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Microstructure and Properties of B_4C-Zrb_2 Ceramic Composites

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Abstract*—Boron carbide (B_4C) ceramic composites containing 20vol.%, 30vol.%, and 40vol.% ZrB_2 as additive were fabricated at 2100 °C for 60 min under 30 MPa load by hot pressing. The conductivity and process ability of the B_4C-ZrB_2 composites were improved when the ZrB_2 content was >20vol.%. The relative density of the composites ranged from 95.2% to 98.0%. The microstructure and mechanical properties of the composites were also investigated. The highest flexural strength (497.82 ± 12.7 MPa) and fracture toughness (7.0 ± 0.3 MPa·m1/2) of the B_4C-ZrB_2 ceramic composites were much higher than that of B4C ceramic, and the Vickers hardness ranged from 28.8 GPa to 32.4 GPa. The toughening mechanism involved a combination of micro crack and residual stress because of the micro crack deflection caused by the different thermal expansion coefficients of B_4C and ZrB_2.

***Keywords*—Boron carbide ceramic composite; ZrB2 additive; conductivity; mechanical properties.**

I. INTRODUCTION

Boron carbide, known as the third hardest material after diamond and cubic boron nitride, is best recognized for its hardness and abrasion resistance. Under highly abrasive conditions B_4C outperforms other hard materials [1-3]. Boron carbide has a density of about 2.52 g/cm^3 and a hardness of 35–45 GPa, which is even higher than those of diamond and cubic boron carbide at >1300 °C. Boron carbide is the most ideal high-temperature wear-resistant material, considered even better than silicon carbide and corundum [4,5]. Another important feature of boron carbide is its relatively high neutron absorption ability, including high absorption cross-section, wide absorption spectrum, no strong secondary radiation after absorption, low cost, and abundant sources of raw materials [6,7,8]. Therefore, boron carbide is widely applied in nuclear reactor control as a neutron absorber[9]. Given the strong covalent bond of boron carbide ceramics, they are hardly sinter able and relatively brittle, which are both serious obstacles for any structural material. a very poor sintering property, high sintering temperature, low fracture toughness (about 2–3 MPa·m$^{1/2}$), and very low workability [8,10,11]. Thus, the processing performance of boron carbide composites must be improved because they are difficult and costly to process into complex components using only mechanical processing of grinding [6,12,13]. Traditionally the sinter ability of B_4C ceramics has been improved by using sintering additives. In this regard, different additions have been added to B_4C to promote its properties. The addition of metals can benefit the densification, but not the mechanical properties. On the contrary, carbide and boride second phases, either added directly or formed in situ during sintering, have been observed to benefit the fracture toughness and flexural strength of B_4C [5]. in this paper, a series of boron carbide ceramic composites with ZrB_2 as additive was prepared. The introduction of additive improved the toughness of the composites especially their processing performance. The results can serve as a technical foundation for preparing and processing boron carbide ceramic composites to complex components.

II. EXPERIMENTAL PROCEDURE

The starting powders used were ZrB_2 (Northwest Institute for Non-ferrous Metal Research, China) with an average particle size of 2 μm (N99%) and B_4C (Mudanjiang Jingangzuan Boron Carbide Co., Ltd., China) with an average particle size of 3.2 μm (N99%). The powder mixture containing ZrB_2 and xvol.% B_4C (x=20, 30, and 40) nanoparticles was ball milled using ZrO_2 ball media and ethanol at 180 rpm for 12 h. All ball-milling processes were performed in polyethylene bottles. After mixing, the resulting slurry was dried with a rotary evaporation and then screened. The obtained powder mixtures were hot pressed at 2100 °C for 60 min at a uniaxial pressure of 30 MPa in an argon atmosphere. The micro structural features of the hot-pressed specimens were investigated by examining the fractured surfaces and polished cross-sections using a scanning electron microscopy (SEM) system (FEI Sirion, Holland) with simultaneous chemical analysis using an energy-dispersive spectroscopy (EDS) system (EDAX Inc.). The grain sizes of the high-density ceramics were determined from SEM images with an image analysis software package (Image J). The flexural strength (σ) was tested by 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. Each specimen was ground

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and polished with diamond slurries to a 1 μm finish. The edges of all specimens were chamfered to minimize the effect of stress concentration resulting from machining flaws. Micro hardness (Hv1.0) was measured by Vickers' indentation with a 9.8 N load applied for 15 s on polished sections. The fracture toughness (KIC) was evaluated by the single-edge notched-beam test with a 16 mm span and a crosshead speed of 0.05 mm/min using 2 mm × 4 mm × 22 mm test bars on the same jig used for the flexural-strength determination. All flexural bars were fabricated with the tensile surface perpendicular to the hot-pressing direction. A minimum of five specimens were tested under each experimental condition.

III. RESULTS AND DISCUSSION

A Density and relative density

The density and relative density of the B_4C-ZrB_2 ceramic composites were tested with six samples per group. As shown in Table 1, the density increased with increasing additive content. The relative density initially increased and then decreased little. The highest relative density was 98% when the ZrB_2 content was 30vol.%.

