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Journal of the European Ceramic Society 32 (2012) 1813–1820
www.elsevier.com/locate/jeurceramsoc

# Multiple crack healing of a $Ti_2AlC$ ceramic

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Received 23 November 2011; received in revised form 4 January 2012; accepted 16 January 2012
Available online 6 February 2012

**Abstract**

A highly attractive self-healing material would be one which combines excellent mechanical properties with a multiple healing capability. Self-healing ceramics have been studied for over 40 years to obtain some performance recovery and to prevent material failure during service, but so far only materials with the capability of single healing event per damage site have been realized. Here we report on a self-healing $Ti_2AlC$ ceramic capable of repeatedly repairing damage events. The $Ti_2AlC$ ceramic achieves at least seven healing cycles after repeated cracking at a given location. The main healing mechanism at high temperature is the filling of the cracks by the formation well adhering $\alpha$-$Al_2O_3$ and the presence of some rutile $TiO_2$. For healed samples, the flexural strength returned or even slightly exceeded the virginal strength. The fracture toughness recovery has been quantified for multiple healing cycles.


*Keywords:* Carbides; Crack healing; Electron microscopy; X-ray methods; Mechanical properties

## 1. Introduction

Advanced ceramics with extraordinary mechanical, thermal and electrical properties have been used in a wide range of applications. The main drawback of these ceramics is their brittle character that makes them sensitive to the presence of surface cracks, resulting in loss in performance or even a sudden catastrophic failure. Inspired by healing processes in nature, for some years material scientists have tried to develop self-healing engineering materials combining adequate mechanical properties and autonomous crack healing ability to restore their load bearing capacity.[1–3] The earliest crack healing study on a ceramic, viz. corundum could be traced back to the year 1966.[4] After that damage repair in some oxide ceramics such as ZnO, MgO, $UO_2$, $Al_2O_3$ has been investigated.[5–7] The main crack healing mechanism for these oxide ceramics is grain growth similar to the mechanism responsible for densification during sintering. Since then, another crack healing mechanism driven by oxidation has been developed for SiC, $Si_3N_4$ and ternary carbides as well as their composites.[8–14] This is potentially a very attractive concept because the additional atoms required to fill the crack are automatically supplied by the gaseous environment and the material itself had not to be 'weakened' to allow self healing. For such system, both the ceramic matrix and the gaseous environment act as "reservoirs" for providing the healing agent. It is reasonable to believe that multiple healing events in such ceramics should be possible. However, over 40 years, autonomous healing of ceramics has only been demonstrated for single or one-time-only healing event and the effect of such healing on the mechanical properties was not quantified either.

Recently, a novel ternary ceramic, viz. $Ti_2AlC$ has attracted much attention. $Ti_2AlC$ belongs to the so-called MAX-phase family, where M is an early transition metal, A is mostly a group IIIA or IVA element, and X is either C or N.[15] $Ti_2AlC$ has an unusual combination of attractive properties up to high temperatures, such as high strength, high oxidation resistance, ductility and nonsusceptibility to thermal shock. These properties make $Ti_2AlC$ attractive for high temperature applications in which the material is exposed to thermal cycles, mechanical loading and oxidative environments. Such conditions are encountered in installations for power generation or propulsion, raw material production, recycling, etc. Hence, autonomous crack healing is

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0955-2219/$ – see front matter 
doi:10.1016/j.jeurceramsoc.2012.01.017

highly desirable for $Ti_2AlC$ upon application in high temperature environment. $Ti_2AlC$ ceramic with multiple self-healing capability could significantly extend its service life and reliability. Our previous work[14] showed that $Ti_3AlC_2$ has self-healing ability to completely heal a crack with a length of 7 mm and a width of 5 μm after healing at 1100 °C in air for 2 h. The main healing mechanism for $Ti_3AlC_2$ is that the crack can be filled by the formation of α-$Al_2O_3$ and rutile-$TiO_2$ at high temperature. However, a larger percentage of $TiO_2$ present in the oxidation layer leads to spallation failure in $Ti_3AlC_2$ owing to the unmatched thermal expansion coefficients. This further implies that a larger fraction of $TiO_2$ formed within the crack gap weakens the adhesion between matrix and oxides, and correspondingly causes loss of the strength recovery. Hence, it is expected that a deposit of only α-$Al_2O_3$ in the crack may further improve the performance recovery owning to that the adhesion between α-$Al_2O_3$ and $Ti_2AlC$ substrate is strong.[16,17] It has been demonstrated that $Ti_2AlC$ has an excellent oxidation resistance due to the formation of a continuous protective α-$Al_2O_3$ scale,[18–20] and that it exhibits a superior spallation resistance because of the well-matched thermal expansion coefficients between α-$Al_2O_3$ layer and $Ti_2AlC$ substrate.[16] Previous work showed that narrow cracks or small pores in $Ti_2AlC$ can be filled by just $Al_2O_3$ after treatment at high temperature, indicating that $Ti_2AlC$ has a potential crack healing ability.[21] However, a quantification of the performance recovery of both $Ti_3AlC_2$ and $Ti_2AlC$ ceramics has not been demonstrated yet.

