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RESEARCH

Conventional and two-step sintering of boron carbide ceramics with a sintering additive

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Abstract

Sintering refers to the consolidation of particulate matter into dense solids. Boron carbide is a material of choice for a wide variety of engineering applications, due to its unique properties. On the other hand, it is a highly covalent non-oxide ceramic, which has low diffusivity. Densification of boron carbide via thermally activated process is extremely hard and requires additional driving forces. In this study, the production of boron carbide with 0–20% Ti_3SiC_2 by both single-step and two-step pressureless sintering was investigated. The resultant ceramics were subjected to density measurement and microstructure and phase characterization. Boron carbide samples with 20 vol% Ti_3SiC_2, which were held 3 h at 1750 °C, yield ~ 81% density regardless of the number of sintering steps. Ti_3SiC_2 additive resulted in the formation of boron carbide–based composite with TiB_2 and SiC phases in all experiments.

Keywords Densification · Boron carbide · Sintering additive · MAX phase

Introduction

Boron carbide is a prominent ceramic in the defense industry and advanced technology applications due to its high melting temperature (2700 °C), high hardness (~ 30GPa), low density (2.52 g/cm^3), high chemical resistance, and good neutron absorption. However, its covalent bond causes low atomic mobility (diffusivity), making the densification of boron carbide by thermally activated processes very difficult, and that limits its widespread usage. Also, low fracture toughness (3.5 MPa.m$^{1/2}$) makes boron carbide industrially disadvantageous [1–4]. Boron carbide dense pellets are commercially produced by pressureless sintering and hot press (HP). Sintering temperatures can be reduced below 2000 °C with the spark plasma sintering (SPS) technique, one of the electric field–assisted sintering methods. However, SPS is not very convenient for commercial use due to its high investment cost. Moreover, both SPS and HP limit the sample geometry due to the use of a die. As mentioned above, high densification temperatures (≥ 2000 °C) and long processes (hours) are required for the pressureless sintering techniques. However, it is a more economical and straightforward process than other sintering methods and has the advantage of fabrication complex shapes [5–9].

A decrease in the sintering temperature of boron carbide was observed (1750–1900 °C) by decelerating the grain growth with sintering additives. In order to reduce the sintering temperature of boron carbide, carbon, metallic phases (Al, Si, Ti), and oxide phases (ZrO_2, Al_2O_3) were used [10–12].

The addition of boride and carbide phases (such as TiB_2 and SiC) in boron carbide leads to the formation of boron carbide–based composites. Studies show that the addition of the second phase could activate a toughening mechanism, which improves the sinterability and mechanical properties of ceramics. Studies on B_4C/TiB_2 composites have shown that fracture toughness of composites (3–6 MPa m$^{1/2}$) are higher compared to boron carbide (3.5 MPa m$^{1/2}$). Tan et al. have carried out a study with the addition of Ti_3AlC_2 phase, one of the MAX phases, into boron carbide. They showed

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that the 15% Ti_3AlC_2 additive significantly increased the mechanical properties of boron carbide, Vickers hardness of 40.2 GPa, and fracture toughness of 4.7 MPa $m^{1/2}$ [13–15].

Carbides are very hard materials and have good wear and oxidation resistance. Powder forming technologies are often used in the manufacture of these materials. Forming processes of carbides often requires high temperatures and pressure assistance. Studies on the production of carbides showed that the presence of the reinforcing phases promote densification and improve mechanical properties. Recently, new materials, produced using metal and ceramics together, attract attention in many application areas. The most important point in these materials is the interaction between metal and ceramic. Ternary metal carbides are excellent example for this new materials group [16, 17]. Ti_3SiC_2, a ternary carbide phase (MAX phase), has low density (4.5 g/cm^3), high oxidation resistance, and better thermal and electrical conductivity than titanium. Despite the carbide in its structure, its hardness is very low (~4GPa), but it has good fracture toughness (~8 $MPa^{1/2}$) compared to boron carbide [18, 19].

In this study, the pressureless sintering behavior of boron carbide with Ti_3SiC_2 phase will be investigated. As the density of boron carbide reaches low densities with pressureless sintering at temperatures below 2000 °C, the method called two-step sintering (TSS) was also applied for comparison with single-step sintering (SSS). The studies with high-temperature ceramics by two-step sintering are presented in the literature and show that it is a promising method for obtaining high density and smaller grain sizes for high-temperature non-oxide ceramics [20–22].

