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In situ boron carbide–titanium diboride composites prepared by mechanical milling and subsequent Spark Plasma Sintering

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Abstract Boron carbide–titanium diboride composites were synthesized and consolidated by Spark Plasma Sintering (SPS) of mechanically milled elemental powder mixtures. The phase and microstructure evolution of the composites during sintering in the 1,200–1,700 °C temperature range was studied. With increasing sintering temperature, the phase formation of the samples was completed well before full density was achieved. The distribution of titanium diboride in the sintered samples was significantly improved with increasing milling time of the Ti–B–C powder mixtures. A bulk composite material of nearly full density, fine uniform microstructure, and increased fracture toughness was obtained by SPS at 1,700 °C. The grain size of boron carbide and titanium diboride in this material was 5–7 and 1–2 μm, respectively.

Introduction

The outstanding properties of boron carbide, such as extremely high hardness, chemical stability, and low specific weight, make it an attractive component for hard and wear-resistant materials. Being intrinsically brittle and difficult to sinter, boron carbide often requires different additives to improve its sintering behavior and mechanical properties [1–4]. The general trends in the development of boron carbide-based composites are aimed at the possibility of sintering such materials at temperatures lower than those required for single-phase boron carbide and obtaining higher fracture toughness and strength.

Titanium diboride has been proposed as a promising second phase for tailoring boron carbide properties [5–15]. Pairing boron carbide and titanium diboride in a composite can be beneficial for the design of thermoelectric materials [8, 13] and composites with increased fracture toughness and bending strength relative to pure boron carbide [6, 7, 9, 10, 12, 14, 15]. Also, titanium diboride was suggested as a possible grain growth inhibitor [5] for boron carbide. Several attempts have been made to develop boron carbide–titanium diboride composites by two major approaches: sintering boron carbide and titanium diboride powders [3, 5, 6, 13, 15], and in situ reactive sintering of boron carbide with additions of Ti, TiO_2 [9], or TiO_2 and carbon [7, 10–12, 14]. The mere addition of titanium diboride to boron carbide still creates difficult-to-sinter composites [3, 13]. Hot pressing of boron carbide with 20 vol.% of titanium diboride at 1,900 °C results in a material of 20% porosity [13]. Similarly, pressureless sintering of boron carbide with addition of 5 wt.% of titanium diboride retards densification even at a temperature as high as 2,375 °C, the resultant bulk composite materials having only 82% of theoretical density [3]. The work performed by Kim et al. demonstrates the possibility of consolidating boron carbide and titanium diboride powders by utilizing pressureless sintering; however, to achieve high densities, iron should be added to the composite [5]. The role of iron in the process is the formation of an iron-rich liquid phase during sintering, which makes enhanced densification possible. The drawbacks of this method are rapid grain

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growth due to the presence of the liquid phase during sintering and a concomitant decrease in the strength of the composite. Skorohkhod and Krstic [11] experimentally verified the significance of in situ formation of titanium diboride in a boron carbide matrix containing TiO_2 and free carbon. Though the in situ reaction of conversion of titania to titanium diboride was completed before the densification occurred, the densities of the samples formed by reactive sintering were higher than those of the samples consolidated from boron carbide and titanium diboride powders. Accordingly, the in situ formation of titanium diboride seems to enhance densification at lower temperatures.

In the present work, we suggest a new synthesis route for boron carbide–titanium diboride composites based on the in situ formation of both phases. This approach aims to achieve a more flexible microstructural control of the final materials. As confirmation of this approach, a study conducted by Anselmi-Tamburini et al. [16] showed the improvement in the final density during sintering of hafnium diboride when this compound was in situ synthesized during the sintering process. To simultaneously synthesize the composite from the elemental powders and consolidate it into a bulk material, we employed an advanced sintering technique, Spark Plasma Sintering (SPS), which allows fast and effective densification of ceramic materials [17, 18]. SPS is based on the application of pulsed electric current and pressure to the sample. The key advantage of this technique is achieving very high heating rates and short sintering times at a lower temperature compared to conventional sintering techniques, such as pressureless sintering or hot pressing. These features of SPS allow for the control of grain growth in a material during densification. To our best knowledge, no study has been performed on the fabrication of dense boron carbide–titanium diboride composites from the elemental powders. High-energy mechanical milling [19] was chosen for this study for the preparation of a powder precursor suitable for the subsequent reacting and consolidation. The goal of the present work was to study the phase formation and microstructure evolution during the SPS of boron carbide–titanium diboride in situ composites synthesized from mechanically milled Ti-B-C mixtures.

