JOURNAL OF MATERIALS SCIENCE 26 (1991) 3491–3496

Pressureless-sintered and HIPed $SiC–TiB_2$ composites from $SiC–TiO_2–B_4C–C$ powder compacts

TOSHIHIKO TANI, SHIGETAKA WADA
Toyota Central Research and Development Laboratories, Inc., Nagakute, Aichi, 480-11, Japan

Dense $SiC–TiB_2$ composites with prescribed compositions were obtained through pressureless sintering of $SiC–TiO_2–B_4C–C$ powder compacts. During the process, TiO_2, B_4C and C reacted to form TiB_2, followed by the consolidation of SiC matrix with the aid of excess B_4C and C. The effects of the composition of the starting powders on the final density were investigated and the mechanical properties of the composite were evaluated. The sintered body with additional HIPing at 1900 °C exhibited the average four-point flexural strength of more than 700 MPa at both 20 and 1400 °C.

1. Introduction

Silicon carbide-based ceramic composites with improved fracture toughness and electrical-discharge machinability have been developed by incorporating electrically conductive particulates such as titanium diboride or carbide [1–3]. These materials are prepared by moulding SiC powder mixed with the reinforcing particles and some additives, and sintering or hot-pressing the moulded body. In the conventional method, however, the characteristics of the supplied particles often dominate the fabrication process and the properties of the final composite. When fine TiB_2 particles are used, for example, mixing powders with water would be unfavourable because of the high reactivity [4]. On the other hand, using coarse TiB_2 particles would deteriorate the fracture strength of the composites.

One of the industrial processes of preparing fine TiB_2 particle is milling the TiB_2 agglomerates produced by the following carbothermal reaction of TiO_2, B_4C and C at about 2000 °C [5]

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

The removal of the CO gas from the system is important to enhance the reaction at lower temperatures. In the pressureless sintering process of SiC with boron and carbon, CO gas generated by the reaction of carbon and silica on the surface of SiC particle hinders densification [6] and must also be removed. This gives rise to the idea that the synthesis of TiB_2 particles and the sintering of SiC could be done in a single process to prepare $SiC–TiB_2$ composites. The internal synthesis is advantageous also because both boron carbide and carbon work not only as reactants for TiB_2 but also as sintering aids for the SiC matrix [7]. It should be noted that TiB_2 is more stable than TiC or TiO_2 in the presence of boron carbide in the high temperature range where SiC matrix can be densified.

Miyamoto *et al.* [8] proposed the high-pressure combustion sintering, by which $SiC–TiB_2$ composite was prepared from the powder compact of titanium and boron mixed with SiC under a mechanical pressure of 3 GPa. The reaction,

$$Ti + 2B \rightarrow TiB_2 \quad (2)$$

is exothermic and does not need external heating nor a long reaction time. The explosive reaction would cause defects in the specimen without high mechanical pressure and the application to the ceramic parts with complicated shapes is difficult.

In previous work [9], we reported that the dense SiC matrix composites with 10, 20 and 30 vol % TiB_2 were obtained by the reactive hot-pressing of $SiC–TiO_2–B_4C–C$ powder mixtures. The hot-pressed SiC matrix composite with 20 vol % internally synthesized TiB_2 exhibited an average four-point flexural strength of more than 700 MPa up to 1400 °C. The internal synthesis process is considered to be more suitable to pressureless sintering than to hot-pressing, because the semi-closed system in hot-pressing dies is unfavourable for the removal of the CO gas from the specimen.

The preliminary study on the pressureless sintering demonstrated that the preheating conditions strongly influenced the progress of the carbothermal reaction and the final density of the sintered composite [10]. The vacuum-soaking treatment at 1400 to 1600 °C for several hours prior to the densification stage at 2150 °C in argon is essential to produce a dense $SiC–TiB_2$ composite from the $SiC–TiO_2–B_4C–C$ powder compact.

This paper describes the effect of the excess boron carbide and carbon on the final density of the $SiC–TiB_2$ composite and the mechanical properties of the internally synthesized and pressureless-sintered $SiC–TiB_2$ composites with varied TiB_2 contents.

