Preparation of silicon-based oxide layer on high-crystalline SiC fiber as an interphase in SiC/SiC composites

N. Igawa [a,*], T. Taguchi [a], R. Yamada [b], Y. Ishii [a], S. Jitsukawa [b]

[a] *Neutron Science Research Center, Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki-ken 319-1195, Japan*
[b] *Department of Materials Science, Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki-ken 319-1195, Japan*

Abstract

New silicon-based oxide layers, SiO_2 and SiO_2–MgO, as the interfacial materials of SiC/SiC composites were prepared on Hi-Nicalon Type S SiC fiber by sol–gel method. The fibers were completely coated by only dipping twice in a coating solution of $[Si] = 1.0$ mol/dm^3 or that of $[Mg] = 0.50$ mol/dm^3 and $[Si] = 0.25$ mol/dm^3. These coated layers were amorphous up to 1200 °C for the SiO_2 coated fibers, or consisted of a mixture of SiO_2 and Mg_xSi_zO up to 1400 °C in SiO_2–MgO coated fibers. The tensile strength of coated Hi-Nicalon Type S SiC fiber after heating at 1200 °C was similar to that of unheated Hi-Nicalon Type S SiC fiber without heating and was reduced by 15% after heating to 1400 °C.

© 2004 Elsevier B.V. All rights reserved.

1. Introduction

Silicon carbide has a high specific strength, high temperature strength and excellent thermal stability material, however monolithic SiC is extremely brittle with low fracture toughness. Continuous SiC fiber reinforced SiC matrix composites (SiC/SiC) were developed and significantly improved these properties [1,2]. In addition to these good properties, SiC has a low induced radioactivity after neutron irradiation, therefore SiC/SiC are attractive candidate materials for fusion reactor structural applications [3–6].

In SiC/SiC, the interphase between SiC fibers and SiC matrix is very important for excellent mechanical properties [7,8] since they allow the deflection of cracks at the interphase, the fiber pullout during fracture leading to excellent interfacial shear strength and the ductile failure modes to produce good mechanical properties. In the previous study [9,10], several interphases, such as carbon and boron nitride, were investi-

gated and these interphases degraded under neutron irradiation and oxidation environments. Also, conventional SiC fiber, such as Hi-Nicalon contains the excess amorphous carbon [11]. Since that carbon can degrade oxygen resistance, an oxide material could not be applied as an interphase for SiC/SiC. Recently, advanced SiC fibers have been produced, including Hi-Nicalon Type S [12] and Tyranno SA [13] which possess superior mechanical, thermal properties and oxidation resistance as well as excellent performance under neutron irradiation. Therefore oxide interphases become a potential candidate to improve the thermal stability, oxidation and radiation-resistance of SiC/SiC composites.

In this study, we investigated a silicon-based oxide for the interphase of SiC/SiC because of its thermal stability and low induced radioactivity. The interaction between SiC fibers and the interphase was examined and the mechanical properties of coated fibers were evaluated.

2. Experimental procedure

The SiC fiber used in the present work was Hi-Nicalon Type S (Nippon Carbon Co. Ltd., Tokyo, Japan).

---

[*] Corresponding author. Tel.: +81-29 282 6099; fax: +81-29 282 5922.

E-mail address: igawa@maico.tokai.jaeri.go.jp (N. Igawa).

Table 1
Coating parameters of the SiC fiber

	Coating solution (mol/dm³)		Number of dips
	[Si]	[Mg]	
Sample-1	0.5	–	2
Sample-2	1.0	–	2
Sample-3	1.0	–	5
Sample-4	0.25	0.5	2
Sample-5	0.25	0.5	5

Hi-Nicalon Type S has a low-oxygen content and is a high-crystalline SiC fiber derived from polycarbosilane fiber possessing has excellent mechanical properties, such as high tensile strength and elastic modulus, at high temperature. The diameter, elastic modulus and tensile strength of Hi-Nicalon Type S are approximately 12 µm, 420 and 2.6 GPa, respectively [11].

A silicon-based oxide layer on SiC fiber as the interphase of SiC/SiC composites was prepared by sol–gel method. Two types of coating solutions were prepared: Si-alkoxide and Si-2Mg-alkoxide solutions. Silicon tetrapropoxide and magnesium dipropoxide were dissolved in 2-propanol. The Si and Mg concentration of these coating solutions are shown in Table 1. The coating on the SiC fibers was prepared by a dip method. After dipping, the coating layer on the fibers was hydrolyzed at room temperature in air. This dip-and-hydrolyzed process was a maximum of repeated 5-times. Finally, the coated fibers were heated up to 1400 °C in air for 1 h to oxidize those hydrolyzed layers: the heating and cooling rates were controlled to be 7 K/min. The phases of the coating layer were analyzed by using X-ray diffraction; CuKα radiation of 40 KV and 20 mA was used with a step-scanning technique in the 2θ range from 25 to 80°. The surface of the coated layers was examined by using a scanning electron microscopy (SEM). The tensile strength of the coated fibers was also measured at room temperature by single filament method using an Instron-type tensile testing machine with a gauge length of 25 mm and crosshead speed of 0.5 mm/min.

