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Spark Plasma Sintering of Boron Carbide Using Ti_3SiC_2 as a Sintering Additive

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Abstract: Boron carbide has unique properties for wide application possibilities; however, poor sinterability limits its applications. One approach to overcome this limitation is the addition of secondary phases into boron carbide. Boron carbide based composite ceramics are produced by the direct addition of secondary phases into the structure or via reactive sintering using a sintering additive. The present study investigated the effect of Ti_3SiC_2 addition to boron carbide by reactive spark plasma sintering in the range of 1 700-1 900 °C. Ti_3SiC_2 phase decomposed at high temperatures and reacted with B_4C to form secondary phases of TiB_2 and SiC . The results demonstrated that the increase of Ti_3SiC_2 addition (up to 15 vol%) effectively promoted the densification of B_4C and yielded higher hardness. However, as the amount of Ti_3SiC_2 increased further, the formation of microstructural inhomogeneity and agglomeration of secondary phases caused a decrease in hardness.

Key words: reactive sintering; SPS; boron carbide; MAX phase

1 Introduction

Boron carbide (B_4C) is one of the most significant non-oxide covalent solids, combining superior properties such as outstanding hardness (as high as 47 GPa), high melting point (2 763 °C), and low density (2.52 g/cm³). The grain size, porosity, and the amount and type of defects in the ceramics affect the mechanical properties such as hardness and fracture toughness. Therefore, variable hardness values of boron carbide are reported in the literature. Due to its high strength to weight ratio, there is a great interest in the application of boron carbide in the defense industry as a light armor material. The abrasive wear resistance of boron carbide is high; therefore, it is used as abrasive powders and coatings. Boron carbide is also used as both reactor control rods and neutron-absorbing shielding owing to its high absorption cross-section and chemical stability. However, due to the strong covalent nature of boron carbide and

low self-diffusion coefficient, it is very challenging to obtain fully dense boron carbide ceramics with conventional techniques^[1-5]. The poor sinterability and low fracture toughness of boron carbide limit its widespread application. High temperatures (> 2 200 °C) and long sintering times (hours) are required for the industrial non-pressure production of boron carbide. Dense stoichiometric boron carbide samples are commercially produced by hot press. Although the sintering temperatures can be relatively reduced with the hot press, it is not possible to reduce the sintering temperature below 2 000 °C. Spark plasma sintering (SPS) is an electricaly assisted densification technique in which moderate pressure is also applied simultaneously. SPS provides many advantages for densifying high temperature ceramics by reducing the sintering temperature and time. Rapid process during SPS can effectively prevent grain growth, which results in an improvement in the mechanical properties of the ceramics. The ceramics are densified with the Joule heating, created by the high current flow through the system. Boron carbide was densified to 98% theoretical density at 1 600 °C under 70 MPa pressure in the studies by Tamburini *et al*, and Sairam *et al* reached full density at 1 800 °C in

15 minutes. Studies report various sintering parameters depending on the particle size of starting powder and different additives used^[6-8].

Another approach to enhancing densification is researching the influence of sintering additives on the matter diffusion process. Some additives used for boron carbide are graphite, metals (Al, Fe, Ni, etc), carbon fiber, and carbon nanotube^[9]. Although carbon and metallic additives positively affect densification, in most cases, the negative effect of these additives on the mechanical properties of boron carbide is inevitable. Production of boron carbide-based composites by incorporating secondary phases is an alternative way to promote densification of boron carbide and improve mechanical properties such as hardness and fracture toughness. The limited number of phases can be adopted as a secondary phase for boron carbide based composite since boron carbide belongs to high temperature ceramic family. TiB_2 and SiC are good candidates to enhance boron carbide's sinterability and mechanical properties. These composites are prepared by adding secondary phases directly to the B_4C matrix or using advanced *in situ* reactive sintering techniques. Li *et al* prepared (SiC, TiB_2)/ B_4C composite by reactive hot pressing from B_4C , Si_3N_4 , and TiC ^[10]. In another study, the composites were prepared by *in situ* reactive spark plasma sintering using B_4C and $TiSi_2$ by Wang *et al*^[11]. $Ti_{x+1}SiC_x$ is one of the MAX phases known for its remarkable properties. It has a low density of $4.5g/cm^3$, high oxidation resistance, and excellent thermal and electrical conductivity. MAX phases have good fracture toughness ($7-9.5 MPa.m^{1/2}$ for Ti_3SiC_2) and machinability compared to other ceramics^[12]. Tan *et al* reported improved sinterability and fracture toughness of boron carbide by adding Ti_3AlC_2 (one of the MAX phases) by SPS. Full densification of composite was achieved at temperatures as low as $1500^\circ C$ ^[13]. He *et*

