

Article

Effect of Additive Ti_3SiC_2 Content on the Mechanical Properties of B_4C – TiB_2 Composites Ceramics Sintered by Spark Plasma Sintering

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Abstract: B_4C – TiB_2 composite ceramics with ultra-high fracture toughness were successfully prepared via spark plasma sintering (SPS) at 1900 °C using B_4C and Ti_3SiC_2 as raw materials. The results showed that compared with pure B_4C ceramics sintered by SPS, the hardness of B_4C – TiB_2 composite ceramics was decreased, but the flexural strength and fracture toughness were significantly improved; the fracture toughness especially was greatly improved. When the content of Ti_3SiC_2 was 30 vol.%, the B_4C – TiB_2 composite ceramic had the best comprehensive mechanical properties: hardness, bending strength and fracture toughness were 27.28 GPa, 405.11 MPa and $18.94 \text{ MPa}\cdot\text{m}^{1/2}$, respectively. The fracture mode of the B_4C – TiB_2 composite ceramics was a mixture of transgranular fracture and intergranular fracture. Two main reasons for the ultra-high fracture toughness were the existence of lamellar graphite at the grain boundary, and the formation of a three-dimensional interpenetrating network covering the whole composite.

Keywords: spark plasma sintering; boron carbide; Ti_3SiC_2 ; fracture toughness

1. Introduction

Boron carbide is an attractive engineering material with a high melting point, low density, high hardness, high thermal conductivity and a large neutron absorption surface, which makes it a candidate material for wear-resistant parts, cutting tools, light armor products and neutron radiation shielding [1,2]. However, its low sintering property (due to the strong B–C covalent bond and B_2O_3 oxide layer) and poor fracture toughness limits its excellent performance. Spark plasma sintering (SPS) is a kind of electric current-assisted sintering technology, which can enhance the bonding and densification of particles through the combination of mechanical pressure, an electric field and a thermal field [3,4]. SPS adopts the same stamping/die system concept as hot pressing, although the heating methods are fundamentally different. Hot pressing sintering is heated by heater radiation, while the SPS heat source is Joule heat generated by the current of the mold or sample [5,6]. A heating rate of up to 1000 °C/min can be obtained by SPS, and the heating-up time is greatly shortened, which is beneficial to limit the grain growth [7]. In addition, currents can also enhance powder sintering by activating one or more parallel mechanisms, such as surface oxide removal, electromigration and electroplasticity [8].

Reasonable use of additives can stimulate boron carbide densification without any deterioration of mechanical properties. Some additives can react with boron carbide in situ to form nonvolatile second phases, which is helpful for densification and can enhance properties. Ti_3SiC_2 can react with B_4C to form TiB_2 with high hardness and a high melting point, which can be used as an ideal toughening phase for B_4C ceramics [9]. In this study, B_4C – TiB_2 composite ceramics with ultra-high toughness were prepared by the SPS process with different contents of Ti_3SiC_2 as additives, and the influence mechanism of Ti_3SiC_2 content on the microstructure and properties of B_4C – TiB_2 composite ceramics was studied.

2. Experimental Procedure

Commercially available B_4C powders (purity 99.9%, 1 μm , 4.53 g/cm^3 , Nangong Naiyate Alloy Welding Material Co., Ltd., Nangong, China) and Ti_3SiC_2 powders (purity 99.9%, <74 μm , 4.53 g/cm^3 , Nanjing Mingchang New Material Co., Ltd., Nanjing, China) were used as raw materials. Ti_3SiC_2 – B_4C powders containing 20 vol.%, 25 vol.%, 30 vol.% and 35 vol.% Ti_3SiC_2 , respectively, were mixed for 24 h through a small vertical mixer at 80 r/min without adding solvent. Samples were prepared by SPS equipment (HP D 25/4-SD, FCT Systeme GmbH, Frankenblick, Germany) in a vacuum with 35 MPa mechanical pressure at 1900 °C for 5 min. The heating rate was 100 °C/min and the cooling rate was 50 °C/min.

