JOURNAL OF MATERIALS SCIENCE **37** (2002) 1101 – 1106

Effect of structure of interfacial coating layer on mechanical properties of continuous fiber reinforced reaction sintered silicon carbide matrix composite

S. SUYAMA
Power & Industrial Systems Research & Development Center, Toshiba Corporation, 2–1, Ukishima-cho, Kawasaki-ku, Kawasaki, 210–0862, Japan

T. KAMEDA, Y. ITOH
2–4, Suehiro-cho, Tsurumi-ku, Yokohama 230–0045, Japan

A dense silicon carbide matrix composite reinforced by Hi-Nicalon fibers CVD coated with boron nitride and silicon carbide was fabricated by slurry impregnation and subsequent reaction sintering with molten silicon. The effect of the structure and the thickness of the silicon carbide layer of the fiber coating on the mechanical properties of the composite were investigated. That is, three types of silicon carbide layers, namely a dense structure with a thickness of 0.15 μm and two porous structures with a thickness of 0.15 μm and 0.48 μm, respectively, were investigated. As a result, excellent strength property of ceramic matrix composite (CMC) was obtained in the case of the dense silicon carbide (SiC) layer. The thickness effect of the SiC layer on the strength was smaller than that of the structure.

1. Introduction

Fiber-reinforced ceramic matrix composites are some of the most promising candidate materials for high temperature structural applications. SiC matrix composites are expected to be used as materials for gas turbine hot section parts, aiming at the improvement of the gas turbine efficiency due to the reduction of cooling air, and the potential reduction of NOx [1, 2]. The typical fabrication processes for SiC matrix composites are chemical vapor infiltration (CVI) and precursor impregnation and pyrolysis (PIP). With regard to protection of fibers and interfaces from the oxidation environment of the gas turbine, a dense matrix is preferable. The reaction sintering process is one of the processes suitable for forming a dense matrix without firing shrinkage [3–7]. The recent development of a low oxygen content SiC fiber (Hi-Nicalon), which shows both excellent high temperature stability and weaving ability, enables various matrix consolidation processes at high temperature.

In our previous work [8–12], a dense SiC matrix composite reinforced by Hi-Nicalon fibers was developed by slurry impregnation and subsequent reaction sintering process. In this work another processing route was selected by selecting appropriate processing conditions for the BN/SiC dual coating and Si-B metal infiltration for this composite, high strength and large fracture energy properties were achieved. In order to obtain the excellent mechanical properties, it was necessary to control the reaction of fiber with molten Si during sintering [13–18].

In this work, the effects of the structure and the thickness of the SiC layer of the fiber coating on the mechanical properties of the composite were investigated. The barrier effect of SiC layer to prevent the reaction with molten Si during sintering was discussed.

2. Experimental procedure

The fabrication method for composite test samples is shown in Fig. 1. Filaments of SiC fiber (Hi-Nicalon/Nippon Carbon Co., Ltd.) were coated with BN/SiC by chemical vapor deposition (CVD), to provide the appropriate interfacial weak bonding and to prevent the interfacial reaction. The BN coating thickness was about 0.4 μm. The SiC coatings were three types: a dense structure with a thickness of 0.15 μm and two porous structures with a thickness of 0.15 μm and 0.48 μm, respectively. The dense and porous structures of SiC coatings were obtained under different CVD conditions. The fiber yarn consisted of 500 filaments, and the filament diameter was about 14 μm. After 4 yarns were gathered into one fiber bundle unit, flat braided preforms made of 13 bundle units were fabricated. Alternatively, the fiber yarns were gathered uni-directionally. The fibrous preforms were set in a porous mold and the green composites were obtained by pressure impregnating and casting of the matrix slurry. The slurry was a mixture of SiC, carbon powders and water with some dispersant. The green composites were dried and then reaction sintered at 1450°C

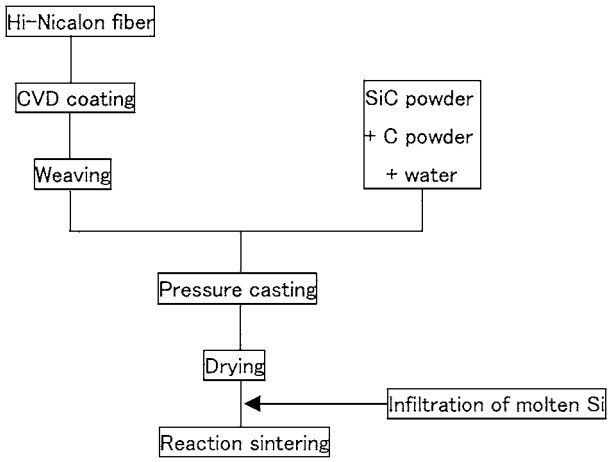

Figure 1 Flow chart of the fabrication process for the composite samples.