al added 5 wt% and 10 wt% Ti_3SiC_2 into boron carbide and used a hot press for reactive sintering of boron carbide based composite and observed improvement in mechanical properties^[14]. The authors produced boron carbide-based composites using Ti_3SiC_2 as a sintering additive by pressureless sintering in the previous study. A solely temperature-dependent process promoted phase transformation, which leads to the composite formation, albeit without reaching high densities^[15]. In this study, the effect of Ti_3SiC_2 addition on boron carbide's sintering behavior and properties is investigated by reactive SPS.

2 Experimental

Boron carbide ($<5 \mu m$, 98.5% purity, H. C. Starck) and Ti_3SiC_2 ($<10 \mu m$ New Material Technology Co. Ltd., China, $\geq 98\%$) are starting powders, and the XRD patterns of which are shown in Fig.1. The free carbon was detected in the boron carbide structure. The microstructure of boron carbide with a particle size of a few microns is displayed in Fig.2. Mixtures of boron carbide powder with 5-20 vol% Ti_3SiC_2 were ball-milled for 5 h using silicon carbide balls as the milling media with a ball/powder weight ratio of 1/4. Table 1 lists the name of samples based on the composition of starting powders. The mixed powder in ethanol was dried at $80^\circ C$ for 36 h, and the obtained powder was subsequently sieved.

A (3.5 ± 0.2) g powder (mixed powders and monolithic B_4C) was poured into the graphite mold (inner diameter 20 mm) and then sintered by the FCT HP D 25-SD spark plasma sintering furnace. The sintering was performed under vacuum with applied pressure at $1700-1900^\circ C$. A moderate initial pressure of 16 MPa was applied to all specimen up to $1550^\circ C$. Between room temperature to $1550^\circ C$, the heating rate was 200

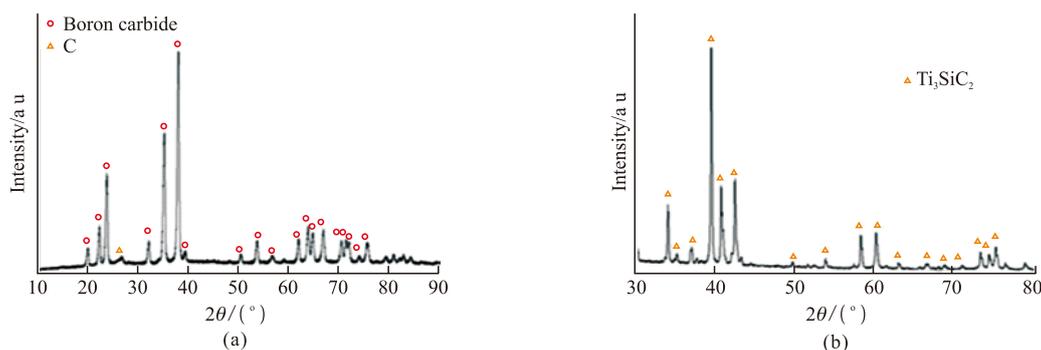


Fig.1 XRD pattern of starting powder: (a) boron carbide; (b) Ti_3SiC_2 ^[15]

°C/min. At 1 550 °C, the heating rate was decreased to 50 °C/min and the pressure was increased to 70 MPa. The dwell time at sintering temperature was 10 min.

