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SiC matrix composites reinforced with internally synthesized TiB_2

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A new process of preparing particulate-reinforced ceramic composites by internal synthesis has been developed. SiC powder mixed with TiN and amorphous boron was hot-pressed above 2000° C in an argon atmosphere. The boron molar content in the mixture was designed to be more than twice that of TiN. In the process of hot-pressing, the following reaction took place between 1100 and 1700° C

$$TiN + 2B \rightarrow TiB_2 + \tfrac{1}{2}N_2\uparrow$$

The synthesis of TiB_2 was followed by the densification of SiC matrix with the aid of the excess boron. The new process provides SiC matrix composites in which fine TiB_2 particulates are dispersed. Compared with hot-pressed monolithic SiC, the composite containing 20 vol % TiB_2 exhibits a 80% increase in fracture toughness and about the same flexural strength of 490 MPa at 20° C in air and 750 MPa at 1400° C in a vacuum.

1. Introduction

SiC ceramics are promising candidates for heat engine applications. However, they have a low fracture toughness value, which causes them to suffer from serious damage under contact stress or solid particle impingement. Therefore, one of the most important problems of silicon carbide ceramics is to improve their fracture toughness. Recent investigations [1, 2] have demonstrated that the addition of a transition metal boride particulate is effective in increasing the mechanical properties of SiC. Janney [1] obtained a 45% increase in fracture toughness and 28% increase in flexural strength in hot-pressed SiC containing 15 vol % TiB_2. Pressureless-sintered SiC containing 16 vol % TiB_2 was reported to have up to 90% higher fracture toughness than monolithic SiC [2]. Hot-pressed SiC–ZrB_2 was also described as an electroconductive ceramic composite [3]. These composites are fabricated by sintering or hot-pressing mixtures of SiC powder, reinforcing particulates, and sintering aids. Transition metal boride powders are generally available in large particle diameter and furthermore are difficult to treat owing to their high reactivity [4]. McMurtry *et al.* [2] suggested that special nonaqueous blending and drying procedures should be used in producing a homogeneous mixture of presized TiB_2 and submicrometre SiC powders.

Thus it is a new idea to produce a reinforcing particulate, synthesized *in situ* from its source materials in the sintering process when the commercial powder is so large or highly reactive that it is not favourable as a starting material. It was expected that an internally synthesized TiB_2 particulate would be finer than commercial TiB_2 powders. Titanium nitride, carbide and oxide are commercially available in finer particle size and are less sensitive to water than titanium diboride. It is advantageous for the internal synthesis that the boron or boron compound works not only as a reactant for TiB_2 but also as a sintering aid for the SiC matrix, and that TiB_2 is more stable than TiC, TiN or TiO_2 in the presence of boron in the high-temperature range where the SiC matrix can be densified. This paper describes the partially reactive hot-pressing of the mixture of SiC, titanium source material and boron source material to produce SiC–TiB_2 composites, and also reports the properties of the composites obtained.

2. Experiments

2.1. Selection of reaction system

Among the several methods available for synthesis of TiB_2 [4–10], the following solid state reactions between TiC, TiN or TiO_2 for a titanium source and boron, B_4C or BN for a boron source have been considered as candidates for the internal synthesis reaction.

$$TiC(s) + 2B(s) \rightarrow TiB_2(s) + C(s) \tag{1}$$

$$TiC(s) + \tfrac{1}{2}B_4C(s) \rightarrow TiB_2(s) + 1\tfrac{1}{2}C(s) \tag{2}$$

$$TiC(s) + 2BN(s) \rightarrow TiB_2(s) + C(s) + N_2(g) \tag{3}$$

$$TiN(s) + \tfrac{1}{2}B_4C(s) \rightarrow TiB_2(s) + \tfrac{1}{2}C(s) + \tfrac{1}{2}N_2(g) \tag{4}$$

$$TiN(s) + 2B(s) \rightarrow TiB_2(s) + \tfrac{1}{2}N_2(g) \tag{5}$$

$$TiN(s) + 2BN(s) \rightarrow TiB_2(s) + 1\tfrac{1}{2}N_2(g) \tag{6}$$

$$TiO_2(s) + 2B(s) + 2C(s) \rightarrow TiB_2(s) + 2CO(g) \tag{7}$$

$$TiO_2(s) + 2BN(s) + 2C(s) \rightarrow TiB_2(s) + 2CO(g) + N_2 \tag{8}$$

$$TiO_2(s) + \tfrac{1}{2}B_4C(s) + 1\tfrac{1}{2}C(s) \rightarrow TiB_2 + 2CO(g) \tag{9}$$

