

Fabrication and thermal shock resistance of HfB_2 -SiC composite with B_4C additives

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A HfB_2 based ceramic matrix composite containing 20 vol.% SiC particles with 2 vol.% B_4C as sintering additives was fabricated by hot-pressed sintering. The microstructure and properties, especially the thermal shock resistance of the composite were investigated. Results showed that the addition of B_4C improved the powder sinterability and led to obtaining nearly full dense composite. The flexural strength and fracture toughness of the composite were 771 MPa and $7.06 \text{ MPa m}^{1/2}$, respectively. The thermal shock resistance tests indicated that the residual strength decreased significantly when the thermal shock temperature difference was higher than 600 °C. The large number of microcracks on the sample surface was the main reason for the catastrophic failure.

Keywords: *ceramic matrix, mechanical properties, microstructure*

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1. Introduction

Transition metal diborides such as ZrB_2 and HfB_2 , due to their unique combination of high melting point (3040 °C for ZrB_2 and 3250 °C for HfB_2), high strength, good thermal stability and corrosion resistance [1–3], have been under active development for demanding elevated temperature applications, as the most promising high-temperature ceramic materials. Fields within which transition metal diborides have found utilization include hypersonic flight, atmospheric reentry or rocket propulsion, such as the leading edges and nose-cones for a new generation of sharp-shaped hypersonic reentry vehicles [4]. However, due to its low self-diffusion coefficient and thermodynamic surface energy, pure borides ceramics cannot be sintered to fully dense composites even at temperatures over 2100 °C if no sintering additives are used [5, 6]. This low sinterability of metal diborides greatly

limited the application of these materials [7]. Therefore, the investigation of some new sintering aids yielding high sintered density at low sintering temperatures and obtaining clean grain boundary should be considered as an effective way to enhance the mechanical properties of refractory borides.

Recently, the intentional introduction of some nonmetal materials as sintering additives, such as nitrides and carbides, including AlN [8], Si_3N_4 [9], HfN [10] and B_4C [11] has consistently improved the sinterability, microstructure and properties of metal diboride ceramics. Among these new sintering aids, the use of B_4C as an additive was found to have more advantages than the others due to limited occurrence of secondary grain boundary phases [12]. However, behavior of B_4C as a sintering aid has not been well understood yet by researchers and its effect on the microstructure and properties of UHTCs needs to be investigated deeply.

In this study, a HfB_2 based composite containing 20 vol.% SiC particles and 2 vol.% B_4C

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as a sintering aid was prepared by hot pressing. The microstructure and mechanical properties of this composite were studied. The thermal shock resistance was investigated by water-quenching method. Even though similar heat treatments did not fully reproduce the real operative reentry conditions, the results may provide precious complementary information for the understanding the thermal shock behavior.

2. Experiment

Commercially available HfB_2 powder (over 96 % purity, Northwest Institute for Non-ferrous Metal Research, China), SiC powder (over 99.5 % purity, Xuzhou Hongwu Nanometer Materials Co. Ltd., China), B_4C powder (over 98 % purity, Jingangzuan Boron Carbide Co., Ltd, China), were used. The starting powder mixtures, HfB_2 +20 vol.% SiC+2 vol.% B_4C were milled for 24 hours in a polyethylene jar using absolute ethanol and zirconia balls, and then dried and sieved. The as-processed powder mixtures were hot-pressed at Ar gas atmosphere, with an applied pressure of 35 MPa. The set point of the hot-pressed run was 1850 °C and the soaking time was 30 min.

The microstructural features on a polished and fractured surface of the composite were observed using scanning electron microscopy (SEM, FEI Sirion, Holland) and transition electron microscopy (TEM, JEOL 2010).