Experimental

Titanium (99.5%, −325 mesh, Alfa Aesar), amorphous boron (95–97%, submicron, Fluka, Sigma-Aldrich), and carbon black (99.99%, 42 nm, Alfa Aesar) powders were used as the raw materials. The contents of the elemental powders in the mixtures were calculated according to 23 vol.% TiB_2 and 77 vol.% $B_{4.5}C$ in the composite product. It is well known that boron carbide has a broad non-stoichiometry range (9–20 at.% C). The boron carbide synthesized in this work is close to the congruently melting composition [1].

Mechanical milling was conducted in a SPEX 8000 mill (SPEX CertiPrep, Metuchen, NJ) with a tungsten carbide ball and a tungsten carbide vial. The O-ring seals were used to firmly close the vial to prevent any ingress of air during milling. The powder mixture load in the milling vial was 2.5 and 5.0 g. The weight of the tungsten carbide ball was 10 g. The milling time was 4, 8, and 16 h. The mechanically milled powders were cold pressed at a pressure of 10 MPa, the green density of the samples being 50–55% of the theoretical density of the two-phase boron carbide–titanium diboride composite.

Spark Plasma Sintering was performed in a 1050 Dr. Sinter apparatus (Sumitomo Coal Mining Co., Japan). The heating rate was 200 °C/min from room temperature up to 600 °C and then the temperature was increased with a rate of 100–200 °C/min until a maximum temperature was reached. The direct current pulsing cycle was set at 12 pulses on and 2 off. The applied voltage at the maximum temperature was 4.3–5.5 V. The maximum current reached 1,300 A when the sample was heated up to 1,200 °C and 1,600–2,000 A when the temperature increased up to 1,700 °C. The holding time varied from 2 to 5 min at the maximum temperature. A graphite die and graphite punches were used. The weight of the powder loaded in the die was 0.85 g. To avoid interaction between the powder mixture components with the punches and the die, graphite foil was used. A unidirectional pressure of 50–100 MPa was applied during the SPS. For monitoring the temperature, an optical pyrometer was focused on a near-through hole in the wall of the die.

Fracture surfaces of the composites were obtained in mode I fracture by cleaving a partial diamond saw cut. To study the microstructure and phase distribution polished cross-sections of the samples were obtained. For this purpose, the sintered samples were cut using a diamond saw and then polished to a 1 μm diamond finish.

Archimedes' method was employed to measure the density of the sintered samples. Deionized water was used as the immersion liquid.

XRD phase analysis of the powder mixtures and the sintered samples was performed with a XDS 2000 X-ray diffractometer using Cu Kα radiation (Scintag Inc., Cupertino, CA, USA). Scanning electron microscopy (SEM) characterization of the powders and sintered composites was conducted with a FEI XL30-SFEG high-resolution scanning electron microscope (USA) using secondary electron and back-scattered electron (BSE) imaging.

Hardness and fracture toughness measurements were performed using a Wilson Tukon (American Chain &

Cable Company Inc., USA) hardness tester with a Vickers diamond indenter. The fracture toughness estimations from indentation crack lengths were done with the Anstis equation [20]. The elastic modulus of the composite was calculated according to the rule of mixtures based on the Voigt model. The values of 465 and 565 GPa for the elastic modulus of boron carbide and titanium diboride, respectively, were taken for the calculation. The fracture toughness was estimated for the fully dense sample.