0022-2461/91 $03.00 + .12

We also report that the additional HIP treatment improved the density and strength of the sintered composite.

2. Experimental procedure

2.1. Determination of optimum amounts of B_4C and C

The optimum amounts of the excess boron carbide and carbon as sintering aids were investigated using the powder mixture of α-SiC powder (Showa Denko Co., average particle size 0.48 μm), TiO_2 powder (Fuji Titan Kogyo, TM-1, rutile type, average particle size 0.4 μm), B_4C powder (Denki Kagaku Kogyo, average particle size 1.5 μm) and carbon black powder (Mitsubishi Chemical, average particle size 0.018 μm). The mixing ratio of SiC and TiO_2 was designed so that the volume ratio of SiC matrix to TiB_2 particulate formed by the carbothermal reaction should be 7:3. The amounts of boron carbide and carbon added were more than the stoichiometrically required for the synthesis of TiB_2. In one series of the mixing lots, the excess B_4C amount was changed from 1 to 5 wt % of the SiC powder while the excess carbon was kept constant at 2 wt % of the SiC. In the other series of mixing lots, the amount of excess carbon was changed from 1 to 5 wt % and from 0 to 2.5 wt % of the SiC powder while the excess B_4C was kept constant at 1 and 2 wt %, respectively, of the SiC. The 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. Screened powders under 32-mesh were moulded in 10×50 mm^2 dies at a pressure of 20 MPa and isostatically pressed at 300 MPa. The green compacts in a graphite container were heated in a vacuum at 1500 °C for 4 h. After the vacuum-soaking treatment, argon gas was introduced into the furnace and the compacts were sintered in an argon atmosphere at 2150 °C for 1 h. The density of the sintered body was measured. Crystalline phases of the sintered bodies were identified by X-ray diffraction (XRD) analysis. The chemical compositions of the soaked specimen and the sintered body were determined by ICP-AES for Ti 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.

2.2. Preparation of pressureless-sintered SiC–TiB_2

The compositions of the raw materials used for the preparation of pressureless-sintered SiC containing 10, 20 and 30 vol % TiB_2 are shown in Table I. They have the same compositions as those used in the study on hot-pressing [9]. The mixed ratios of SiC to TiO_2 powders in lots 1, 2 and 3 were designed in such a way that the volume ratios of SiC to TiB_2 were 9:1, 8:2 and 7:3, respectively, in the final products. Excess amounts of 1.5 wt % B_4C and C to SiC powder were added to each lot as sintering aids, besides the stoichiometrically required amounts for the reaction with TiO_2. The other powder mixture of SiC with only B_4C and C was also prepared for a single phase specimen.

TABLE I Compositions of the starting powder mixtures

Lot	SiC	TiO_2	B_4C	C
0	100	0	0.5	1.9
1	100	18.0	7.7	5.6
2	100	40.5	15.5	10.6
3	100	69.4	25.4	17.1

Each powder lot was mixed in water by ball milling. Slurries were spray-dried and the granular powders were die-pressed (50×60 mm^2) at 20 MPa 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 as shown in Fig. 1. SiC containing B_4C and C was sintered at 2100 °C for 1 h.

Sintered specimens were machined into rectangular bars (size $4 \times 3 \times$ more than 35 mm^3). Density was measured and Young's modulus was determined through the composite-bar method [11]. 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 fracture toughness value was determined by the indentation-fracture (IF) method [12] and the single-edge-precracked-beam (SEPB) method [13].

