Effect of Additive Ti$_3$SiC$_2$ Content on the Mechanical Properties of B$_4$C–TiB$_2$ Composites Ceramics Sintered by Spark Plasma Sintering

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Abstract: B$_4$C–TiB$_2$ composite ceramics with ultra-high fracture toughness were successfully prepared via spark plasma sintering (SPS) at 1900 °C using B$_4$C and Ti$_3$SiC$_2$ as raw materials. The results showed that compared with pure B$_4$C ceramics sintered by SPS, the hardness of B$_4$C–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$_3$SiC$_2$ was 30 vol.%, the B$_4$C–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 MPa·m$^{1/2}$, respectively. The fracture mode of the B$_4$C–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$_3$SiC$_2$; 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$_2$O$_3$ 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$_3$SiC$_2$ can react with B$_4$C to form TiB$_2$ with high hardness and a high melting point, which can be used as an ideal toughening phase for B$_4$C ceramics [9]. In this study, B$_4$C–TiB$_2$ composite ceramics with ultra-high
toughness were prepared by the SPS process with different contents of Ti$_3$SiC$_2$ as additives, and the influence mechanism of Ti$_3$SiC$_2$ content on the microstructure and properties of B$_4$C–TiB$_2$ composite ceramics was studied.

2. Experimental Procedure

Commercially available B$_4$C powders (purity 99.9%, 1 μm, 4.53 g/cm$^3$, Nangong Naiyate Alloy Welding Material Co., Ltd., Nangong, China) and Ti$_3$SiC$_2$ 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$_3$SiC$_2$–B$_4$C powders containing 20 vol.%, 25 vol.%, 30 vol.% and 35 vol.% Ti$_3$SiC$_2$, 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$_4$C–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 × 4 mm × 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 × 4 mm × 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$_4$C and Ti$_3$SiC$_2$ are shown in Figure 1. The SEM images show that B$_4$C particles have ladder-like surface undulation, a typical transgranular fracture which appears during the particle crushing process; Ti$_3$SiC$_2$ 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$_4$C–TiB$_2$ ceramic composites prepared at 1900 °C with a different content of additive Ti$_3$SiC$_2$. There is no diffraction peak of Ti$_3$SiC$_2$ in any of the XRD images, which indicates that Ti$_3$SiC$_2$ had completely reacted with B$_4$C. When the temperature is above 1200 °C, the following reactions occur [10]:

$$\text{B}_4\text{C} + \text{Ti}_3\text{SiC}_2 \rightarrow 2\text{TiB}_2 + \text{TiC} + \text{SiC} + \text{C} \quad (1)$$

$$\text{B}_4\text{C} + 2\text{TiC} \rightarrow 2\text{TiB}_2 + 3\text{C} \quad (2)$$

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]:

$$3\text{B}_4\text{C} + 2\text{Ti}_3\text{SiC}_2 \rightarrow 6\text{TiB}_2 + 2\text{SiC} + 5\text{C} \quad (3)$$

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$_4$C are the main phase composition of the composites, and a small amount of SiC and C exist. With the increase in Ti$_3$SiC$_2$ content, the proportion of TiB$_2$, B$_4$C and C (graphite) in the composite increases, while the content of B$_4$C decreases.
Figure 1. (a) SEM image of Ti$_3$SiC$_2$; (b) SEM image of B$_4$C; (c) XRD pattern Ti$_3$SiC$_2$; (d) XRD pattern of B$_4$C.

Figure 2. XRD patterns of B$_4$C–TiB$_2$ ceramic composites sintered at 1900 °C with different contents of the additive Ti$_3$SiC$_2$. 
Table 1. Contents of different phases in B$_4$C–TiB$_2$ composite ceramics sintered at different temperatures.

| Sample Name | Content of Ti$_3$SiC$_2$ (vol.%) | TiB$_2$ (wt.%) | B$_4$C (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 sample prepared with different contents of Ti$_3$SiC$_2$. In our experiment, the pure B$_4$C samples sintered by SPS were broken when they were taken out of the mold, so the pure B$_4$C 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$_3$SiC$_2$, and its hardness, bending strength and fracture toughness were 33.5 GPa, 224.43 MPa and 5.96 MPa·m$^{1/2}$, respectively. Compared with BT0, all of the samples containing Ti$_3$SiC$_2$ 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$_4$C 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$_3$SiC$_2$ (4 GPa) was much smaller than that of B$_4$C; Ti$_3$SiC$_2$ can be extruded and deformed without leaving voids between particles under an external load. After reaction sintering, TiB$_2$, B$_4$C, 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.

