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Self-healing ceramic coatings that operate in extreme environments: A review F FREE

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ABSTRACT

This paper provides an overview of the latest research developments in the design and exploration of ceramic coatings with high temperature adaptive behavior. The adaptive behavior, triggered by thermal or thermomechanical stimulus, may be used to create smart surfaces that are able to change their chemistry and structure to achieve the desired functionality. The initial focus of the paper will be to provide an overview on the basics of self-repairing materials. This will be followed by a brief outline of the work that has been reported on self-healing/adaptive mechanisms in bulk ceramics. We will then focus on providing a thorough review on self-healing ceramics with a focus on adaptation/healing in tribology as well as thermal barrier, anticorrosion, and oxidation resistant coatings. Advantages and disadvantages of using hybrid polymer-ceramic coatings will also be discussed toward the end of the article. This overview will provide a fundamental understanding of the changes in the structural and chemical properties of these materials and how that correlates to their performance. This review also includes a discussion on anticipated future developments in this important and upcoming area of research.

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I. INTRODUCTION

Self-healing materials are intelligent materials that have the ability to heal porosity or cracks. These materials are also called self-repairing, autonomic-healing, and autonomic-repairing materials.^{1,2} The concept of self-repairing materials was first proposed in the 1980s.³ The creation of such materials was primarily inspired by the concept of self-healing of the human body and other living systems. Since then, self-repairing materials have been developed for all classes of materials, i.e., polymers, metals, ceramics, and composites. The majority of the studies focuses on using self-healing polymer-based systems due to their high mobility and adaptability to applied stresses.¹⁻³ Meanwhile, self-repair is a more challenging endeavor for metals and especially for ceramics given that these materials are not inherently viscous. A relatively large viscosity for at least one phase in a composite is an important condition for the design of a self-repairing material.^{1,4,5} Moreover, the concept of self-healing has almost exclusively been used in bulk structural materials to help restore strength and avoid mechanical failure. Potential applications of these bulk materials include aerospace, automotive, and construction industries.^{1,6} Very little work has been devoted to self-healing ceramic coatings,

which is an important area of research that has the potential to revolutionize the coating industry.

The goal of this contribution is to provide an overview of the research that has taken place in the last few years in the area of self-healing ceramic coatings. Self-healing ceramic coatings are a relatively new class of coatings that are metastable in nature. Their metastability, if controlled properly, may be the mechanism that facilitates repair of damage and enhance material functionality. In [Sec. II](#), the basics of the fundamental mechanisms that are needed to design a self-repair material will be discussed. [Section III](#) highlights the major achievements that have been reported in the literature in the design and fabrication of self-repairing bulk ceramics. [Section III](#) starts with a discussion on the challenges associated with the transition from bulk to coatings and focuses on the main areas used for self-healing ceramic coatings. This section is then divided into four subsections that pertain to tribologically, thermally, oxidatively, and humidity-activated self-healing coatings, as depicted by the schematic diagram in [Fig. 1](#). The last section of this review paper provides a conclusion of the major achievements made in this field and a discussion of potential future directions of this technology.

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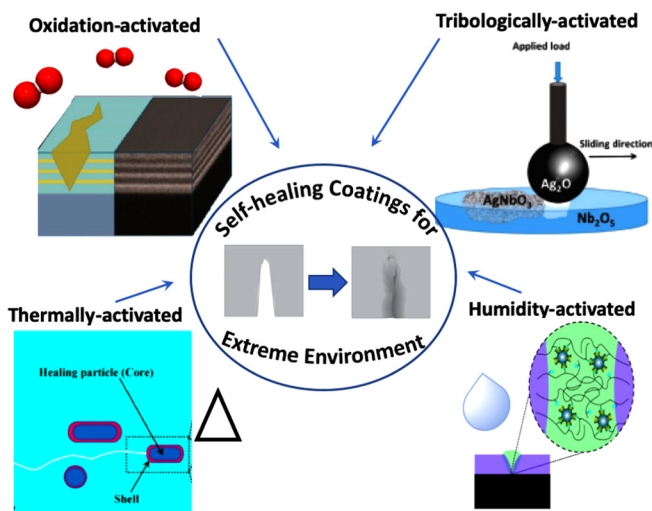


FIG. 1. Outline of the ceramic-based coatings discussed in this review article.

II. BASICS OF SELF-HEALING

Self-healing processes may be classified into two categories: (1) autonomic processes whereby damage healing is activated without the need to provide additional energy and (2) nonautonomic processes whereby energy in the form of heat, light, or any other external trigger is needed to stimulate the self-healing process.^{1,7,8} Self-repairing materials are further classified into extrinsic and intrinsic self-healing subclasses.^{1,9,10} Extrinsic self-healing requires additional external agents in the form of nano- or micro-capsules, hollow fibers, vascular, or particles to facilitate repair, whereas intrinsic self-repairing materials do not require the addition of such materials.¹

The fundamental mechanisms that take place during the healing process are shown in Fig. 2.⁸ When a crack forms [Figs. 2(a) and 2(b)], a “mobile phase,” caused by the damage or by an external trigger, is generated [Fig. 2(c)]. To effectively contribute to the self-repair mechanism, this “mobile phase” needs to (1) be relatively viscous, (2) be able to fill the crack/pore by direct mass transport, and (3) result in a repair reaction in the damaged zone [Fig. 2(d)]. When the healing process is complete, the mechanical properties of

the damaged material can be partially or fully restored [Fig. 2(e)]. The healing temperature will vary with the types of materials, which is ambient temperature for concrete, low temperatures for polymers (<120 °C), medium temperature for metals (<600 °C), and elevated temperatures for ceramics (>800 °C).⁸ Ceramics, which are the focus of this review paper, are therefore highly nonautonomic and that makes their design much more challenging given the high temperature levels that are required to trigger healing. When ceramics are used at high temperatures, however, they become more autonomic demonstrating great potential for adaptability.

Table I highlights potential design strategies that give rise to self-healing behavior for different material classes. The different shades indicate the expected level of healing success. Dark gray, light gray, and white depict positive, potential, and unlikely design, respectively.^{1,8} Due to the relatively low healing temperature range and the molecular structure of polymers and their composites, more effective healing design strategies may be applied to them compared to ceramics, concretes, and metals. Encapsulation, channel transport, expanding phases, heating, and electrochemical processes are used for ceramics, while biological healing processes are mainly used for concretes.^{1,8} In bioinspired self-healing concrete, bacteria are immobilized in crevices to be activated if water penetrates into the produced cracks, thus preventing the precipitation of minerals.⁸ All of these design strategies can be utilized individually or cooperatively in the self-healing process for the various material classes.

The performance of all natural or synthetic materials deteriorates during their service period. Their prolonged use can lead to the formation of microcracks followed by materials degradation and failure once the crack accumulation eventually exceeds a critical level. If the material is capable of self-healing, the damage can be reversed or prevented, preferably multiple times. This way, the service life and reliability of the device will be extended effectively. Moreover, self-healing materials may provide an early means of detection to avoid any human intervention to replace damaged parts. The advantages of using a self-repairing material highlighted above can dramatically cut down the cost.

The fundamental principles of crack-healing ceramics were previously discussed by Greil in a nice 2012 review article on self-healing ceramics.¹¹ He focused on providing a fundamental understanding of the thermodynamic and kinetic aspects governing the healing process as well as useful approaches to accelerate the healing reaction and reduce the healing temperature. In addition, the guiding principles of microstructure modifications to facilitate

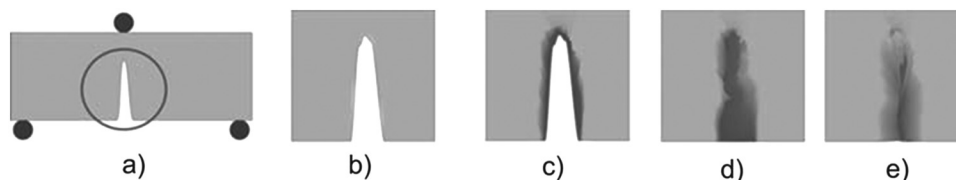


FIG. 2. Common basic principle of self-healing materials. (a) The mechanical load induces a crack; (b) detailed view of the crack; (c) a “mobile phase” is induced; (d) closure of the crack by the “mobile phase;” (e) immobilization after healing. Reprinted with permission from Hager *et al.*, Adv. Mater. **22**, 5424 (2010). Copyright 2010, John Wiley & Sons, Inc.

