Microstructure and mechanical properties of B₄C matrix composites sintered with (TiB₂+Al)

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Abstract. The B₄C matrix composites were obtained with the addition of (24.5 % TiB₂+2 % Al) using spark plasma sintering method at 1600 °C with the pressure of 80 MPa for 5 min. Compared with the monolithic B₄C ceramics, due to the (24.5 % TiB₂+2 % Al) additive in B₄C matrix composite, the densification temperature of B₄C matrix composite was obviously decreased and the flexural strength was significantly improved. The B₄C matrix composites exhibited the high flexural strength of 528 MPa, and a moderate Vickers hardness of 24.2 GPa. The excellent flexural strength attributed to the second phases in the composites can prevent the cracks from extending and the energy dissipation effect resulted from the intergranular fracture.

1. Introduction
Covalent bonded boron Carbide (B₄C) ceramics are characterized by ultrahigh hardness (55-67 GPa), low relative density (2.52 g/cm³), excellent chemical inertness, good neutron absorption performance, ultrahigh melting point (~2623 K) high elastic modulus and so on [1-3]. These attractive physical and chemical properties make B₄C ceramics become the promising materials for many applications, such as lightweight armors, wear-resistant and abrasive materials [4-7]. However, because of the high melting point (2450 °C), the existence of surface oxide layer-B₂O₃, the low coefficient of self-diffusion and the strong covalent bonding, the fully-dense B₄C ceramics are difficult to fabricate by traditional methods [8-9]. High sintering temperature and long holding time are needed to obtain the high relative density B₄C ceramics, and the grain carsening man happen during sintering process. In addition, the sinterng parameters can cause energy waste[10-12]. Therefore, how to enhance the sintering characteristics of B₄C ceramics is a significant task in this field.

Many researches have been carried out to solve this problem and improve the mechanical properties of B₄C ceramics, the introduction of the second phase is considered to be the most effectively way to overcome the problem [13-15]. Many B₄C matrix composite systems, such as B₄C-oxide [13], B₄C-carbide [14] and B₄C-metal [15] with excellect mechanical properties were synthesized.

In addition, as an emerging technology, spark plasma sintering (SPS) is known as the fast sintering and low temperature sintering because of the electrical discharge effect and the use of electric-pulsed current on the electrodes. SPS is expected to be an excellent method to fabricate fully-dense B₄C ceramic at lower sintering temperature and shorter holding time compared to traditional sintering methods. During the process of the SPS, the surface oxide layer (B₂O₃) on the B₄C ceramics can be effectively removed, meanwhile, the densification temperature of ceramics is reduced. Therefore, the SPS process
should be used to fabricate the B\textsubscript{4}C ceramics [16-19], and this sintering method has been shown to be effective in obtaining the fine-grained as-sintered compact.

In this paper, the B\textsubscript{4}C matrix composites with the addition of (24.5 \% TiB\textsubscript{2}+2 \% Al) (abbreviated as BTA composites) were obtained by the SPS technology at the relative low temperature of 1600 °C. The effect of the additive on the flexural strength and the Vickers hardness of the composites will be investigated.

2. Material and experimental producer
Commercial B\textsubscript{4}C powders (99.99 \%, Shanghai, China) with the average size of 1 μm, TiB\textsubscript{2} powders (99.99 \%, Shanghai, China) with the average size of 1 μm and Al powders (99.99 \%, Shanghai, China) with the average size of 50 nm were used as the raw materials. The mixture consisted of 73.5 wt. \% B\textsubscript{4}C, 24.5 wt. \% TiB\textsubscript{2} and 2 wt. \% Al was sealed in the agate jars, then mixed by ball milling for 3h with the revolution speed of 300 rpm and the ball-to-powder of 3:1. After the ball milling process, the slurry was evaporated and dried at 70 °C. The mixed powder of B\textsubscript{4}C and BTA are shown in Fig. (1). It can be observed from Fig. 1 (b) that the mixed powder of BTA ceramic is uniform distribution.

SPS (DR. SINTER type SPS-3.20, Sojitz Machinery Corporation, Tokyo) technology was utilized to sinter the B\textsubscript{4}C ceramics and BTA composite. The ball-milled B\textsubscript{4}C-TiB\textsubscript{2} Al powder mixtures were loaded into the cylindrical graphite dies with an inner diameter of 25 mm and a height of 55 mm, then the mixtures were heated to 1650 °C at the pressure of 80 MPa in a 0.5 Pa vacuum chamber for 5 min. Meanwhile, the monolithic B\textsubscript{4}C ceramics were loaded into the cylindrical graphite dies with an inner diameter of 25 mm and a height of 55 mm, then the mixtures were heated to 1850 °C at the pressure of 80 MPa in a 0.5 Pa vacuum chamber for 5 min. The average heating rate is about 100 °C/min in both of the sintering producers.

