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Properties of SiC/SiC Composites with Surface Modified SiC Fiber

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The thin carbon film was formed on the SiC fibers by hydrothermal treatment at 573 K under 22 MPa for 4h. In-depth profile of X-ray photoelectron spectroscopy, XPS, and PACKTEST results revealed that carbon film of approximately 50 nm was formed on the surface of SiC fiber. Monofilament of SiC maintained the original strength after hydrothermal treatment.

Bulk specimens of SiC/SiC composites were prepared by repeating the process of infiltrating polycarbosilane binder in the bundle of SiC fiber by pressure and pyrolyzing. The bending strength of hydrothermally treated fiber reinforced specimen, here after HT specimen, was 5 % larger than that of untreated fiber reinforced specimen. On the other hand, average deflection value by bending test of HT specimen was 10 % larger than that of the other specimen. From these results, the thin carbon film on the SiC fibers was effective to decrease the stress concentration at the interface.

Inferring from the morphology of the fractured surface, optimization of the thickness of the carbon film is essential to improve the strength.
Key words: SiC, hydrothermal treatment, composite, surface modification.

1. INTORDUCTION

Saving energy and saving resources are serious problem in advanced industries. Developing light and heat- resistant materials with high specific strength and high specific modulus are essential for high efficient energy conversion in these fields. Though ceramic is one of candidates, practical application is strictly limited because of their brittleness. SiC is useful ceramic at a temperature higher than 1300 K in air because it has high specific strength, high heat resistance and high anti-oxidation properties [1].

If the toughness of SiC is improved, the utility will be expanded widely. Fabricating a Fiber Reinforced Ceramics (FRC) is one of promising method to eliminate the brittleness. SiC fiber is a promising candidate as the reinforcement, as it has desirable properties for high temperature materials and no thermal stress between the reinforcement and the matrix. Therefore the combination of these materials is expected to have high performance for an ecological conscious material.

Optimal interfacial bonding strength is essential for this combination to avoid crack propagation from the matrix to the fiber and v.v. Forming a thin carbon film on the fiber is one of the solutions to restrain the crack propagation due to decrease the stress concentration at the interface [2]. The thin carbon film was formed on the SiC fibers by hydrothermal treatment (hereafter H-treatment). The effect of the carbon layer on the mechanical properties of the composites was examined.

2. EXPERIMENTAL PROCEDURES

2.1 SiC monofilament

HI-NICALON of SiC fiber made by Nippon Carbon Co. Ltd. was used as the reinforcement. A thin carbon film was formed on the fiber by H-treatment. The treatment was carried out by using a super critical salt bath (TSC-B600) and a reaction tube which were made by Taiatsu techno Co. Ltd. The treatment was performed with the water of 65.40 cm^3 at 573 K under 22 MPa for 4 hours.

The surface of the SiC fiber was decomposed to form a thin C-layer on the fiber. Remained Si dissolves in ambient water as the form of SiO_2. It is difficult to detect the thickness of the C-layer, as it is very thin. Then a sintered SiC plate was also used for precise examination of the carbon film formed by H-treatment besides the SiC fiber. The surface of the SiC plate of 3 mm$\times$12 mm$\times$1.5 mm was cleaned and carbon film was also formed on the surface of SiC plate by H-treatment at the same condition as the reinforcement fiber. SiO_2 concentration in ambient water was detected after H-treatment by using PACKTEST made by Kyoritsu Chemical-check Lab., Corp. The concentration should be proportional to the decomposed SiC. Then the thickness of the C-layer formed by the H-treatment was determined from the amount of the SiO_2.

Binding condition of C at the SiC plate surface was examined by X-ray photoelectron spectroscopy, XPS. The examination was carried out to the depth

direction by applying Ar sputtering. Morphological observation of the SiC fiber surface was performed by field emission scanning electron microscopy, FE-SEM.

Strength of the monofilament before and after treatment was examined to check the deterioration. The diameter of the monofilament was determined by using He-Ne laser. The laser was applied to the monofilament on a cardboard mount. The diameter of the monofilament (d) was precisely determined from the wave length of the laser (l= 633 nm), distance between a pair of the diffraction fringes (D) and the distance from the fiber to the screen (s) as follows [3];

$$d=2ls/D \qquad (1)$$

The tensile strength for the monofilament was determined from the load at the fracture and cross section area from "d". 30 monofilaments were examined for each condition.

