Available online at www.sciencedirect.com
ScienceDirect
Scripta Materialia 58 (2008) 13–16
Scripta MATERIALIA
www.elsevier.com/locate/scriptamat

Oxidation-induced crack healing in Ti_3AlC_2 ceramics

G.M. Song,[a,*] Y.T. Pei,[b] W.G. Sloof,[c] S.B. Li,[d] J.Th.M. De Hosson[b] and S. van der Zwaag[a]

[a] *Fundamentals of Advanced Materials, Faculty of Aerospace Engineering, Delft University of Technology, Kluyverweg 1, 2629 HS Delft, The Netherlands*
[b] *Department of Applied Physics, The Netherlands Institute for Metals Research, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands*
[c] *Department of Materials Science and Engineering, Delft University of Technology, Mekelweg 2, 2628 CD Delft, The Netherlands*
[d] *Materials Engineer Center, Beijing Jiaotong University, Beijing 100044, China*

Received 27 August 2007; accepted 4 September 2007
Available online 1 October 2007

Crack healing of Ti_3AlC_2 was investigated by oxidizing a partially pre-cracked sample. A crack near a notch was introduced into the sample by tensile deformation. After oxidation at 1100 °C in air for 2 h, the crack was completely healed, with oxidation products consisting primarily of α-Al_2O_3 as well as some rutile TiO_2. The indentation modulus and hardness of the crack-healed zone are slightly higher compared with those of the Ti_3AlC_2 base material. The preferential oxidation of Al atoms in Ti_3AlC_2 grains on the crack surface results in the predominance of α-Al_2O_3 particles forming in a crack less than 1 μm wide.

Keywords: Crack healing; Ti_3AlC_2; High-temperature oxidation; Preferential oxidation; Mechanical property

Crack healing in ceramic materials via surface oxidation or thermal diffusion has been well documented in the literature [1–8]. The oxidation mechanism [1–5] exhibits better healing efficiency than the diffusion mechanism because the volume expansion induced by crack surface oxidation can effectively fill the crack opening, whereas the diffusion mechanism relies on the mass flux from the base material to the crack zone [6–8]. In the past 20 years, investigation into crack-healing in engineering ceramics has mainly concentrated on SiC and Si_3N_4 and their composites because their microcracks can be effectively healed with high-temperature oxidation products such as SiO_2 [1–5]. The good crack-healing ability undoubtedly increases the reliability and competitive potential of these ceramics as high-temperature structural components.

The recently developed ternary carbide Ti_3AlC_2 has an excellent combination of properties of both ceramics and metals, and is a very promising material for high-temperature applications [9–15]. Given the potential application of Ti_3AlC_2 ceramics at high temperatures, it would be very attractive if damage to Ti_3AlC_2 ceramics could be healed autonomously during service at a high operating temperatures. Information about the crack-healing ability of Ti_3AlC_2 ceramics, which has not yet been reported in literature, will be the topic of this paper.

The present work concentrates on the crack-healing ability of Ti_3AlC_2 in a high-temperature oxidizing environment. A crack in a Ti_3AlC_2 sample was created by tensile loading. The cracked sample was then exposed to high temperatures in an oxidizing environment to heal the crack. The mechanical properties of healed crack zone were evaluated using nanoindentation.

The Ti_3AlC_2 bulk sample was prepared by an in situ solid–liquid reactive hot-pressing method. Ti, Al and graphite powders with the desired atomic ratio of 3:1.1:2 were mixed by ball-milling for 4 h in an ethanol solution. The slurry was dried at 60 °C and cold-pressed into blocks in a graphite die under 8 MPa, and then hot-pressed at 1425 °C under 20 MPa for 30 min in flowing argon gas. The final dimensions of these Ti_3AlC_2 blocks were $35 \times 25 \times 5$ mm^3.

In order to introduce a crack in Ti_3AlC_2 ceramics in a controllable manner, a Ti_3AlC_2 specimen $8 \times 2 \times 0.3$ mm^3 was glued onto a steel tensile bar, as sketched in

* Corresponding author. Tel.: +31 15 2781607; fax: +31 15 2784472; e-mail: g.song@tudelft.nl

1359-6462/$ - see front matter
doi:10.1016/j.scriptamat.2007.09.006

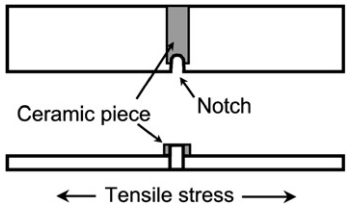

Figure 1. Sketch showing the methid used to make a single edge notch and microcrack in a Ti_3AlC_2 specimen bonded to a steel tensile bar.

Figure 1. A notch was made on one side of the ceramic piece and the steel bar with a saw. The depth of the notch in the Ti_3AlC_2 piece and the steel bar was 0.5 and 2.5 mm, respectively. Next, the tensile bar was mounted on a micro tensile stage (Deben Micro Tensile Device-5KN) installed in a scanning electron microscope (SEM, JEOL JSM 6500F). Tensile load was applied to the bar until a crack was initiated near the center of the notch in the Ti_3AlC_2 specimen, which was monitored with SEM observations. Thereafter, the sample was unloaded.