Materials and methods

Boron carbide ceramics were produced using commercial powders: B_4C powders (< 10 µm, 98%; HC Starck) and Ti_3SiC_2 powders (%99; Kanthal, Sweden). The XRD patterns of powders are displayed in Fig. 1. Ti_3SiC_2 of 5–20 vol% were mixed with boron carbide (SiC balls as grinding media) in ethanol for 5 h by ball milling, then dried at 80 °C for 36 h and sieved through 200 mesh sieve. The homogeneously mixed powders were pressed by uniaxial pressing into disc-shaped with a diameter of 10 mm.

A high-temperature tube furnace (Protherm, ≤ 1800 °C) was used for the sintering process. The heating rate was 5 °C/min, and Ar gas was used for preventing oxidation.

The densification parameters are graphically explained in Fig. 2 and tabulated in Table 1. Two different routes for two-step sintering have been conducted. One of them starts with lower temperature (1550 °C) pretreatment, followed by a second stage at elevated temperature (1750 °C). It is proposed that pretreatment retards the abnormal grain growth in the early stage of sintering and thus helps the formation of homogenous microstructure in the end. The second one is the relatively new one; the sample is heated to a high temperature (1750 °C) and immediately after cooled and kept at a lower temperature (1550 °C). This technique is also based upon suppressing grain growth. Using lower temperature in the second stage, it has been reported that smaller grains are obtained after densification [23–25].

Archimedes method was used for determining the densities of the samples. The crystallographic phases were characterized by X-ray diffraction (XRD, PANALYTICAL-EMPYREAN) using copper Kα radiation. The micrographs of fractured surfaces for specimens were determined by scanning electron microscopy (SEM, Nova).

Results and discussion

The densities of samples are shown in Fig. 3. The densities of the samples increased with the increase of MAX phase addition for all sintering processes. The maximum density of ~81% was obtained when the samples were kept 3 h at 1750 °C whether it is a single- or two-step sintering. Preheating process at 1550 °C during the TSS-T3-3 experiment

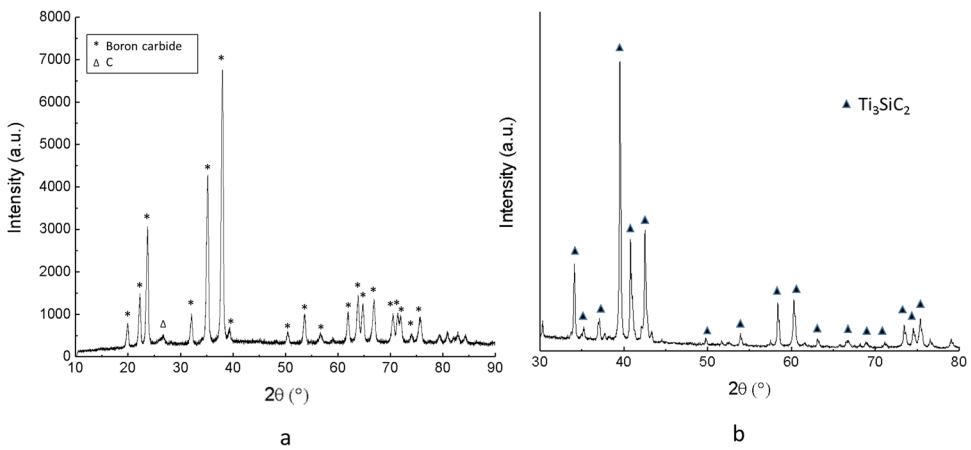

Fig. 1 XRD patterns of boron carbide (**a**) and Ti_3SiC_2 (**b**)

