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Densification, microstructure and mechanical properties of hot pressed ZrB_2–SiC ceramic doped with nano-sized carbon black

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ABSTRACT

The effect of nano-sized carbon black on densification behavior, microstructure, and mechanical properties of zirconium diboride (ZrB_2) – silicon carbide (SiC) ceramic was studied. A ZrB_2-based ceramic matrix composite, reinforced with 20 vol% SiC and doped with 10 vol% nano-sized carbon black, was hot pressed at 1850 °C for 1 h under 20 MPa. For comparison, a monolithic ZrB_2 ceramic and a ZrB_2–20 vol% SiC composite were also fabricated by the same processing conditions. By adding 20 vol% SiC, the sintered density slightly improved to ~93%, compared to the relative density of ~90% of the monolithic one. However, adding 10 vol% nano-sized carbon black to ZrB_2–20 vol% SiC composite meaningfully increased the sinterability, as a relatively fully dense sample was obtained (RD=~100%). The average grain size of sintered ZrB_2 was significantly affected and controlled by adding carbon black together with SiC acting as effective grain growth inhibitors. The Vickers hardness, flexural strength and fracture toughness of SiC reinforced and carbon black doped composites were found to be remarkably higher than those of monolithic ZrB_2 ceramic. Moreover, unreacted carbon black additives in the composite sample resulted in the activation of some toughening mechanisms such as crack deflections.

1. Introduction

Zirconium diboride is a potential candidate for ultrahigh-temperature structural applications, such as thermal protection systems in hypersonic reentry aerospace vehicles, due to its relatively low density, outstanding chemical inertness, high melting point, and high electrical and thermal conductivities. However, monolithic ZrB_2 has some disadvantages including poor oxidation resistance and low fracture toughness. In addition, it is difficult to fabricate fully dense monolithic samples due to the characteristics of strong covalent bonding, low self-diffusion coefficient, and the formation of oxide impurities on the surfaces of raw materials [1–4].

Different reinforcement phases (e.g. SiC) have been added to enhance thermal/mechanical properties and high temperature oxidation resistance as well as prevent the overstated grain growth of ZrB_2-based ceramics. Nevertheless, SiC could not significantly improve the sinterability of ZrB_2; hence, higher sintering temperatures were needed to fabricate fully dense materials [5–12].

Some additives (e.g. carbon) have shown a twofold effect as a sintering aid to enhance the sintering process and/or a reinforcement phase to improve the mechanical properties of ZrB_2-based ceramics and ZrB_2–SiC composites [13–21]. The sinterability improvement in such ultrahigh-temperature ceramics is related to the elimination of oxide impurities (such as zirconia, silica and boria) from the surfaces of ZrB_2 and SiC powders as raw materials. By the addition of graphite or graphene, the fracture toughness of ZrB_2-based ceramics was improved via activating several toughening mechanisms such as crack deflection, crack bridging, and the additives pull-out [22–29]. The sinterability and fracture toughness of hot pressed and spark plasma sintered ZrB_2-based ceramics were also enhanced by adding carbon nanotubes [30,31]. Crack deflection, fiber deboning, bridging, and pull-out were also detected as the toughening mechanisms in hot pressed short carbon fiber reinforced ZrB_2–SiC composites [9,32–35]. However, by increasing the amount of short carbon fiber in pressureless sintered ZrB_2–SiC ceramics, the fracture toughness and densification process were descended [36]. Adding carbon black, nano-sized powders in the shape of porous compactable agglomerates, was also led to the improvement in the fracture toughness of hot pressed ZrB_2–SiC composites by activation of crack deflection, bridging and branching as toughening mechanisms [37].

In this work, the ceramic samples were fabricated by hot pressing at the temperature of 1850 °C for a holding time of 60 min under an

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applied pressure of 20 MPa. Densification behavior, microstructural evolution and mechanical properties (hardness and fracture toughness) of undoped ZrB_2, ZrB_2–SiC and nano-carbon black doped ZrB_2–SiC samples were studied. This article is the fourth part of a series of papers dealing with the impact of several *nano-carbon* additives with different morphologies on the properties of hot pressed ZrB_2–SiC ultrahigh-temperature ceramics. The effects of *graphite nano-flakes*, *graphene nano-platelets*, and *carbon nanotubes* have been reported elsewhere [22,24,39].

2. Experimental procedure

2.1. Materials and process

ZrB_2 powder (purity > 99%, particle size ~2 μm, density 6.1 g/cm^3, Leung Hi–tech Co., China), α-SiC powder (purity ~99%, particle size ~5 μm, density 3.2 g/cm^3, Carborundum Universal Ltd., India), and research grade nano-sized carbon black powder (purity > 95%, particle size ~15 nm, density 1.86 g/cm^3, US Research Nanomaterials Inc., USA) were purchased to form different ceramic compositions. Powder mixtures with the following compositions were prepared: ZrB_2 (hereafter termed Z), ZrB_2–20 vol% SiC (hereafter termed ZS), and ZrB_2–20 vol% SiC–10 vol% carbon black (hereafter termed ZSC). For preparing ZSC sample, nano-sized carbon black powder was initially wet stirred in ethanol for 60 min using an ultrasonic mixer (40 kHz frequency, 265 W output power, Mercury UC 4, Turkey). Then, ZrB_2 and SiC powders were also supplemented to the slurry and stirred once more for 60 min; afterward, ethanol was evaporated at 80 °C on a rotatory oven (Tebazma HMS 14, Iran). As–received powders of Z and ZS samples were also prepared similar to that of ZSC sample. Finally, the dried powder mixtures were supplementarily ball-mixed in zirconia media for 60 min.