Table 1 Composition of the powder mixture

Composition	Designation
B ₄ C-5 vol%Ti ₃ SiC ₂	BTSC5
B ₄ C-10 vol%Ti ₃ SiC ₂	BTSC10
B ₄ C-15 vol%Ti ₃ SiC ₂	BTSC15
B ₄ C-20 vol%Ti ₃ SiC ₂	BTSC20

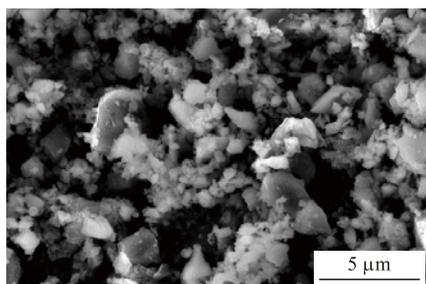


Fig.2 The microstructure of boron carbide powder

The densities of the sintered samples were determined by the Archimedes method. The theoretical densities of powders are determined with the rule of mixtures. The XRD analysis for phase determination was carried out with PANALYTICAL-EMPYREAN. The microstructure and chemical analysis (EDX) were examined with the scanning electron microscope (SEM-NOVA). The samples were cut with a diamond disc and polished for SEM analysis and Vickers hardness measurement (under 1 kg load for 10 s dwell time).

3 Results and discussion

The relative densities for each specimen as a function of sintering temperature are shown in Fig.3. All samples were sintered under 70 MPa pressure and 10 min holding time. The relative density of boron carbide without additive sintered at 1 700 °C is extremely low. The sintering additive displays its impact on densification even with 5 vol% addition and increased the relative density from 65.6% to 71.8% of the theoretical density. MAX phase decomposes at temperatures below 1 700-1 900 °C range, and reacts with B₄C to form new phases (Fig.4). The defects created during such process can alter the diffusion kinetic during densification^[8]. It is known that the diffusion coefficient increases with the decrease in particle size. Therefore, the low density of boron carbide without additive at all temperatures may also be attributed to the absence of

the pre-sintering process (milling). Overall, the density of the samples increased with increase in percentage of additives. The maximum relative density obtained at 1 700 °C remained at 81.8%. The relative densities for the specimen sintered at 1 800 °C ranged from 75.2% to 91.1%. Densities around 98% of the theoretical density are only reached at 1 900 °C with 10 vol%-20 vol% Ti₃SiC₂ phase additive into boron carbide. The samples did not exhibit densities $\geq 99\%$ of theoretical density.

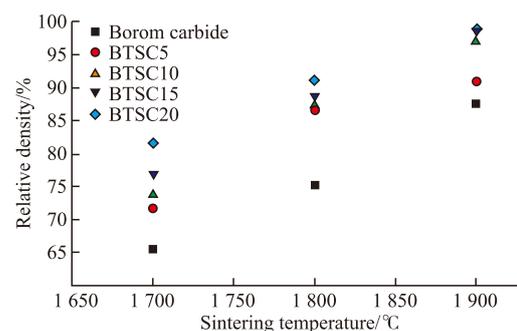


Fig.3 Densities of the specimen as a function of sintering temperature

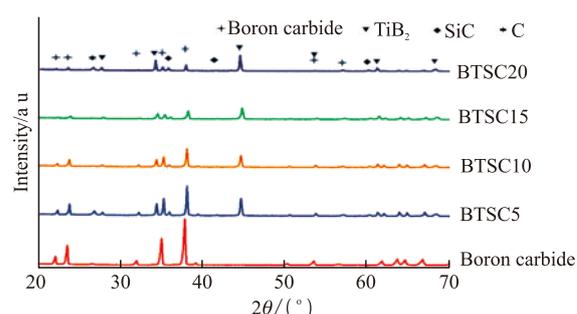


Fig.4 XRD patterns of samples with different amounts of Ti₃SiC₂ densified at 1 800 °C by SPS

In Fig.4, XRD patterns for all specimens sintered at 1 800 °C are given for comparison. No Ti₃SiC₂ diffraction peak was observed in all XRD patterns indicating that Ti₃SiC₂ decomposes at high temperatures. B₄C, TiB₂, and SiC phases exist in the structure, and TiB₂ peaks become more distinctive compared to boron carbide as the amount of Ti₃SiC₂ increases. No additional peak is observed except for residual carbon.

