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Improvement of mechanical properties of SiC/SiC composites by various surface treatments of fibers

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Abstract

In order to make an interfacial shear strength control layer (ISSCL), such as pyrolytic C layer, effective and improve SiC/SiC composites' mechanical properties, heat treatment at 1500°C under Ar flow in quite low O_2 partial pressure or a CVI SiC coating were applied to Hi-Nicalon™ SiC fibers. Interfacial microstructures between fiber and matrix were examined by SEM and TEM. Interfacial shear properties were evaluated by single-fiber push-out tests and compared with the results of three-point bend tests and tensile tests. Fracture surfaces after mechanical tests were examined by SEM with EDS and optical interferometric profilometry. Active oxidation of the fibers decreased fiber mechanical properties and made the composites brittle, although it was successful in making the ISSCL rough. SiC fiber coating induced strong bonding between fiber and ISSCL and turned the crack path from between the fiber and the ISSCL to the inside of the ISSCL. Interfacial frictional stress was increased and the mechanical properties of tensile tests were improved.

1. Introduction

Ceramic matrix composites (CMCs) are expected to be applied to not only airplanes and spacecraft but also advanced energy systems such as high thermodynamic efficiency gas cycles and fusion systems because of their high-temperature mechanical properties and low activation [1,2].

The importance of interfacial fracture behavior between fiber and matrix on the mechanical properties of CMCs has long been emphasized [3]. The authors have concentrated their efforts on the relationship between interfacial fracture behavior and the interfacial microstructure of SiC/SiC composites [4,5]. As for SiC/SiC composites, SEM and TEM observation showed that, almost always, the interfacial crack propagated at the interface between the fiber and the interfacial shear stress control layer (ISSCL), such as the pyrolytic C layer. This behavior was not limited only to C layers. Multiple SiC layers and 'porous' SiC layers, which are expected for nuclear applications [6], showed the same behavior. The fracture surface of the fibers was smooth. This led to low frictional stress of the debonded interface and made crack propagation easy. This fracture behavior is attributed to a smooth fiber surface and a weak bond between the ISSCL and the fiber. This interfacial fracture behavior has been reported, and chemical treatment of the fiber surface has been applied to get a stronger bond between fiber and ISSCL and keep the crack within the ISSCL. Mechanical properties were improved by such surface treatment [7,8].

The objective of this work is to make the ISSCL effective and to improve mechanical properties by fiber surface treatment. As the simplest way to treat fiber surface, SiC was coated onto fibers to strengthen the bond between fiber and ISSCL, for the interfacial bond between ISSCL and SiC matrix was stronger than the interfacial bond between fiber and ISSCL. The

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interfacial crack was expected to propagate not at the interface between fiber and ISSCL, but within the ISSCL in a complicated manner as shown in Fig. 1. Heat treatment of fiber was applied as another surface treatment to make the fiber surface rough by active oxidation [9].

Interfacial strength depends on clamping stress and frictional stress [3]. One of the functions of the ISSCL is to reflect crack propagation at the fiber–matrix interface back into the ISSCL. For this function, an appropriate interfacial clamping stress is required. To keep interfacial strength after debonding, a large interfacial frictional stress is also desired. The concept of the ISSCL in this work is to have both an appropriate clamping stress and a large frictional stress.

