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In-situ Synthesized TiB_2 Toughened SiC

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Abstract

A new process of preparing SiC–TiB_2 particulate-reinforced composite by in-situ *synthesis has been developed. TiB_2 particles were formed* in situ *by chemical reaction between TiH_2, Si and B_4C; the particle size of the TiB_2 is usually about 2 μm. The composite containing 30 vol% TiB_2 exhibited a fracture toughness of 6·21 MPa $m^{1/2}$ and a flexural strength of 400 MPa. It was suggested that the main toughening mechanisms are the thermal residual stress field, crack bridging by TiB_2 particles and crack deflection around TiB_2 particles.*

1 Introduction

SiC ceramics have many good properties and are prospective structural materials. But their low fracture toughness make them very sensitive to defects and less reliable. Prior studies found that by adding a second phase particle, such as TiC[1,2] or TiB_2,[3-5] into the SiC matrix, the strength and fracture toughness can be greatly improved. The above authors considered that the main toughening mechanism is crack deflection caused by the second phase particles via induced residual stresses. Taya *et al.*[6] reasonably explained the experimental results by calculating and theoretically analysing the residual stress toughening mechanisms. Table 1 shows the main physical properties of TiB_2 and SiC.[7]

The above discussed SiC matrix composites were all prepared by directly adding the second phase particles. By internally synthesizing TiB_2, Tani and Wada[8,9] obtained SiC–TiB_2 ceramic composites from the chemical reactions $TiN + 2B \rightarrow TiB_2 + 0{\cdot}5N_2 \uparrow$ and $TiO_2 + 0{\cdot}5B_4C + 1{\cdot}5C \rightarrow TiB_2 + 2CO \uparrow$. This kind of processing avoids the difficulties of treating TiB_2 powders (owing to their slow reaction with water), and the internally synthesized TiB_2 particles are finer and more uniformly distributed. The reactant B simultaneously improved the sintering of the SiC matrix. According to the above reactions, there are gases such as N_2 and CO released in the reaction processes, which prevent sintering to some extent. So the following *in situ* chemical reaction was developed to internally synthesize TiB_2:

$$TiH_2 \rightarrow Ti + H_2 \uparrow$$
$$x\,SiC + Si + 2Ti + B_4C \rightarrow (1 + x)SiC + 2TiB_2 \quad (1)$$

According to this reaction, when no extra SiC is added, the phase composition of the product is 28·89 vol% SiC and 71·11 vol% TiB_2, and the volume content of the second phase TiB_2 can be conveniently adjusted by adding extra SiC. This paper describes the effect of the TiB_2 content on the mechanical properties and the toughening mechanisms. The mechanism of the above reaction has been discussed elsewhere.[10]

2 Experimental Procedure

The raw materials were used as-received. They are α-SiC (6H) (particle size ~ 1 μm, BET specific surface area 7·5 m^2 g^{-1}, major impurity = oxygen at < 0·5 wt%), Si (≥ 99% phase pure, particle size < 45 μm) and TiH_2(≥ 99·5% phase pure, particle size < 45 μm), B_4C (> 99% phase pure, particle size 5–8 μm). There were three composites, designated ST-1 (monolithic SiC), ST-2 (containing 15 vol% TiB_2) and ST-3 (containing 30 vol% TiB_2). According to the content of SiC, 1 wt% C and 1 wt% B_4C were added as sintering additives. After being ball-milled with a WC-Co media in alcohol for 4 h and dried, the mixed powders were hot pressed at 2000°C in Ar for 60 min under 30 MPa, and a disc of $\phi60 \times 5$ mm was then obtained.

The densities of the hot pressed specimens were obtained by liquid displacement. X-ray diffraction (XRD) was used to determine the phase composition of the fabricated bodies. The microstructure was examined by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and HREM. Vickers hardness was tested at a load of 98 N. The fracture toughness K_{IC} was measured

Table 1. Properties of TiB_2 and SiC

Property	*SiC*	*TiB_2*
Density (g cm^{-3})	3·21	4·52
Melting point (°C)	2540*	2790
Thermal expansion coefficient (× 10^{-6} °C^{-1})	4·0	8·1
Poisson's ratio	0·14	0·28
Elastic modulus (GPa)	414	529
Vickers hardness (GPa)	25·5	34

*Decomposition temperature.

on bars (2 × 4 × 20 mm) machined from the hot-pressed specimens by the SENB method (notch width <0·2 mm, depth ~1·6 mm, load speed 0·5 mm min^{-1}). The flexural strength 6_f was measured on bars (3 × 4 × 36 mm) by the three-point bending method (span 30 mm, load speed 0·5 mm min^{-1}).