3. Results and discussion

3.1. SiO₂ coating on the fiber

Fig. 1 shows the SEM photographs of Hi-Nicalon Type S SiC fiber with the SiO₂ coated layer after heating at 1000 °C. That of uncoated Hi-Nicalon Type S fiber is also shown in Fig. 1 for comparison. The uncoated fiber has a smooth surface. Though the fibers in sample-1 were only partially coated after a single dip, the surface of the fibers was fully coated and smooth after only two dips in the coating solution consisting of [Si] = 1.0 mol/dm³.
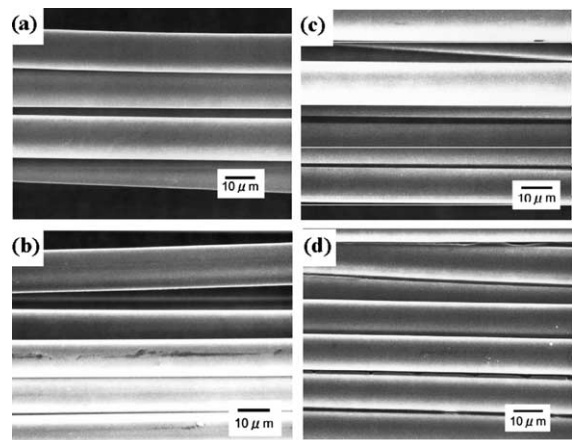

Fig. 1. SEM microphotographs of SiO₂ coated Hi-Nicalon Type S fibers; (a) uncoated fiber, (b) sample-1, (c) sample-2 and (d) sample-3.

Fig. 2 shows the X-ray diffraction patterns of the sample-2 after dipping and processing the coating. For comparison, uncoated Hi-Nicalon Type S SiC fiber is also shown in Fig. 2. The XRD pattern of uncoated Hi-Nicalon Type S SiC fiber shows 5 peaks around the 2θ of 35.7°, 41.4°, 60.4°, 71.8° and 75.5° (d = 0.251, 0.218, 0.154, 0.131 and 0.125 nm) which correspond to the (1 1 1), (2 0 0) (2 2 0) (3 1 1) and (2 2 2) reflections of β-SiC. Though no other peaks were observed in sample-2 below 1200 °C which indicated the oxide layer was amorphous phase, a small peak attributed to SiO₂ was observed around a 2θ of 22.5° at 1400 °C. While the diffraction peak widths of Hi-Nicalon SiC fiber narrowed following heating in the previous study [14], no change of the peak shape and position of Hi-Nicalon Type S SiC fiber were observed in the present work. This suggests that the microstructure of Hi-Nicalon Type S fiber is very stable under those conditions.
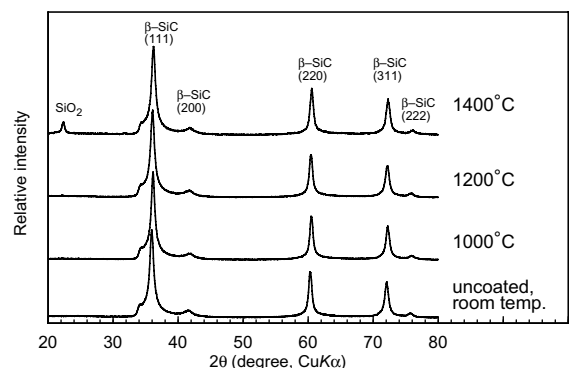

Fig. 2. X-ray diffraction patterns of SiO₂ coated Hi-Nicalon Type S fiber as a function of coating fabrication temperature.
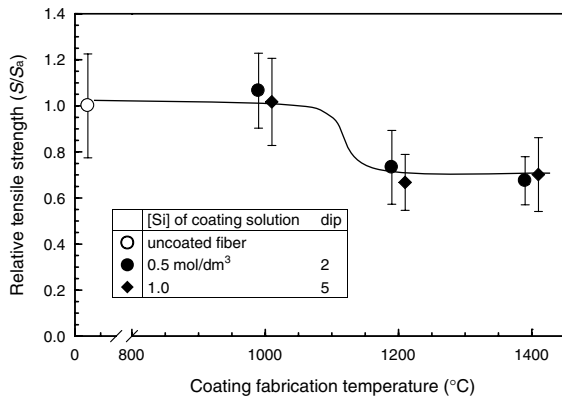
Fig. 3. Tensile strength of SiO_2 coated Hi-Nicalon Type S fiber as a function of coating fabrication temperature.

