A review of some of experimental and numerical studies of self-crack-healing in ceramics

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Abstract
Ceramics can be used in many applications including aeroengine turbine blades, gas turbine blades, high-performance bearings, and many other applications that require high temperature service; however, these ceramics are subjected to thermal and mechanical stresses during/while being used in service. Residual stresses may eventually cause microcracks (internal and surface cracks) and the failure of the component in use, hence limiting their use as structural engineering materials; for this reason, applying or inducing self-crack-healing ability would be the solution to overcome such problems. Developing new materials with an inherent ability to heal the cracks and increasing resistance to fracture wear and corrosion has been the goal for many researchers in the field of science and engineering and manufacturers. Great benefits can be expected from the components in use while applying self-healing ability, such as reducing maintenance, inspection, and the cost of machining and polishing, which enhance the reliability and the lifespan of the component in use hence meeting the needs of many industries like automotive, space, aerospace. Consequently, many attempts have been made to imitate the mechanisms of biological systems to design self-healing materials and coatings which can result in complete recovery and functionality of the component. These research studies are reviewed and summarized in this review manuscript.

Keywords
ceramics, microcracks, self-healing

1 | INTRODUCTION

Self-crack-healing materials have the capability of partial or complete healing cracks and the damage imposed on them as well as the capability of recovering the functionality and the integrity of the structure.1,2 Self-crack-healing mechanisms inspired by the natural healing ability of biological systems can be categorized as either extrinsic or intrinsic. In the case of extrinsic healing, the system requires healing agents. On the other hand, intrinsic healing is inherent, the healing process is inherent in the material itself.

Autonomic self-healing would make the materials ideal for aerospace and automotive applications. Among the many types of healing, only self-crack healing induced by oxidation can attain complete recovery. The crack-healed zone should be mechanically as strong as the original material to achieve...
complete strength recovery; thus, the crack-healed zone should satisfy the following requirements:

- The volume between the crack walls should be completely filled with the product formed by the self-healing reaction.
- The formed product should have the same or higher strength as the base material.
- The formed product should strongly bond to the crack walls.

For intrinsic self-healing, the healing agent is embedded into the matrix and the healing process is due to physicochemical reaction. The damage triggers the healing process through the healing agent. The mechanical properties can be recovered upon the healing process. In the case of extrinsic self-crack healing, the healing agent would be foreign particles added to the material during the manufacturing process. In this case, the healing agent is encapsulated and dispersed within the matrix. Upon cracking, the healing agent in the capsules flows into and fills the gap between the crack faces causing the bridging of these crack faces (the healing agent interacts with the cracks). The crack causes the rupture of the capsules, releasing the healing agent, which flows to fill the cracks. This is followed by a physical or chemical reaction to mend the crack faces, consequently resulting in mechanical integrity of the component/composites.

Another classification of the self-healing materials depending on the trigger is as follows:

- Autonomic self-healing Materials:
  - In this type of self-healing, the healing process is inherent in the system itself, and the healing process does not require a stimulus to initiate the healing process.
- Nonautonomic Self-healing Materials:
  - The healing process in this type of self-healing materials requires an external trigger such as heat or light. In order to initiate the healing process, an external stimulus is needed, which triggers the healing process through chemical reaction.

Some requirements and common parameters utilized in the self-crack-healing process are shown in Figure 1.

Ceramics have low fracture toughness, which means that they are brittle and sensitive to flaws such as micro and macro cracks, which limit their applications as structural components. The present research is focused on the self-crack-healing ability of different materials and composites. Self-crack-healing behavior is reviewed as a function of the healing conditions (time, temperature, and chemical composition) as well as the mechanism responsible for healing the cracks not to mention utilizing a numerical model to simulate the healing behavior of the cracks. In the current manuscript, a review and summary of research studies on self-healing behavior in ceramics is provided.

### 2 | SELF-HEALING IN CERAMICS, THIN FILMS, AND ITS COMPOSITES/ CONCEPTS AND PREVIOUS STUDIES

Inspired by nature, inducing crack-healing capability in ceramics can bring many benefits including less maintenance, enhancing the reliability, and the structural strength, and reducing maintenance. Designing a self-healing system with self-crack-healing ability has been a research topic for many researchers in the field of science and engineering. Investigations on the self-crack healing can be traced back to 1958 by Hummel and Bush. They reported that the mechanical properties (Strength and Young’s Modulus) of magnesium dititanate increased at high temperatures (1000°C) and the healing of the cracks was the reason behind enhancing the properties. The self-healing of the cracks was investigated by several researchers; Petrovic and Jacobson. They showed that at high temperatures, SiC reacts with oxygen to form SiO₂, which flows to fill the cracks.

Figure 2 shows the analogy of the self-healing process to wound healing in human bodies. In human beings, the first step of the healing process starts after the bleeding through the coagulation, blood clotting; in this process, activation, adhesion, and aggregation of the platelets, and deposition and maturation of the fibrin (a protein involved in the blood clot); a polymerization process of the fibrin alongside with the platelets form clot which would cover the wound site and heal it. Inspired by the healing process of the wound and tissues in biological systems, the first

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**FIGURE 1** Self-crack-healing requirements and parameters

| I | Self-crack-healing Requirements are: |
|---|---|
| | • The healing agent must flow into the crack site |
| | • Fill the volume opened by the cracks |
| | • Adhere to the cracks’ walls |

| II | Self-crack-healing Parameters are: |
|---|---|
| | • Chemical composites |
| | • Healing temperature |
| | • Time |
| | • Partial pressure |
| | • Self-healing particle size |
| | • Environments |
step is a sintering process, which is an external stimulus to trigger the self-healing. The next step is the grain growth phenomenon and crack closure, and finally the formation of new bonds and healing of the crack.  

The crack-healing behavior of Spinel (MgAl$_2$O$_4$) ceramics has been investigated by several researchers. Tavangarian and Li investigated the crack-healing behavior and the strength recovery of SiC/Spinel nanocomposites. The results of their work showed that the complete healing of the induced cracks was attained at a temperature of 1545°C in a holding time of 1 minute in an air atmosphere. A recovery of the strength was achieved for the samples healed at a temperature of 1550°C and 1 minute holding time, and a healing efficiency of about 99% was recorded for the samples healed at a temperature of 1550°C and 1 minute holding time. In the ternary systems they studied SiC/Al$_2$O$_3$/Y$_2$O$_3$, a liquid eutectic compound (Y$_2$Si$_2$O$_7$) was formed which flowed due to the low viscosity to fill the cracks and heal the surface.

Self-crack-healing behavior of SiC was investigated by Osada et al. at temperatures ranging from (1000-1500)°C for different pressures of oxygen (1 atm, 5 × 10$^{-4}$ atm, and 0.05 atm). The strength was recovered completely owing to the passive oxidation of the SiC. Ando et al. investigated the self-healing ability of SiC/Spinel nanocomposites; they demonstrated that cracks can be healed completely at temperatures ranging from (900-1400)°C in an air environment. The optimum conditions for healing the cracks were (1200-1300)°C for 1 hour in air only. Also, the crack-healing behavior of Si$_3$N$_4$/SiC was investigated by Ando et al. at high temperatures under cyclic stress. Their results showed that the composite has an excellent healing ability, a complete healing of the cracks can be achieved at temperatures (1100-1200)°C regardless of the healing time.