3 Results and Discussion

According to the XRD pattern of sample ST-2, as shown in Fig. 1 (to which that of ST-3 is similar) it can be seen that there are only phases of SiC and TiB_2, and no other phase existed, indicating that the high temperature reaction was in accordance with reaction (1). The SiC formed from reaction (1) was β-SiC,[10] but the starting powder of SiC was α-SiC, thus the SiC existing in the samples was a mixture of α- and β-SiC.

The relative densities of the hot-pressed specimens are shown in Fig. 2. It can be seen that the density was obviously improved by increasing the volume content of TiB_2. The relative density of sample ST-3 was 99·33%, indicating the reactants simultaneously improved the density of the SiC matrix. Figure 3 shows the flexural strength and fracture toughness versus volume content of TiB_2. It can be seen that the properties of sample ST-3 were relatively better; its fracture toughness was 6·21 ± 0·59 MPa $m^{1/2}$ and fracture strength was 392 ± 30 MPa. The 'lower' properties of monolithic SiC and sample ST-2 may be mainly due to their low sintering densities. So, the following discussion is based on the ST-3 specimen.

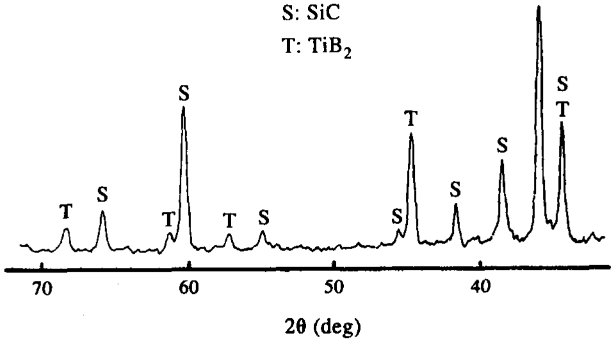

Fig. 1. XRD pattern of specimen ST-2 (CuKα).

Figure 4 is the TEM micrograph of sample ST-3. It can be seen that the particle size of TiB_2 formed *in situ* is ~2 μm. Figure 5 is the HREM image of the interface between an *in situ* synthesized TiB_2 particle and the α-SiC matrix, which shows that the interface is 'clean' and free from any interfacial phase. Such a characteristic is attributed to the high surface energy of the newly formed TiB_2 by *in situ* reaction and indicates that

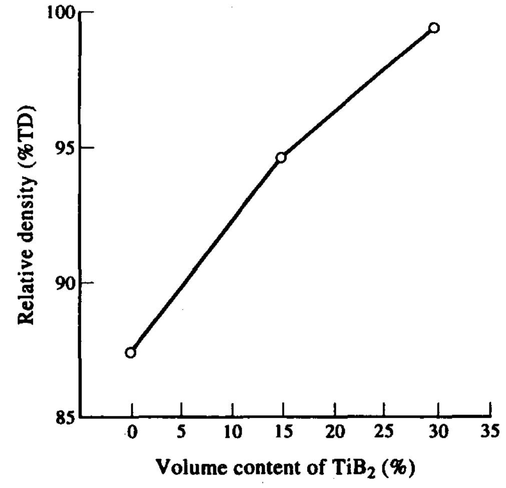

Fig. 2. Relative density of specimen versus volume content of TiB_2.

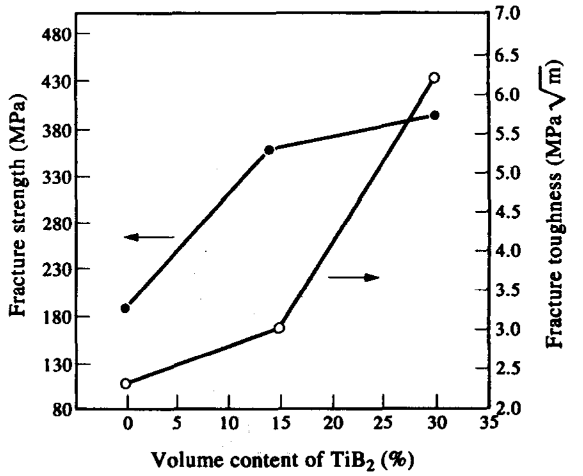

Fig. 3. Flexural strength and fracture toughness versus volume content of TiB_2.

Fig. 4. TEM micrograph of sample ST-3. The dark phase is TiB_2 and the grey phase is SiC.