31 July 2023 20:18:16

TABLE I. Selected potential design strategies for self-healing behavior of the different material types as described in Ref. 8. The shading shows the expected level of healing success (dark gray—positive; light gray—potential; white—unlikely).

Design strategies	Encapsulation	Channel transport	Expanding phases	Temperature increase	Phase separation	Reversible crosslinks	Biological processes	Electro-chemical process
Polymers and composites	Dark Gray	Dark Gray	Dark Gray	Dark Gray	Dark Gray	Dark Gray	Light Gray	White
Ceramics	Dark Gray	Dark Gray	Dark Gray	Dark Gray	Light Gray	White	Dark Gray	Dark Gray
Metals	Light Gray	Light Gray	Dark Gray	Dark Gray	Light Gray	White	White	Dark Gray

crack repair are provided: (1) acceleration of material transport by grain boundary decoration and grain size reduction and (2) reduction of thermal activation barrier by repair filler activation.¹¹ In the next sections of this review paper, it will become apparent how researchers used these strategies to create ceramics that are able to self-repair.

III. SELF-HEALING IN BULK CERAMIC MATERIALS

The creation of self-healing ceramics has been a very challenging task for researchers, which explains the relatively smaller number of publications in this area. Ceramics are inert materials that are stable at elevated temperatures and hence do not display low viscosity unless they reach temperatures in the vicinity of their melting point. This is due to the high activation energies of the diffusive mass transport in the covalent or ionic structures of ceramics.⁸ Researchers have focused on incorporating self-healing centers inside the materials during their synthesis, resulting in the creation of a composite structure. The self-repairing process, facilitated by the presence of the healing center, occurs because of one of the following mechanisms: (1) oxidization or (2) precipitation. This section offers a brief discussion on these mechanisms. This discussion is meant to provide an overview of self-healing mechanisms that have been successfully used in bulk materials and that could be applied for thin film coatings.

A. Oxidation-induced healing

Oxidation healing is usually carried out by adding carbide or nitride particles in a ceramic matrix. These particles oxidize at elevated temperatures. This oxidation is accompanied by a volume expansion of more than 50% to facilitate crack healing. Oxidation is usually triggered by providing energy to the material in the form of heat or electricity. The thermal or electrical stimulus may be supplied to the material as part of its working environment or as needed as part of a repair strategy. Both of these scenarios will require a different material architecture and design.

1. Thermal stimulus

Ando *et al.*^{12,13} investigated the crack-healing behavior of hot-pressed mullite/SiC composite ceramics. They found that the strength of precracked specimen was recovered by an oxidation healing mechanism at elevated temperatures. Optimum healing conditions were achieved when specimen were annealed at 1300 °C in air for 1 h. A three-point bending-test was used to evaluate the bending strength of the healed specimen as a function of SiC

content.¹² These healed samples had recovered their bending strength when tested up to about 1200 °C. The main crack-healing mechanism observed for these materials was caused by the following oxidation reaction: $\text{SiC} + 3/2 \text{O}_2 = \text{SiO}_2 + \text{CO}$ ($\Delta H = -943 \text{ kJ/mol}$). For complete strength recovery, the optimal volume fraction of SiC was found to be in the 7.5%–15% range. For optimum crack-healing ability, a volume fraction of SiC > 10% was recommended since a lower volume fraction does not allow for a significant volume expansion. A follow-up study¹⁴ revealed that the use of a healing activator could be beneficial in expediting the healing process of the mullite/SiC system. They concluded that doping the mullite/SiC composite with 0.2 vol. % MnO promoted the healing process by lowering the viscosity of the formed oxide and facilitating flow of matter as well as crack repair. Several other researchers have used the same concept to create self-healing composites, whereby SiC particles are added as repair agents and were used in combination with a wide variety of other phases to produce composites that include SiC/BN/SiC-B₄C,¹⁵ SiC/spinel,¹⁶ Al₂O₃/SiC,^{17,18} SiC/(SiC-SiBCN)_x,¹⁹ SiCf/SiC and PyC/SiC,²⁰ C/SiC-SiBCN,²¹ ytterbium disilicate ceramic reinforced with silicon carbide nanofillers,²² Cf/SiC composites modified by a boron-containing phase,²³ SiC-BN composites,²⁴ and ZrO₂/SiC.²⁵

A separate attention should be given to MAX phase ceramics as materials that show great potential for self-repairing via oxidation.²⁶ MAX phases are a group of ternary carbides and nitrides exhibiting unique thermal, mechanical, and electrical properties originating from their layered hexagonal crystallographic structures. In MAX phases, layers of MX ceramic (combining early transition metal with either carbon or nitrogen) alternate with layers of pure metals (usually Al or Si) creating the general formula M_{n+1}AX_n for the material. Such alternating structures provide the MAX phases with high temperature strength and stiffness of ceramic and high toughness, ductility, and electrical thermal characteristics of the metals.^{27–29}

MAX phases, as nonoxidic materials, undergo oxidative decomposition once exposed to high temperatures. Depending on the structure of the materials, this oxidative composition can vary from being very slow, as in the case of Ti₂AlC forming protective oxide layer, to very fast, as in the case of Hf₂SnC undergoing fast and full conversion into the oxidic state.^{26,30} Such control over the oxidative behavior of the MAX phases can be used for oxidation-assisted healing of the cracks and defects in the materials. Song *et al.*³¹ successfully demonstrated healing of up to 5 μm wide cracks in Ti₃AlC₂ after annealing the samples for 2 h at 1100 °C in air. It was shown that the indentation modulus and hardness of the healed cracks are higher than for the original Ti₃AlC₂ material

31 July 2023 20:18:16

which is attributed to the formation of primarily α - Al_2O_3 particles in the crack. Similar self-healing mechanism was observed in Ti_2AlC ceramic.³² Importantly, slow oxidation of the Ti_2AlC allowed damage repair repeatedly. This is an outstanding result given that not many self-repairing materials allow repair over damage cycles. In this study, Ti_2AlC ceramics were synthesized by hot pressing using 30 MPa a mixture of Ti, Al and C at 1450 °C for 8 h in an Ar atmosphere.³² The synthesized ceramic displayed a

significant crack healing ability, as shown in Fig. 3. A three-point bending test was conducted to determine the initial, the residual, and the recovered strength, respectively. After indentation and cycle fatigue test, many microcracks were introduced around 3 Knoop indents in the predamaged samples [Fig. 3(a)]. After healing at 1200 °C in air, the microcracks disappeared completely [Fig. 3(b)]. The main healing mechanism was shown to consist of the filling of the crack by well adhering α - Al_2O_3 grains