Several studies on self-crack healing linked the self-crack-healing phenomena and the oxidation behavior of the crack-healing agent. The structural integrity can be enhanced through inducing the healing ability through the chemical reaction of the healing agent. The rate of the chemical reaction is affected by the temperature. Tikare and Choi showed that the healing process can occur in different environments around 800°C through mass transport. Haung and Wen investigated the self-crack-healing mechanism of Al$_4$SiC$_4$ ceramics. They showed that the healing process occurs through oxidation and release of the residual stresses (Sintering process at 1300°C in air rather than in vacuum). Radford and Lange showed that the healing of cracks can be achieved through the sintering process of samples fabricated from alumina, at a temperature of 1700°C for a healing time of 1 hour (the healing process is a result of the grain growth from one side to the other side of the crack surface). In other cases, the healing process can be achieved by the pore evolution of the microstructure during the annealing process of alumina as demonstrated by Gupta. After sintering for 1 hour, most of the cracks were healed and around 95% of the strength was recovered.

Nakatani et al. studied the crack-healing ability of SiN/SiC nanolaminated films at elevated temperatures ranging from (600-1200)°C in an air environment. Their results...
showed that the inserted layers of SiC may heal the cracks in SiN thin films. They also reported that the healing ability can be enhanced upon increasing the time and temperature.\textsuperscript{26} Chen et al.\textsuperscript{27} investigated the crack-healing ability in Zr$_2$Al$_4$C$_5$ composite ceramics at high temperatures ranging from 800-1200°C. They reported that this composite has an excellent ability to heal induced cracks and damage through the oxidation process. Their results showed that the optimum temperatures to heal the cracks was 1000°C. They reported that the cracks could be healed completely at a temperature greater than 1000°C in an air environment, the main mechanism to heal the cracks was found to be the oxidation process and forming of the oxides mainly t-ZrO$_2$ and α-Al$_2$O$_3$. Chu et al.\textsuperscript{28} investigated self-healing of SiC ceramics and showed that the strength of the healed samples increased as a result of the residual stresses due to the thermal expansion mismatch of SiO$_2$ and SiC. The self-crack-healing ability was investigated by Chuo et al.\textsuperscript{29} They showed that cracks in SiC/Al$_2$O$_3$ ceramic can be partially healed in an argon atmosphere. Thompson et al.\textsuperscript{30} investigated the self-healing ability of SiC/Al$_2$O$_3$ nanocomposites. They showed that pre-cracked specimens could be healed at 1300°C for 2 hours holding time in an argon atmosphere. Adhesion of the cracks was the responsible mechanism for healing of the precracked specimens. Self-crack-healing ability was investigated by Wang and Steven.\textsuperscript{31} They showed that Zirconia has excellent self-healing ability. At 1700°C the ZrO$_2$(m) transforms into ZrO$_2$(t), which heals the cracks and recovers the strength. The responsible mechanisms for healing the cracks are the rearrangement of the grains through the transformation as well as the diffusion process. Takahashi et al.\textsuperscript{32} investigated the crack-healing ability of mullite/SiC multi-composite under stress. The results of their work showed that the composite has an excellent healing ability. The induced cracks healed under cyclic and static stresses at a temperature of 1473 k. The self-healing of C/SiC composites modified with Si-B-C was investigated by Zuo et al.\textsuperscript{33}

The self-healing of cracks was investigated to extend the lifetime of thermal barrier coatings through the oxidation and decomposition of MoSi$_2$(B) healing particles at high temperatures leading to the formation of amorphous silica which flows to seal the cracks and/or fill the gap between the crack faces. This is followed by the reaction of ZrO$_2$-based TBC, which leads to the formation of ZrSiO$_4$, and this reaction leads to strong bonding between the healing agent and the matrix material and hence filling/sealing/mending the cracks.\textsuperscript{34} The self-healing behavior of thermal barrier coatings fabricated by spark plasma sintering was investigated by Nozahic et al.\textsuperscript{35} The coating consists of yttria partially stabilized zirconia (YPSZ) with dispersed core-shell particles of MoSi$_2$-Al$_2$O$_3$ as a healing agent (self-healing TBC made of YPSZ and core-shell encapsulated MoSi$_2$(B)-based particles). The coating was applied on MCrAlY-coated Ni-based superalloys through SPS). The self-healing ability of carbon composites containing B$_4$C and SiC particles have been investigated by Kobayashi et al.\textsuperscript{36}

The self-healing ability of C/SiC composites modified with Si-B-C was investigated by Cao et al.\textsuperscript{37} at elevated temperatures and due to the thermal mismatch, the cracks can be healed. Li et al.\textsuperscript{38} investigated the crack-healing ability of Ti$_2$AlC ceramic at high temperature. Their investigation showed that the cracks could be healed completely at 1200°C for 2 hours in air and the Ti$_2$AlC shows significant crack-healing ability as the cracks can be completely healed and filled with the oxidation products and the flexural strength can be recovered or even slightly enhanced.

Parohit et al.\textsuperscript{39} made an investigation on manufacturing of the self-healing materials. In this paper, they searched the modern approaches to the self-crack healing. The crack-healing behavior in yttria stabilized zirconia thermal barrier coatings was investigated by Derelioglu et al.\textsuperscript{40} through embedding the encapsulated particles of MoSi$_2$(B) as a healing agent. They reported that the cracks healed through the oxidative decomposition of the embedded particles at high temperatures and the formation of silica, which flows to the gap between the crack faces and react with zirconia to form ZrSiO$_4$ to adhere the crack surfaces.

The mechanism behind the self-healing of the cracks can be attributed to the oxidation, diffusion, and grain growth during the sintering process. During the sintering process the particles diffuse through the grain boundaries and as a consequence bridge the crack planes. During the sintering process, the system can fill the induced cracks with the formed transition compounds (glassy phases) and heal it. The generation of the mobile glassy phase is a necessity for the self-healing process. The crack-healing behavior of mullite/SiC/Y$_2$O$_3$ composite was investigated by Lee et al.\textsuperscript{41} They showed that the cracks can be healed due to sintering at temperatures ranging between (1200-1400)°C in an air environment. Yoshioka et al.\textsuperscript{42} made an investigation of using the TiC particles as a healing agent to heal the induced cracks in Al$_2$O$_3$-based composites at high temperatures. In their study, they reported that TiC has potential ability to heal the cracks in ceramic systems extrinsically. The crack-healing behavior of SiC/Al$_2$O$_3$ composites was investigated by Ando et al.\textsuperscript{43} They showed that the cracks can be healed completely at healing conditions of 1300°C for 1 hour healing time in an air environment. As a result of the reaction between SiC and O$_2$, the oxide SiO$_2$ forms, which is responsible for healing the cracks. MoSi$_2$ was found to be a self-healing agent in TBCs by Sloof and Kochuby.\textsuperscript{44} When the crack is initiated, the healing agent reacts with O$_2$ to form the mobile phase which flows to fill the cracks. The self-healing behavior of structural ceramics was investigated by Ando et al.\textsuperscript{45} In their research they investigated the crack-healing conditions (temperature, time, and chemical composition), and their influence on the healing...
behavior. They also showed that it is important to induce the self-healing ability in ceramics to improve the reliability and induce the structural integrity and reduce the machining and maintenance cost.

