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Effect of TiB_2 content on microstructure and mechanical properties of in-situ fabricated TiB_2/B_4C composites

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Abstract: The fully dense boron carbide matrix composites containing 10%−40% (volume fraction) TiB_2(TiB_2/B_4C) were in-situ fabricated via chemical reaction of B_4C, TiO_2 and graphite powders at 2 050 °C under a pressure of 35 MPa. Scanning electron microscopy (SEM) and transmission election microscopy (TEM) observations show that the sub-micron/nano-sized TiB_2 particles are uniformly located within the matrix grains and at the B_4C grain boundaries. With the increase of TiB_2 content, the elastic modulus and fracture toughness of composites increase remarkably. However, the situation is reversed for Vickers hardness and flexural strength. The fracture toughness exhibits a maximum value of 8.2 MPa·$m^{1/2}$ for the 40% (volume fraction) TiB_2/B_4C composite. The main toughening mechanisms of TiB_2/B_4C composites are microcrack toughening and crack deflection toughening.
Key words: TiB_2/B_4C composites; in-situ reaction; toughening mechanisms

1 Introduction

Boron carbide (B_4C) ceramics have been widely used for a variety of structural applications due to their extremely high hardness, wear resistance, low specific gravity and high chemical stability. However, the boron carbide used as a structural material was limited by two major drawbacks, namely, the low fracture toughness of B_4C and the very high temperature required for its sintering. Nearly, fully densification cannot be achieved by pressureless sintering and can be attained in pure B_4C only by hot pressing above 2 300 °C [1]. Many efforts have been made to improve the densification of B_4C by introducing sintering aids including metals (Al, Ti) [2−3], oxides (Al_2O_3, ZrO_2) [4−5] and non-oxides (W_2B_5, TiC) [6−7], as well as B and C [8−9].

Recently, it has been found that the addition of TiO_2 into B_4C along with the stoichiometric amount of C greatly reduces the sintering temperature and increases the toughness and strength [10]. The sintering process involves the conversion of TiO_2 to TiB_2 according to the following reaction:

$$2TiO_2+3C+B_4C\rightarrow 2TiB_2+4CO\uparrow \quad (1)$$

The TiB_2 phase serves as a strengthening and toughening agent whose presence results in an increase in bend strength to over 500 MPa [10−15]. A flexural strength of 866 MPa and fracture toughness of 3.2 MPa·$m^{1/2}$ were reported for fully dense B_4C-15% (volume fraction) TiB_2 composites prepared from a mixture B_4C/TiO_2/carbon black powders via reactive hot pressing for 1 h at 2 000 °C under a pressure of 50 MPa [16]. A mixture of fine-sized B_4C with 40% (mass fraction) TiO_2 was transformed into a 95% dense B_4C-TiB_2 composite fabricated at 2 160 °C for 1 h [17]. In the present study, in order to improve the mechanical properties of B_4C ceramics, B_4C-TiB_2 composites were in-situ synthesized by hot pressing. Furthermore, the effect of the in-situ TiB_2 on microstructure and mechanical properties of TiB_2/B_4C composites was investigated.

2 Experimental

Commercially available B_4C powder with an average particle size of 3.5 μm was used. The B_4C powder was mixed with high purity (99.9%) nano-size TiO_2 (smaller than 50 nm) and graphite powders by

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ball-milling for 12 h using alcohol as a vehicle. Mixing was performed in a plastic jar with agate balls as a milling media. In order to gain the sintered compositions containing 10%, 20%, 30%, and 40% (volume fraction) TiB_2, the levels of TiO_2 and C were adjusted according to the stoichiometry of Eq. (1) (see Table 1 for the green compositions). The blended powders were dried at 75 °C for 20 h. All samples were sintered at 1 850 °C for 0.5 h, and then hot-pressed for 1 h at 2 050 °C under a pressure of 35 MPa in a vacuum of 1.3×10^{-3} Pa. The heating rates were 20 °C/min from room temperature to 1 850 °C and 10 °C/min from 1 850 to 2 050 °C, respectively.

Table 1 Green specimen compositions

Green			Sintered		
$w(B_4C)$/%	$w(TiO_2)$/%	$w(C)$/%	$\varphi(B_4C)$/%	$\varphi(TiB_2)$/%	Theoretical density/($g\cdot cm^{-3}$)
79.42	16.79	3.79	90	10	2.718
65.19	28.41	6.40	80	20	2.916
54.75	36.92	8.33	70	30	3.114
46.77	43.44	9.79	60	40	3.312

Phase structure was identified by X-ray diffraction (XRD) analysis. The bulk density was measured by the Archimedes method. The hardness was evaluated by Vicker's indentation. The flexural strength was measured by a three-point bending test. The fracture toughness was measured by a single edge notch beam test. The polished surfaces were examined by SEM. The microstructure of the composites was investigated by TEM.