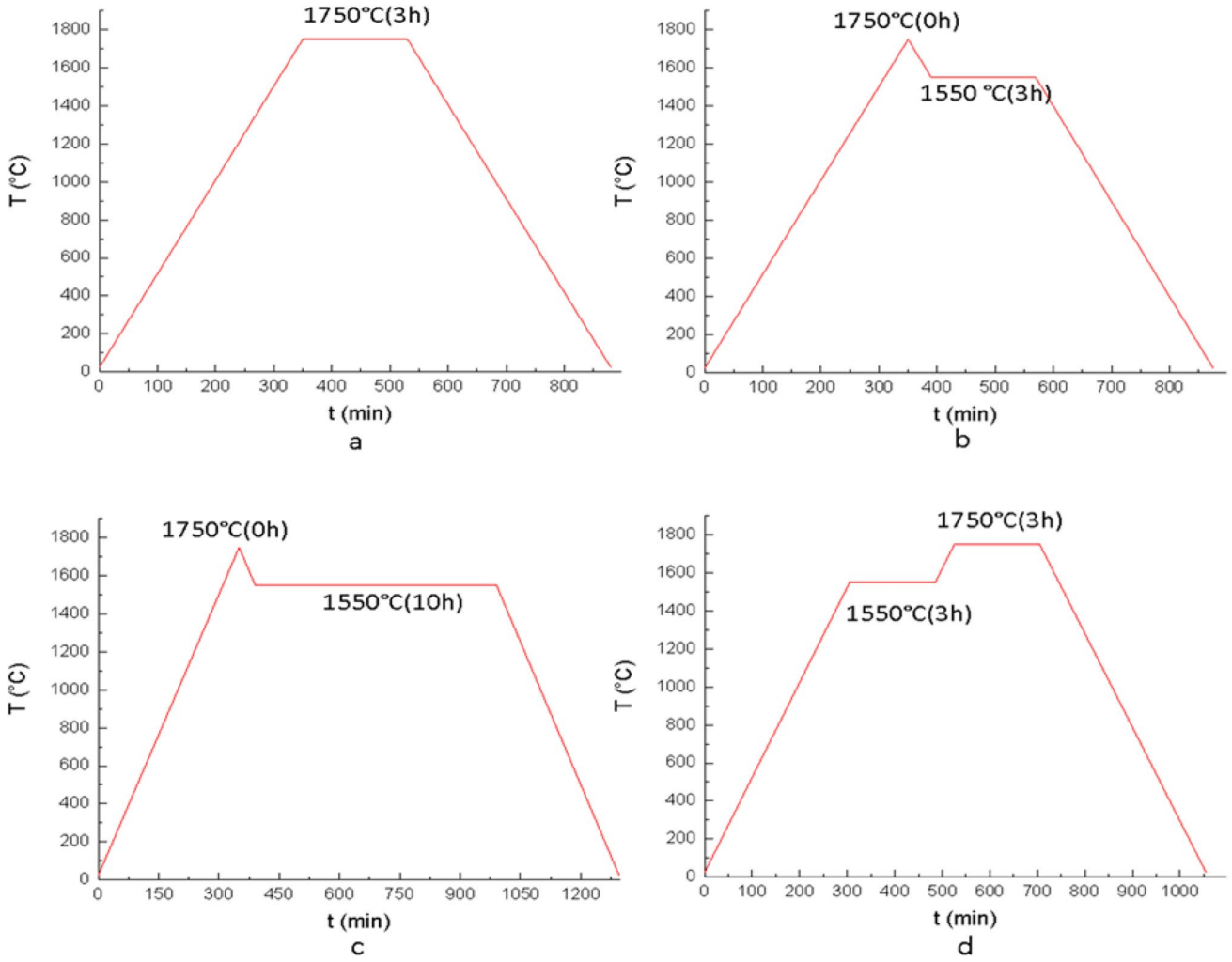

Fig. 2 The graphical description of densification parameters of single-step sintering (**a**), TSS-T0-3 (**b**), and TSS-T0-10 (**c**), and TSS-T3-3 (**d**)

Table 1 Designation for sintering condition

Designation	Temperature 1 (°C)	Holding Time 1 (h)	Temperature 2 (°C)	Holding time 2 (h)
SSS-T3	1750	3	-	-
TSS-T0-3	1750	0	1550	3
TSS-T0-10	1750	0	1550	10
TSS-T3-3	1550	3	1750	3

did not cause a change in density. TSS-T0-3 and TSS-T0-10 samples could not reach the same densities as single-step sintering and remained at maximum density of ~ 76%. Although the holding time at 1550 °C was increased from 3 to 10 h, such increase also did not contribute to the density of the samples. Overall, the density results show that sintering additive contributed the density of samples, while two-step sintering did not.

