Strength of hot pressed ZrB$_2$–SiC composite after exposure to high temperatures (1000–1700 °C)

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Abstract

Residual strength (room temperature strength after exposure in air at high temperatures) of hot pressed ZrB$_2$–SiC composites was evaluated as function of SiC contents (10–30 vol%) as well as exposure temperatures for 5 h (1000–1700 °C). Multilayer oxide scale structures were found after exposures. The composition and thickness of these multilayered oxide scale structure was dependent on exposure temperature and SiC contents in composites. After exposure to 1000 °C for 5 h, the residual strength of ZrB$_2$–SiC composites improved by nearly 60% compared to the as-hot pressed composites with 20 and 30 vol% SiC. On the other hand, the residual strength of these composites remained unchanged after 1500 °C for 5 h. A drastic degradation in residual strength was observed in composites with 20 and 30 vol% SiC after exposure to 1700 °C for 5 h in ZrB$_2$–SiC. An attempt was made to correlate the microstructural changes and oxide scales with residual strength with respect to variation in SiC content and temperature of expsoure.
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Keywords: A. Hot pressing; D. Borides; Ultra High Temperature Ceramics; Oxidation; Flexural strength

1. Introduction

In the recent past, considerable work has been carried out in the field of ultra high temperatures ceramics, especially on ZrB$_2$ based ceramics and composites, due to interest in technologies associated with hypersonic flight, atmospheric re-entry, and rocket propulsion. Materials in such applications must possess high melting temperature (∼3500 °C) along with high electrical and thermal conductivities, good oxidation and chemical attack resistance.[1–3] The high temperature oxidation resistance of pure ZrB$_2$ is not sufficient for the aggressive environments associated with the above applications. Addition of SiC as reinforcement in ZrB$_2$ is known to improve the oxidation resistance by enabling the formation of protective borosilicate glass layer[4–5] which offers a higher viscosity, higher boiling point and lower vapor pressure than B$_2$O$_3$, thereby providing more efficient oxidation protection.[6] It was found that the oxide scale of ZrB$_2$–SiC composites generally had a layered structure. Based on detail work by Zhang et al.,[7] the structural changes in the oxide scale revealed:

(i) In the temperature range from 700 °C to 1200 °C, the oxide structure consists of a B$_2$O$_3$-rich outer layer, a subscale of ZrO$_2$ that contained unoxidized SiC, and unaffected ZrB$_2$–SiC in the substrate.

(ii) In the temperature range 1200–1600 °C, the outer layer changed to a SiO$_2$-rich glassy oxide followed by a subscale of ZrO$_2$ that contained some SiO$_2$ and, finally, unaffected ZrB$_2$–SiC.

(iii) At temperatures above 1600 °C, an additional SiC-depleted layer forms before one reaches the unaffected ZrB$_2$–SiC. The SiC-depleted layer develops due to the change of oxidation kinetics of SiC from passive to active.[8]

For re-usable applications, it is essential to know the effect of these oxide layer structures on residual strength of the ZrB$_2$–SiC composites at room temperature after exposure to high temperatures. Few reports are available on residual strength of ZrB$_2$–SiC composite after thermal exposure at high temperatures.[9–11] Guo

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and Zhang[9] have shown that the flexural strength of ZrB_2 with 10 and 30 vol% SiC increased sharply after exposure at 1500 °C for 30 min and then gradually decreased for longer times. Recently, it was shown that the oxide scale structure has a great influence on the improvement of strength of ZrB_2–SiC–graphite composite after exposure to 1100 °C.[12] Previous work by authors shows the effect of B_4C content on residual strength of hot pressed ZrB_2 after exposure to high temperatures.[13] It was found that the residual strength of hot pressed ZrB_2 with 0.5 and 1 wt% of B_4C dramatically increased after exposure to 1000 °C for 5 h. In contrast, larger volume fractions of B_4C (3 and 5%) did not lead to any improvement.

Previous studies on residual strength of ZrB_2–SiC composites have been limited to specific exposure temperature.[9–12] But there is a need to measure residual strength after exposure to a range of temperatures since the oxide layer structure changes with temperatures. The present work seeks to address this gap by measuring the dependence of residual bend strength on thermal exposure under oxidizing conditions at different temperatures and times.