Results and discussion

XRD patterns of the Ti-B-C mechanically milled mixtures are shown in Fig. 1. The reflections observed in the 17°–21° 2θ range are due to the presence of some crystalline boron as an admixture in the amorphous boron powder. The presence of tungsten carbide is due to contamination from the milling media and the vial walls. The amount of tungsten carbide increases with increasing milling time of the powders. Also, cubic boron oxide appears in the mixture upon milling for prolonged periods of time. As is seen from the XRD patterns, neither the titanium diboride nor boron carbide phase forms during the milling process. This result can be explained considering the following. The possibility for a combustion reaction during milling can be examined by the adiabatic temperature of the mixture, the same criterion used for the self-propagating high-temperature synthesis (SHS) [21]. If a reaction cannot occur in the SHS mode without pre-heating, it is also unlikely to initiate combustion in the mixture of reactants during milling. Titanium diboride is well known for its ability to be formed in the SHS mode starting from the elemental constituents [22]. Such a reaction, as expected, can be easily ignited during mechanical milling of the binary mixtures of the stoichiometric composition [23, 24]. However, the enthalpy of formation of boron carbide is relatively low [25] and, as a consequence, it is not considered as an SHS-compound. The study performed by Ramos et al. [26] shows that prolonged milling of B–C powder mixtures in a planetary Fritsch P-5 ball mill does not lead to formation of boron carbide; however, during the annealing at 1,200 °C the milled mixture does transform to boron carbide. Thus, the synthesis of boron carbide phase by mechanical milling could not be realized without the heating stage following milling. The powder composition studied in the present work can be described as a stoichiometric mixture of titanium and boron taken to produce titanium diboride highly "diluted" by boron and carbon black taken to form boron carbide. Therefore, at room temperature this mixture is not capable of an SHS reaction and is not likely to be ignited during milling. For the boron carbide–titanium diboride

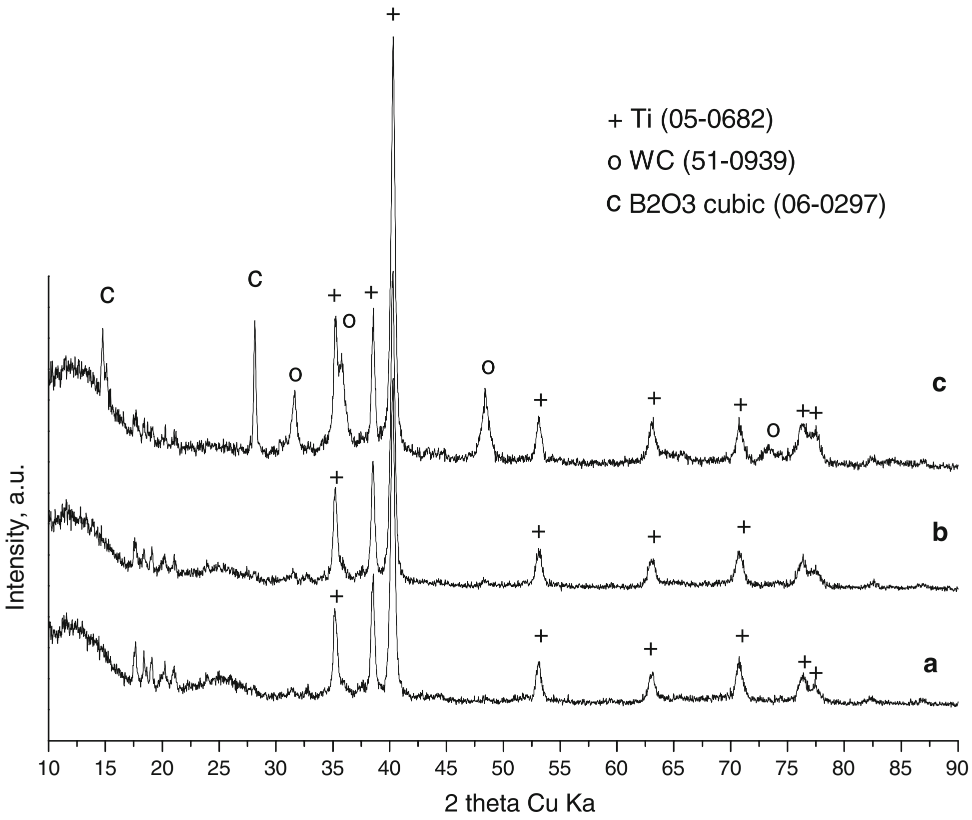


Fig. 1 XRD patterns of the Ti–B–C powder mixtures mechanically milled for: (**a**) 4 h, (**b**) 8 h, (**c**) 16 h (powder load 5.0 g)

