SiC matrix composites containing transition metal boride particulates internally synthesised by carbothermal reaction

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SiC matrix composites reinforced with the various borides of the transition metals in group IV a-VI a, which were synthesized from the transition metal oxide, boron carbide and carbon mixed with SiC powder. Dense composites containing boride particulates of titanium, zirconium, niobium and chromium were prepared through reactive hot-pressing. The morphology of the internally synthesized boride particles reflected that of the starting oxide powders. SiC–NbB_2 composites with four-point flexural strength of 500 to 600 MPa and better oxidation resistance than SiC–TiB_2 were prepared even through pressureless sintering process. Pressureless-sintered and HIPed SiC–20 vol% NbB_2 exhibited the four-point flexural strength of 760 MPa at 20 °C and 820 MPa at 1400 °C.

1. Introduction

A silicon carbide–titanium diboride composite with improved fracture toughness and electrical-discharge machinability was developed by the pressureless sintering of the powder compact of SiC and TiB_2 [1]. A SiC matrix composite with fine TiB_2 particulate was obtained through the reactive pressureless-sintering of a SiC–TiO_2–B_4C–C powder compact [2]. In this process, the TiB_2 particles are formed in the vacuum-soaking at 1400 to 1600 °C and the SiC matrix is densified above 2000 °C. The SiC–TiB_2 composite through the internal-synthesis method exhibited a four-point flexural strength of more than 700 MPa up to 1400 °C [3]. This composite system is, however, vulnerable to the oxidation degradation at high temperatures [4]. The SiC matrix composites containing the other boride particulates were also known as excellent refractory materials. The SiC–ZrB_2 composites, for example, were reported to have good oxidation resistance at 1200 °C [5]. The other investigation showed that the SiC–HfB_2 system was more oxidation resistant than SiC–ZrB_2 above 1800 °C [6].

Meerson and Samsonov [7] reported that not only TiB_2 but also ZrB_2, VB_2, NbB_2 and TaB_2 powders with nearly stoichiometric compositions can be synthesized by heating TiO_2, ZrO_2, V_2O_5, Nb_2O_5 and Ta_2O_5, respectively, with B_4C and C in a vacuum. It is, therefore, possible to prepare SiC matrix composites containing the various transition metal borides mentioned above through the internal synthesis method. It is also expected that the composite with more excellent properties can be prepared through the internal synthesis process than the conventional method.

This paper describes the preparation of hot-pressed SiC-various borides through the internal synthesis and the oxidation resistance of the composites is compared. Pressureless sintering and HIPing were applied to the SiC–NbB_2 system with good oxidation resistance and its mechanical properties were evaluated.

2. Thermodynamic consideration

The required conditions to prepare a dense SiC matrix composite with internally synthesised boride particulates using carbothermal reaction are the following:

1. The boride can be formed from the oxide–B_4C–C powder mixture at lower temperatures than where the densification of the SiC matrix proceeds.
2. The boride must be more stable than the carbide of the metal up to the sintering temperature of SiC in the presence of B_4C and C.
3. The melting point of the boride is higher enough than the sintering temperature of SiC.

The free energy changes of the following formation reactions of the seven transition metal diborides are shown in Fig. 1, including extrapolated data [8]

$$TiO_2 + 0.5B_4C + 1.5C \rightarrow TiB_2 + 2CO\uparrow \quad (1)$$

$$ZrO_2 + 0.5B_4C + 1.5C \rightarrow ZrB_2 + 2CO\uparrow \quad (2)$$

$$HfO_2 + 0.5B_4C + 1.5C \rightarrow HfB_2 + 2CO\uparrow \quad (3)$$

$$0.5V_2O_5 + 0.5B_4C + 2C \rightarrow VB_2 + 2.5CO\uparrow \quad (4)$$

$$0.5Nb_2O_5 + 0.5B_4C + 2C \rightarrow NbB_2 + 2.5CO\uparrow \quad (5)$$

$$0.5Ta_2O_5 + 0.5B_4C + 2C \rightarrow TaB_2 + 2.5CO\uparrow \quad (6)$$

$$0.5Cr_2O_3 + 0.5B_4C + C \rightarrow CrB_2 + 1.5CO\uparrow \quad (7)$$

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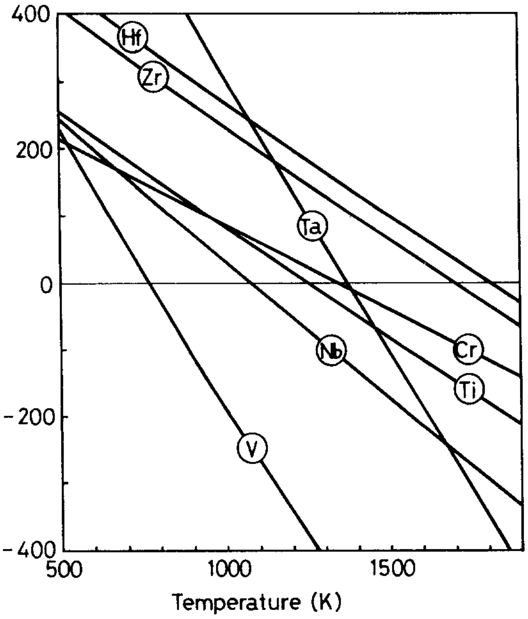