2.3. HIP Treatment after pressureless sintering

The pressureless-sintered SiC–20 vol % TiB_2 prepared through the above process was hot-isostatically pressed in a graphite container at 1750 to 1900 °C for 1 h in argon atmosphere of 200 MPa and the density of the HIPed specimens were measured. The changes of the crystalline phases and the microstructure were investigated by XRD and SEM, respectively. The specimens HIPed at 1900 °C were machined into rectangular bars with the same size of the pressureless-sintered specimens. The Young's modulus and flexural strength were measured and compared with those of

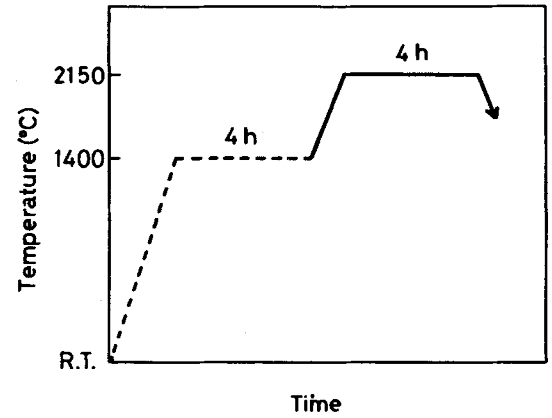

Figure 1 Pressureless-sintering schedule (--- in a vacuum, — in Ar (1 atm)).

the pressureless sintered bodies before HIPing. The sintered body with open porosity was also HIPed under the same conditions.

3. Results

3.1. Amounts of B_4C and C

Fig. 2 shows the density and open porosity of the sintered body as a function of the excess amount of boron carbide when the excess carbon amount was 2 wt % of the SiC powder. The open porosity was zero at the excess boron carbide amount of more than 2 wt % of the SiC. Maximum density was 3.54 $g\,cm^{-3}$ when the excess boron carbide amount was 2 wt %. Fig. 3 shows the density against the excess amount of carbon black when the excess boron carbide amount was 1 and 2 wt % of the SiC. The maximum density, 3.55 $g\,cm^{-3}$, 98.7% of the theoretical value, was attained when the excess amounts of boron carbide and carbon were 2 and 1 wt %, respectively. The XRD analysis showed that the sintered specimens did not contain unreacted phases and was composed of α-SiC and TiB_2 though the outside surface of the specimen indicated a diffraction peak of graphite as well. Even the vacuum-soaked specimen at 1400 °C for 4 h showed a diffraction pattern of only SiC and TiB_2, as shown in Fig. 4.

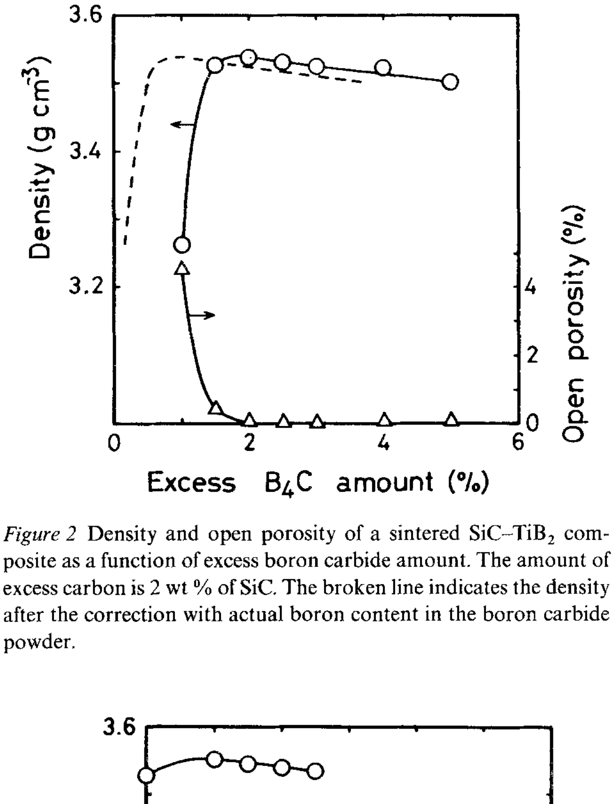

Figure 2 Density and open porosity of a sintered SiC–TiB_2 composite as a function of excess boron carbide amount. The amount of excess carbon is 2 wt % of SiC. The broken line indicates the density after the correction with actual boron content in the boron carbide powder.