composites formed from elements, Halverson et al. reported a series of experiments and thermodynamic calculations, establishing the necessary requirements for an SHS reaction [25]. The SHS mode of the reaction for the composition studied in the present work is possible only when the mixture is initially heated up to 1,200 K [25]. According to Takacs and McHenry, the ball temperature in a SPEX mill does not exceed 100 °C provided that no exothermic reaction takes place during milling [27]. Presumably, the local temperatures can be much higher; however, they do not cause the overall heating of the mixture up to temperatures required for the SHS to occur.

SEM images of the milled powders show that with increasing milling time the agglomerates grow in size from 40 to 60 μm after milling for 4 h to 60–100 μm after milling for 16 h; however, their fine microstructure remains basically unchanged: the particles ranging in size from 50 to 500 nm are present in the mixtures (Fig. 2).

The choice of the sintering temperatures was dictated by the goal of obtaining the fully reacted and consolidated composites. Anselmi-Tamburini et al. showed that in the mixtures of carbon black and amorphous boron, formation of boron carbide was nearly complete after sintering in the SPS at 1,200 °C; however, the densities higher than 90% could be achieved only after sintering at 1,700 °C [28]. In that study, the temperature was controlled by a thermocouple inserted in a hole drilled axially through the lower punch. Such a set-up ensured direct contact of the thermocouple with the bottom of the sample representing its true temperature. It was found experimentally that in the high-temperature range, the real temperature of the sample could be 200–250 °C higher than those measured by an optical pyrometer focused on the external wall of the die [16]. In the present work, the optical pyrometer used to monitor the temperature was focused on a near-through hole in the wall of the die. Taking this into account, one can assume that the real temperatures in the sample were approximately 100 °C higher than those recorded by the pyrometer. Considering the above and aiming at the goal for high-density composites, the Ti–B–C mechanically milled powders were sintered at the 1,600 and 1,700 °C temperatures. In the discussions of the results of the present work, the reported temperatures are pyrometer measured as was described in the experimental section. In a preliminary investigation, we did perform a number of lower-temperature SPS tests. In the sample heated in the SPS up to 1,000 °C, we still found unreacted titanium along with small amounts of boron carbide and titanium diboride. Since the stoichiometric mixture of titanium and boron with the mole ratio 1:2 was "diluted" by the excessive amount of boron and carbon, the reaction between titanium and boron did not proceed in an explosive, self-sustaining mode. Instead, one can assume that the reaction occurred gradually during sintering. The powder mixture was almost fully reacted to form boron carbide and titanium diboride at 1,200 °C (Fig. 3, the powders used in those experiments were milled for 4 h at 2.5 g powder load). This observation is in good agreement with previous results on the synthesis of pure boron carbide by SPS [28]. Small amounts of phases other than boron carbide or titanium diboride are

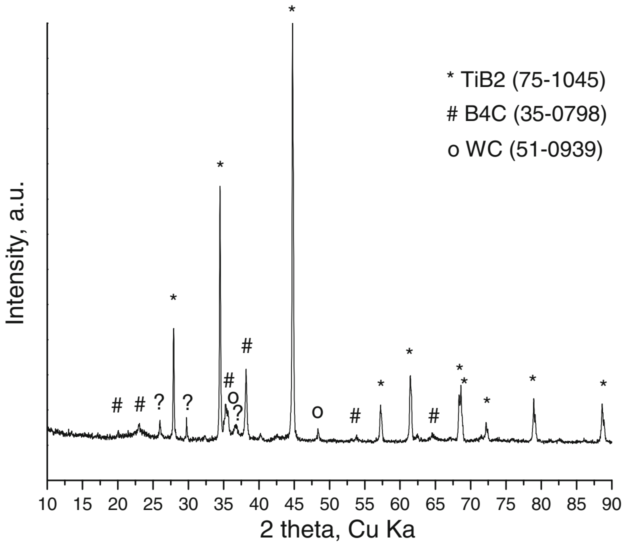


Fig. 3 XRD pattern of the boron carbide–titanium diboride composite sintered at 1,200 °C (milled for 4 h, powder load 2.5 g)