(1723 K) in vacuum for 18 ks. The infiltrating metals were 99.9 mass% pure silicon metal and 5 mass% boron-doped silicon metal. The sintered bodies were machined into $1 \times 10 \times 40$ mm bending test bars. For the uni-directional samples, the fiber direction was 90° to the tensile stress direction in the bending test.

The microstructures of the SiC coatings of the fibers were observed by a scanning electron microscope (SEM). Densities of the fabricated composite were evaluated by the Archimedes' method. Fiber volume fractions of the braided samples were evaluated by the observation of polished cross sections. The mechanical properties, which were first matrix cracking strength (σ_1) and ultimate strength (σ_2) for braided samples were evaluated in the 3-point bending test. The 90° fiber direction strength ($\sigma_\perp$) was evaluated in the 3-point bending test for uni-directional samples. The span and the crosshead speed of the 3-point bending test were 30 mm and 0.5 mm/min, respectively.

3. Experimental results and discussion

3.1. Microstructure of SiC coatings

In previous studies on the reaction between SiC and molten Si [13–18], it was reported that a small amount of SiC dissolved into molten silicon, and then re-precipitated. Different silicon carbide materials showed extremely different reaction behavior in liquid silicon. The polycarbosilane-derived silicon carbide fibers showed the highest reaction rate, CVD-formed silicon carbide fibers showed the slower reaction with molten Si [18]. So, to prevent the reaction between the fibers and the molten silicon, the CVD-silicon carbide barrier coating was applied.

Fig. 2 shows a SEM microphotograph of the contact region of Hi-Nicalon and silicon after heat treatment at 1420°C (1693 K) in vacuum. The fiber-material in the contact region to the Si-melt had dissolved and then re-precipitated. This remarkable morphology change was thought to have caused the drastic degradation of the fiber strength. Therefore, controlling the contact and the reaction between fiber and molten silicon in the fabrication process is thought to be important for obtaining desirable mechanical properties. The effects of the structures and the thickness of the SiC barrier coating were investigated.

Fig. 3 shows the microstructures of the surfaces of the three SiC coatings observed by SEM. The SiC coating thickness conditions are 0.15 μm for fiber (a) and fiber (b), and 0.48 μm for fiber (c). It is clearly observed that the microstructures of the SiC coatings are dense for fiber (a), and porous for fiber (b) and (c). The dense coating has a glassy morphology. On the other hand,