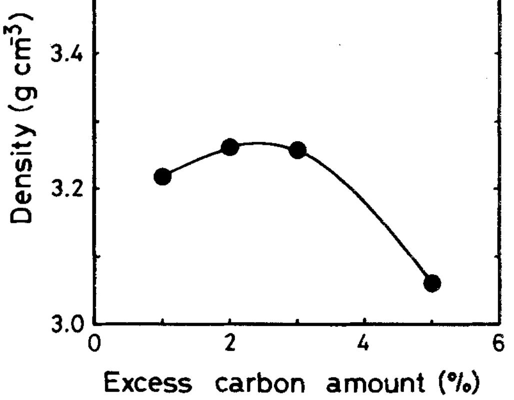

Figure 3 Density of the sintered composite as a function of amount of excess carbon. (○ excess $B_4C = 2\%$, ● excess $B_4C = 1\%$)

The results of the chemical analysis for the vacuum-soaked specimen and the sintered specimen with density of 3.54 $g\,cm^{-3}$ are shown in Table II with the calculated values. The purity of the starting powders are taken into consideration and the stoichiometric TiB_2 formation reaction is assumed for the calculation. Both experimental values are close to the calculated composition. The volume ratio of SiC to TiB_2 determined from the experimental weight ratio of Si to Ti in the sintered specimen is 69.5:30.5, which is very close to the designed ratio.

3.2. Properties of pressureless-sintered SiC–TiB_2

All the specimens pressureless-sintered at 2150 °C for 4 h from the SiC–TiO_2–B_4C–C powder compacts were

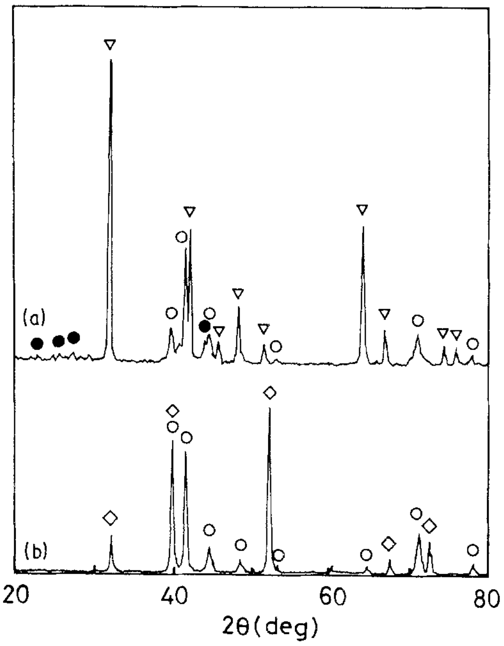

Figure 4 X-ray diffraction patterns of mixed powder (a) before and (b) after vacuum soaking at 1400 °C for 4 h. (○ SiC, ▽ TiO_2, ● B_4C, ◇ TiB_2).

TABLE II Results of the chemical analysis for pressureless-sintered SiC–30 vol % TiB_2

Element	Experimental composition (wt %)		Calculated composition (wt %)
	Soaked specimen at 1400 °C for 4 h	Sintered specimen at 2150 °C for 4 h	
Si	40.9	42.1	42.5
C	20.7	21.1	20.1
Ti	25.8	25.5	25.5
B	11.9	11.8	11.9
O	1.2	0.0	—
Total	100.5	00.5	100.0

composed of α–SiC and TiB_2 and do not contain open porosities. The density and Young's modulus of the sintered body are shown in Fig. 5, with the properties of the hot-pressed specimen. The pressureless sintered composite with each composition attained approximately 99% of the density of the hot-pressed composite. The Young's modulus increased linearly with increasing content of TiB_2. The flexural strength and K_{IC} of the composites are shown in Fig. 6. The strength of the composites with more than 20 vol % TiB_2 are 500 to 600 MPa at both 20 and 1400 °C, which are the same level as that of the single phase SiC. Spherical pores of 20 to 50 μm in diameter were observed at most of the fracture origins of the sintered composites. K_{IC} increased with increasing TiB_2 content and it is higher than that of the hot-pressed composite for each composition.

