B4C-TiB2 Composite Ceramics with Ultra-High Fracture Toughness Fabricated by Spark Plasma Sintering

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Abstract

B₄C-TiB₂ composite ceramics with ultra-high fracture toughness were successfully prepared via spark plasma sintering using B₄C and 30 vol.% Ti₃SiC₂ as raw materials at different sintering temperatures. The results show that compared with pure B₄C ceramics sintered by SPS, the flexural strength and fracture toughness are significantly improved, especially the fracture toughness has been improved by leaps and bounds. When the sintering temperature is 1900 °C, the B₄C-TiB₂ composite ceramic has the best comprehensive mechanical properties: hardness, bending strength and fracture toughness are 27.28 GPa, 405.11 MPa and 18.94 MPa·m^{1/2}, respectively. The main two reasons for the ultra-high fracture toughness are the formation of TiB₂ three-dimensional network covering the whole composites, and the existence of lamellar graphite at the grain boundary.

1. Introduction

Boron carbide is widely used in wear-resistant parts, armor protection and aerospace^[1–3]. These excellent properties are due to the strong covalent bond, but this structure also leads to the low self-diffusion coefficient of B₄C. Low self-diffusion ability, high melting point and the oxygen-rich layer (B₂O₃) on the surface of B₄C particles make it difficult to sinter B₄C compactly, which greatly limits its application^[4].

There are three common methods to obtain high density B₄C ceramics: increasing sintering temperature, applying high pressure and using additives. Increasing sintering temperature and pressure has great requirements for the equipment, so the use of additives has become the most convenient method. Metal additives are very effective for the densification of B₄C ceramics, but the hardness of B₄C ceramics decreases obviously with the soft metal phase^[5]. Ti₃SiC₂ can react with B₄C to form the second phase with high hardness, i.e. TiB₂ and SiC, which can achieve the second phase toughening effect at the same time of promoting sintering. Meanwhile, the reduction of hardness can be controlled in a small range.

The traditional hot pressing sintering of B₄C needs to be kept above 2000 °C for more than 1h^[3]. SPS (Spark Plasma Sintering) is a kind of low-temperature rapid sintering process which is widely concerned. The combination of mechanical pressure, electric field and thermal field can enhance the bonding and densification of particles^[6–8]. In this study, B₄C-TiB₂ composite ceramics with high toughness were prepared by SPS process (using 30 vol.% Ti₃SiC₂ + B₄C mixed powder as raw materials). In addition, the effect of sintering temperature on the microstructure and properties of B₄C ceramics was also studied.

2. Experimental Procedure

Commercially available B₄C powders (purity 99.9%, 1 μm, 4.53 g/cm³, Nangong Naiyate Alloy Welding Material Co., Ltd), Ti₃SiC₂ powders (purity 99.9%, < 74 μm, 4.53 g/cm³, Nanjing Mingchang New Material Co., Ltd) were used as raw materials. 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 Fig. 1. It can be observed from SEM images that B_4C particles have sharp edge and ladder-like surface undulation, which is a typical transgranular fracture appearance during the particle crushing process; Ti_3SiC_2 particles have larger grain size and 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). 30 vol.% Ti_3SiC_2 - B_4C powders were mixed for 24 h through a small vertical mixer at 80 r/min without adding solvent. The specimens were prepared by SPS equipment (HP D 25/4-SD, FCT Systeme GmbH, Germany) in vacuum with 35 MPa mechanical pressure at 1800 °C, 1850 °C, 1900 °C and 1950 °C for 5 min. The heating rate was 100 °C/min and the cooling rate was 50 °C/min. The SPS method was used to prepare the sample under vacuum environment with 35 MPa mechanical pressure at 1800 °C, 1850 °C, 1900 °C and 1950 °C for 5 min. the heating rate was 100 °C/min and the cooling rate was 50 °C/min.

Absolute density of B_4C - TiB_2 composite ceramics were determined using the Archimedes method. Hardness was measured by a Vickers-indentation tester (Shimadzu, HMV-2TADW E, Japan) at 9.81 N load with a holding time of 15 s on the polished surface. Flexural strength was determined by three-point bending test with the span of 30 mm and the loading speed of 0.5 mm/min, and the specimens used in the test were $3 \times 4 \times 35$ mm bars. SENB method was used to determine the fracture toughness of the specimens, with dimensions of $2 \times 4 \times 20$ 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, Netherlands), scanning electron micro-scope (SEM, S-4800N, Hitachi, Japan), transmission electron microscope (TEM, JEM-2100, JEOL, Japan) and energy dispersive spectrometer (EDS, INCA, OXFORD INSTRUMENTS, England).

