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Self-healing of indentation damage in Ti_2AlC MAX phase ceramics

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ABSTRACT

Although the crack-healing capacity of Ti_2AlC ceramics has been sufficiently studied, the ability of Ti_2AlC to self-heal large-scale damage, such as foreign object damage (FOD), remains unknown. This paper investigates the self-healing ability of Ti_2AlC ceramics with large-scale damage (~1000 μm in diameter). Extensive healing was observed even in the plastic damage and radial cracks. The damage and cracks caused by indentations made using a tungsten carbide sphere were filled and covered with newly formed oxides, such as titanium oxide and alumina, by the oxidation of Ti_2AlC after heat treatment in air at 1000 °C. The strength, hardness, toughness, and elastic modulus of the Ti_2AlC samples were measured before and after healing. The results show that the mechanical properties of Ti_2AlC were similar or even slightly higher after the damage had been healed. Thus, Ti_2AlC ceramics are attractive healing agents for foreign object damage in high-temperature applications.

1. Introduction

Ceramic materials have low reliability because of their brittleness and low impact resistance. Self-healing of damage during operation can provide a significant advantage by prolonging the lifetime of materials [1]. Previous research on self-healing of crack in materials involved the contact of the sample surface with a Vickers or Knoop indenter above the critical load of crack initiation [2,3]. However, foreign object damage (FOD) was found to be the main cause of failure of ceramic components owing to the mechanical contact [4,5]. Nevertheless, the healing capacity of materials with large-scale damage has not received sufficient research attention.

In a previous study, large-scale damage was introduced using a spherical tungsten carbide (WC) indenter [6], which caused significant damage to the surface of MAX (a ternary carbide or nitride expressed as $M_{n+1}AX_n$ phase) material [7,8]. Indentation damage with a diameter of 500 μm to > 1 mm (1000 μm) was produced.

Self-healing in engineering ceramics was primarily studied on the cracks using post-heat treatment techniques in an oxygen atmosphere [3,9]. Since the healing on the large diameter of imprints by FOD has not been reported, the present study investigates the oxidation-induced self-healing capacity of the Ti_2AlC MAX phase for larger indentation damages.

2. Experimental details

Titanium aluminum carbide (Ti_2AlC, 211 MAX phase) powder was first synthesized from titanium (Ti, 99 %, 5 μm, US Research Nanomaterials Inc., USA); titanium carbide (TiC, 99.99 %, 3 μm, Kojundo Chemical Laboratory Co., Japan); and aluminum powder (Al, 99.5 %, 3 μm, Kojundo Chemical, Japan). The detailed process was described in our previous study [9]. The synthesized Ti_2AlC powder was sintered at 1570 °C to make a coin sample with a diameter of 25.4 mm.

The densities of the Ti_2AlC sintered samples were measured using the Archimedes principle. The surface of the sample was polished with diamond paste. Hertzian indentation was performed in air on the top surface of the Ti_2AlC samples using a WC sphere of radius $r = 1.98$ mm (J&L Industrial Supply Co., MI, USA) at load $P = 3500$ N. Post-heat treatment was conducted at 1000 °C for 2 h in air to heal cracks and damage on the Ti_2AlC. The cracked, damaged, and healed areas were observed by optical microscope (OM, Olympus, Japan), scanning electron microscope (SEM, JSM-6701F, JEOL, Japan) and digital microscope (Zeiss, Smartzoom 5, Switzerland). The phases of the Ti_2AlC sample after healing were analyzed by X-ray diffraction (XRD, RINT-2500HF, Rigaku, Japan).

A four-point flexural strength test was conducted on bar-shaped samples, of dimensions 3 × 4 × 40 mm, where the undamaged or healed areas were positioned in the tensile region. Vickers indentation (HM-114, Mitutoyo, Japan) was performed to measure the hardness and