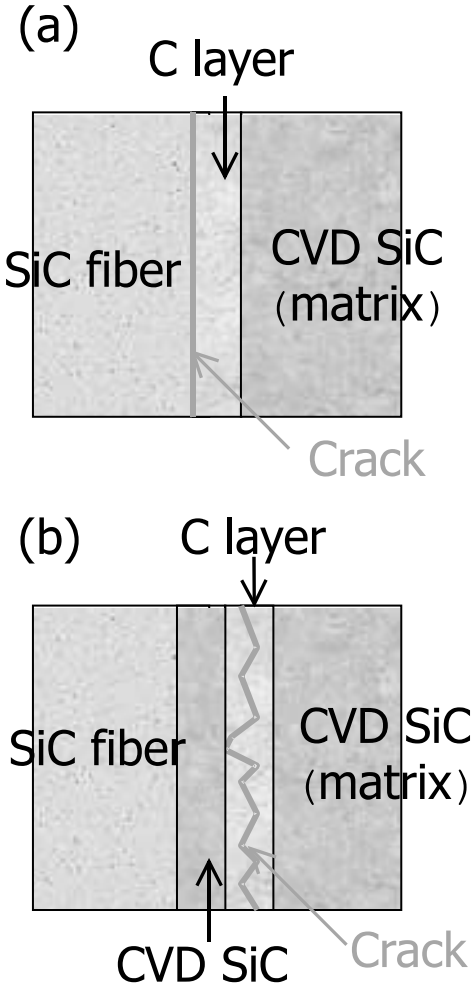


Fig. 1. Images of crack propagations at fiber–matrix interfaces: (a) without fiber surface treatment; (b) with the fiber SiC coating.

2. Experimental procedure

2.1. Materials

The materials used in this study were flat-woven Hi-Nicalon™ SiC-fiber-reinforced SiC matrix composites. SiC/SiC composites were fabricated by the chemical vapor infiltration (CVI) method [10]. Methyltrichlorosilane (MTS) was used for SiC deposition. As one of the fiber surface treatments, fibers were coated with SiC, whose thickness was 0.25 μm, by the CVI method, prior to the deposition of an ISSCL of C of 0.13 μm thickness, and matrix SiC deposition. The fibers were heated for 1 h at 1500°C under ultra-high-purity Ar flow (oxygen content < 0.1 ppb) as another fiber surface treatment [9]. The heating rate was 100°C/h. After heat treatment, pyrolytic C of 0.40 μm thickness and matrix SiC were deposited. The reference material, which had a 0.15-μm thick ISSCL of C without any surface treatment, was also fabricated.

2.2. Examination of microstructure

The microstructure of the composites was examined by optical microscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The thin film for TEM observation was prepared by a focused ion beam (FIB). The details of the FIB process have been described elsewhere [5]. The fracture surfaces after mechanical tests were observed by SEM. The pull-out fibers' surfaces were analyzed by EDS equipped with SEM and by optical interferometric profilometry to evaluate roughness.

2.3. Mechanical tests

Interfacial shear properties were obtained by single-fiber push-out tests [4]. The specimens were sliced into 500-μm-thick samples. After mechanical polishing, the specimens reduced in thickness to approximately 50 μm. They were placed on a holder with a groove of 50 μm width. Isolated fibers with fiber direction perpendicular to holder surface on the groove were selected with a video microscope. They were pushed out by a Berkovich-type pyramidal diamond indenter tip with a maximum load of 1 N. Both the pushed-in and pushed-out sides were observed by SEM after push-out tests.

Three-point bend tests were carried out at ambient temperature. The sample geometry was $25^{l} \times 4.0^{w} \times 1.6^{t}$ mm. The support span was 18 mm. The cross-head speed was 0.03 mm/s.

Tensile tests were carried out at ambient temperature. The strain of the composites was measured by means of bonded strain gauges. Tensile specimens with reduced-gauge section were used (Fig. 5). The gauge sizes were $5.0^{l} \times 2.0^{w} \times 1.6^{t}$ mm. In order to accommodate test

specimen with wedge-type grips, 1.0-mm-thick aluminum end tabs were attached to both sides of the specimen. All tests were conducted with a cross-head speed of 0.5 mm/min.

3. Results

3.1. Interfacial microstructure

Fig. 2 shows a TEM image of the interfacial microstructure of the fiber SiC coating sample. The interface between fiber SiC coating and C layer was as rough as the interface between C layer and matrix SiC. Mixed layers of C and SiC were also observed. These layers were deposited prior to SiC deposition, because MTS gas includes a slight amount of free C, and C was more sensitive to reaction than SiC.