Houjou et al.\(^5\) studied the self-healing behavior of Si\(_3\)N\(_4\)/SiC composites as a function of temperature, time, crack size and environment and the oxidation behavior as a function of the temperature and time. They reported that cracks could be healed completely in an air environment but not in N\(_2\), Ar nor in vacuum. The optimum temperature to heal the cracks completely ranged between (900-1400)\(^\circ\)C, the maximum size of the cracks to be healed completely was reported to be 200 \(\mu\)m in diameter. The crack-healing ability of Al\(_2\)O\(_3\)/Ti\(_2\)AlC was investigated by Pedimonte et al.\(^4\) The addition of the MAX phase served as a healing agent which reacts with the O\(_2\) present to form oxidation products which flow to fill the gap between the crack faces. The oxidation products were Ti\(_2\)AlC and Ti\(_2\)SnC. The crack-healing behavior of Al\(_2\)O\(_3\)/SiC composite was investigated under various conditions by Ono et al.\(^4\) The healing process was accomplished through the sintering of the composites. The heat treatment conditions to heal the cracks completely ranged from (1000\(^\circ\)C-1400\(^\circ\)C) in air. Various healing conditions were applied to heal the surface cracks of the machined specimens. The self-crack-healing performance of Ti\(_2\)AlC ceramics was investigated by Yang et al.\(^4\) Their results showed that cracks can be healed after heat treatment of 1200\(^\circ\)C in air for 10 minutes, the healing of the cracks was due to an oxidation process. The analysis of the self-healing effect of the crystalline admixtures in concrete was studied in 4 different environments. The results showed that the healing behavior differs depending on the exposure and the presence of the crystalline admixtures.\(^5\)

The crack-healing ability of Al\(_2\)O\(_3\)/SiC was investigated by Takahashi et al.\(^5\) Complete healing of the induced cracks was achieved at temperatures 1200\(^\circ\)C or 1300\(^\circ\)C for holding time of 1 hour. A partial healing of the cracks was observed. Lu X. et al reported in their article the oxidation process and the formation of the oxide (\(\alpha\)-Al\(_2\)O\(_3\)) as the main mechanism to heal the cracks.\(^5\) SiC is one of the most investigated self-healing agents when a crack occurs, SiC reacts with the oxygen in an air environment during the sintering process at high temperatures to form SiO\(_2\), which flows to fill initial cracks or cracks induced upon service.\(^5\) The crack-self-healing in ceramics has been investigated by many researchers on single oxide crystals, amorphous silicates, polycrystalline oxide and nonoxide materials. A number of studies can be found in the literature regarding self-healing behavior of engineering ceramics, such as Al\(_2\)O\(_3\)/SiC composite, Si\(_3\)N\(_4\) composite, ZrB\(_2\)/SiC ceramics and ternary carbides (eg, Ti\(_2\)AlC\(_2\), Zr\(_2\)Al\(_4\)C\(_5\),…etc). Many of these studies showed that the crack-healing ability of these materials was induced by surface oxidation. Oxidation products, such as SiO\(_2\), Al\(_2\)O\(_3\), and TiO\(_2\) can easily penetrate into the defects and flaws, which lead to the closure of cracks and healing. Systems like Si\(_3\)N\(_4\)/SiC, Mullite/SiC, and Al\(_2\)O\(_3\)/SiC have been investigated and showed significant self-healing abilities.\(^3,5,5\) The crack-healing behavior in Al\(_2\)O\(_3\) was investigated by Kim et al.\(^6\) Their results showed that cracks can be healed by sintering the samples above 1400\(^\circ\)C for 1 hour. The crack-healing behavior of Cr\(_2\)AlC ceramic as a function of temperature, time, and crack size was investigated by Li et al.\(^7\) In their study they showed that healing of the cracks was due to annealing of the specimens at temperatures above 1000\(^\circ\)C. The crack-healing behavior of UO\(_2\) has been investigated by Bain.\(^8\) The responsible mechanism for healing cracks is the grain growth due to the irradiation of UO\(_2\) at conditions of 1400\(^\circ\)C and 600 hours. Sung-Po Liu and Kotoji Ando\(^9\) showed that monolithic alumina can heal the cracks at a temperature of 1000 celsius or 1450 celsius for an hour healing time.

In his article, routes and mechanisms toward self-healing behavior in engineering materials, Van der Zwaag S., provided a glimpse on the self-healing behavior in materials.\(^5\)

Farle et al.\(^1\) studied the crack-healing behavior of Ti-containing materials and composites under combustion chamber conditions. The mechanism that is responsible for healing the cracks is oxidation induced sintering. The main ceramics that they used in their study were Al\(_2\)O\(_3\), Ti\(_2\)AlC, and Cr\(_2\)AlC. The results of their research showed that the MAX phase ceramics Ti\(_2\)AlC and Cr\(_2\)AlC have an intrinsic ability to heal the cracks. In alumina, the healing was achieved through the dispersion of the TiC particles. In Al\(_2\)O\(_3\)/TiC, the crack closure was achieved through filling of the cracks with the oxides, TiO\(_2\). In Ti\(_2\)AlC, the main oxides formed were TiO\(_2\) and Al\(_2\)O\(_3\). In the case of Cr\(_2\)AlC, the cracks were filled with Al\(_2\)O\(_3\).

In general, the healing process is triggered by a chemical oxidative reaction while specimens are being sintered/heat treated. The size of the particles plays a role in the self-healing process, the smaller the particle size, the more efficient the healing process, and the better mechanical properties. The size of the nanoparticles used should be similar.

Some studies have shown that the healing process or the rate of healing depends on the crack width; the healing rate or the degree is reduced as the cracks width is increased.\(^2\) Tao et al studied the crack-healing behavior of MoSi\(_2\)/borosilicate glass composite through comparing the flexure strength before and after the healing process of the prescratched samples. A partial recovery of the strength was reported for the samples healed at temperatures greater than 800\(^\circ\)C. A healing of the induced cracks was reported for the samples heat treated/healed at temperatures of 900\(^\circ\)C and 1400\(^\circ\)C. The main mechanisms to heal the scratches were reported as the oxidation of MoSi\(_2\) into MoO\(_3\) and SiO\(_2\) for the samples healed at 900\(^\circ\)C, whereas the viscous flow of borosilicate glass for the samples healed at a temperature of 1400\(^\circ\)C.\(^2\)
Zhang et al investigated the crack-healing behavior and strength recovery of ZrO₂(YS₂O₃)-Al₂O₃-MoS₂ ceramics in air at different conditions (heat treatment, time, and the content of the base material MoS₂ in the composite). The results of their investigation showed that cracks could be healed completely at 1100°C for 3 hours in air and the strength recovered. The oxidation products such as SiO₂ (glassy phase) were responsible for healing the cracks and recovering the strength (the glassy phase formed by the oxidation reaction is responsible for closing the cracks and rebindign the crack walls). Increasing the MoS₂ content increased the flexural strength; however, it was lower than that of the original samples. Takahashi et al studied the crack-healing behavior of Si₃N₄/SiC composites under cyclic stress of 210 MPa at temperatures: 900, 1000, 1100, and 1200°C in an air environment. The results showed that the samples healed at temperatures of 900°C and 1000°C. Brochu et al made a review on the self-healing biomaterials, in which, they introduce new approaches to the self-healing in biomaterials.

