

Processing and characteristics of TiB_2 toughened B-Ti-C composites^①

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Abstract: B-Ti-C composites toughened by TiB_2 particles were produced by reaction sintering of B_4C , TiC and TiB_2 powders. Microstructure and mechanical properties of the composites were studied. A notable improvement on flexure strength and fracture toughness were achieved in B_4C composites containing 10% TiB_2 and 20%–30% TiC (volume fraction). The highest flexure strength and fracture toughness, 425 MPa and $8.2 \text{ MPa}\cdot\text{m}^{1/2}$, respectively, resulted for B_4C -10% TiB_2 -30% TiC composite, are much higher than those for monolithic B_4C . The main toughening mechanism is microcrack toughening and crack deflection toughening.

Key words: B-Ti-C composites; microstructure; mechanical properties; toughening mechanism

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1 INTRODUCTION

Boron carbide has many outstanding properties, such as extremely high hardness ($3\ 850 \text{ kg}\cdot\text{mm}^{-2}$, lower only to diamond and cubic boron nitride), excellent stability toward the effect of various acids, high melting point ($2\ 450\ ^\circ\text{C}$), high value of elastic modulus (450 GPa) and low density ($2.52 \text{ g}\cdot\text{cm}^{-3}$). All these properties allow boron carbide to cover a wide range of technological applications including cutting tools, wear resistant components and light armor materials^[1-4].

However, owing to the strong covalent bonds in its lattice, boron carbide is difficult to sinter to high density. Even at temperatures in excess of $2\ 300\ ^\circ\text{C}$, pure boron carbide can only be sintered to 75%–80% theoretical density^[5]. Another problem restricting the application of boron carbide is its relatively low strength (less than 300 MPa) and fracture toughness (about $2.2 \text{ MPa}\cdot\text{m}^{1/2}$) compared to other ceramics^[6]. The drawback in sintering B_4C is generally overcome by using of submicrometer starting powders and of promoting densification dopants. Carbide has been the most common additive for the densification in the industrial processing of boron carbide. Generally, bodies with relative density of more than 95% theoretical value can be achieved by adding a few percent element carbon to the submicrometer powders^[4, 7-9]. However, boron carbide activated by element carbon has low strength and toughness. In order to improve the toughness and increase the reliability of this ceramics for structural applications, different second phase has been introduced in the host

matrix to develop the boron carbide based ceramics^[10-13]. Among which, titanium diboride was the most effective in improving mechanical properties. In a recent study^[14], polycrystalline composites of B_4C - TiB_2 with relative densities exceeding 97% can be obtained by pressureless sintering with the addition of 1% Fe (mass fraction). Another important route, namely reaction sintering, has been employed for the fabrication of B_4C matrix composites. With the addition of TiO_2 as one of the starting materials, the B_4C - TiB_2 composites were formed, and a maximum strength of 513 MPa and toughness of $3.71 \text{ MPa}\cdot\text{m}^{1/2}$ have been reported^[5]. Here the fine grain reinforcement and crack deflection have been believed to be responsible for the improvement of mechanical properties.

The present work is planned to improve the poor sinterability and toughness of B_4C by introducing both direct and in-situ TiB_2 particles. At the same time, element carbon can be obtained by reaction sintering. The purpose of present work is to study the processing, microstructure and mechanical properties of TiB_2 toughened B-Ti-C composites.

2 EXPERIMENTAL

Two materials were investigated in this study, whose compositions are presented in Table 1. The starting materials were B_4C , TiB_2 and TiC powders, with the average grain size of $3\text{--}5\ \mu\text{m}$, $4\text{--}6\ \mu\text{m}$ and $3\text{--}5\ \mu\text{m}$, respectively. The powders were mixed in alcohol for 8 h, and after drying, were cold pressed at 200 MPa. The cold pressed billets were then hot pressed in vacuum at $2\ 050\ ^\circ\text{C}$

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Table 1 Composition, sintering parameters and properties of materials

Material	Composition/ %			Sintering condition			Porosity/ %	Flexural strength/ MPa	Fracture toughness/ (MPa·m ^{1/2})
	B ₄ C	TiB ₂	TiC	Temp/ °C	Pressure/ MPa	Time/ min			
B ₄ C	100	0	0	—	—	—	> 10	309	3.7
BT20	70	10	20	2 050	17	30	0	380	7.7
BT30	60	10	30	2 050	17	30	0	462	8.2

and 25 MPa for 30 min to a size of $d 55 \text{ mm} \times 5 \text{ mm}$.