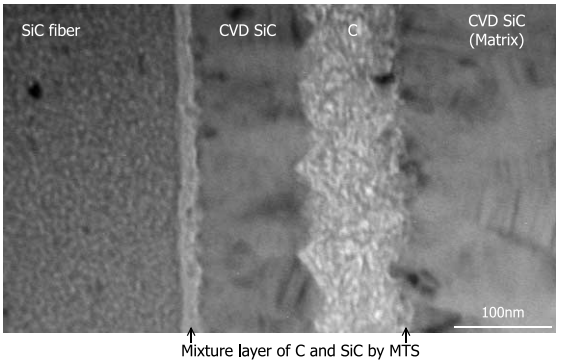


Fig. 2. A TEM image of the fiber–matrix interface of SiC/SiC composites with the fiber SiC coating.

The Hi-Nicalon™ fiber after heat treatment for 1 h at 1500°C and interfacial microstructure of its composites are shown in Fig. 3. Self-decomposition of the SiC fiber, for quite low O_2 partial pressure, happened during the annealing process. During this process SiC crystals grew outward on the fiber surface, and a rough C layer was produced.

3.2. Interfacial shear properties

Representative loading curves of single-fiber push-out tests are shown in Fig. 4. The curve indicated as SiC/C is the fiber SiC coating sample. Another is the sample without surface treatment. The loading curves are parabolic at first as the indenter penetrates into a fiber. The gradient change labeled 'push-in' indicates the initiation of interfacial debonding at the surface. The crack between a fiber and matrix propagated, and a fiber was deformed elastically and pushed in. Then, the whole interface was debonded, and a fiber was pushed out. Details regarding push-out tests are given in our previous papers [4,5].

'Push-in' load does not depend on specimen thickness, but on fiber diameter, since push-in load is used to debond the interface near the surface, although it is

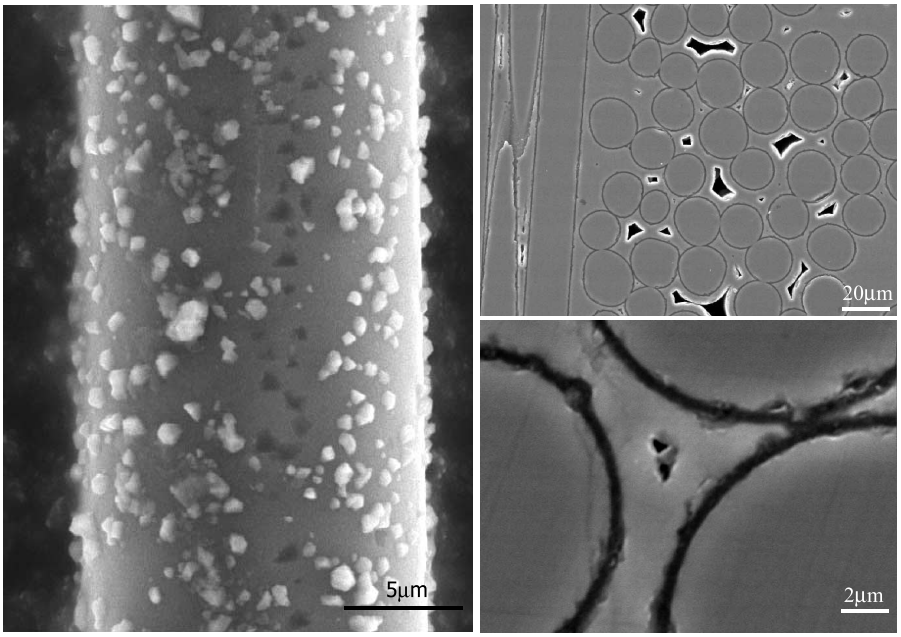


Fig. 3. SEM images of Hi-Nicalon™ fiber after heat treatment and its composites.