Recently, ternary carbides and nitrides such as Ti₃AlC, Zr₂AlC₅, and Cr₂AlC, also called MAX phase (where M denotes an early transition metal, A is a III A, or IV A group elements, and X is either C or N) have received much attention due to their unique combination of properties including low density, high modulus and strength, high electrical conductivity, good thermal conductivity, low coefficient of friction, good thermal stability and oxidation resistance, and have shown efficient crack-healing capability at 1100°C and 1200°C in air.

Li et al investigated the crack healing of Ti₃SnC ceramic in an air environment at low temperature and within a short period of time. At a temperature of 800°C, Ti₃SnC showed a capability of repairing the cracks induced by thermal shocks within just 1 hour. Their study showed a full recovery of the strength and conductivity; filling the cracks by the formation of the solid oxides, such as Al₂O₃, TiO₂ and Cr₂O₃ was identified as the main mechanism for healing surface cracks. Ando and Nakao applied the concept of self-healing ability to ensure the reliability of ceramic materials through the service life of a component. Nakao et al studied the self-healing ability of mullite/SiC whisker/SiC particles multi-composites. In their paper, they reported the oxidation process of SiC admixture as a healing mechanism. They reported that the cracks healed by only the SiC(W) was weaker than the matrix (base) unlike the cracks healed by the oxidation of SiC(W, P), which yielded a part superior in mechanical properties to the matrix at every tested temperature. Nam studied self-healing behavior to heal the large cracks in SiC ceramics as a function of the heat treatment, coating method and coating times.

Cracks were healed through the heat treatment at high temperatures of 1000°C or above which causes a chemical reaction that mends the induced flaws and cracks. Electrochemical anodization was used to heal the cracks induced in Al₂O₃/Ti composites, a full recovery of the strength to its original level was reported.

Self-crack healing of Al₂O₃/SiC nanoparticles was investigated by using a kinetic model. The crack healing was investigated at different conditions. A complete recovery of the strength was achieved at conditions of 1000°C-1550°C in partial oxygen pressure above active to passive pressure transition PO₂=1, their results made a contribution to design materials with self-healing capabilities for gas turbine applications. During the sintering process, the nanoparticles bond together to enhance the mechanical and physical properties of the final product. A percentage of shrinkage about 10%-20% and deformation occurs during the physical process. Jun et al studied the crack-healing behavior of Al₂O₃ matrix composites mainly TiC/Al₂O₃, SiC/Al₂O₃ and ZrO₂/Al₂O₃, which are used in many applications, such as heat engines, cutting tools. The prepared specimens of these composites were indented at different loads of 49, 98, and 196 N and were annealed for 1 hour at different temperatures of 1000, 1200, and 1400°C in an air environment and at 1200°C for 1 hour in vacuum. For this process, the main healing mechanism is a chemical reaction, and in the case of vacuum it is stress relaxation, which produces less strength recovery. However, the main mechanisms to heal the cracks in ZrO₂/Al₂O₃ composite were believed to be the existence of the eutectic phase and the rearrangement of the grains which is caused by the phase transformation of zirconia from monoclinic to triclinic, ZrO₂(m) → ZrO₂(t), when increasing the healing temperature.

Bontemaa et al studied the autonomous healing of the cracks of Al₂O₃ at high temperature through the use of SiC as a healing agent which forms silica, which serves as a healing agent to heal the cracks at high temperatures. In their study, they selected heating particles composites of transition metals and their carbides and nitrides to heal the damage and restore the strength. They reported oxidation as a healing mechanism through the filling of the cracks with the transition metal oxide. The oxidation process is accompanied with a volume expansion of 50% or higher. The selected oxides were TiO₂, ZrO₂, ZnO, HfO₂, N₂O₅ and Y₂O₃. Nakao et al studied the self-healing behavior of mullite/SiC whisker multi-composites and mullite/SiC whisker composites. They reported that a mullite/15% SiC whiskers 10 Vol% SiC particle multi-composite (MS15W10P) to be used as a material for springs, could heal the cracks at a temperature of 10 hours at heat treatment temperatures ranging from (1273-1473) K. They reported a superior healing ability of MS15W10P to that of MS25W. The healing ability of silicon carbide particles and whiskers multi-composite compared with whiskers only was attributed to the difference in the distribution and geometry of SiC. Kilicli et al studied
the self-healing behavior in metallic materials and their composites. In their study they reviewed, summarized and evaluated the healing mechanisms involved in the healing process. They reported the lack of studies on the self-healing in metallic materials/MMCs.\textsuperscript{79}

Zhang et al. studied the self-healing behavior of TZ3Y20A-SiC ceramics and ZrO\textsubscript{2}(Y\textsubscript{2}O\textsubscript{3})\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}-SiC ceramics as a function of temperature, time, crack size, and SiC content. They reported crack healing through the oxidation mechanism in which the SiC reacts with the oxygen in the atmosphere and forms SiO\textsubscript{2}. They reported optimum healing conditions of 0.54 \textmu m crack size, 10 hours healing time, 10 Vol\% SiC, and 1000°C healing temperature. They also reported a complete healing ability of the composite-at conditions of 10 Vol\% SiC at a heat treatment temperature of 1073 K for a holding time of 30 hours, 1273 K for 10 hours or 1373 K for 5 hours for a crack width of 0.45 \textmu m.\textsuperscript{80} Castanie et al. studied the self-healing of cracks in glass-boron composites. Their results showed that the healing occurs at 700°C by the oxidation process of boron in molten B\textsubscript{2}O\textsubscript{3}, which flows to fill the crack walls. They observed the healing behavior through using X-ray nanotomography. They reported that the healing process occurs through the chemical reaction between the boron oxide (B\textsubscript{2}O\textsubscript{3}) and the glass matrix as observed using coupled NMR, electron microscopy, and nano-XRF analysis which leads to the diffusion of barium and calcium and the formation of borosilicate phases, which heal the cracks. This behavior was observed using 2D and 3D observations, x-ray nanotomography, nano-x-ray fluorescence imaging, electron microprobe, and NMR.\textsuperscript{81} Barbero and Ford conducted research to characterize the self-healing of fiber-reinforced polymer matrix, laminated composites.\textsuperscript{82}

