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Microstructure, mechanical properties and thermal shock resistance of ZrB_2-SiC-C_f composite with inhibited degradation of carbon fibers

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ABSTRACT

ZrB_2-SiC-C_f composite with carbon coated carbon fibers was successfully prepared by low temperature hot pressing. This composite showed an excellent thermal shock resistance compared with those composites fabricated by hot pressing and spark plasma sintering using as-received carbon fibers. Toughening mechanisms such as crack deflection, crack branching, fibers pull-out and fibers bridging were obviously detected in ZrB_2-SiC-C_f owing to the inhibited degradation of carbon fibers and the relatively weak fiber/matrix interfacial bonding, leading to a non-brittle fracture mode of the composite. Moreover, the composite exhibited an excellent thermal shock resistance with a high critical thermal shock temperature difference of 773 °C which is about twice those of the reported ZrB_2-based ultra-high temperature ceramics. This work provides valuable guidance in the preparation of ZrB_2-based ultra-high temperature ceramics with a combination of excellent properties.

1. Introduction

ZrB_2 is typically grouped in a family of materials deemed ultra-high temperature ceramics (UHTCs) due to its high melting point (3250 °C) [1–3]. The combination of attractive properties, such as high melting temperature, high hardness and strength, high electrical and thermal conductivities and low density relative to others, makes ZrB_2 the most promising candidate for use in extreme environments [4–6]. The addition of SiC has been proved to be an effective way to improve the densification, mechanical properties as well as oxidation resistance of ZrB_2 [7,8]. Unfortunately, in spite of its distinguished properties, ZrB_2-SiC is still not capable of withstanding the extreme service environment owing to the susceptibility to brittle fracture and poor thermal shock resistance of this material [9]. In order to improve the fracture toughness and thermal shock resistance of ZrB_2-based ceramics, a verity of toughening phases have been introduced into ZrB_2 matrix, such as particles [10], graphite flakes [11], whiskers [12] and fibers [12–14]. Researches have shown that the addition of graphite (G) flakes improved the thermal shock resistance of ZrB_2-based ceramics through crack deflecting and the releasing of residual stress in the composites, while the composites still show a low fracture toughness and exhibit a typical brittle fracture mode during fracturing [15]. More recently, researchers have paid more attention to carbon fiber reinforced ZrB_2-based ceramics since the carbon fiber shows more advantages in improving the fracture toughness [14,16] and having great potential in significantly improving the thermal shock resistance of ZrB_2-based ceramics compared with other reinforcements. However, the severe degradation of carbon fibers in carbon fiber reinforced ZrB_2-based ceramics caused by the high sintering temperature has plagued researches on such materials. Therefore, it is necessary to seek ways to inhibit the degradation of carbon fibers in the fabrication of carbon fiber reinforced ZrB_2-based ceramics and the general methods should include reducing the sintering time, decreasing the sintering temperature and using carbon coated carbon fibers [16]. Spark plasma sintering (SPS) is an effective method to rapidly consolidate powders to near-theoretical density by the combined effects of rapid heating, powder surface cleaning and pressure [17], which might show advantages in reducing the sintering time of carbon fiber reinforced ZrB_2-based ceramics. The strategy typically adopted to decrease the sintering temperature of ZrB_2 is to use nanosized powders as starting material instead of micrometer powders because the sintering activity of nanosized particles is dramatically higher than that of their micrometer sized counterparts [18]. Additionally, research has

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shown that deposition of carbon coating on the carbon fibers benefits to protect carbon fibers from the process corrosion during sintering [16]. However, no open literature has reported the fabrication of carbon fibers reinforce ZrB_2-based ceramics at low temperature with combination of using nanosized ZrB_2 powders and adopting carbon coated carbon fibers, and the thermal shock resistance of such material has not been investigated so far.

In this paper, as-received and carbon coated carbon fibers were adopted to fabricate ZrB_2-SiC-C_f composites using nanosized ZrB_2 powders by SPS or HP with the aim of inhibiting the degradation of carbon fibers and obtaining excellent properties of the composites. The microstructures, mechanical properties and the thermal shock behaviors of the composites were investigated.

2. Experimental procedure

Commercially available powders and carbon fibers were used in this study: ZrB_2 powders (Beijing HWRK Chem Co. Ltd., China) and SiC powders (Kaihua, China) with average particle sizes of 150 and 450 nm, respectively, and T800 carbon fibers (Tokyo, Japan) with an average diameter size of 5 μm. Prior to the fabrication process of the ZrB_2-SiC-C_f composites, continuous carbon fibers were chopped into short fibers with an average length of 2 mm. Certain amount of short carbon fibers were coated with pyrolytic carbon (PyC) using CVD process in a hot-wall tube reactor, and mixture of methane and argon gases was used to deposit PyC on the surfaces of carbon fibers at 1100 °C. The powders consisting of 50 vol% ZrB_2, 20 vol% SiC and 30 vol% carbon fibers (as-received or PyC coated) were ultrasonically dispersed in ethanol for 1 h and then ball milled for 8 h in a polyethylene bottle using WC balls and ethanol as the grinding media. To minimize segregation by sedimentation, the slurry was dried in a rotary evaporator at a temperature of 75 °C and a rotation speed of 30 rpm. The dried powders were sintered by SPS or hot pressing (HP) in a graphite die under vacuum. For SPS, the powders were heated to 1900 °C at a rate of 100 °C/min and then held at this temperature for 10 min. A uniaxial load of 30 MPa was applied at 500 °C. For HP, the powders were heated to 1600 °C at a rate of 15 °C/min and then held at this temperature for 2 h. A uniaxial load of 30 MPa was applied at 1200 °C. The shrinkage curve of the sample was recorded by a dilatometer at a resolution of 0.005 mm. The expansion of the graphite punches during sintering has a significant influence on the shrinkage curves of the powder compacts. In order to take into account the thermal expansion of punches, the entire die assembly was heated to the same temperature without the sintered powder compact inside the die. The powder shrinkage data reported in present study was obtained by subtracting the thermal expansion of the graphite punches from the original recorded shrinkage data, which could be the actual shrinkage data of the powder compact. The samples with as-received carbon fibers by SPS and HP were signed as SPS-ZSC-R and HP-ZSC-R, respectively. The sample with PyC coated carbon fibers by HP was signed as HP-ZSC-C.

