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Multiple crack healing of a Ti_2AlC ceramic

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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 α-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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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