Effects of boron content on the microstructure and properties of $B_xC$-$TiB_2$ ($x$=4.5, 6.5 or 8.5) ceramic composites by the reactive spark plasma sintering

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ABSTRACT

$B_xC$-$TiB_2$ ceramic composites were fabricated via reactive spark plasma sintering using TiC and B as the raw materials. The impact of B/TiC mole ratios on the phase compositions, densification behaviors, microstructure, and mechanical properties of the ceramic composites were investigated. The results showed that the stoichiometry of $B_xC$ could be tailored by changing initial boron content and the obtained $B_{4.5}C$, $B_{6.5}C$ and $B_{8.5}C$ phases have the same crystal structure (R-3m). The excess of B enhanced the reaction between TiC and B, which released a large amount of hot energy and promoted the densification of the composites. The TB8.5 composite sintered at 1900°C had the best comprehensive mechanical properties, with hardness and flexural strength of 40.36 GPa and 551 MPa, respectively. The formation of nano-sized TiB$_2$ grains induced by reaction were beneficial for improving the mechanical properties of these composites.

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1. Introduction

Due to its extreme hardness (Vickers hardness 40–60 GPa), high melting point (2450°C), low specific gravity (Density 2.52 g/cm³), and chemical inertness to corrosive media, boron carbide ($B_xC$) has shown great potential for a variety of structural applications such as wear-resistant components, lightweight armor products, and neutron radiation hardening.
shields, etc [1–3]. However, because of the high hardness and electrical resistance, it is particularly difficult to machine B₄C ceramic using either traditional diamond tools or electrical discharge machining (EDM) [4]. In addition, due to the strong covalent bond of B-C, low surface diffusion ability, and high resistance to grain boundary sliding of B₄C grains, it is very difficult to condense monolithic B₄C even at a temperature higher than 2000°C with the assistance of external pressure [5,6]. Du et al. [7] investigated hot-pressing kinetics and densification mechanisms of boron carbide. It can be found that high density of B₄C requires long holding time, high sintering temperature and high applied pressure, which is accompanied by significant grain coarsening.

In order to improve its machinability and sinterability, a variety of second phases have been added to the B₄C matrix as sintering aids [8–10]. It has been shown that the addition of TiB₂ can promote densification, decrease the porosity level and improve mechanical properties [11–13]. Yuan et al. [14] reported that TiB₂ as a sintering aid would significantly improve the hardness (19.7%), flexural strength (24.1%), and fracture toughness (19.7%). Dense B₄C-TiB₂ composites can be easily machined using electrical discharge machining (EDM) since TiB₂ possesses good electrical conductivity [4]. Furthermore, B₄C-TiB₂ ceramics with in situ generated TiB₂ phase were reported to have finer microstructures and better mechanical properties compared with a material in which TiB₂ was added into B₄C via simple powder blending [15–18]. According to the work from Gorle et al. [19], dense B₄C composite compacts can be obtained using B₄C-Ti-B mixtures at lower sintering temperature of 1400°C.

Spark plasma sintering (SPS) is a novel sintering method incorporating multi-physical effects and has exhibited many significant advantages compared to conventional sintering methods [20]. Recently, fully dense B₄C-TiB₂ composites were successfully synthesized via SPS technique from a mixture of 1 mol TiC and 6 mol B [21,22]. Pure B₄C-TiB₂ composite powders were obtained at 1200°C for 0 min or 1000°C for 15 min via a carbide boronizing process according to the reaction of TiC+6B = TiB₂+ B₄C [23]. Based on the B-C phase diagram [24], as shown in Figure 1, it can be found that there is a wide phase homogeneity range in 'B₄C' from B₃C to B₁₀.₅C. The research on B₄C-ZrB₂ composites suggested that the excess of B leads to the formation of B₄C (>4), which has beneficial effects on densification and hardness improvement of B₄C based composites [25]. In the present study, boron-rich 'B₄C'-TiB₂ ceramic composites were fabricated by reactive SPS. The effect of the initial boron amounts on the densification, phase constitution, microstructure, and hardness of the sintered compacts was assessed.

