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Oxidation behavior and mechanical properties of low-oxygen SiC fibers prepared by vacuum heat-treatment of electron-beam-cured poly(carbosilane) precursor

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EB-cured PCS fibers were heat-treated at 1273–1673 K under a reduced pressure of 1.33 Pa, and subsequently they were exposed to 1773 K in air. The thermal stability and oxidation resistance of the fibers were investigated through TG, XRD analysis, specific resistivity measurement, SEM observation and tensile tests. The oxidation rates at initial stage are thought to be strongly dependent upon the microstructure of the fibers in the as-heat treated state and the presence of water vapor. Incomplete ceramization and the occurrence of active-oxidation during heat-treatment yielded poor oxidation resistance to the fibers. The oxidation caused the grain growth of SiC, drop of resistivity and degradation of strength. The oxidation of the fibers was retarded at later stage. The fibers heat-treated at 1573 K had high strength and high oxidation resistance. *© 2003 Kluwer Academic Publishers*

1. Introduction

Poly(carbosilane)-derived silicon carbide fibers are of great importance as a reinforcing material for ceramic-matrix composites for a variety of high-temperature applications. The SiC fibers have a microstructure consisted of SiC crystallites, amorphous silicon oxycarbide (SiC_xO_y) and free carbon phase. The exposure of SiC fibers to high temperatures leads to the thermal decomposition of SiC_xO_y phase; the crystallization into β-SiC and the evolution of SiO and CO gases. Consequently, a degradation of fiber strength is caused by the grain growth of β-SiC, increase in porosity and flaw growth. A curing process of poly(carbosilane) (PCS) fibers using electron beam (EB) irradiation under an inert atmosphere enabled the manufacturing of low-oxygen SiC fibers (Hi-Nicalon, Nippon Carbon Co., Tokyo, Japan). Hi-Nicalon fibers are much more heat-resistant than Si—C—O fibers (Nicalon, Nippon Carbon Co., Tokyo, Japan) which are manufactured by an oxidation curing process [1, 2].

In order to develop the high-temperature strength of low-oxygen SiC fibers, the heat-treatment of EB-cured PCS fibers under reduced pressure has been investigated instead of a conventional heat-treatment under inert atmosphere [3–5]. The improvement of thermal stability of the fibers could be achieved by absence of retained hydrogen, that is, complete ceramization. However, the heat-treatment above 1673 K caused the active-oxidation of SiC grains in the fibers, resulting in marked degradation of fiber strength. The oxidation resistance also is one of controlling factors in the high-temperature application of SiC fibers. The objective of this work was to determine the feasibility of improving the oxidation resistance of the fibers heat-treated under a reduced pressure. The fibers heat-treated at 1273–1673 K were subjected to oxidation test at 1773 K in air. The chemical, structural and mechanical changes of oxidized fibers were investigated as a function of heat-treatment temperature. In order to make clear the oxidation mechanism of the fibers, the oxidation behavior was discussed by relating the morphology of the fibers in the as-heat treated state.

2. Experimental method

In this study, electron beam irradiation-cured poly(carbosilane) (EB-cured PCS) fibers manufactured by Nippon Carbon Co. (Tokyo, Japan) were used. The EB-cured PCS fibers had an overall composition $SiC_{1.83}O_{0.035}H_{3.78}$ and a mean diameter of 23.5 μm.

Four grams of EB-cured PCS fibers of 60 mm in length were placed in an alumina boat and those were positioned in the hot zone of a horizontal SiC resistance furnace (alumina reaction tube of 50 mm in inner diameter). After evacuation, they were continuously heated at 300 K/h and were held for 3.6 ks at each temperature from 1273 to 1673 K under a reduced pressure of 1.33 Pa (0.01 mmHg). The gas generation from PCS fibers during heat-treatments were investigated by gas analysis using a gas chromatograph and pressure measurements of a reaction tube.

Low-oxygen fibers (after heat-treatment of EB-cured PCS fibers under reduced pressure), 500 mg and 3 cm long, were placed in a platinum crucible and subjected to the oxidation tests of 72 ks at 1773 K in air. During oxidation, the mass change of the fibers was determined by a digital-type automatic recording balance.

The crystallized phase and the SiC crystallite size of the fibers were determined by X-ray diffraction (XRD). After the SiO_2 film formed on the fibers had been removed with an $NH_4OH + HF$ solution, specific resistivity was measured at room temperature. Direct current was applied between both ends of the fiber which were attached with electron-conductive resin to copper electrode plates spaced 0.8 mm apart. Ten measurements were made for each fiber. The morphologies of the as-oxidized fibers and the SiO_2-removed fibers were examined by field emission scanning electron microscopy (FE-SEM, Hitachi Limited., Type S5400, Tokyo, Japan). The room-temperature tensile strength of an SiO_2-removed fiber of 10 mm gauge length was determined using a universal tensile testing instrument (Orientec Co., TENSILON UTM-II-20, Tokyo, Japan) with a load cell of 9.8 N and a crosshead speed of 2 mm/min.