The absolute density of B_4C – TiB_2 composite ceramics was determined using the Archimedes method. Hardness was measured by a Vickers indentation tester (HMV-2TADW E, Shimadzu, Kyoto, Japan) at a 9.81 N load with a holding time of 15 s on the polished surface. Flexural strength was determined by a three-point bending test with a span of 30 mm and a loading speed of 0.5 mm/min, and the specimens used in the test were 3 mm $\times$ 4 mm $\times$ 35 mm bars. The SENB (Single-Edge Notched Beam) method was used to determine the fracture toughness of the specimens, with dimensions of 2 mm $\times$ 4 mm $\times$ 20 mm (with 2 mm high notch). The microstructures of the composite ceramics were characterized by X-Ray powder diffraction (XRD, X' Pert PRO-MPD, Holland Panalytical, Almelo, Netherlands), scanning electron microscope (SEM, S-4800N, Hitachi, Tokyo, Japan), transmission electron microscope (TEM, JEM-2100, JEOL, Tokyo, Japan) and energy dispersive spectrometer (EDS, INCA, OXFORD INSTRUMENTS, Oxford, UK).

3. Results and Discussion

The scanning electron microscope (SEM) images and X-ray diffraction (XRD) patterns of the as-received powders of B_4C and Ti_3SiC_2 are shown in Figure 1. The SEM images show that B_4C particles have ladder-like surface undulation, a typical transgranular fracture which appears during the particle crushing process; Ti_3SiC_2 particles have an obvious lamellar structure. It can be seen from the XRD images that the two kinds of powders are relatively pure and almost no oxide exists (the content of oxide is too small to be detected in XRD). Figure 2 shows the phase composition of B_4C – TiB_2 ceramic composites prepared at 1900 °C with a different content of additive Ti_3SiC_2 . There is no diffraction peak of Ti_3SiC_2 in any of the XRD images, which indicates that Ti_3SiC_2 had completely reacted with B_4C . When the temperature is above 1200 °C, the following reactions occur [10]:



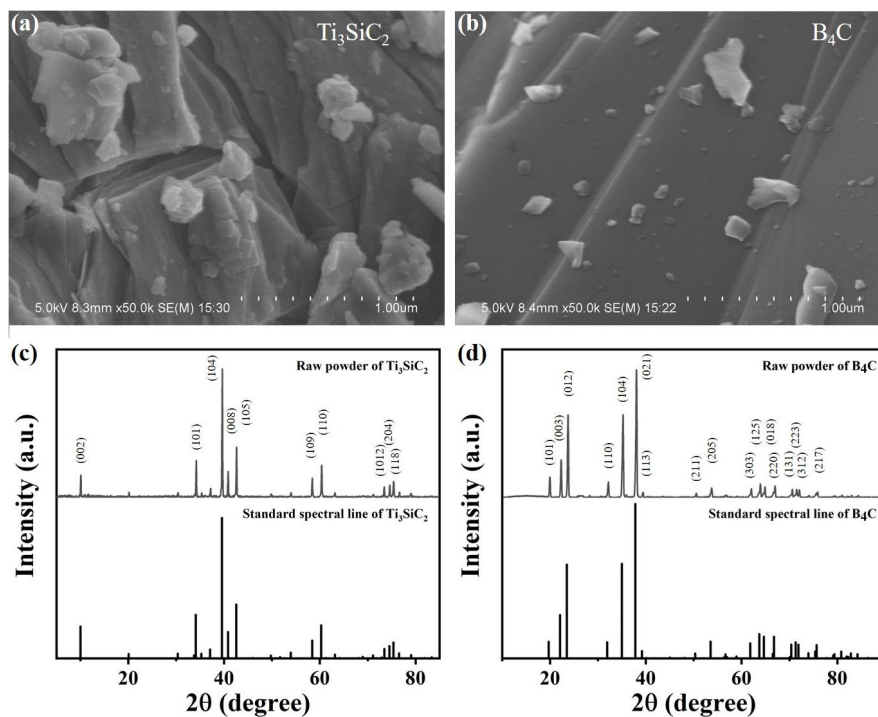


Figure 1. (a) SEM image of Ti_3SiC_2 ; (b) SEM image of B_4C ; (c) XRD pattern Ti_3SiC_2 ; (d) XRD pattern of B_4C .

