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Thermal stability of SiO_2-coated SiC fiber (Hi-Nicalon) under argon atmosphere

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Thermal stability of low-oxygen SiC fiber (Hi-Nicalon) coated with SiO_2 film was investigated. The SiO_2 film of same thickness but different crystal structure was formed by heating low-oxygen SiC fiber (Hi-Nicalon) under different oxidation conditions. The oxidation treatment and the subsequent exposure at 1773 K in argon caused very little loss of strength for unoxidized core. For as-oxidized fiber with SiO_2 film which contained imperfections, further loss of strength was caused after exposure in argon. There was little degradation of core strength on being exposed repeatedly at rapid heating and cooling rate in argon. The fiber oxidized at 1773 K kept high level of strength even after exposure at 1823 K. This is because the change in crystal structure of SiO_2 film before and after exposure in argon, which was the controlling factor in the degradation of strength, was diminished with increasing oxidation temperature.

1. Introduction

Polycarbosilane-derived low-oxygen silicon carbide fiber fabricated by electron beam irradiation curing method (Trade name: Hi-Nicalon, Nippon Carbon Co., Tokyo, Japan) has been often utilized as reinforcing material in ceramic matrix composites because of its excellent thermal stability [1, 2]. Hi-Nicalon fiber is composed from β-SiC nanocrystallite, free carbon and a small amount of amorphous silicon oxycarbide (SiC_XO_Y) phase [3, 4]. The SiC_XO_Y phase is thermodynamically unstable at elevated temperatures. Long time of heating above 1673 K causes thermal decomposition of SiC_XO_Y phase, resulting in the gradual degradation of fiber strength. The promising method for improvement of the thermal stability is a suitable covering to restrict the outward transport of decomposed gases, SiO and CO. In particular, SiO_2 film produced by oxidation treatment was very effective in retarding the decomposition reaction of silicon carbide fiber fabricated by oxidation curing method (Trade name: Nicalon, Nippon Carbon Co., Tokyo, Japan) [5, 6]. The formation of SiO_2 film can be less expensively achieved by using a relatively simple equipment. Furthermore, the ceramics produced by hot-pressing pre-oxidized fibers were found to have excellent high-temperature characteristics [7].

The SiO_2-coating developed the thermal stability of Hi-Nicalon fiber as well as that of Nicalon fiber [8]. Consequently, coatings of 0.3–0.4 μm thick were found to be most effective in suppressing the thermal decomposition of unoxidized core and keeping high levels of strength. In present work, the SiO_2 films of 0.3–0.4 μm thick but different crystal structure such as amorphous, nanocrystalline or highly crystallized phase were formed by oxidizing Hi-Nicalon fiber for different oxidation times at 1073–1773 K. Subsequently the oxidized fibers were exposed for at 1773 or 1823 K in argon. In addition, the resistance of SiO_2 film to the exposure repeated at a rapid heating and cooling rate was investigated. The microstructure and strength of both as-oxidized and exposured fibers were determined to evaluate the thermal stability of SiO_2 coated fiber. The oxidation treatment of making most protective SiO_2 film was well established.

2. Experimental procedure

The sample used in this study is the low-oxygen silicon carbide fiber (Hi-Nicalon) manufactured by Nippon Carbon Co. It has molar composition of $SiC_{1.40}O_{0.05}$ and mean diameter of 15 μm . Fibers were oxidized at temperatures from 1073 to 1773 K in air by using the SiC resistance furnace. The oxidation conditions of fibers and the characterization of as-oxidized fibers are given in Table I. The mass gain due to the oxidation of fiber was measured by an automatic recording balance. The oxidation time was controlled to form the SiO_2 film of 0.3–0.4 μm thickness. The thickness of SiO_2 film, b was calculated from the oxidized fraction of fibers determined by a digital-type automatic recording balance as follow:

TABLE I Oxidation treatment of low-oxygen SiC fiber (Hi-Nicalon)