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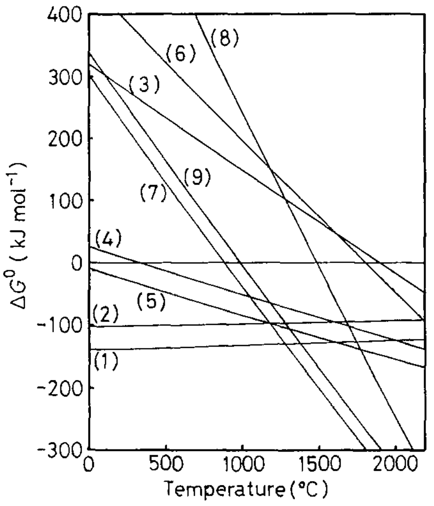

Figure 1 The standard free energy changes, ΔG^0, with temperature for various titanium diboride forming reactions: (1) $TiC(s) + 2B(s) \rightarrow TiB_2(s) + C(s)$; (2) $TiC(s) + \frac{1}{2}B_4C(s) \rightarrow TiB_2(s) + 1\frac{1}{2}C(s)$; (3) $TiC(s) + 2BN(s) \rightarrow TiB_2(s) + C(s) + N_2(g)$; (4) $TiN(s) + \frac{1}{2}B_4C(s) \rightarrow TiB_2(s) + \frac{1}{2}C(s) + \frac{1}{2}N_2(g)$; (5) $TiN(s) + 2B(s) \rightarrow TiB_2(s) + \frac{1}{2}N_2(g)$; (6) $TiN(s) + 2BN(s) \rightarrow TiB_2(s) + 1\frac{1}{2}N_2(g)$; (7) $TiO_2(s) + 2B(s) + 2C(s) \rightarrow TiB_2(s) + 2CO(g)$; (8) $TiO_2(s) + 2BN(s) + 2C(s) \rightarrow TiB_2 + 2CO(g) + N_2$; (9) $TiO_2(s) + \frac{1}{2}B_4C(s) + 1\frac{1}{2}C(s) \rightarrow TiB_2(s) + 2CO(g)$.

The standard free energy changes of the above reactions are shown in Fig. 1 [11]. Reactions 1 and 2 are exothermic, so that they may cause a too rapid formation of TiB_2, as observed in the $Ti + 2B \rightarrow TiB_2$ system [7]. Reactions 1 to 4 produce carbon as well as TiB_2; on the other hand, reactions 7 to 9 require carbon to reduce TiO_2. Reactions 5 and 6 are endothermic, in which carbon is not involved. The standard free energy change of Reaction 5 is negative above room temperature and that of Reaction 6 is positive up to about 1800° C. Furthermore, the nitrogen gas volume evolved by Reaction 6 is three times as large as that evolved by Reaction 5. They suggest that Reaction 5 is more advantageous than Reaction 6 because the gas-generating reaction at high temperature will prevent the densification of SiC matrix.

With the above considerations, boron and TiN were selected as source materials for the internal synthesis of TiB_2. TiN powder is commercially available in submicrometre sizes. Matsudaira *et al.* [10] reported that TiB_2 powder, particle size 0.5 to 2 μm, was synthesized at 1400° C for 6 h in an argon atmosphere from submicrometre TiN and amorphous boron with a composition containing excess boron.

2.2. Experimental procedure

The starting materials used were β-SiC powder (Ibiden, Co., Ogaki, Japan average particle size 0.3 μm, purity > 98 wt %), TiN powder (Nihon Shin-Kinzoku Co., Toyonaka, Japan average particle size 0.8 μm, purity > 99 wt %) and amorphous boron powder (Cerac, Inc., Milwaukee, USA average particle size 1 μm, purity 99.5%). These starting materials were mixed with ethanol by ball milling. The mixing ratio was designed so that the volume ratios of SiC matrix to TiB_2 particular formed by the reaction of TiN and boron would be 10 : 0, 9 : 1, 8 : 2 and 7 : 3 in the final products, for lots 0, 1, 2 and 3, respectively. Excess boron was still added as a sintering aid upto as much as 3 wt % of the SiC powder, in addition to the stoichiometric necessity for the synthesis of TiB_2. For comparison with the SiC–TiN–B system, mixed powders of SiC, TiN and BN (Denki Kagaku Kogyo, Co., Tokyo, Japan average particle size 3.5 μm, purity was 99 wt %) was also prepared in a equivalent molar ratio to the lot 3. The slurries were filtered by suction, and dried at 80° C.