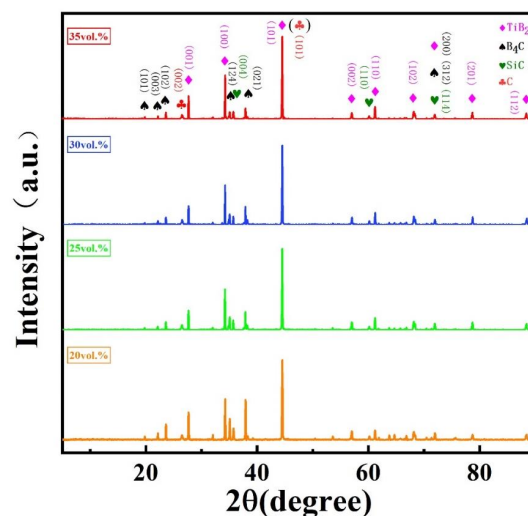
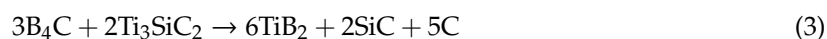


Figure 2. XRD patterns of B_4C – TiB_2 ceramic composites sintered at 1900 °C with different contents of the additive Ti_3SiC_2 .

The reactions (1) and (2) ended at 1600 °C, and based on the above results, the overall reaction in the system can be described as the following reaction [10]:



TiC appears as an intermediate product in the whole reaction process but does not exist in the final product. According to the XRD test results, the content of each phase is shown in Table 1. TiB_2 and B_4C are the main phase composition of the composites, and a small amount of SiC and C exist. With the increase in Ti_3SiC_2 content, the proportion of TiB_2 , B_4C and C (graphite) in the composite increases, while the content of B_4C decreases.

Table 1. Contents of different phases in B_4C – TiB_2 composite ceramics sintered at different temperatures.

Sample Name	Content of Ti_3SiC_2 (vol.%)	TiB_2 (wt.%)	B_4C (wt.%)	SiC (wt.%)	C (Graphite) (wt.%)
BT20	20	9.4	87.4	1.6	1.7
BT25	25	19.7	73.2	3.3	3.8
BT30	30	29.6	61.9	4.2	4.4
BT35	35	40.6	47.7	6.1	5.6

Table 2 shows the properties of the samples prepared with different contents of Ti_3SiC_2 . In our experiment, the pure B_4C samples sintered by SPS were broken when they were taken out of the mold, so the pure B_4C sample BT0 prepared by Direct Current Sintering at 1800 °C for 10 min was used as the control group. BT0 was the reference sample without Ti_3SiC_2 , and its hardness, bending strength and fracture toughness were 33.5 GPa, 224.43 MPa and 5.96 $MPa \cdot m^{1/2}$, respectively. Compared with BT0, all of the samples containing Ti_3SiC_2 had a higher relative density. Figure 3 shows the BSE (Backscattered Electron) images of BT0 and BT30 after polishing. There were some closed pores in BT0, but not in BT30. This is because the B_4C particles have sharp edges and corners, and its hardness (55 GPa) is very high. Thus, they cannot be extruded and deformed under pressure, leaving a non-contact space inside, and form pores. The hardness of Ti_3SiC_2 (4 GPa) was much smaller than that of B_4C ; Ti_3SiC_2 can be extruded and deformed without leaving voids between particles under an external load. After reaction sintering, TiB_2 , B_4C , SiC and C (existing in the form of graphite) in the composites have different thermal expansion coefficients, which makes the ceramics more compact after cooling.