Meanwhile, the monolithic B\textsubscript{4}C ceramics were sintered at 1850 °C at 80 MPa for 5 min by SPS as the comparative study. The heating rates were maintained at 100 °C/min. In addition, the phases analysis of the two kinds of ceramics were observed by x-ray diffraction (XRD, X' Pert PRO-MPD). The scanning electron microscopy (SEM, Hitachi S-4800N) was used to analyze the microstructures of the monolithic B\textsubscript{4}C ceramics and BTA ceramics. The Vickers hardness was tested by microstructure tester (HMV-2TADW). The flexural strength of the ceramics was measured at the room temperature by electromechanical universal testing machine (USA, Instron-5980, Instron Corporation) with the dimension of 3 mm×4 mm×20 mm.

3. Results and discussion
The XRD patterns of the monolithic B\textsubscript{4}C ceramics and BTA composites are shown in Fig. 2 (a) and Fig. 2 (b), respectively. In Fig. 2 (a), only B\textsubscript{4}C phase could be observed in the XRD patterns in B\textsubscript{4}C ceramics. The diffraction peaks of B\textsubscript{4}C, TiB\textsubscript{2} and AlB\textsubscript{12}C\textsubscript{2} are shown in Fig. 2 (b) in the BTA composites, which suggested that the nano-Al reacted with B\textsubscript{4}C matrix and formed the AlB\textsubscript{12}C\textsubscript{2} new phase during the sintering process.

![Fig. 1. SEM images of the powders: (a) B\textsubscript{4}C powder (b) BTA mixed powder](image-url)
Fig. 2. XRD patterns of (a) monolithic B₄C ceramics and (b) BTA composites.

Fig. 3 shows the flexural strength and the Vickers hardness of the monolithic B₄C ceramics and BTA composites. As shown in Fig. 3 (a), the monolithic B₄C ceramics exhibited low flexural strength of 378 MPa. However, the value of the flexural strength of the BTA composites was 528 MPa, which was about 39.7 % percent increase in flexural strength over the value of corresponding monolithic B₄C ceramics. Because of the present of second phases TiB₂ and AlB₁₂C₂, the cracks in the B₄C matrix composites could be hindered and the grain sizes could be refined [20], so the structure was strengthened and the flexural strength was improved. In addition, the relative density is also an important influence factor on mechanical properties, the relative density of these two ceramics will be discussed in detail in the next section. Therefore, the addition of (TiB₂+Al) was beneficial for the flexural strength of the B₄C ceramics.

As shown in Fig. 3 (b), the Vickers hardness of monolithic B₄C ceramics was 34.5 GPa, which was higher than that of BTA composites (24.2 GPa). Due to the TiB₂ second phase and the AlB₁₂C₂ second phase were softer than the B₄C matrix [21], therefore, the formation of the second phases could lead to the decreased of the Vickers hardness in the BTA composites.

Fig. 3. (a) The flexural strength and (b) the Vickers hardness of the monolithic B₄C ceramics and BTA composites.
Fig. 4. The SEM images of the fracture surfaces of (a) the monolithic B₄C ceramics and (b) the BTA composites.

The fracture surfaces of the monolithic B₄C ceramics and BTA composites are shown in Fig. 4 (a) and Fig. 4 (b), respectively. It can be seen that there were pores in the monolithic B₄C ceramics, which was detrimental to the mechanical properties of the ceramics. While, the fully-dense structure was obtained in the BTA composites, as shown in Fig. 4 (b). Therefore, the densification temperature was 1600 °C for the B₄C ceramic with the addition of 24.5 wt. % TiB₂ and 2 wt. % Al. In comparison to the sintering temperature of monolithic B₄C ceramics (1850 °C), in the BTA composites, the sintering temperature reduced obvious due to the existence of second phases TiB₂ and AlB₁₂C₂.

In addition, the fracture mode was typical transgranular fracture in the monolithic B₄C ceramics in Fig. 4 (a), while in the BTA composites in Fig. 4 (b), the fracture mode translated into a combination of transgranular and intergranular fracture. The combination of the two fracture modes was beneficial to the flexural strength, due to the effect of the energy dissipation resulted from the intergranular fracture. Therefore, compared with the monolithic B₄C ceramics, the BTA composites we obtained exhibited better flexural strength.

4. Conclusion

In the present study, the BTA composites were fabricated with the addition of 24.5 wt. % TiB₂ and 2 wt. % Al at 1600 °C with the pressure of 80 MPa for 5 min by the SPS technology. The results indicated that the densification temperature of BTA composites reduced obviously due to the existence of second phases TiB₂ and AlB₁₂C₂. Compared with the monolithic B₄C ceramics, the BTA composites exhibited better flexural strength. The dense microstructure and the transformation of the fracture mode were the major reason for the relative high flexural strength. However, the Vickers hardness of the BTA composites was lower than that of the B₄C ceramics, because the TiB₂ and AlB₁₂C₂ were softer than B₄C matrix.

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