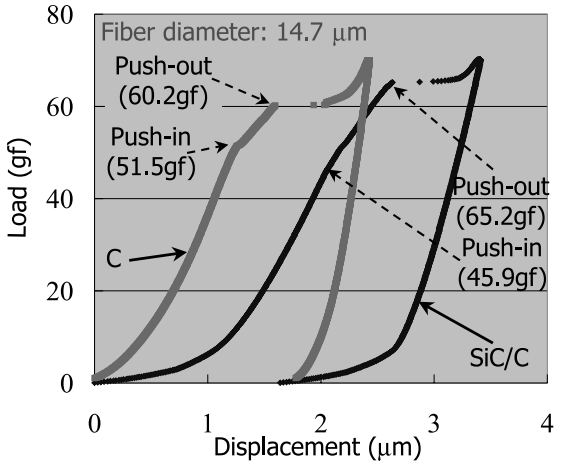


Fig. 4. Effect of the fiber SiC coating on the loading curves of single-fiber push-out tests.

impossible to measure the depth of the debonded region at push-in. The push-in load was divided by fiber diameter to normalize data. Interfacial shear stress was obtained from 'push-out' load in Fig. 4 and calculated from Eq. (1). The push-out load was divided by debonded area [8]. Eq. (1) is presented as follows:

$$\tau_{is} = P/\pi Dt, \tag{1}$$

where τ_{is} is the interfacial shear stress, P the load at push-out, D the fiber diameter and t is the specimen thickness. The effects of fiber surface treatments on interfacial shear properties are summarized in Table 1.

Although the push-in load of the sample with SiC coating was slightly less than that of the reference sample without SiC coating, the push-out load of the material with SiC coating was larger than that of the reference sample without SiC coating. The value, where push-in load is divided by fiber diameter, depends on the clamping stress of the interface. Interfacial shear stress includes clamping stress and frictional stress at the debonded region. These results indicate that the frictional stress of the interface was increased by the fiber SiC coating, although the clamping stress of the fiber SiC coating sample was little lower than that of the reference sample without surface treatment. Both interfacial properties were decreased by the heat treatment of the fiber.

Table 1
Effect of the fiber surface treatments on interfacial mechanical properties

Interphase	Push-in load/diameter	ISS[a] (MPa)
SiC/C	3.01	280
Heat treat./C	2.23	89
C	3.32	212

[a] Interfacial shear stress (push-out load/interfacial area).

Table 2
Effect of the fiber surface treatment method on bend properties[a]

ID	Modulus (GPa)	Proportional limit stress (0.01%, MPa)	Bend strength (MPa)
SiCB1	112	438	645
SiCB2	116	319	635
HTB1	153	186	195
HTB2	186	153	167

[a] SiCB: SiC coating; HTB: heat treatment.

3.3. Effect of surface treatment method on bend properties

Bend properties of the fiber surface treatment samples are shown in Table 2. Proportional limit stresses in Table 2 were obtained from 0.01% strain offset. The fiber heat treatment samples showed very brittle fracture behavior. Although modulus was increased, both proportional limit stress and bend strength greatly decreased. The fiber SiC coating samples showed superior mechanical properties to the fiber heat treatment samples. In the fiber SiC coating samples, the critical change of slope was not seen at proportional limit stress.

3.4. Effect of fiber SiC coating on tensile properties

Tensile tests of the fiber SiC coating samples and the reference samples without fiber surface treatment were carried out. The tensile properties, modulus,

