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Preparation and Microstructure of TiB_2–TiC–SiC Platelet-Reinforced Ceramics by Reactive Hot-Pressing

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Abstract

Using TiH_2, Si and B_4C as raw materials, a platelet-reinforced ceramic composite of TiB_2–TiC–SiC was prepared by reactive hot-pressing. The product has three phases: TiB_2 (in plate-like shape), TiC and β-SiC. The microstructural characteristics of the composite were observed by scanning electron microscopy and the phase chemistry was analysed by energy-dispersive X-ray analysis. The mechanical properties of the composite were also determined. © 1996 Elsevier Science Limited.

1 Introduction

In the ternary system of TiB_2–TiC–SiC, the binary composites of TiB_2–TiC, SiC–TiB_2 and SiC–TiC have better mechanical properties than the corresponding monolithic ceramics. Furthermore, de Mestral and Thevenot reported that the mechanical properties of TiB_2–TiC–SiC ternary composites are better than those of the above three binary composites.[1]

Ceramic composites prepared by reaction techniques exhibit several advantages when compared with conventionally processed ceramics.[2] The main advantages are low-cost raw materials, simple processing and the ability to produce special microstructures and mechanical properties in the resulting materials. In the ternary system of TiB_2–TiC–SiC, SiC–TiB_2 composites were prepared by *in situ* synthesis of TiB_2 in a SiC matrix from the reaction of TiN and B or TiO_2, B_4C and C[3,4] or TiC and B[5] or TiH_2, Si and B_4C.[6] Ti(C, N)–SiC composites were prepared by the reaction of TiC and Si_3N_4 when TiN was added.[7] TiB_2–SiC composites were prepared by the reaction of TiH_2, Si and B_4C.[8] Recently, TiB_2-TiC composites were fabricated by liquid infiltration of titanium into a B_4C preform at 1600–1800°C in an Ar atmosphere[9] and titanium–boron–carbon composites with plate-like Ti_3B_4 phase by transient plastic phase processing (TPPP) using Ti and B_4C as starting materials.[10]

In consideration of the low oxidation resistance of TiB_2–TiC composites, SiC was thought to be an effective additive. Therefore, a series of TiB_2–TiC–SiC ternary composites was prepared by reaction synthesis, which was reported in a previous paper.[11] This present paper presents the preparation process and the microstructure of the composite ceramics produced by reactive hot-pressing according to the following reaction:

$$TiH_2 \rightarrow Ti + H_2\uparrow$$

$$4Ti + 0{\cdot}5Si + 1{\cdot}5B_4C \rightarrow 3TiB_2 + TiC + 0{\cdot}5SiC \quad (1)$$

The volume contents of the phase composition according to the above reaction are 71·52% TiB_2, 18.79% TiC and 9·68% SiC.

2 Experimental Procedure

The starting powders were TiH_2 (purity 99·5%, particle size <45 μm), Si (purity > 99%, particle size <45 μm) and B_4C (purity 99%, particle size 5–8 μm). The stoichiometric powders were mixed in alcohol with WC–Co balls for 4 h in a nylon pot and then dried. The composite was fabricated by reactive hot-pressing in a graphite die with BN coating at 2000°C under 30 MPa for 60 min in an Ar atmosphere. Figure 1 shows the temperature and pressure as a function of time in the process of reactive hot pressing. As shown in the plot, there is a 15 min stage at the temperature of 1500°C in order to give enough time for chemical reaction, then the pressure was gradually applied. Otherwise, if the pressure was applied too early and too fast, some metal melt would flow out of the die.

The product was electrical-discharge machined to specimens and then ground and polished. Phase composition was determined by X-ray diffraction (XRD). The water displacement method was used to

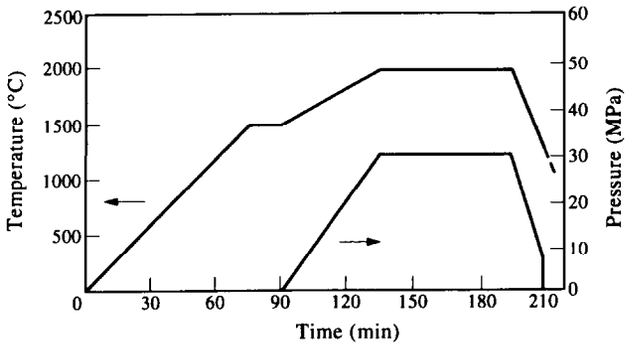


Fig. 1. Reactive hot-press control showing the temperature and pressure as function of time.