In Fig. 4, XRD patterns of samples with the highest density values for each experimental condition are displayed. XRD patterns of boron carbide with 20 vol% Ti_3SiC_2 ceramics for each experiment exhibit the formation of composite materials consisting of three different phases. However, the Ti_3SiC_2 peak was not observed, indicating that Ti_3SiC_2 was completely decomposed at high temperatures used in this study. B_4C matrix composite with the formation of secondary phases of TiB_2 and SiC exists in the final structure. The reactive sintering occurs in all experimental conditions and contributes to the sintering of boron carbide.

Based on observed phase composition, the following reactions are predicted:

$$Ti_3SiC_2 \rightarrow Ti_3C_2 + Si \quad (1)$$

$$Ti_3C_2 \rightarrow 3TiC_{2/3} \quad (2)$$

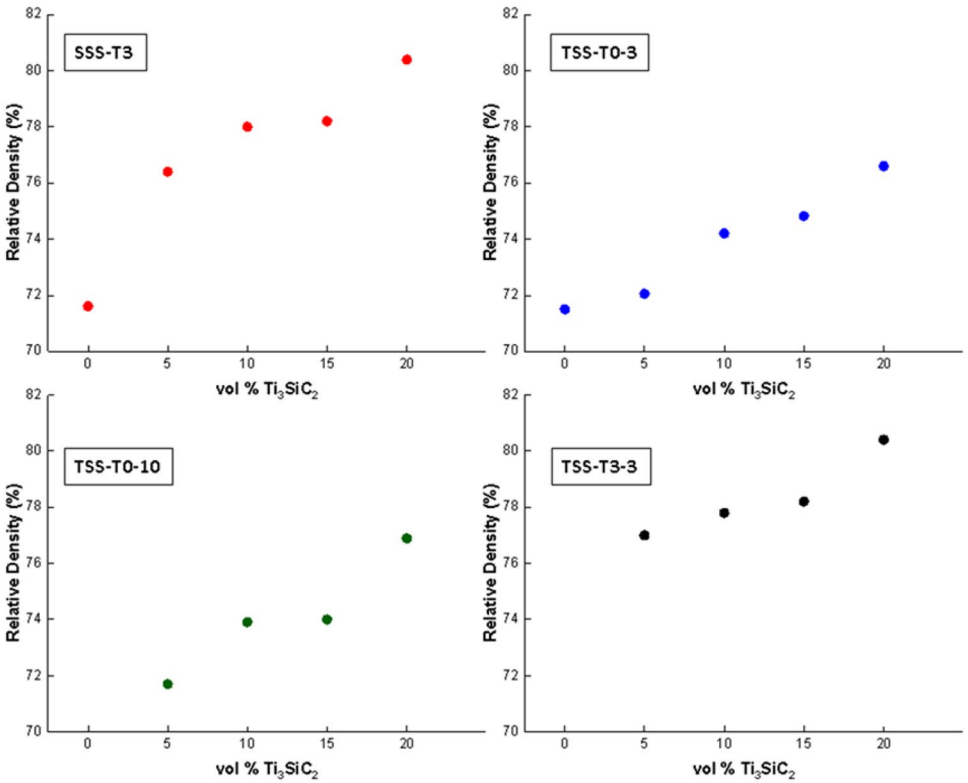

Fig. 3 The densities of samples as a function of vol% Ti_3SiC_2 for single-step sintering (**a**), TSS-T0-3 (**b**), and TSS-T0-10 (**c**), and TSS-T3-3 (**d**) experiments

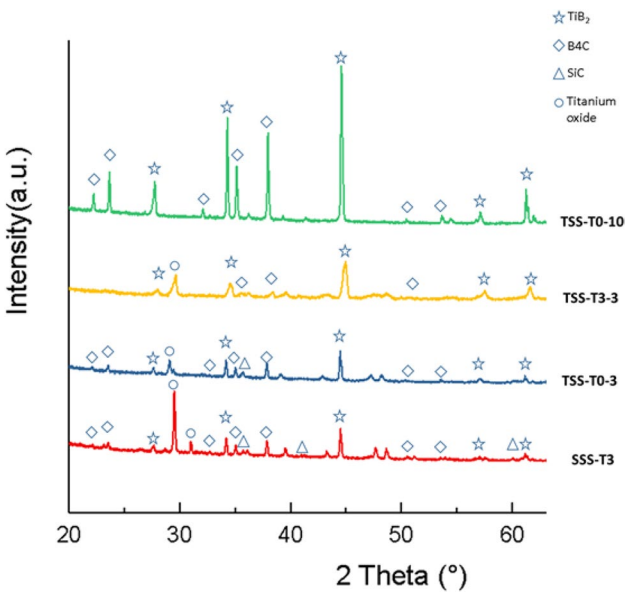

Fig. 4 The XRD patterns of boron carbide with 20 vol% Ti_3SiC_2 for each experiment