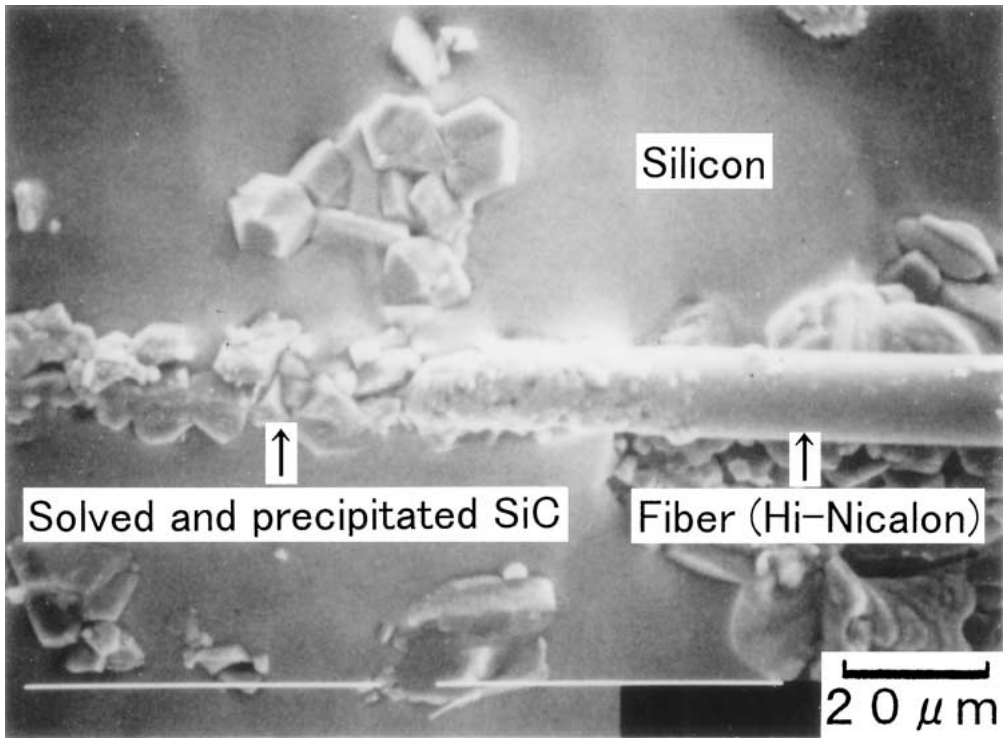

Figure 2 SEM microphotograph of the contact region of Hi-Nicalon and silicon after heat treatment at 1420°C (1693 K) in vacuum.