3 Results and discussion

All the TiB_2/B_4C composites fabricated by reaction hot-pressing exhibit almost fully densities. The TiB_2 synthesized by in-situ reaction clearly promotes the densification of boron carbide in the sintering process. From XRD analysis, no TiO_2 or C was detected in all of samples (as shown in Fig. 1). Only B_4C and TiB_2 phases were identified, although the presence of a small amount of oxygen or carbon cannot be ruled out.

Typical polished microstructures of various sintered TiB_2/B_4C composites (as shown in Fig. 2), consist of boron carbide (gray) and titanium diboride (white). In all the specimens, TiB_2 particles were dispersed in the B_4C matrix homogeneously. The average B_4C grain size decreases with the increase of TiB_2 volume fraction. The TiB_2 particles inhibit the increase of grain size. Most of grain sizes of the TiB_2 and B_4C are less than 5 μm. The largest B_4C grains have visible twinned structure (as shown in Fig. 3(a)). These grains might have been

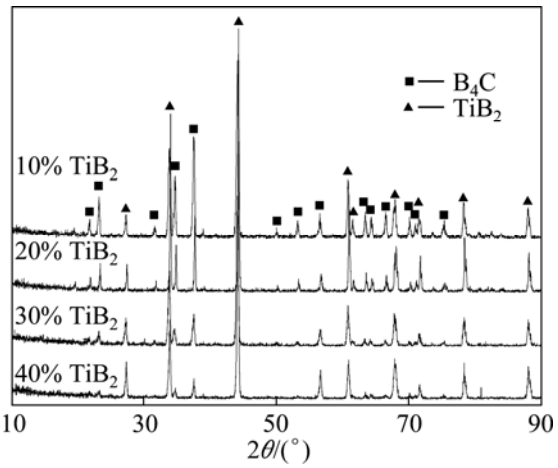

Fig. 1 XRD patterns of TiB_2/B_4C composites

subjected to high internal shear stress in cooling from the elevated temperatures, most likely due to thermal expansion anisotropy. In addition, some dislocation lines or loops were found near the small TiB_2 particles in the B_4C grains (as shown in Fig. 3(b)). It may be attributed to the thermal mismatch between TiB_2 and B_4C. From Figs. 3(c) and (d), the TiB_2 particles can be classified into two types: as above-mentioned small equiaxial nano-sized TiB_2 particles (20−150 nm) confined within larger boron carbide grains, and large, irregularly shaped TiB_2 particles (or particle clusters) located at the grain boundaries or triple junctions. The particles with grain boundary tend to coarsen, while those confined within the grains retain their initial size. This implies that the grain boundary is the major mass-transfer path for TiB_2 coarsening.

The variations of Vicker's hardness (Hv), elastic modulus (E), flexural strength and fracture toughness of B_4C/TiB_2 composites with TiB_2 volume fraction are shown in Figs. 4 and 5. The increase of TiB_2 content from 10% to 40% (volume fraction) results in a decrease in Hv due to the lower hardness of TiB_2 than that of B_4C and the rule of mixtures. The elastic modulus increases with increase of TiB_2 content, which is attributable to high elastic modulus for TiB_2. With adding 40% (volume fraction) TiB_2, the elastic modulus of the composite is 526 GPa, which is 15% higher than that of 10% (volume fraction) TiB_2/B_4C.

As shown in Fig. 5, the addition of TiB_2 has significant effects on the flexural strength and the fracture toughness of B_4C. The fracture toughness increases steadily with the increase of TiB_2 content, as shown in Fig. 5. The maximum value is 8.2 $MPa\cdot m^{1/2}$ for 40% (volume fraction) TiB_2. It depends upon the presence of uniformly distributed TiB_2 particles and a well sintered fine-grained B_4C matrix. The thermal