$$B_4C + 6TiC_{2/3} \rightarrow 6TiB_2 + 7C \quad (3)$$

$$Si + C \rightarrow SiC \quad (4)$$

The binary carbides (SiC, TiC) and the binary silicides (TiSi, $TiSi_2$, Ti_5Si_3) present in the Ti-Si–C phase diagram represented below 1300 K. At elevated temperatures, the formation of Ti_3C_2 phase and loss of Si from the structure occur, because Si-Ti bonds are weaker than Ti-C bonds. Moreover, Ti_3SiC_2 is chemically stable up to 1600 °C, but its resistance to carburization is low above this temperature. Carbon, from graphite pot or from boron carbide, diffuses into ternary carbide structure and leads to the growth of TiC layers with the loss of Si [26, 27].

Figure 5 shows the microstructure images of the fractured surfaces of the sintered samples for single-step sintering. The formation of particle–particle contact in the samples with Ti_3SiC_2 additives compared to boron carbide sample was observed. However, no significant change of the relative density was observed from microstructures of samples except for the one with 20 vol% Ti_3SiC_2 additive. In the microstructure, the matrix is boron carbide and the light gray is TiB_2, and the gray phase is SiC.

Density values for the samples with 20 vol% additive are in the range of 76–81%. As can be seen from the microstructures in Fig. 6, the densification of each sample is low. SEM images also confirm the higher density of the samples produced in the SSS-T3 and TSS-T3-3 processes. Elemental mapping of TSS-T3-3 sample (20 vol% Ti_3SiC_2) was also performed and presented in Fig. 7 using high-resolution FESEM. The presence of a small amount of oxide confirms the formation of oxide in the sample (bright area in the oxygen map). The distribution of elements is not entirely uniform and there are regions deficient of Ti or Si