To determine the temperature intervals of shrinkage, the dilatometric study (fixed heating rate 50 °C/min and fixed compression pressure 35 MPa) was performed for BTSC10 (Fig.5). Some shrinkage (convergence of B₄C particles) beginning from 1 450 °C is observed. Activation of shrinkage starting from 1 670 °C can be explained by the decomposition of the MAX phase, *i.e.*, reaction sintering with the formation of TiB₂ and SiC. The XRD patterns of BTSC20 sintered at 1 700 and 1 800 °C are given in Fig.7. No extra peak

was observed (except carbon) in the sample sintered at 1 700 °C, indicating the decomposition of MAX phase had been completed. Based on these data, the following sintering mode was chosen for all composites: quickly heated (200 °C/min) to 1 550 °C at relatively low pressing pressure (16 MPa), then the heating rate was reduced to 50 °C/min, and the pressure was raised to the working pressure (70 MPa) in the temperature range of 1 550-1 700 °C.

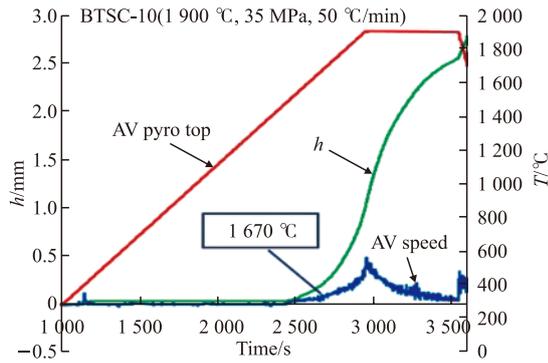


Fig.5 Shrinkage (h) and shrinkage rate (speed) of BTSC-10 composite material at constant heating rate 50 °C/min and compression pressure 35 MPa

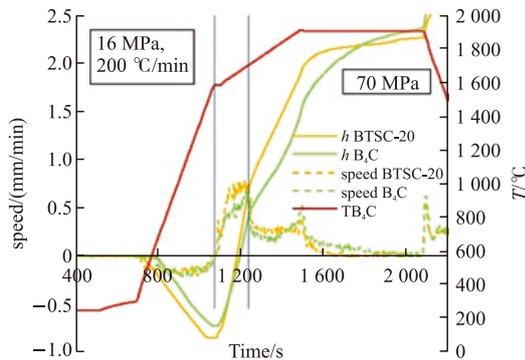


Fig.6 Shrinkage (h) and shrinkage rate (speed) for pure B_4C and BTSC-20 composite material at variable heating rate and compression pressure

Fig.6 illustrates the kinetic dependences for pure B_4C and BTSC20 composite material. There was an increase in pressing pressure to the working in the interval between the vertical lines. After using the working pressure (70 MPa, 1 700 °C), the shrinkage rate of pure B_4C increases above 1 820 °C and remains quite significant throughout the holding time. In case of BTSC20, the shrinkage rate remains almost constant up to a holding temperature of 1 900 °C, and the shrinkage during exposure is negligible. The difference in shrinkage's dependencies can be explained by the significant amount of TiB_2 formed due to the decay of the MAX phase. The shrinkage kinetics for BTSC10 (15)

composites are very similar to the kinetics of BTSC20, *i e*, the amount of TiB_2 formed by the decomposition of 10 vol% and 15 vol% Ti_3SiC_2 is sufficient to obtain a high material density at 1 900 °C, but at lower temperatures the more prolonged exposure is needed. The shrinkage kinetics of BTSC5 are intermediate, *i e*, the formed TiB_2 is insufficient to obtain a material with high density at the selected temperature (1 900 °C) and compression pressure (70 MPa).