3. Results

3.1. Heat-treatment of EB-cured PCS fibers under reduced pressure

Fig. 1 shows the amounts of gases evolved from EB-cured PCS fibers during heating up to 1773 K under reduced pressure. The 900 K peak is principally attributed to the evolution of H_2 and CH_4 gases, though C_2H_4 and C_2H_6 is contained as the minor gases. The gases evolved at 900 K is responsible for the decomposition of Si—H and Si—CH_3 bonds [6, 7]. The H_2 gas peak at about 1400 K is due to the decomposition of C—H bonds. CO gas begins to evolve at about 1400 K and its amount increases rapidly with increasing temperature. CO evolution is due to both a thermal decomposition of amorphous SiC_xO_y phase and a reduction of the phase by free carbon (carbothermic reduction).

Fig. 2 shows the change in the pressure of reaction tube in which EB-cured PCS fibers were placed for the purpose of heat-treatment. Three peaks of gas evolved were observed at 470, 900 and 1360 K during heating from room-temperature to each heat-treatment temperature. In addition, the forth peak was observed during holding at 1673 K. The sizing treatment by water is performed for the purpose of bundling the EB-cured PCS fibers. Therefore, the first peak at 470 K is presumably due to the dissociation of adsorbed water. As can be seen from Fig. 1, the second peak at 900 K corresponds to the CH_4 and H_2 evolution by the decomposition of Si—H and Si—CH_3 bonds, and the third peak at 1360 K corresponds to the H_2 evolution by the decomposition of C—H bonds. Furthermore, the fourth peak during holding at 1673 K corresponds to the SiO and CO evolution by the thermal decomposition and carbothermic reduction of SiC_xO_y phase. Therefore, the decomposition of C—H bonds did not occur at all after heat-treatment at 1273 K, and hence the fibers were insufficiently strengthened [4]. While the heat-treatment temperature was kept for 3.6 ks at 1373–1573 K, the thermal decomposition of C—H bonds was completed. Although the decomposition of C—H bonds was completed during heating to 1673 K, the SiC_xO_y phase in the fibers was decomposed during keeping of 3.6 ks. Consequently, marked degradation of strength was caused by the heat-treatment at 1673 K [4].

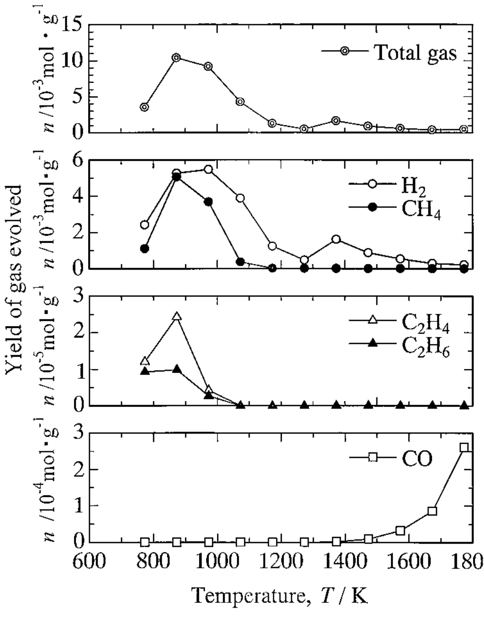

Figure 1 Gas evolution during heat-treatment of EB-cured PCS fibers under reduced pressure.

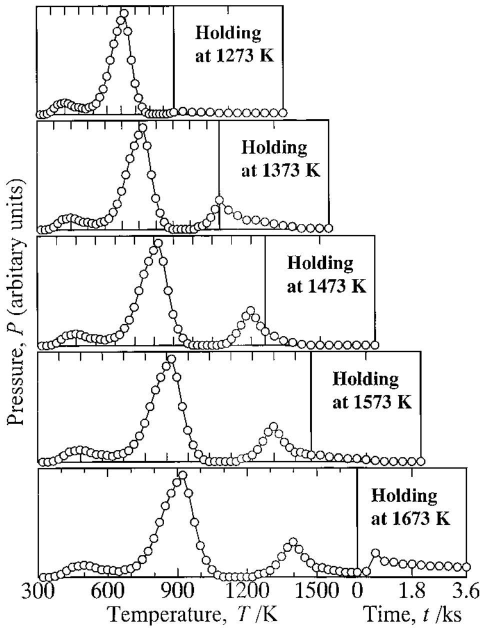

Figure 2 Change in pressure in reaction tube during heat-treatment of EB-cured PCS fibers under reduced pressure.