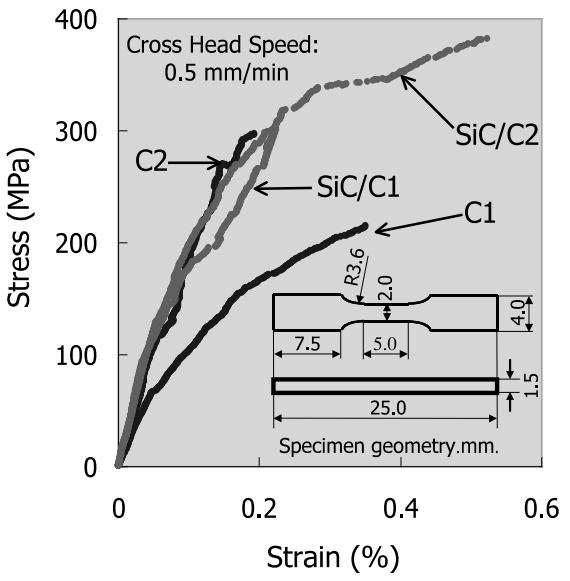


Fig. 5. Effect of the fiber SiC coating on the loading curves and the specimen geometry of tensile tests.

proportional limit stress and tensile strength, were improved by fiber SiC coating as shown in Fig. 5 and Table 3, although data scatter was large because the specimen size was small, and flat-woven fibers were used. The curves for the fiber SiC coating samples are indicated as SiC/C. The others are for the samples without surface treatment.

SEM observation showed a quite different fracture surface between the fiber SiC coating samples and the reference sample as shown in Figs. 6 and 7. Fiber pull-out lengths of the SiC coating samples were approximately 10–20 μm, but more than 100 μm in the reference samples. The fiber bundle pull-out length of the fiber SiC coating samples was also longer than that of the reference samples.

The difference in pull-out fiber surface between the fiber SiC coating samples and the reference samples without surface treatment was not clear from SEM observation. However, EDS analysis of the pull-out fiber surface showed a clear difference of interfacial debonding between fiber and matrix (Fig. 8). Both C and SiC were detected from fiber surfaces of the reference samples without surface treatment, and the atomic ratio of C to Si corresponded to that of the Hi-Nicalon™ fiber [11]. In the case of the fiber SiC coating samples, almost all species detected on fibers surfaces were C. Although the crack propagated at the interface between the fiber and C layer in the case of the reference samples without fiber surface treatment, the crack propagated within the C layer in the case of the fiber SiC coating samples. Pull-out fiber surface roughness was evaluated by optical interferometric profilometry. The root mean square (RMS) of measured surface height of the SiC coating samples was 9.0 nm compared to 2.5 nm in the reference samples. The pull-out fiber surface of the fiber SiC coating samples was rougher than that of the reference samples.

Table 3
Effect of the fiber SiC coating on tensile properties[a]

ID	Modulus (GPa)	Proportional limit stress (0.01%, MPa)	Tensile strength (MPa)
SiC/Cl	242	125	268
SiC/C2	230	163	382
C1	130	78	215
C2	201	126	297

[a] SiC: SiC coating, C: without surface treatment.

4. Discussion

4.1. The effect of fiber heat treatment

The Hi-Nicalon™ fiber surface was successfully modified by self-decomposition of fiber during heating