2. Experimental procedure

Commercially available TiC (>99%, 2 ~ 4 μm, Aladdin Reagent Co. Ltd., Shanghai, China, as shown in Figure 2(a)) and amorphous boron powders (>99%, <10 μm, Zhongnuo Advanced Material Co. Ltd., Beijing, China, as shown in Figure 2(b)) were used as starting materials. The molar ratio between TiC and B was set as 1:6.5, 1:8.5, and 1:10.5, according to reactions (1)-(3). The proportioned TiC and B powders were mixed and then dry-milled for 48 h in a polyethylene bottle using a small amount of WC-8 wt% Co balls. In this study, the corresponding powders and sintered ceramics were designated as TB6.5, TB8.5, and TB10.5, respectively.
The blended TiC-B powders were sintered by SPS (LABOX-350, Sinter Land Inc., Japan) in a 20.4-mm inner diameter graphite die. Graphite foils of 0.2 mm thickness were placed between the punches and the powders, and between the die and the powders for easy removal and significant reduction of temperature inhomogeneities. In addition, the exterior of the die was covered by graphite felt with a thickness of ~10 mm, which was used as a thermal insulation to reduce the radiation losses and possible temperature gradients. Sintering was performed in a vacuum (residual pressure <20 Pa), and a constant pressure of 30 MPa was applied from the beginning of the heating step to the end of the dwell. For all sintering, the heating from room
temperature to 600°C was controlled by a preset heating program and completed within 8 minutes. From 600°C to the desired temperature, a heating rate of 80°C/min was used. When the required temperature reached up to 1800 or 1900°C, the sample was then soaked for 6 minutes. Subsequently, the electric current was directly cut off and the sample was rapidly cooled by the cooling water. Some other cycles below the dwell temperature have also tried to understand the real reaction process. The heating rate, applied pressure, and holding time are 80°C/min, 30 MPa, and 0 min, respectively. The temperature and vacuum curves during the heating process were recorded by the computer of the SPS furnace.

The disk was ground to remove the outer carbon contaminated layers with a final thickness of about 3.0 mm in thickness and 20.0 mm in diameter. The bulk density was measured by the Archimedes method. X-ray diffraction (XRD, Rigaku, Tokyo, Japan) was used to determine the crystal phases and lattice parameters of obtained specimens. The microstructure of the sample was examined by scanning electron microscopy (SEM, Sigma, Zeiss, Germany) and transmission electron microscopy (TEM, JEM-2100 F, JEOL, Japan). Based on these micrographs, the average grain size of TiB₂ was counted using ‘Nano Measure’ software, and as many grains as possible were measured for each specimen to improve accuracy.

The flexural strength at room temperature was measured in a three-point bending test (IBTC-5000, CARE Measurement & Control Co., Ltd., China) with a span width of 12 mm and a crosshead displacement of 0.5 mm/min on rectangular (16 mm x 3 mm x 3 mm) bars, which were cut from the SPS discs by EDM. The reported flexural strength values are the mean and standard deviation of five measurements. The Vickers hardness (HV) was measured at room temperature with a Vickers hardness tester (Shanghai Shangcai Testermachine Co., Ltd., China) at a load of 9.8 N and a dwell time of 15s.

3. Results and discussion

3.1. Phase evolution and densification behavior

Figure 3 shows the X-ray diffraction analysis of different samples after being heated to 1800 and 1900°C with a holding time of 6 min. It can be seen that pure B₄C and TiB₂ without any residual reactants were observed in all samples, which indicated that the reaction between TiC and B went to completion during the reactive spark plasma sintering process. In addition, no oxides or impurity phases were observed in XRD patterns, which was attributed to the minimization of oxygen during powder processing, and surface oxide removal during the isothermal holds. As shown in Figure 3, the peaks of TiB₂ were remarkably stronger than those of B₄C because of the atomic number of Ti being significantly higher than those of B and C. The intensity of the B₄C peaks increased as B content increased, which was consistent with the change in designed compositions. With the increase of temperatures, the diffraction peaks of B₄C also became stronger, which indicated that the specimens prepared at 1900°C had a higher crystalline degree. The lattice constants of the B₄C and TiB₂ phases for composite ceramics were calculated using the Jade software, as present in Table 1.
Variations of the measured temperature, shrinkage displacement, and the corresponding shrinkage rate along with the heating time for TB6.5–1900, TB8.5–1900, and TB10.5–1900 are shown in Figure 4. It can be seen that the densification curves of these three specimens showed a similar trend. In the early stage, the powders began to expand due to thermal effects. Subsequently, a brief contraction occurred, and then the samples continued to expand. After reaching a certain temperature node, the alloy powder began to shrink rapidly, in which the shrinkage rate first increased and then decreased. In the dwelling stage, the shrinkage rate approached 0.
In order to further investigate the brief contraction in the early stage, the TB6.5 powders and the corresponding alloys sintered at 1179 (Beginning temperature of shrinkage) and 1261 (End temperature of shrinkage) °C with a holding time of 0 min were analyzed by the XRD method, as plotted in Figure 5. For the starting powder mixture, the TiC and B phases were identified. XRD patterns of the TB6.5–1179 specimen revealed that the TiB₂ and BₓC phases had formed at 1179°C. When the sintering temperature increased to 1261°C, the XRD intensity of the TiC phase was almost non-existent, which indicated that TiC almost completely reacted with B and formed the TiB₂ and BₓC phases. It can be concluded the brief contraction of the displacement in the temperature ranges from 1179 to 1261°C for the TB6.5 powders were ascribed to the exothermic reaction between TiC and B. In addition, the reaction temperature ranges for TB6.5 (1179 to 1261°C), TB8.5 (1150 to 1245°C), and TB10.5 (1115 to 1227°C) decreased with the increase in the ratios of B/TiC, indicating that the excess of B content promoted the reaction between TiC and B.