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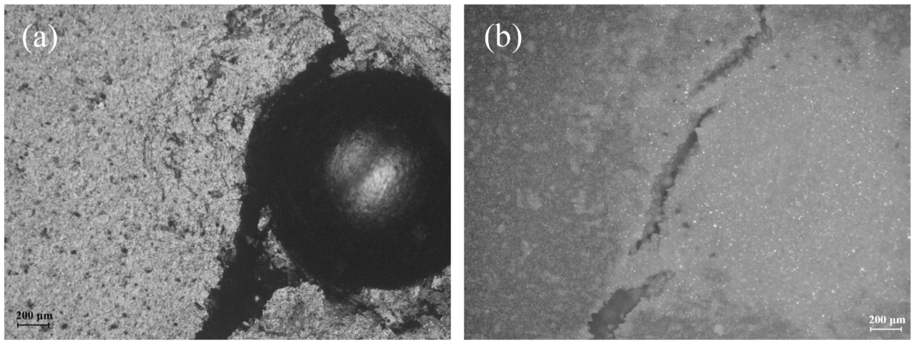

Fig. 1. Optical micrographs of Ti_2AlC indentation damage: The damage was indented using a WC ball with a radius of 1.98 mm at load $P = 3500$ N. The damage areas (a) before and (b) after healing in air at 1000 °C for 2 h.

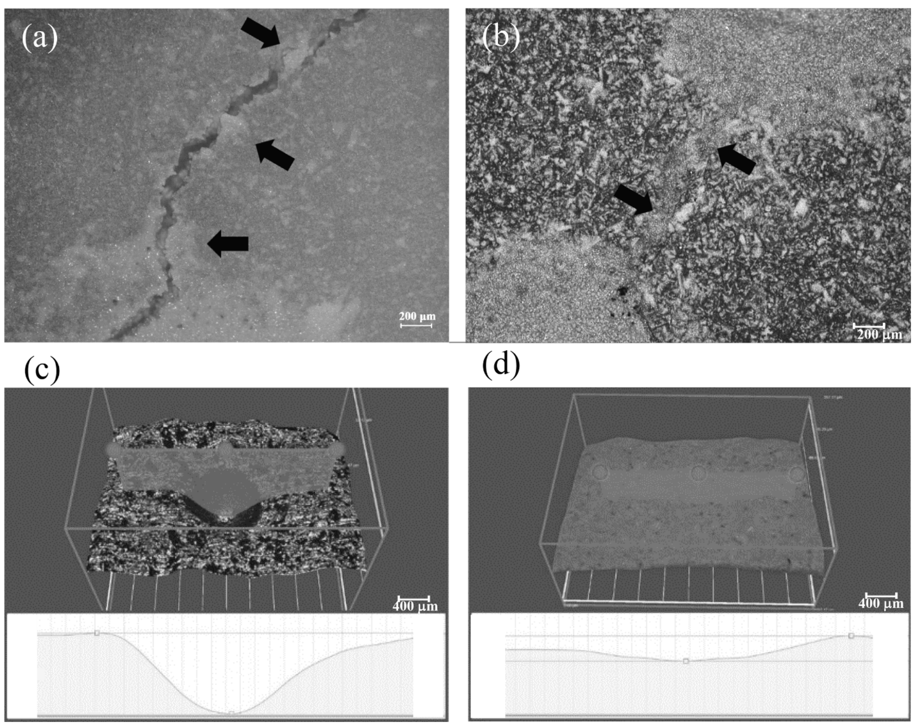

Fig. 2. Optical and digital micrographs of Ti_2AlC. Figure (a) shows optical micrographs of Ti_2AlC radial cracks after healing. Figure (b) shows digital micrographs of Ti_2AlC radial cracks and indentation damages after healing. Figures (c) and (d) show depth measurement profiles before and after healing, respectively. Damages were indented using a WC ball with a radius of $r = 1.98$ mm at load $P = 3500$ N. Healing was conducted in the air at 1000 °C for 2 h.

toughness, using a diamond indenter at a load $P = 9.8$ N on the polished samples. Furthermore, the relative hardness and elastic modulus were analyzed from the sphere indentation load–displacement curve before and after healing [9].

3. Results and discussion

Fig. 1 (a) shows an optical micrograph showing indentation damage on the surface of the Ti_2AlC ceramics using a WC sphere with a radius of $r = 1.98$ mm at load $P = 3500$ N. The damage was observed in the Nomarski illumination of the optical microscope [6,7]. The damage type was not typical of brittle ceramics, but rather an irreversible plastic damage zone as observed in tough ceramics [10]. Previous studies showed that the microstructure of the plastic zone consists of micro-cracks [6,7]. The diameter of the damage zone was > 1000 µm. In addition, a large radial crack developed from the indentation damage. Micrometer-sized wing cracks could coalesce to develop radial cracks if they are subjected to higher load or repeated stress [6,10]. Fig. 1(b) shows re-observation of the developed damage shown in Fig. 1(a) after the heat-treatment of Ti_2AlC at 1000 °C for 2 h in air. The micrograph indicate that the extensive indentation damage was filled and completely healed. Some of the radial cracks began to be filled by newly formed materials. As a result, Ti_2AlC ceramics could heal even a large plastic damage.