Illhan et al. studied the self-healing behavior of plasma sprayed spinel coatings through the incorporation of silicon carbide and yttria as healing agents. They reported that after 1 hour of the heat treatment, the silica reacted with Y\textsubscript{2}O\textsubscript{3} to form a crystalline phase Y\textsubscript{2}SiO\textsubscript{3} and vitreous phase Y\textsubscript{2}Si\textsubscript{2}O\textsubscript{7}. They reported that the results obtained from the experiments are the same as the results obtained from the microstructural simulations. The oxidation process was reported as a healing mechanism to heal the cracks in MgAl\textsubscript{2}O\textsubscript{4} coatings.\textsuperscript{83} Muhammad et al. performed an analysis and comparison of several methods and tests that were developed to evaluate the efficiency of healing in concrete. They reviewed, analyzed, and compared the different methods tests that are available.\textsuperscript{84} Nakao and Abe studied the self-healing behavior of Al\textsubscript{2}O\textsubscript{3}-SiC nanocomposite, they reported the enhancement of the self-healing through using SiC nanosized particles. They reported the oxidation process as the main mechanism to heal the damage through using nanosized particles could lower the temperature at which the oxidation reaction occurs. The size range at which they could attain complete recovery varied from (30-270) nm at a temperature range varied from 950°C through 1300°C; using particle size <10 nm is not beneficial for the recovery of the strength under any conditions due to the fact that the gap between the crack walls cannot be filled with the oxidation products as a result of the small volume of SiC on walls of the crack.\textsuperscript{85} Nam and Kim studied the self-healing behavior of SiC ceramics as a function of temperature and crack size. The cracks could be healed at optimum conditions of 1100°C for an hour in an air environment. The strength could be recovered after heat treatment of the specimens. They reported that a combination of SiC ceramics with SiO\textsubscript{2} as an additive had excellent healing ability.\textsuperscript{86}

Kunz and Klemm studied the crack-healing behavior of environmental barrier coating for nonoxide ceramic matrix composites and the healing mechanism. They reported an oxidation process as the healing mechanism, which was the transformation of the microstructure and the formation of SiO\textsubscript{2} and its reaction with ytterbium silicate.\textsuperscript{87} Yoshioka and Nakao studied the crack-healing behavior of Al\textsubscript{2}O\textsubscript{3}/TiC ceramic composite. The self-healing behavior was investigated as a function of the temperature and time. They reported strength recovery at a temperature of 800°C for a holding time of 1 hour. The cracks were filled with the formed TiO\textsubscript{2}.\textsuperscript{88} Song et al studied the crack-healing behavior in advanced machinable Ti\textsubscript{3}AlC\textsubscript{2} through oxidizing the cracked samples. The results of their study showed that the ceramic has an excellent ability to heal the cracks through the oxidation process at elevated temperatures, they reported a complete healing of the cracks time through the oxidation and the formation of the oxides after heat treatment at a temperature of 1100°C in an air environment for 2 hours.\textsuperscript{89} Burton et al proposed a constitutive model to simulate the crack-healing behavior of a shape memory alloy composite.\textsuperscript{90} Kong et al studied the self-crack-healing behavior and the mechanism behind it of SiBCN ceramics derived from hyperbranched polysiloxazine and the effect of temperature on the healing behavior. They reported that the high content of B and Si in the ceramic yield a higher compatibility of the healing process as a consequence of its tendency toward reacting with oxygen at elevated temperatures. The formed glassy phases and the formed oxides fill the cracks and heal it. They found that the healing process occurs at a temperature of 1000°C in an air environment. Increasing the content of the boron in the ceramic increases the healing efficiency in the ceramic in the presence of O\textsubscript{2} at high temperatures. The main oxides formed which heal the cracks are SiO\textsubscript{2}, B\textsubscript{2}O\textsubscript{3} and B\textsubscript{2}O\textsubscript{3}SiO\textsubscript{2}. These oxides fill the cracks and prevent further damage of the substrate.\textsuperscript{91} Nguyen et al studied the self-healing behavior of ytterbium disilicide. In their study, they reported that the composite (Yb\textsubscript{2}Si\textsubscript{2}O\textsubscript{7}–Yb\textsubscript{2}SiO\textsubscript{3}/SiC) has the ability to heal the cracks. The cracks could be healed owing to the reaction between the monosilicate and the silica which yields the formation of Si\textsubscript{2} (disilicide)\textsuperscript{92,93} Nakao et al studied the healing behavior of
surface cracks, in ceramics as well as the mechanical behavior. They stated that inducing the healing ability to heal these cracks can ensure the integrity of the structural ceramics.94 Keller and Crall described the methods of the self-healing in composite materials95 Boatemaaa et al studied the crack-healing behavior of Al2O3/Ti2AlC composite. They studied the addition of Ti2AlC particles as a healing agent to the Al2O3 ceramics. They reported that the induced cracks could be healed through the oxidation process and formation of oxides. TiO2 formed as a result of the decomposition of the matrix phase. Ti2Al formed after the annealing at temperatures ranging between (800-1000)°C at high temperatures in an air environment. The healing behavior was studied at temperatures ranging between (800-1000)°C for a holding time of 0.25, 1, 4 and 16 hours. The recovery of the strength was about 90% after annealing/heat treatment of 1000°C for a holding time of 15 minutes. A full recovery of the strength was attained after annealing at 1000°C for 1 hour. They reported the oxidation process as the healing mechanism.96

Greil studied the crack-healing behavior. In his paper, he reported that the oxidation process is the main mechanism to heal the cracks.97 Boatemaaa et al studied the healing behavior of the damage through using healing particles composed of transition metals and their carbides and nitrides in order to be used in high-temperature applications. They reported that the oxidation process and formation of the oxides followed by filling the crack gap with the formed oxides. The oxidation process is accompanied by 50% volume expansion. In their research, they demonstrated a procedure to select the healing agents to heal alumina at high temperature, the main mechanism to heal the cracks is the formation of oxides and filling of the crack faces with these formed oxides, these formed oxides are in charge of bonding the cracks.98 Pei et al studied the healing process/behavior of Cr2AlC MAX phase; they reported that the main mechanism to heal the cracks is surface oxidation at high temperatures; they reported the optimum conditions to completely heal the cracks as follows: Crack width of 4.8 and 10 μm respectively, heat treatment time of 4 and 12 hours/ for a time period/holding time of 4 and 12 hours respectively and healing temperature of 1200°C. In their research, they used time-lapse X-ray computed tomography (CT).99 Lee et al studied the crack-healing behavior of Al2O3 composites with different percentages of SiC (10 wt%, 15 wt and 20 wt%) and Y2O3 (3 wt%) through the sintering process in an air environment at temperatures 1473 K, 1573 K and 1673 K for 1 hour holding time.100 Li et al studied the crack-healing behavior of Al2O3-TiB2-TiSi2 ceramic composite fabricated through a vacuum hot pressing method. They reported the oxidation process at high temperatures and the formation of oxides, SiO2 and TiO2 as the main mechanism to heal the cracks. They reported a complete recovery of the strength for the samples heat treated and healed at 800°C for a holding time of 90 minutes with a percentage recovery of up to 107.25%. The recovery of the strength was reported for a crack length of 150 and 300 μm.101 Li et al studied the crack-healing behavior of Ti2SnC through the oxidation induced repair in an oxidative environment/through the mechanism of precipitation induced repair in vacuum.102 Hu et al studied the crack-healing behavior of Si3N4/SiCw. The oxidation reaction and the formation of the glassy phases was reported as the mechanism to heal the damage.103

In Si-containing ceramics, the main mechanism to heal the induced cracks/surface cracks were reported to be the oxidation and the formation of the silica-based oxides and products. The formation of a viscous, glassy phase is responsible for filling the gap between the crack faces. In ceramics and ceramic-based composites, a combination of the oxidation reaction and the viscous flow of the glassy phase or the healing agent were found to heal the induced damage or crack in an air environment. The key parameter that governs the healing process is the reduction in the surface free energy.