Figure 1 The standard free energy changes, ΔG^0, with temperature for the various diborides formation reactions:

$$TiO_2 + 0.5B_4C + 1.5C \rightarrow TiB_2 + 2CO\uparrow \quad (1)$$

$$ZrO_2 + 0.5B_4C + 1.5C \rightarrow ZrB_2 + 2CO\uparrow \quad (2)$$

$$HfO_2 + 0.5B_4C + 1.5C \rightarrow HfB_2 + 2CO\uparrow \quad (3)$$

$$0.5V_2O_5 + 0.5B_4C + 2C \rightarrow VB_2 + 2.5CO\uparrow \quad (4)$$

$$0.5Nb_2O_5 + 0.5B_4C + 2C \rightarrow NbB_2 + 2.5CO\uparrow \quad (5)$$

$$0.5Ta_2O_5 + 0.5B_4C + 2C \rightarrow TaB_2 + 2.5CO\uparrow \quad (6)$$

$$0.5Cr_2O_3 + 0.5B_4C + C \rightarrow CrB_2 + 1.5CO\uparrow \quad (7)$$

The data show that the seven transition metal diborides can be thermodynamically formed through the above carbothermal reactions below 1800 K even under the CO gas pressure of 0.1 MPa. The other data base shows that the formation of Mo_2B_5 and W_2B_5 through the carbothermal reaction is also possible below 1400 K [9]. It must be considered, however, that the actual formation reactions proceed through some elementary ones.

Every boride mentioned above is more stable than the carbides of each transition metal in the presence of boron carbide or boron. There may be some difficulties in the use of volatile oxide such as V_2O_5 or Cr_2O_3 and in the densification of the SiC matrix containing CrB_2 whose melting temperature is as low as 2200 °C [9].

Among the borides of the transition metals in group IV a-VIa, the ZrB_2, NbB_2 and CrB_2 were selected as internally synthesized particulates in the SiC matrix.

3. Experimental procedure

3.1. Hot-pressed SiC-borides

The powder lots of raw materials are shown in Table I, including the reference lot used for SiC–TiB_2 in the previous work [10]. The SEM images of the starting oxide powders are shown in Fig. 2. The TiO_2 and Nb_2O_5 powders are fine and have narrow particle size distributions, while Cr_2O_3 and ZrO_2 powders include coarse clusters of strongly agglomerated primary particles. The mixed ratios of SiC and oxides were designed so that the volume ratio of SiC matrix to diboride particulates formed by the carbothermal reaction should be 8:2. Excess amounts of 1.5 wt % B_4C and C to the SiC powder were added to each lot as sintering aids, besides the stoichiometrically required amounts for the reaction with the oxides. Starting materials were mixed with water by ball milling for 20 h, using a polyethylene pot and nylon-coated iron balls. The slurries were filtrated by suction, and dried at 100 °C. The screened powders under 32-mesh were die-pressed at 20 MPa. Powder compacts were heated in graphite dies (inner diameter of 60 mm). They were heated in a vacuum at 1500 °C for 6 h without pressing. After the vacuum-soaking treatment, argon gas was introduced into the furnace and a mechanical pressure of 25 MPa was applied. The fabrication process was completed by hot-pressing in an argon atmosphere at 2100 °C for 1 h. Only the SiC–Cr_2O_3–B_4C–C powder mixture (lot 1–1) was hot-pressed at 2000 °C because of the low melting point of CrB_2.

TABLE I Powder lots of raw materials for hot-pressing

Lot	Matrix powder	Reactants for boride	Sintering aids
1–0	SiC[a]	TiO_2[b] + B_4C[c] + C[d]	B_4C + C
1–1	SiC	Cr_2O_3[e] + B_4C + C	B_4C + C
1–2	SiC	ZrO_2[f] + B_4C + C	B_4C + C
1–3	SiC	Nb_2O_5[g] + B_4C + C	B_4C + C

[a] Showa Denko, Densic Ultrafine A-1 (alpha type).
[b] Fuji Titan Kogyo, TM-1 (rutile type).
[c] Denki Kagaku, #1200.
[d] Mitsubishi Chemical, Diablack A.
[e] Wako Pure Chemical Industries.
[f] Hokuko Chemical, HZ-N, monoclinic type.
[g] Mitsui Mining & Smelting.

The hot-pressed specimens were machined into rectangular bars (size: 4 × 3 × more than 35 mm^3). The density was measured and Young's modulus was determined through the composite-bar method [11]. The four-point flexural strength was measured at 20 °C in air and at 1400 °C in a vacuum. The upper and lower spans were 10 and 30 mm, respectively, and the crosshead speed was 0.5 mm min^{-1}. The crystalline phases of the hot-pressed specimens were identified by X-ray diffraction (XRD) analysis.