In the present study, we explored the autonomous mechanical property recovery after repeated cracking at a specific location for $Ti_2AlC$.

## 2. Experimental procedures

$Ti_2AlC$ samples were prepared by hot pressing a mixture of Ti, Al and graphite (C) with a molar ratio of Ti:Al:C = 2:1:1 at 1450 °C for 8 h with 30 MPa in an Ar atmosphere. The phase composition of the produced sample was identified by X-ray diffraction analysis with a Bruker AXS D5005 diffractometer (Germany) using monochromatic Co Kα radiation. The microstructure of the synthesized samples were observed by a scanning electron microscopy (SEM) using a JEOL JSM 6500F field emission gun scanning electron microscope (Tokyo, Japan) equipped with energy-dispersive spectroscopy (EDS) and optical microscopy (OM) using a Neophot 30 optical microscope (Carl Zeiss, Germany). Oxidation behavior of $Ti_2AlC$ was performed at 1200 °C for 0–8 h in air. The microstructure of oxide scale was characterized by SEM.

A three-point bending test was performed in a Deben Microtester (Woolpit, UK) using virginal, pre-damaged and healed samples of 4 mm wide, 3 mm thick and 36 mm long. The span size and crosshead speed were 30 mm and 0.5 mm/min, respectively. The virginal samples, beveled and polished to 0.25 μm using diamond paste, were used to determine the initial strength. Three indents were made at the center of the long virginal specimen using a Knoop diamond indenter to create crack damage. The indentation test was controlled in a Zwick/Z2.5 hardness tester (Ulm, Germany). The load is 10 kg and the constant contact time is 15 s. The impressed specimens were then subjected to a fatigue cycle test in the Deben Microtester to make further propagation of microcracks around the indents. Constant load amplitude test was conducted at a load ratio $R = P_{min}/P_{max} = 0.1$, where $P_{max}$ is the maximum load of 150 N and $P_{min}$ is the minimum load of 15 N. The number for the fatigue cycle is 30 times. The predamaged specimens were heat treated at 1200 °C for 2 h in air in an Lenton furnace (Hope Valley, UK) to heal the micro cracks. The predamaged specimens and the healed specimens were respectively used to determine the residual strength and recovered strength.

Single edge notched beam (SENB) samples were prepared with a width of 2 mm, a height of 4 mm and a length of 36 mm and a notch of about 0.2 mm width and 1.5 mm length cut in the center with a thin diamond blade. Through-thickness cracks were created by loading in 3-point bending rig (span 30 mm and crosshead speed of 0.05 mm/min). The fracture toughness ($K_{IC}$) was measured using the SENB method. The precracked specimens were healed at 1200 °C for 2 h in air in the Lenton furnace and then loaded in the next bend test. This process was repeated until the crack was no longer healed within 2 h at 1200 °C.

After each fracture and healing cycle, scale on the oxidized surface was slightly polished off using 4000# SiC paper to observe the healed crack. The introduced cracks before and after healing were observed by OM and SEM. The detailed micrograph of the healed damaged zone was analyzed using electron backscatter diffraction (EBSD). The phase composition in the healed crack was identified by EDS and electron probe micro analysis (EPMA) with a JEOL JXA 8900R microprobe (Tokyo, Japan).

## 3. Results

The synthesized samples have a typical microstructure consisting of larger rod-shaped grains as shown in Fig. 1(a). $Ti_2AlC$ as the main phase companied with small amount of $Ti_3AlC_2$ and $Ti_{1.25}Al_{2.75}$ was detected by XRD; see Fig. 1(b).

The oxidation rate of $Ti_2AlC$ increases rapidly when the temperature is increased to 1200 °C in a range of 1000–1400 °C.[19,20] At 1200 °C, just an $Al_2O_3$ scale is formed on $Ti_2AlC$. Fig. 2 further confirms the above observation. A typical SEM micrograph shows that a continuous and dense α-$Al_2O_3$ formed after oxidation at 1200 °C for 2 h; see Fig. 2(a). Few $TiO_2$ grains are visible more or less homogeneously distributed on the α-$Al_2O_3$ layer. This scale increases in thickness with prolonging oxidation time at 1200 °C. The increase of scale thickness as a function of time can be fitted to an exponential law. Given the rate of scale formation and crack width introduced (discussed below), a healing treatment of damaged $Ti_2AlC$ samples at 1200 °C for 2 h was chosen.