2. Experimental details

Commercially available ZrB_2 powders ($d_{50} \sim 1.5$–$3\,\mu m$), supplied by H.C. Strack, Germany, SiC powders ($d_{50} \sim 1.5\,\mu m$), supplied by H. C. Strack, Germany and B_4C powders ($d_{50} \sim 7\,\mu m$), supplied by Electro Abrasive Corporation, USA were used as raw materials. ZrB_2–SiC composites with 10, 20 and 30 vol% SiC were prepared. All these composites had small amount of B_4C (1 wt% of ZrB_2 contents) as additive. Powders were mixed for 24 h in a polythene bottle with alumina balls and then hot-pressed in graphite dies at 2000 °C with a heating rate of 15 °C/min under a uni-axial pressure of 25 MPa for 1 h. Hot pressed composites were named as Z10S, Z20S and Z30S for 10, 20 and 30 vol% of SiC. The bulk density was measured using the Archimedes displacement method with water as the immersing medium and the relative density was calculated with respect to theoretical density. The theoretical density was estimated using rule-of-mixtures calculations based on the initial composition of the samples. The polished surface of the hot pressed sample was revealed by SEM without etching. Flexural strength was measured by the three-point bending method with a span of 40 mm and a cross-head speed of 0.5 mm min^{-1} using an Instron 5500R universal testing machine. The size of the samples was $3 \times 4 \times 50$ mm. Bend test samples were prepared from diamond ground, hot pressed discs by EDM wire cutting. For residual strength measurement at room temperature, the bend test specimens of hot pressed ZrB_2–SiC composite were exposed to 1000 °C, 1500 °C and 1700 °C in an air furnace. Specimens were supported on Al_2O_3 fixtures for 1000 °C and 1500 °C and ZrO_2 fixture for 1700 °C. Specimens were heated to the designated temperature at a heating rate of 10 °C/min. Specimens were held for 5 h at the designated temperature and furnace cooled to room temperature. Residual strength of exposed specimens was measured at room temperature as described previously. X-ray diffraction of the oxide layer was performed using a Philips

X-ray diffractometer with copper radiation as the X-ray source. The relative composition of monoclinic ZrO_2 and tetragonal ZrO_2 was calculated from XRD pattern using the polymorph method[14] which uses the (1 0 1) peak of tetragonal (t) ZrO_2 and (−1 1 1) and (1 1 1) peaks of monoclinic (m) ZrO_2 as shown below:

$$V_{t-ZrO_2} = 1 - \frac{1.311(1 - X_{t-ZrO_2})}{1 + 0.311(1 - X_{t-ZrO_2})}$$

$$X_{t-ZrO_2} = \frac{I_{(1\,0\,1)}(t)}{I_{(1\,0\,1)}(t) + I_{(\bar{1}\,1\,1)}(m) + I_{(1\,1\,1)}(m)}$$

where X_m is the intensity ratio and I(t) and I(m) are the peak intensities of tetragonal (t) and monoclinic (m) ZrO_2, respectively and V is the volume fraction.

The weight of specimens before and after exposure was measured for calculation of weight change due to oxidation. The oxide layer thickness was measured from fracture cross-sections. Fracture surfaces of the specimens were examined by scanning electron microscopy. Micro-hardness was measured by Vickers indentation tests using a load of 500 g and a dwell time of 10 s. The indentation fracture toughness was measured from direct crack measurement from following equation[15]:

$$K_C = 0.016 \left(\frac{E}{H}\right)^{1/2} \left(\frac{P}{c}\right)^{3/2}$$

where E is the elastic modulus, H is the hardness, P is the load and c is the crack length from the center of indent. Average micro-hardness and indentation fracture toughness was calculated from five indents. Elastic modulus was measured by pulse–echo technique, using following relation:

$$E = \rho V_L^2 \left\{ \frac{(1 - 2\nu)(1 + \nu)}{(1 - \nu)} \right\}$$

where ρ is density of the sample, V_L is longitudinal velocity of ultrasonic waves and ν is the Poisson ratio. The Poisson ratio was assumed to be 0.16 of ZrB_2–SiC composites.[1] Longitudinal ultrasonic velocity was measured using a 10 MHz transducer.

3. Results

3.1. As hot pressed composite

Fig. 1 shows the microstructure of hot pressed ZrB_2–SiC composites. The light phase is ZrB_2 whereas the dark phase consists of SiC. Near-theoretical density of composite was achieved by hot pressing for ZrB_2–SiC composites with different content of SiC (Table 1). The average grain size of ZrB_2 decreased with increase of SiC contents. The average grain size of ZrB_2 in Z10S samples was found to be $4.3 \pm 1.4\,\mu m$. It decreased marginally to $3.9 \pm 0.9\,\mu m$ in Z30S samples suggesting a small role of SiC in restricting the coarsening of ZrB_2. The average micro-hardness and fracture toughness of ZrB_2–SiC composites increased with SiC content. The average micro-hardness of Z10S was found to be 18.0 ± 0.9 GPa and increased to 24.4 ± 0.6 GPa for Z30S, reflecting the higher hardness of SiC (27 GPa) compared to ZrB_2 (15–18 GPa). The flexural strength of as hot