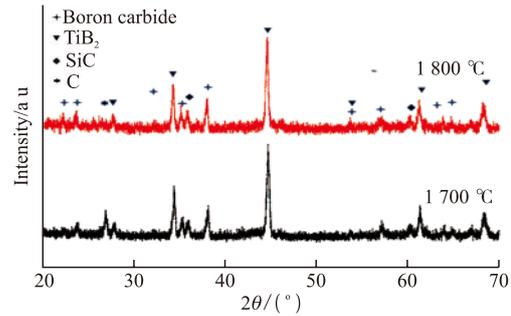


Fig.7 XRD patterns of BTSC20 sintered at 1 700 and 1 800 °C

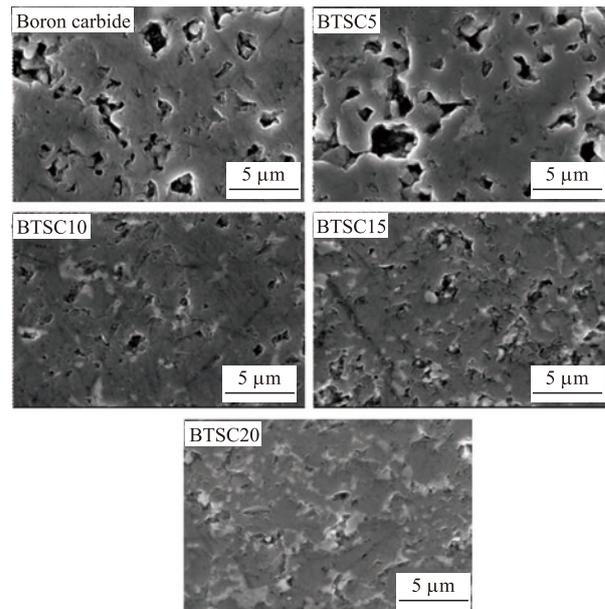
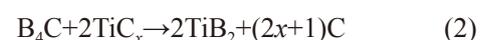


Fig.8 Microstructure images of polished surfaces for all samples sintered at 1 900 °C

Based on the XRD patterns and SPS data, the following reactions are predicted;



Unlike borides, carbides are non-stoichiometric with a wide range of nonmetal-to-metal concentration ratios^[16]. The decomposition of Ti_3SiC_2 to form TiC_x and Si (Reaction 1) around 1 450 °C is reported in

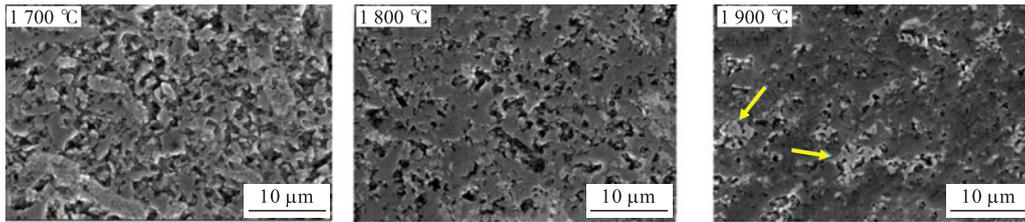


Fig.9 SEM images of the polished surface of BTSC20 sintered at different temperatures