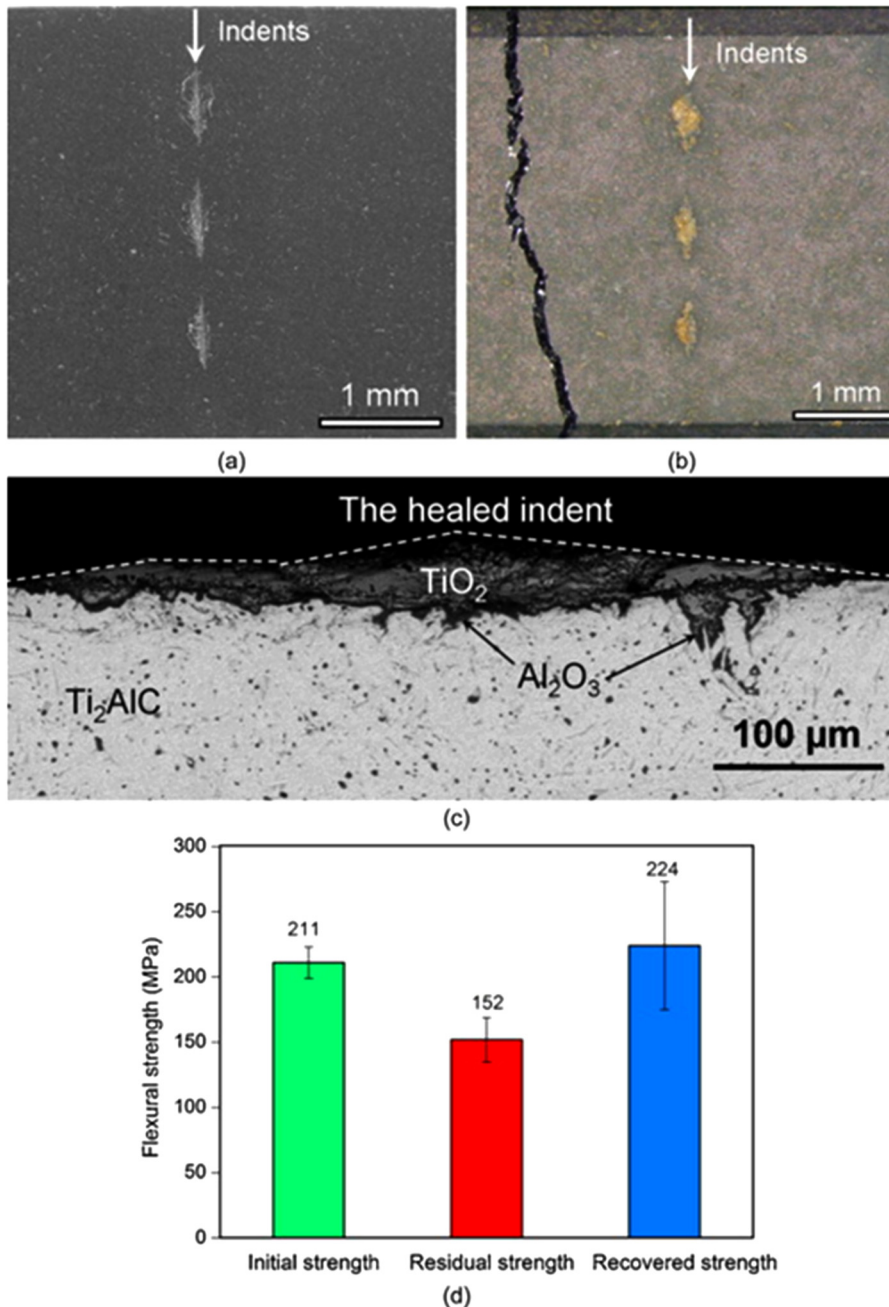


FIG. 3. Strength recovery of Ti_2AlC specimens after crack healing at 1200 °C for 2 h in air. (a) Optical image of the 3 Knoop indents at the center of the long sample to create crack damage. (b) Optical image of the healed sample after flexural strength testing. (c) Cross-sectional backscattered scanning electron image for the healed indent. (d) Flexural strength of the virginal Ti_2AlC , after creating crack damage and after crack healing, respectively. Each data point is the average of five measurements and the error bars represent the standard deviation. Reprinted with permission from Li *et al.*, *J. Eur. Ceram. Soc.* **32**, 1813 (2012). Copyright 2012, Elsevier.

31 July 2023 20:18:16

(black color) and the presence of the rutile phase (deep gray color) [Fig. 3(c)]. The flexural strength of the self-repaired sample slightly exceeded the initial strength of 211 MPa [Fig. 3(d)]. More importantly, this MAX phase was shown to be able to repair damage under cycling events. Seven successful damage repair cycles were demonstrated after repeated cracking at the same location.³² In another study on the same system, Yang *et al.*³³ used an *in situ* microcantilever bending test to evaluate the healing efficiency of prenotched Ti₂AlC ceramic after annealing at 1200 °C for 1.5 h. This *in situ* bending test provided a quantitative method for the evaluation of the strength of Ti₂AlC–Al₂O₃ interface after healing. Boatema *et al.*³⁴ revealed the dynamics of the Ti₂AlC conversion into corundum (α -Al₂O₃) and rutile (TiO₂) as a function of temperature and time of the material annealing toward the full-strength recovery of the material. These results suggested the modifications to the crack healing recipe in order to receive various compositions of the crack filling. The structure of the MAX phase ceramic can be further modified, as in the case of Ti₂Al_{0.5}Sn_{0.5}C, but still show similar oxidative crack-healing mechanism.³⁵

Farle *et al.*³⁶ extended their study on understanding the self-healing mechanism in various MAX phases of more than 75 compositions. Four major criteria for the self-healing to work were proposed: (1) preferential oxidation of the A-element over the M-element, (2) fast diffusion of the A-element to the crack region, (3) volume expansion upon the oxidation of the MAX phase, and (4) good adhesion of the oxidation product to the MAX phase matrix. By evaluating the Gibbs energy of the oxide formation, a list of the self-healing MAX phases was shortened to Al containing MAX phases (such as Ti₂AlC, Ti₂AlN, Ti₃AlC₂, Ti₃AlN₂, Cr₂AlC, Cr₃AlC₂, V₂AlC, V₃AlC₂, Nb₂AlC, Zr₂AlC, Zr₂AlN, Ta₂AlC, and Ta₃AlC₂) and Si-containing MAX phases (such as Cr₂SiC, Cr₃SiC₂, V₂SiC, V₃SiC₂, Nb₃SiC₂, Mo₃SiC₂, and Ta₃SiC₂). Analysis of the diffusion coefficient of the metals in the MAX phases to ensure their faster diffusion further shortened the selection of potentially attractive crack-healing MAX phases to Ti₂AlC, Ti₃AlC₂, V₂AlC, V₃AlC, Nb₂AlC, Zr₂AlC, Zr₂AlN, Ti₂SnC, Ti₃SnC₂, Nb₂SnC, Zr₂SnC, Ti₂InC, Nb₂InC, Zr₂InC, Zr₂InN, Ti₃SiC₂, and the theoretical Nb₃SiC₂, Zr₃SiC₂. In all of these materials, it is important that the formed A-element oxides inhibit further oxidation of the material and protect the underlying matrix from further oxidation. The third criteria for the self-healing MAX phase ceramics characterizes the capability of the material to heal larger cracks. The higher the volume expansion upon oxidation is observed, the larger cracks can be filled. Meanwhile, adhesion of the oxidation products filling the cracks largely affects the strength recovery of the MAX phase materials. In addition to these criteria, it is important to ensure similar coefficients of thermal expansion of the MAX phase and the crack-filling oxidation products to prevent the damage to the material upon temperature changes, as well as close values for the elastic moduli of the materials to avoid residual stress concentration in the recovered region.

2. Electrical stimulus

In addition to the traditional high-temperature activation of the self-healing process, anodization may be another process that triggers the healing process. This is a topic that is still in its infancy

and it is believed that research in this area will increase substantially in the near future. In an example of such study, Shi *et al.*³⁷ successfully demonstrated crack repair for Al₂O₃-Ti composites at room temperature. 20–30 vol. % of titanium powder³⁷ were dispersed in an alumina matrix in an attempt to improve the electrical conductivity of the initially insulating matrix. Anodization of the composite to form titanium oxide in H₃PO₄ electrolyte solution resulted in the healing of the damaged composite structure by bridging oxides. Though the oxidized Ti particles retained their shapes during healing, an inclusion of conductive Ti particles to create conductive paths was important to efficiently allow materials recovery (Fig. 4).³⁷

B. Precipitation-induced healing

Very few articles on precipitation-induced healing of ceramics were published since it is not a fully developed area of research. Gu *et al.*³⁸ studied the healing process of pressed Nb₂O₅ cylindrical pellets that were sintered at 1100 °C for 4 h. In this study, a notch was created in these pellets using a diamond scribe. The notch was healed by adding Ag₂O in the cracked region followed by a heat treatment at 950 °C for 12 h. Raman spectroscopy confirmed the precipitation of a silver niobate (AgNbO₃) ternary phase in the crack region. The strength of the following sets of samples was evaluated using a four-point bending test: smooth, pre-cracked, and healed specimen. The average strength for the smooth, precracked, and healed specimen was measured to be 486 ± 12, 175 ± 10, and 434 ± 15 MPa, respectively. These results indicated that a recovery rate of 90% was achieved, which was a major achievement given that the newly formed repairing phase was relatively soft. In another study, Vickers indentation impressions and cracks in SiC/Ag composites were healed by a vacuum heat treatment via a dissolution-reprecipitation mechanism.³⁹ At temperatures above the melting point for Ag, liquid Ag reacts with SiC to form carbon and an AgSi alloy. Upon cooling, a reprecipitation of SiC occurs. The newly formed SiC grains were able to heal indentation impressions. The main advantage of this process is its reversibility (works well for components that go through multiple heating cycles). Its main disadvantage is that it requires vacuum annealing, which would not be possible for components that operate in air.