Fig. 2. SEM photograph of the composite. The grey phase is TiB_2, white phase TiC and dark phase β-SiC.

test the density. Fracture toughness was determined using the single-edge notched beam (SENB) method (three-point bending, just broken from the notch);[12] the specimen size was 2 × 4 × 20 mm, the notch width was <0·2 mm and the notch depth was about 1·6 mm, and the crosshead speed was 0·5 mm min^{-1}. Fracture strength was tested using the three-point bending method; the specimen size was 3 × 4 × 36 mm and the crosshead speed was 0·5 mm min^{-1}. The microstructure of the composite was examined by scanning electron microscopy (SEM). Energy-dispersive X-ray analysis (EDAX) associated with SEM was used to determine phase chemistry.

3 Results and Discussion

According to the XRD patterns shown in a previous paper,[11] there are only TiB_2, TiC and β-SiC in the composite, indicating that the high-temperature reaction was in accordance with reaction (1). Actually, reaction (1) is a sum of the two following reactions:

$$3Ti + B_4C \rightarrow 2TiB_2 + TiC \quad (2)$$

$$Ti + 0{\cdot}5Si + 0{\cdot}5B_4C \rightarrow TiB_2 + 0{\cdot}5SiC \quad (3)$$

The above two reactions were almost finished at 1350°C after 30 min in an Ar atmosphere,[8,13] and TiB_2 and TiC or TiB_2 and β-SiC were formed.

The properties of the composite are listed in Table 1, in which each value is an average of five or six measurements. Table 1 shows that a dense body can be obtained by reactive hot-pressing under the present sintering condition, and the mechanical properties of the composite are satisfactory.

Figure 2 is an SEM photograph of the polished surface of the composite, in which the grey phase is TiB_2, the white phase is TiC and the black phase is β-SiC. It can be seen from the picture that TiB_2 phase is generally plate-like in shape, and the phases are not uniformly distributed. This kind of microstructure can be attributed to the coarse particle size of the starting powders and the dispersion process of the starting powders. Therefore, the microstructure of the composite can be improved by the use of finer starting powders and a more effective dispersion process.

Figure 3 presents the EDAX spectra of TiB_2, TiC, β-SiC and the whole area in Fig. 2. No Si was detected in the TiB_2 phase indicating that there is no reaction between TiB_2 and SiC. However, Si and Ti were detected in TiC and SiC, respectively, revealing that there is a reaction between the TiC and SiC and solid solutions formed. These results are consistent with the investigation of de Mestral and Thevenot.[1]

It can also be seen from Fig. 2 that the TiB_2 platelets grew very well in TiC-rich regions, as shown in Fig. 4(a), and grew relatively imperfectly in SiC-rich regions, as shown in Fig. 4(b). According to results reported for the TiB_2/SiC system prepared by reaction (3), the SiC phase was converted from the previously formed TiC phase and the TiB_2 phase was quasi-spherical in shape.[8] Therefore, it is suggested that the formation of TiB_2 platelets is closely related to the existence of the TiC phase, and the existence of the SiC phase prohibited the growth of TiB_2 platelets. Details of this phenomenon will be reported after further investigation.

In TiB_2-rich regions, the growth of TiB_2 platelets was prohibited and, if the agglomeration

Table 1. Properties of TiB_2–TiC–SiC platelet composite

Relative density (% of theoretical)	*Fracture strength (MPa)*	*Fracture toughness (MPa $m^{1/2}$)*	*Phase composition*
99·8	680·5 ± 69·3	6·90 ± 0·18	TiB_2, TiC, β-SiC