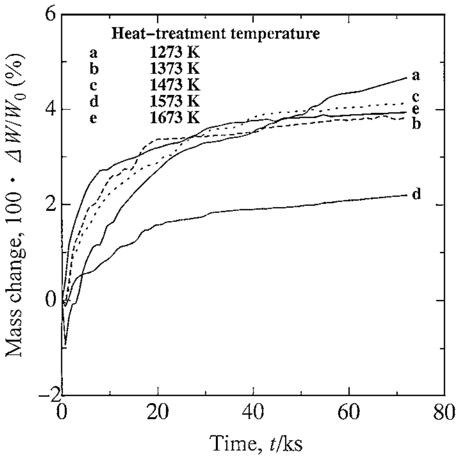

Figure 3 TG curves for fibers oxidized for 72 ks at 1773 K in air after heat-treatment at 1273–1673 K under reduced pressure.

3.2. Oxidation curves

The low-oxygen SiC fibers prepared by the heat-treatment at 1273–1673 K under a reduced pressure of 1.33 Pa were oxidized at 1773 K in air. Fig. 3 shows the oxidation curves, where ΔW and W_0 are the mass-change value determined by thermogravimetry (TG) and the initial mass of the fibers. For the fiber heat-treated at 1273 K, a large mass loss at earliest stage of oxidation ($100\cdot\Delta W/W_0 \fallingdotseq -1$) was followed by a marked mass gain. As can be seen from Figs 1 and 2, the heat-treatment at lower temperatures let to incomplete decomposition of the C—H bonds in the fibers. Therefore, the rapid mass loss observed during oxidation at 1773 K may be attributable to a rapid evolution of retained hydrogen. At earliest stage of oxidation, the slight mass loss caused by the thermal decomposition of amorphous silicon oxycarbide (SiC_xO_y) phase and the oxidation of free carbon was observed in the fibers heat-treated at 1373–1573 K.

Such initial mass losses were then followed by a large mass gain in TG curves. Obviously, the mass gain is due to the passive-oxidation of the fibers with atmospheric oxygen. After oxidation of 72 ks, the fibers heat-treated at 1273 K showed a large mass gain of $100\cdot\Delta W/W_0 \fallingdotseq 6$. The passive-oxidation of the fibers heat-treated at 1373 and 1473 K was retarded, and the mass gain was $100\cdot\Delta W/W_0 \fallingdotseq 4$. The fibers heat-treatment at 1573 K showed a significant reduction of mass gain ($100\cdot\Delta W/W_0 \fallingdotseq 2.5$), i.e., high oxidation resistance. The heat-treatment at 1673 K resulted in the enhancement of passive-oxidation ($100\cdot\Delta W/W_0 \fallingdotseq 4$).

3.3. XRD analysis

Fig. 4 shows the XRD patterns of the fibers oxidized for 72 ks at 1773 K in air. A very sharp peak of cristobalite at $2\theta = 22^\circ$ implies that the fibers heat-treated at 1273 K were severely oxidized in the passive-oxidation regime. The oxidation of the fibers was gradually retarded with increasing heat-treatment temperature, and the fibers heat-treated at 1573 K was mildly oxidized. The fibers heated at 1673 K were again subjected to a high degree of oxidation. These results appear to be consistent with TG data.

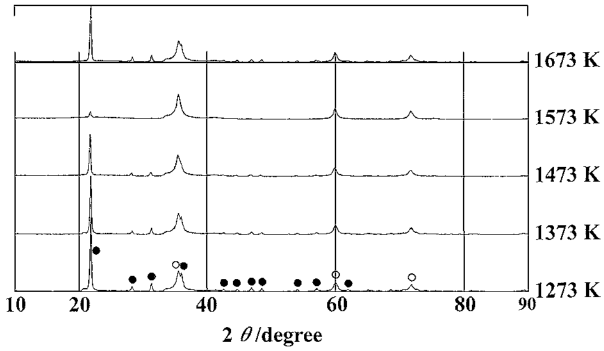

Figure 4 XRD patterns for fibers oxidized for 72 ks at 1773 K in air after heat-treatment at 1273–1673 K under reduced pressure: ○, SiC; ●, cristobalite.

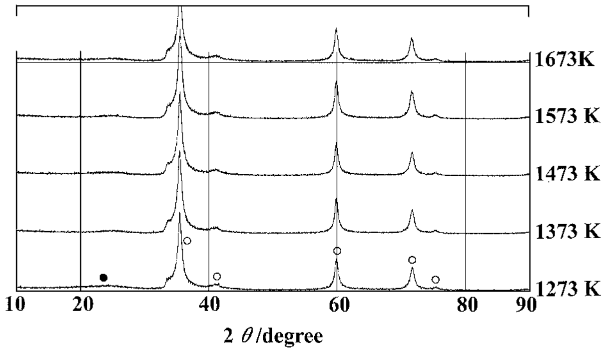

Figure 5 XRD patterns for SiO_2 removed fibers (unoxidized cores) after heat-treatment at 1273–1673 K under reduced pressure and subsequent oxidation of 72 ks at 1773 K in air; ○, SiC; ●, carbon.