The oxidation resistance of the composites was evaluated with the flexural testing bars. The specimens were heated at 1400 °C for 100 h in static air. After the oxidation, the four-point flexural strength was measured at 20 °C for the specimens which survived. The hot-pressed SiC–20 vol % TiB_2 prepared in the previous work [10] was also heated in air under the same conditions and its oxidation resistance was compared with that of the composites in this work.

3.2. Pressureless-sintered and Hiped SiC–NbB_2

The compositions of the raw materials used for the preparation of pressureless-sintered SiC containing 10, 20, and 30 vol % NbB_2 are shown in Table II. The mixed ratios of SiC to Nb_2O_5 powders in lots 1, 2 and 3 were designed in such a way that the volume ratios of SiC to NbB_2 were 9:1, 8:2 and 7:3, respectively, in

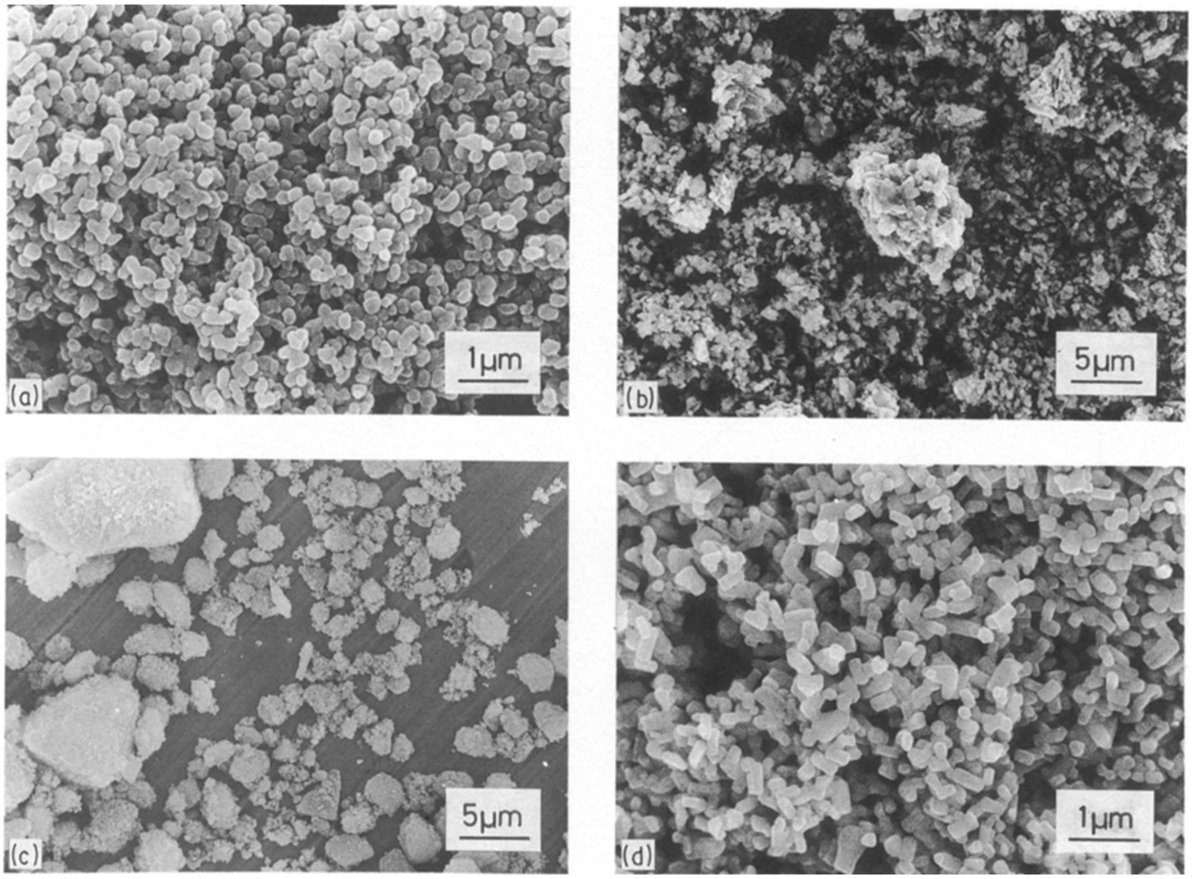

Figure 2 SEM images of starting oxide powders: (a) TiO_2, (b) Cr_2O_3, (c) ZrO_2 and (d) Nb_2O_5.

TABLE II Compositions of the starting powder mixtures

Lot	SiC	Nb_2O_5	B_4C	C
2–0	100	0	0.5	1.9
2–1	100	27.8	7.0	6.5
2–2	100	62.6	14.5	12.8
2–3	100	107.4	24.1	20.9

the final products. The other powder mixture of SiC with B_4C and C was also prepared for comparison in the mechanical properties with the composites.