Table 2. Properties of ceramics prepared with different contents of additive Ti$_3$SiC$_2$.

| Simple Name | Content of Ti$_3$SiC$_2$ (vol.%) | Density (g/cm$^3$) | Relative Density (%) | Hardness (GPa) | Flexural Strength (MPa) | Fracture Toughness (MPa·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$_4$C, especially the graphite phase, therefore it is inevitable that the hardness of the composite ceramics is lower than that of the pure B$_4$C 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$_4$C matrix, and the light gray rough area is TiB$_2$ particles, which indicates that the fracture modes of the B$_4$C 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$_4$C, TiB$_2$ and C, respectively. Due to the mismatch of thermal expansion coefficients between B$_4$C, TiB$_2$ and graphite (B$_4$C: 4.5 × 10$^{-6}$ k$^{-1}$; TiB$_2$: 8.1 × 10$^{-6}$ k$^{-1}$; Graphite: 1 × 10$^{-6}$ k$^{-1}$ in the parallel direction, 29 × 10$^{-6}$ 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$_4$C matrix will introduce internal stress, which will strengthen the B$_4$C 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.
It should be noted that the fracture toughness of the composites was greatly improved by adding more than 20 vol.% of Ti3SiC2. The fracture toughness of BT30 was 18.94 MPa·m^1/2, which was more than three times of that of BT0 (5.80 MPa·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 μm B4C powders and 0.5–10 μm Ti3SiC2 powders as raw materials, and their process was 1850 °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 (B4C: 1 μm; Ti3SiC2: <74 μm), 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 °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 TiB2 and B4C, 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 B₄C–TiB₂ composite ceramics reported in recent years.

| Serial No. | Starting Powder                                      | Relative Density (%) | Kᵢc, (MPa·m⁰.⁵) | Flexural Strength (MPa) | Ref. (Year) |
|-----------|-----------------------------------------------------|----------------------|------------------|------------------------|-------------|
| 1         | B₄C + 5 wt% (Ti₃SiC₂ + Si)                          | -                    | 5.61             | 457.6                  | [14] (2019) |
| 2         | B₄C + 30 wt% (TiB₂ + Si)                            | 99.6                 | 5.77             | 531.2                  | [15] (2018) |
| 3         | B₄C + 20 mol%TiB₂                                   | 97.9                 | 3.7              | -                      | [16] (2020) |
| 4         | B₄C + 15 wt%SiC + 20 mol%TiB₂                       | 98.6                 | 4.2              | 343.8                  | [17] (2020) |
| 5         | B₄C + 6.45 vol.%SiC + 7.78 vol.%TiB₂               | 99.62                | 6.38             | 632                    | [12] (2019) |
| 6         | B₄C + 30 vol.% Ti₃SiC₂                              | 98.72                | 8.0              | 492.3                  | [9] (2017)  |
| BT30      | B₄C + 30 vol.% Ti₃SiC₂                              | 101.54               | 18.94            | 405.11                 | This work  |

Figure 4. (a) SEM image of fracture surface of BT0; (b) SEM image of fracture surface of BT30; (c) Energy spectrum of B₄C; (d) Energy spectrum of TiB₂; (e) Energy spectrum of C.

Figure 5 shows the variation of the relative density and hardness of B₄C–TiB₂ composite ceramics with the content of Ti₃SiC₂. 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 Ti₃SiC₂ content, resulting in an increase in the relative density. The hardness decreases with the increase in Ti₃SiC₂ content, because the proportion of the second phase with lower hardness, especially graphite, increases.
Figure 5. Relative density and hardness of the B$_4$C–TiB$_2$ composite ceramics sintered with different contents of Ti$_3$SiC$_2$.

Figure 6 shows the variation of flexural strength and fracture toughness of B$_4$C–TiB$_2$ composite ceramics with additive Ti$_3$SiC$_2$ content. When the content of Ti$_3$SiC$_2$ is in the range of 20 vol.%–30 vol.%, the flexural strength and fracture toughness are positively correlated with the content of Ti$_3$SiC$_2$. 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$_3$SiC$_2$ content. In this region, TiB$_2$, graphite and B$_4$C 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$_4$C concentration area into small parts and surrounds them, so that there is no large area of a continuous B$_4$C phase in the composites. The large area of a continuous B$_4$C phase is very unfavorable to the toughness of the composite. With the increase in interlacing degrees of TiB$_2$, SiC, graphite and B$_4$C, 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$_4$C–TiB$_2$ composite ceramics is greatly improved by the overall three-dimensional interpenetrating network structure.

However, when the content of Ti$_3$SiC$_2$ 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$_4$C, 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.
Figure 6. Flexural strength and fracture toughness of the B₄C–TiB₂ composite ceramics sintered with different contents of Ti₃SiC₂.

Figure 7. (a–d) BSE images of B₄C–TiB₂ composite ceramics sintered with 20 vol.%, 25 vol.%, 30 vol.%, 35 vol.% Ti₃SiC₂ in order; (e) Local magnification BSE image of (c); (f) Local magnification BSE image of (d).
4. Conclusions

Ultra-high toughness B$_4$C–TiB$_2$ composite ceramics were prepared by the SPS method at 1900 °C. The content of additive Ti$_3$SiC$_2$ has a great influence on the microstructure and mechanical properties. With the increase in Ti$_3$SiC$_2$ 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$_3$SiC$_2$ is 30 vol.%, B$_4$C–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 MPa·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$_4$C–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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