Table 1 Density and Relative Density of B_4C-Zrb_2 Ceramic Composites

Material	Theoretical density ($g \cdot cm^{-3}$)	Actual density ($g \cdot cm^{-3}$)	Relative density (%)
B_4C-20vol.%ZrB_2	3.234	3.08	95.2%
B_4C-30vol.%ZrB_2	3.591	3.52	98.0%
B_4C-40vol.%ZrB_2	3.948	3.86	97.8%

B. Mechanical properties

The mechanical properties of the B_4C-ZrB_2 ceramic composites are listed in Table 2. The measured fracture toughness ranged from 6.3 ± 0.3 $MPa \cdot m^{1/2}$ to 7.0 ± 0.3 $MPa \cdot m^{1/2}$, which was highly higher than that of monolithic B_4C ceramic (3–4 $MPa \cdot m^{1/2}$) [14]. The improvement in fracture toughness can be attributed to the introduction of ZrB_2 particles, which can result in crack deflection.

Table 2 Mechanical properties of B4C-ZrB2 ceramic composites

Material	Flexural strength (MPa)	Fracture toughness ($MPa \cdot m^{1/2}$)	Microhardness (GPa)
B_4C-20vol.%ZrB_2	497.82 ± 12.7	6.3 ± 0.3	30.4 ± 1.6
B_4C-30vol.%ZrB_2	401.49 ± 13.3	7.0 ± 0.3	32.4 ± 1.9
B_4C-40vol.%ZrB_2	326.30 ± 14.1	6.6 ± 0.3	28.8 ± 2.1

Alien from the increase in fracture toughness, the flexural strength did not significantly increase after the introduction of ZrB_2 particles. The experimental value flexure strength ranged from 326 MPa to 497 MPa, which was close to the recently reported value for monolithic B_4C ceramic (~400 MPa) [15]. High residual stress may exist at the interfaces between the additive particles and matrix grains (interfaces) because of the difference between the thermal expansion coefficients (TECs) of B_4C and ZrB_2, which may result in the formation of numerous micro cracks in grain boundaries.

As shown in Table 2, different volume fractions of additives introduced to the B_4C-ZrB_2 ceramic composites exerted varied influences on their mechanical properties. The flexural strength declined with increased ZrB_2 additive, which ranged from 497.82 ± 12.7 MPa to 326.30 ± 14.1 MPa when the ZrB_2 content increased from 20vol.% to 40vol.%. According to literatures and the present experimental results, a moderate amount of additive can significantly increase the flexural strength, and 20vol.%ZrB_2 realized the highest flexural strength in this study. As shown in Table 2, the fracture toughness and micro hardness increased with increased ZrB_2 content and then decreased slightly. When the ZrB_2 content was 30vol.%, the fracture toughness value was 7.0 ± 0.3 $MPa \cdot m^{1/2}$ and the micro hardness value was 32.4 ± 1.9 GPa, which was slightly lower than the micro hardness value (33–36 GPa) of pure B_4C ceramics. The introduction of ZrB_2 particles undoubtedly played an important role in improving the mechanical properties of B_4C-ZrB_2 ceramic composites.

C. Microstructure

Figure 1 shows the fracture scanning electron micrographs of B_4C-ZrB_2 ceramic composites containing different vol.ume fractions of ZrB_2 tested for flexural strength. The fracture surfaces of the composites revealed a uniform distribution of ZrB_2 (white contrast) particles in B_4C (dark contrast) matrix. Some ZrB_2 particles with sizes ranging within 2–5 μm located along the grain boundaries of B_4C were also shown in Fig. 1. There are some pores existed in these B_4C-ZrB_2 ceramic composites. Compared to B_4C-30vol.%ZrB_2 and B_4C-40vol.%ZrB_2, there are more and bigger pores located in B_4C-20vol.%ZrB_2. While the amount and size of pores existed in B_4C-30vol.%ZrB_2 and B_4C-40vol.%ZrB_2 are almost same, which is consistent to the density of B_4C-ZrB_2 given in table 1.

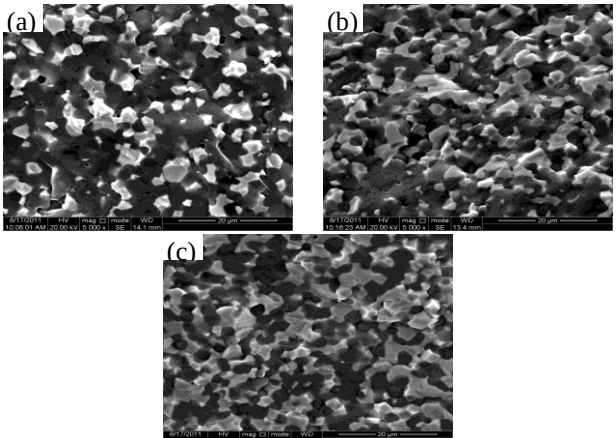

Fig. 1. SEM images of fracture surface: (a) B_4C-20vol.%ZrB_2;(b) B_4C-30vol.%ZrB2;(c) B_4C-40vol.%ZrB_2

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Porosity, grain size, micro cracks, and residual stress are the main factors influencing material fracture toughness. After introducing different volume fractions of ZrB_2, the relative density of the composites ranged from 95.2% to 98%. Moreover, analysis of the fracture SEM images (Fig. 2) revealed that ZrB_2 addition did not significantly change the grain sizes of B_4C-ZrB_2 ceramic composites. Toughening was not significantly affected by porosity and grain size, and instead depended on the combined action of micro crack and residual stress.