Fig. 5 shows the XRD patterns of the SiO_2-removed fibers, i.e., the unoxidized cores. After oxidation of 72 ks at 1773 K, similar XRD patters were obtained in the fibers heat-treated at 1273 to 1673 K. A broad pattern at $2\theta = 26^\circ$ indicates that the organization of the carbon phase in the fiber core during oxidation at 1773 K is very limited. Using Scherrer's formula, the apparent SiC crystallite size, D_{SiC}, was calculated from the half-value width at mid height of (111) peak for the SiO_2-removed fibers. Fig. 6 shows the relationship between D_{SiC} and heat-treatment temperature. The D_{SiC} values of the fibers in the as-heat

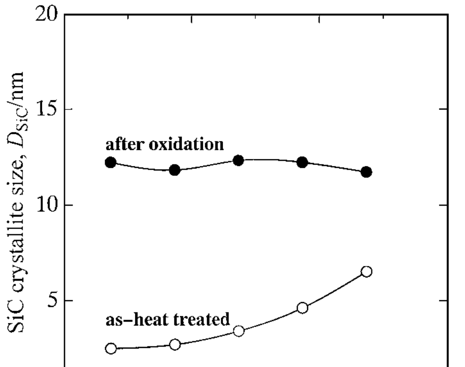

Figure 6 SiC crystallite size of fibers heat-treated at 1273–1673 K under reduced pressure and those oxidized subsequently for 72 ks at 1773 K in air.

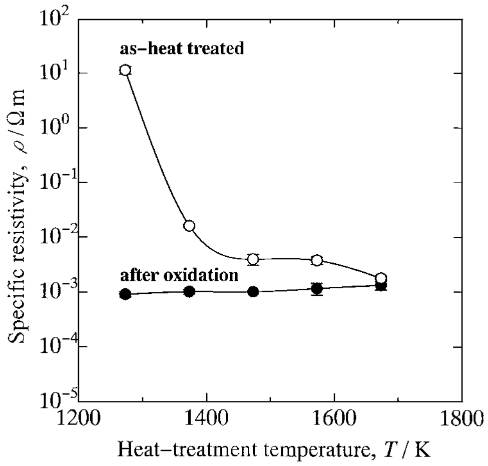

Figure 7 Specific resistivity of fibers heat-treated at 1273–1673 K under reduced pressure and those oxidized subsequently for 72 ks at 1773 K in air.

treated state increased with an increase in heat-treatment temperature. Although the β-SiC crystallite coarsened significantly during oxidation of 72 ks, its value was almost identical (11.7–12.3 nm), regardless of heat-treatment temperature.

3.4. Specific resistivity

The specific resistivity, ρ, is one of structure-senstive properties of silicon carbide fibers. Fig. 7 shows the relationship between ρ and heat-treatment temperature. The ρ value of oxidized fibers were measured after having removed SiO_2-film. The resistivity of the fibers heat-treated at 1273 K was exceedingly high, implying that an organic structure was still left in the fibers. At higher heat-treatment temperatures, as a consequence of sufficient ceramization, the ρ value was lowered by 3–4 orders of magnitude. Further drop of