Densities of ZrB_2-SiC-C_f composites were measured by the Archimedes method with deionized water as the immersing medium. Relative density was calculated via dividing bulk density by the theoretical density based on the law of mixture. Microstructures were analyzed by scanning electron microscopy (SEM, FEI Sirion, Holland) with energy dispersion spectroscopy (EDS). Flexural strength was tested in three-point bending on 3 mm × 4 mm × 36 mm bars, using a 30 mm span and a crosshead speed of 0.5 mm/min. Fracture toughness was evaluated by a single-edge notched beam (SENB) method with a 16 mm span using 2 mm × 4 mm × 22 mm test bars and a crosshead speed of 0.05 mm/min. The reported average values and standard deviations of flexural strength and fracture toughness were calculated from a minimum of six bars polished by diamond to a 0.5 μm finish. The thermal shock behaviors of the composites were investigated by a water-quenching technique. The specimens were heated to a preset temperature (200–900 °C) at a rate of 10 °C/min in a resistance furnace in air and held at this temperature for 30 min, and then the specimens were subjected to a thermal shock by quenching them into a water bath from the preset temperatures. The residual flexural strengths of the specimens after quenching were measured by three-point bending test. The reported critical thermal shock temperature difference ($\triangle Tc$) value was defined as 70% of the room temperature strength according to the linear interpolation of the residual strength values as described in ASTM C1525-04 [19].

3. Results and discussion

Fig. 1 displayed the typical fracture surfaces of SPS-ZCS-R prepared by SPS at 1900 °C for 10 min. It can be clearly seen that serious degradation of carbon fibers occurred in the composite during the SPS process. Most of the carbon fibers were transformed into carbon clusters as shown in Fig. 1a. A small portion of carbon fibers seemed to survive in the composite while they were also severely destroyed during the SPS process as indicated in Fig. 1b and c. ZrC was obviously detected by EDS on the surfaces of the carbon fibers, as shown in inset of Fig. 1b, indicating that some reactions occurred between carbon fibers and other compositions containing zirconium element. According to the results of thermodynamic calculation, the change in Gibbs free energy of the reaction between carbon and ZrB_2 was positive at the present condition, which demonstrated that the carbon fiber should not react with ZrB_2. In general, surface oxidation of commercially available ZrB_2 and SiC powders, especially for nanosized powders, was inevitable to be hindered during production or reserve, and the equimolar amounts of ZrO_2 and B_2O_3 impurities could be formed on the surfaces of ZrB_2 powders due to the oxidation of the powders under ambient conditions [20]. The reaction between carbon and ZrO_2 impurity were thermodynamically favorable at the present condition, which should be the main reason for the formation of ZrC phase causing the degradation of carbon fibers. In addition, the reactions between carbon fibers and B_2O_3 and SiO_2 impurities existed on the surfaces of the ZrB_2 and SiC powders, respectively, should be also responsible for the serious degradation of carbon fibers. From the microstructure analysis of ZrB_2-SiC-C_f composite by SPS, it can be concluded that the degradation of carbon fibers could not be inhibited by reducing the sintering time at high temperature (1900 °C).

In order to reduce the sintering temperature and achieve an acceptable level of density, ZrB_2-SiC-C_f composite with as-received carbon fibers was hot pressed at 1600 °C with a holding time of 2 h. As expected, most of the carbon fibers in HP-ZSC-R preserved their integrity during the hot pressing process compared with those in SPS-ZCS-R shown in Fig. 2, although a much longer sintering time was used to densify HP-ZSC-R. Comparing with the different microstructure evolutions of carbon fibers in SPS-ZCS-R and HP-ZSC-R, it can be concluded that the high sintering temperature was the main factor leading to the degradation of carbon fibers and reducing the sintering temperature was an effective way to inhibit fiber degradation. Even so, surface erosion of carbon fibers was inevitable in HP-ZSC-R (Fig. 2c) because of the reactions between carbon fibers and other compositions. In order to further understand the surface erosion mechanisms of carbon fibers, the element distribution near the fiber/matrix interface was investigated by EDS as exhibited in Fig. 3. It can be clearly seen that the amounts of oxygen and silicon located at the fiber/matrix interface were significantly higher than those located in the matrix and carbon fibers implying a segregation of SiO_2 at the fiber/matrix interface.