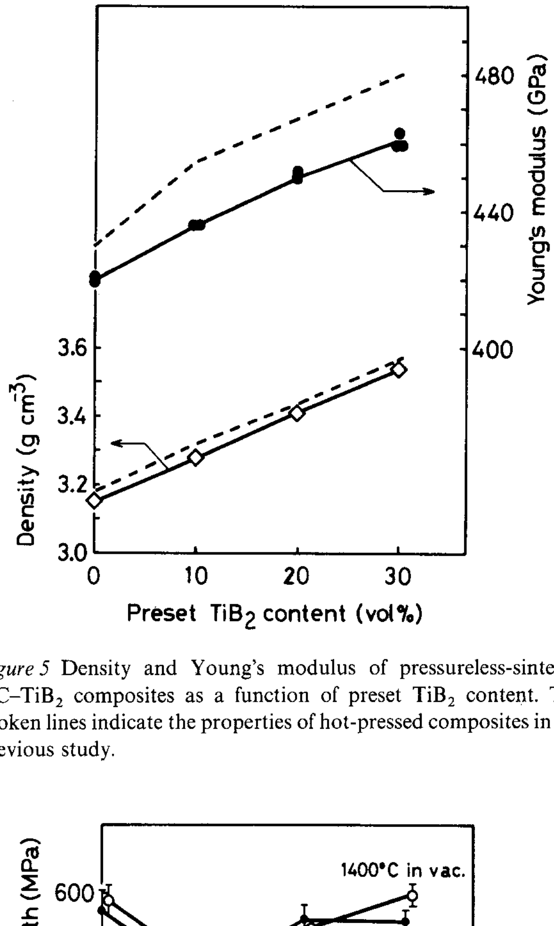

Figure 5 Density and Young's modulus of pressureless-sintered SiC–TiB_2 composites as a function of preset TiB_2 content. The broken lines indicate the properties of hot-pressed composites in the previous study.

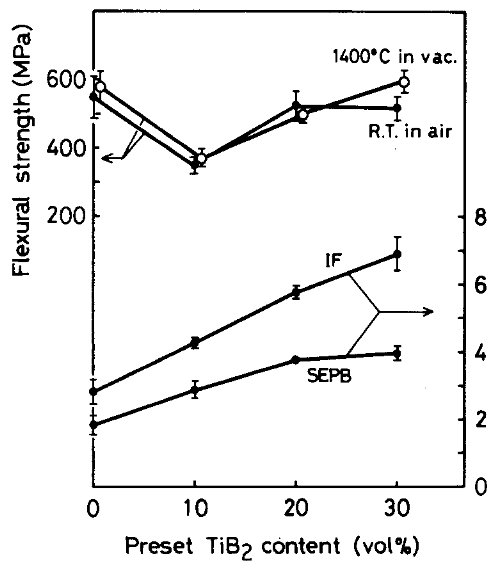

Figure 6 Four-point flexural strength and K_{IC} of pressureless-sintered SiC–TiB_2 composites as a function of preset TiB_2 content.

3.3. Properties of HIPed composites

The relationship between HIP temperature and the relative density of SiC–20 vol % TiB_2 composite are shown in Fig. 7. The density increased with increased temperature and reached the theoretical one by the 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 SEM photographs of the fracture surfaces of the specimens before and after the HIPing at 1900 °C are shown in Fig. 8. The HIP treatment up to 1900 °C did not cause the grain growth of SiC nor TiB_2. The small pores among SiC grains and TiB_2 particles disappeared after the HIPing.

The flexural strength of the specimen HIPed at 1900 °C was constant from room temperature to 1400 °C and at the same level as the hot-pressed composite, as shown in Fig. 9. The average four-point strengths were 726 MPa at 20 °C and 715 MPa at 1400 °C. They are about 40% higher than those of the pressureless sintered specimen while K_{IC} remained the same value. The Weibull plots of the strength of the HIPed specimen are shown in Fig. 10. The Weibull modulus of the strength at 1400 °C would be 15.3 if calculated without a singular point and nearly equal to that of the room-temperature strength. Most of the fracture origins in the HIPed specimens were not spherical pores but small agglomerates of carbon or TiB_2 particles.