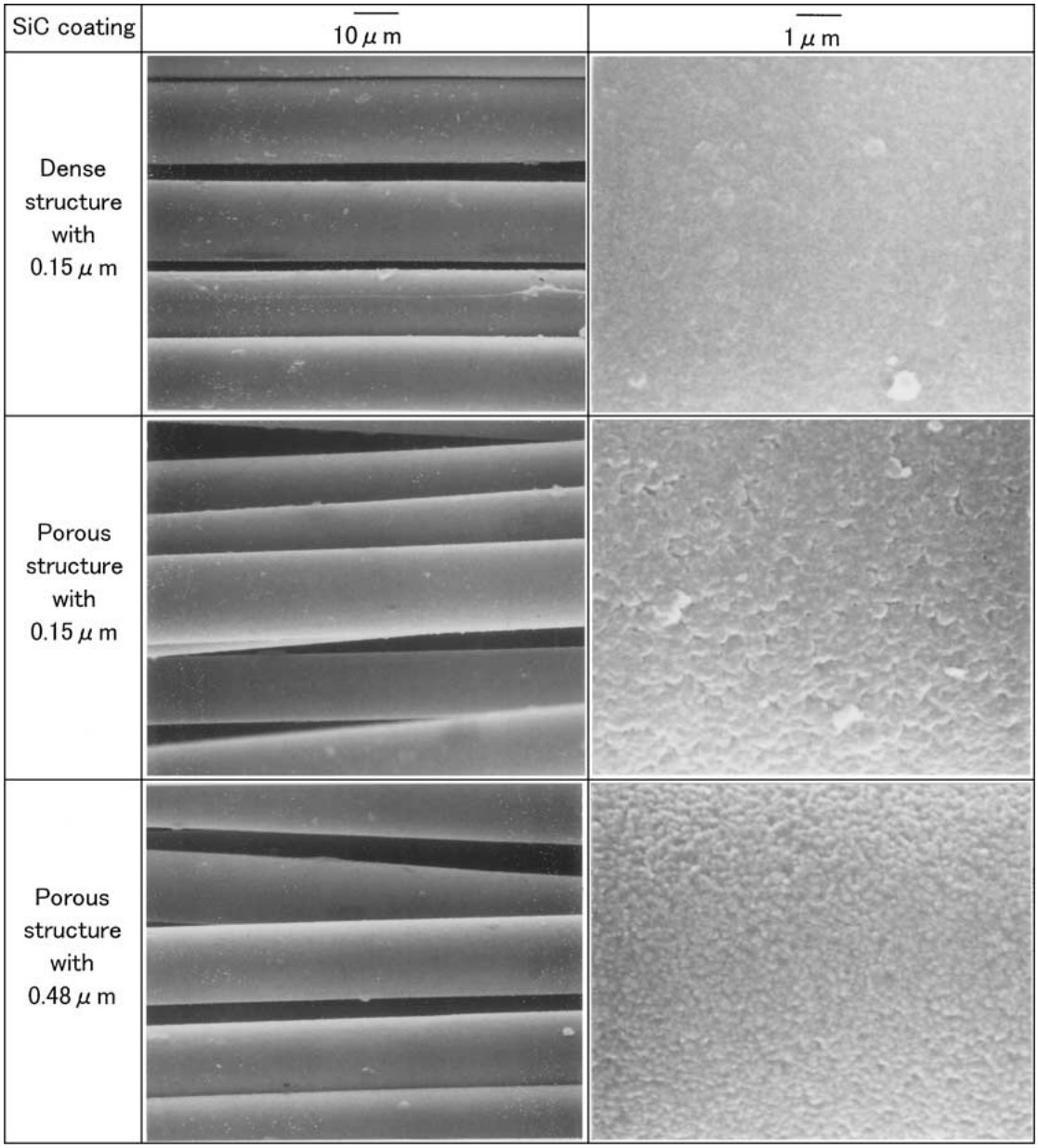

Figure 3 SEM microphotographs of the SiC coating surfaces of Hi-Nicalon.

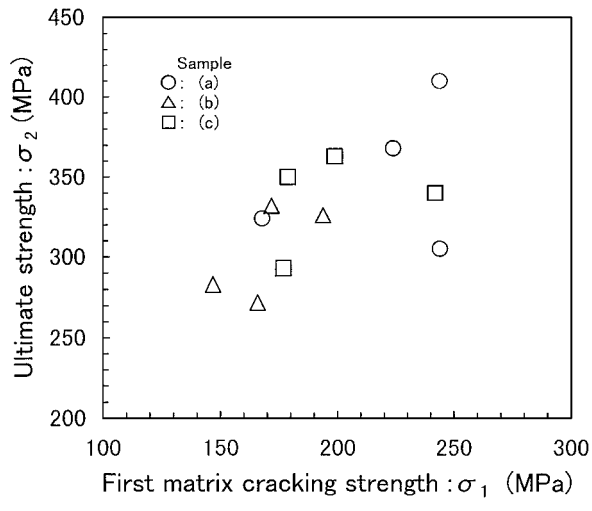

Figure 4 The relation between the first matrix cracking strength and the ultimate strength for the braided samples, with dense structure and 0.15 μm-thickness SiC coating (a), with porous structure and 0.15 μm-thickness SiC coating (b), with porous structure and 0.48 μm-thickness SiC coating (c).

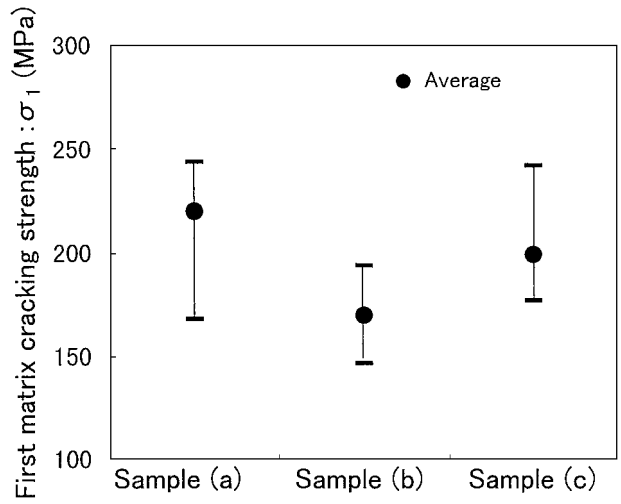

Figure 5 The first matrix cracking strength for the braided samples, with dense structure and 0.15 μm-thickness SiC coating (a), with porous structure and 0.15 μm-thickness SiC coating (b), with porous structure and 0.48 μm-thickness SiC coating (c).