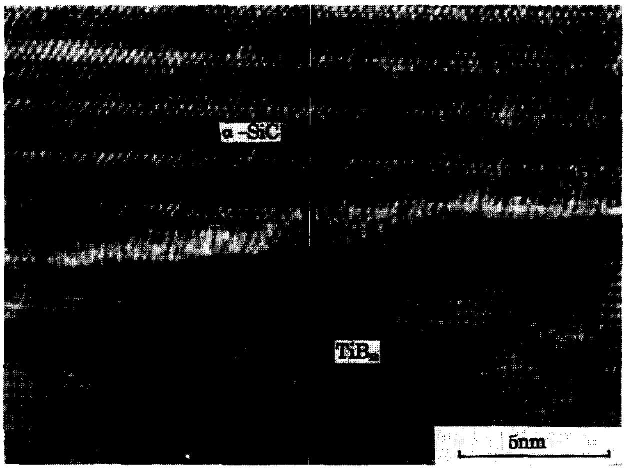

Fig. 5. HREM image of α-SiC–TiB_2 interface.

the second phase particles formed *in situ* directly connect with the matrix and the interfacial connection will be strong; which is markedly different from the weak TiB_2–SiC interface of the composites produced by directly adding TiB_2 particles.[4,11]

The mismatch between the linear thermal expansion coefficient (α) and elastic moduli (E) in the SiC matrix and the TiB_2 particle results in the generation of residual stresses in the particles and around the matrix (tensile residual stress and compressive tangential stress).[1] A crack would be expected to propagate in a direction parallel to the axis of the local compressive stress and perpendicular to the axis of the local tensile stress in the matrix surrounding the particle, which will induce crack deflection.

Figure 6 shows the crack interaction with TiB_2 particles on the polished surface of sample ST-3. It can be seen that the crack deflected around the TiB_2 particles and crack branching occurred. Figure 7 shows crack bridging by a TiB_2 particle at the crack tip. Because the interfaces between the *in situ* synthesized TiB_2 particles and SiC matrix are strong, TiB_2 particulate bridging is easily formed. According to the crack bridging toughening mechanism,[12] higher interfacial strength will induce a better toughening effect.

Fig. 6. Crack deflection by TiB_2 particles in sample ST-3.

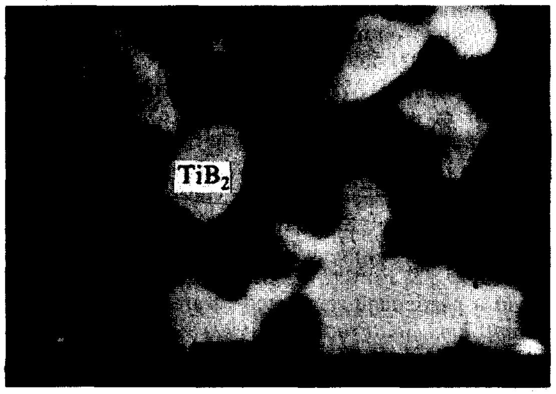

Fig. 7. Crack bridging by TiB_2 particle. The light-grey phase is TiB_2 and dark-grey phase SiC.

According to the calculation method proposed by Taya *et al.*,[6] the calculated average residual stresses for the SiC matrix and TiB_2 particle in composite ST-3 are (using the data in Table 1 and setting ΔT, the temperature range over which stresses are not relieved, to be 1200 K):

$$\langle\sigma\rangle_{\mathrm{SiC}} = -595\ \mathrm{MPa}, \quad \langle\sigma\rangle_{\mathrm{TiB_2}} = +1388\ \mathrm{MPa}$$

This compressive stress in the SiC matrix will increase the fracture toughness according to the thermal residual stress toughening mechanism.[6] As discussed above, it was suggested that the toughening mechanisms for the ST-3 composite were the thermal residual stress field, crack bridging by TiB_2 particles and crack deflection around TiB_2 particles.

4 Conclusions

(1) TiB_2 can be synthesized *in situ* in a SiC matrix by the chemical reaction of TiH_2, Si and B_4C. The particle size of TiB_2 is generally ~2 μm.
(2) The reactant simultaneously improved the densification of the SiC matrix.
(3) The fracture toughness and flexural strength of SiC–30 vol% TiB_2 were, respectively, 6·21 ± 0·59 MPa $m^{1/2}$ and 392 ± 30 MPa. The toughness was twice as high as that of monolithic SiC ceramics. It was suggested that the main toughening mechanisms were the thermal residual stress field, crack bridging by TiB_2 particles and crack deflection around TiB_2 particles.

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