IV. SELF-HEALING CERAMIC-BASED COATINGS

Research in the area of self-healing coatings is still in its infancy. Self-healing coatings, just like self-healing bulk materials, require the incorporation of self-healing centers that may be triggered by an external stimulus. We believe that the design of self-repairing coatings is extremely challenging because of the following reasons:

- **Need of good knowledge of the selected thin film process:** Many of the thin film processes do not result in the formation of a thermodynamically stable architecture. Hence, understanding the processing-structure-performance paradigm is a key to the creation of an effective self-healing material.
- **Understand the effect of the mobile phase on the healing process:** Coatings being thin and having a coating-air and a coating-substrate interface will greatly affect the migration of the

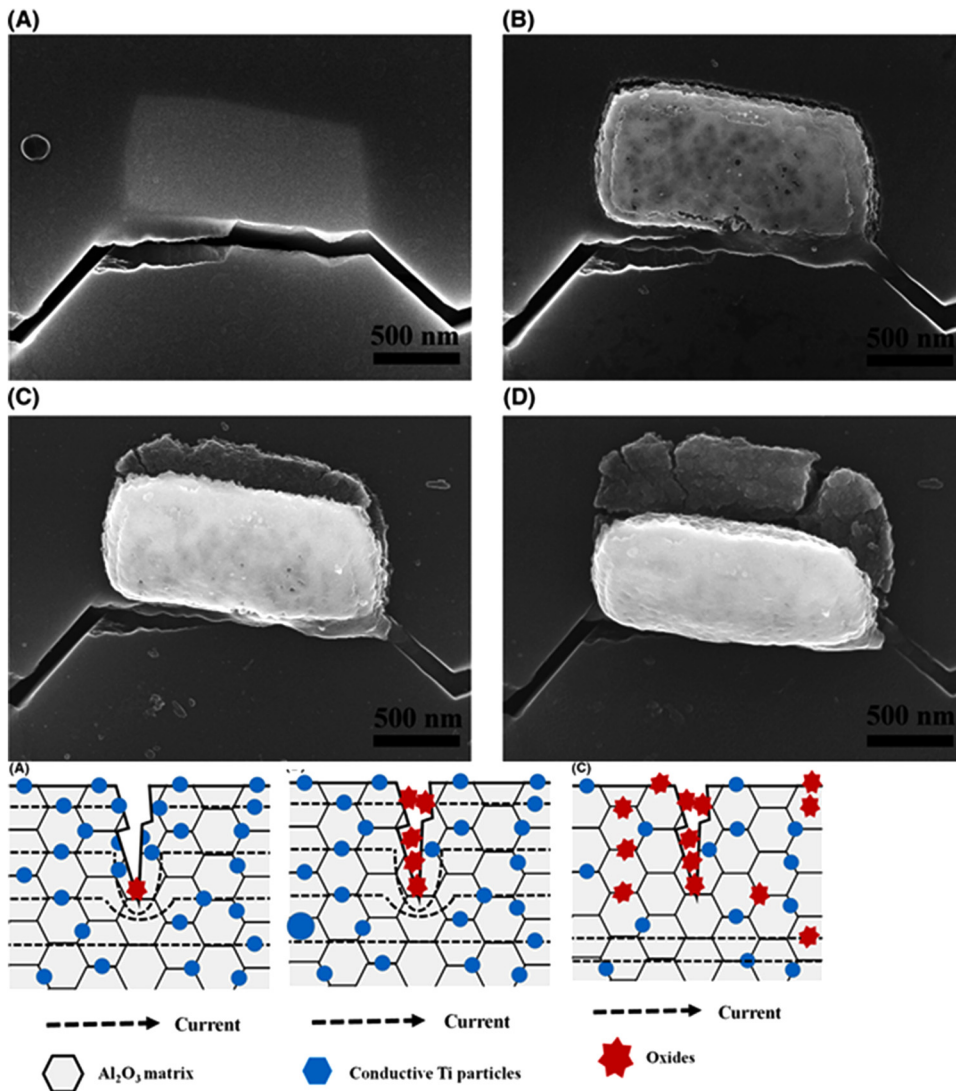


FIG. 4. SEM micrograph of the surface morphology changes of a representative Ti particle in cracked $\text{Al}_2\text{O}_3/20$ vol. % Ti composites (a) before anodization, and after A2 crack healing: (b) first step; 3 h with a current density of 2 A/dm^2 , (c) second step, which involves further anodization, an additional 1 h with a current density of 4 A/dm^2 , and (d) third step, even further anodization, an additional 1 h with a current density of 6 A/dm^2 . These micrographs were obtained from the same sample. Applied load was 29.4 N. The crack length before anodization was $140 \mu\text{m}$. Table I shows the chemical composition after each step. Mechanism of the self-healing. Reprinted with permission from Shi *et al.*, *J. Am. Ceram. Soc.* **102**, 4236 (2019). Copyright 2019, John Wiley & Sons, Inc.

31 July 2023 20:18:16

healing centers. The viscous phases should not react with the substrate, which could cause delamination or change the properties of the coatings.

A. Self-healing in tribology

Surface adaptation during sliding contact is a new and efficient method to design smart materials that are able to create and maintain a very thin low-friction material on the surface, while preserving a very thick hard ceramic coating underneath for strength/wear resistance. The production of the traditional two-layer system that consists of a lubricious layer on a hard surface will not provide lubrication over extended periods of time since once the former is worn out, what is left is a nonshearing hard ceramic that has a high coefficient of friction. The use of metastable composites opened up a new realm of smart materials whereby a lubricious phase

continuously replenishes sliding surfaces to provide the best solution to minimize friction and wear. Moreover, activating a self-healing process is a viable approach for preventing the failure of ceramics experiencing mechanically induced crack propagation.

Surface self-organization during sliding contact has recently received more attention from the research community since it seems to have the potential to create both a self-healing and a self-lubricating surface. These properties are crucial for implementing environmentally friendly tribological practices. Friction and wear are usually viewed as irreversible processes that lead to energy dissipation (friction) and material deterioration (wear). These adverse effects can be mitigated using solid lubricants that are able to self-organize on sliding surfaces to minimize friction and/or wear. The formation of an optimum solid lubricant at the interface between sliding surfaces is crucial to the efficiency and lifetime of applications, especially when operating in harsh environments.

The first nanocomposite coating design that was able to provide continuous lubrication was based on the concept of noble metal diffusion.⁴⁰ These self-lubricating coatings are nanocomposite materials that consist of a hard-ceramic matrix to impart wear resistance and inclusions of a noble metal that are highly mobile at elevated temperatures (>~300 °C) to slowly migrate to the surface to provide enhanced lubricity. The temperature that triggers silver migration may be regulated by controlling grain size of the matrix, which is achieved through the selection of the right substrate temperature during deposition.^{41,42} Examples of systems that were investigated include TiC-Ag,⁴³ YSZ-Ag,⁴⁴ Cr₂AlC-Ag,⁴⁵ CrN-Ag,⁴¹ CrAlN-Ag,⁴⁶ Mo₂N-Ag,⁴⁷ and MoCN-Ag.⁴⁸ This design concept results in a large volume fraction of grain boundaries, which provides toughness enhancement through stress minimization, crack deflection, and ductility.^{49,50} This self-lubricating concept may be used to create a lubricious ternary oxide film^{51–53} on the surface of a hard coating, which is also able to heal damage that occurs as a result of the sliding process. Conditions to successfully create an adaptive/self-repairing coating include (1) the presence of a mobile phase that is able to migrate to the surface at a controlled rate; (2) the phase migration, usually facilitated by thermal and/or mechanical stimuli, should result in the formation of a ternary oxide layer on the surface of the hard coating; and (3) the newly formed oxide needs to be able to shear easily under sliding conditions.