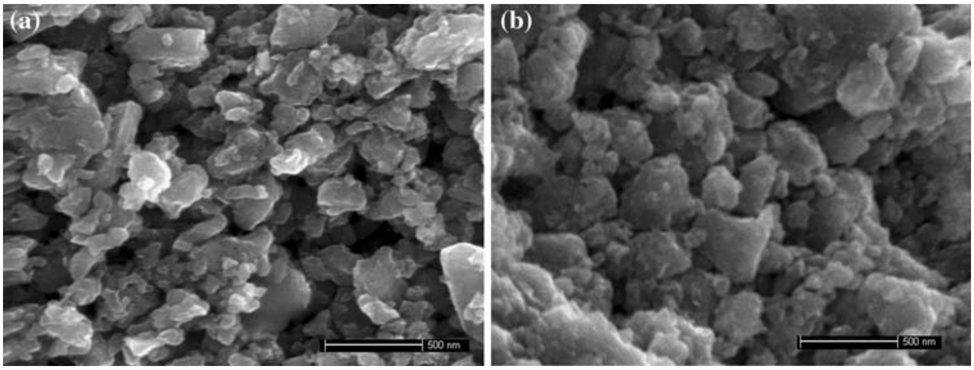


Fig. 2 Microstructure of the Ti–B–C powder mixtures mechanically milled for: (**a**) 4 h; (**b**) 16 h (powder load 5.0 g)

present in the sample; however, they decompose or react with increasing sintering temperature and are no longer found in the samples sintered at higher temperatures. The sample sintered at 1,200 °C was only 84% dense and at 1,000 °C the densification did not occur at all. To reduce tungsten carbide contamination in the dense composites, higher-temperature SPS tests reported below were performed on the samples milled at 5.0 g powder load.

XRD patterns of the samples sintered at 1,600 and 1,700 °C show the presence of the two phases in the composite (Fig. 4). In the sample sintered at 1,700 °C boron carbide is well crystallized. It is worth mentioning that tungsten carbide phase is absent in the XRD patterns of the samples sintered at 1,600–1,700 °C though it is present in the milled powders (Fig. 1) and after sintering at 1,200 °C (Fig. 3). At temperatures higher than 1,100 °C [29] boron carbide reacts with tungsten carbide to form tungsten boride W_2B_5 and carbon:

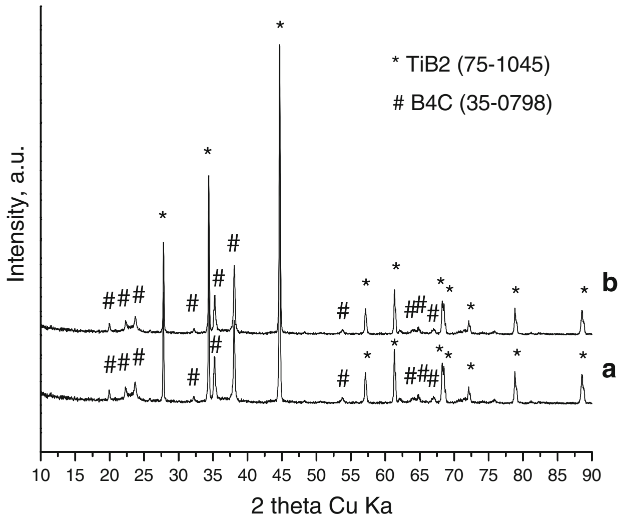


Fig. 4 XRD patterns of the boron carbide–titanium diboride composite sintered at: (**a**) 1,600 °C (milled for 4 h), (**b**) 1,700 °C (milled for 16 h)

Table 1 Relative density and hardness of the SPS-ed B_4C-TiB_2 samples sintered at different conditions

Milling time, h	Maximum SPS-temperature (°C)	Heating rate (°C min^{-1})	Holding time (min)	Pressure (MPa)	Relative density (%)	Hardness (kg mm^{-2})
4	1,600	100	2	50	90.6	–
4	1,700	100	2	100	95.3	2,359
8	1,700	100	2	100	96.2	1,949
16	1,700	200	5	100	>99	2,117