2.2 SiC/SiC composites

Composites with two kinds of fibers, i.e. before and after H-treatment, were fabricated. Polycarbosilane binder, the raw material of SiC, was infiltrated into the bundle of the SiC fiber under the pressure of 0.5 MPa by N_2 gas after evacuation. Then the polycarbosilane was pyrolyzed to form SiC in a furnace. The space among the fibers was filled by SiC after 6 times of the process described above.

The strength of bulk specimens was examined by three point bending test. Sample size for three point bending test was 3 mm×2 mm×48 mm. Fractured surfaces after bending test were observed by FE-SEM.

3. RESULTS AND DISCUSSIONS

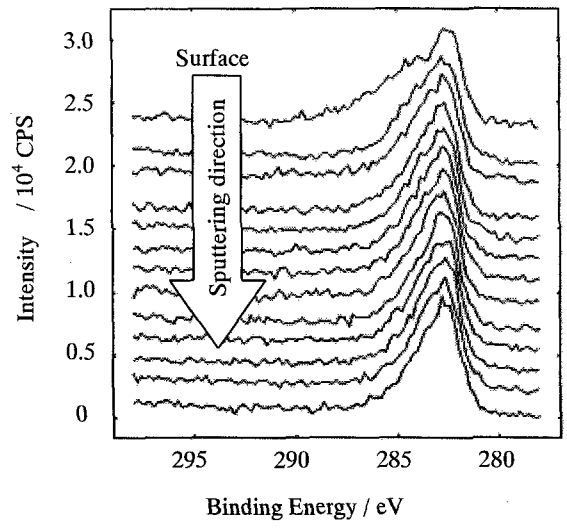
3.1 SiC monofilament

Figures 1 (a) and (b) show the transition in the depth direction of carbon peak of SiC plate before and after H-treatment. The peak at 284.2 eV in Figure 1 shows free carbon and the peak at 282.3 eV shows the carbon in SiC [4]. As the peak is obviously observed at 284.2 eV in Figure 1 (b), it was confirmed that the carbon films of nanometer in thickness was formed by H-treatment at 573 K under 22 MPa for 4 hours though the thickness of the films is not clear at the moment. From the results and literatures [5], the process of forming the carbon film on the fiber is presumed as follows;

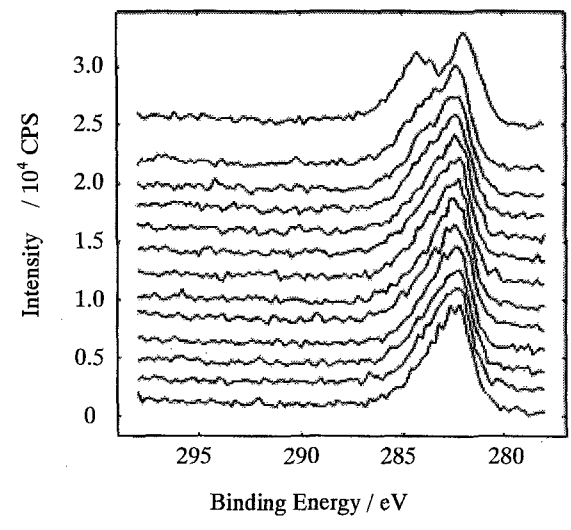
$$SiC + 2H_2O \Leftrightarrow SiO_2 + C + 2H_2 \qquad (a)$$