Oxidation condition			Tensile strength (GPa)	
Temperature (K)	Time (h)	Crystal structure of SiO_2 film	with SiO_2	without SiO_2
1073	200	amorphous	3.04	3.08
1173	150	amorphous	2.79	3.09
1273	100	amorphous	2.57	2.83
1373	50	amorphous	2.33	2.83
1473	30	cristobalite	2.46	2.94
1573	24	cristobalite	2.27	2.79
1673	12	cristobalite	2.11	2.80
1773	5	cristobalite	1.98	2.84

$$b = r_0\{1 - (1 - X)\}^{1/2} \tag{1}$$

where r_0 is the radius of fiber and X is the oxidized fraction of fiber.

$$X = \frac{\Delta W}{\Delta W_{100}} \tag{2}$$

ΔW and ΔW_{100} are the mass gain after oxidation treatment and that after 100% oxidation of fiber, respectively.

The oxidized fibers were subsequently exposed under argon atmosphere as follows: 500 mg of oxidized fibers, 3 cm in length were charged in a magnesia crucible and then was rapidly positioned in the hot zone of furnace controlled at the given temperature. Argon was flowed from the bottom of the furnace at flow rate of 8.33×10^{-6} m^3/s. Upon completion of exposure test, the fibers were quenched by raising the crucible to the low temperature zone of the furnace.

The exposure tests of fiber were conducted under three types of heat-treatment condition:

(1) the heat treatment which consists of the heating to 1773 K, the holding of 18 ks and the cooling to room temperature (test A)

(2) the heat treatment which consists of the heating to 1823 K, the holding of 18 ks and the cooling to room temperature (test B)

(3) five times repetition of the heat treatment which consists of the heating to 1773 K, the holding of 3.6 ks and the cooling to room temperature (test C).

Both the oxidized fibers and exposed fibers were characterized in the following way : The crystal structure of fibers was studied by X-ray diffraction, and the morphology of fibers was observed by the scanning electron microscope. The room-temperature tensile strength of a fiber of 10 mm gauge length was determined with a universal tensile testing instrument (Orientec Co., Type TENSILON UTM-II-20, Tokyo, Japan) using a load cell of 100 g and a crosshead speed of 2 mm/min. An average of 20 measurements was tested for each heat-treated fiber. Tensile tests also were conducted for the fibers of which SiO_2 film was removed with $NH_4F + HF$ solution, in order to determine the strength of unoxidized core.

3. Results

Fig. 1 shows the Auger electron spectroscopic measurement of surface concentration for the fiber oxidized for 30 h at 1473 K in air. The oxide layer of about 0.34 μm thickness is distinctly formed around the fiber. This implies that the oxidized fibers are coated with a smooth and continuous SiO_2 film. The smooth appearance of the oxidized fibers is observed by SEM observation. The SiO_2 film shifts to the unoxidized core via the region having the linear concentration gradients of oxygen and carbon. AES depth profile shows that the value calculated by Equation 1 is found reasonable as the SiO_2 film thickness.

X-ray diffraction patterns are shown in Fig. 2 for fibers oxidized at the oxidation conditions which are given in Table I. The broad pattern at diffraction angle of $2\theta \fallingdotseq 22°$ reveals that SiO_2 film formed around fibers is amorphous silica below 1373 K. The very week diffraction peak of cristobalite was observed in the fibers oxidized at 1473 and 1573 K, showing that the SiO_2 film is in the nanocrystalline structure. On the other hand, the fibers oxidized at 1673 and 1773 K have the highly crystallized SiO_2 film, owing to the sharp cristobalite peak. Thus, it is found that the crystallization of SiO_2 film develops with increasing the oxidation temperature. In addition, the diffraction pattern of β-SiC becomes sharp

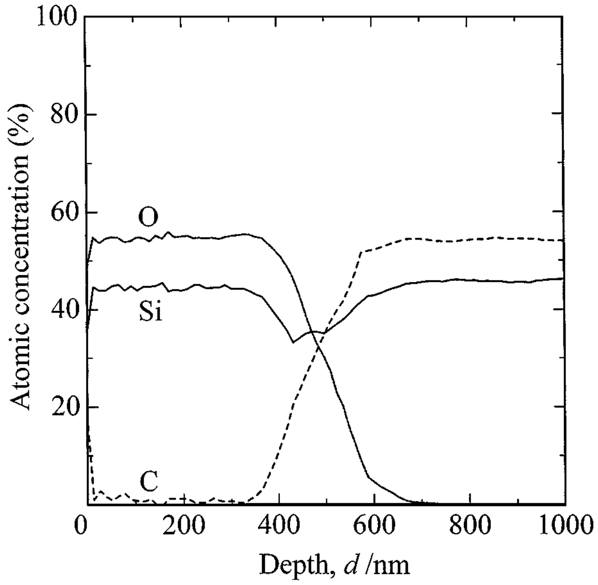

Figure 1 AES depth profile of fiber oxidized for 30 h at 1473 K in air.

