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Strengthening of porous TiB_2–SiC ceramics by pre-oxidation and crack-healing

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ABSTRACT

Low porosity TiB_2–SiC ceramics were prepared by Cold Isostatic Pressing–Pressureless Sintering (CIP–PS). The crack-healing behavior of these ceramics was investigated by pre-oxidizing the samples at 800–1200 °C in air for various durations ranging from 5 to 240 min. The effects of pre-oxidation temperature and time on the microstructure and mechanical properties of porous TiB_2–SiC ceramics were studied. The strength of porous ceramics obviously improved after pre-oxidation, with a maximum increase in strength of 134.4% for samples pre-oxidized at 1200 °C for 120 min. The strengthening mechanism of porous TiB_2–SiC ceramics after pre-oxidation was also investigated and discussed. This study provides a novel concept for improving the strength and structural integrity of porous ceramics in practical applications.

1. Introduction

TiB_2–SiC ceramics are materials of particular interest, because they have a unique set of properties. These include high melting point, high strength and hardness, thermal conductivity, electrical conductivity, good chemical stability, and superb wear resistance, all of which makes them promising candidates for high-temperature structural applications [1–4]. Porous ceramic materials with tailored microstructures have potential application as structural components because of their unique properties such as light weight and good thermal shock resistance. However, high porosity decreases ceramic resistance to moisture and mechanical erosion [5]. The fabrication of porous ceramics with a dense surface is necessary to overcome this.

Pre-oxidation has been known to increase mechanical properties, hot corrosion resistance, and thermal shock behavior by forming a dense surface, which can cause or heal surface flaws. Moreover, several works on the crack-healing behavior of engineering ceramics such as Al_2O_3/SiC composites [6], $MoSi_2$-based composite [7], Si_3N_4 matrix composites [8,9], ZrB_2–SiC ceramics [10,11], and ternary carbide $Zr_2Al_4C_5$ ceramics [12] have been reported. Zhang and his co-workers [10] studied the effect of pre-oxidation temperature and time on the flexural strength of ZrB_2–20 vol. % SiC composites. The flexural strength improved after pre-oxidation, with a maximum increase in strength of 15% for samples pre-oxidized at 800 °C for 180 min. Liu et al. [13] investigated the hot corrosion resistance of Ti_3SiC_2 ceramics in a mixture of 75 wt.% Na_2SO_4 + 25 wt.% NaCl, which melts at 850 °C, could be improved greatly by pre-oxidation treatment. These studies introduced a self-healing ability for fractures, which increases the reliability of dense ceramics by pre-oxidation. Moreover, in our previous study [14], highly porous Si_3N_4 ceramics were pre-oxidized to improve their mechanical properties by forming a dense layer, however, the flexural strength of the pre-oxidized specimens remained almost constant.

To the best of our knowledge, few studies have been conducted to determine the effects of pre-oxidation on the mechanical properties of low-porosity ceramics. In this study, low porosity TiB_2–SiC composite ceramics with relatively high mechanical properties were produced by employing the pre-oxidation process. The effects of the process parameters on the composition, microstructure, and mechanical properties of the porous TiB_2–SiC ceramics were measured and analyzed.

2. Experimental procedures

Commercially available raw materials were used to prepare low porosity TiB_2–SiC ceramics composites by CIP-PS in this study. The initial TiB_2 powder (purity > 99.9%, Alfa Aesar, USA) with a mean size of 2 μm and SiC powders (purity > 99.9%, 1 μm, Weifang Kaihua Micro-powder Co. Ltd., China) with 20 vol.% were ball-milled for 12 h in a polyethylene bottle using ZrO_2 balls and ethanol as the

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grinding media, and the milling speed of planetary ball mill (SFM-1, Shenyang Kejing Auto-instrument Co., Ltd, China) is 200 rpm. After milling, the slurry was dried with a rotary evaporator and then subjected to pestle and sieving with 100 mesh. The mixed powders were subsequently dried and compacted uniaxially under a pressure of 10 MPa in a graphite mold pre-sprayed with a layer of BN. To improve the green strength of the layers, 1 wt.% PVA was added as binder to each layer before die pressing. After demoulding, the green bodies were cold-pressed at 250 MPa by cold isostatic press machine (CIP-50MA, Shenyang Kejing Auto-instrument Co., Ltd, China). Finally, the porous green bodies were heated by vacuum sintering furnace (CXZT-200-22Y, Shanghai ChenXin Electric Furnace Co., Ltd, China) with 5 °C/min up to 1900 °C followed by a dwell time of 1 h and then cooled down with 5 °C/min to 1000 °C, under pure argon. Low heating and cooling rates were selected in order to relax the mismatch stresses during sintering.

The water-immersion technique was conducted using the Archimedes method to determine open porosities and densities of the sintered samples. The density of dried green bodies was calculated from the mass and dimension of samples. Porosity was calculated from the ratio of apparent density of porous sample to the theoretical density of dense TiB_2-20 vol.%SiC ceramic ($\rho = 6.92\ g/cm^3$). Each parameter was an average of the results of at least three samples. Thermal conductivity was measured by the guarded heat flow test method (DTC-300, TA Instruments Co., America).