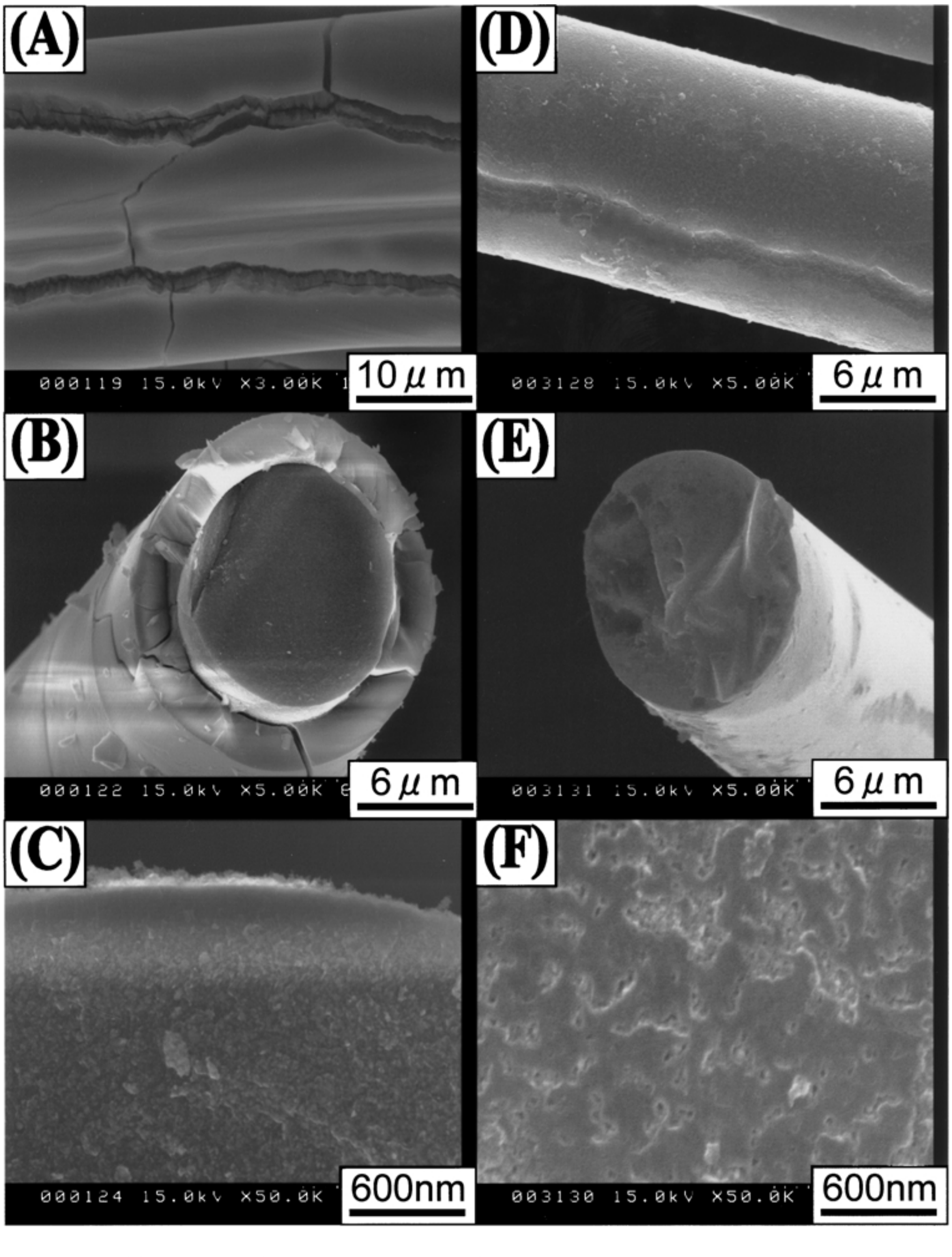

Figure 8 SEM photographs of fibers oxidized for 72 ks at 1773 K in air after heat-treatment at 1273 K under reduced pressure. (A), (B) and (C): in as-oxidized state, (D), (E) and (F): after removal of SiO_2 film with NH_4F HF solution.

ρ value was caused after oxidation, and a similar resistivity, $\rho \fallingdotseq 10^{-3}$ Ωm was produced in all the fibers heat-treated at 1273–1673 K and further oxidized at 1773 K.

3.5. Fiber morphology

Figs 8, 9 and 10 show SEM photographs of the fibers oxidized for 72 ks in air after heat-treatment at 1273, 1573 and 1673 K, respectively. Fiber morphologies were observed for the as-oxidized fibers (photos A, B and C) and the unoxidized cores (photos D, E and F). For the fiber heat-treated at 1273 K (Fig. 8), an SiO_2 film developed significantly during oxidation and cracked on cooling to room temperature (photos A and B). A groove observed in the unoxidized core (SiO_2-film removed fiber) implies that the cracks of SiO_2-film was formed even during oxidation (photo D). In addition, the cross-sectional area and the surface of the unoxidized core were minutely porous (photos C and F). As shown in Fig. 9, the surfaces of both SiO_2 film and unoxidized core were very smooth for the fibers heat-treated at 1573 K (photos A and D). The SiO_2 film was comparatively thin (photo B), and the dense structure was found in both the fractured surface and the surface of unoxidized core. Fig. 10 indicates that the fibers heat-treated at 1673 K were significantly porous throughout the cross-sectional area and the surface of