For a quantitative assessment of the strength recovery of damaged $Ti_2AlC$ for single damage and healing event, virginal, pre-damaged and healed samples were prepared and loaded in 3-point bending to determine the initial strength, the residual strength and the recovered strength, respectively. After indentation and cycle fatigue test, many microcracks were introduced around 3 Knoop indents in the pre-damaged samples

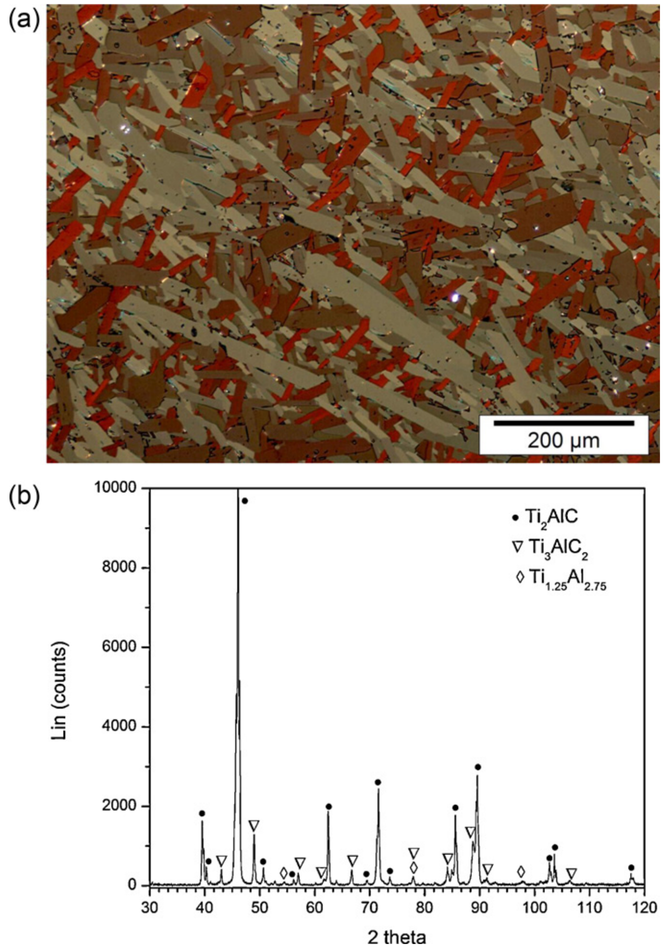


Fig. 1. (a) Optical micrograph of synthesized $Ti_2AlC$. (b) XRD pattern of $Ti_2AlC$. The identification of phases was according to the ICDD cards No. 04-001-6044 ($Ti_2AlC$), 00-052-0875 ($Ti_3AlC_2$), and 04-007-2383 ($Ti_{1.25}Al_{2.75}$), respectively.

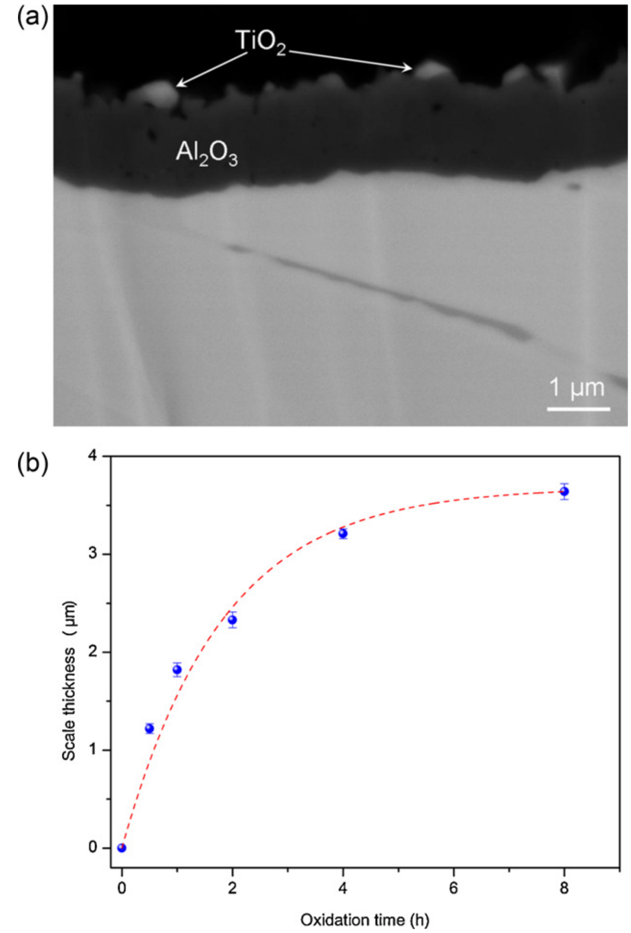


Fig. 2. Oxidation behavior of $Ti_2AlC$ at 1200 °C in air. (a) A dense and continuous $\alpha$-$Al_2O_3$ scale formed after oxidation at 1200 °C for 2 h. (b) Scale thickness versus oxidation time.

(Fig. 3(a)). After healing at 1200 °C for 2 h in air, the indents were completely filled by oxides, around which the microcracks disappeared completely (Fig. 3(b)). Cross-sectional image clearly shows that the damaged zone is filled by a mixture of oxides, $\alpha$-$Al_2O_3$ (black color) and rutile $TiO_2$ (deep gray color) (Fig. 3(c)). After bending test, the fracture propagation of the predamaged samples was through the dents, while the final fracture of the healed $Ti_2AlC$ samples did not coincide with the induced damage site but was always some distance away from it (Fig. 3(b)). The residual strength decreases from 211 MPa of the initial strength to 152 MPa. Damage of this type leads to a 30% drop in flexural strength (Fig. 3(d)). For the healed samples, the flexural strength returned or even slightly exceeded the initial strength; see Fig. 3(d).