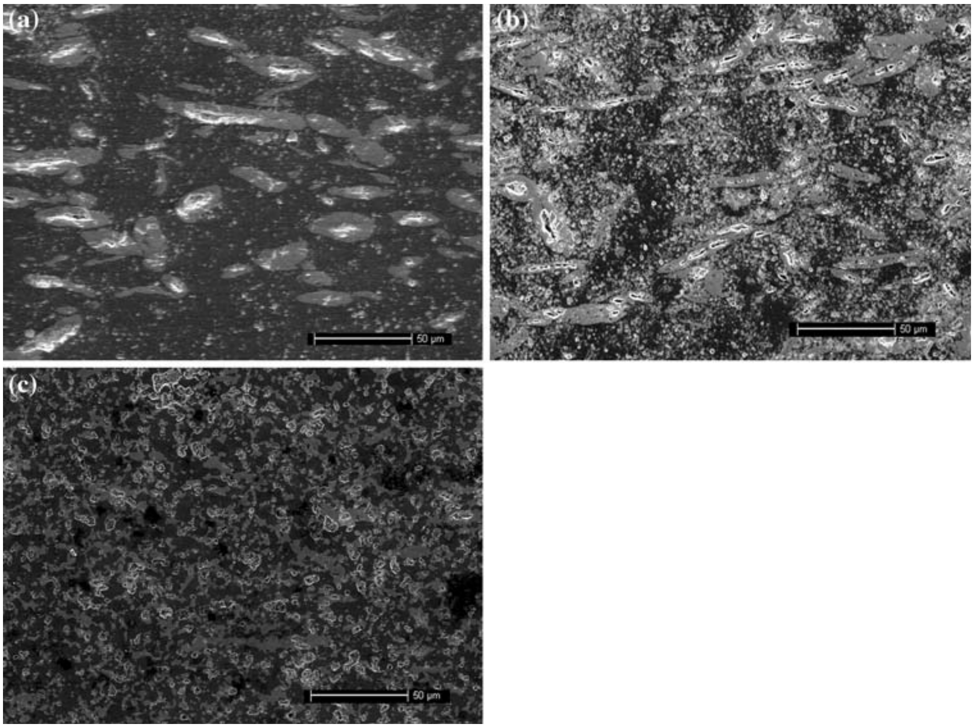
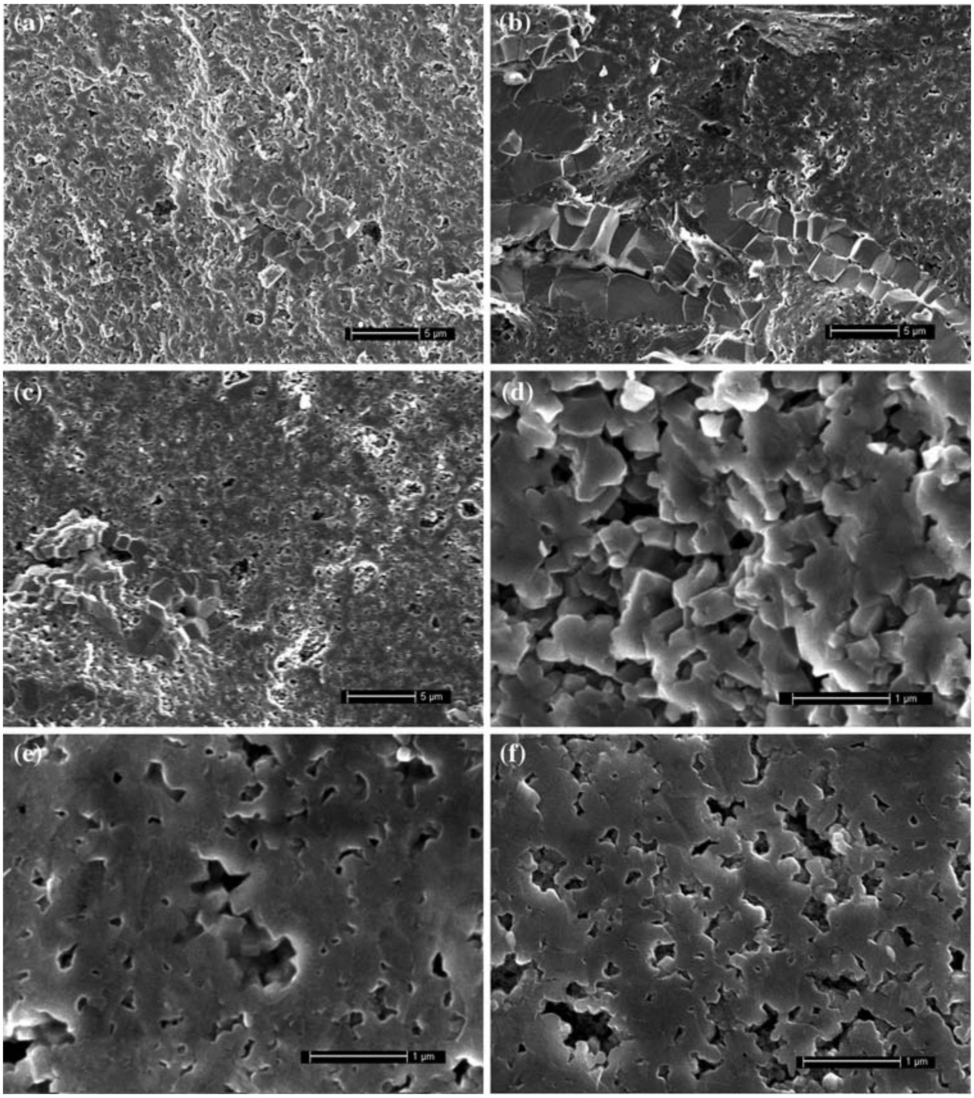