3. Results And Discussion

Fig.2 XRD patterns of B_4C - TiB_2 ceramic composites sintered at different temperatures

Fig.2 shows the phase composition of B_4C - TiB_2 ceramic composites prepared at different sintering temperatures. There is no diffraction peak of Ti_3SiC_2 in all XRD images, which indicates that Ti_3SiC_2 has completely reacted with B_4C and transformed into TiB_2 and SiC in the sintering process at four different sintering temperatures. When the temperature is above 1200 °C, the following reactions occur^[9]:

The reaction (1) and (2) ended at 1600 °C, on the basis of the above results, the overall reaction in the system can be described as the following reaction^[9]

TiC does not exist in the final product, appearing as an intermediate product during the whole sintering process. According to the XRD test results, the content of each phase is shown in Table 1. It can be seen that the composition of the composite ceramics changes little when sintered at different sintering temperatures, which is mainly composed of TiB₂ and B₄C, with a small amount of SiC and C. When the temperature rise, the content of SiC decreases and the content of C increases, which may be due to the slight evaporation of silicon in the sintering process. It can be inferred that the evaporation of Si also increases with the increase of temperature.

Table 1 contents of different phases in B₄C-TiB₂ composite ceramics sintered at different temperatures

Simple name	Sintering Temperature (°C)	TiB ₂ (wt.%)	B ₄ C (wt.%)	SiC (wt.%)	C (wt.%)
BT1800	1800	30.3	61.4	5	3.3
BT1850	1850	30.1	61.6	4.7	3.6
BT1900	1900	29.6	61.9	4.2	4.4
BT1950	1950	30.6	61.2	3.5	4.7

Table 2 Properties of ceramics prepared by different sintering processes

Simple code	Content of Ti ₃ SiC ₂ (vol.%)	Sintering Temperature [°C]	Density (g/cm ³)	Relative Density (%)	Hardness (GPa)	Flexural Strength (MPa)	Fracture Toughness (MPa·m ^{1/2})
B1800	0	1800	2.50	99.20	33.5	224.43	5.96
BT1800	30	1800	3.12	99.84	28.03	358.30	16.41
BT1850	30	1850	3.13	100.32	28.44	351.10	17.15
BT1900	30	1900	3.17	101.54	27.28	405.11	18.94
BT1950	30	1950	3.17	101.44	28.16	398.01	17.53

Table 2 shows the mechanical properties of the samples prepared by different sintering processes. The sample B1800 is pure B₄C ceramic sintered by SPS as comparative group, whose hardness, bending strength and fracture toughness are 33.5 GPa, 224.43 MPa and 5.96 MPa·m^{1/2}, respectively. The density

of samples BT1800 to BT1950 is slightly higher than that of pure B_4C ceramic sintered by SPS. Because of the slight evaporation of silicon, the density of B_4C-TiB_2 composite ceramic is even slightly higher than the theoretical density. Fig.3(a) shows the variation of relative density and hardness of B_4C-TiB_2 composite ceramic versus sintering temperature. The relative density becomes larger with the increase of temperature, reaches the highest point at 1900 °C, and decreases slightly at 1950 °C. When the ceramic composition is basically the same, the density is the key factor affecting the hardness of ceramics, while the ceramics sintered at 1800 °C and above are almost dense (The relative density of all samples are above 99.8%), so the influence of sintering temperature on the hardness of ceramics is negligible. The hardness of the sample containing 30 vol.% Ti_3SiC_2 decreases to a certain extent compared with that of pure B_4C . However, due to the high hardness of the main second phase TiB_2 formed by the reaction, the hardness of the composite ceramics still remains at a high level between 27.18 GPa and 28.44 GPa.

Fig.3(b) shows the variation of flexural strength and fracture toughness of B_4C-TiB_2 ceramics with sintering temperature. Simple and BT1850 have similar flexural strength and fracture toughness, and the properties of BT1900 are obviously higher than the former two. This change trend is consistent with the relative density in Fig.3(a). Fig.4(a)-(d) are the SEM pictures of fracture appearance of samples BT1800 to BT1950 in turn. Fig.4(b) shows there are some large-size B_4C grains in the samples sintered at 1850 °C, resulting in a small decrease in the flexural strength of the samples sintered at 1800 °C. The comparison of Fig.4(a)-(c) shows that the samples sintered at 1800 °C, 1850 °C and 1900 °C have similar grain sizes (excluding a small part of large grains in Fig.5(b)), so the significant increase of density at 1900°C is the reason for the improvement of flexural strength and fracture toughness of sample BT1900. Compared with BT1900, the bending strength and fracture toughness of BT1950 are decreased, especially the latter. The main reason for that is the obvious grain growth of B_4C as shown in Fig.5(d), and the secondary reason is the slight decrease of the relative density as shown in Fig.3(a). Fig.4(f) is the BSE image of the ceramics sintered at 2000 °C. It can be clearly seen that if the temperature is further increased, the grains grow furthermore, which is not conducive to the integrated mechanical properties of the B_4C-TiB_2 composite ceramic. Moreover, when the sintering temperature is 2000 °C, the raw materials reacted with graphite mold and damage it. So, the bending strength and fracture toughness reach the maximum values of 405.11 MPa and $18.94 \text{ MPa}\cdot\text{m}^{1/2}$ when the sintering temperature is 1900 °C. Compared with the fracture appearance of pure B_4C ceramic (Fig. 4 (e)), the fracture surface of the samples with additive Ti_3SiC_2 (Fig. 4(a)-(d)) is much rougher, showing a mixed fracture mode. Intergranular fracture and transgranular fracture correspond to the rough and flat surface in the figure respectively^[10]. In Fig.4, the dark gray flat area is the B_4C matrix, and the light gray rough area is TiB_2 particles, which indicates that in B_4C-TiB_2 composite ceramics, the fracture mode of B_4C phase and TiB_2 phase is the transgranular fracture and intergranular fracture respectively.