The density of the sintered samples was estimated by the SEM analysis of polished surfaces. The phase analysis of the composites was conducted by X-ray diffractometer with CuK_α ray. The microstructure of the composites was evaluated using light microscopy on polished surfaces, SEM on polished and fracture surfaces, and TEM on ion-thinned sections. Flexural strength was measured by the three-point flexural test, with the bar size of $3 \text{ mm} \times 4 \text{ mm} \times 36 \text{ mm}$ and a span length of 30 mm. Fracture toughness was measured by the SENB method, with the bar size of $2 \text{ mm} \times 4 \text{ mm} \times 25 \text{ mm}$ and a span length of 16 mm. Both flexure strength and fracture toughness of the composites were measured in air at room temperature using an Instron 1186 machine.

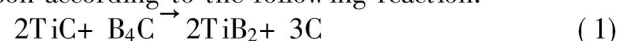
The starting composition, sintering parameters and the resulting mechanical properties of the sintered materials are all listed in Table 1.

3 RESULTS AND DISCUSSION

3.1 Microstructure of B-Ti-C composites

The X-ray diffraction result of BT30 sample is given in Fig. 1, with the major phases listed first. No TiC peak is found and the phases presented in

the specimen are TiB₂, B₄C and active carbon. It is indicated that, during the sintering process, the starting TiC has been fully transformed to TiB₂ and free carbon according to the following reaction.



The newly formed active carbon causes the diffusion in the bulk and along the grain boundaries of the available phase, which contributes to the formation of the dense structure of the sintered composites. The relative densities of the two specimens are all nearly 100%.

Figs. 2 (a) and (b) show typical microstructure of B-Ti-C composites. It is noteworthy, that

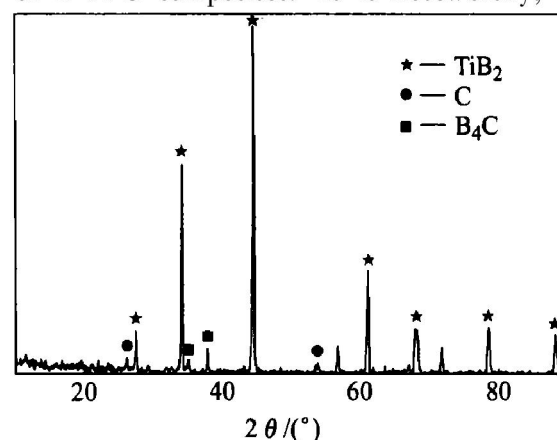


Fig. 1 XRD spectrum of BT30 composite

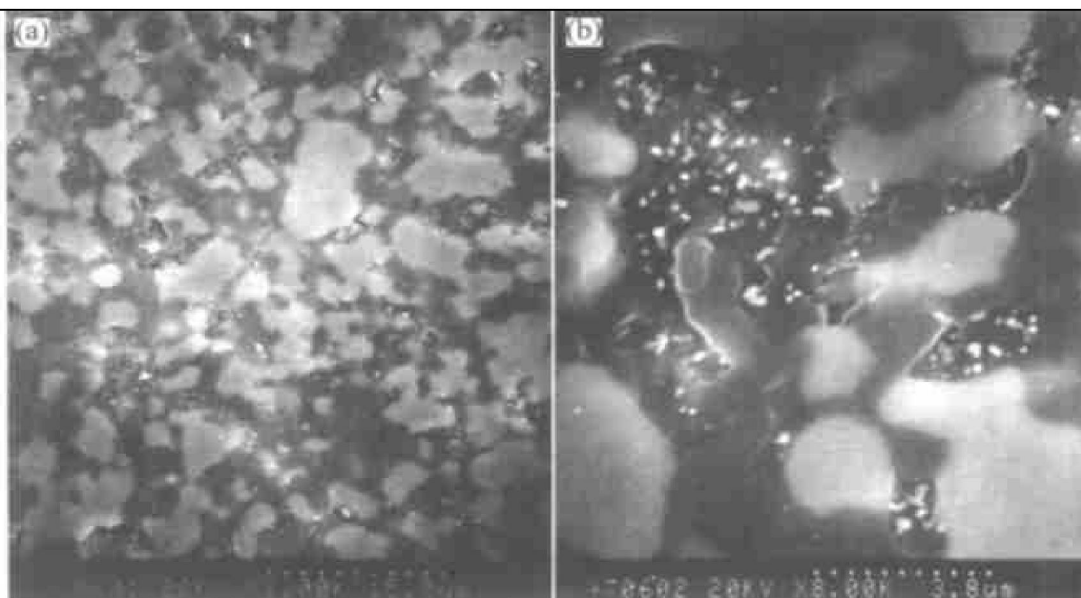


Fig. 2 SEM micrographs of polished surfaces of composites
(a) —Polished surface of BT30; (b) —Reaction zone of BT30