Based on the B-C phase diagram [24] and Thermo-Calc software [26], the corresponding thermodynamics data of the reaction equations (1)-(3) varied with reaction temperature can be calculated to verify the possibility of the above chemical reactions, as described in Figure 6. It can be seen that the Gibbs free energies for all reactions between 800°C and 2000°C were negative, indicating that all of these reactions could occur during the process. The Gibbs free energy of reaction (3) was more negative than of reactions (1) and (2) in the whole temperature ranges, and this was also consistent with the above densification behavior.

Figure 4. Variations of the measured temperature, shrinkage displacement, and the corresponding shrinkage rate along with the heating time for (a) TB6.5–1900, (b) TB8.5–1900, and (c) TB10.5–1900.
3.2. Microstructure

The microstructure and grain size distribution of sintered samples for TB6.5, TB8.5, and TB10.5 are shown in Figures 7 and 8. It can be clearly seen from Figure 7 that the BₓC-TiB₂ composites consisted of two phases, the BₓC matrix appeared as a dark phase and the bright phase was TiB₂. By comparing the contrast in SEM images, the following...
observations can be made. With the increase of B content, the volume fraction of TiB$_2$ in the composites decreased. The composites sintered at 1900°C showed smaller amounts of pores in comparison with other composites sintered at 1800°C. For all the composites except for TB10.5–1900, the fine TiB$_2$ grains gathered together, corresponding to the unreacted TiC grains. In addition, the sizes of the TiB$_2$ grains decreased with the increase of the B/TiC mole ratios, which was attributed to the sufficient reaction between TiC and B. It should be noted that the TiB$_2$ grains in the composite of TB10.5–1900 grew significantly compared to those in the composite of TB6.5–1900 and TB8.5–1900, which also indicated that the TiB$_2$ powder was easier to achieve densification, and then the TiB$_2$ grains coarsened. For the composites of TB8.5–1800, TB8.5–1900, and TB10.5–1800 in Figure 8(c-e), the grain sizes of the TiB$_2$ grains were 0.96 ± 0.49, 1.15 ± 0.53 and 0.85 ± 0.33 μm, respectively. According to the Hall-Petch relationship, the existence of nano-sized TiB$_2$ is helpful to realize the high hardness in the composites.

A bright-field TEM image of the TB6.5–1900 composite is shown in Figure 9(a). The phases of different areas in Figure 9(a) were identified by the selected area electron diffraction (SAED) pattern in Figure 9(b,c). The [010] and [00] electron diffraction patterns of TiB$_2$ and B$_x$C, respectively, were observed. Based on the SEAD results, the phases of
Different areas can be detected on Figure 9(a), where the region_A (dark contrast) was TiB₂ and the region_B (bright contrast) was B₄.₅C. High-resolution TEM micrographs of the B₄.₅C-TiB₂ interfaces adjacent to regions A and B are also presented in Figure 9(b,c). The interplanar distances of the TiB₂ grain corresponding to the (100) and (001) planes were...
0.27 and 0.32 nm, respectively. The interplanar distances of the B_{4.5}C grain corresponding to the (010) and (012) planes were 0.45 and 0.37 nm, respectively. Figure 10 presents the TEM image and high-resolution micrograph of the TB10.5–1900 composite. The [010] zone axis diffraction spots of TiB_2 and the [100] zone axis diffraction spots of B_xC were observed. By comparing the experimental results of the TB6.5–1900 and TB10.5–1900 composites, the obtained B_{4.5}C and B_{8.5}C phases all were the B_4C phase in the B-C binary system with R-3 mm structure. The grain boundary in both composites was clean and no other phase was observed, indicating good interfacial compatibility of TiB_2 and B_xC. This is necessary for the composite to hold great mechanical properties. In addition, the TiB_2 grains were close to a nanometer in TB6.5–1900 composites and grew significantly in TB10.5–1900 composite.

