing temperature and shortening of the healing time period. Encapsulation with an oxidation barrier layer might be necessary to avoid uncontrolled reaction of high reactivity healing agent particles. Extending the activation to nonthermal electrochemical oxidation was demonstrated to achieve healing even at room temperature which may be of interest for opening future application fields of engineering ceramics at lower temperatures.

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