Each powder lot was mixed in water by ball milling. Slurries were freeze-dried and the screened powders were die-pressed at 20 MPa (50×60 mm^2) and isostatically pressed at 300 MPa. Powder compacts were soaked in a vacuum at 1400 °C for 4 h and sintered in an argon atmosphere at 2150 °C for 4 h. SiC containing B_4C and C was sintered at 2100 °C for 1 h.

The pressureless-sintered single phase SiC and SiC–20 vol % NbB_2 composite prepared through the above process were hot-isostatically pressed in a graphite container at 1750 to 1900 °C for 1 h in an argon atmosphere at 200 MPa. The pressureless-sintered composites containing 10, 20 or 30 vol % NbB_2 were hot-isostatically pressed at 1900 °C for 1 h in an argon atmosphere at 200 MPa.

The chemical compositions of the HIPed SiC–NbB_2 composites were determined by ICP–AES for Nb and B, by the alkali fusion–gravimetric method for Si, by the inert gas fusion-thermal conductivity method for O and the combustion-infrared absorptiometric method for C.

Sintered and HIPed specimens were machined into rectangular bars of the same size as the hot-pressed specimens. The density was measured and the crystalline phases were identified by X-ray diffraction (XRD) analysis. Four-point flexural strength was measured at 20 °C in air and at 1400 °C in a vacuum. Fracture toughness value was determined by the indentation-fracture (IF) method [12].

4. Results

4.1. Hot-pressed SiC–boride

The XRD patterns of the hot-pressed bodies from the powder lots 1 and 3 are shown in Fig. 3. The XRD analysis showed that they did not contain unreacted phases nor by-products and was composed of SiC and diboride of each metal. The density, Young's modulus and four-point flexural strength of the hot-pressed specimens are shown in Table III with their crystalline phases. All the specimens were densified to more than 97% of the theoretical density. The density of the composite containing TiB_2, and NbB_2 would reach each theoretical value if it is calculated with the assumption that the excess B_4C and C remain in the hot-pressed body. The SEM images of the polished surface of the composites were shown in Fig. 4. The morphology of the internally synthesised boride particle is obviously related to that of the each starting oxide powder. The boride particles in the SiC–CrB_2 and SiC–ZrB_2 have a wide size distribution and the

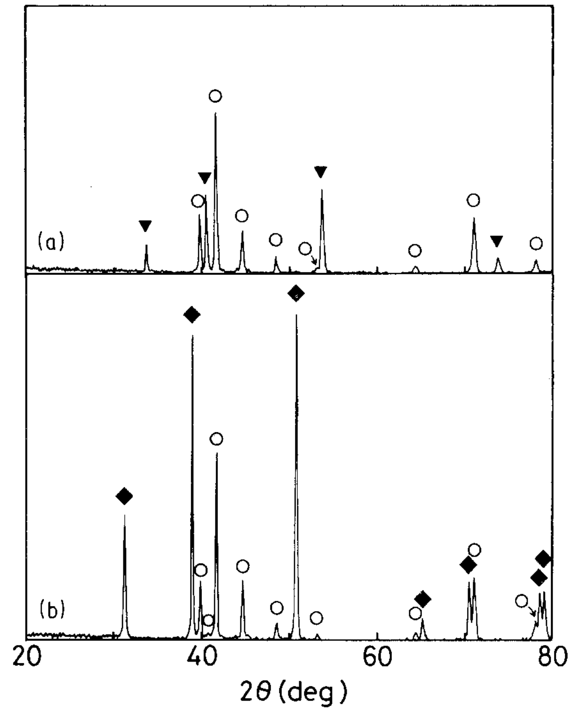

Figure 3 X-ray diffraction patterns of the polished surface of the hot-pressed bodies from the powder mixtures. (a) 1–1 (A) and (b) 1–3. (○ SiC, ▼ CrB_2, ◆ NbB_2).

coarse ones worked as fracture origins. On the other hand, TiB_2 and NbB_2 particles were dispersed in the uniform sizes in the composites and most of the fracture origins were agglomerates of carbon particles.

Among the composites prepared through the internal synthesis, SiC–CrB_2, SiC–ZrB_2 and SiC–NbB_2 survived the oxidation test at 1400 °C. The SiC–20 vol % NbB_2 held the strength of more than 500 MPa after the oxidation.

3.2. Pressureless-sintered and hiped SiC–NbB_2

All the specimens pressureless-sintered at 2150 °C from the SiC–Nb_2O_5–B_4C–C powder compacts were composed of α-SiC and NbB_2 and did not contain open porosities, though the outside surface of the specimen indicated a diffraction peak of graphite as well. The density and the room-temperature four-point flexural strength of the sintered body are shown in Fig. 5, compared with the properties of the hot-pressed specimen. The pressureless sintered composite containing 20 vol % NbB_2 attained approximately 98% of the density of the hot-pressed composite with the same composition. The strength of the composites was 500 to 600 MPa, which is the same level as that of the pressureless-sintered single phase SiC or SiC–TiB_2 prepared through the internal synthesis [3].