Some mechanical properties of the composite were investigated. The final densities of the composites were measured by Archimedes water-immersion method, and the theoretical density was estimated by the rule of mixture. The flexural strength (σ) was tested in a three-point configuration on 3 mm by 4 mm by 36 mm bars, using a 30 mm span and a crosshead speed of 0.5 mm/min. Each specimen was ground and polished with diamond slurries down to a 1 μm finish. The edges of all the specimens were chamfered to minimize the effect of stress concentration. Hardness was measured by Vickers' indentation with a 50 N load applied for 15 s on

the polished sections. Fracture toughness (K_{IC}) was evaluated by a single-edge notched beam test with a 16 mm span and a crosshead speed of 0.05 mm/min using 2 mm by 4 mm by 22 mm test bars, on the same jig as used for the flexural strength. A minimum number of five specimens were tested for each experimental condition.

The thermal shock resistance was studied by the method of the retained flexure strength after water-quenching. The test specimens were cut into 4×3×36 mm³ rectangular bars and polished with diamond pastes. After that, the specimens were placed in a muffle furnace at the testing temperature and maintained at each temperature for 10 min to eliminate any temperature gradient within the specimen. Then the specimen was immersed into the boiling water bath (100 °C). The samples were dropped parallel to their longer axis into the water, and the time between leaving the furnace and immersion in the quenching bath did not exceed 5 s. For each condition, at least five specimens were tested. The retained strength was measured at room temperature at a crosshead speed of 0.5 mm/min by three-point bending using an Instron universal testing machine. The microstructure of the specimen after thermal shock was analyzed by scanning electron microscope (Hitachi S-4700) equipped with an energy dispersive X-ray spectroscope.

3. Results and Discussions

3.1. Microstructure and mechanical properties

A typical microstructure observed on the polished section of HfB_2 -SiC composite is presented in Fig. 1(a). In this figure, the gray phase and the black phase correspond to HfB_2 and SiC respectively. The composite was found to be nearly full dense with no residual porosity, in accordance with the high relative density of 99.6%. It should be noted that no B_4C phase was found in the composite. That is presumably the result of the reactions between B_4C and oxide impurities (mainly HfO_2) in the raw powders. The removal of oxygen contamination could greatly improve the

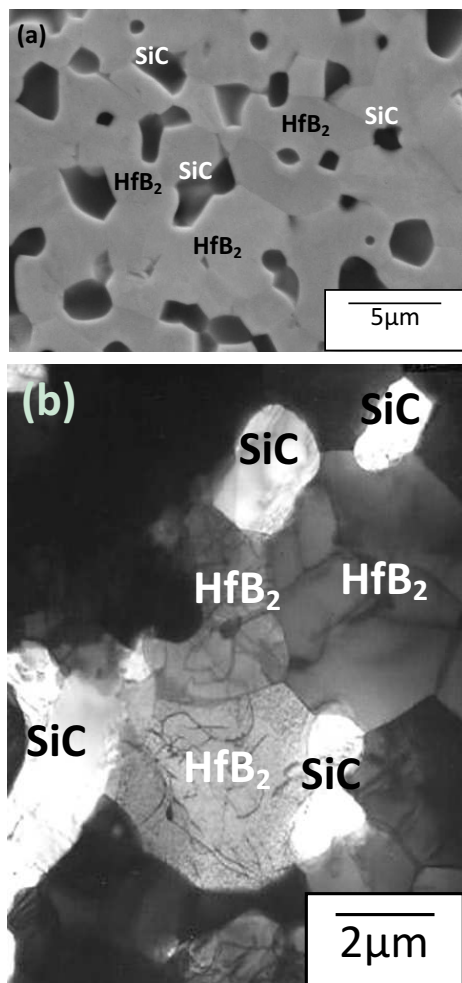


Fig. 1. Typical micro-structural images of the composite. (a) SEM; (b) TEM.

densification of diborides through the increased boron activity [13]. The possible reaction can be as follows:

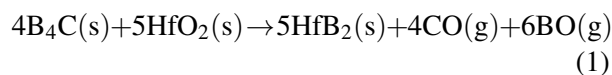


Fig. 1(b) shows a TEM micrograph of the sample. The distribution of SiC and HfB₂ grains is very homogeneous. HfB₂ grains form a three-dimensional network and SiC grains in a discrete state are surrounded by HfB₂ grains.