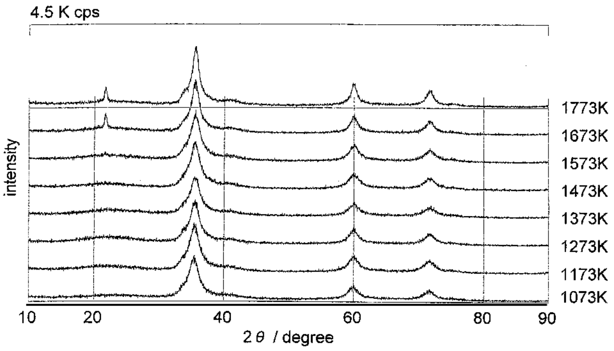

Figure 2 X-ray diffraction patterns of fibers oxidized under oxidation conditions shown in Table I.

at 1673 and 1773 K. This means that the thermal decomposition of fiber occurs at the earliest stage of oxidation because of incomplete coating of fiber with SiO_2 film.

The oxidation-treated fibers were exposed for 18 ks at 1773 K in argon (test A). Figs 3 and 4 show the room-temperature tensile strength for as-oxidized fibers and SiO_2-removed fibers (unoxidized core) before and after exposure, respectively. As can be seen from Fig. 3, the strength of the as-oxidized fiber with SiO_2 film decreases gradually with increasing oxidation temperature. It clearly shows that the further degradation of fiber strength occurs during exposure in argon. While the strength of as-received (unoxidized) fiber decreases markedly, virtually to zero, the oxidized fiber retains 56–75% of as-received strength. Fig. 4 exhibits that the strength of SiO_2-removed fiber, that is, unoxidized core, retains almost unchanged in the as-oxidized state independently on the oxidation temperature. In addition, there is little the decrease in strength of unoxidized core even after the exposure in argon. Thus, the strength of unoxidized core is kept in the level comparable to as-received strength of 3.08 GPa. As a result, the strength of the fibers with SiO_2 film is lower than that of SiO_2-removed fiber. This is thought to be because the SiO_2 film often contains imperfections such as pores, voids and flaws.

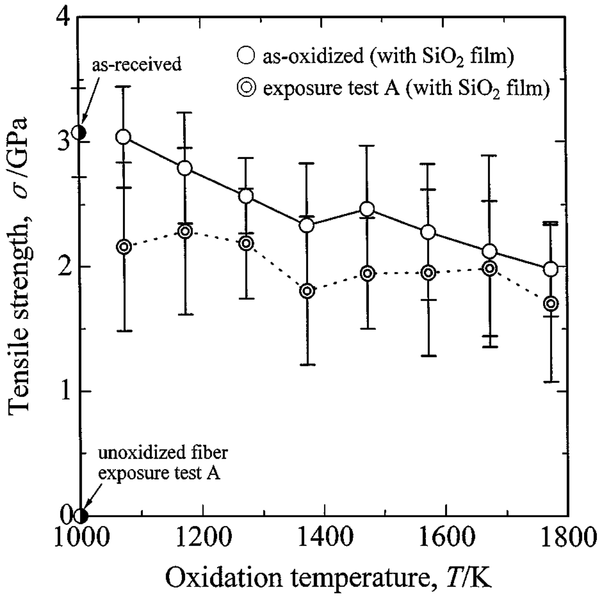

Figure 3 Relationship between tensile strength of fibers with SiO_2 film and oxidation temperature.