In practical applications, it is likely that new cracks will develop at specific locations and that after the healing process; this would again be the location for the formation of a crack. Therefore, it is more interesting to study ability of the material to heal new cracks developed at positions where old cracks were healed in previous cycles. To this aim, a new set of single edge notched beam (SENB) samples was prepared. Through-thickness cracks with lengths of large than 1000 μm were created by loading in 3-point bending rig. Subsequently, the first crack was healed by oxidation at 1200 °C in air for 2 h and the crack was completely filled and gone as shown in Fig. 4(a). The second crack introduced by 3-point bending almost propagated and deflected near the previously healed crack in $Ti_2AlC$; see Fig. 4(a). After healing under the same condition as for the first treatment, the second crack was completely filled again, but the healed crack gap became wider; see Fig. 4(b). The same $Ti_2AlC$ sample was repeatedly re-cracked and healed in this manner. Up to the fourth fracture and healing cycle, the crack was still fully filled but became wider upon repeatable crack healing (Fig. 4(c)). So in later fracture cycles the newly introduced crack runs mainly through this wider healed-zone; see Fig. 4(c) and (d). After sixth cycle of healing, a part of crack in particular in the region close to the notch was no longer completely filled in the 2 h annealing treatment at 1200 °C in air. In the subsequent fracture and healing cycles, the unhealed part of the crack extended (Fig. 4(d)).

To determine the restoration of the fracture toughness for multiple cracking and healing, each of three $Ti_2AlC$ samples was repeatedly cracked and healed in the same manner as just described, and the three point bending loads for open cracks were monitored and the fracture toughness was determined