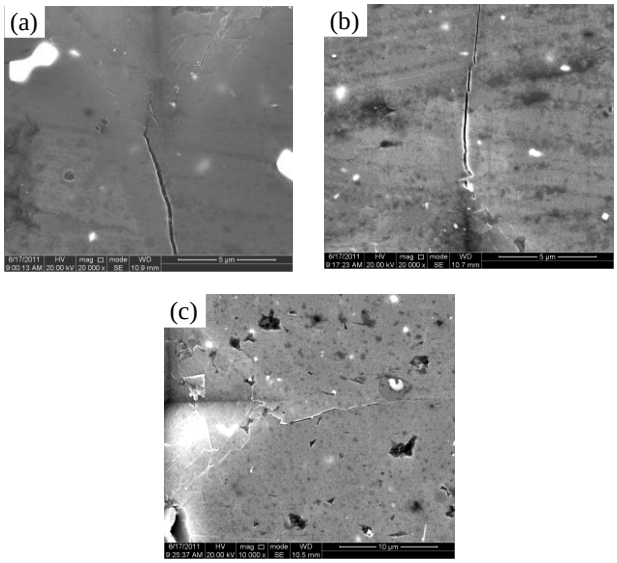

Fig. 2. SEM images of indentation-induced crack propagation on a polished surface: (a)B_4C-20vol.%ZrB_2;(b) B_4C-30vol.%ZrB_2;(c) B_4C-40vol.%ZrB_2

Given that the TEC of ZrB_2 ranges from 6.3×10^{-6} K^{-1} to 6.8×10^{-6} K^{-1}, the TEC of B_4C is 4.2×10^{-6} K^{-1} to 4.4×10^{-6} K^{-1}. This difference in TECs among sintered materials resulted in the formation of micro cracks, which caused path deflection and improved fracture toughness. At the same time, the differences in TECs generated a large amount of residual stress in the grain boundary, which further increased the fracture toughness to varying degrees by promoting crack deflection. This could be confirmed by observing the fracture surfaces of B_4C-ZrB_2 ceramics after flexural strength tests, as shown in figure 1. It is obvious that the addition of ZrB_2 changes the fracture mode from a predominantly Tran granular mode of B_4C-20vol. ZrB_2% to the combination of transgranular and intergranular mode as shown in fig.1(b) and (c). The high fracture toughness and micro hardness of B_4C-30vol. ZrB_2% is consistent to the high proportion of intergranular mode shown in the SEM image. As shown in figure 2, the increasing content of ZrB_2 leads to the deflection of micro cracks slightly due to the increasing residual stress. Notably, B_4C ceramic possesses nonconductive and hard characteristics; thus, B_4C ceramic is difficult to process into complex components using only the mechanical process of grinding. With increased volume fraction of ZrB_2 additive, the boron carbide ceramic composites changed from insulator to conductor because ZrB_2 is a good conducting material. The experiments proved that when the ZrB_2 content was >20vol.%, B_4C-ZrB_2 ceramic composites with good conductive performance were formed. The precision electro machining method can be used to realize complicated shapes of B_4C-ZrB_2 ceramic composites that have good conductive performance. The processing parameters are shown in Table 3. Compared with the traditional machining method, electro machining can greatly reduce the cost and residual stress of hard, brittle materials as well as improve the machining efficiency and machining quality.

Process	Pulse width	Pulse interval	Floating voltage	Peak current	Processing voltage	Processing current
Meso-machining	100 μs	20 μs	120 V	45 A	30 V	15–16 A
Finishing	30 μs	10 μs	120 V	15 A	30 V	4.5–5 A

Table 3 Electric machining parameters of B_4C-ZrB_2 composites

IV. CONCLUSION

B_4C-based ceramic composites containing micro sized *x*vol.%ZrB_2(*x* = 20, 30, and 40) particles were fabricated at 2100 °C for 60 min under 30 MPa load by hot pressing. The mechanical properties of the composites especially flexural strength and fracture toughness (average values of 497.82 MPa and 7.0 MPa·$m^{1/2}$, respectively) were much higher than those of monolithic B_4C ceramic. The micro crack initiation and propagation mode were investigated, and results showed that the combined mixed action of micro cracks and residual stress, which caused micro cracks to deflect upon micro cracks propagation, were the main mechanisms of additive toughening.

V. ACKNOWLEDGMENT

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AUTHOR'S PROFILE

Han Wenbo received Ph.D of Materials Engineering in Harbin Institute of Technology. His research work contains ultra high temperature ceramic composites and nano ceramic. More than 40 academic papers were published in international journals.