### 3.3. Relative density and mechanical properties

Figure 11 shows the densities and relative densities of composite ceramics. The densities and relative densities of composites sintered at 1900°C were overall higher than these of composites sintered at 1800°C. With the increase in the ratios of B/TiC, the densities of the composite ceramics reduced and the corresponding relative densities increased. The
results of the relative densities were in good agreement with the morphologies of the composites. Due to the difficulty of obtaining accurate density of Bₜ₀.₅C phases, the relative density of TB10.5–1900 composite material exceeded 100%.

The Vickers hardness and flexural strength of composites sintered at 1800 and 1900°C were measured and the results are shown in Figure 12. It can be seen that the Vickers hardness of the composites sintered at 1900°C was higher than that of the composites sintered at 1800°C, as the hardness has the positively correlation with the relative density. The finer TiB₂ grain size and the higher relative density led to the highest hardness of 40.36 GPa for the TB8.5–1900 composite. The flexural strength of the obtained Bₜ₀.₅C-TiB₂ composites varied from 329 to 551 MPa and the composites sintered at 1900°C showed the trend of increasing first and then decreasing, which should be attributed to the finer TiB₂ grains of the TB8.5–1900 composite. Densities, relative densities, and mechanical properties of composite ceramics were summarized in Table 2.

Figure 13 shows the fracture surfaces of the Bₜ₀.₅C-TiB₂ composites after the bending test. Except for the TB10.5–1900, all the ceramic composites showed the mixed fracture mode with cleavage and intergranular fracture, corresponding with flat and rough features, respectively. The flat regions with river pattern were the Bₜ₀.₅C phases, and the rough regions with rock sugar shape referred to TiB₂ particles. It indicates that Bₜ₀.₅C phases exhibited a typical cleavage fracture mode while TiB₂ phases presented an intergranular fracture mode. Due to the grain growth of the TiB₂ particles, the failure model for the composite of TB10.5–1900 was mainly cleavage fracture, which led to its undesirable flexural strength of 369 MPa.

Table 2. Densities, relative densities, and mechanical properties of composite ceramics.

| Composite ceramics | Density (g/cm³) | Relative densities (%) | Hardness (GPa) | Flexural strength (MPa) |
|--------------------|----------------|------------------------|----------------|------------------------|
| TB6.5–1800         | 3.137 ± 0.007  | 94.50 ± 0.20           | 28.86 ± 2.50   | 382 ± 58               |
| TB6.5–1900         | 3.251 ± 0.010  | 97.91 ± 0.30           | 38.25 ± 2.40   | 405 ± 53               |
| TB8.5–1800         | 2.994 ± 0.011  | 95.18 ± 0.35           | 30.21 ± 5.19   | 329 ± 16               |
| TB8.5–1900         | 3.143 ± 0.005  | 99.90 ± 0.15           | 40.36 ± 3.14   | 551 ± 57               |
| TB10.5–1800        | 2.981 ± 0.014  | 98.56 ± 0.45           | 29.12 ± 2.06   | 344 ± 36               |
| TB10.5–1900        | 3.069 ± 0.008  | 101.50 ± 0.25          | 39.13 ± 4.35   | 369 ± 31               |
4. Conclusions

A solid-state reaction between TiC and B was used to fabricate the BₓC-TiB₂ composites using a reactive spark plasma sintering process. The effects of B/TiC mole ratios and sintering temperatures on the densification, microstructural and mechanical properties of BₓC-TiB₂ composites were examined. Several conclusions were drawn as follows:

(1) With the increased amount of B contents, all the reaction products of TiC and B consisted of two phases of BₓC and TiB₂. Excess B can form boron-rich boron carbide, which was located in the solid solubility range of BₓC.

(2) The increase in B contents reduced the exothermic reaction temperature between TiC and B and promoted the densification of the composites. Dense ceramics were obtained for the TB8.5–1900 and TB10.5–1900.

Figure 13. Fracture surfaces of the TiB₂-BₓC composites after bending test: (a) TB6.5–1800, (b) TB6.5–1900, (c) TB8.5–1800, (d) TB8.5–1900, (e) TB10.5–1800 and (f) TB10.5–1900.
(3) Although coarse TiC precursor was used, refined TiB₂ grains were observed in the sintered samples. The formation of nano-sized TiB₂ was helpful to realize the mechanical performance of the TB8.5–1900 (40.36 GPa and 551 MPa).

(4) After the full densification of the TB10.5–1900 composite, excess energies (high sintering temperature or excess holding time) led to significant grain growth of TiB₂. The fracture mechanism for the TiB₂ phase transformed from intergranular fracture to cleavage fracture, which resulted in a significant decline in mechanical properties.

Disclosure statement
No potential conflict of interest was reported by the author(s).

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