Stone *et al.*⁵⁴ produced Ta₂O₅/Ag coatings by unbalanced magnetron sputtering with the premise that silver would migrate to the surface and form a thin lubricious AgTaO₃ film while maintaining a hard underlayer for Ag content <15 at. %. These coatings were found to possess a surface that adapts because of the high operating temperatures and the relatively larger sliding pressures. Low CoF values and, more importantly, very low wear rates were recorded. The wear rates for this adaptive system were superior than those of single-phase AgTaO₃ films because of the formation of a thin lubricious layer on a hard phase that is primarily made of Ta₂O₅. This surface reconstruction was accompanied by a self-repairing process that contributed to the observed low wear rates. Molecular dynamics simulations were carried out to understand the fundamental mechanisms that differentiate the tribological properties of Ta₂O₅ and AgTaO₃ films. Simulations and experiments highlighted the migration of silver to the surface to form the lubricious ternary phase, which had a major effect on the friction and wear response of the sliding interface. In addition, this study revealed that friction decreased, while wear increased with the increase in silver content in Ta₂O₅/Ag films, when the Ag content was >5 at. %. However, both methods also showed that the lowest friction was always observed on AgTaO₃. More importantly, the study suggests that it may be possible to tune the friction and wear response of Ag-Ta-O films by controlling the amount of embedded silver for a given set of operating conditions. Zhu *et al.*⁵⁵ recently combined the following three phases NiCrAlY, Ag₂O, and Ta₂O₅, to create a composite that is able to use the synergistic lubrication of Ag, NiO, CrO₂, AgTaO₃, and Ag₂Ta₄O₁₁. The formation of these phases enabled the self-lubrication of the composite coating in a wide temperature range in addition to the self-repair that was needed to maintain low friction and wear rates. Various surface reconstruction processes were observed at different temperature regimes. The main lubricious phases were found to be Ag and NiO

up to 350 °C. When the temperature reached 550 °C, a newly formed glaze layer made of NiO and CrO₂ provided lubrication since Ag was no longer effective. At 750 °C, AgTaO₃ and Ag₂Ta₄O₁₁, formed by the *in situ* chemical reaction discussed earlier, formed a lubricious and wear resistant glaze.

Shirani *et al.*⁵⁶ explored the mechanism of lowering the high-temperature healing requirement by assisting the process of crack repair with a normal load and shear stresses to induce an adaptive tribochemical event between sliding surfaces (Fig. 5). For this, the material system consisting of niobium oxide and silver has been studied using macroscale pin-on disk tests. The selection of this particular sliding chemistry led to the formation of a lubricious ternary AgNbO₃ phase at the interface once the temperature reached ~600 °C. Interestingly, in the absence of sliding, the temperature needed for the ternary phase formation exceeds 945 °C. The observed formation of the ternary phase was accompanied by a threefold decrease in the friction coefficient value as compared to niobium oxide/silicon nitride system. The enhanced tribo-performance was associated with a tribologically activated surface reconstruction process initiated inside the wear track. The formation of the lubricious ternary oxide at a much lower than thermodynamically required temperature suggests that the self-healing process can be initiated with mechanically induced stresses. Such a process is a new recipe for improving wear and crack resistance characteristics of ceramic components and may be tuned to provide the desired frictional response.

In a very recent study, our group produced a hybrid dual-phase coating that consists of an A356 aluminum alloy modified by plasma electrolytic oxidation (PEO) and that was burnished with graphite-MoS₂-Sb₂O₃ chameleon solid lubricant powders.⁵⁷ The PEO coating was selected to provide high mechanical strength, superior hardness, and thermal protection to the aluminum alloy. The chameleon coating's role was to impart a lubricous behavior from 25 up to 300 °C. COF values were measured to be 0.2 at room temperature down to 0.02 at 300 °C.⁵⁷ These outstanding results are due to the adaptive nature of the coatings that are able to both maintain the right lubricious phase on the surface as well as heal any cracks that form due to the sliding process.

B. Self-healing for thermal barrier coatings

Thermal barrier coatings (TBCs) are ceramic-based materials that are widely applied to protect superalloy blades in gas and jet turbines to allow operation at elevated temperatures in a highly corrosive environment.^{58,59} Gas turbines, which are essential energy sources for propulsion and power generation, can provide significantly higher powers as the operating temperatures are increased.^{60–62} TBCs are usually deposited on the surface of the rotating blades and shrouds as well as on the fixed guide vanes in the hot section area of the combustion chamber.⁶³ Typically, for a ~250 μm thick TBC coating, the temperature gradient will decrease by about 150 °C, depending on the thermal resistance of the coating, from the hot gas flow surface to the superalloy surface.^{63–65}

The intrinsic brittleness of ceramics is derived from the strong and directional covalent and ionic bonds of their constituent atoms.⁶⁶ Therefore, TBCs have low fracture toughness and are sensitive to flaws. A reduction in strength results in a decrease in the

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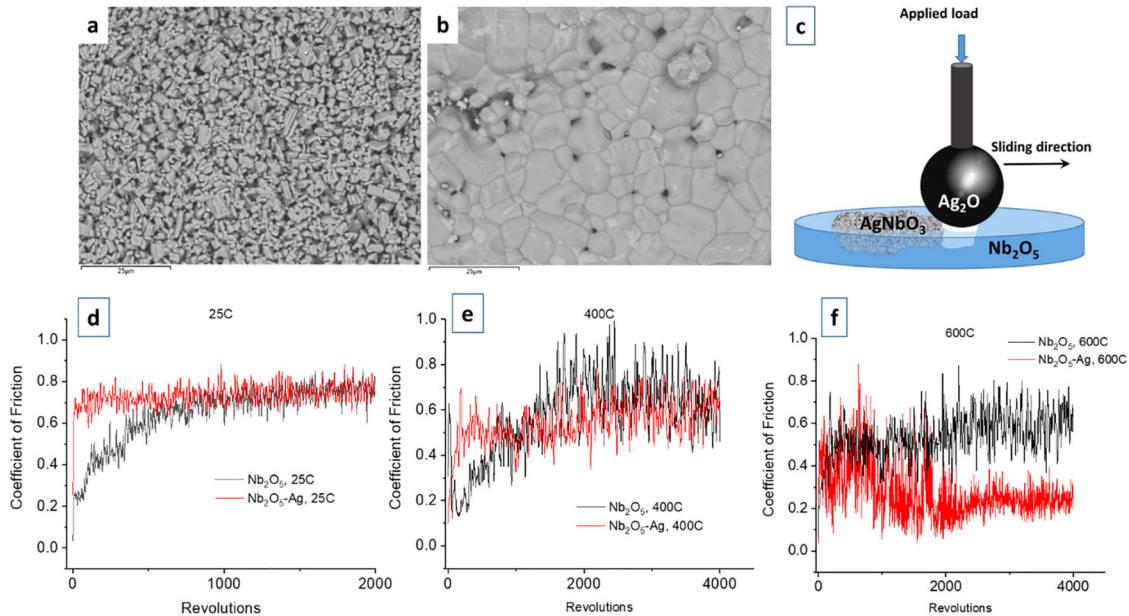