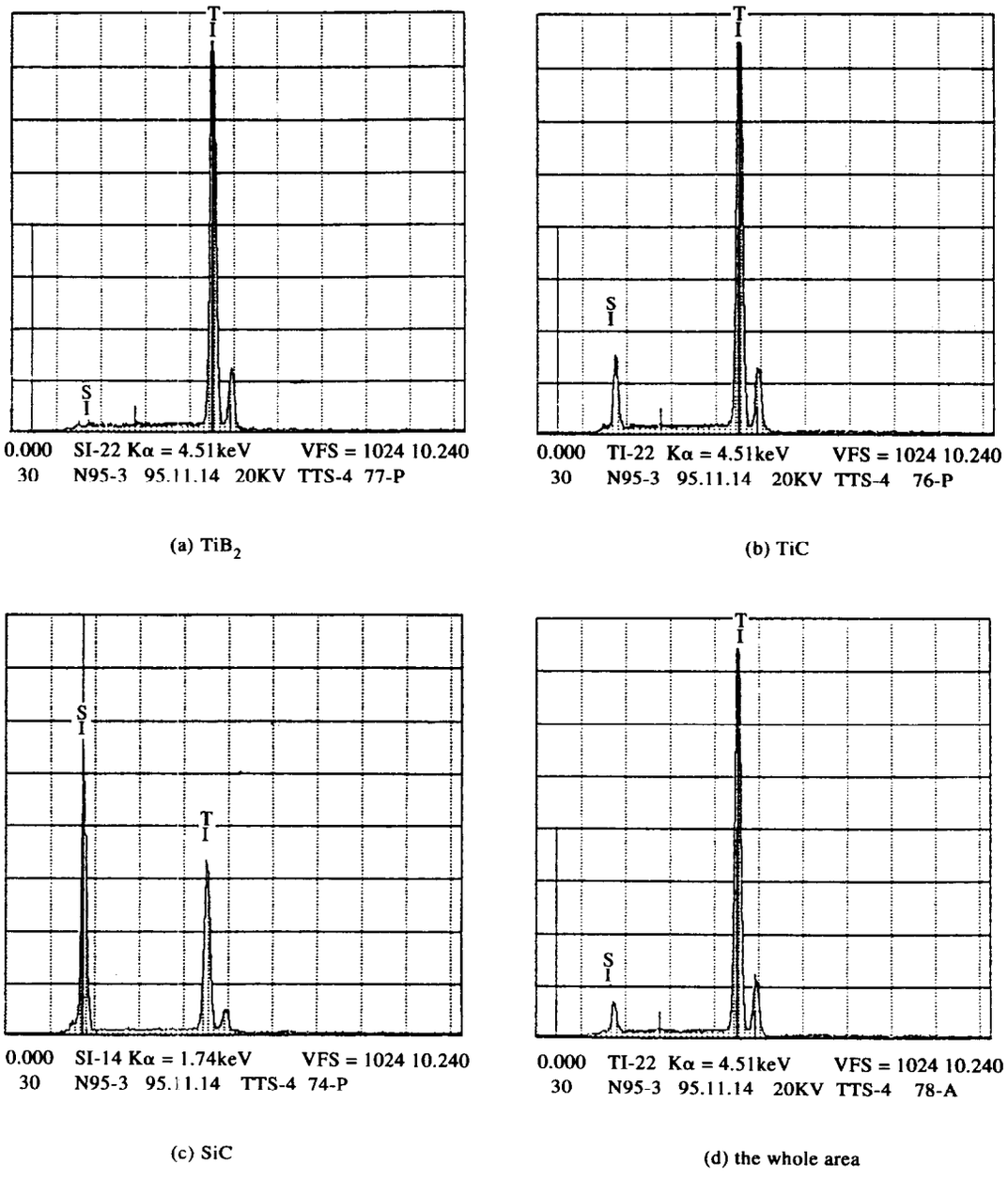


Fig. 3. EDAX spectra of (a) TiB_2, (b) TiC, (c) SiC and (d) the whole area in Fig. 2.