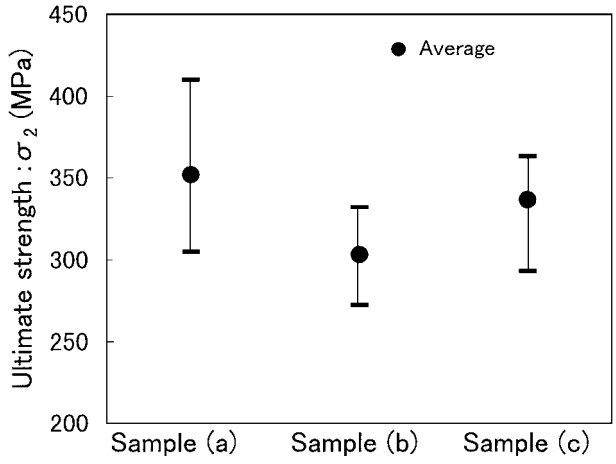

Figure 6 The ultimate strength for the braided samples, with dense structure and 0.15 μm-thickness SiC coating (a), with porous structure and 0.15 μm-thickness SiC coating (b), with porous structure and 0.48 μm-thickness SiC coating (c).

the porous coating has a granular morphology. This difference in the coating structures is caused by the SiC CVD process conditions.

3.2. Effect of SiC coating structure on the mechanical properties of composites

Densities of the fabricated composites were about 3.0 Mg/m^3. Fiber volume fractions of the braided samples were about 20 vol%. The mechanical properties, which are first matrix cracking strength (σ_1) and ultimate strength (σ_2) for braided samples in the 3-point bending test are shown in Figs 4–6. Fig. 4 shows the relation between the first matrix cracking strength and the ultimate strength for all samples. The ultimate strength is higher than the first matrix cracking strength. Therefore, the fracture strength of the composed fibers is thought to control the ultimate strength. From Fig. 5, it is recognized that the sample of fiber (a) with dense