the composites consist of two main solid phases, i. e. TiB_2 particles in B_4C matrix. Additionally, some pores are observed on the polished surfaces. Further observation of the pores, just as Fig. 2 (b) shows that large numbers of fine TiB_2 particles disperse at the bottom of these pores. EDAX analysis subsequently identifies the traces of carbon at the same place. Based on these evidences, we can conclude that reaction (1) proceeded in the above pore regions, producing fine in-situ TiB_2 and graphite phase. When the specimens were rubbed and polished, graphite phase together with some TiB_2 particles were pulled away from the surface, leading to the formation of the pores.

Details of the microstructure are shown in selected TEM micrographs, which are presented in Fig. 3. It can be seen from Fig. 3 (a) that TiB_2 and graphite contact directly, indicating the simultaneous formation of both compounds consistent with the reaction

(1), further proving our speculation. Free carbon precipitates between the boundaries of B_4C and TiB_2 , characterized by a turbulent structure with a high level of defection. The poor crystallization is verified by the diffraction pattern in Fig. 3(c). In addition, free carbon in B-Ti-C composites could exist as thin layers according to the Lorenz's observation to B_4C - TiB_2 composites added by 4% - 6% free carbon^[8]. Also, Microcracks are found in our B-Ti-C composites, whose formation results from the thermal expansion mismatch between matrix and reinforcement. The mutual inhibition of the matrix and second phase particles contributes to the fine microstructure of the B-Ti-C composites.