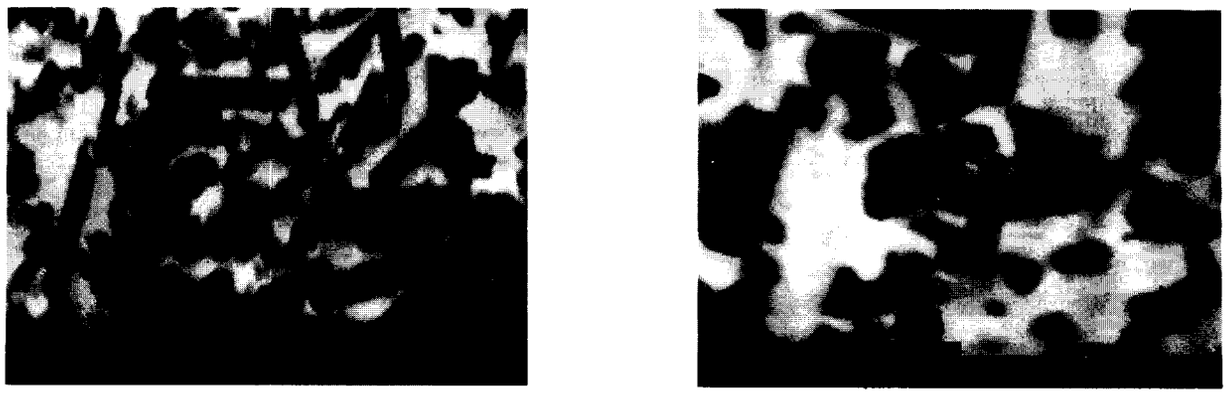
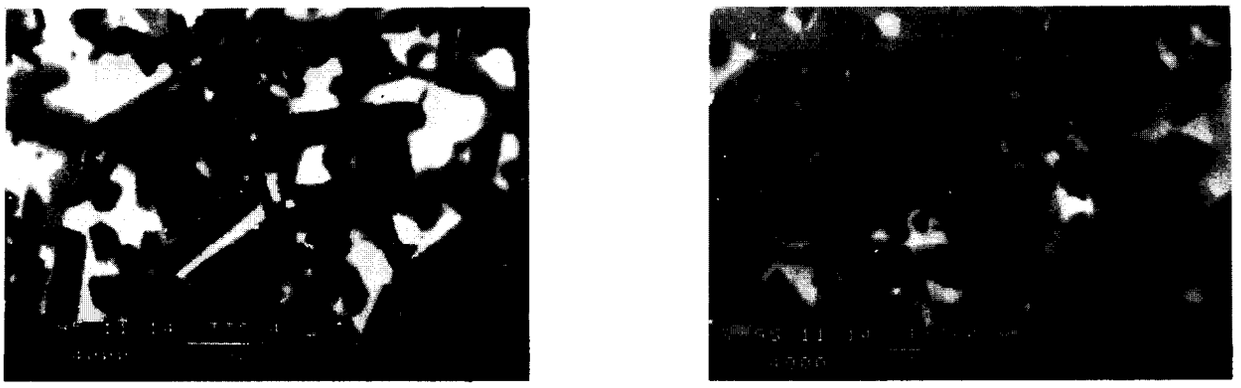


Fig. 4. The shape of the TiB_2 phase in different regions: (a) TiC-rich region; (b) SiC-rich region.

region of TiB_2 was large enough, quasi-spherical TiB_2 particles were formed, as shown in Fig. 5. This means that good distribution of each phase in the composite and/ or reducing the TiB_2 content will help the growth of TiB_2 platelets, and better mechanical properties of the composite may be obtained.



(a) (b)

Fig. 5. Effect of TiB_2 agglomeration on the shape of the TiB_2 phase: (a) in TiB_2-rich region; (b) in a large agglomeration region of TiB_2.

4 Conclusions

A platelet-reinforced ceramic composite of TiB_2–TiC–SiC was prepared by reactive hot-pressing using TiH_2, Si and B_4C as starting materials. The growth of TiB_2 platelets was different in different regions of the composite. The platelets grew very well in the TiC-rich regions and imperfectly in the SiC-rich regions, with agglomeration of TiB_2 prohibiting the growth of TiB_2 platelets. Additionally, the EDAX results show that there is no reaction between TiB_2 and SiC while there is reaction between TiC and SiC, forming solid solutions. The mechanical properties of the composite are satisfactory.

Acknowledgement

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