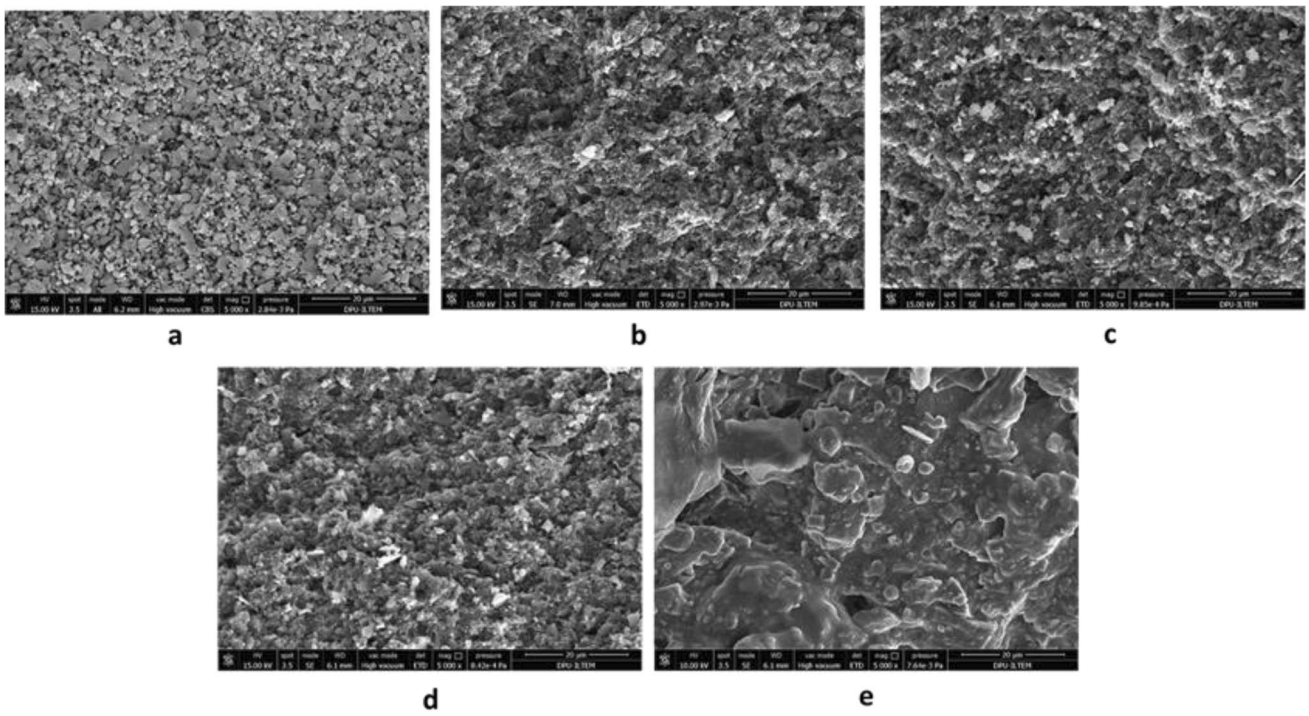

Fig. 5 The microstructure of boron carbide(**a**), boron carbide with **b** 5 vol% Ti_3SiC_2, **c** 10vol% Ti_3SiC_2, **d** 15vol% Ti_3SiC_2, and **e** 20vol% Ti_3SiC_2. All samples are densified with single-step sintering at 1750 °C, 3 h

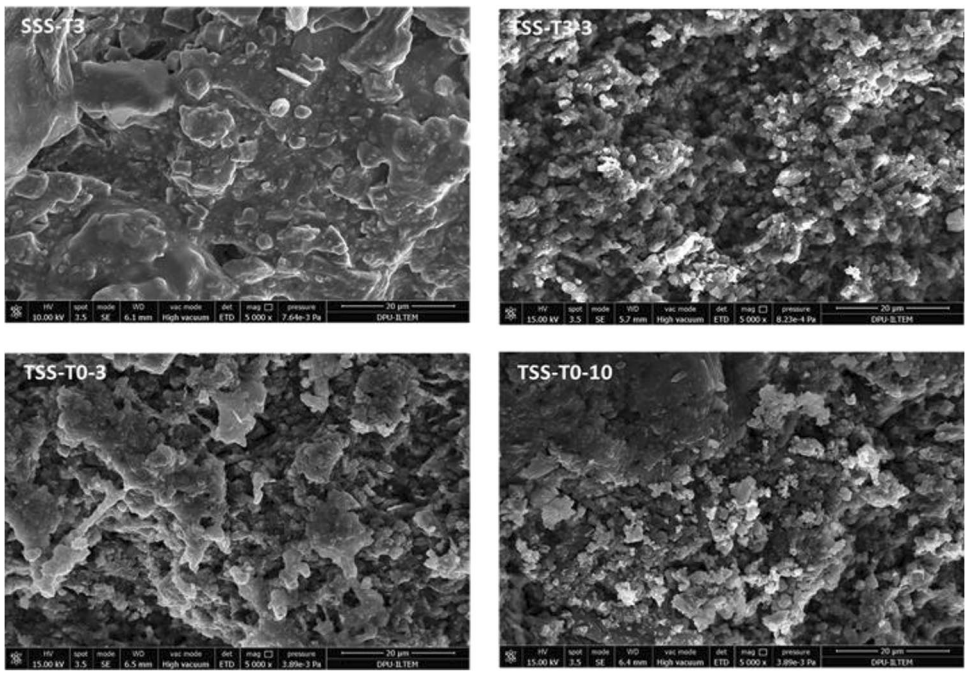

Fig. 6 Microstructure images of 20 vol% Ti_3SiC_2 added boron carbide powders are shown for each experimental condition

confirming the existence of different phases in the boron carbide matrix.

Although the density has been increased with the amount of additive, it is still challenging to sinter boron carbide ceramics with a solely temperature-based process. Due to low densification, mechanical properties of samples have not been analyzed. Different sintering techniques (HP, SPS) can be used to determine the effect of Ti_3SiC_2 additive on the mechanical properties of boron carbide.