$$SiC_xO_y + (n\text{-}y)H_2O \Leftrightarrow SiO_2 + xC + nH_2 \qquad (b)$$

$$SiO_2 + nH_2O \Leftrightarrow SiO_2 \cdot nH_2O \qquad (c)$$



a) before H-treatment



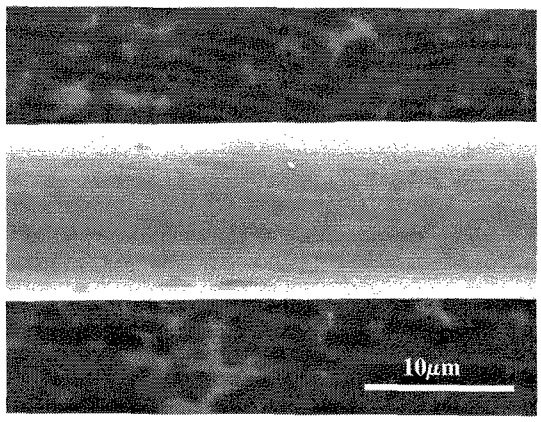
b) after H-treatment

Fig. 1 Depth profile of carbon peak of SiC plate before and after H-treatment.

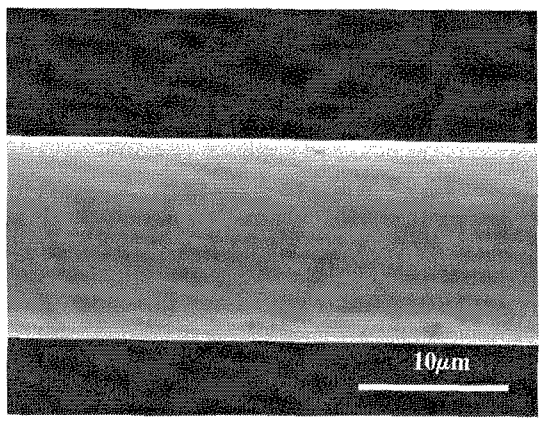
After the H-treatment, increase of 0.5 to 1 ppm SiO_2 in the water of 65.40 cm^3 was confirmed by the PACKTEST. This means that the SiC was decomposed to Si and C at the surface of the plate, and the carbon was left as a film on the SiC plate. The separated Si formed the SiO_2 on the plate and the reaction of (c) was caused. SiO_2 dissolved in the water by reaction of (c). Then the amount of carbon is obtained. Depth profile of XPS and PACKTEST results coincide and we can estimate that carbon film of at least 50 nm was formed on the surface of SiC by H-treatment.

The surface of the monofilament was investigated by FE-SEM. Figures 2 (a) and (b) show the morphology of SiC monofilament before and after H-treatment. Both surfaces of two monofilaments were

smooth, and no pit which might cause degradation was observed even after H-treatment.



a) before H-treatment



b) after H-treatment

Fig. 2 FE-SEM photographs of the surface of SiC fiber before and after H-treatment.

Figure 3 shows the result of tensile strength for the monofilament. The strength of the monofilament after H-treatment was 2690 MPa, and it was the almost same value as strength of the monofilament before treatment.

3.2 SiC/SiC composites

Figure 4 shows the results of three point bending test for SiC/SiC composites. Average strength of the composites with the fiber after H-treatment is approximately 6 % higher with small scattering, and the deflection to fracture in bending is 9.6 % larger than the other composite.

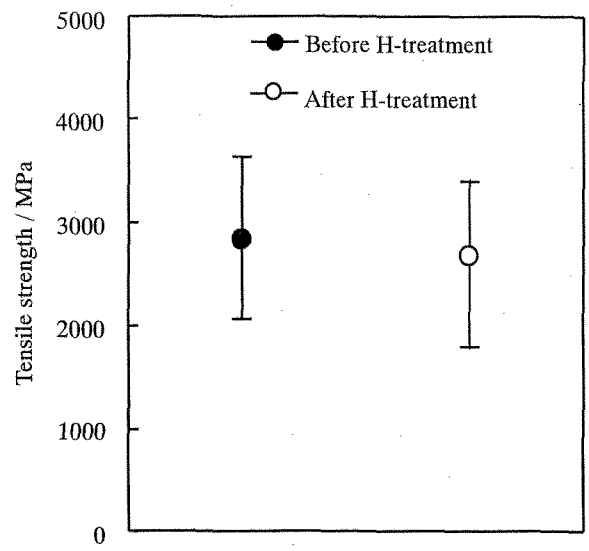


Fig. 3 Tensile strength of SiC fiber before and after H-treatment.