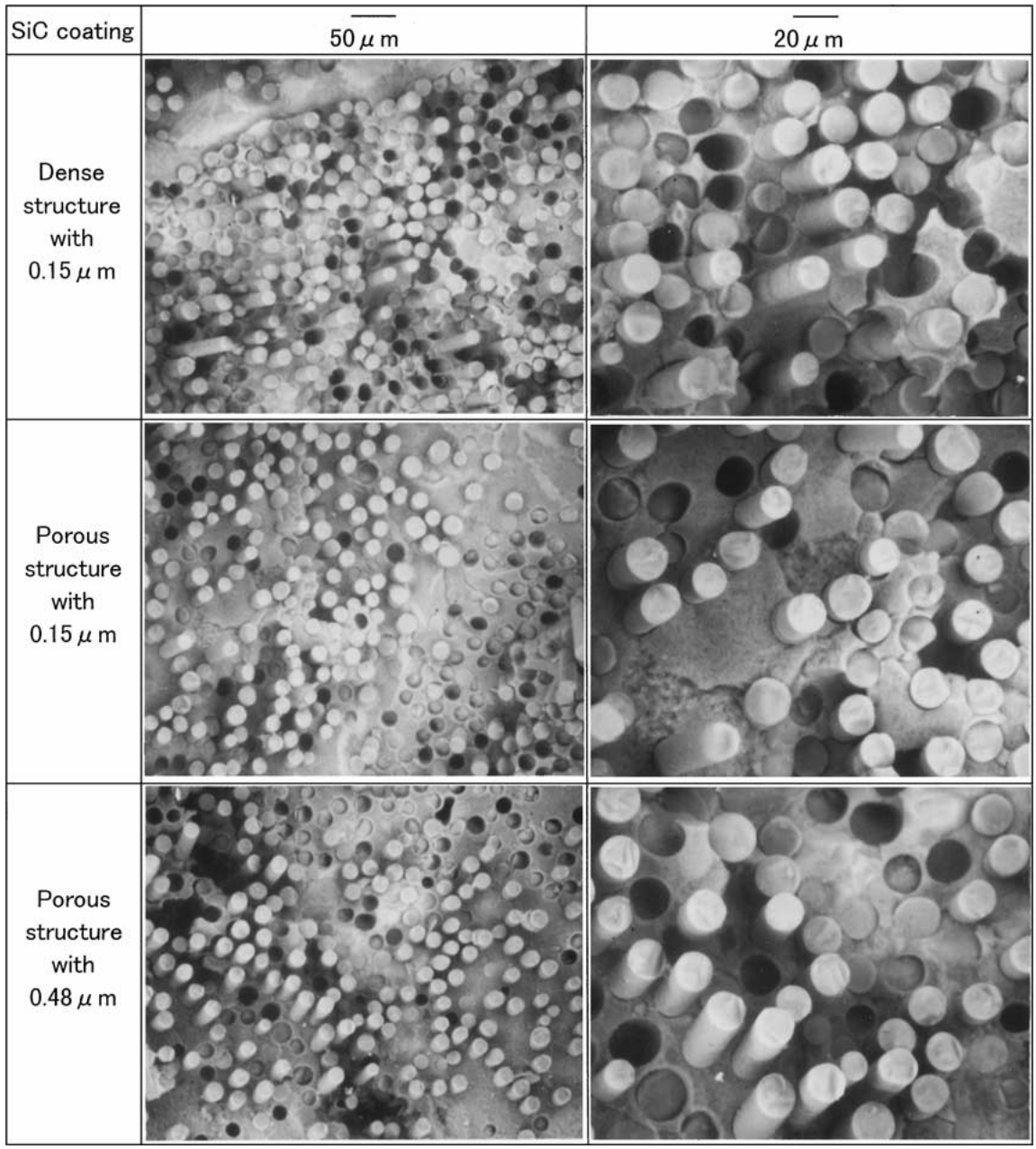

Figure 7 SEM microphotographs of fracture surfaces after 3-point bending test at room temperature, with dense structure and 0.15 μm-thickness SiC coating (a), with porous structure and 0.15 μm-thickness SiC coating (b), with porous structure and 0.48 μm-thickness SiC coating (c).

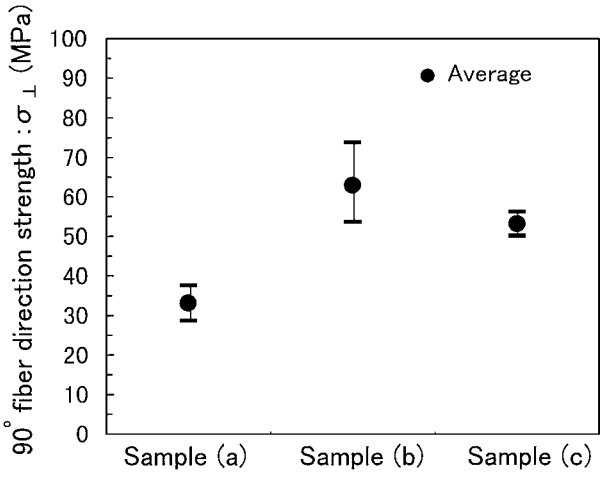

Figure 8 The 90° fiber direction strengths for the uni-directional samples, with dense structure and 0.15 μm-thickness SiC coating (a), with porous structure and 0.15 μm-thickness SiC coating (b), with porous structure and 0.48 μm-thickness SiC coating (c).

structure and 0.15 μm-thickness SiC coating shows the highest first matrix cracking strength, the sample of fiber (c) with porous structure and 0.48 μm-thickness SiC coating shows the middle strength, and the sample of fiber (b) with porous structure and 0.15 μm-thickness SiC coating shows the lowest strength. From Fig. 6, it is recognized that the sample of fiber (a) with dense structure and 0.15 μm-thickness SiC coating shows the highest ultimate strength, the sample of fiber (c) with porous structure and 0.48 μm-thickness SiC coating shows the middle strength, and the sample of fiber (b) with porous structure and 0.15 μm-thickness SiC coating shows the lowest strength. This difference is thought to correspond to the composed fiber strength. As mentioned above, the composed fiber strength property is mainly dependent on the degradation caused by the reaction between molten Si during sintering. So, the dense structure SiC coating is effective for preventing the contact with molten Si. The thicker SiC