The pre-oxidation tests were carried out in a convention furnace in ambient laboratory atmosphere. In order to eliminate the effect of thermal shock on the mechanical properties, specimens were heated at 10 °C/min to the target temperature, held at that temperature for different durations of time, and then left to cool freely inside the furnace. After pre-oxidation, the oxidized specimens were kept in a sealed container, which was protected from ambient moisture to prevent hydration of B_2O_3. The room-temperature flexural strength of as-sintered and pretreated samples was tested in three point bending on 3 mm × 4 mm by 36 mm bars, using a 30 mm span and a crosshead speed of 0.5 mm min^{-1}. All flexural bars were fabricated with the tensile surface perpendicular to the cold isostatic pressing direction. To obtain the average value, at least five samples were tested under each experimental condition. The microstructures of TiB_2–SiC composites before and after testing were observed by scanning electron microscope (FEI Quanta 200, FEI Company, Hillsboro, USA) equipped with X-ray energy dispersive detector systems (EDS).

3. Results and discussion

3.1. The effect of pre-oxidation temperature

Fig. 1 summarizes the flexural strength of the porous TiB_2–SiC composite after pre-oxidation at 800–1400 °C for 60 min. The flexural strength values of untreated specimens was 77.6 ± 11 MPa, and the flexural strength of specimens pre-oxidized at 800, 1000, 1200, and 1400 °C for 60 min was 170.7 ± 6.4, 140.1 ± 28, 116.5 ± 14 and 40 ± 2.4 MPa, respectively. This indicates that an approximate 120% increase in strength, compared with that of the corresponding polished specimen, was achieved after pre-oxidizing at 800 °C for 60 min. This increase in strength suggests that the initial cracks and pores, introduced through the surface-finishing procedure for brittle materials, were healed during the pre-oxidation process. Similar results have been reported for Al_2O_3/SiC and Si_3N_4/SiC composites [6–10].

The crack-healing effect can be seen in Fig. 2, which shows a surface micrograph of the porous ceramics after oxidation at 800–1400 °C for 60 min. The SEM images of the sintered TiB_2–SiC

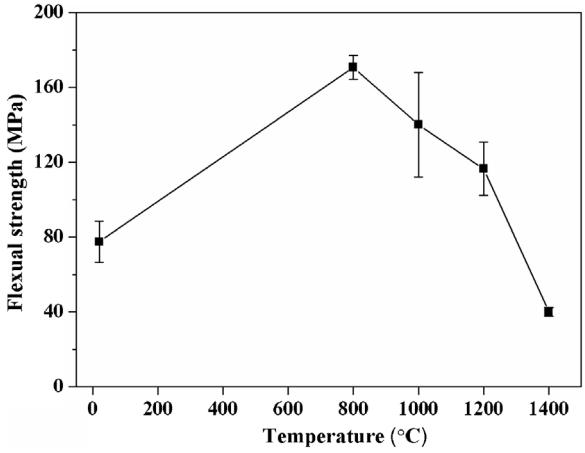

Fig. 1. Flexural strength of samples after pre-oxidation at 800–1400 °C for 60 min.

composite (Fig. 2a) show that the TiB_2 grains with mean grain size of about 2 μm have an isotropic microstructure consisting of hexagonal grains. The porosity of obtained porous TiB_2–SiC ceramics was 29.4 ± 2.1 vol.%, and the pore radius was about 8 μm. The SiC particulate (dark features) is homogenously distributed in the matrix and no agglomeration was detected. After oxidizing the sample at 800 °C, TiB_2 begins to oxidize to boria and TiO_2. EDS analysis shows that Ti, B and O are the main composition of this zone (Fig. 2b). This is consistent with the reported oxidation studies of TiB_2 system composites [16]. At this temperature, boric oxide is glassy and flows to fill pores and flaws in the TiB_2–SiC composite, which in turn leads to an increase in flexural strength. However, oxide evaporation and formation of gas (i.e., B_2O_3 and CO) were found to be detrimental to the crack-healing ability. In our previous work, B_2O_3 started to evaporate above 1000 °C [10,15]. As shown in Fig. 2c, despite a glassy B_2O_3 film observed on top of the ($TiO_2 + B_2O_3$) scale at 1000 °C, the gaseous B_2O_3 evaporates at open surface sites without disrupting the scale. This may be the reason for the slight decrease in flexural strength compared to the specimens oxidized at 800 °C.

To the best of our knowledge, the SiC phase begins oxidizing appreciably at temperatures above 1100 °C. At higher temperatures of 1200 °C, this silica-based glass offers greater resistance to evaporation than B_2O_3 alone [10]. Moreover, the microstructure of the TiO_2 appears to change from equiaxial grains at temperatures below 1000 °C to columnar grains at 1200 °C and higher. The pores in the porous TiO_2 layer are filled with silica (Fig. 2d). Although the silica-based glass offers greater crack-healing ability, the strength of the columnar TiO_2 grains were lower than that of the equiaxial TiB_2 and/or TiO_2 grains. This was the reason for the further slight decrease of flexural strength when oxidizing at 1200 °C. The samples oxidized at 1400 °C showed the worst crack-healing effect; a 48.4% decrease in strength compared to that of the corresponding polished specimen. The glass phase (B_2O_3 and silica) evaporated rigorously and the fragile columnar TiO_2 grains grew larger, thus causing a decrease in the crack-healing ability (Fig. 2e).

3.2. The effect of pre-oxidation time at different temperature

Crack-healing behavior is also very sensitive to crack-healing time. The effect of crack-healing time on the flexural strength of the specimens oxidized at 800 °C and 1200 °C was investigated. Fig. 3 shows the flexural strength of the TiB_2–SiC composite after pre-oxidation at 800 °C for different times (5, 60, 120, 240, and 360 min). Compared to the flexural strength of untreated specimens (77.6 MPa), the strength was improved greatly after pre-oxidation at 800 °C for 5–360 min, with a more than 99.4% increase in strength. The greatest increase, 134.4%, occurred in the porous