Table 1 summarizes some physical and mechanical properties of the composite. The flexural strength and fracture toughness of the

composite are 771 MPa and 7.06 MPam^{1/2}, respectively. Compared with the similar material system reported in reference [14], the mechanical properties of obtained composite exhibit a large increase, which can be attributed to the increase in relative density and decrease in grain size. In addition, the Vicker's hardness of the composite was about 21 GPa.

3.2. Thermal shock resistance of the composite

The thermal shock resistance of the composite was evaluated by the method of retained flexural strength after water-quenching. It should be noted that the boiling water, not cold water, was used in the present test. Compared to quenching into room-temperature water [15], the quenching bath in boiling water was used due to several attractive features, such as temperature maintenance, turbulent heat-transfer conditions, and less variable surface heat-transfer coefficients compared to quenching into room-temperature water. Moreover, the size of the flexural bars was large enough (>1.8 mm) to minimize the effect of size.

The curves of the residual strength of the composite after thermal shock versus water-quenching temperature difference (ΔT) were plotted in Fig. 2. The figure also represents the critical thermal shock temperature difference reported by reference [14]. The results reveal that the bending strength of the composite shows no decrease after quenching with $\Delta T < 600$ °C. However, when the temperature difference was over 600 °C, the residual bending strength drastically decreased. This indicates that the critical temperature difference (ΔT_c) is 600 °C, which is 100 °C higher than that of the data reported by other researchers [14]. It shows that a higher critical temperature difference under thermal shock was achieved in our composite. The improvement in the thermal shock resistance is believed to be attributable to the high fracture toughness. A high K_{IC} and rather low strength represent a high resistance to the fracture propagation during steady-state heat flow down

Table 1. Mechanical properties of composite.

Materials	H_v (GPa)	K_{IC} ($\text{MPa m}^{1/2}$)	σ (MPa)	Relative density (%)
HfB_2 -SiC- B_4C	21.6 ± 0.8	7.06 ± 0.4	771 ± 30	99.6

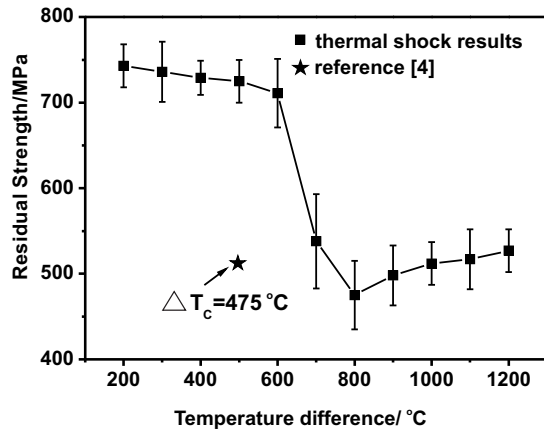
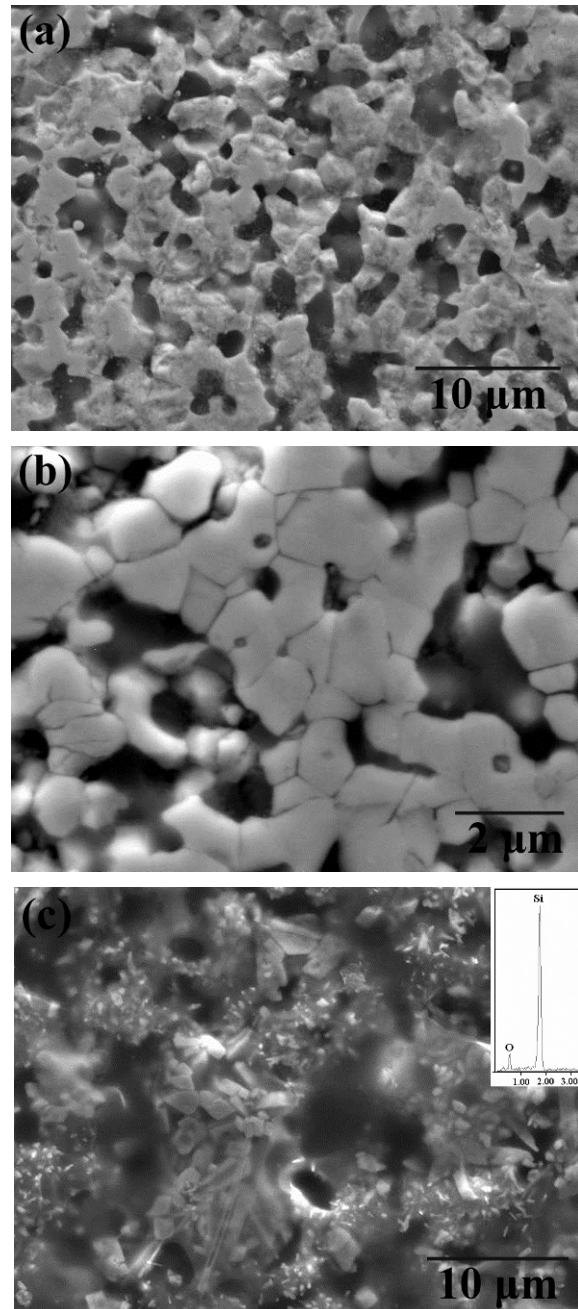