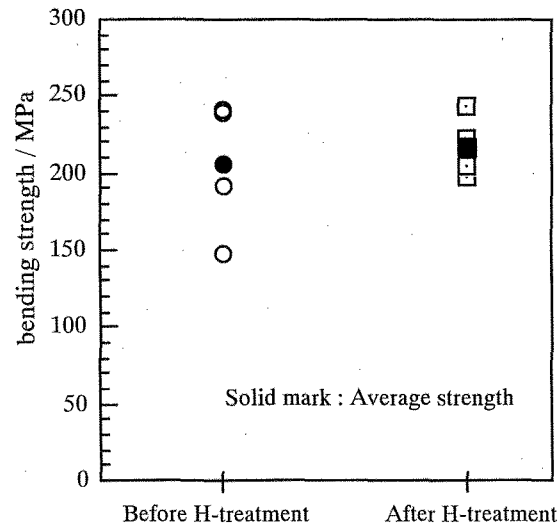
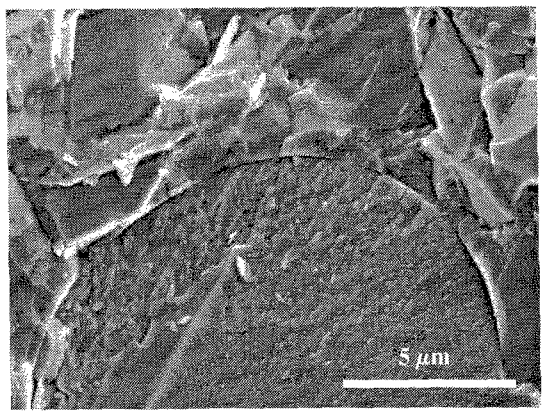
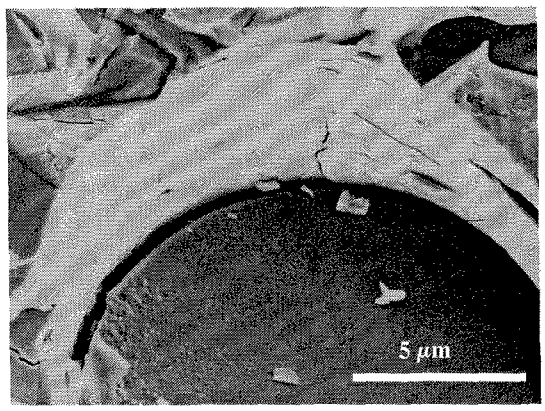


Fig. 4 the results of three point bending test for SiC/SiC composites with SiC fiber before and after H-treatment.

Figures 5 (a) and (b) show fractographs of bending fracture for SiC/SiC composites with SiC fiber before and after H-treatment. The fractured surface of the composite with the fiber before H-treatment is flat as shown in Figure 5 (a). On the other hand, a step between the fiber and the matrix and a gap at the interface were obviously observed as shown in Figure 5 (b). It seems that this step was caused by pull out. From these results, the thin carbon film on the SiC fibers was effective to decrease the stress concentration at the interface. Inferring from the morphology of the fractured surface, optimization of the thickness of the carbon film is essential to improve the strength.



a) before H-treatment



b) after H-treatment

Fig. 5 fractographs of bending fracture for SiC/SiC composites with SiC fiber before and after H-treatment.

4. CONCLUDING REMARKS

XPS analyses and PACKTEST revealed the carbon film on the surface of SiC which was formed by hydrothermal treatment. The thickness of the film was approximately 50 nm. The strength of the fiber was approximately 2700MPa after hydrothermal treatment, and degradation was hardly observed.

Average strength of the composites with the hydrothermally treated fiber was approximately 6 % higher, and the deflection to fracture in bending was 9.6 % larger than the other composite. A step and a gap were obviously observed at the interface between the fiber and the matrix on the fractured surface of the composites with hydrothermally treated fiber. These phenomena indicate that the crack was split along the weak interface, and the stress concentration was released at the tip of the crack.

From these results, it is expected that the strength of SiC/SiC composites will be improved by optimizing the thickness of the carbon film on the SiC fiber

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