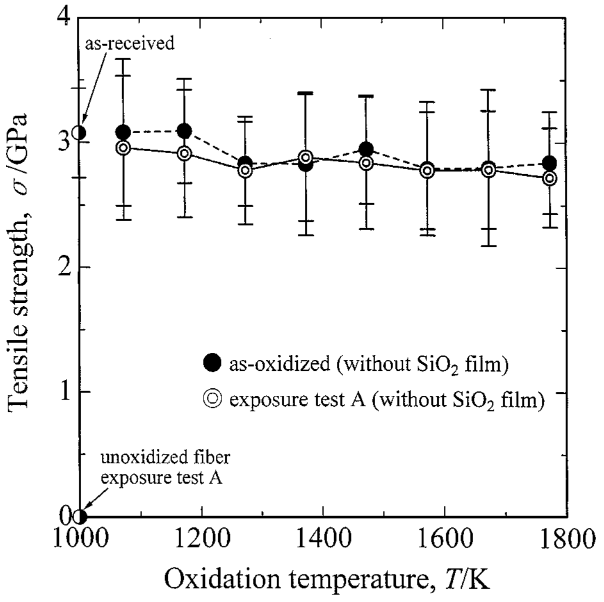

Figure 4 Relationship between tensile strength of SiO_2-removed fibers and oxidation temperature.

After exposure of 18 ks at 1773 K in argon, considerable level of strength was retained even in the fiber with SiO_2 film. Therefore, the exposure tests for the SiO_2-coated fibers were carried out under more severe conditions: the exposure test at 1823 K (test B), and the exposure test in which rapid heating and cooling is repeated five times at temperatures between room-temperature and 1773 K (test C).

Figs 5–7 show the X-ray diffraction patterns of fibers oxidized at 1073, 1473 and 1773 K, respectively. The SiO_2 film formed by the oxidation at 1073 K is amorphous. It crystallizes into cristobalite during continuous exposure of 18 ks at 1773 K (test A) and repeated exposure at 1773 K (test C). After exposure of 18 ks at 1823 K (test B), the SiO_2 film disappears and the unoxidized core crystallizes highly into β-SiC. For the fiber oxidized at 1473 K, the marked crystallization of SiO_2 film is observed after test B. On the other hand,

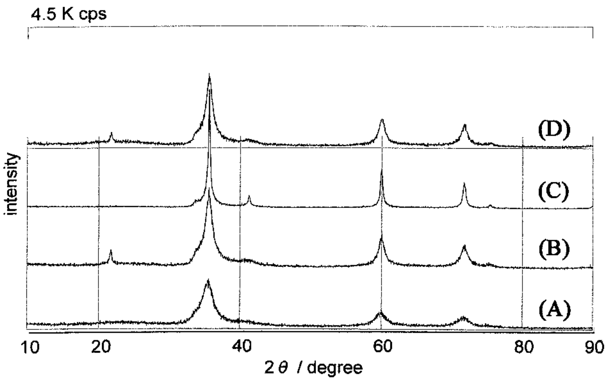

Figure 5 X-ray diffraction patterns of fibers exposed in argon after oxidaton of 200 h at 1073 K. (A): as-oxidized, (B): continuous exposure of 5 h at 1773 K (test A), (C): continuous exposure of 5 h at 1823 K (test B), (D): repeated exposure of 1 h at 1773 K (test C).

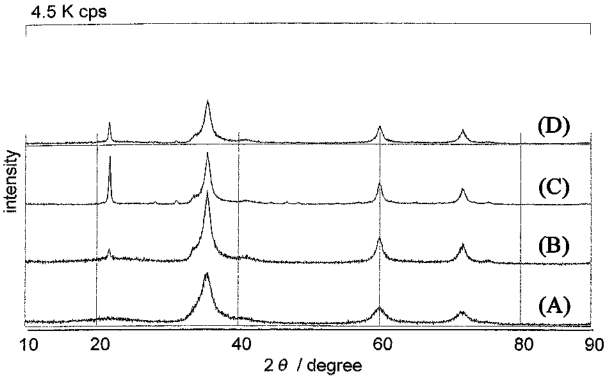

Figure 6 X-ray diffraction patterns of fibers exposed in argon after oxidaton of 30 h at 1473 K. (A): as-oxidized, (B): continuous exposure of 5 h at 1773 K (test A), (C): continuous exposure of 5 h at 1823 K (test B), (D): repeated exposure of 1 h at 1773 K (test C).