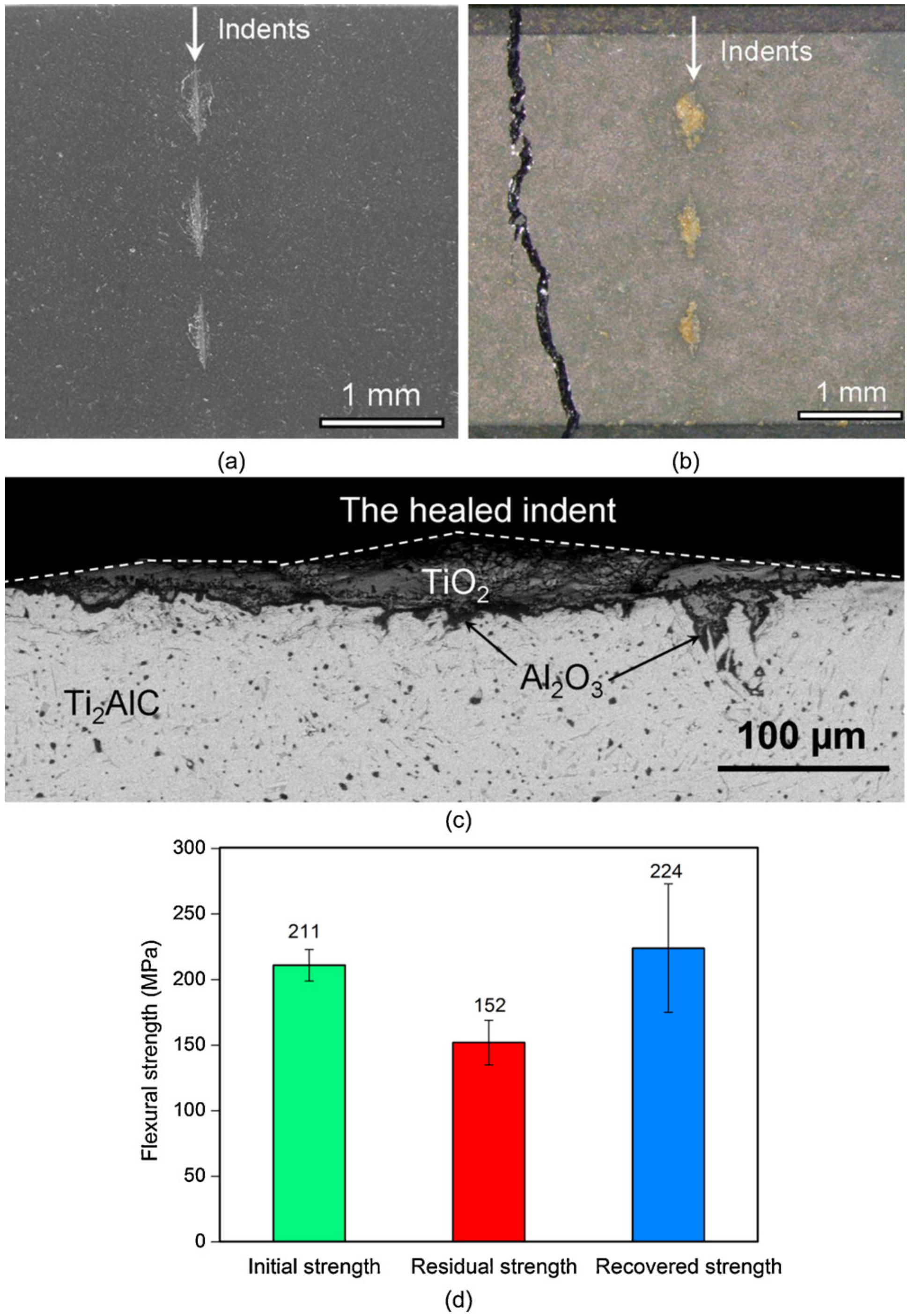


Fig. 3. Strength recovery of $Ti_2AlC$ specimens after crack healing at 1200 °C for 2 h in air. (a) Optical image of the 3 Knoop indents at the center of long sample to create crack damage. (b) Optical image of the healed sample after flexural strength testing. (c) Cross-sectional back-scattered scanning 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 5 measurements and the error bars represent the standard deviation.

quantitatively according to the equation given in Refs. 22 and 23. Fig. 5 describes the relationship between the fracture toughness recovery and healing cycle. The fracture toughness ($K_{IC}$) decreases from 6.4 MPa $m^{1/2}$ for the virginal material to about 3 MPa $m^{1/2}$ for the material after 7 healing cycles. This decrease in fracture toughness is associated with filling of the crack gap with $Al_2O_3$ and some $TiO_2$ and the presence of unfilled parts of the crack for cracks already healed several times; see Fig. 4(d). The drop in fracture toughness is the result of the lower fracture toughness of the reaction products ($K_{IC}$ ($Al_2O_3$) = 3–4 MPa $m^{1/2}$ [24,25], $K_{IC}$ ($TiO_2$) = 2–4 MPa $m^{1/2}$ [26] and $K_{IC}$ for $Al_2O_3/TiO_2$ composites is 4–5 MPa $m^{1/2}$)[27] as well as the lower microstructural perfection of the reaction products in the crack gap. Such a drop in toughness is comparable to the drop in toughness of