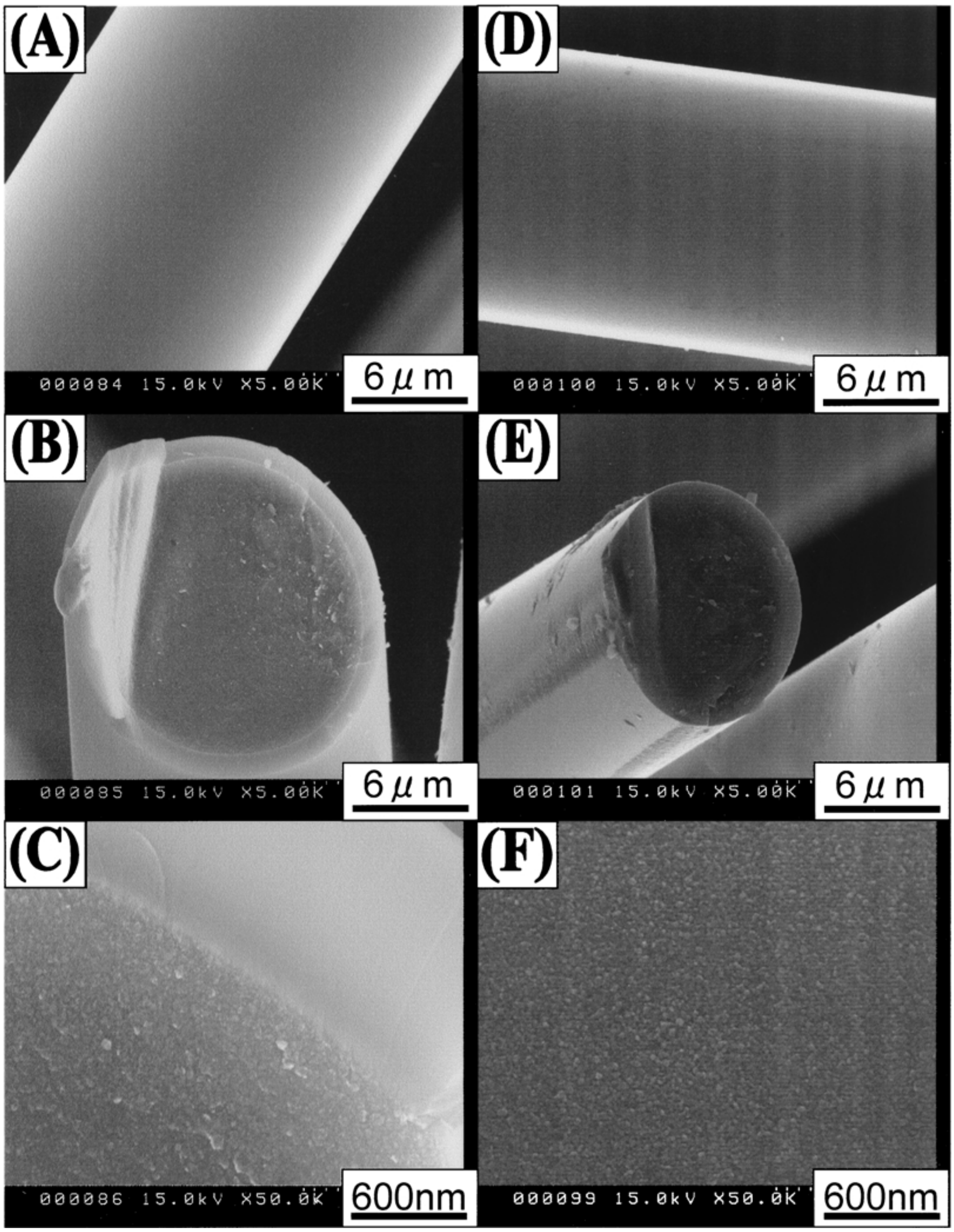

Figure 9 SEM photographs of fibers oxidized for 72 ks at 1773 K in air after heat-treatment at 1573 K under reduced pressure. (A), (B) and (C); in as-oxidized state, (D), (E) and (F): after removal of SiO_2 film with NH_4F HF solution.