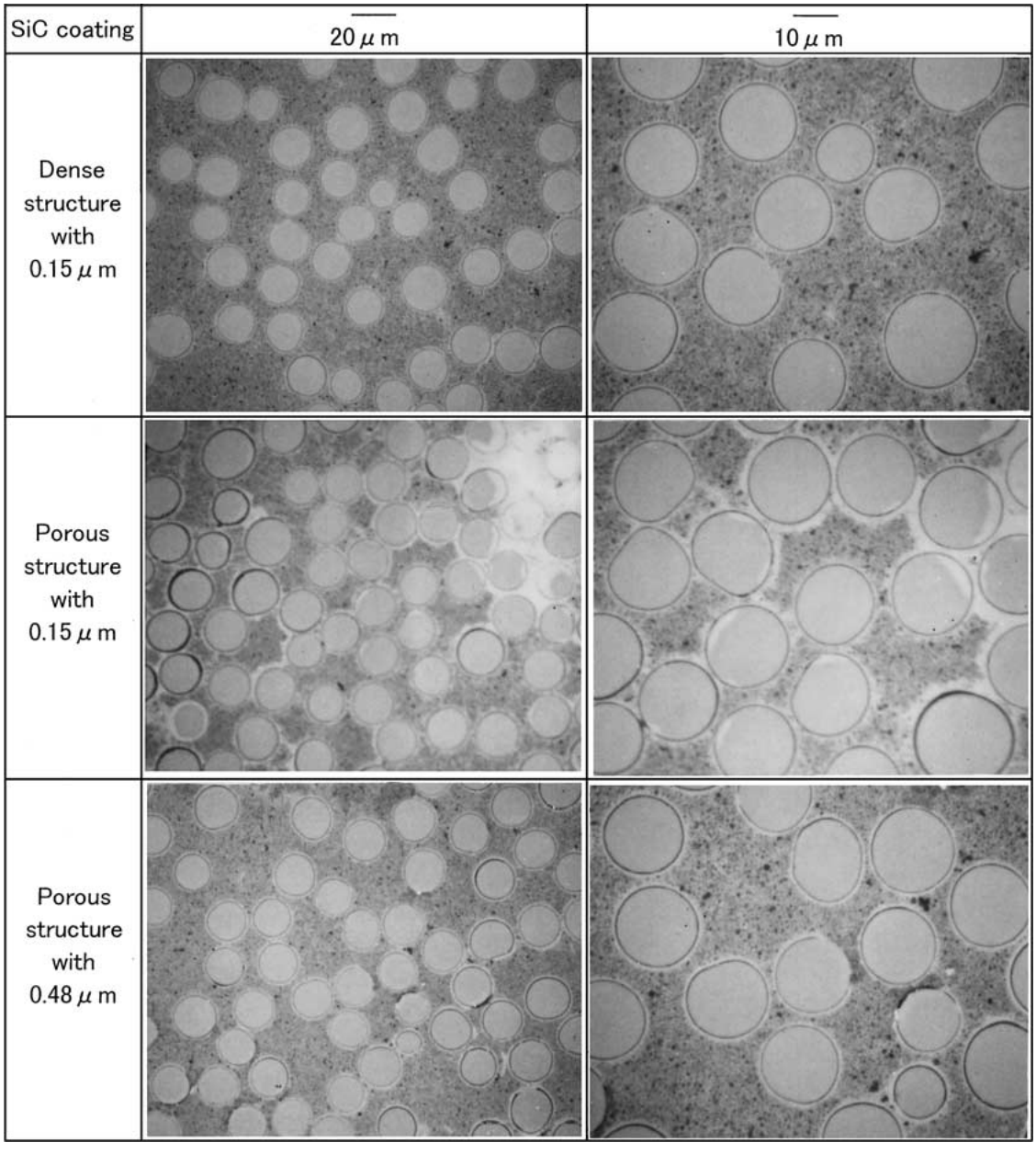

Figure 9 SEM-BEI microphotographs on polished section of the specimen, with dense structure and 0.15 μm-thickness SiC coating (a), with porous structure and 0.15 μm-thickness SiC coating (b), with porous structure and 0.48 μm-thickness SiC coating (c).

coating shows the middle ultimate strength. The effect of the thickness of SiC coating is smaller than that of the structure. The fracture energy properties show a little difference. Fig. 7 shows SEM microphotographs of the corresponding fracture surfaces. Fiber pull-out was clearly observed for all fracture surfaces. However, no regions without fiber pull-out were observed. The tendency was recognized that the regions with no fiber pull-out were large for porous SiC coating samples, but small for the dense SiC coating sample.

The 90° fiber direction strengths ($\sigma_{\perp}$) are shown in Fig. 8. They show the highest value for the sample of fiber (b), the middle value for the sample (c), and the lowest value for sample (a). This is thought to correspond to the interfacial bonding strength. Fig. 9 shows SEM-BEI microphotographs for polished section of the specimen. For porous structure SiC coatings of fiber (b) and (c), a part of the composite fibers showed a region with changed contrast, which had reacted with molten silicon during sintering. These results explain that the effectiveness of the SiC layer as a barrier for preventing the reaction with molten Si is in the descending order of the samples of fiber (a), (c) and (b).