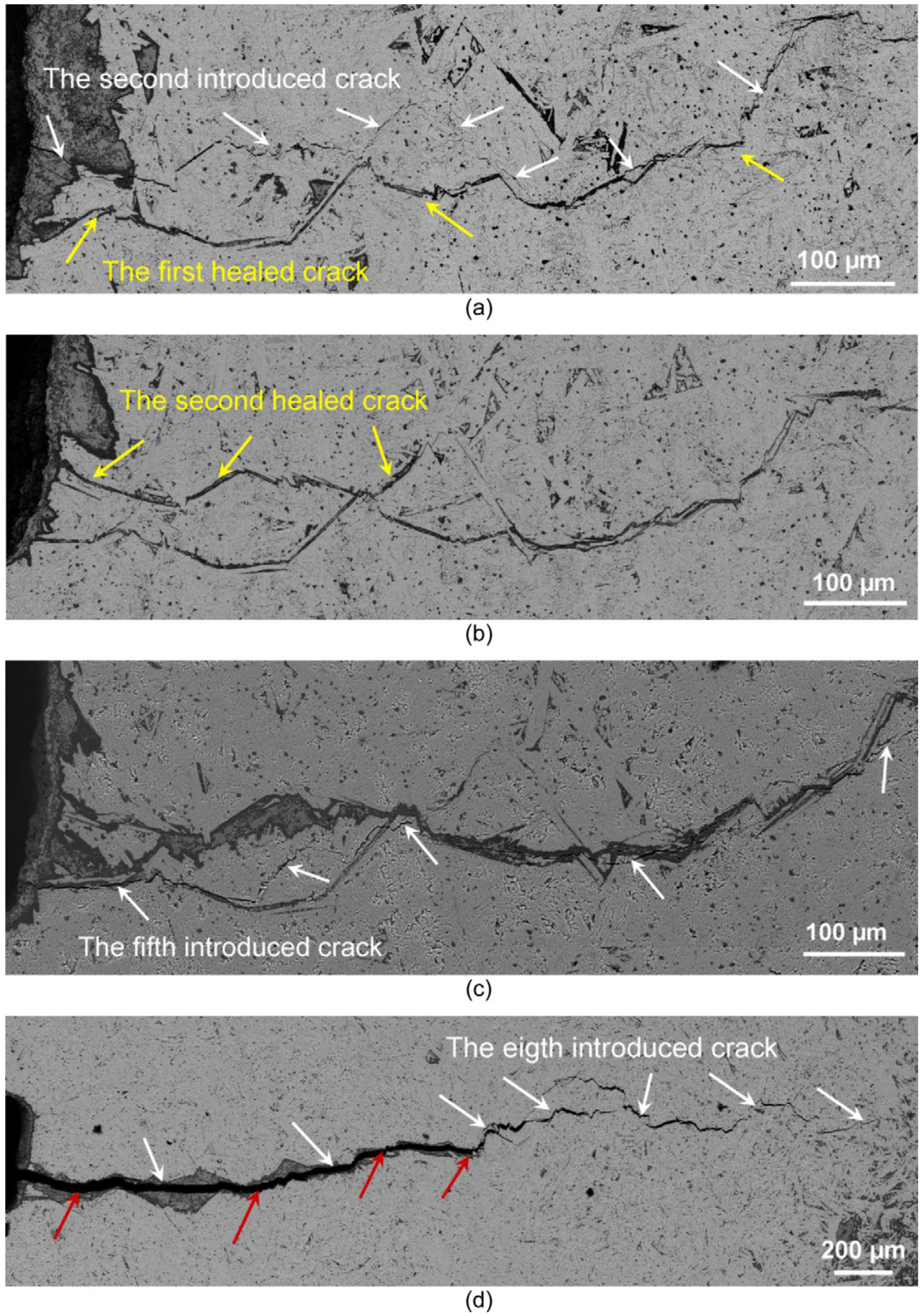


Fig. 4. Black-scattered scanning electron micrographs of fracture and crack healing of $Ti_2AlC$ samples. (a) Crack path after one cycle of healing and subsequent fracture. The yellow arrows indicate the crack completely filled, the white arrows indicate the new introduced crack. Note that the subsequent crack almost deflects around the healed zone of the first crack. (b) After two cycles of healing, the second crack was completely filled again. (c) Crack path after four cycles of healing, and subsequent fracture. (d) Crack path after seven cycles of healing, and subsequent fracture. The red arrows indicate the location of remnant crack parts. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

scar tissue with respect to the original tissue for humans and animals.

## 4. Discussions

From the recovery of the flexural strength, it can be concluded that the damage-healed zone itself has a good tensile strength. The strength recovery also implies that the adhesion between the oxides in the crack gap and the $Ti_2AlC$ matrix must be strong. It is beneficial that the thermal expansions of $\alpha$-$Al_2O_3$ ($8.8 \times 10^{-6}\,^{\circ}C^{-1}$ along *c*-axis direction, and $7.9 \times 10^{-6}\,^{\circ}C^{-1}$ normal to *c*-axis direction)[19] and of rutile $TiO_2$ ($7 \times 10^{-6}\,^{\circ}C^{-1}$ along *a*-axis direction, and $9.4 \times 10^{-6}\,^{\circ}C^{-1}$ along *c*-axis direction)[28] are only a little bit smaller than that

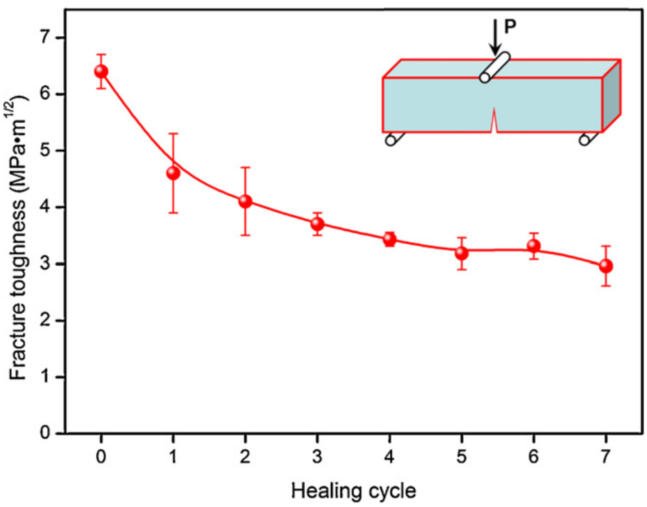


Fig. 5. Fracture toughness as a function of the number of fracture and healing cycles. The first value for the fracture toughness (i.e. for cycle number 0) pertains to the virginal material. Each data point is the average of 3 measurements. The error bars indicate the standard deviation.

of $Ti_2AlC$ ($9–9.6 \times 10^{-6}\,°C^{-1}$).[19,20] This implies that small compressive stress is generated in the oxides when the healed material is cooled down from the oxidation temperature. The recovered flexural strength increase is also due to the fact that small imperfections like pores in the materials were also filled with oxides by the healing treatment.

In this work we demonstrate for the first time that it is possible to heal a ceramic by thermal treatment for at least seven cycles. Further extension of the number of healing cycles may be possible through optimization of healing conditions. Obviously, the healing process in the unhealed section does not stop upon high temperature exposure but is retarded by oxides that cover the fracture surfaces. To bridge the crack gap in these unhealed sections, much longer healing times will be required. This is evidenced by the sample that was subjected to 7 cycles of fracture and healing but which was annealed for 100 h after the 8th fracture; see Fig. 6(a). The crack was filled with oxides both parallel and perpendicular to the direction that the crack propagated, even if the crack is several millimeters long. For wider crack sections the reaction product in the crack is a mixture of $\alpha$-$Al_2O_3$ and rutile $TiO_2$, the former covering the crack faces and the latter distributed in the center of the healed zone; see Fig. 6(b). However, in the thinner crack gap sections, only $\alpha$-$Al_2O_3$ was observed. This feature is identical to the previous observations on other wider cracks such as presented in Fig. 3(c). Fig. 6(c) further provides definitive evidence for the presence of $\alpha$-$Al_2O_3$ and small amount of rutile $TiO_2$ in the healed damage zone with relative thinner crack gaps. It is remarkable that the oxides grown from the two opposing fracture surfaces have merged into one oxide layer (Fig. 6(c)). Apparently, the mobility of the oxygen and aluminium atoms is sufficient to establish chemical bonding across the oxide/oxide interface at the center of the crack gap.