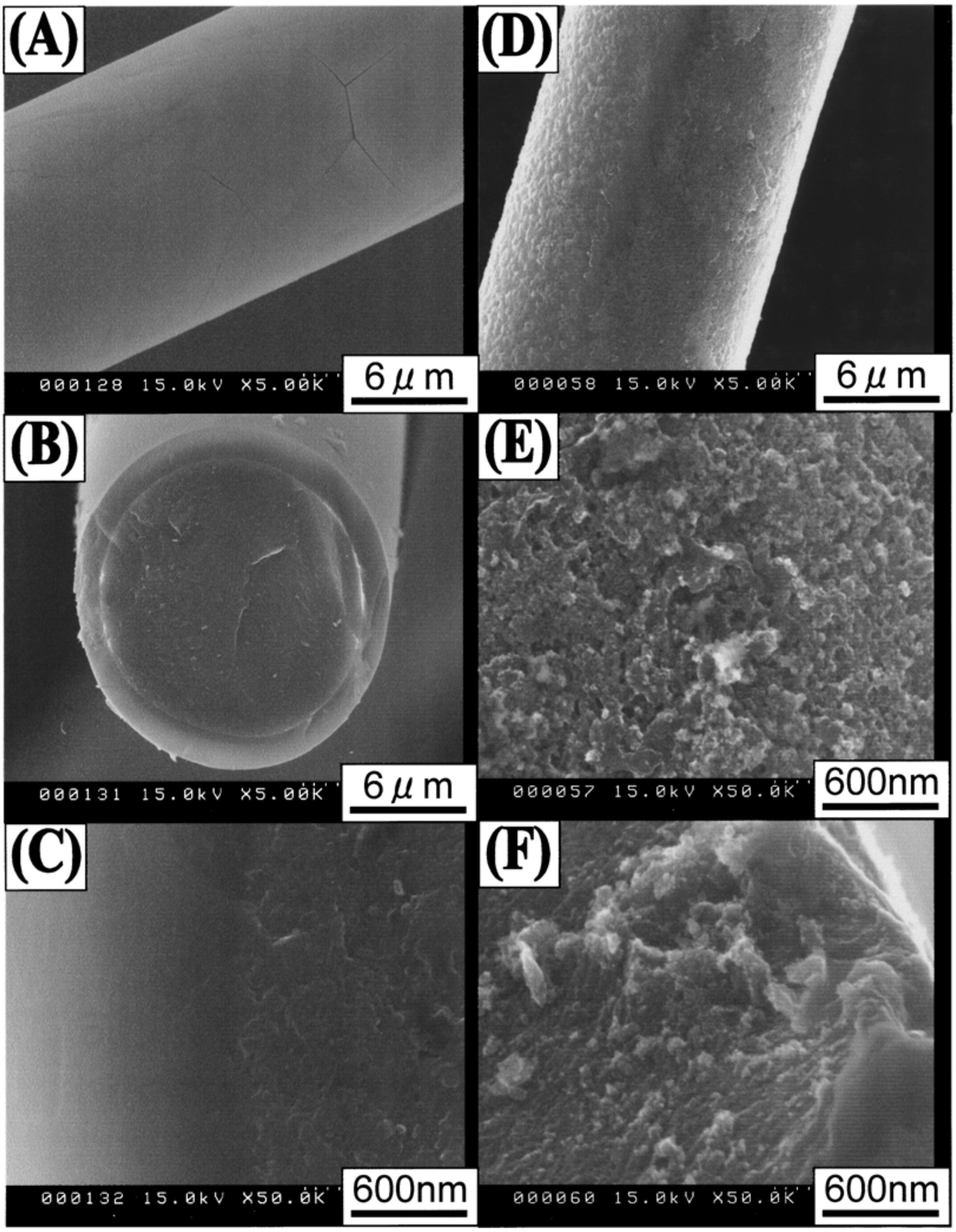

Figure 10 SEM photographs of fibers oxidized for 72 ks at 1773 K in air after heat-treatment at 1673 K under reduced pressure. (A), (B) and (C): in as-oxidized state, (D), (E) and (F): after removal of SiO_2 film with NH_4F HF solution.

unoxidized core (photos C and F). The SiO_2 film grew considerably and was finely broken (photos A and B).

3.6. Tensile strength

Room-temperature strength, σ, of the as prepared and further oxidized fibers is shown in Fig. 11. The adherence of SiO_2 film let to the difficulty in determining the tensile strength of the as-oxidized fibers. Therefore, the SiO_2-removed fibers (unoxidized cores) were subjected to tensile test. The heat-treatment at 1473 K gave the highest strength in the as-heat treated state, i.e., $\sigma = 3.5$ GPa. Although the oxidation treatment caused some degradation of fiber strength, a strength of 2.1 GPa was retained in the fiber heat-treated at 1573 K.

4. Discussion

The passive-oxidation of SiC fibers is controlled by the diffusion of oxygen molecules throughout SiO_2 film formed on the fiber surface [8, 9]. The oxidation kinetics of SiC fibers has been analyzed using a parabolic rate law [10–12]:

$$(\Delta W/W_0)^2 = k_p \cdot t \qquad (1)$$

Application of TG data to rate Equation 1 is shown in Fig. 12. At each heat-treatment temperature, a plot of $(\Delta W/W_0)^2$ against t gave two straight lines having different slope gradient (i.e., parabolic rate constant, k_p) in short time and long time oxidation. Fig. 13 shows the

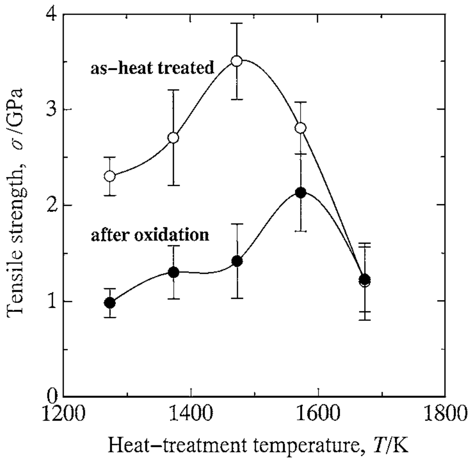

Figure 11 Room-temperature tensile strength of fibers heat-treated at 1273–1673 K under reduced pressure and those oxidized subsequently for 72 ks at 1773 K in air.