FIG. 5. Preparation of the bulk niobium oxide sample by (a) pressing and (b) sintering the pellet. The sample was further tested for the tribological performance (c). Tribology test of Nb_2O_5 with and without the presence of Ag at (d) 25 °C, (e) 400 °C, and (f) 600 °C. Results indicate a reduction in the coefficient of friction in the case of silver presence at 600 °C (f). Reprinted with permission from Shirani *et al.*, *Surf. Coat. Technol.* **397**, 126016 (2020). Copyright 2020, Elsevier.

lifespan and reliability of gas turbine engines.⁵⁵ Flaws in the TBCs can be due to a number of reasons that include the fabrication process, impinging debris, fatigue, thermal shock, chemical attack, high pressures, and high stresses.^{67–69} In addition, porosity is an inherent property of the deposition processes, such as electron beam evaporation or air plasma spray, used to create TBCs. This porosity has the advantage of reducing thermal conductivity and substantially enhances film adhesion to the substrate by accommodating stresses related to thermal expansion differences at the coating-substrate interface.^{70,71} A major challenge for TBCs is that their porosity acts as a pathway for CMAS (calcia-magnesia-alumina-silicate) infiltration and for oxygen diffusion.⁷² Most researchers that have investigated the self-healing concept in TBCs did so to mitigate CMAS attack. When engines operate at low altitudes, external siliceous minerals from dust, sand, and volcanic ash can be ingested by the air intake and pass through the engine.^{73–77} The melting temperature of CMAS varies between 1190 and 1260 °C depending on the composition,⁷⁸ while the inlet temperature of high-pressure gas turbine blades is typically around 1300–1600 °C.^{79,80} Therefore, when the temperature is below the melting point of CMAS, the debris can cause erosive wear by impact damage, and when exceeding the CMAS melting point, the siliceous debris melts, deposits, and infiltrates into the TBCs through pores, cracks, and at a much slower rate through grain boundaries because of its predominant wetting ability (Fig. 5).^{73,81–83} During CMAS infiltration, a portion of YSZ is chemically dissolved by CMAS leading to the generation of new phases (such as zirconium silicate, calcium feldspar, spinel, etc.) and the tetragonal to monoclinic phase transformation of YSZ.^{84–87}

Upon cooling, the glassy CMAS solidifies and fills the porous coating resulting in the increase in stiffness and thermal conductivity of TBCs, and acceleration of the substrate oxidation rate.^{88–91}

Four technical methods have been exploited to overcome the low fracture toughness of ceramics, ensure the structural integrity and reliability, and extend components' durability:^{12,92–94} (1) enhance the fracture toughness of ceramics by controlling microstructure or adding strengthening phases (e.g., fibers, whiskers, or particles); (2) utilize a nondestructive testing apparatus to inspect components and repair cracks before service; (3) apply a proof test to avoid the use of unreliable materials; and (4) modify currently used ceramics with phases that provide self-healing ability. The latter concept seems to be a viable approach to extend the life cycle of these materials and reduce the cost of operation of gas turbine engines.^{95,96} For TBCs, the design requires the deposition of a two-layer system that consists of a self-healing top layer over a traditional porous structure. The top layer's function is to seal the TBC to mitigate oxygen and CMAS infiltration. The underlayer maintains the desired porosity to enhance thermal resistance and accommodate thermal stresses.

Ouyang *et al.*⁹⁷ were the first researchers to design, produce, and test self-healing thermal barrier coatings. Their model was based on the oxidation of SiC at elevated temperatures (concept already discussed in Sec. III) to create a self-healing layer on top of the traditional YSZ layer (Fig. 6). This bilayer coating was created by air plasma spray (APS) and any cracks that formed as a result of APS processing were repaired by the reaction of SiC particles in the crack with the oxygen in the atmosphere for temperatures above

31 JULY 2023 20:18:16

720 °C. The self-repairing concept was used to reduce oxidation of the thermally grown layer, which will eventually lead to coating spallation. The effectiveness of this concept for CMAS mitigation was not reported. Gu *et al.*⁹⁸ used a similar concept to create YSZ-Al₂O₃-TiC and YSZ-Al₂O₃-SiC self-healing composite overlayers by laser processing, which is an alternative to the traditional processes, such as electron beam evaporation and air plasma spray. The study suggested a design whereby coatings should consist of a two-layer system: (1) a porous ceramic single-phase underlayer that maintains a low thermal conductivity and that is able to accommodate stresses due to coating-substrate thermal mismatch and (2) a dense self-healing composite overlayer that prevents the infiltration of CMAS and oxygen. In this study, processing conditions were optimized to create an adherent TBC coating. Laser processing was demonstrated to be a viable technique that has the potential to create a self-healing layer that seals YSZ-based underlayers from diffusion. In a follow-up study, Gu *et al.*⁶⁹ carried out a CMAS infiltration study on the YSZ-Al₂O₃-SiC system. Cross-sectional SEM images revealed a threefold improvement in CMAS resistance for this system over that of the reference YSZ system. Another type of self-healing strategy that was employed to enhance the resistance of YSZ-based TBCs to CMAS attack was via precipitation-induced self-healing.⁶⁹ Two different composites were investigated, namely, YSZ-Al₂O₃-Ta₂O₅ and YSZ-Al₂O₃-Nb₂O₅. Self-repair occurs via the following chemical reactions: Nb₂O₅ + Al₂O₃ → 2AlNbO₄ or Ta₂O₅ + Al₂O₃ → 2AlTaO₄. Cross-sectional SEM figures revealed a 33-fold improvement in

CMAS resistance for the YSZ-Al₂O₃-Nb₂O₅ system and a sixfold improvement for YSZ-Al₂O₃-Ta₂O₅ over that of the reference YSZ system.

Nozahic *et al.*⁹⁹ created self-healing TBC coatings that consist of a mixture of YPSZ powder and encapsulated MoSi₂(B) based particles using spark plasma sintering (Fig. 7). The ceramic coatings were produced on MCrAlY coated inconel substrates. The TBC self-healing mechanism was shown to consist of cracks being filled with silica and a zircon phase. In addition, an Al₂O₃ shell was found to protect the MoSi₂-based particles against premature oxidation under thermal cycling conditions at 1100 °C in air. When such a protective shell is present, the particles oxidize at a rate almost 100 times slower than unprotected MoSi₂(B) based particles. These observations confirmed the intended self-healing mechanism of MoSi₂(B) based particles reinforced yttria partially stabilized zirconia based TBCs.

C. Self-healing ceramic coatings for oxidation and corrosion protection

Coatings of ZrB₂-SiO₂ were produced on SiC coated C/C composites by infiltrating a silica sol into a porous ZrB₂ layer.¹⁰⁰ These would be potentially used to protect space vehicles against thermal shock upon re-entry. It was concluded that these coatings were effective at protecting the underlying composites from oxidation for 330 h at 1500 °C. The excellent oxidation resistance of