The surface cracks or the damage may be induced through the indentation via using micro or nano-indentation, Vickers indentation, thermal shock, machining, fatigue or the overuse of the component in service. The relaxation phenomena of the crack surface stimulated by the type of bonding in ceramics prevent the healing process of the nano-cracks. The main mechanisms to heal the induced damage is a combination of diffusion controlled sintering, viscous flow, redistillation of the glassy phase, and rebonding of the crack faces with the glassy phase. Another mechanism to heal the damage, the induced crack in multi-component and multi-phase ceramic materials is through the formation of the eutectic glassy phase and the rearrangement of the particles. Some research studies mentioned that the healing temperature for single crystals exceeds/in the range of 0.7-0.9 of the melting point and equal to the sintering temperature in the case of polycrystalline ceramics.

Upon the thermal activated oxidation on the crack interface/ in most cases, the healing process in ceramics takes place due to the thermal activation upon the sintering process followed by the oxidation process through which an oxidation process occurs leading to the formation of oxidation products/oxides which fill the crack gap and bond its faces. The healing process of the intentionally induced cracks on the surface or through machining and/or the thermal shock takes place through the sintering process/heat treatment in an oxidized environment. The healing process of the cracks and damage in ceramics is enhanced/induced through the sintering process via the thermal activation. The closure/sealing/healing of the crack gap occurs through the rearrangement of the atoms (healing agent/healing particles) and the viscous flow of the healing agent/glassy phase into the crack gap. The solid reaction in an oxidized environment is responsible for the crack gap. The healing temperature is as high as the sintering temperature for some ceramics such
as alumina for example with a healing time no longer than 10 hours. Ceramics such as SiC and MAX phase ceramics were found to heal the damage/cracks at lower temperatures (<1400°C), the healing temperature for SiC for instance is less than 870°C, and for Ti2SnC is <500°C. Boatemaa et al. studied the self-healing behavior of the surface cracks in Al2O3 containing 20 Vol.% of Ti2AlC MAX phase ceramic particles, the oxidation process and the formation of the oxides, TiO2 and Al2O3, was reported as the main mechanism to heal the surface cracks. They reported an efficient healing of the cracks between 800°C and 1000°C and filling of the cracks with the formed oxides, TiO2 and Al2O3. They reported a strength recovery of the composite at a temperature of 900°C for 1 hour and 1000°C for 15 minutes. At 800°C the healing process required a healing time of 16 hours.104 Boatemaa et al. studied the effect of TiC particle size on the kinetics of the oxidation process including its temperature; different sizes ranging from nanometer to micrometer were used in order to study the effect of the particle size on the oxidation process as a kinetic to heal the cracks. In their study, they used a model to determine/predict the healability of the particles used in their research.104 Shi et al. studied the crack-healing behavior in ceramic-based composites through utilizing the electrochemically assisted anodization process at room temperature in 1 mol/L H3PO4 electrolyte solution (galvanostatic). In this process, the composites were used as anodes and Pt as cathode, the distance between the cathode and anode is 15 mm. The obtained/formed oxides (TiO2) after the anodization process could heal the cracks and seal its faces.105 Takashi reported a complete rebonding of the cracks after heat treatment at a temperature of 600°C for a holding time of 10 minutes with high-temperature oxidation of the nonoxide interlayer healing agent as the main mechanism to heal the cracks106. Sitnikov et al. discussed in their paper the basic concepts and mechanisms of self-healing in different types of materials including ceramics; in their paper, they provided a brief summary of the physical and chemical aspects of self-healing in materials.107

The phenomena of self-crack healing was also investigated based on numerical simulations using finite element analysis108,109. Baranger et al. proposed a model to predict the behavior and lifetime of crack-healing behavior of ceramic composites; this model can be used to compare experimental and numerical results.110 Ozaki et al. developed a constitutive model to analyze the behavior of self-crack-healing ceramics.111 Stumpf et al. studied the crack-healing behavior of ZrO2 ceramic composites loaded with Nb2AlC (MAX phase) healing particles. They reported oxidation induced healing upon annealing at a temperature of 1200°C in an air environment with a healing time of (10-20) mins. In their article, they derived a semi-empirical oxidation cohesive zone healing model.112 Greil reviewed the kinetic and thermodynamic aspects that govern the healing process in ceramics through the solid state reaction, which facilitate the internal and surface cracks healing, or through vapor solid oxidation reaction, to heal the surface cracks and pores.113 Yoshitomo et al. used a framework of FEM to simulate the crack generation and crack propagation of self-healing fiber-reinforced ceramic (shFRC) with high-temperature oxidation as a main mechanism to heal the crack.114 Perrot et al. proposed a numerical model that depends on an image of the cross-section of the material or on virtual meshes to simulate the self-healing process; in their model, they featured the oxidation kinetics and the flow of the glassy liquid oxide.115 Doquet et al. used a finite element model to simulate the crack healing in a nuclear glass/inactive borosilicate glass; they reported the closure of the induced cracks through the annealing process in an ESEM at a temperature of 400°C.116

Fei Liu et al. reported a high-temperature healing capability of SiCBN through the oxidation process of the ceramic derived from hyperbranched polyborosilazanes at conditions of 1000°C in an air environment as a result of the high content of boron and silicon in the ceramic. Self-crack-healing behavior as demonstrated by Fei Liu et al. is shown in Figure 3 below.117

### 2.1 Thermodynamics of the Healing Reaction

In order to have a healing process of the induced cracks/to initiate the healing process in ceramics, an oxidation process has to occur. The oxidation reaction of the healing agent can be summarized as follows:

\[
\chi + M^{x+}O_{y/2} \leftrightarrow \chi^{x+}O_{y/2} + M
\]

Provided that the following condition is achieved/the free energy of the reaction is:

\[
\Delta_r G (T) = \Delta_r G_{(\chi O_{y/2})}^0 - \Delta_r G_{(MO_{x/2})}^0 > 0
\]

The healing agent/particles react with the oxygen on the crack surface/surface of the crack.

\[
2y\chi + O_2 \rightarrow \chi_{2y}O_2
\]

The exothermic reaction enthalpy can be expressed as follows:
Hence

The formation of a strong bond between the healing agent and the crack faces is favorable in this reaction/a strong bonding between the crack faces and the formed oxides is favored in this reaction.

The kinetic triplet, the activation energy $E_A$, the Arrhenius Constant, and the reaction model were used by researchers working on the self-healing to predict the healing parameters of the used healing agent.