Before hot-pressing, the feasibility of the internal synthesis of TiB_2 was examined. The mixed powder of SiC, TiN and boron (lot 2) was die-pressed at pressure of 20 MPa. Pellets obtained were heated in a graphite container at 1000 to 1800° C for 1 h in an argon atmosphere and then the conversion ratio of TiN to TiB_2 was determined by X-ray diffraction analysis. To investigate the effect of the existence of SiC on the conversion ratio, pellets of the equivalent mixture of TiN and amorphous boron powders, excluding SiC powder, were heated under the same conditions. The effect of the atmosphere on the internal synthesis of TiB_2 was also examined by the phase determination of pellets heated at 1400 or 1500° C for 4 h in argon, nitrogen and vacuum.

Mixed powders were hot-pressed in graphite dies lined with boron nitride powder in an argon atmosphere at 2000 or 2080° C for 1 h, and 2160° C for 30 min at 20 MPa. Some samples were soaked at 1500° C for 4 h during temperature elevation. Hot-pressing in nitrogen was also carried out for powder mixture 3.

Four-point bend loading was used to measure the fracture strength at 20° C in air and 1400° C in a vacuum. Bending specimens were cut from each hot-pressed billet and then were ground, parallel to the long axis, with a 325 grit diamond wheel to dimensions of 3 mm × 3 mm × 35 mm. To avoid the effect of machining on bending strength, test pieces were annealed at 1500° C for 4 h in a vacuum. The elastic modulus was also determined by the composite-bar method [12] using the bending test bar. The bending strength was measured at a cross-head speed of 0.5 mm min^{-1}. The outer and inner load spans were 30 and 10 mm, respectively. The fracture toughness was determined by the indentation method using Niihara's equation [13].

3. Results

The conversion ratio from TiN to TiB_2 in SiC–TiN–B compacts after heating in argon for 1 h is shown in Fig. 2, together with that in TiN–B compacts. X-ray diffraction (XRD) patterns of the specimens heated at 1100, 1400 and 1700° C for 1 h are shown in Fig. 3. The synthesis of TiB_2 begins at 1100° C and is almost completed after heating at 1700° C for 1 h. Although the conversion ratio in SiC–TiN–B compact is much lower than that in TiN–B compact below 1300° C, both ratios are nearly equal above 1600° C. Increasing the time to 4 h at 1400 or 1500° C had little effect on the conversion ratio, but heating in a vacuum promoted the reaction. A weight gain was observed when the compact was heated in nitrogen. In this case, TiB_2 was not synthesized, but boron nitride was

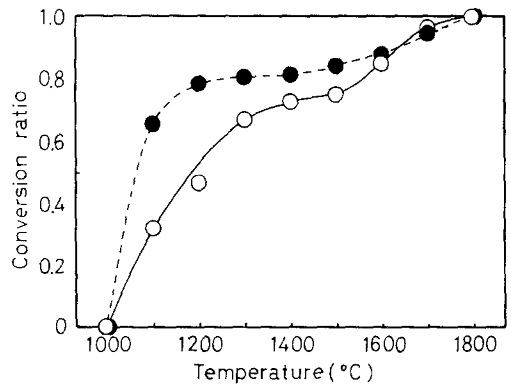

Figure 2 The conversion ratios from TiN to TiB_2 in (●) TiN–B compacts and (○) SiC–TiN–B compacts as a function of treatment temperature at a holding time of 1 h in an argon atmosphere.

detected by infrared absorption analysis.

Samples from lots 1 and 2 were densified to over 99% theoretical density by hot-pressing at 2080° C. Hot-pressing at 2160° C enabled even a sample from lot 3 to attain over 99% theoretical density. XRD analysis of all specimens hot-pressed in argon revealed that the crystalline phases were β-SiC and TiB_2 and that no TiN could be detected. Soaking treatment at 1500° C for 4 h during temperature elevation had no effect on density or phase composition of the hot-pressed specimens. A sample hot-pressed at 2160° C in nitrogen was also composed of SiC and TiB_2, but its density was 93% theoretical. The mixture of SiC–TiN–BN could be hot-pressed to a relative density of only 85%, and was composed of SiC, TiB_2 and BN.

TiB_2 particles formed by the internal reaction were finely dispersed in the hot-pressed composite, as shown in Fig. 4. By quantitative image analysis of polished surfaces of composites, average diameters of TiB_2 particles were found to be 0.97, 1.01 and 1.03 μm for lots 1, 2 and 3, respectively. The areas occupied by TiB_2 particles in the polished surfaces were 7.2, 18.5 and 27.0% for lots 1, 2 and 3, respectively. These values were similar to the preset volume fractions of TiB_2.