The experimental and calculated chemical compositions of the HIPed specimen with the preset TiB_2 content of 20 vol % are shown in Table III. The experimental values are close to the calculated composition and the volume ratio of SiC to TiB_2 determined from the experimental weight ratio of Si to Ti in the HIPed specimen is 79.8:20.2, which is again very close to the designed ratio.

The sintered specimen with open pores was also densified by the HIPing at 1900 °C. TiC phase was, however, identified on the HIPed surface, besides SiC, TiB_2 and graphite.

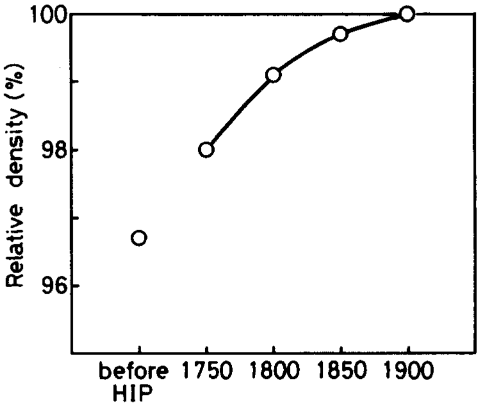

Figure 7 Relative density of SiC–20 vol % TiB_2 composite as a function of HIP temperature. (HIP conditions: argon pressure 200 MPa, time 1 h).

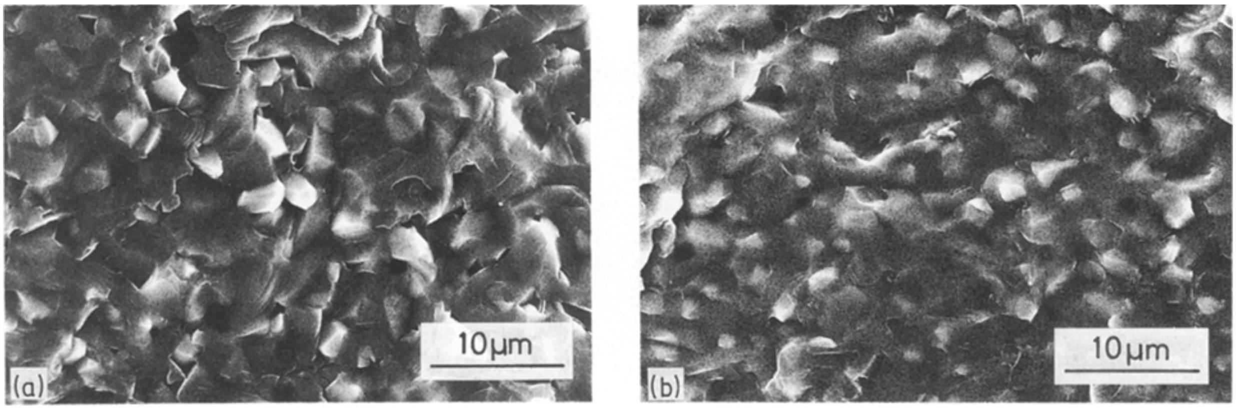

Figure 8 SEM photograph of the fracture surfaces of pressureless-sintered SiC–20 vol % TiB_2 composites (a) before and (b) after HIPing at 1900 °C.

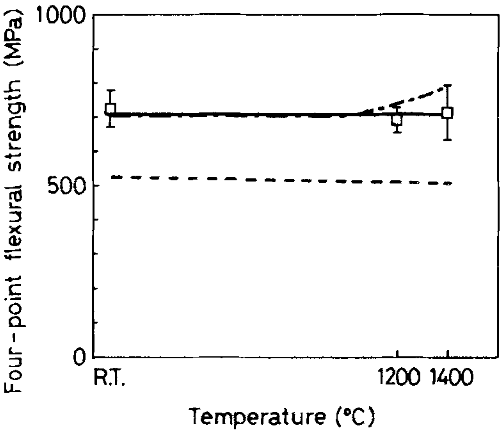

Figure 9 Four-point flexural strength of HIPed SiC–20 vol % TiB_2 as a function of temperature, with the data of hot-pressed (-----) and pressureless-sintered (----) composites with the same compositions.