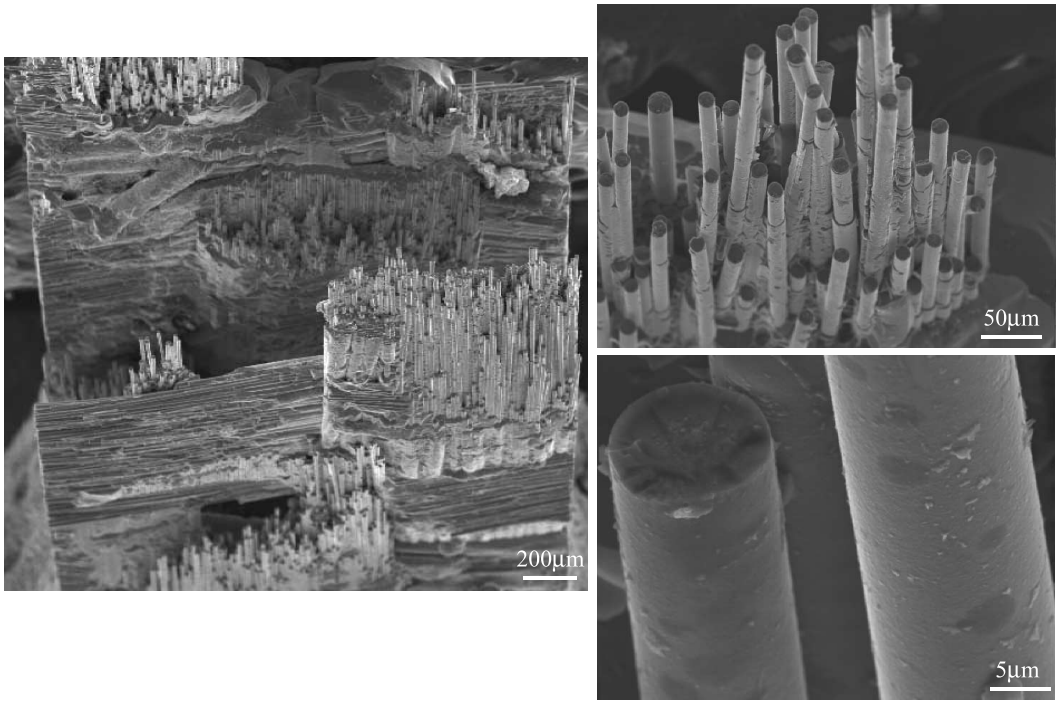


Fig. 6. Fracture surface of the SiC/SiC composites without fiber surface treatment.

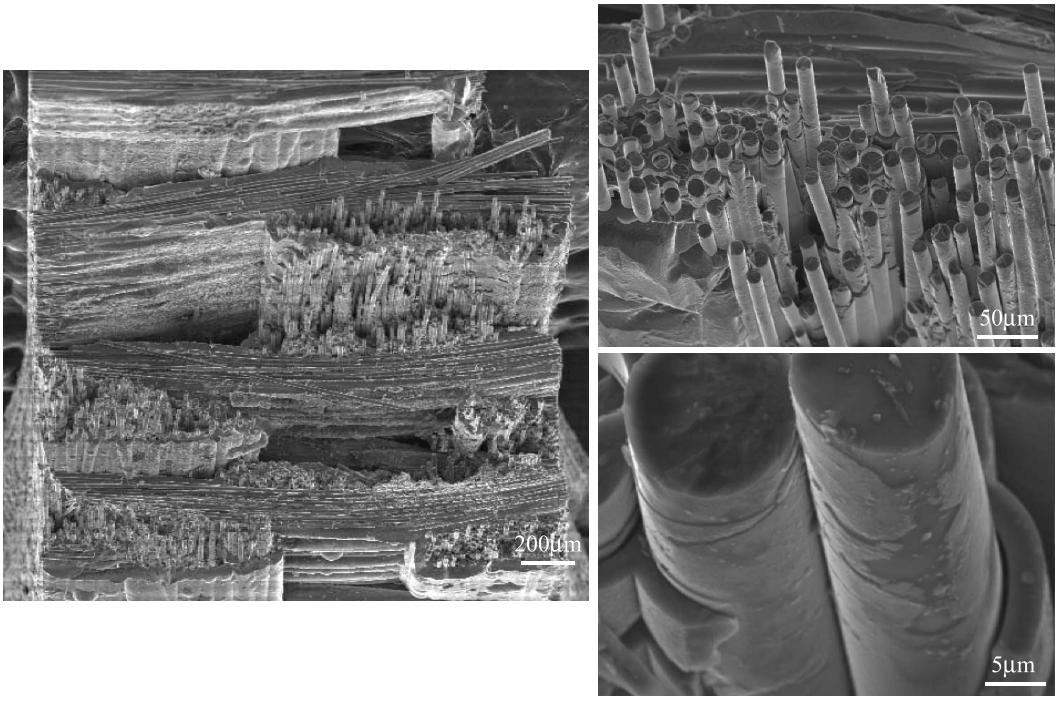
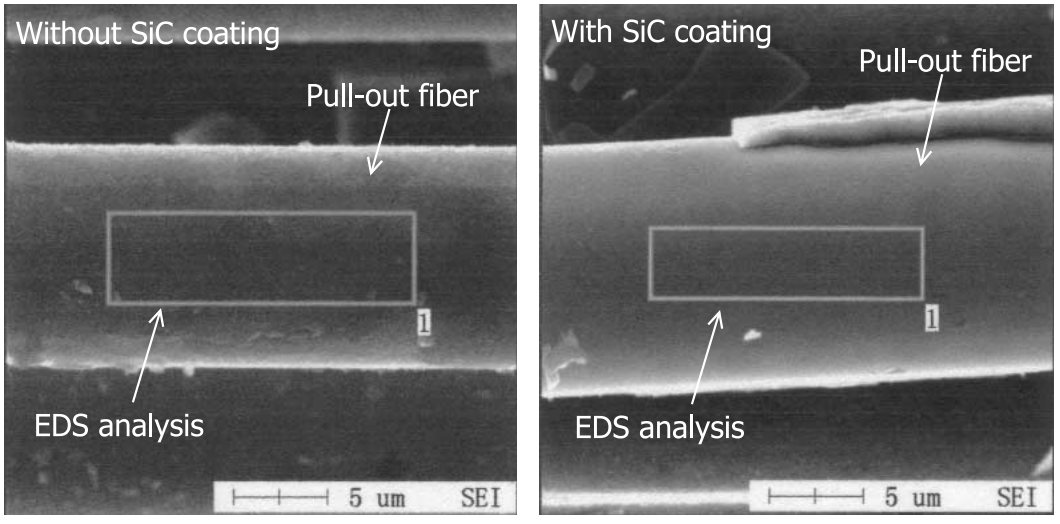