Fig. 2(a) shows the radial cracks using the same WC sphere at the same load, $P = 3500$ N. Figure shows the cracks after heat treatment in air at 1000 °C for 2 h. New material was formed (indicated by arrows in the figure) that began filling the cracks. Fig. 2(b) shows the digital micrograph indicating radial cracks that developed from each indentation damage and coalesced. The damage and radial cracks are observed to be completely healed, when the displacement of crack-opening is not as large as shown in Fig. 2(a), as shown in the micrograph observed using a digital microscope. Farle et. al. reported that Ti_2AlC could heal the crack gap by diffusion, volume expansion and adhesion [11].

The depths of indentation damages were measured during observation in the digital microscope before and after healing as shown in Fig. 2 (c) and 2(d), respectively. The maximum depth of damage diminished after healing, and the change is evident after healing from peak-to-valley

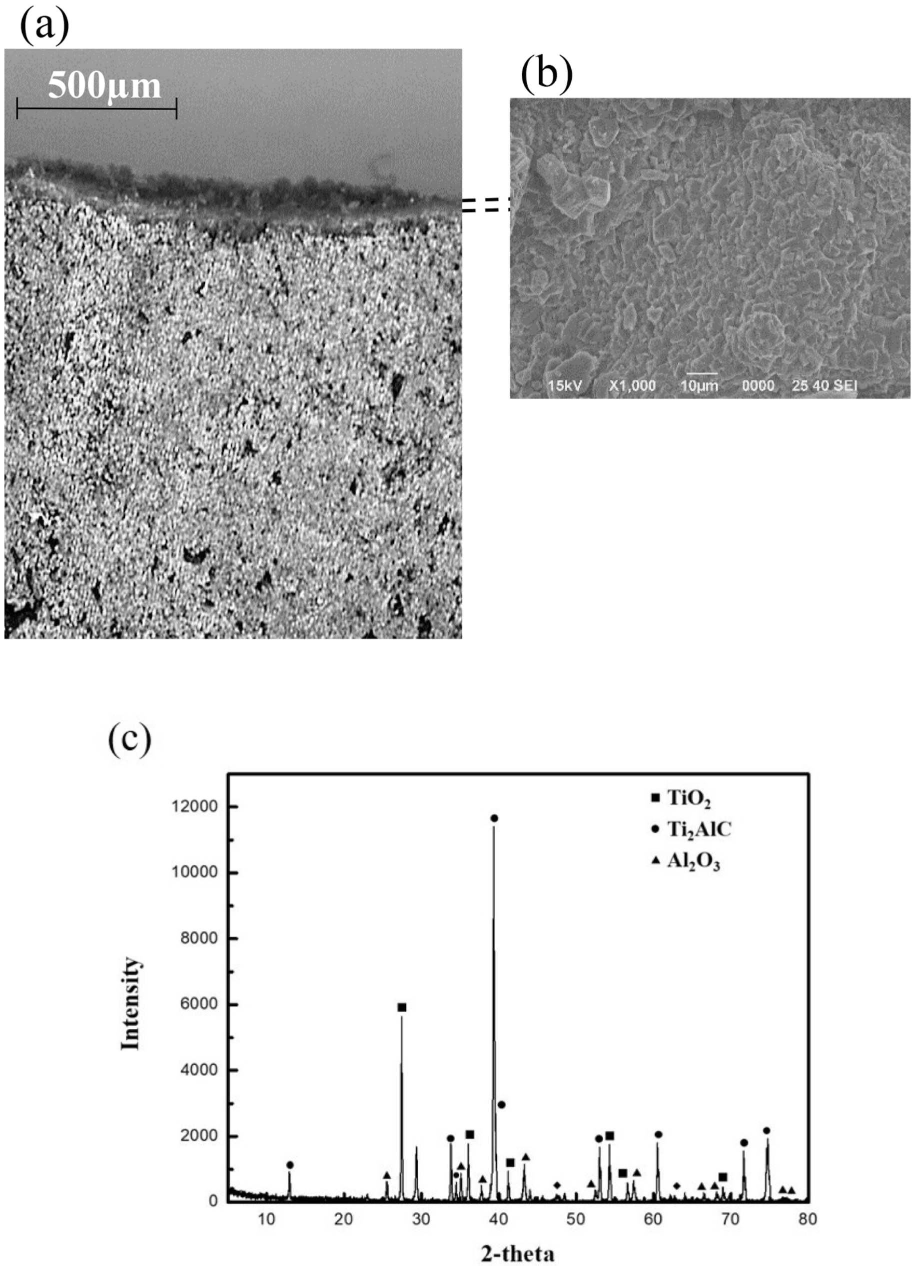

Fig. 3. (a) Optical micrographs of Ti_2AlC section views after damage healing. Newly formed oxide materials are observed in the subsurface; (b) the oxide material on the surface is clearly seen by SEM observation; (c) XRD peaks of Ti_2AlC after healing in the air at 1000 °C for 2 h.

to smooth surface profile.

Fig. 3 shows the analysis results of the phases to fill the developed indentation damage. Fig. 3 (a) shows an optical micrograph of the damage on the section view of the Ti_2AlC ceramic sample. A microscopy examination of the section (Fig. 3(a)) and surface (by SEM, Fig. 3(b)) of the crack-healed Ti_2AlC ceramic sample show that most irreversible damage had been filled and covered with new phases.

The XRD peaks of the Ti_2AlC ceramic sample after healing revealed titanium oxide (TiO_2) and alumina (Al_2O_3) on the Ti_2AlC sample surface. We confirmed the covered phase of the damaged zone by EDS, thereby resulting in only Ti, Al, C and O elements being detected. Therefore, the healing mechanism is the oxidation of Ti_2AlC in air.

Table 1
Basic characteristics of Ti2AlC before and after healing the indentation damage.

Material	**Relative Density**	**Strength** (MPa)		**Hardness** * (GPa)		**Toughness** * ($MPa \cdot m^{1/2}$)		**Relative hardness****		**Relative elastic modulus****	