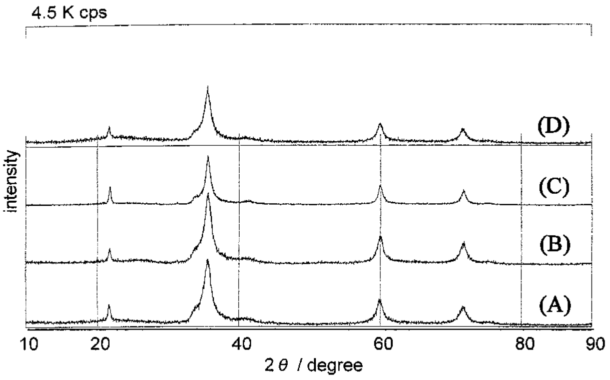

Figure 7 X-ray diffraction patterns of fibers exposed in argon after oxidaton of 5 h at 1773 K. (A): as-oxidized, (B): continuous exposure of 5 h at 1773 K (test A), (C): continuous exposure of 5 h at 1823 K (test B), (D): repeated exposure of 1 h at 1773 K (test C).

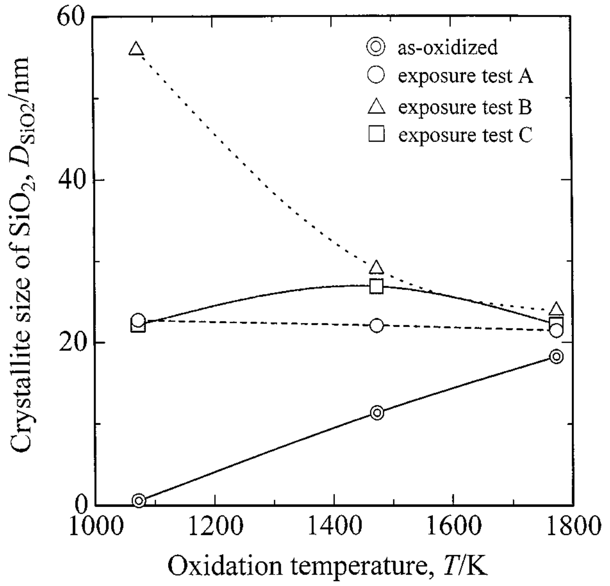

Figure 8 Relationship between SiO_2 crystallite size and oxidation temperature.

the SiO_2 film of the fiber oxidized at 1773 K is crystalline, and further crystallization is not caused after all the exposure tests.

The crystallite size of SiO_2 was calculated from the half-width value of peak at diffraction angle of $2\theta \fallingdotseq 22°$ using Scherrer's equation. Fig. 8 shows the crystallite size of SiO_2, D_{SiO_2} for the fibers oxidized at 1073, 1473 and 1773 K. It is can be seen that SiO_2 film has a tendency to crystallize and coarsen during exposure in argon. This tendency is enhanced with decreasing the oxidation-treatment temperature of fiber. In particular, marked coarsening of SiO_2 crystals was observed in the fibers oxidized at 1073 K and subsequently exposed at 1823 K (test B). The value D_{SiO_2} of 56 nm was measured just before the fiber was completely decomposed.

Fig. 9 shows the relationship between the room-temperature strength of SiO_2-removed fiber (unoxidized fiber) and oxidation temperature. As mentioned earlier, only a slight loss of strength is observed after exposure of 18 ks at 1773 K (test A). After exposure of 18 ks at 1823 K (test B), the strength for the fibers oxidized at 1073 K is completely lost, virtually to zero value, though that for the fibers oxidized at 1473 and 1773 K is kept in high levels. Furthermore, the repeated exposure test (test C) demonstrates that the rapid heating and cooling between room-temperature and 1773 K occurs only a slight degradation of fiber strength. It may be noted that the strengths of the fiber oxidized at 1773 K are nearly identical to that of as-oxidized fiber after exposure tests.