Fig. 7. Fracture surface of the SiC/SiC composites with the fiber SiC coating.



without SiC coating		with SiC coating	
C (at.%)	Si (at.%)	C (at.%)	Si (at.%)
64.33	35.67	**97.77**	2.33

Fig. 8. Effect of the fiber SiC coating on interfacial fracture.

under Ar flow in quite low O_2 partial pressure. A rough C layer between fiber and matrix was produced. However the composites produced with these fibers showed very brittle fracture behavior and their mechanical properties greatly decreased. This degradation might be attributed to fiber degradation by self-decomposition. A

preliminary experiment on fiber heat treatment was carried out to decide on a heat treatment condition in which the fiber surface became rough, and the fiber kept most of its strength. However, these experiments were unsuccessful in optimizing the heat treatment conditions.

4.2. The effect of fiber SiC coating

In marked contrast to fiber heat treatment, the fiber SiC coating improved mechanical properties and fracture behavior. This coating made the bond between fiber and C layer strong, and cracks propagated not at the interface between fiber and C layer, but within the C layer. Complicated interfacial fractures made the debonded interface rough and increased interfacial frictional stress. Large interfacial frictional stress is considered to increase apparent proportional limit stress because high interfacial strength can be maintained after interfacial debonding. Shorter fiber and fiber bundle pull-out length might correspond to less scatter of pull-out length. Tensile strength depends on fiber strength and the number of fiber retained at maximum load. Less scatter of pull-out length means that many fibers broke at the same time. This is the one of the reasons why the tensile strength increased. Another function of the fiber SiC coating is to protect the fiber. This protection might also increase composite tensile strength by increasing retained fiber tensile strength in the composite.

5. Conclusions

1. Both fiber SiC coating and fiber heat treatment made the C interface rough.
2. Interfacial mechanical properties and bend properties were not improved by fiber heat treatment because of fiber degradation.
3. Interfacial frictional stress and tensile properties were improved by fiber SiC coating.
4. Fiber and fiber bundle pull-out length of the composites with fiber SiC coating were shorter than those of the composites without fiber surface treatment.
5. The crack propagated within the C layer in a complicated manner in the composites with fiber SiC coating, and between the fiber and C layer in the composites without fiber surface treatment.

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