		Before	**After**	**Before**	**After**	**Before**	**After**	**Before**	**After**	**Before**	**After**
Ti_2AlC	91.33 %	170.7 ± 16.7	169.1 ± 15.9***	3.03 ± 0.34	3.25 ± 0.35***	4.76 ± 0.66	5.61 ± 0.39***	100 %	122 %***	100 %	104 %***

*data from Vickers indentation, $P = 9.8$ N.
**data from spherical indentation, $P = 1,000$ N.
***after 1000 °C, 2hr, 1cycle.

Preferential oxidation is believed to occur at the damaged site because the site is not faceted but rounded, and titanium and aluminum can diffuse easily into the rounded surface during oxidation. Therefore, it is certain that the extensive damage healing of Ti_2AlC MAX-phase ceramics occurs by high-temperature oxidation.

Table 1 summarizes the relative density and mechanical properties, such as strength, hardness, toughness, relative hardness, and elastic modulus before and after crack healing. In general, the strength properties of ceramics are crucially affected by surface damage [6,11], on the other hand, the mechanical properties of Ti_2AlC ceramics are similar or better after healing, according to the results in the table. The increase of the properties after healing is associated with filling of the damage with Al_2O_3 [3]. Therefore, all these results indicate that the original mechanical properties can be recovered by the healing of extensive damage using MAX phases.

4. Conclusions

This study demonstrated that extensive self-healing of indentation damage and radial crack is possible in Ti_2AlC MAX phase ceramics. The damage is filled and covered with newly formed oxides via heat treatment in air. The recovery rates of the strength, hardness, toughness, and relative elastic modulus after healing were 99 %, 107 %, 118 %, and 104 %, respectively. These results suggest that at high temperatures, the Ti_2AlC MAX phase can heal even large damage of diameter > 1000 μm.

CRediT authorship contribution statement

Kee Sung Lee: Conceptualization, Methodology, Writing – original draft. **Hyeonji Ahn:** Visualization, Investigation. **Gye Won Lee:** Data curation. **Willem G. Sloof:** Conceptualization, Methodology, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors do not have permission to share data.

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