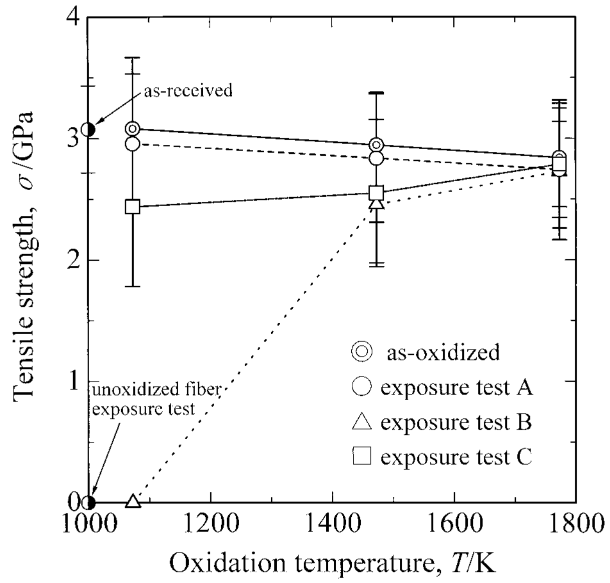

Figure 9 Relationship between tensile strength of SiO_2-removed fiber and oxidation temperature.

The morphologies of fiber surface are shown in Fig. 10. The SiO_2 films of all as-oxidized fibers have very smooth appearance (photos A and D). The double structure consisting of rough surface and smooth core was observed only for the fiber which was exposed to 1823 K after oxidation treatment at 1073 K (photos B and C). Fiber surface and fractured surface for all the other fibers were smooth and glassy, as well as that for the fiber exposed to 1823 K after oxidation treatment at 1473 K (photos E and F).

4. Discussion

Hi-Nicalon has an excellent thermal stability, owing to small amounts of unstable silicon oxycarbide phase, SiC_XO_Y. The fiber strength remains almost unchanged below 1673 K in argon. The degradation of strength is gradual at 1673 to 1873 K and then is serious above 1873 K [4, 5]. As can be seen from Fig. 2, the strength of unoxidized core (SiO_2-removed fiber) was reduced by about 10% even after oxidation of 18 ks at 1273 K. This degradation of strength is not due to the thermal decomposition of SiC_XO_Y phase which occurs above 1473 K [4, 5]. Hi-Nicalon fiber also contains SiC nanocrystals and the intergranular free carbon phase. The free carbon phase forms a continuous framework between the SiC nanocrystals [4]. The unoxidized core is oxidized by the inward diffusion of oxygen molecules through SiO_2 film [9, 10]. Therefore, microimperfections are probably formed on the surface of unoxidized core by the preferential oxidation of the free carbon