Fig. 5 Cross-section of the sintered boron carbide–titanium diboride composites (pressing direction is vertical relative to the page): (**a**) milled for 4 h, sintered at 1,600 °C; (**b**) milled for 8 h, sintered at 1,700 °C; (**c**) milled for 16 h, sintered at 1,700 °C

Fig. 6 Fracture surface of the boron carbide–titanium diboride sintered composites showing titanium diboride agglomeration (**a**–**c**) and boron carbide-rich areas (**d**–**f**) (pressing direction is vertical relative to the page): (**a**, **d**) milled for 4 h, sintered at 1,600 °C; (**b**, **e**) milled for 4 h, sintered at 1,700 °C; (**c**, **f**) milled for 8 h, sintered at 1,700 °C



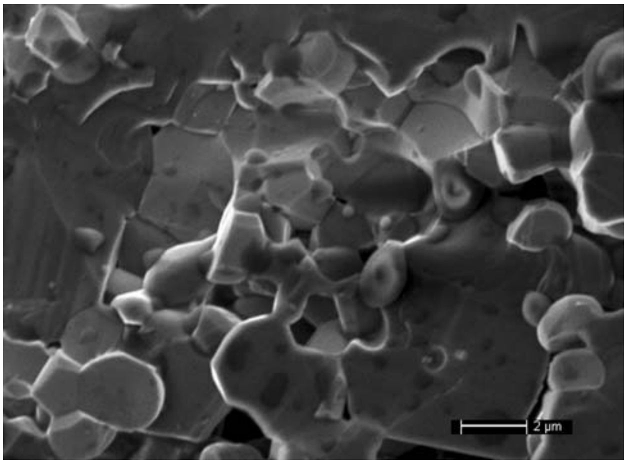


Fig. 7 Fracture surface of the nearly fully dense boron carbide–titanium diboride sintered composite (milled for 16 h, sintered at 1,700 °C. Pressing direction is vertical relative to the page)

$B_4C + WC = W_2B_5 + C.$

Since the initial stoichiometry of boron carbide was a little shifted from B_4C to boron-enriched composition, residual carbon will not remain in the sintered samples. The reason tungsten boride phase does not appear on the XRD patterns is the formation of (Ti, W)B_2 solid solutions during sintering. They exhibit a crystallographic structure of titanium diboride [30, 31] and very close lattice parameters due to small difference in the atomic radii of Ti and W.