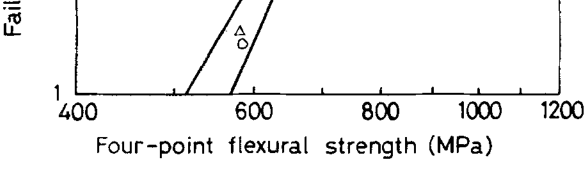

Figure 10 Weibull plots of the strength of HIPed SiC–20 vol % TiB_2 at 20 °C in air and 1400 °C in a vacuum. (△ $\bar{\sigma}_{4f}^{1400\,°C} = 715$ MPa, $m = 12.4$, $n = 18$; ○ $\bar{\sigma}_{4f}^{RT} = 726$ MPa, $m = 16.7$, $n = 22$).

TABLE III Results of the chemical analysis for HIPed SiC–20 vol % TiB_2

Element	Experimental composition (wt %)	Calculated composition (wt %)
Si	50.1	50.6
C	23.3	23.1
Ti	18.3	17.7
B	8.5	8.6
O	0.0	—
Total	100.2	100.0

4. Discussion

Dense $SiC–TiB_2$ composite was obtained by the pressureless sintering of $SiC–TiO_2–B_4C–C$ powder compact with excess boron carbide of 1.5 to 2.5 wt % and excess carbon of 1 to 2 wt % of the SiC. With the consideration of the purity of the starting boron carbide and carbon powders, the effective optimum excess amounts turn out to be 0.6 to 1.4 wt % B_4C and 0.9 to 2.0 wt % C of the SiC. These amounts are the same level as B_4C (or B) and C required as sintering aids for the pressureless sintering of single phase SiC [14–16].

The results of the XRD and chemical analysis for the composite demonstrated that the internal synthesis of TiB_2 was almost completed by the vacuum-soaking at 1400 °C for 4 h and the composition of the sintered body was very close to the designed value. The optimum soaking condition is, however, supposed to be dependent on the amount of generated CO gas, the thickness of samples and the evacuation capacity of a furnace, so that it should be found in each case. The pressureless-sintered SiC matrix composites with more than 20 vol % TiB_2 exhibited slightly higher strength than the pressureless sintered SiC–16 vol % TiB_2 composite prepared through the conventional method [1].

Although it has been known that the density and strength of single phase SiC with boron (or boron carbide) and carbon was improved by HIPing at 1900 to 2200 °C at an argon pressure of 100 to 200 MPa [17, 18], HIP treatment for the pressureless sintered SiC matrix composites has not been reported. Densification of SiC matrix–TiB_2 particulate composite during HIPing is essentially the same as that of single phase SiC because it is driven through the plastic deformation of the SiC grains by the external pressure. HIP treatment at 1900 °C extinguished both small pores among grains and large pores caused by the contamination during processing, and the pressureless sintered SiC–20 vol % TiB_2 attained theoretical density after HIPing. Its strength was also increased to the same level as that of the hot-pressed composite. The preparation of the slurry with more uniform powder dispersion will further improve the strength of the composite. HIPing at 1900 °C did not cause the grain growth of SiC nor TiB_2 as in the case of the single phase SiC. The treatment temperature is a decisive factor for the grain growth, for the pressureless sintering above 2200 °C causes the grain growth of SiC, which leads TiB_2 particulates to the grain growth as well.

The TiC phase identified on the surface of the HIPed specimen with open pores was formed by the reaction of TiB_2 and carbon-containing gas phase species in the HIP furnace. The species is considered to be CO caused by the reaction of graphite heater and the oxygen impurity in argon at a pressure of 200 MPa. That accounts for the fact that TiC was not formed during the pressureless sintering process in argon at a pressure of 0.1 MPa.