Fig. 2. Residual strength of composite versus thermal shock temperature differences.

a steep temperature gradient. Other researchers observed similar improvement in thermal shock resistance with increase in toughness [16].

In order to further clarify the mechanism of thermal shock resistance of the composite, the fracture surfaces of the flexural bars were examined with a scanning electron microscope (SEM), as it is seen in Fig. 3. The surfaces of the test bars which were not subjected to the shocks (Fig. 1(a)) and single quenched with $\Delta T = 600^\circ\text{C}$ (Fig. 3(a)) show little difference in appearance. However, the fracture surface of the bars quenched at $\Delta T = 800^\circ\text{C}$ is considerably different. As shown in Fig. 3(b), a typical fracture surface of the thermal shocked composite shows microcracking and fracturing in the matrix around the SiC particles. This microcracking behavior could explain the decrease in flexural strength observed.

Fig. 2 also indicates that when the ΔT was over 800°C , the residual strength of composite after thermal shock exhibited a gradual increase. The microstructural investigation of the thermally shocked surfaces revealed the existence of severe surface oxidation as the thermal shock temperature

Fig. 3. Surfaces SEM images of HfB_2 -SiC- B_4C composite after thermal shock: (a) $\Delta T=600^\circ\text{C}$; (b) $\Delta T=800^\circ\text{C}$; (c) $\Delta T=1200^\circ\text{C}$.

difference increased above 1000 °C (Fig. 3(c)). Surface blistering and swelling were the result of SiC particles oxidation and the formation of carbon monoxide gas bubbles. Moreover, a small amount of melted amorphous SiO₂ was also detected by EDS analysis. This kind of amorphous SiO₂ had some beneficial effect on the thermal shock behavior, sealing the surface microcracks and resulting in the increase of residual strength.

4. Conclusions

HfB₂-20 vol.%SiC-2 vol.%B₄C ceramic matrix composite was fabricated by hot-pressed sintering. The composite exhibited a homogeneous microstructure and a good combination of mechanical properties (771 MPa for flexural strength and 7.06 MPa m^{1/2} for fracture toughness). In comparison with other materials, the composite had an excellent thermal shock resistance due to the higher fracture toughness and lower flexural strength. Microstructural analysis of the sample surface indicated that the microcracks induced by thermal shock were the major reason for the decrease in residual strength.

Acknowledgements

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