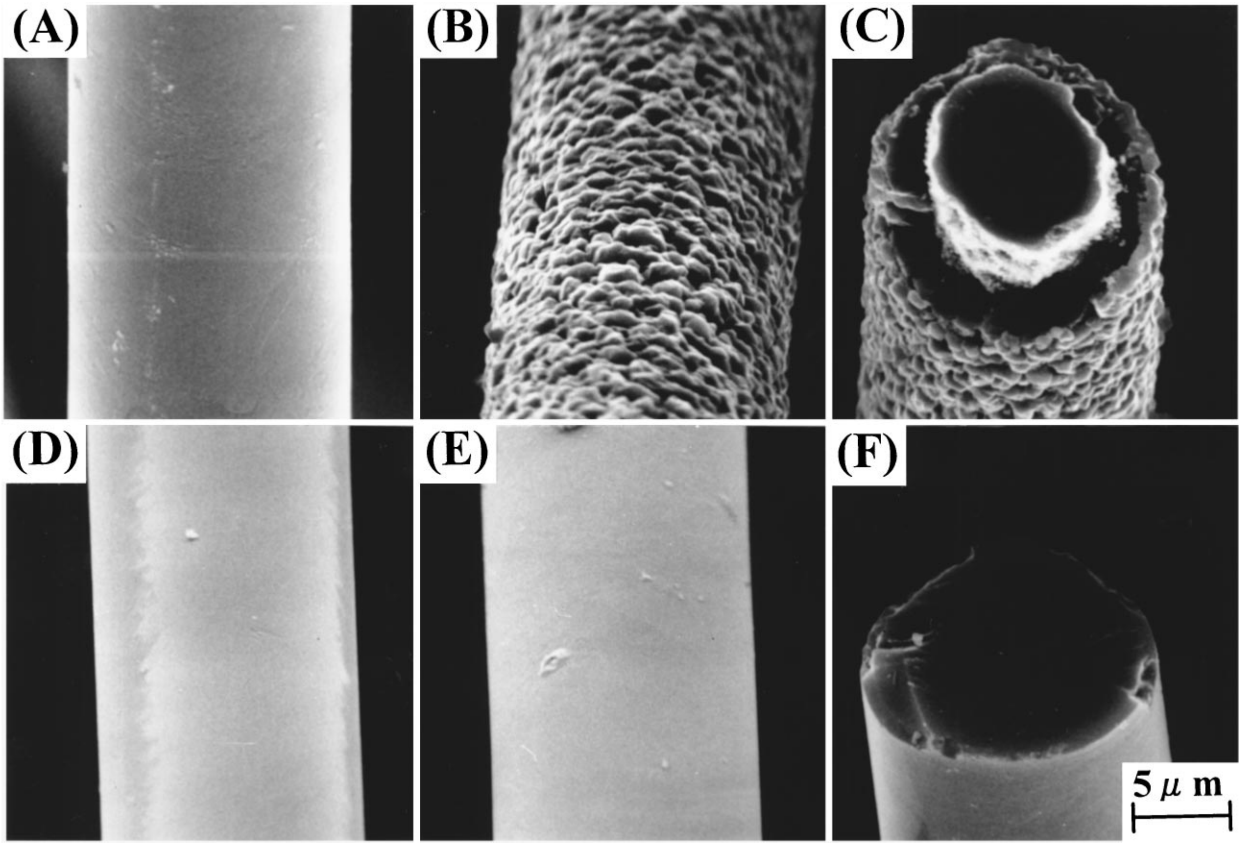

Figure 10 Morphology of fiber surface. photo A: as-oxidized at 1073 K, photos B and C: exposed at 1823 K after oxidation at 1073 K, photo D: as-oxidized at 1473 K, photos E and F: exposed at 1823 K after oxidation at 1473 K.

phase, resulting in a slight reduction of strength. If the oxidation temperature exceeds the decomposition temperature of amorphous SiC_XO_Y phase (about 1473 K), the liberation of decomposed gases, i.e. SiO and CO, and the crystallization into SiC occur at earliest stage of oxidation because of imperfectly coating with SiO_2 film. This is substantiated by X-ray diffraction result (Fig. 2). The formation of protective SiO_2 film seems to suppress further decomposition of unoxidized core by restricting the outward diffusion of both SiO and CO gases. Therefore, the thermal decomposition occurs only slightly in an oxidizing gas such as air.

From comparison of Fig. 2 with Fig. 3, the strength-controlling imperfections are thought to be principally contained in SiO_2 fillm. In addition, the strength of as-oxidized fiber with SiO_2 film, as a consequence of the crystallization of SiO_2 film and coarsening of SiO_2 grains, decreases with increasing oxidation temperature. X-ray diffraction reveals that the exposure of oxidized fibers in argon has a tendency to cause further the crystallization of SiO_2 film and the coarsening of SiO_2 grains. Since new imperfections such as pores, voids and cracks are produced in SiO_2 film, further degradation of fiber strength occurs during continuous exposure of 18 ks at 1773 K in argon (test A). The degradation of strength is more severe for the fiber oxidized at lower temperatures. As can be seen from Fig. 8, this is attributable to not the SiO_2 grain size after exposure, but the magnitude of increase in SiO_2 grain size during exposure. In particular, marked increase in SiO_2 grain size, as well as the crystallization of amorphous silica into to cristobalite, was observed for the fiber oxidized at 1073 K. As mentioned above, a considerable degradation of strength is to be avoided for the as-oxidized fibers with SiO_2 film, owing to the formation of imperfections in SiO_2 film. On the other hand, the strength of unoxidized cores is little lost during oxidation treatment and continuous exposure at 1773 K (test A).