The tensile strength of the fibers (S) as a function of the coating fabrication temperature is shown in Fig. 3. The tensile strength of uncoated Hi-Nicalon Type S SiC fiber without heating (S_a) was 2.6 GPa. The tensile strength of SiO_2-coated fibers was the same as S_a up to 1000 °C. While that heated at 1200 °C was degraded to 80% of S_a, no more degradation was observed between 1200 and 1400 °C.

3.2. SiO_2–MgO coating on the fiber

Fig. 4 shows the SEM photographs of Hi-Nicalon Type S SiC fiber with the SiO_2–MgO coated layer after heating at 1000 °C. The fibers were coated completely but the surface was rough in sample-4 compared with the SiO_2 coated fibers (see Fig. 1). The surface became rougher with increasing number of dips and the excess coating layers were only partially formed.

Fig. 5 shows X-ray diffraction patterns of the sample-5 after coating processing at several temperatures. The peaks attributed to MgO were observed around 2θ of 43.4° and 62.8° at 700 °C, these peaks decreased with increased processing temperature and completely disappeared at 1400 °C, and the peaks attributed to $MgSiO_3$ around 2θ of 28.7°, 34.4° and 56.8° were increased. A small amount of Mg_2SiO_4 was also observed around 2θ of 46.4° at 1400 °C in this sample. The SiO_2
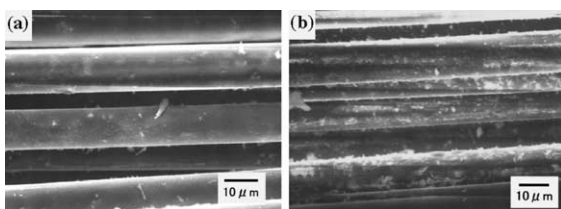

Fig. 4. SEM micrographs of SiO_2–MgO coated Hi-Nicalon Type S fibers; (a) sample-4 and (b) sample-5.
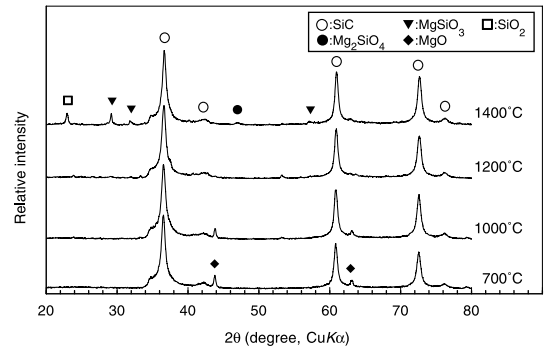

Fig. 5. X-ray diffraction patterns of SiO_2–MgO coated Hi-Nicalon Type S fiber as a function of coating fabrication temperature.
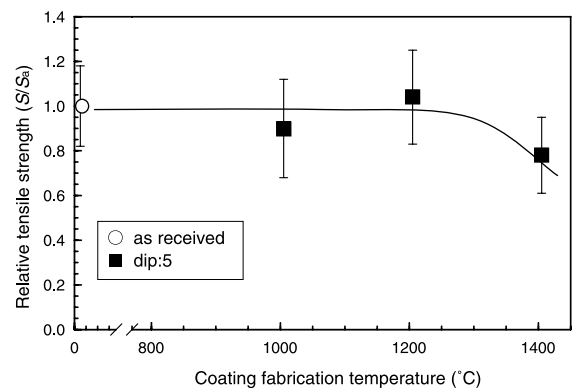

Fig. 6. Tensile strength of SiO_2–MgO coated Hi-Nicalon Type S fiber(sample-5) as a function of coating fabrication temperature.

peak was observed around 2θ of 22.5° at 1400 °C. These SiO_2 peaks in samples-2 and 5 at 1400 °C were attributed to the decomposition and crystallization of the coating but it was not determined if it was due to oxidation of SiC fiber. No change in the peaks attributed to the SiC fiber itself were observed.

Fig. 6 shows the tensile strength of sample-5. The tensile strength was the same as S_a up to 1200 °C and showed higher thermal degradation resistance compared with the SiO_2 coated fiber. The strength was degraded to 85% of S_a after heating to 1400 °C. Ichikawa reported that the tensile strength of Hi-Nicalon Type S SiC fiber after heating to 1400 °C in air was degraded to 60% of S_a [11]. The reason for the strength degradation was that the oxide layer damaged the fiber at the interface between the fiber and coating, however, once the coating was applied, it prevented a direct interaction between the fiber and oxygen in air: viscous silica formed in the coating gives the fiber improved oxidization resistance, because oxygen diffusion is limited in this material [15].