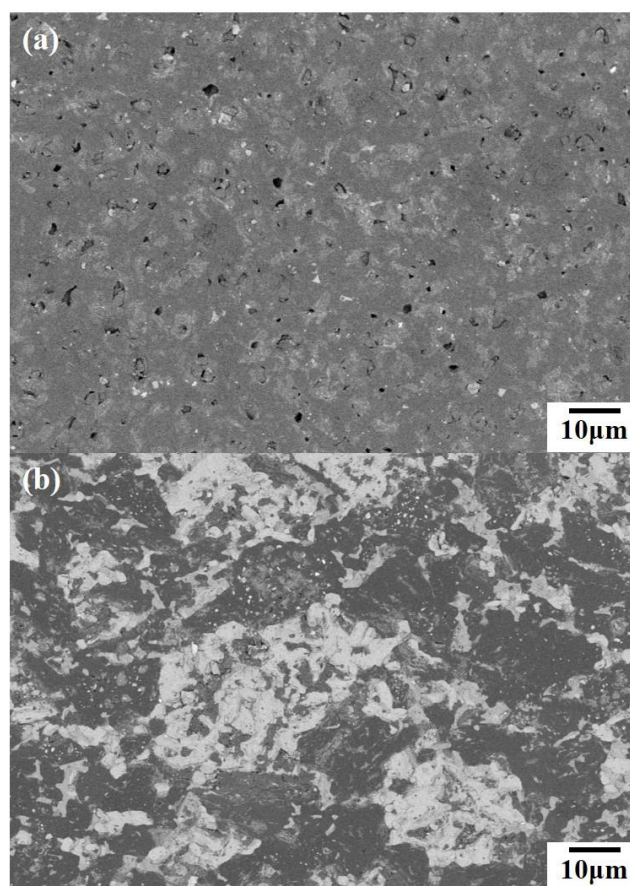
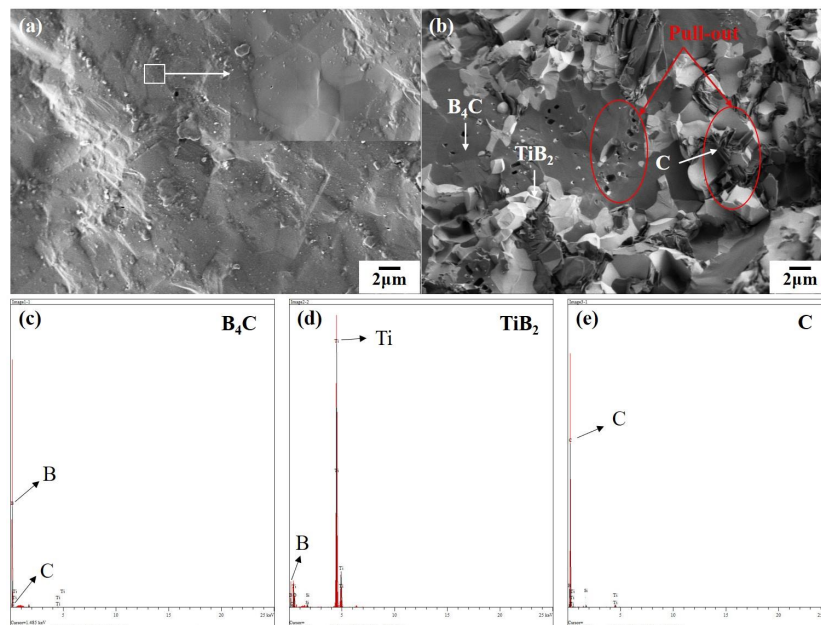
**Figure 3.** (a) BSE image of BT0; (b) BSE image of BT30.

Table 2. Properties of ceramics prepared with different contents of additive Ti_3SiC_2 .

Simple Name	Content of Ti_3SiC_2 (vol.%)	Density (g/cm^3)	Relative Density (%)	Hardness (GPa)	Flexural Strength (MPa)	Fracture Toughness ($\text{MPa}\cdot\text{m}^{1/2}$)
BT0	0	2.50	99.20	33.50	224.43	5.96
BT20	20	3.12	101.16	31.14	317.55	17.68
BT25	25	3.13	101.51	28.70	383.25	18.37
BT30	30	3.17	101.54	27.28	405.11	18.94
BT35	35	3.17	102.28	26.71	343.95	19.00