Previous research addressed the oxidation mechanism of $Ti_2AlC$.[19,21,29] Upon exposure of $Ti_2AlC$ to a high temperature in an oxidizing environment, the selective oxidation of Al into $Al_2O_3$ takes place since Al atoms easily diffuse from the cell structure of $Ti_2AlC$.[15] The Al atoms meet and react with O to form $Al_2O_3$. More and more $Al_2O_3$ forms on the two surfaces of crack. If the crack gap is narrow, quickly it is filled with $\alpha$-$Al_2O_3$ and this is the only reaction product (Fig. 6(a) and (b)). Also the decrease of oxygen partial pressure with oxidation in oxide/$Ti_2AlC$ interface favors the formation of $Al_2O_3$. However, the formation and growth of $\alpha$-$Al_2O_3$ results in the Al depletion of the $Ti_2AlC$ near the $Al_2O_3$ interface. The Al depletion, if severe, results in the damage in structural integrity of $Ti_2Al_xC$ ($x = 0.5–1$)[30] and leads to outward diffusion of Ti, which reacts with O to form $TiO_2$. Even a continuous and dense $Al_2O_3$ scale covers the crack surfaces, Ti and Al atoms can still diffuse through pores and along grain boundaries in the $Al_2O_3$ scale to the crack gap. Therefore, the outward diffusion of Al and Ti reacts with O to fill wide crack gaps results in the formation both $TiO_2$ and $\alpha$-$Al_2O_3$.

So far only self-healing polymers based on microvascular networks have shown the ability to multiple healing.[31,32] But the fabrication of such highly engineered multi-phase materials is complex and the healing process after multiple fractures will be restricted due to the depletion of healing agents. The present study is the first demonstration of multiple healing in a simple monolithic ceramic. Upon crack healing, both the $Ti_2AlC$ matrix and the gaseous environment can act as reservoirs to supply the element required to fill the crack autonomously and continuously. Hence, the easy fabrication and the repeatable crack healing ability make $Ti_2AlC$ a highly attractive material.

The implications of multiple healing of the type recorded for this MAX phase material on the life time of a final product is schematically shown in Fig. 7, in which also the behavior for single healing and ideal healing is indicated. A single self-healing material exhibits one healing action only. It repairs the damage almost completely and then fractures to failure if a new damage event occurs.[2] An ideal self-healing material is most attractive because it can heal damage many times and in such a manner that the healed material has comparable mechanical properties to the base material. For such a material there is no accumulation of damage to the level of catastrophic failure and the material has an infinite lifetime under applied damage and healing conditions.[2] For the multiple self-healing $Ti_2AlC$ material, the crack and the notch dimensions were chosen such that a damage level of 55% was obtained. After the first healing cycle, the damage level decreased to 32% (the notch dimension). During the next 4 cycles, the damage level is still constant. However, during the 6th cycle the crack is no longer fully filled (Fig. 4(d)), leading to an increase in the damage level after healing. Upon further damaging and healing the damage levels increase rapidly until complete failure takes place and healing is no longer possible within 2 h. Of course, the number of damage and healing cycles up to complete catastrophic failure depend on the initial damage levels imposed; lower initial damage levels will lead to a larger number of cycles. More perfect healing, i.e. the material in the crack gap having better properties, will also lead to a larger number of cycles. A fracture mechanical model describing the