The relationship between the HIP temperature and the relative density of the SiC–20 vol % NbB_2 composite are shown in Fig. 6 with that of the single phase SiC. The density increased with increasing temperature and attained the density of the hot-pressed composite by HIP treatment at 1900 °C. The weight and the crystalline phases of the open-pore-free specimen did not change by the HIP treatment.

The four-point flexural strength and K_{IC} of the HIPed specimen are shown in Fig. 7. The composites

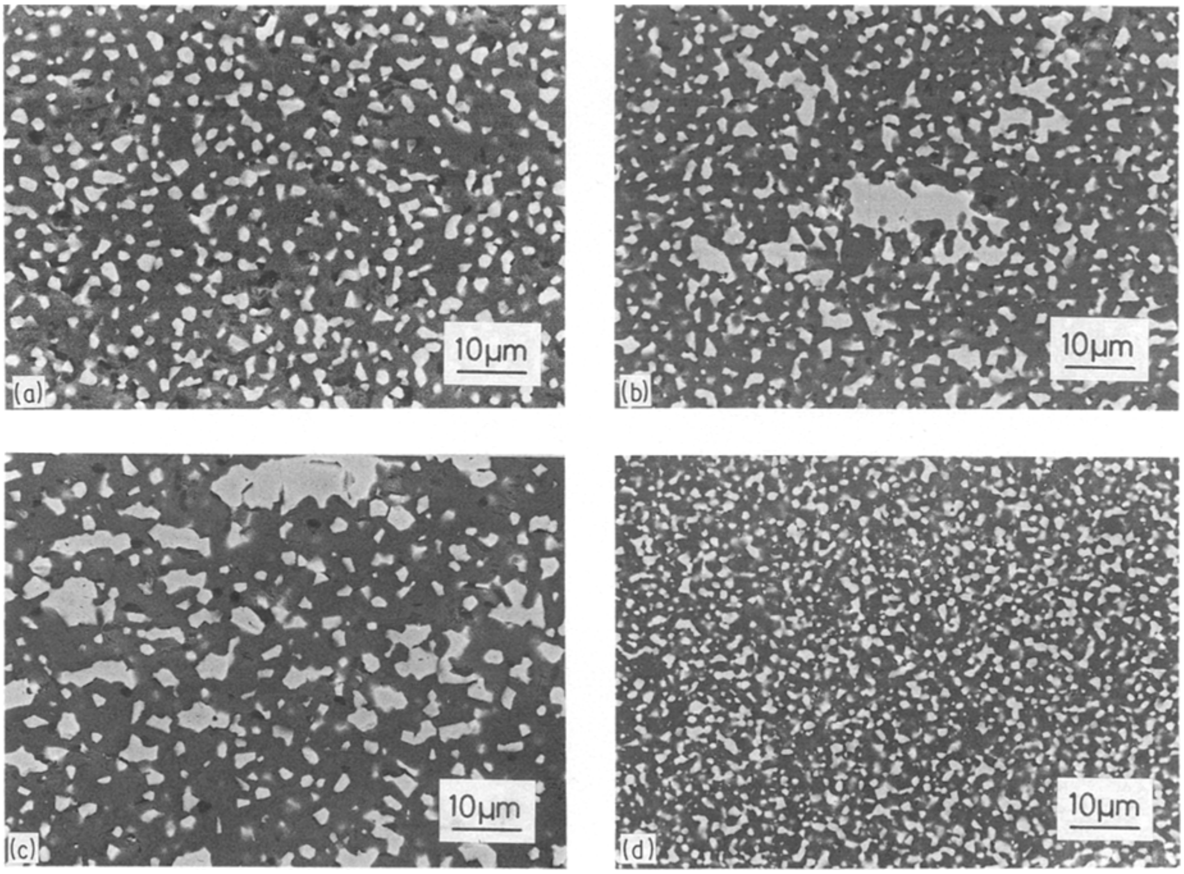

Figure 4 SEM images of the polished surfaces of the hot-pressed SiC–diboride composites prepared from: lot (a) 1–0, (b) 1–1, (c) 1–2 and (d) 1–3.

TABLE III Properties of hot-pressed SiC–20 vol % boride composites

Lot	Density ($g\,cm^{-3}$)	Identified phases	E (GPa)	Four-point flexural strength (MPa)	
				As-machined	After oxidation
1–0	3.44 (99.1 %)	SiC + TiB_2	467	700	disintegration
1–1	3.61 (97.9 %)	SiC + CrB_2	432	430	300
1–2	3.73 (98.5 %)	SiC + ZrB_2	451	360	380
1–3	3.93 (99.4 %)	SiC + NbB_2	460	740	550