As shown in Fig. 9, the unoxidized core (SiO_2-removed fiber) also deteriorates for the fibers exposed under severe conditions. While the continuous exposure of 18 ks at 1823K (test B) causes a slight degradation of the strength for the fibers oxidized at 1473 and 1773 K, test B causes marked degradation of the strength for the fiber oxidized at 1073 K, practically to 0 Gpa. The SiO_2 grains coarsen markedly after exposure at 1823 K: the increase in grain size from 0.6 to 56 nm, resulting in the production of serious imperfections in SiO_2 film. Since the SiO_2 film is proof no longer against the decomposition pressure of unoxidized core (i.e. the pressures of SiO and CO) at 1823 K, the disappearance of SiO_2 film and the resultant decomposition of unoxidized core occur. The center of the fiber has a smooth and glassy fracture surface (Fig.10, photo C), showing that thermal decomposition is retarded in this region. However, the fiber strength is nearly perfectly lost. This seems to be because the cracks from coarsened surface propagate to the center.

From Fig. 10, it can be seen that the SiO_2 grain size after repeated exposure test (test C) is nearly identical to that after continuous exposure test (test A). However, test C causes greater loss of strength than test A, particularly for the fiber oxidized at low temperature of 1073 K. Therefore, the repeated exposure, that is, a rapid repetition of heating and cooling produce the imperfections in unoxidized core as well as in SiO_2 film.

Finally, the fiber oxidized at 1773 K has the most excellent thermal stability, owing to the small change in crystal structure of SiO_2 film before and after all exposure tests.

5. Conclusions

Low-oxygen silicon carbide fiber (Hi-Nicalon) was coated with the SiO_2 film with different crystal structure of 0.3–0.4 μm thickness by oxidizing for different times at 1073–1773 K in air. Subsequently, the fiber was heated in argon under three type of exposure condition: continuous exposure of 18 ks at 1773 K (test A), continuous exposure of 18 ks at 1823 K (test B) and five times-repeated exposure of 3.6 ks at 1773 K (test C).

The strength of SiO_2-removed fiber (unoxidized core) retained 91–100% of as-received strength after oxidation treatment. There was little degradation of strength after test A. On the other hand, the strength of as-oxidized fiber with SiO_2 film decreased significantly with increasing oxidation temperature, and it decreased further after test A. This tendency was enhanced after test B. Test B caused large change in the crystal structure of SiO_2 film for the fiber oxidized at 1073 K, resulting in the disappearance of SiO_2 film and the degradation of fiber strength to 0 GPa. All the SiO_2 film were proof of test C, although there was a considerable reduction of strength for the fiber oxidized at low temperature. The change in the crystal structure of SiO_2 film is thought to be the controlling factor in the degradation of fiber strength. Since the highly crystallized SiO_2 film remained almost unchanged during exposure, the fiber oxidized at 1773 K was retained a high level of strength after all the exposure tests.

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References

1. M. TAKEDA, Y. IMAI, H. ICHIKAWA, T. SEGUCHI and K. OKAMURA, *Ceram. Eng. Sci. Proc.* **12** (1991) 1007.
2. *Idem., ibid.* **13** (1991) 209.
3. G. CHOLLON, R. PAILLER, R. NASLAIN, F. LAANANI, M. MONTHIOUX and P. OLRY, *J. Mater. Sci.* **32** (1997) 327.
4. G. CHOLLON, R. PAILLER, R. NASLAIN and P. OLRY, *ibid.* **32** (1997) 1133.
5. T. SHIMOO, H. CHEN, K. KAKIMOTO and K. OKAMURA, *J. Ceram. Soc. Japan* **101** (1993) 295.
6. T. SHIMOO, H. CHEN and K. OKAMURA, *Nippon Kinzokugakkai-shi* **57** (1993) 652.
7. T. ISHIKAWA, S. KAJII, K. MATSUNAGA, T. HOGAMI and Y. KOHTOKU, *J. Soc. Mat. Sci. Japan* **45** (1996) 593.
8. T. SHIMOO, F. TOYODA and K. OKAMURA, *J. Am. Ceram. Soc.* submitted.
9. *Idem. J. Ceram. Soc. Japan* **106** (1998) 447.
10. *Idem. J. Mater. Sci.* submitted.

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