The powder mixtures were sintered in a graphite resistance heated hot pressing furnace (Shenyang Weitai Science & Technology Development Co. Ltd., China). Three disc-shaped samples, for each composition, with diameter of 25 mm and as-sintered thickness of 5 mm were packed into a graphite die and covered with graphite foil and boron nitride. A sintering temperature of 1850 °C, a heating rate of 15 °C/min maintained with an external uniaxial pressure of 20 MPa and a holding time of 60 min were selected as the hot pressing conditions in 5×10^{-2} Pa vacuum. The die temperature, above 1000 °C, was monitored using an infrared thermometer (Dikai IT-6, China) through a sapphire window.

2.2. Characterization

Bulk density of the hot pressed samples was determined by Archimedes' principles using distilled water as the immersing medium. Geometrical technique was also employed to approve the validity of experimentally measured values. Relative density was estimated through dividing bulk density by theoretical density which was calculated using the rule of mixtures. Moreover, phase characterization was performed with X-ray diffraction (XRD) method in a Siemens D5000 diffractometer using Cu lamp (λ=1.54 Å, 40 kV, 30 mA). Microstructural investigations were carried out by field emission scanning electron microscopy (FESEM: Mira3, Tescan, Czech Republic). Also, specimens for microstructure analysis were prepared by grinding and polishing processes with diamond slurries down to a 1-μm finish. Energy dispersive spectroscopy (EDS: DXP-X10 P digital X-ray processor) was used for chemical composition identification. The mean ZrB_2 grain size of the sintered ceramics was determined from FESEM micrographs of the fractured surfaces by an image analysis software package (ImageJ 1.44p, Wayne Rasband, National Institute of Health, USA) and approximated by assessing at least 100 grains. In addition, hardness (HV 5.0) was determined by a Vickers diamond indenter (Zwick Roell, ZHV 10, Germany) with a 49 N load for 15 s on the polished sections as an average of 5 indentations. Young (elastic) modulus was appraised by an equation (Eq. (1)) proposed by Nielsen [39]:

$$E = E_0 \frac{(1-P)^2}{1+\frac{P}{\rho-1}} \quad (1)$$

where E_O is modulus of fully dense sample calculated by the rule of mixtures, P is volume percentage of porosities and ρ is shape factor of 0.4. Indentation fracture toughness (K_{IC}) was estimated using a formula (Eq. (2)) proposed by Anstis et al. [40] from the lengths of the diagonal indentation-induced cracks after Vickers hardness measurements:

$$K_{1C} = (0.016 \pm 0.004)\left(\frac{E}{H_V}\right)^{1/2}\frac{L}{c^{3/2}} \quad (2)$$

where E is Young modulus, H_V is Vickers hardness, L is indentation force (49 N), and c is half of the crack length. The fracture toughness values were also reexamined by single-edge notched beam test on 2×4×18 mm^3 test bars, employing a 16-mm span with crosshead speed of 0.05 mm/min. Flexural strength was obtained by three-point bending test on 2×3×18 mm^3 bars, using a 12-mm span with crosshead speed of 0.5 mm/min on the same jig employed for the K_{IC} assessment.

3. Results and discussion

3.1. Starting materials and powder mixture analyses

Fig. 1 shows the field emission scanning micro/nano-graphs and X-ray diffraction patterns of starting materials. The only detectable crystalline phases in Fig. 1(a) and (b), by XRD methodology, are ZrB_2 and SiC, respectively. XRD pattern of the nano-sized carbon black powder is presented in Fig. 1(c), which verifies the amorphous nature of this additive.

FESEM micro/nano-graphs of the powder mixture of ZSC sample are shown in Fig. 2. A relatively homogeneous dispersion of carbon black powders with ZrB_2 and SiC particles is observed in Fig. 2(a). As it can be clearly seen in Fig. 2(b), the nano-sized carbon black powders are in vicinity or contact with the surface of ZrB_2 particles.

3.2. Densification behavior and microstructural evolution

Table 1 presents the characteristics of as-sintered ceramics such as relative density, average ZrB_2 grain size, Vickers hardness and fracture toughness values. After sintering process, the relative density of monolithic ZrB_2 ceramic (Z sample) reached ~90% but rose to ~93% by adding 20 vol% SiC to the matrix (ZS sample). By adding the same amount of SiC together with 10 vol% nano-sized carbon black, a fully dense ZSC sample was obtained. Therefore, it can be concluded that the relative density of ZrB_2–SiC ceramic was remarkably affected by the addition of carbon black. Zhou et al. [37] fabricated a fully dense ZSC sample by addition of 20 vol% SiC and 5 vol% nano-sized carbon black after hot pressing at 1900 °C for 60 min under 30 MPa in argon atmosphere.

It seems that the main effect of well-dispersed nano-sized carbon black particles on densification behavior of ZrB_2–SiC system is the reaction of carbon with surface oxide impurities of staring materials, i.e. zirconia (ZrO_2) and boria (B_2O_3) on ZrB_2 as well as silica (SiO_2) on SiC particles. It was reported that homogenous dispersion of carbon additives in ZrB_2–SiC composites has an important role on sinterability and densification process [22,24,38,41].

Fig. 3 shows the field emission SEM images of the polished surfaces of hot pressed ceramic samples. Although the porosities in monolithic Z sample (Fig. 3(a)) are larger than those in ZS sample (Fig. 3(b)); the addition of SiC in ZS sample, compared to Z sample, seems to reduce the amount of porosities only about 3%. No obvious porosity can be