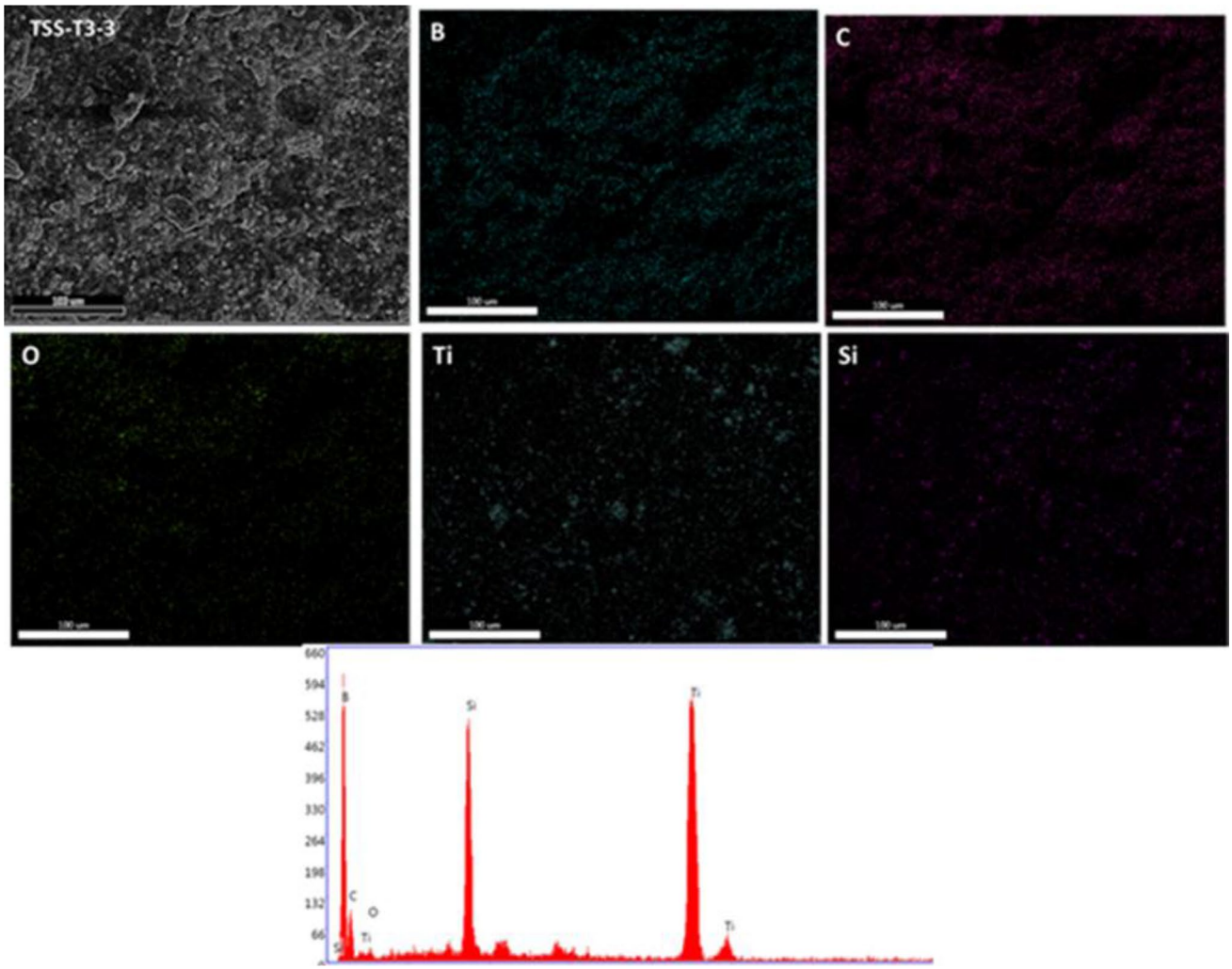

Fig.7 The elemental mapping of 20% Ti_3SiC_2 added boron carbide sintered by TSS-T3-3 process for all elements (B, C, O, Ti, and Si)

Conclusion

Ti_3SiC_2 addition into boron carbide produced boron carbide matrix with TiB_2 and SiC composites. The two-step sintering process makes no difference in the density of ceramic bodies, whereas the amount of additive did. Addition of 20 vol% Ti_3SiC_2 into boron carbide results in density as high as 81%. Such density is only achieved where the sample is held 3 h at 1750 °C.

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