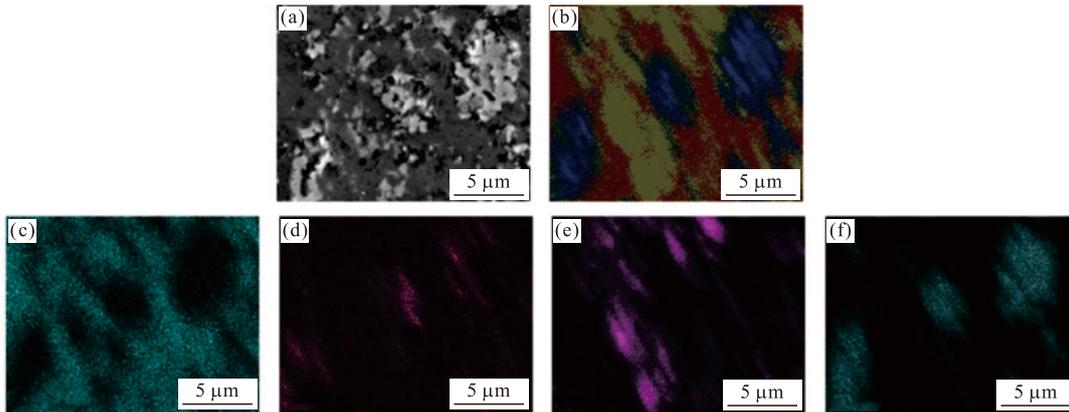


Fig.10 SEM EDX-Mapping analysis: (a) BSE image of BTSC20; (b) SEM-EDX mapping of the selected region; (c) B-atoms rich region; (d) C-atoms rich region; (e) Si-atoms rich region; (f) Ti-atoms rich region

various studies^[17]. TiC_x reacted with boron carbide by Reaction (2) and resulted in the TiB_2 phase. SiC phase formed through the reaction between Si and C and both were produced based on Reactions (1) and (2), respectively. Also, as mentioned before, free carbon exists in the as-received boron carbide.

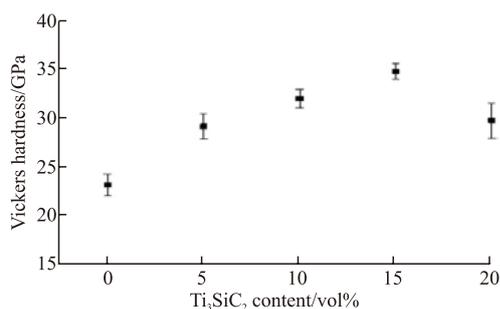


Fig.11 Vickers hardness variation as a function of the amount of Ti_3SiC_2 additive (densified at 1900 °C)

The microstructures of the polished surface of the samples sintered by SPS at 1900 °C are shown in Fig.8. As the amount of additive into boron carbide increased, the porosity decreased, as seen from the SEM images in Fig.8. Fig.9 displays the microstructure of boron carbide with 20% Ti_3SiC_2 ceramics densified at different temperatures. At higher temperatures with a higher amount of additive, the porosity is reduced.

In Fig.11, Vickers hardness values of all samples sintered at 1900 °C are presented. Boron carbide sample has low Vickers hardness due to its high porosity. The hardness value increased with 5 vol% Ti_3SiC_2 addition, but it is still low compared to 10 vol% and 15 vol% Ti_3SiC_2 addition due to higher porosity of BTSC5 sample than BTSC10 and BTSC15 samples, which can be seen from the microstructures of samples in Fig.8. Despite its high density compared to other samples, the hardness of BTSC20 decreased. Such behavior can be attributed to the aggregation of second phases, shown with arrows in the SEM images of BTSC20 sintered at 1900 °C in Fig.9. The chemical composition distribution is also displayed in BSE image and elemental mapping of the BTSC20-1900 °C sample in Fig.10.

4 Conclusions

$B_4C/TiB_2/SiC$ composites were synthesized using B_4C and Ti_3SiC_2 as starting powders. The reactive spark plasma sintering enabled producing highly dense boron carbide composite at relatively low temperatures. Increasing sintering temperature and additive amount led to ceramics with higher densities. The decomposition of the MAX phase and its reaction with B_4C during

heating under pressure may change the stoichiometry of B₄C, and this deficient structure causes an increase in the driving force for mass transport by changing diffusion kinetics. The hardness of samples increased with the Ti₃SiC₂ addition up to 15 vol%, and then decreased due to the agglomeration of second phases in the composite.

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Conflict of interest

All authors declare that there are no competing interests.

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