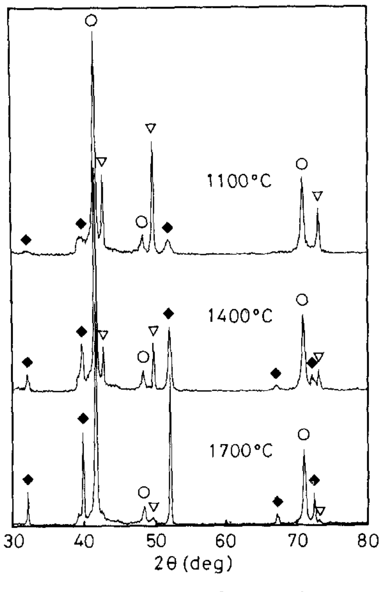

Figure 3 X-ray diffraction patterns of the specimens treated at 1100, 1400 and 1700° C for 1 h in an argon atmosphere: (○) β-SiC, (▽) TiN, (◆) TiB_2.

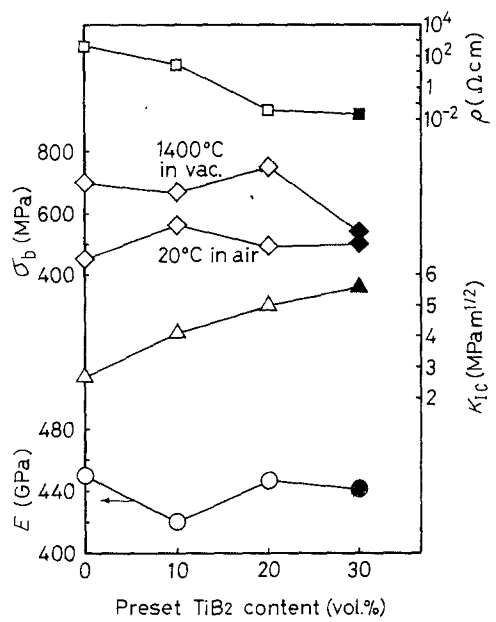

Figure 4 Electrical conductivity (□, ■) ϱ, four-point flexural strength (◇, ◆) σ_b, fracture toughness (△, ▲) K_{IC}, and elastic modulus (○, ●) *E*, of SiC composites hot-pressed at 2080° C (open marks) or 2160° C (solid marks) as a function of preset TiB_2 content.

The dependence of the electrical conductivity, flexural strength, fracture toughness and elastic modulus on the preset volume fraction of TiB_2 are shown in Fig. 5. The room-temperature strength of the composite containing 10 vol % TiB_2 was 560 MPa, 25% higher than that of monolithic SiC. Although the room-temperature strengths of composites containing 20 and 30 vol % TiB_2 were nearly equal to that of monolithic SiC, the fracture toughnesses were increased by about 80 and 100%, respectively. The flexural strength at 1400° C of all the specimens is higher than that at room temperature. Most of the fracture origins of the composites were large agglomerates of TiB_2 particles, an example of which is shown in Fig. 6.

The electrical resistivity of composites containing more than 20 vol % TiB_2 falls below 0.1 Ω cm and they can be easily wire-cut by electrical discharge at the rate of about 100 mm h^{-1}. The wire-cut surfaces appear molten-looking with craters, as described by Ramulu [14].

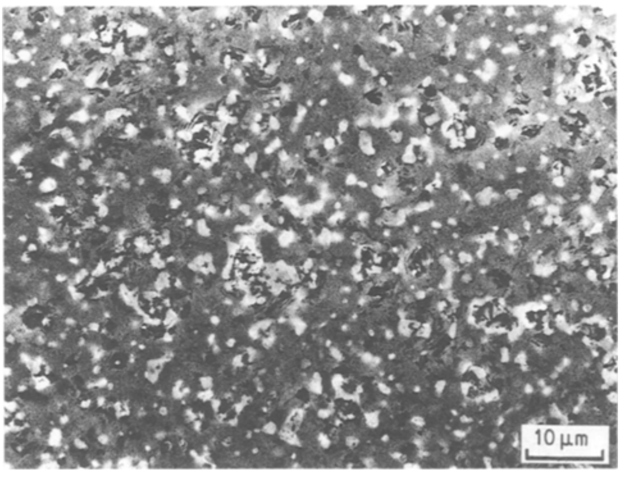

Figure 5 Scanning electron micrograph of a polished section of SiC–TiB_2 composite containing 20 vol % TiB_2 internally synthesized.