The rate of transformation of any substance for nonisothermal experiments is represented by/can be given by:

$$
\frac{da}{dt} = \frac{da}{dt} \cdot \frac{dt}{dT}
$$

(1)

where $\alpha$ can be defined as the function converted at any time and is given by/can be described:

$$
a = m_t - m_0 / m_\infty - m_0
$$

(2)

$m_0$, $m_t$, $m_\infty$ are the masses at time 0, $t$ and $\infty$ respectively.

$$
\beta = \frac{dT}{dt} \text{ – the heating rate}
$$

$\Delta f \chi^0 = \Delta_f G^0_{(x_{0}/2)} - T \Delta_f S^0$

$$
\Delta_f G(T) > 0
$$

Hence

$$
\Delta_f G^0_{(1/2)} > \Delta_f G^0_{(MO_{0}/2)}
$$

The formation of a strong bond between the healing agent and the crack faces is favorable in this reaction/a strong bonding between the crack faces and the formed oxides is favored in this reaction.

The kinetic triplet, the activation energy $E_A$, the Arrhenius Constant, and the reaction model were used by researchers working on the self-healing to predict the healing parameters of the used healing agent.

The rate of transformation of any substance for nonisothermal experiments is represented by/can be given by:

$$
\frac{da}{dt} = Ae^{-E_A/RT}f(\alpha)
$$

(3)

From Equations 1 & 2 we have the nonisothermal conversion rate:

$$
\frac{dT}{dt} = A/\beta e^{-E_A/RT}f(\alpha)
$$

(4)

Integrating of Eq. 4 yields the nonisothermal transformation rate law:

$$
g(\alpha) = A/\beta \int_0^T e^{-E_A/RT} dT
$$

(5)

Rewriting Equation (3) and Equation (5) yield:

$$
\frac{da}{d\xi} = A f(\alpha)
$$

(6)

$$
g(\alpha) = A\xi
$$

(7)

The experimentally determined conversion rate can be given by:

$$
\frac{da}{d\xi} = \frac{da}{dt} e^{E_A/RT}
$$

(8)

$$
\frac{da}{d\xi} = \beta \frac{da}{dT} e^{E_A/RT}
$$

(9)
The Arrhenius constant can be determined from nonisothermal experimental data.

The reaction time required or generalized time can be determined from/given by:

\[ \xi = \frac{E_A}{\beta T} \cdot P_{(x)} \]  

\[ P_{(x)} = \int_{x}^{\infty} e^{-x/x^2} dx dT \]

where

\[ X = \frac{E_A}{RT} \]

From the nonisothermal transformation rate law, we have:

\[ g(a) = A/\beta \int_{0}^{T} \exp \left( \frac{E_A}{RT} \right) \]

Yield

\[ \int_{0}^{T} \exp \left( \frac{E_A}{RT} \right) dT = \frac{E_A}{R} \int_{x}^{\infty} e^{-x/x^2} dx \]

The equation that governs the activation energy is given by:

\[ \ln(\beta / T_p^2) + \left( \frac{E_A}{RT_p} \right) = C \]

where

\[ T_p \] The peak temperature, which represent the temperature at which the reaction rate occurs is at its maximum; \( R \) - Gas constant; \( C \) - Constant; \( E_A \) - Activation energy and can be obtained by plotting.

\[ \ln(\beta / T_p^2) \text{vs. } 1/T_p \]

Upon the sintering process chemical and physical reactions occur, which result in conversion process of the substances, the solid-state reaction can be described using analytical model, an example of such model is the master curve plot which uses/employ the generalized time (\( \xi \)), which is the time required to obtain a function converted at infinite temperature, describe the isothermal or nonisothermal reactions respectively:

\[ \xi = \int_{0}^{T} \exp \left( \frac{E_A}{RT} \right) dt \]

\[ \xi = 1/\beta \int_{0}^{T} \exp \left( \frac{E_A}{RT} \right) dT \]

\[ 2.2 \quad \text{Self-Healing Mechanism in Ceramics} \]

In ceramics, the self-healing of the damage is initiated/induced through the thermal activation followed by the sintering process, rearrangement of the particles/atoms, viscous flow of the glassy phase(s) and hence sealing of the cracks and/or the solid-state oxidation reaction.

The healing temperatures were recorded to be in the range of the sintering temperatures (>1400°C); some studies reported lower temperatures <1000°C, in the range of 870°C and below).

The healing reaction of the induced cracks was reported to occur through the annealing process in an oxidation environment at temperatures in the range of 1000°C-1200°C for ceramics like SiC, Al2O3, ZrO2, Si3N4, ZrB2, 3Al2O3·2SiO2 at low oxygen partial pressures and under constant or cyclic stresses.

The oxidation process is accompanied by volume expansion of an estimated percentage of greater than 50% with the lowest possible values of the thermal stresses. TiO2, ZrO2, Al2O3, SiO2, HfO2, Nb2O5, and Y2O3 are among the most promising/effective oxides to have an effective healing process.

After the sintering process, residual stresses are formed due to the mismatch of the thermal expansion/coefficients of the constituents components/the matrix and the healing agent/particles. The volume expansion upon the oxidation process is a prerequisite for the healing process and filling of the crack gap upon the oxidation process.

The oxidation reaction can be determined as:

\[ MX_n + (a + b) O_2 \rightarrow MO_{a/2} + nXO_{b/2} \]

where \( MX \): Carbide or nitride; \( MO_{a/2} \) & \( XO_{b/2} \) - The oxidation reaction products.

Examples of elements with high volume expansion of up to 100% are Nb, Ta, Cr, NbC, and SiC and these with volume expansion of <100% are Ti, Hf, Zr, TiC, TaC, Cr3C2, TiN, ZrN, TaN, Cr2N, and Si3N4. These are considered elements with positive volume expansion; however, these may not be able to heal the cracks/damage completely. The size of the healing particles and the crack dimensions are among the factors that have impact on the self-healing process.

The most important prerequisite to heal the damage is the strong bonding between the crack faces. Hence, the adhesion energy/bonding energy can be described using a macroscopic atomic model and can be defined as the work of adhesion/bonding/the work done to bond or adhere the surfaces.

\[ W_{Bonding} = - \left( \gamma_{\text{matrix}(Al_2O_3)} + \gamma_{\text{oxide}} \right) + \gamma_{\text{interface}} \]
where
\( \gamma_{\text{surface}}^{\text{matrix(Al}_2\text{O}_3)} \): The surface energy of Al\(_2\)O\(_3\).
\( \gamma_{\text{oxide}}^{\text{oxide}} \): The surface energy of the oxide and can be determined from the enthalpy of the surface of each of the constituents/elements which composes the interface weighted by the molar density of the system.
\( \gamma_{\text{interface}}^{\text{Al}_2\text{O}_3} \): The interface energy of Al\(_2\)O\(_3\) which can be determined or estimated from the energies of the interactions of the atoms on the sides of the interface, or from the enthalpy of the solutions.

All oxides have both high surface and bonding energies which enable them to well adhere/bond to the matrix. The residual stresses are generated due to the mismatch of the coefficients of thermal expansion of the constituent components/or the matrix/the main substance and the healing agent.

For MAX phase materials, the main approach to heal the cracks is the intrinsic self-crack healing, in which a decomposition reaction of the matrix occurs. In contrast to the approach used to heal the cracks/damage in alumina or other oxides, in which the material is at its lowest energetic state, wherein the most applicable approach to heal the cracks is the extrinsic self-crack healing. The healing process is accompanied by up to >100% volume expansion.