The densities of the samples sintered at 1,600 and 1,700 °C are presented in Table 1. It can be seen that the samples of more than 95% theoretical density can be obtained after sintering at 1,700 °C. The SEM images of the cross-sections of the composites are shown in Fig. 5. Severe agglomeration of titanium diboride is seen in the sample milled for 4 and 8 h, while a substantially improved dispersion of titanium diboride is observed in the sample milled for 16 h apparently due to better dispersion of titanium in the mixtures prior to sintering. The correspondence of the bright phase on the SEM micrographs to titanium diboride was confirmed by the BSE imaging. The microstructural evolution of the composites can also be traced from the fracture surface of the sintered samples (Fig. 6). The agglomerates of titanium diboride appear as areas consisting of poorly sintered faceted particles 1 μm–2 μm in size or larger (Fig. 6a–c). In the areas where large titanium diboride agglomerates are present, the fracture occurs in the intergranular mode. These agglomerates seem to comprise a disproportionate part of the porosity of the composites. To eliminate the porosity of the material, the distribution of titanium diboride should be more uniform, which can be achieved by using prolonged mechanical milling of the pre-reacted mixtures. In reactive sintering of boron carbide from the elemental constituents, the improvement in the final density with increasing preliminary mechanical milling time was observed by Heian et al. [32]. In the present work, the role of mechanical milling becomes even more important since it helps disperse titanium in the Ti–B–C mixtures. As a result, the problem of agglomeration of titanium diboride particles can be overcome in the final sintered composite. Fig. 6d–f shows the boron carbide-rich areas, which consist of 300–500 nm grains. With increasing sintering temperature it becomes denser so that in the boron carbide-rich areas the fracture occurs in a transgranular fashion. Fig. 7 reveals the fracture surface of the nearly fully dense material, which consists of titanium diboride grains 1–2 μm in size uniformly distributed among the boron carbide grains of 5–7 μm. So, prolonged mechanical milling was advantageous for the development of a more uniform microstructure. The growth of boron carbide grains is due to holding the sample at a high temperature during the SPS.

As can be seem from Table 1, the hardness of the composites is lower than the value calculated from the rule of mixtures. According to Gusev [33], the composition studied in this work is close to the pseudobinary eutectic $B_{4.5}C$-TiB_2. The reduced hardness of the eutectic compositions of ceramic compounds was observed earlier by other researchers [34]. However, those compositions were found to exhibit elevated resistance to brittle fracture and crack resistance. Indeed, as was estimated from the indentation measurements, the sample sintered to full density showed a relatively remarkable fracture toughness of 5.9 MPa $m^{1/2}$ as compared to monolithic boron carbide, which has a fracture toughness ranging from 2.9 to 3.7 MPa $m^{1/2}$ [1]. The 5.9 MPa $m^{1/2}$ value is in good agreement with the results obtained by Skorokhod et al. [10] for hot-pressed B_4C–TiB_2. So, the processing developed in this study is suitable for the preparation of fine-grained high toughness boron carbide–titanium diboride composites. By using elemental powders in conjunction with mechanical milling and SPS it is possible to control the microstructure, grain size, and fracture behavior of boron carbide–titanium diboride composites.

Conclusions

The present study showed that the combination of high-energy mechanical milling and Spark Plasma Sintering is a promising route for preparation of fine-grained in situ composites in the boron carbide–titanium diboride system. Neither B_4C nor TiB_2 was formed during milling. The reason for the lack of the reaction between titanium and boron during milling is the “dilution” of the mixture by boron and carbon taken to form boron carbide. No phases other than B_4C or TiB_2 were detected in the samples sintered at 1,600–1,700 °C SPS temperatures. The density of the sintered composites increased with sintering temperature. Densities higher than 95% were obtained at SPS temperatures as high as 1,700 °C. Increasing the time of mechanical milling helped significantly improve the distribution of titanium diboride in the sintered composites. The nearly fully dense material obtained in this study consisted of titanium diboride grains 1–2 μm in size uniformly distributed among the boron carbide grains of 5–7 μm. The sintered fully dense composite showed an increase in fracture toughness (5.9 MPa $m^{1/2}$) compared to monolithic boron carbide.

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