The cracked ceramic piece was removed from the steel bar by dissolving the glue in acetone for 24 h, and was thoroughly cleaned twice with isopropanol. The sample was heated at 1100 °C for 2 h in air.

The microstructures of the sample were studied via the JSM 6500F-SEM equipped with an energy dispersive spectrometer (EDS). The crystalline phases present in the sample before and after heat treatment were identified by X-ray diffractometry (XRD) using a Bruker AXS D5005. An MTS Nano Indenter XP equipped with a Berkovich indenter was used to measure the indentation modulus (E) and hardness (H) on the local healed zone. The averaged values of E and H were obtained over a range of indentation depth of 60–150 nm.

A crack with a length of ~7 mm in the Ti_3AlC_2 sample is shown in Figure 2a. Once the crack had been nucleated, it propagated rapidly perpendicular to the tensile loading direction. The average width of the crack is about 5 μm. Images at higher magnification (Fig. 2 inset) show that the crack propagates in a zigzag mode so as to follow the basal planes of the hexagonal Ti_3AlC_2 randomly oriented lamellar grains. This zigzag crack pattern in combination with local crack bridging is responsible for the high toughness of the ceramic material ($K_{IC} \sim 8$ MPa $m^{1/2}$).

The crack was invisible after oxidation treatment at 1100 °C for 2 h because an oxide layer covered the sample. After removing the oxide scale of the sample by mechanical polishing, it was found that the crack was fully healed, i.e. filled with oxidation products as shown in Figure 2b. Elemental Ti, Al and O maps of the healed crack zone show that high Al content bands adjacent to the Ti_3AlC_2 base material are always accompanied by high O content and low Ti content. EDS analysis reveals that the crack opening has been filled by two Al_2O_3 layers adjacent to the crack surfaces and a TiO_2 layer in between (see Fig. 3). An interesting observation is that when the crack opening is less than 1 μm, the filling materials consist mainly of Al_2O_3. For instance, the composition of the narrowest filled crack (point A, see Fig. 4) on the cross-section of a healed sample is 62 at.% O, 31 at.% Al and 7 at.% Ti. As the crack width increases, the TiO_2 content becomes higher. For instance, the composition at point A in Figure 3 is 51 at.% O, 20 at.% Al and 31 at.% Ti.

To explore the crack-healing mechanism, the oxidation behavior of Ti_3AlC_2 ceramic was investigated by a stepwise oxidation procedure of the fracture surface, as shown in Figure 5. First, a thin continuous oxide scale consisting of nanosized particles covered the fracture surface after oxidation for 180 s (Fig. 5a). The oxide scale then grew with nanosized faceted particles on top when the oxidation time was prolonged to 360 s (Fig. 5b). The faceted particles grew further and the oxide scale thickened with time. After oxidizing for 900 s, the mean size of the faceted particles increased

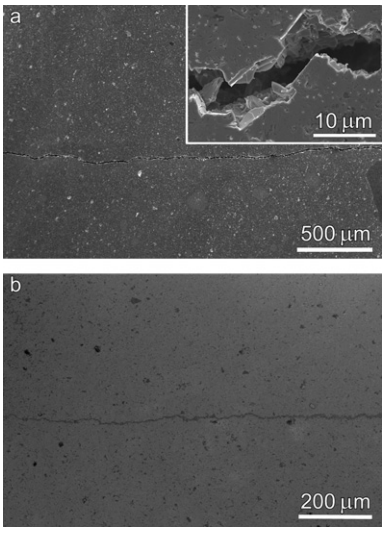

Figure 2. (a) A crack with a length of ~7 mm and an average width of 5 μm introduced into the Ti_3AlC_2 sample. The inset is a higher-magnification image of the crack. (b) A healed crack.

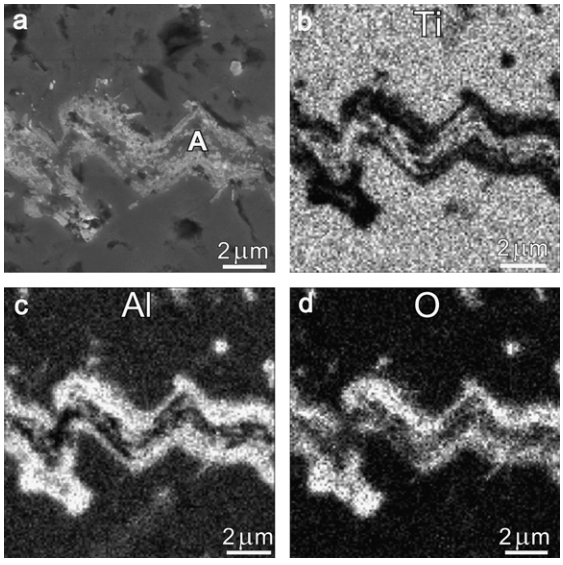

Figure 3. Cross-section of the healed Ti_3AlC_2 sample. (a) SEM image; (b) Ti map; (c) Al map; (d) O map.