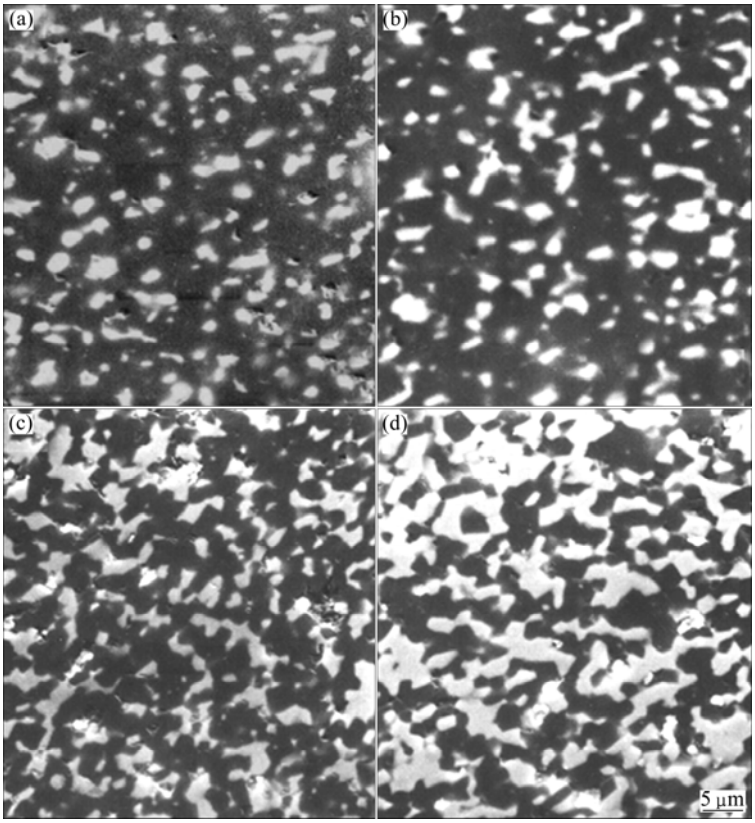

Fig. 2 SEM images of polished TiB_2/B_4C composites: (a) 10%TiB_2/B_4C; (b) 20%TiB_2/B_4C; (c) 30%TiB_2/B_4C; (d) 40%TiB_2/B_4C

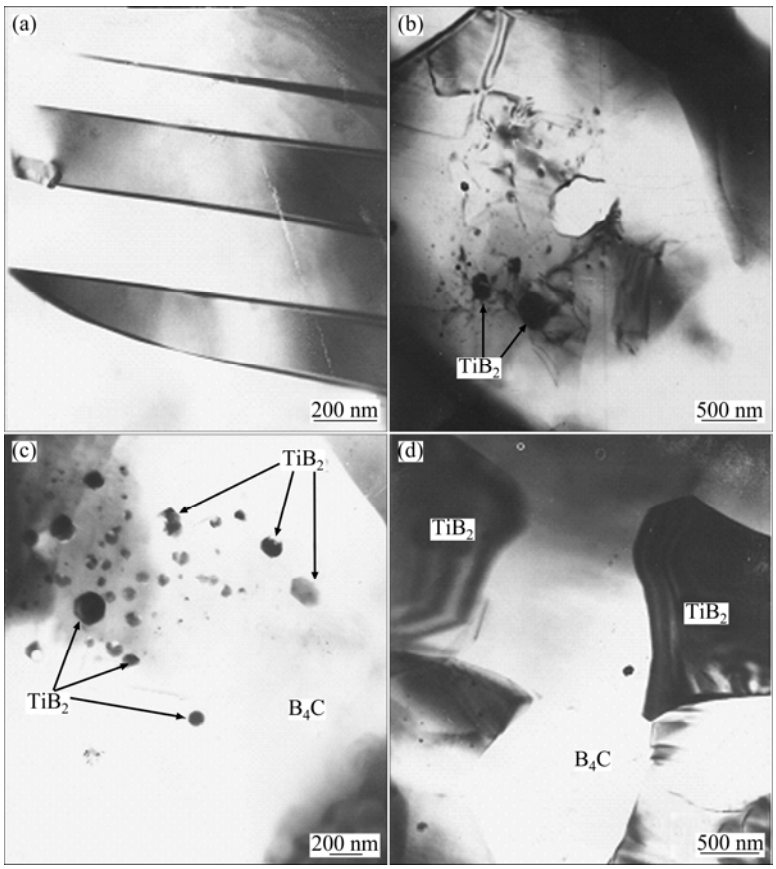

Fig. 3 TEM images of TiB_2/B_4C composites: (a) Twinned structure in B_4C; (b) Dislocation microstructure near small TiB_2 particles in B_4C grains; (c) Nano-sized TiB_2 particles in B_4C grain; (d) Large TiB_2 particles located at grain boundaries or triple junctions

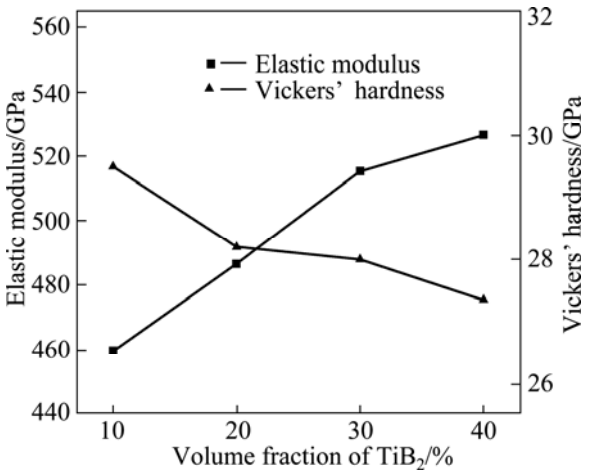

Fig. 4 Elastic modulus and Vickers' hardness as function of TiB_2 volume fraction for TiB_2/B_4C composites