3.2 Mechanical properties and fracture mechanism of B-Ti-C composites

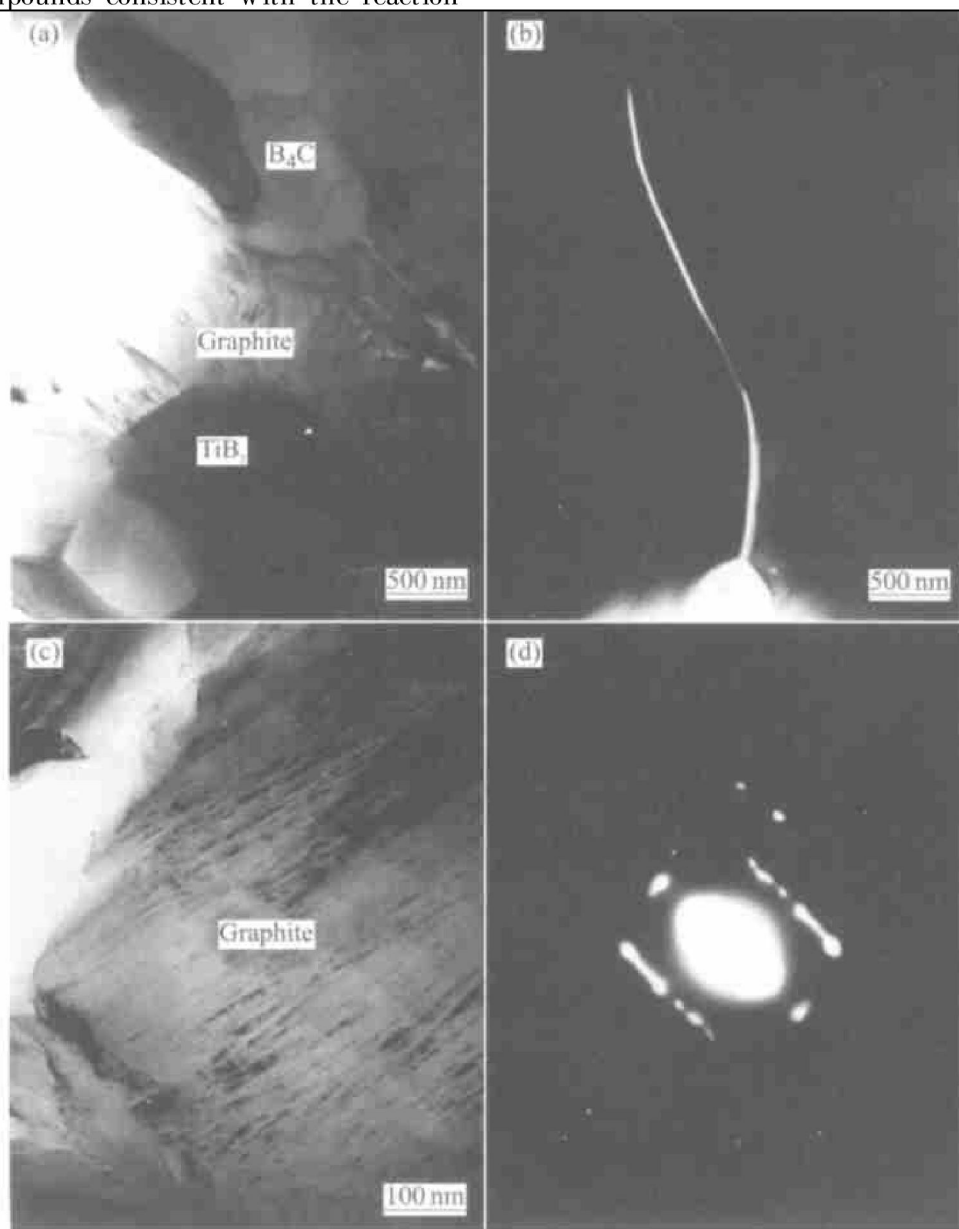


Fig. 3 TEM micrographs of BT30 composite

(a) —Microstructure of composite; (b) —Microcrack in composite;
(c) —Microstructure of graphite; (d) —Diffraction pattern of graphite

Table 1 lists the mechanical properties of the B-TiC composites. Since our sintering technique did not allow the sintering of pure B₄C, the data corresponding to 0 particles was from Ref. [8]. With the incorporation of the TiB₂ and TiC into B₄C matrix, both the flexural strength and the fracture toughness of the composites are efficiently improved. Particularly, the value of the fracture toughness of BT30 composite is 8.2 MPa·m^{1/2}, which is two times higher than that of pure B₄C and 4.5 MPa·m^{1/2} higher than that of B₄C-TiB₂ materials^[5], respectively.

In the present composites, the increase of strength results directly from high density and refined microstructure. Furthermore, monolithic TiB₂ has a much higher strength than that of B₄C, which also contributes to the high strength of the B-TiC composites.

The toughening mechanism is subject to crack deflection toughening and microcrack toughening. Seen from the micrographs of fracture surfaces (Fig. 4), where grain pull and crack deflection are predominant, the present composites features mostly intergranular fracture in compared with transgranular cracking in monolithic boron carbide. The intergranular fracture may be attribute to carbon layer between phase boundaries, which weaken the strength of the interfaces. Microcracks could be formed on cooling from the sintering temperature, since thermal residual stress above a critical threshold and weak interfaces could be provided simultaneously. According to the methodology of a process zone, toughening effect is represented by the following relation^[15]:

$$k_c = k_0 + \Delta k_t \quad (2)$$

where k_0 is the in situ toughness of the matrix, Δk_t is the toughness increment due to microcracking, which complies with the relationship:

$$\Delta k_t \propto \frac{\lambda E f \theta}{\sigma_c - \lambda E f \theta} \quad (3)$$

where λ is a numeric constant depending on the microcrack initiate criterion, E is elastic modulus, f is the volume fraction of microcrack and θ is the permanent dilatation associated with the thermal expansion mismatch strain $\Delta \alpha \cdot \Delta t$, denotes the critical stress for microcrack formation. Free carbon decreases the fracture resistance thus increases the toughness increment. At the same time, the starting introduced TiB₂ particles contribute to remain the high matrix toughness by limiting an easy path for main crack. Combined with these two effects, the composites obtained a high toughness, which is higher than that of either B₄C-TiB₂^[5] or B₄C-C^[7] composites. Although the appearance of microcrack is harmful to the strength, the strength is still high. As a result, the composites possess a balance of improved strength and toughness.



Fig. 4 SEM micrographs of fracture surfaces of composites
(a) —BT20; (b) —BT30

4 CONCLUSIONS

1) Highly dense B-TiC composites are produced by hot-pressed sintering B₄C, TiB₂ and TiC powders. Active carbon, which is formed during the reaction between B₄C and TiC, contributes to the dense structure of the composites.

2) The elevated values of mechanical properties are reached owing to the strong effect on the microstructure (grain size, intergranular fracture) caused by TiB₂ as well as free carbon. The toughness of 10% TiB₂-30% TiC-B₄C composites is 8.2 MPa·m^{1/2}, which is two times higher than that of pure B₄C, and 4.5 MPa·m^{1/2} higher than that of B₄C-TiB₂ materials, respectively.

3) The main toughening mechanism is crack deflection toughening and microcrack toughening.

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