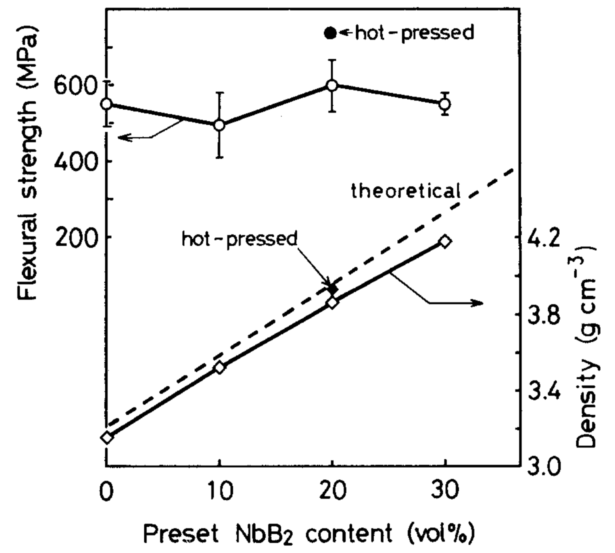

Figure 5 Density and room-temperature strength of pressureless-sintered SiC–NbB_2 composites as a function of preset NbB_2 content.

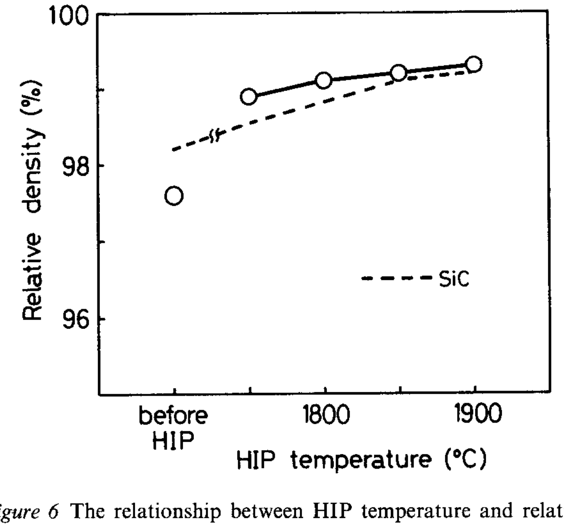

Figure 6 The relationship between HIP temperature and relative density of SiC–20 vol % NbB_2 composite.

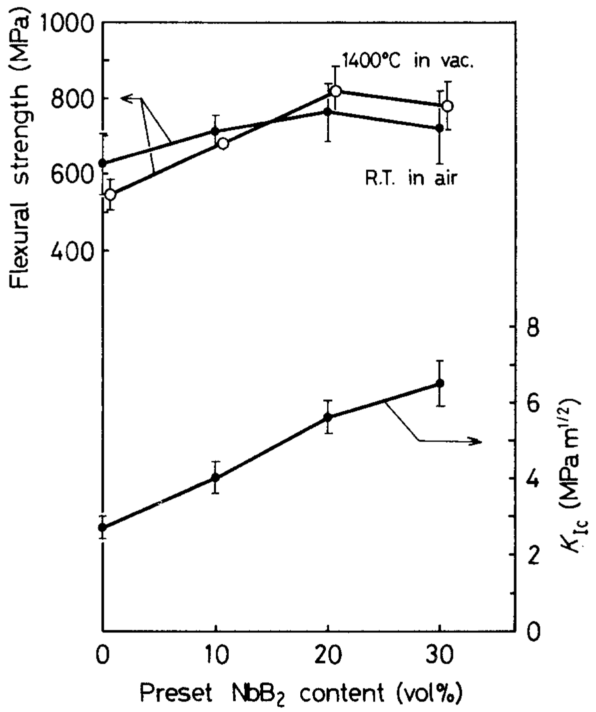

Figure 7 Four-point flexural strength and K_{IC} of pressureless-sintered and HIPed SiC–NbB_2 composites as a function of preset TiB_2 content.

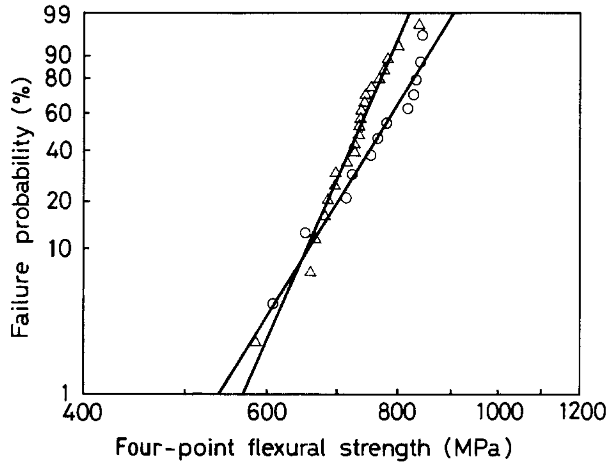

Figure 8 Weibull plot of the room-temperature strength of HIPed SiC–20 vol % NbB_2 (○: $m = 16.7$, $n = 22$), $\sigma_{4F}^{RT} = 763 \pm 77$ MPa) composite with the plot of that of the HIPed SiC–20 vol % TiB_2 (△: $m = 11.8$, $n = 12$, $\sigma_{4F}^{RT} = 726 \pm 54$ MPa).

showed higher strength and fracture toughness than the HIPed SiC. Their strength are about 28 to 44% higher than those of the pressureless sintered specimen and SiC–20 vol % NbB_2 exhibited the strengths of 760 MPa at 20 °C in air and of 820 MPa at 1400 °C in a vacuum. The Weibull plot of the strength of the HIPed SiC–20 vol % NbB_2 is shown in Fig. 8 with that of the strength of the HIPed SiC–20 vol % TiB_2.