The excellent properties of the SiC–TiB_2 prepared through the internal synthesis proves this process to be a useful fabrication method of ceramic composites. The internal synthesis can be applied to the preparation of SiC matrix composites containing boride particulates of the other transition metals in group IVa–VIa, or carbide particulates of such metals.

4. Conclusions

The conclusions are as follows:

1. Dense SiC–TiB_2 composites with prescribed compositions were obtained by the pressureless sintering of SiC–TiO_2–B_4C–C powder compacts. The excess amounts of B_4C and C required for the densification of the SiC matrix were the same level as the amounts of the additives doped for the pressureless-sintering of single phase SiC.
2. Additional HIPing at 1900 °C at argon pressure of 200 MPa excluded residual closed pores and made a composite with theoretical density. The HIPed SiC–20 vol % TiB_2 composite exhibited an average four-point flexural strength of more than 700 MPa at both 20 and 1400 °C.

Acknowledgements

We express our thanks to Mr Y. Kawai and Mr Y. Kondo within this company for the chemical analyses of the composites. We are also grateful to Dr S. Hori of our laboratory for useful discussion.

References

1. C. H. McMURTRY, W. G. D. BOECKER, S. G. SESHADRI, J. S. ZANGHI and J. E. GARNIER, *Amer. Ceram. Soc. Bull.* **66** (1987) 325.
2. R. JIMBOU, K. TAKAHASHI and T. KOSUGI, *Adv. Ceram. Mater.* **1** (1986) 341.
3. H. ENDO, K. TANEMOTO and H. KUBO, in Sintering '87, Vol. 2, edited by S. Somiya, M. Shimada, M. Yoshimura and R. Watanabe (Elsevier Science Publishers, Essex, UK, 1988) p. 1052.
4. H. R. BAUMGARTNER and R. A. STEIGER, *J. Amer. Ceram. Soc.* **67** (1984) 207.
5. J. J. KIM and C. H. McMURTRY, *Ceram. Eng. Sci. Proc.* **6** (1985) 1313.
6. S. PROCHAZKA, C. A. JOHNSON and R. A. GIDDINGS, Proceedings of the International Symposium of Factors in Densification and Sintering of Oxide and Non-oxide Ceramics (Gakujutu Bunken Fukyu-Kai, Tokyo, Japan, 1979) p. 366.
7. S. PROCHAZKA, *Spec. Ceram.* **6** (1975) 171.
8. Y. MIYAMOTO, Y. C. HYUN, Y. TAKANO, O. YAMADA and M. KOIZUMI, *J. Jpn Soc. Powder Metall.* **35** (1988) 651.
9. T. TANI and S. WADA, *Nippon Seramikkusu Kyokai Gakujutu Ronbunshi* **97** (1989) 1195.
10. T. TANI and S. WADA, *J. Mater. Sci. Lett.* **9** (1990) 22.
11. S. KUDO and M. OZAWA, *Jpn J. Appl. Phys.* **28** Supplement 28-2 (1989) 184.
12. K. NIIHARA, R. MORENA and D. P. H. HASSELMAN, *J. Mater. Sci. Lett.* **1** (1982) 13.
13. T. NOSE and T. FUJII, *J. Amer. Ceram. Soc.* **71** (1988) 328.
14. Y. MURATA and R. H. SMOAK, Proceedings of the International Symposium of Factors in Densification and Sintering of Oxide and Non-oxide Ceramics (Gakujutu Bunken Fukyu-Kai, Tokyo, Japan, 1979) p. 382.
15. W. BOECKER and H. HAUSNER, *Powder Metall. Int.* **10** (1978) 87.
16. T. HASE and H. SUZUKI, *Yogyo-Kyokai-Shi* **86** (1978) 12.
17. G. K. WATSON, T. J. MOORE and M. L. MILLARD, *Amer. Ceram. Soc. Bull.* **64** (1985) 1253.
18. K. HOMMA, T. TATSUNO and H. OKADA, *J. Jpn Soc. Powder Metall.* **34** (1987) 66.

Received 31 May
and accepted 26 June 1990