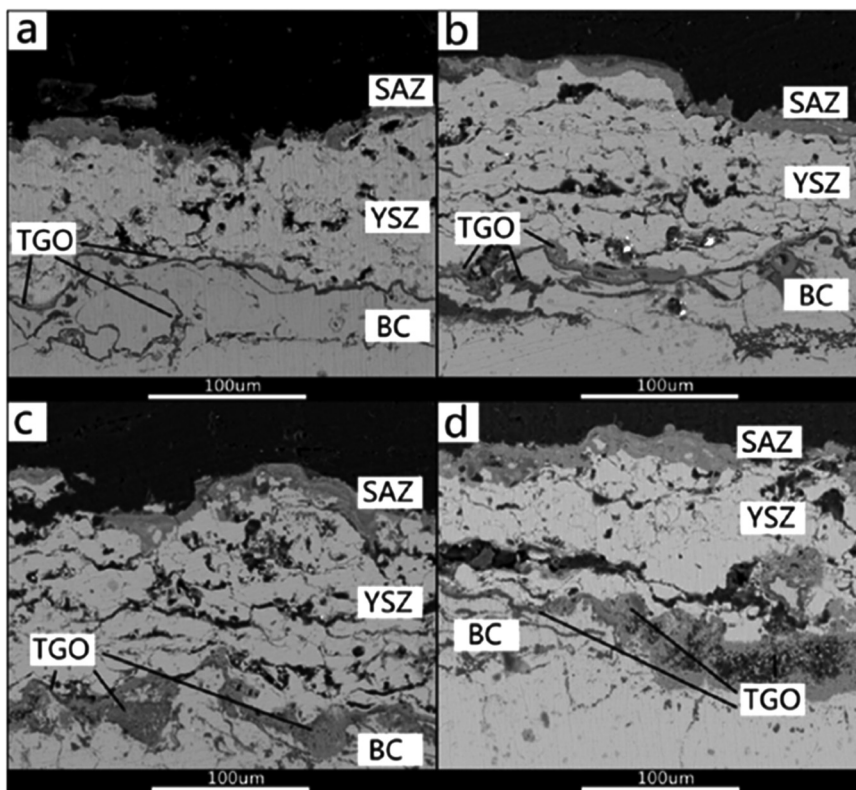


FIG. 6. Cross-sectional SEM images of SAZ TBC samples after high temperature oxidation for (e) 5 h, (f) 10 h, (g) 15 h and (h) 20 h. Reprinted with permission from Ouyang *et al.*, *Surf. Coat. Technol.* **286**, 365 (2016). Copyright 2016, Elsevier.

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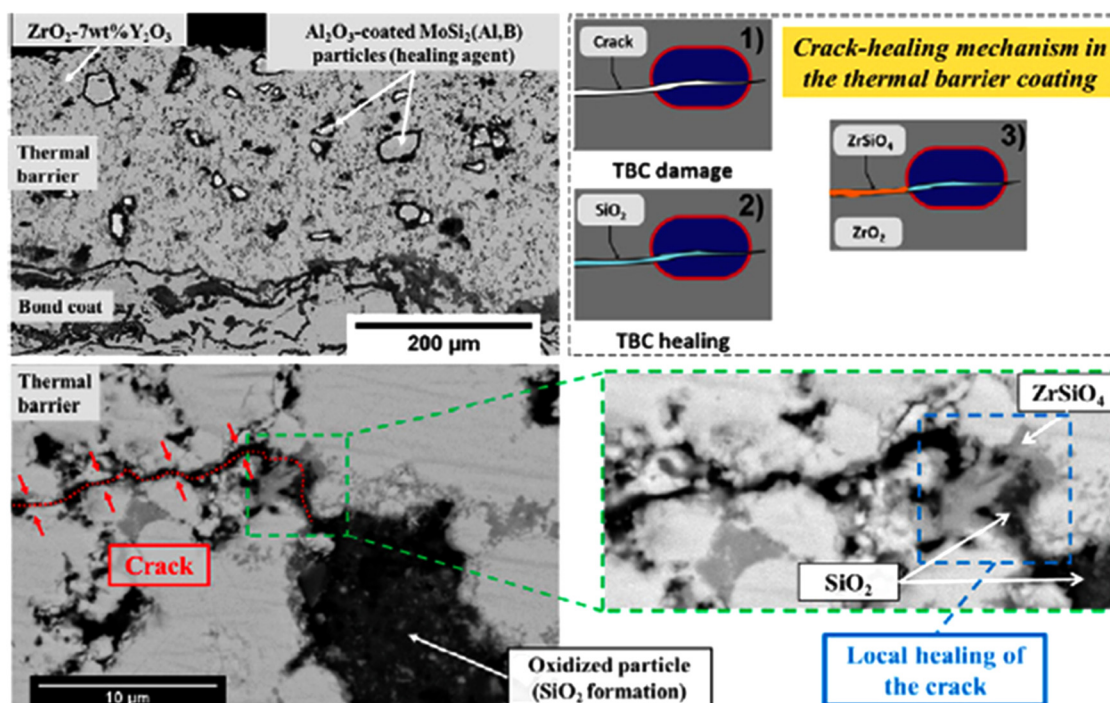


FIG. 7. (a) Cross-sectional SEM backscattered images of a TBC made of a mixture of YPSZ powder and 10 vol. % encapsulated MoSi₂ (B); (b) suggested crack-healing mechanism; (c) SEM backscatter electron image of a cross-sectional view of a TBC made of a mixture of YPSZ and 5 vol. % of encapsulated MoSi₂ (B) based particles after 151 cycles of 1 h at 1100 °C. Reprinted with permission from Nozahic *et al.*, Mater. Des. **143**, 204 (2018). Copyright 2018, Elsevier.

these coatings was attributed to the volume expansion that resulted from the formation of ZrO₂ (13.6% volume expansion) and ZrSiO₄ (98% volume expansion) through the oxidation of the ZrB₂ phase. Upon cooling, these phase transformations created compressive stresses in the coatings. These compressive stresses restrained cracks from forming, hence improving the overall oxidation protection of the composite. Similarly, a self-healing oxidation resistant coating with a double layer of SiC was prepared using a two-step technique by chemical vapor reaction and chemical vapor deposition.¹⁰¹ It was observed that a good adhesion was built between the inner SiC layer and the outer SiC layer. Compared with single layer SiC coatings, the double layer SiC coatings exhibited a better oxidation resistance. After a 24 h static oxidation test in air at 1773 K, no mass loss of the double layer SiC coatings was observed. A mass gain of 1.73 mg cm⁻² was measured instead which was suggested to be the mechanism that helped seal the coating to improve its oxidation resistance.

Glassy materials have potential to self-repair surfaces since they have lower viscosity at elevated temperatures. For example, thermally stable boro-silicate glass coatings with excellent wetting properties and viscosity were used to protect SiCf/SiC composites from oxidation.¹⁰² The glass-coated composites were produced using a low-cost slurry, which was subsequently treated in air for 100 h at 1200 °C. Three-point bending tests were carried out on the glass-coated and uncoated composites after the thermal treatment.

The results of this tests suggested that, unlike for the uncoated samples, the mechanical properties of the glass-coated composites remained almost virtually unaffected by the heat treatment process. In a similar investigation of self-healing using borosilicate glass for thermal protection, B₄C was added to the glass matrix.¹⁰³ A study of the thermal properties as a function of temperature up to 900 °C revealed that the repair capability depended on the content of the carbide phase. The B₂O₃ generated from this carbide was able to dissolve into the borosilicate glass and significantly change the coefficient of thermal expansion and the softening temperature of the glass. A protective coating with the lowest porosity and oxygen permeability was formed when the B₄C content was ~25 wt.%. Fan *et al.*¹⁰⁴ demonstrated the enhanced oxidation resistance and thermal shock properties of SiCN/borosilicate glass-B₄C-Al₂O₃ coatings for C/C aircraft brake materials. These properties are improved because of the oxidation of boron to form B₂O₃ that can repair cracks. Glassy coatings that contain VB as a healing agent embedded between glassy layers were produced by atomic layer deposition (Fig. 8).¹⁰⁵ This new coating was effective at healing any cracks that formed on the surface via oxidation of VB to form V₂O₅ and B₂O₃ that have a low viscosity and are able to migrate to the desired locations for operating temperatures in the 700–900 °C range.