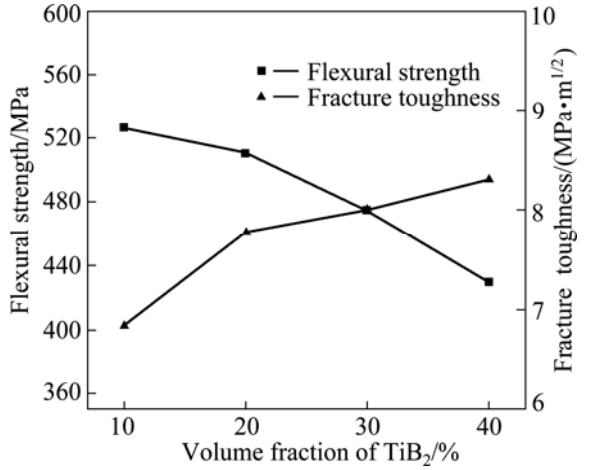

Fig. 5 Flexural strength and fracture toughness as function of volume fraction of TiB_2 for TiB_2/B_4C composites

expansion mismatch stress developed in cooling to room temperature places the TiB_2/B_4C boundary under the tensile stress and leads to partial or full fracture of the interface due to a large difference in the linear thermal expansion between B_4C and TiB_2. As calculated by SKOROKHOD and KRSTIC [10], the residual stress is about 1 GPa. The large boundary stress is sufficient to break the interface and cause microcracking followed by a partial or full relaxation of the stress. The crack with size less than their presence has positive effects on the fracture toughness. In addition, from Fig. 6, crack deflection occurs around the TiB_2 particles for the 20% (volume fraction) TiB_2/B_4C composite.

Different from fracture toughness, the flexural strength decreases slowly from 526 to 429 MPa with adding 40% (volume fraction) TiB_2. It may weaken the effect of residual stresses and microcracks.

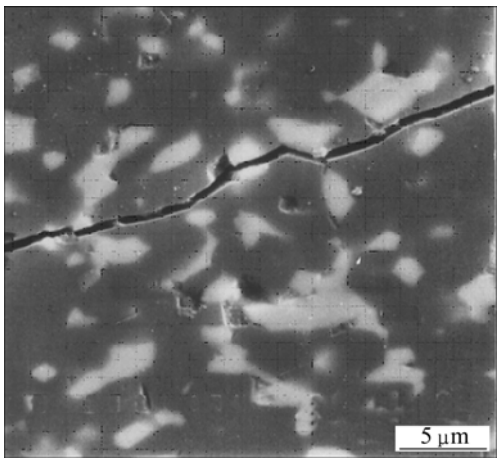

Fig. 6 Crack deflection on 20% (volume fraction) TiB_2/B_4C composite specimen

4 Conclusions

1) TiB_2/B_4C composites exhibit a composite microstructure where TiB_2 particles are dispersed uniformly in a fine grained B_4C matrix.

2) The fracture toughness increases steadily with increasing TiB_2 content, reaching the maximum value of 8.2MPa·$m^{1/2}$ at 40% (volume fraction) TiB_2.

3) The main toughening mechanisms are microcracks toughening and deflection toughening of propagating cracks caused by the thermal expansion mismatch between TiB_2 and B_4C.

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TiB_2 含量对原位反应合成 TiB_2/B_4C 复合材料的组织结构和力学性能的影响

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摘 要：以 B_4C, TiO_2 和石墨粉为原料，采用原位反应热压烧结工艺(2 050 °C，35 MPa，1 h)制备了致密的 TiB_2 含量为 10%~40%(体积分数)的 TiB_2/B_4C 复合材料，并对复合材料的组织结构和力学性能进行了研究。扫描电子显微镜和透射电子显微镜分析结果表明：在 B_4C 晶内及晶界处均匀分布着纳米或亚微米级的 TiB_2 颗粒，随着 TiB_2 含量的增加，弹性模量和断裂韧性明显增大，而弹性模量和抗弯强度却随之减小。40%(体积分数)TiB_2/B_4C 复合材料具有高的断裂韧性，高达 8.2 $MPa·m^{1/2}$，主要增韧机制由微裂纹增韧和裂纹偏转增韧。

关键词：TiB_2/B_4C 复合材料；原位反应；增韧机理

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