4. Conclusions

A dense SiC matrix composite reinforced by Hi-Nicalon fibers was fabricated by slurry impregnation and subsequent reaction sintering process. The effects of the structure and the thickness of the silicon carbide layer over the SiC fiber on the mechanical properties of the composites were investigated. The following was concluded.

1. The effects of the structure and the thickness of the SiC layer of the fiber coating on the mechanical properties of the composite were investigated.

2. In the case of SiC coating with dense structure, the SiC layer was effective as a barrier for preventing the reaction with molten Si during reaction-sintering.

3. The barrier effect of the thickness of SiC coating layer on the strength of CMC was smaller than the effect of the dense structure.

References

1. G. S. CORMAN, J. T. HEINEN and R. H. GOETZE, ASME Paper 95-GT-387, in International Gas Turbine and Aeroengine Congress and Exposition (Houston, Texas, USA, June 5–8, 1995).
2. M. H. VAN DE VOORDE and M. R. NEDELE, *Ceramic Eng. & Sci. Proc.* **17**(4) (1996) 3.
3. K. L. LUTHRA, R. N. SINGH and M. K. BRUN, *Am. Ceram. Soc. Bull*. **72** (1993) 79.
4. A. SZWEDA, T. E. EASLAR, D. R. PETRAK and V. A. BLACK, ASME Paper 99-GT-189, in International Gas Turbine and Aeroengine Congress and Exposition, Indianapolis, Indiana, USA, June 7–10, 1999.
5. G. S. CORMAN, M. K. BRUN and K. L. LUTHRA, ASME Paper 99-GT-234, in International Gas Turbine and Aeroengine Congress and Exposition, Indianapolis, Indiana, USA, June 7–10, 1999.
6. A. J. DEAN, G. S. CORMAN, B. BAGEPALLI, K. L. LUTHRA, P. S. DIMASCIO and R. M. ORENSTEIN, ASME Paper 99-GT-235, in International Gas Turbine and Aeroengine Congress and Exposition, Indianapolis, Indiana, USA, June 7–10, 1999.
7. T. KAMEDA, A. SAYANO, N. AMIJI, H. ICHIKAWA, H. HAMADA, A. FUJITA and T. UOZUMI, in Proc. 21st An. Conf. Compos., Cocoa Beach, FL, USA, 1997 p. 419.
8. Y. ITOH, T. KAMEDA, K. NISHIDA, M. UMEZAWA, K. IMAI and H. ICHIKAWA, *J. Ceram. Soc. Japan* **106** (1998) 830 (in Japanese).
9. Y. ITOH, T. KAMEDA, S. SUYAMA and K. NAGATA, *ibid.* **106** (1998) 1190 (in Japanese).
10. T. KAMEDA, S. SUYAMA, Y. ITOH and Y. GOTO, *ibid.* **107** (1999) 327 (in Japanese).
11. Y. ITOH, T. KAMEDA and S. SUYAMA, *ibid.* **107** (1999) 425 (in Japanese).
12. T. KAMEDA, S. SUYAMA, Y. ITOH and K. NISHIDA, *ibid.* **107** (1999) 622 (in Japanese).
13. J.-G. LI and H. HAUSNER, *J. Am. Ceram. Soc.* **79** (1996) 873.
14. E. FITZER and R. GADOW, "Ceramic Components for Engine 1993 Japan," (KTK Scientific Publishers, Tokyo and D. Reidel Publishing Co., Dordrecht, 1984) p. 561.
15. H. ICHIKAWA and HOSYASENKAGAKU, **58** (1994) 21 (in Japanese).
16. R. W. RICE, "Treatise on Materials Science and Technology," Vol. II (Academic Press, New York, 1978) p. 199.
17. M. UMEZAWA, Nippon Carbon Co. Ltd., private communication.
18. E. FITZER and R. GADOW, in Proc. of International Symposium on Ceramic Components for Engine, 1983 Japan, edited by S. Somiya, *et al*. (KTK Scientific Publishers, Tokyo, 1983) p. 561.

Received 19 April
and accepted 21 November 2001