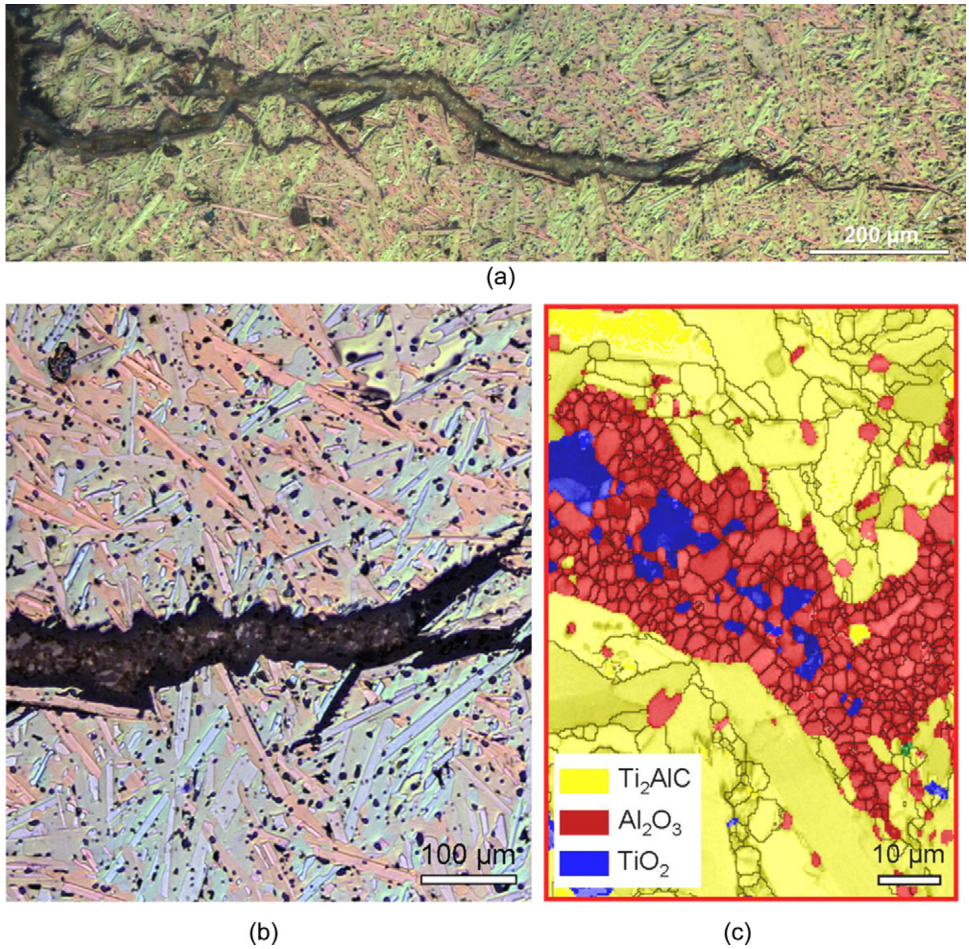


Fig. 6. Low- and high-magnification images showing the completely filled crack in the sample after 8th fracture and then annealing at 1200 °C for 100 h. (a) Optical overview image of the healed crack. (b) An enlarged optical image taken from (a). Two opposite fracture surfaces were covered by the same $Al_2O_3$ layer (black) and the gap between two surfaces was fully filled by a mixture of $Al_2O_3$ (black) and $TiO_2$ (large white particles). (c) Detailed micrograph of the healed-damage zone obtained with scanning electron microscopy using electron backscatter diffraction.

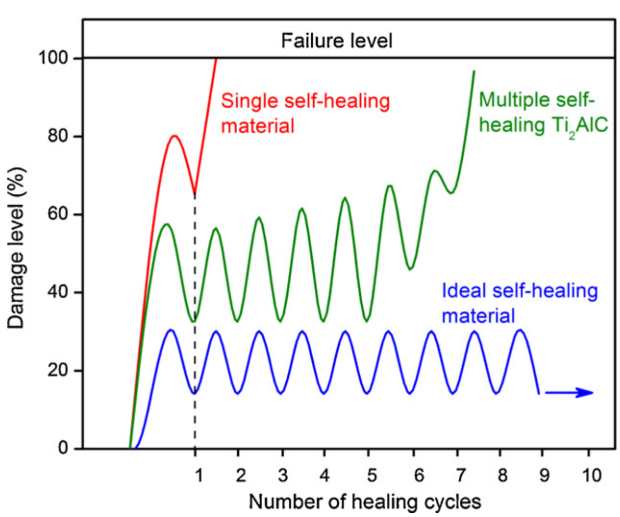


Fig. 7. Schematic diagram of the damage development in self-healing materials. In the curve for $Ti_2AlC$, wave peaks represent the damage levels (a ratio of the crack and the notch dimensions and the sample height), and wave troughs represent the initial damage level (the notch dimension and unhealed crack part after 5 healing cycles).

effect of damage and healing on the lifetime extension will be presented elsewhere.

The excellent properties of $Ti_2AlC$ together with its ability to repetitively healing of cracks demonstrated here are unique for rigid self-healing materials currently being developed. The underlying healing mechanism offers new opportunities for damage management in ceramics for critical high temperature applications.

## 5. Conclusions

A $Ti_2AlC$ ceramic consisting of larger rod-shaped grains and with small amount of $Ti_3AlC_2$ and $Ti_{1.25}Al_{2.75}$ impurities has been synthesized by hot pressing a mixture of Ti, Al and C at 1450 °C for 8 h with 30 MPa in an Ar atmosphere. The synthesized $Ti_2AlC$ ceramic shows a significant crack healing ability. The flexural strength returned from its residual damaged strength value of 152–224 MPa, which even slightly exceeded the initial strength of 211 MPa, after healing of indentation-induced cracks in the $Ti_2AlC$ samples at 1200 °C for 2 h in air. More attractively, the $Ti_2AlC$ ceramic was shown to be capable of repeatedly repairing damage events. It achieved at least seven healing cycles after repeated cracking at a given location. The fracture toughness ($K_{IC}$) recovery in a range of 3–6.7 MPa m$^{1/2}$ has been quantified during the repeatable healing cycles. The main healing mechanism is the filling of the crack by well adhering α-$Al_2O_3$ grains and the presence of some rutile $TiO_2$.

## Acknowledgements

This work was supported by the National Natural Science Foundation of China under Grant No. 51072017, "Hongguoyuan" Talent Foundation of Beijing Jiaotong University, the Delft Center of Materials Research Program on Self Healing Materials, and the Dutch IOP program on Self Healing Materials under Grant No. IOP-SHM 0871.

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