The hardness of the second phase particles produced by the reaction is lower than that of B_4C , especially the graphite phase, therefore it is inevitable that the hardness of the composite ceramics is lower than that of the pure B_4C ceramics. Compared with BT0, the flexural strength and fracture toughness of BT20–BT35 are improved, and the hardness decreases. Figure 4a,b show the fracture morphology of BT0 and BT30, respectively. It can be seen that the fracture surface of BT0 is flat, which is a typical transgranular fracture morphology. Comparatively, the fracture surface of sample BT30 is rough, which is a typically mixed fracture morphology of transgranular fracture and intergranular fracture. In Figure 4b, the dark gray flat area is the B_4C matrix, and the light gray rough area is TiB_2 particles, which indicates that the fracture modes of the B_4C phase and the TiB_2 phase are transgranular fracture and intergranular fracture, respectively. In addition, there is a dark gray lamellar phase around the TiB_2 grain, which can be inferred as carbon phase by energy spectrum analysis. Figure 4c–e show the energy spectrum of B_4C , TiB_2 and C, respectively. Due to the mismatch of thermal expansion coefficients between B_4C , TiB_2 and graphite (B_4C : $4.5 \times 10^{-6} \text{ K}^{-1}$; TiB_2 : $8.1 \times 10^{-6} \text{ K}^{-1}$; Graphite: $1 \times 10^{-6} \text{ K}^{-1}$ in the parallel direction, $29 \times 10^{-6} \text{ K}^{-1}$ in c direction) [11], there will be large residual stress at the interface of the phases, which will induce crack deflection along the grain boundary and extend the crack propagation path to improve the strength and toughness of the material. The nano TiB_2 particles embedded in the B_4C matrix will introduce internal stress, which will strengthen the B_4C matrix by a lattice distortion effect, and can also nail the dislocations and hinder their movement, so as to enhance the strength of the material.

**Figure 4.** (a) SEM image of fracture surface of BT0; (b) SEM image of fracture surface of BT30; (c) Energy spectrum of B_4C ; (d) Energy spectrum of TiB_2 ; (e) Energy spectrum of C.

It should be noted that the fracture toughness of the composites was greatly improved by adding more than 20 vol.% of Ti_3SiC_2 . The fracture toughness of BT30 was $18.94 \text{ MPa}\cdot\text{m}^{1/2}$, which was more

than three times of that of BT0 ($5.80 \text{ MPa}\cdot\text{m}^{1/2}$), and more than twice as high as the highest fracture toughness cited in Table 3. Wen Q et al. [9] adopted the same ratio of raw materials as ours to sinter the ceramics. They used $0.5 \text{ }\mu\text{m}$ B_4C powders and $0.5\text{--}10 \text{ }\mu\text{m}$ Ti_3SiC_2 powders as raw materials, and their process was $1850 \text{ }^\circ\text{C}$ hot pressing sintering for 30 min. Compared with their work, the particle size of the raw powders we used had a greater difference in size (B_4C : $1 \text{ }\mu\text{m}$; Ti_3SiC_2 : $<74 \text{ }\mu\text{m}$), meaning aggregates were formed more easily, which are beneficial for toughness but unfavorable for strength [12]. Besides, our ceramics had a higher relative density and graphite content, which may be due to the evaporation of Si at a higher sintering temperature, and the electric field [13]. In the analysis of XRD data, only graphite matched with the existing peaks, and the diffraction peaks of other existing forms of carbon did not correspond with the peaks in the experimental data. Moreover, the sintering temperature was $1900 \text{ }^\circ\text{C}$, at which point the amorphous carbon would also be graphitized. Therefore, we infer that the lamellar phase in Figure 4b is graphite. Graphite phase exists at the grain boundaries of TiB_2 and B_4C , which reduces the bonding strength of the interface and has an adverse effect on the hardness and strength of the composite ceramics. This is the reason why the flexural strength of BT30 is at a low level in Table 3. At the same time, the existence of graphite can limit grain growth. In the cooling process, microcracks are produced under the effect of interfacial stress produced by different thermal expansion coefficients, and the cracks propagate along the interlayer of graphite during fracture, resulting in lamellar pull-out. This lamellar pull-out process greatly prolongs the path of crack propagation, consumes the energy of cracks, and is beneficial to improving the fracture toughness. It can be seen from Figure 4b that there are traces of particle pull-out and lamellar graphite pull-out in the fracture surface of BT30, which is one of the important reasons for the toughening of the composite.