Most of the research on self-healing in ceramics focused on using SiC, TiC, Al\(_2\)O\(_3\), and MAX phase ceramics as healing agents to heal the damage and surface cracks, which decompose upon the heat treatment to their main oxides. Other ceramics with too low a melting point such as AlN/ceramics such as AlN are not considered as healing agents due to their too low volume expansion (<25%), which yields an insufficient healing process.

3 | SELF-HEALING IN CONCRETE AND CEMENTITIOUS MATERIALS

The self-healing behavior of smart construction material was investigated by employing tailored additives. The so-called crystalline admixtures were used where active chemicals react with water and cement particles in concrete to form calcium silicate hydrates. Self-healing of cementitious material has been investigated using numerical models.\(^{118}\) Beglarigale et al studied the self-healing behavior in cementitious materials through the microencapsulation of the healing agent. In their research, they used sodium silicate as a self-healing agent, which is encapsulated through the polymerization of the monomer on the aqueous sodium silicate droplets/microencapsulation of the sodium silicate with polyurethane shell. The optimum ratio of the sodium silicate and water was 50%.\(^{119}\) Yildirim et al reviewed the ability of the intrinsic healing in engineered cementitious composites. They reported the factors that affect/influence the healing efficiency and the effect of the healing behavior on the mechanical properties of cementitious composites.\(^{120}\)

Vijay et al reviewed the use of bacteria as a healing agent in concrete as well as the variation of the properties based on the addition of bacteria. In their study, they reported that using the bacteria as a healing agent increases the durability and strength of the concrete. They also mentioned that using encapsulation methods yield better results than the direct application method.\(^{121}\) The self-healing ability of hybrid engineered cementitious composites was studied by Nehdi.\(^{122}\) The rapid ability to heal the multiple damage autonomously of the superamphiphobic surfaces based on a smart two layers self-healing network was investigated by Zhang et al.\(^{123}\)

Davis and Jefferson proposed in their work a numerical/analytical model to simulate the self-healing behavior in cementitious materials.\(^{124}\)

Ferrara et al studied the self-healing ability of high performance fiber-reinforced cementitious composites upon exposure to different environmental conditions. They investigated the self-healing ability as a function of the composition, the maximum crack width and the environmental conditions.\(^{125}\) Qiu et al studied the effect of several factors (slag content, crack width, and environmental alkalinity) on the efficiency of the self-healing engineered cementitious composites, these fiber-reinforced strain hardening cementitious composites have the ability to heal the cracks.\(^{126}\) Huang et al studied the self-healing mechanisms in cementitious composites and analyzed the required environmental conditions for each healing mechanism. They reviewed the healing mechanisms in cementitious materials and the conditions of the healing agents, aspects, applications and perspectives in engineering practice.\(^{127}\)

Hilloul et al analyzed the healing ability and efficiency and the nature of healing products as well as the mechanical regains obtained as a consequence of the healing process in cementitious materials. They quantified the healing capability and kinetics of low water to cement ratio concrete. They found that concrete structures subjected to premature cracking can heal with mechanical regains while immersed into water. They investigated self-healing behavior in ultra-high performance concrete. In this study, a model was implemented in finite element code Cast3M to calculate the self-healing potential of a damaged concrete beam after cracking. The model predicted lower strength of the self-healing concrete in the healed region than the strength of the original concrete. They compared the results obtained from the numerical model with that obtained from experiments.\(^{128}\)

Hickman and Evans studied the crack-healing ability of CaCO\(_3\). They showed that the complete healing of the cracks was found to occur at 850°C with a healing time of 25 hours.\(^{62}\)

\[ H_{\text{Al}}^{\text{oxider}} \]
This section summarizes the design, manufacturing, and characterization of self-crack-healing ceramics as follows:

- Selection of particles/nanoparticles
- Preparation method of the samples/compaction and shaping process
- Setting the conditions/healing parameters
- Specific analysis to predict the healing/initiation of the healing reaction, thermogravimetric analysis etc
- Healing method/approach, oxidation, and diffusion upon heat treatment at moderate or high temperature, activator or healing particles at moderate to low temperatures, electromagnetic induction at room temperature etc
- Assessing the healing process through characterization. This could be done by SEM to qualitatively determine the degree of healing, see Figure 4. Quantitative assessment is done through material tests such as a three-point bending test. In these tests, the bending strength of the material before cracks were induced would be compared to bending strength after cracks were induced in the ceramic and to bending strength after self-crack healing occurred in the ceramic.

A review on the self-healing behavior, concept and processes, was done in this paper covering the research that has focused on the experiments and modeling of this behavior in ceramics and its composites.

Many researchers studied the self-healing behavior in ceramics. For this class of materials, self-healing occurs at a specific temperature. The healing process in ceramics occurs at temperatures greater than 800°C.

In order to have a complete and efficient healing process, some requirements have to be met, and these are as follows:

- The healing must be triggered by cracking.
- Healing occurs at high temperatures.
- The strength of the healed zone must be equal to or superior to the base material.
- In ceramics, the healing particles located at the crack walls react with the oxygen in an air environment to produce healing products/resulting in the healing action.
• The volume between the crack walls should be filled with the self-healing reaction products.

In ceramics, the extrinsic healing occurs through adding/ the inclusion of the healing particles in the ceramic matrix during the manufacturing process. An oxidation chemical reaction triggers the crack-healing particles/agent-interface healing reaction through the formation of the oxidation products. An efficient healing process can be described/characterized by the complete and homogenous filling of the cracks through the formation of oxides upon the solid-state oxidation reaction.

In ceramics, the most effective method to heal the damage at high temperatures is the inclusion of transition metals, nitrides, and carbides through the oxidation reaction and formation of transition metal oxides/oxides which lead to/causes sealing of the crack gap. The heat treatment triggers a chemical reaction to heal the cracks.

The main requirements that determine the healability of an oxide to fill the crack gap and heal it are:

• Melting point
• Thermal mismatch
• Adhesion/bonding to the matrix

The requirements of the healing agent are as follows:

• Melting point
• Thermal mismatch
• Volume expansion upon oxidation

There many potential applications for self-healing-ceramics including aerospace applications such as turbine blades, coatings for high-temperature components used in high performance engines such as piston crowns and interior surfaces of exhaust manifolds of high performance engines and components in satellites where repair is difficult. There have been many successful laboratory demonstrations of the effectiveness of self-healing-ceramics where samples are heated in furnaces to induce the healing. In some cases it may not be practical to disassemble components which are not operating at high temperatures and place them in a furnace for repair. In these cases, it may be possible to locally heat the damaged area without disassembly using electromagnetic induction or a high powered laser. Also, in other cases cracks may be too large to repair through self-healing alone. In such cases, additional healing particles could be added to the crack before heating as shown in Figure 5 to assist the healing process. Additional research should be carried out on localized heat sources and optimum use of additional self-healing particles to expand the applications and use of self-healing ceramics.

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How to cite this article: Hammood I, Barber G, Wang B. A review of some of experimental and numerical studies of self-crack-healing in ceramics. Int J Ceramic Eng Sci 2020;2:274–291. https://doi.org/10.1002/ces2.10071