The SEM images of the fracture surfaces of the specimens before and after HIP treatment are shown in Fig. 9. The HIPing at 1900 °C did not cause the grain growth of SiC nor NbB_2. The small pores among grains disappeared after the HIPing and most of the fracture origins in the HIPed specimens were agglomerates of carbon or NbB_2 particles, while most of those of the pressureless-sintered composite are vacant pores. An example of the NbB_2 agglomerate working as a fracture origin is shown in Fig. 9d.

The results of the chemical analysis of the pressureless-sintered or HIPed specimens are shown in

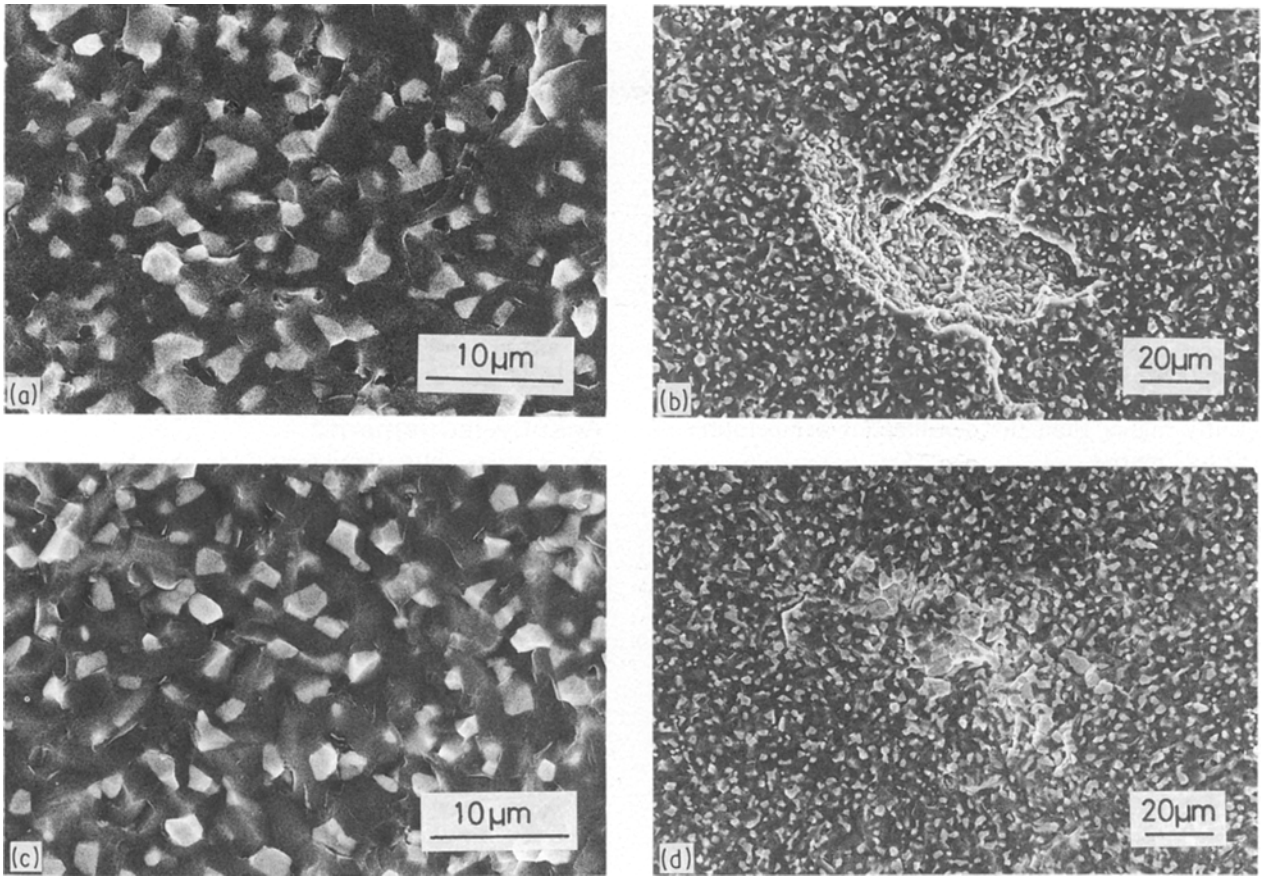

Figure 9 SEM images of fracture surfaces of pressureless-sintered SiC–20 vol % NbB_2 (a, b) before and (c, d) after HIPing at 1900 °C (b) and (d) show typical fracture origins of the composites before and after HIPing, respectively.