Among the various fabrication processes of SiC/SiC, chemical vapor infiltration (CVI) method is one of the best techniques for fusion applications because this method produces a highly pure, stoichiometric, crystalline β-SiC matrix with a low thermal stress. Fabrication of SiC/SiC composites using CVI is typically carried out at about 1100–1200 °C which minimizes fiber damage [16]. The present work shows that the observed degradation of the tensile strength of the coated fiber at 1200 °C was small enough to consider these new interphases, SiO_2 and SiO_2–MgO.

4. Conclusion

Oxide layers consisting of SiO_2 and SiO_2–MgO on Hi-Nicalon Type S SiC fibers for fiber-matrix interphases of SiC/SiC composites were prepared by a sol–gel method. The fibers were satisfactorily coated by dipping twice in coating solutions of $[Si] = 1.0$ mol/dm^3 or that of $[Mg] = 0.50$ mol/dm^3 and $[Si] = 0.25$ mol/dm^3. The interaction between the SiC fiber and the interphase was examined and the mechanical properties of coated fibers were evaluated. The fiber coating was amorphous up to 1200 °C and crystalline SiO_2 was formed in SiO_2 coated fiber, while a mixture of MgO, SiO_2 and Mg_xSi_zO was identified up to 1400 °C in SiO_2–MgO coated fiber. Compared with uncoated and unheated Hi-Nicalon Type S SiC fibers (S_a), the tensile strength of these coated fibers was the same as S_a up to 1200 °C and decreased to 85% of S_a after heating at 1400 °C. These strength values are high enough to consider these new fiber-matrix interphases for SiC/SiC composites up to processing temperatures of 1200 °C.

References

[1] A.G. Evans, Mater. Sci. Eng. A 143 (1991) 63.

[2] A.G. Evans, Philos. Trans. R. Soc. London, A 351 (1995) 511.

[3] L.L. Snead, R.H. Jones, A. Kohyama, P. Fenici, J. Nucl. Mater. 233–237 (1996) 26.

[4] P. Fenici, A.J. Frias Rebelo, R.H. Jones, A. Kohyama, L.L. Snead, J. Nucl. Mater. 258–263 (1998) 215.

[5] S. Nishio, S. Ueda, I. Aoki, R. Kurihara, T. Kuroda, H. Miura, T. Kunugi, Y. Seki, T. Nagashima, M. Ohara, J. Adachi, S. Yamazaki, I. Kawaguchi, T. Hashimoto, K. Shinya, Y. Murakami, H. Takase, T. Nakamura, Fus. Eng. Des. 41 (1998) 357.

[6] A. Hasegawa, A. Kohyama, R.H. Jones, L.L. Snead, B. Riccardi, P. Fenici, J. Nucl. Mater. 283–287 (2000) 128.

[7] R. Naslain, O. Dugue, A. Guette, J. Am. Ceram. Soc. 74 (1991) 2482.

[8] T. Hinoki, L.L. Snead, T. Taguchi, N. Igawa, W. Yang, T. Nozawa, Y. Katoh, A. Kohyama, Ceram. Trans. 144 (2002) 55.

[9] G.N. Morscher, J. Am. Ceram. Soc. 80 (1997) 2029.

[10] L.L. Snead, M.C. Osbone, R.A. Lowden, J. Strizak, R.J. Shinavski, K.L. More, W.S. Eatherly, J. Bailey, A.M. Williams, J. Nucl. Mater. 253 (1998) 20.

[11] H. Ichikawa, Ceram. Trans. 144 (2002) 153.

[12] M. Takeda, A. Urano, J. Sakamoto, Y. Imai, J. Nucl. Mater. 258–263 (1998) 1594.

[13] T. Ishikawa, Y. Kohtoku, K. Kumagawa, T. Yamamura, T. Nagasawa, Nature 391 (1998) 1594.

[14] N. Igawa, T. Taguchi, R. Yamada, S. Jitsukawa, Ceram. Eng. Sci. Proc. 21B (2000) 237.

[15] G. Chollon, R. Pailler, N. Naslain, P. Laanani, M. Monthioux, P. Olry, J. Mater. Sci. 32 (1997) 327.

[16] N. Igawa, T. Taguchi, L.L. Snead, Y. Katoh, S. Jitsukawa, A. Kohyama, J.C. McLaughlin, J. Nucl. Mater. 307 (2002) 1205.