Table 3. Comparison of the properties of the $\text{B}_4\text{C}\text{--TiB}_2$ composite ceramics reported in recent years.

Serial No.	Starting Powder	Relative Density (%)	K_{IC} , ($\text{MPa}\cdot\text{m}^{1/2}$)	Flexural Strength (MPa)	Ref. (Year)
1	$\text{B}_4\text{C} + 5 \text{ wt}\% (\text{Ti}_3\text{SiC}_2 + \text{Si})$	-	5.61	457.6	[14] (2019)
2	$\text{B}_4\text{C} + 30 \text{ wt}\% (\text{TiB}_2 + \text{Si})$	99.6	5.77	531.2	[15] (2018)
3	$\text{B}_4\text{C} + 20 \text{ mol}\%\text{TiB}_2$	97.9	3.7	-	[16] (2020)
4	$\text{B}_4\text{C} + 15 \text{ wt}\%\text{SiC} + 20 \text{ mol}\%\text{TiB}_2$	98.6	4.2	343.8	[17] (2020)
5	$\text{B}_4\text{C} + 6.45 \text{ vol}\%\text{SiC} + 7.78 \text{ vol}\%\text{TiB}_2$	99.62	6.38	632	[12] (2019)
6	$\text{B}_4\text{C} + 30 \text{ vol}\% \text{Ti}_3\text{SiC}_2$	98.72	8.0	492.3	[9] (2017)
BT30	$\text{B}_4\text{C} + 30 \text{ vol}\% \text{Ti}_3\text{SiC}_2$	101.54	18.94	405.11	This work

Figure 5 shows the variation of the relative density and hardness of $\text{B}_4\text{C}\text{--TiB}_2$ composite ceramics with the content of Ti_3SiC_2 . Due to the slight evaporation of silicon [13], the density of the composites is slightly higher than the theoretical density. The evaporation capacity of Si increases with the increase in Ti_3SiC_2 content, resulting in an increase in the relative density. The hardness decreases with the increase in Ti_3SiC_2 content, because the proportion of the second phase with lower hardness, especially graphite, increases.

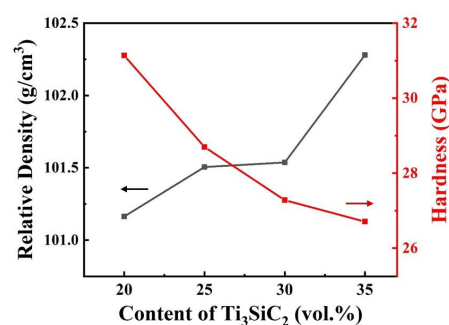


Figure 5. Relative density and hardness of the $\text{B}_4\text{C}\text{--TiB}_2$ composite ceramics sintered with different contents of Ti_3SiC_2 .

Figure 6 shows the variation of flexural strength and fracture toughness of B_4C - TiB_2 composite ceramics with additive Ti_3SiC_2 content. When the content of Ti_3SiC_2 is in the range of 20 vol.%–30 vol.%, the flexural strength and fracture toughness are positively correlated with the content of Ti_3SiC_2 . Comparing Figure 7a–c, it can be seen that the region as shown in Figure 7e becomes larger and more numerous with the increase in Ti_3SiC_2 content. In this region, TiB_2 , graphite and B_4C intersect each other to form a three-dimensional interpenetrating network. During the crack propagation process, multiple two-phase interfaces must be bypassed to disperse into more small cracks and a large number of changes in the propagation direction. The pull-out mechanism of graphite also plays an important role in this agglomeration area. However, this area does not exist in isolation. Every small network links to each other, forming a large network structure covering the whole composite. At the same time, the network divides the B_4C concentration area into small parts and surrounds them, so that there is no large area of a continuous B_4C phase in the composites. The large area of a continuous B_4C phase is very unfavorable to the toughness of the composite. With the increase in interlacing degrees of TiB_2 , SiC, graphite and B_4C , the cracks need to bypass more two-phase interfaces, change direction more often, and disperse into more small cracks, which can consume a lot of energy of crack propagation and hinder the spreading of cracks. Therefore, the fracture toughness of B_4C - TiB_2 composite ceramics is greatly improved by the overall three-dimensional interpenetrating network structure.