Alloys that form multielement glassy materials include Mn_{1.0}Co_{1.9}Fe_{0.1} (MCF)¹⁰⁶ and MoSiAlY.¹⁰⁷ In the first study, atmospherically plasma sprayed MCF protective layers were

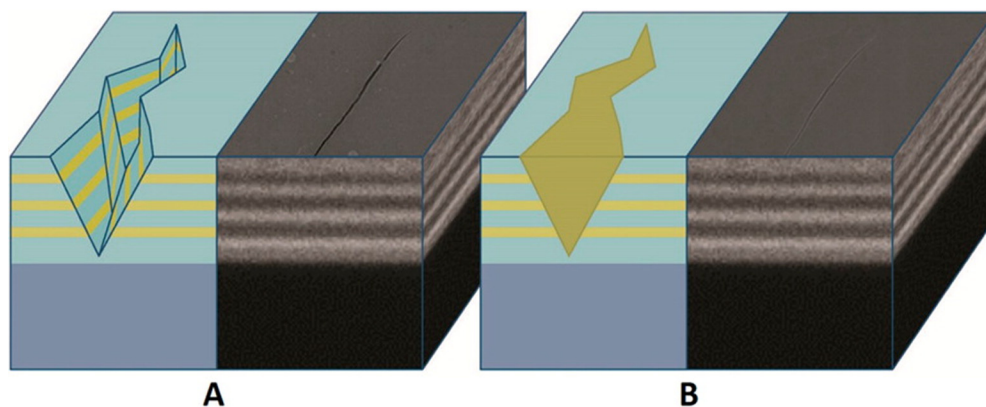


FIG. 8. Schematic description and experimental observation of the self-healing process of thin-film glassy coating: (a) vanadium boride (VB) layers (healing agent) are embedded between glassy layers. Wherever any damage occurs, a crack is formed in the coating; oxidation of the healing layer occurs by reaction with oxygen. (b) V_2O_5 and B_2O_3 produced by the oxidation of VB have a low viscosity at the operating temperature (typically 700–800 °C), which enables them to spread and leads to the crack healing. Reprinted with permission from Castanié *et al.*, ACS Appl. Mater. Interfaces **8**, 4208 (2016). Copyright 2016, American Chemical Society.

shown to reduce chromium related degradation because of their self-repairing ability.¹⁰⁶ Dense coatings on metallic interconnectors are necessary to suppress chromium poisoning of SOFC cathodes. The APS process was designed to operate in reducing conditions to enable the formation of a metastable rock salt structure. Annealing in air resulted in a phase transformation to a spinel phase, which is stable at low temperatures. This phase transformation leads to a volume expansion and a self-healing process that facilitated the sealing of any existing cracks and the overall densification of the coating. In the second study, a self-healing MoSiAlY coating was deposited on a γ -TiAl alloy to improve its oxidation resistance by double glow plasma surface alloying technology.¹⁰⁷ Isothermal oxidation tests carried out at 900 °C indicated that the oxidation resistance of γ -TiAl alloy was effectively improved by the MoSiAlY coating. The volume expansion of the newly formed phases SiO_2 from $MoSi_2$ and Al_2O_3 from $AlMO_3$ was responsible for the self-repairing ability of this coating.

D. Self-healing of ceramic-based hybrid composites

While activation of the self-healing mechanism in all-ceramic systems usually requires exposure to high temperature conditions,

thus limiting the applicability of the coatings, combining ceramics with polymers allowed to design self-healing systems that work for a wider range of requirements. Self-healing coatings based of titanium oxide were designed for UV shielding applications by mixing titanium oxide with 2-hydroxyethyl methacrylate (HEMA).¹⁰⁸ Once the TiO_2 -HEMA composite coating was damaged, the exposure of the system to water resulted in swelling of the HEMA polymer chains that become entangled. This entanglement is the mechanism that promotes crack-healing. The resulting coating demonstrated high UV-shielding performance by absorbing >90% of the UV, as demonstrated by UV-Vis spectroscopy measurements. This UV-shielding ability of the coating, hampered by coating damage, was completely restored by the self-healing activation process (Fig. 9).

Alternatively, a low-temperature self-healing system was designed by joining glass bricks by thin layers of poly(borosiloxane) (PBS)¹⁰⁹ to create materials with up to 90 vol. % of ceramic loading. In this case, glass bricks cut from glass slides were bonded together by pressing after coating with the PBS. The PBS was able to recover the areas of the crack propagation in the materials by forming polymer bridges within the cracks. The materials showed very high mechanical strength once the self-healing mechanism is activated immediately after crack initiation at room temperature.

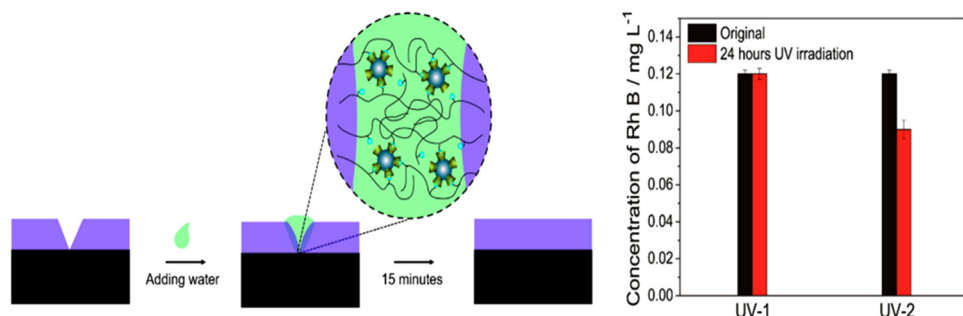


FIG. 9. Schematic of the self-healing mechanism for TiO_2 -HEMA composite. (b) Restoration of the UV-shielding properties with self-healing. Reprinted with permission from Peng *et al.*, Coatings **9**, 421 (2019). Copyright 2019, MDPI.

31 July 2023 20:18:16

Self-healing polymer-ceramic materials were also considered as candidates for corrosion-protection coatings.¹¹⁰ These coatings are usually produced by solgel, electrodeposition, or using plasma techniques. The coatings usually consist of oxides that are covalently bonded to the native oxide layer of metallic substrates. A ceramic matrix also acts as reservoirs for corrosion inhibitors. The inclusion of organic components into the ceramic matrix enhances the ductility, stress resistance, and anticorrosion properties of the coatings. An example of a study that demonstrated the usefulness of this concept is the one by Lamaka *et al.*,¹¹¹ whereby they produced nanostructured hybrid TiO₂-inhibitor films using the solgel technique. These films exhibited enhanced corrosion protection and self-healing ability confirmed using electrochemical impedance spectroscopy and scanning vibrating electrode technique measurements.

V. CONCLUSIONS

Self-healing materials have recently gained increasing interest by the research community. However, this area is still in its infancy especially for ceramic coatings. In this review paper, we provided a broad overview of the advances made in the surface engineering of adaptive and self-repairing ceramic coatings. These are composite-based adaptive materials that automatically adjust their structure and/or chemistry in response to external thermal and/or mechanical stimuli. These materials are usually produced using deposition techniques that include but are not limited to physical vapor deposition, chemical vapor deposition, laser cladding, plasma spray, cold spray, and solgel.^{42,51,112}

Functional ceramic coatings are prone to cracking as a result of external mechanical stresses that could be further exacerbated by thermal stresses. The integrity of the protective surface is significantly compromised by these defects. This review discusses potential solutions with an emphasis on self-healing/surface reconstruction concept to design next-generation protective surfaces. These materials have the potential to significantly increase the lifetime and reliability of coatings and would drastically reduce replacement costs. The focus of the review was to use adaptive/self-healing ceramic surfaces to protect against wear, corrosion, and oxidation. The creation of a self-repairing ceramic is very challenging since healing requires a phase that is mobile and that is able to migrate to the defect site to perform the required material reconstruction, which is usually not a property known for protective materials that are known for their strength and hardness. Self-healing for this class of materials is usually achieved via oxidation-, precipitation-, and phase transformation-induced healing process. Potential applications of these materials were in space, aerospace, power generation, and defense.

In the future, the materials community will have to address many unresolved questions on self-healing ceramic coatings providing a wide variety of opportunities for research in this relatively new field. For example, understanding crack-healing kinetics (solid-state reaction kinetics) is a key to designing materials that are effective at self-repairing. This entails investigating the effect of grain size, viscosity and dispersion of repair agents, and chemical or mechanical activation of these fillers in the healing process.¹¹ This may be achieved by using experimental and theoretical tools to

uncover the fundamental mechanisms that govern self-repair in these complex composite structures. Another potential area of research involves the integration of the concept of materials science tetrahedron to carry out a more efficient and coherent exploration of these materials. Understanding the interdependent relationship between processing, structure, properties, and performance will enable the creation of the most effective self-repairing material compositions. In addition, the effect of crack-healing on the enhanced protective response of a coating needs to be evaluated and quantified. Real time microscopy and spectroscopy techniques may prove to be powerful to achieve this goal.¹¹³⁻¹¹⁶

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