Fig.3 Relative density and mechanical properties of the B_4C-TiB_2 composite ceramics sintered at different temperatures

Fig.4 (a)-(d) SEM images of B_4C - TiB_2 composite ceramics sintered at 1800 °C, 1850 °C, 1900 °C and 1950 °C in turn; (e) SEM image of pure B_4C ceramic sintered at 1800°C; (f) BSE image of B_4C - TiB_2 composite ceramic sintered at 2000 °C

Fig.5 shows the BSE images of the B_4C - TiB_2 composite ceramic prepared by SPS at 1900 °C for 5 min. It can be seen from Fig.5(a) that there are TiB_2 particles with different sizes from nanometer-scale to micron-scale dispersed in the B_4C matrix. Due to the mismatch of thermal expansion coefficients of B_4C and TiB_2 (B_4C : $4.5 \times 10^{-6} \text{ K}^{-1}$; TiB_2 : $8.1 \times 10^{-6} \text{ K}^{-1}$) [11], there is large residual stress at the interface of the two phases, which induces the crack deflection along the grain boundary and prolongs the crack propagation path, which greatly improves the toughness. The nano TiB_2 particles embedded in the B_4C matrix can introduce internal stress, which will strengthen the B_4C matrix by lattice distortion effect, and can also nail the dislocations and hinder their movement. In addition, as shown in Fig.5(c), the nano TiB_2 and SiC particles at the grain boundary of B_4C can also strengthen the grain boundary and prevent the crack growth. Fig.5(b) is the BSE image of TiB_2 - SiC aggregates, in which the dark gray, medium gray and light gray phases are B_4C , SiC and TiB_2 , respectively. In this multiphase mixing region with a large amount of SiC , there is adverse stress effects that have a negative effect on flexural strength[12]. However, the TiB_2 - SiC aggregates can expand the crack propagation path and change the crack propagation direction to consume the crack growth energy, which is helpful to improve the toughness. The crack propagation path in this area is shown in Fig.5(d).

Fig.5 BSE images of different structures of the B_4C - TiB_2 composite ceramic sintered at 1900 °C

Table 3 shows the mechanical properties of B_4C - TiB_2 composite ceramics prepared by different starting materials and sintering methods in recent two years[13-17]. Compared with these works, the flexural strength (405.11 MPa) of the simple that we sintered by SPS at 1900 °C is in the middle to a low level, but the fracture toughness ($18.94 \text{ MPa} \cdot \text{m}^{1/2}$) is much higher than the fracture toughness shown in the table, which can be described as a leap forward improvement. By making an in-depth comparative study of the differences between our work and the work of other researchers, we find that there are two fundamental reasons for the excellent fracture toughness of our B_4C - TiB_2 composite ceramics:

The first is the formation of a three-dimensional network of TiB_2 in the composites. In the area as shown in Fig.5(f), B_4C and TiB_2 are occluded and interlaced, and TiB_2 forms a network structure in the B_4C matrix. In the low magnification backscatter image Fig.5(e), we can find out that this network structure accounts for a large proportion of the whole material composition, and it does not exist in isolation. Links are formed between each small network, connecting a larger network structure covering the whole composite as a whole. At the same time, this network divides B_4C concentrated area and surrounds each one, so that there is no large area of continuous B_4C phase in the material, which is very unfavorable to the toughness of the composite. With higher interlacing degree of TiB_2 and B_4C phases, the cracks need to bypass more multiple two-phase interfaces, change the direction for more times, and disperse into

more small cracks in the process of extension. Therefore, the overall three-dimensional network structure greatly improves the fracture toughness of the B_4C - TiB_2 composite ceramics.