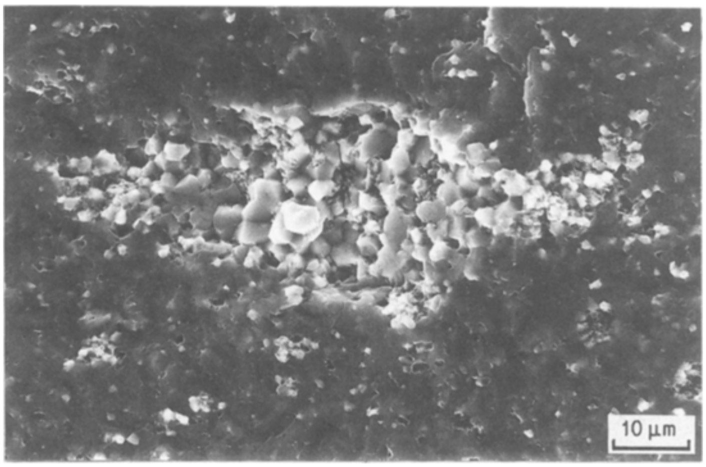

Figure 6 Scanning electron micrograph of a large agglomerate of TiB_2 particles observed in the fractured surface in $SiC-TiB_2$ composite containing 10 vol % TiB_2 internally synthesized.

4. Discussion

Suzuki and Hase [15] have reported that boron was easily diffused over the surface of a β-SiC particle at 1350° C and that the rate of boron diffusion at 1550° C increased by a factor of approximately 30. From their results, it is inferred that internal synthesis of TiB_2 in the SiC–TiN–B compact could proceed as follows; boron diffuses over the surface of the SiC particles and solid state reaction of boron and TiN forms TiB_2, with the evolution of nitrogen.

The conversion ratio from TiN to TiB_2 in SiC–TiN–B compacts is much lower than that in TiN–B compacts below 1300° C. This must be the result of "dilution" of the reactants with SiC particles. However, the conversion ratio in SiC–TiN–B compacts overtakes that in TiN–B compacts at 1600° C and the reaction is completed by heating for 1 h at 1800° C. Internal synthesis of TiB_2 in this system is supposed to have little derogatory effect on the densification of composites, because shrinkage of the SiC matrix proceeds drastically above 1800° C. Nearly fully dense $SiC-TiB_2$ composites were obtained by internal synthesis of TiB_2 from TiN and boron with the help of hot pressure. On the other hand, a composite obtained by the same process from TiN and BN had a poor density. Not only gas generation but also generated nitrogen itself must hinder the densification of SiC [16]. Thus it is obviously a most essential requirement in preparing composites by the internal-synthesis method that the gas-generating reaction should be completed in an early stage.

The flexural strength of the hot-pressed composites in this study were above or equal to that of hot-pressed $SiC-TiB_2$ composites using TiB_2 powder as a starting material [1]. Most of the fracture origins observed in the fractured surfaces after flexural testing were agglomerates or TiB_2 particles, which are considered to be intact remains of agglomerates of TiN particles in the mixed powder. Mixing and drying procedures should be rearranged to improve their strengths.

In this study, internally synthesized particulate-reinforced composites were obtained through (1) hot-pressing, and (2) employing a thermodynamically advantageous reaction system. It is difficult, however, to fabricate a component with complicated configuration through hot-pressing. Furthermore, boron powder with high purity is expensive. A more practical approach is necessary, in which SiC–boride composites could be prepared through (1) pressureless sintering, and (2) employing inexpensive materials as starting reactants.

5. Conclusions

1. Nearly fully dense $SiC-TiB_2$ composites were obtained by means of the internal synthesis method of TiB_2 from TiN and boron. Hot-pressed specimens were compsed of SiC and TiB_2, and no TiN was detected.

2. The average size of TiB_2 particle observed in polished surfaces of the composites is about 1 µm, slightly larger than the size of the starting TiN powder.

3. Room-temperature flexural strengths of the composites were above or equal to that of hot-pressed $SiC-TiB_2$ composites using TiB_2 powder as a starting material. The composite containing 20 vol % TiB_2 exhibits flexural strengths of 490 MPa at 20° C in air and of 750 MPa at 1400° C in a vacuum.

4. The fracture toughness increased with increasing TiB_2 content, and was 50% to 100% higher than that of monolithic SiC.

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