TABLE IV Results of the chemical analysis for pressureless sintered and HIPed SiC–NbB_2 composites

Lot	Designed vol. ratio	Experimental composition (wt %)						Calculated vol. ratio
		Si	C	Nb	B	O	Total	
2–1(PLS + HIP)	90:10	35.0	16.8	39.2	9.2	0.0	100.2	89.7:10.3
2–2(PLS)	80:20	44.3	20.6	27.9	6.7	0.0	99.5	79.9:20.1
2–2(PLS + HIP)	80:20	44.2	20.6	28.1	6.6	0.0	99.5	79.7:20.3
2–3(PLS + HIP)	70:30	54.5	25.3	15.6	4.0	0.0	99.4	69.7:30.3

Table III with the calculated volume ratio of SiC to NbB_2, which were determined from the experimental weight ratio of Si to Nb. All the experimental ratios are very close to the designed ratio. The compositions of the pressureless-sintered SiC–20 vol % NbB_2 remained nearly constant even after the HIPing at 1900 °C.

5. Discussion

Hot-pressed SiC matrix composites containing CrB_2, ZrB_2 and NbB_2 of more than 97% of each theoretical density were fabricated through internal synthesis. The preliminary work showed us that the fabrication of dense SiC matrix composites with internally synthesized molybdenum or tungsten boride is also feasible by hot-pressing at 2100 °C, using MoO_3 and WO_3, respectively, as a starting metal oxide. These experimental results and the thermodynamic consideration suggest that the various kinds of boride particles can be internally synthesised in the SiC matrix. Moreover, SiC matrix composites containing internally synthesised carbide particles can be prepared from SiC–metal oxide–carbon powder mixtures. In this case, however, other densification aids than B_4C or boron-containing material must be used for SiC because metal oxide (or partially reduced oxide) preferentially reacts with B_4C or boron-containing materials to form boride [13].

The particle size distribution of the diboride in the composite depends on that of the starting metal oxide powder. The strengths of SiC–CrB_2 and SiC–ZrB_2 composites, which contain coarse diboride particles, are lower than that of the hot-pressed single phase SiC. The SiC–TiB_2 and SiC–NbB_2, in which fine diboride particles were uniformly dispersed, exhibited a higher flexural strength than 700 MPa. These results suggest that the metal oxide powder with fine particle size must be used as a raw material to prepare a high strength composite through internal synthesis.

The SiC matrix composites incorporating 20 vol % CrB_2, ZrB_2 and NbB_2 were not disintegrated after the oxidation at 1400 °C for 100 h in air although they got much thicker oxidation layers than a single phase SiC did. Among these composites, SiC–NbB_2, exhibiting both good oxidation resistance and excellent mechanical properties, is considered to be most suited as a composite to be fabricated through the internal synthesis, because

1. Nb_2O_5 powder is available in uniform and fine particle size without agglomeration,
2. it has low vapour pressure,
3. the standard formation free energy change of NbB_2 becomes negative as low as below 1000 °C, and
4. the melting point of NbB_2 (3000 °C [9]) is sufficiently higher than the densification temperature of the SiC matrix.

SiC–NbB_2 composites with the relative density of 96.6–98.3% were prepared even through pressureless sintering and the additional HIPing at 1900 °C made the composites denser to 98.9 to 99.3% of the theoretical values. Assuming that the excessively added boron carbide and carbon remained as those in the final composites, each of them reached the full density. And the chemical analysis proved that they had the prescribed compositions. The strength of the composite attained maximum values at the NbB_2 content of 20 vol %, which was 760 MPa at room temperature and 830 MPa at 1400 °C. The composite containing 30 vol % boride particles showed lower strength than that containing 20 vol % boride although the former exhibited higher fracture toughness than the latter. The boride particles were observed to be interconnected each other in the SiC matrix composite containing 30 vol % boride [10] and such microstructure may cause the strength deterioration in the composite.

6. Conclusions

The conclusions are as follows.

1. Dense SiC matrix composites with 20 vol % CrB_2, ZrB_2 and NbB_2 were obtained by the reactive hot-pressing of SiC–respective metal oxide–B_4C–C powder mixtures.
2. The morphology of the internally synthesised diboride particulates reflected that of the starting oxide powder.
3. The composites containing CrB_2, ZrB_2 and NbB_2 exhibited better oxidation resistance than the SiC–TiB_2 system. SiC–20 vol % NbB_2 held the strength of more than 500 MPa even after exposure in air at 1400 °C for 100 h.
4. The SiC – internally synthesised – NbB_2 composites were fully densified by the pressureless sintering at 2150 °C and the additional HIPing at 1900 °C. The HIPed SiC–20 vol % NbB_2 exhibited the four-point flexural strength of 760 MPa at 20 °C and 820 MPa at 1400 °C.

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