Table 3 Comparison of the properties of the B_4C - TiB_2 composite ceramics reported in recent years and produced by us

Serial no.	Starting powder	Relative Density (%)	K_{IC} ($MPa \cdot m^{1/2}$)	Flexural strength (MPa)	Ref. (year)
1	$B_4C + 5 \text{ wt.}\% (Ti_3SiC_2 + Si)$	—	5.61	457.6	[13] (2019)
2	$B_4C + 20 \text{ mol}\%TiB_2$	97.9	3.7	—	[14] (2020)
3	$B_4C + 15 \text{ wt.}\%SiC + 20 \text{ mol}\%TiB_2$	98.6	4.2	343.8	[15] (2020)
4	$B_4C+30 \text{ wt.}\% (TiB_2 + Si)$	99.6	5.77	531.2	[16] (2018)
5	$B_4C + 6.45 \text{ vol.}\%SiC + 7.78 \text{ vol}\%TiB_2$	99.62	6.38	632	[17] (2019)
6	$B_4C + 30 \text{ vol.}\% (Ti_3SiC_2)$	101.54	18.94	405.11	This work

Another reason is the existence of C, which exists in the form of graphite. With the increase of reaction temperature, the content of C increased, and its effect on the properties of the materials cannot be ignored. The graphite formed by the reaction of Ti_3SiC_2 and B_4C exists in the grain boundary in the form of bands, as shown in the TEM image Fig.6. The existence of the graphite layer reduces the bonding strength of the interface, which has an adverse effect on the hardness and strength of the composite ceramics^[18]. But on the other hand, its existence can limit grain growth. In the cooling process, microcracks are produced under the effect of interfacial stress produced by different thermal expansion coefficients, and according to the mechanism of microcrack toughening, it is beneficial to improve the toughness of the material. Combined with the data in Table 1 and Fig3(b), it can be found out that the fracture toughness of the material is positively related to the graphite content before the abnormal grain growth occurs at 1950 °C

Fig.6 TEM image of the B_4C - TiB_2 composite ceramic sintered at 1900 °C

4. Conclusions

The ultra-high toughness and full density B_4C - TiB_2 composite ceramics were prepared by SPS with the addition of 30 vol.% Ti_3SiC_2 . Sintering temperature has a great influence on its microstructure and

mechanical properties, mainly reflected in the sensitivity of density and grain size to temperature. The change of sintering temperature has little effect on the hardness of B_4C-TiB_2 composite ceramics. With the increase of sintering temperature, both bending strength and fracture toughness increase and then decrease. When the sintering temperature is 1900 °C, the B_4C-TiB_2 composite ceramic has the maximum relative density and kept the small grain size, and obtain the best comprehensive mechanical properties: hardness, bending strength and fracture toughness are 27.28 GPa, 405.11 MPa and $18.94 \text{ MPa}\cdot\text{m}^{1/2}$, respectively. The fracture toughness of B_4C-TiB_2 composite ceramics has been greatly improved at the expense of some hardness and bending strength. In B_4C-TiB_2 composite ceramics, the fracture mode is a mixture of transgranular fracture and intergranular fracture. The leap of fracture toughness is attributed to the formation of the TiB_2 three-dimensional network in the B_4C matrix, and the layered graphite exists at the grain boundary.

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Figures

Figure 1

SEM images and XRD patterns of raw powders

Figure 1

SEM images and XRD patterns of raw powders

Figure 2

XRD patterns of B₄C-TiB₂ ceramic composites sintered at different temperatures

Figure 2

XRD patterns of B₄C-TiB₂ ceramic composites sintered at different temperatures

Figure 3

Relative density and mechanical properties of the B4C-TiB2 composite ceramics sintered at different temperatures

Figure 3

Relative density and mechanical properties of the B4C-TiB2 composite ceramics sintered at different temperatures

Figure 4

a)-(d) SEM images of B₄C-TiB₂ composite ceramics sintered at 1800 °C, 1850 °C, 1900 °C and 1950 °C in turn; (e) SEM image of pure B₄C ceramic sintered at 1800 °C; (f) BSE image of B₄C-TiB₂ composite ceramic sintered at 2000 °C

Figure 4

a)-(d) SEM images of B₄C-TiB₂ composite ceramics sintered at 1800 °C, 1850 °C, 1900 °C and 1950 °C in turn; (e) SEM image of pure B₄C ceramic sintered at 1800 °C; (f) BSE image of B₄C-TiB₂ composite ceramic sintered at 2000 °C

Figure 5

BSE images of different structures of the B₄C-TiB₂ composite ceramic sintered at 1900 °C

Figure 5

BSE images of different structures of the B₄C-TiB₂ composite ceramic sintered at 1900 °C

Figure 6

TEM image of the B₄C-TiB₂ composite ceramic sintered at 1900 °C

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TEM image of the B₄C-TiB₂ composite ceramic sintered at 1900 °C