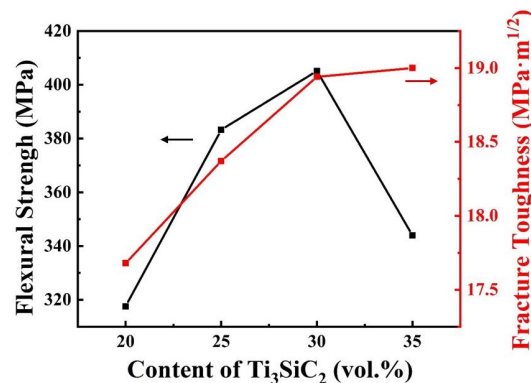


Figure 6. Flexural strength and fracture toughness of the B_4C - TiB_2 composite ceramics sintered with different contents of Ti_3SiC_2 .

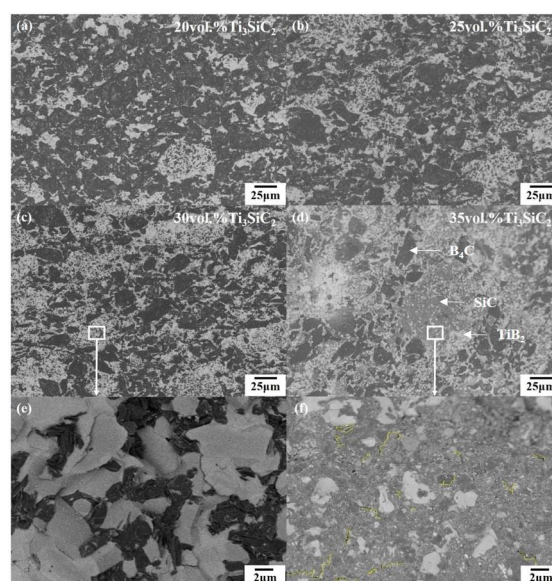


Figure 7. (a–d) BSE images of B_4C - TiB_2 composite ceramics sintered with 20 vol.%, 25 vol.%, 30 vol.%, 35 vol. Ti_3SiC_2 in order; (e) Local magnification BSE image of (c); (f) Local magnification BSE image of (d).

However, when the content of Ti_3SiC_2 is 35 vol.%, as shown in Figure 7d, a large TiB_2 -SiC agglomerated area appears in the BT35 (among which the dark gray, medium gray and light gray phases are B_4C , SiC and TiB_2 , respectively). There is a bad stress effect in the multiphase mixing region with more SiC. As shown in Figure 7f, many microcracks due to mismatching of the thermal expansion coefficient of SiC and TiB_2 can be found in this region. These microcracks are conducive to the toughening of the material, but result in a significant decrease in the bending strength.

4. Conclusions

Ultra-high toughness B_4C - TiB_2 composite ceramics were prepared by the SPS method at 1900 °C. The content of additive Ti_3SiC_2 has a great influence on the microstructure and mechanical properties. With the increase in Ti_3SiC_2 content, the relative density and fracture toughness of the material increase, while the hardness decreases, and the flexural strength first increases and then decreases. When the content of Ti_3SiC_2 is 30 vol.%, B_4C - TiB_2 composite ceramics have the highest bending strength and the best comprehensive mechanical properties: hardness 27.28 GPa, bending strength 405.11 MPa, and fracture toughness $18.94 \text{ MPa}\cdot\text{m}^{1/2}$. The fracture mode of the material is a mixture of transgranular fracture and intergranular fracture. The existence of the graphite phase has a negative effect on the hardness and flexural strength of B_4C - TiB_2 composite ceramics, but it is beneficial to the fracture toughness. The main reason for obtaining high fracture toughness is the formation of a three-dimensional interpenetrating network covering the whole composite.

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Conflicts of Interest: The authors declare no conflict of interest.

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