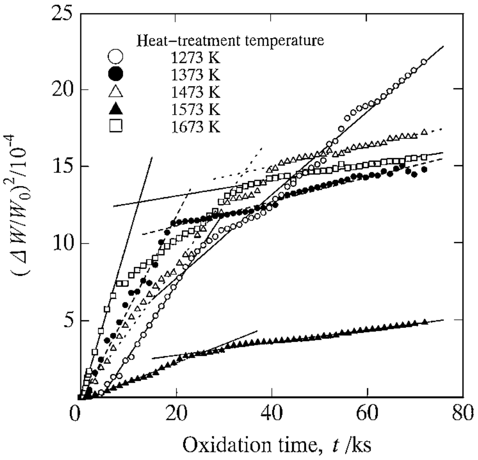

Figure 12 Application of TG data shown in Fig. 3 to parabolic rate equation.

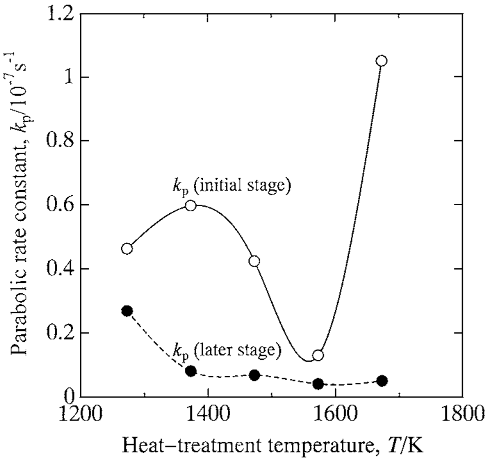

Figure 13 Relationship parabolic rate constant and heat-treatment temperature for fibers oxidized for 72 ks at 1773 K in air.

relationship between k_p and heat-treatment temperature. The k_p value at the initial stage of oxidation is larger than that at the later stage. Since the fibers were incompletely coated by a silica film at the initial stage of oxidation, the oxidation rates are thought to be controlled by the microstructure of the fibers in the as-heat treated state. For the fibers heat-treated at lower temperatures, the defects introduced by rapid generation of H_2 gas at the earliest stage of oxidation increased the permeability to oxygen gas, enhancing the initial rates of passive-oxidation (photos C and F in Fig. 8). H_2 gas evolved may be oxidized into water vapor during exposure to 1773 K in air. The oxidation of SiC in oxidizing environment is known to be greatly accelerated by the presence of a slight amount of water vapor [13, 14]. The formation of water vapor due to the oxidation of retained hydrogen was thought to have a similar effect on the oxidation of Si—C—O fibers (Nicalon) [10]. Therefore, it is possible that large values of k_p at lower heat-treatment temperature appears to be partly responsible for the enhancement effect of water vapor on the oxidation of the fibers. PCS fibers were completely transformed into ceramic fiber by the heat-treatment of 3.6 ks at 1573 K, and hence their structure was observed to be dense both within the cross-sectional area and on the core surface even after oxidation (Fig. 9). The k_p value of such fibers was significantly small, owing to a very low permeability to oxygen gas. Despite complete ceramization, the fibers heat-treated at 1673 K were severely oxidized. The reason is that the heat-treatment at 1673 K under reduced pressure caused the thermal decomposition of amorphous SiC_xO_y phase and the subsequent active-oxidation of the fibers by the retained oxygen in the reaction tube. In particular, the active-oxidation makes the fiber structure highly porous (photos C, E and F in Fig. 10). Such a high permeability to O_2 gas caused a drastic increase in the k_p value. There was a marked decrease in k_p value at later stage of oxidation. When Nicalon fibers were exposed for longer period of time in air, the SiO_2 film on the surface became thicker and denser [15]. Similarly, for the low-oxygen fibers, the development and densification of SiO_2 film is thought to retard the diffusion of O_2 gas throughout it. In addition, the k_p value may be strongly dependent upon the microstructure of SiO_2 film. For the fibers heat-treated at 1273 K, cracks were formed in SiO_2-film during oxidation treatment (photo D in Fig. 8). Consequently, the k_p value was considerably larger than that for the fibers heat-treated above 1373 K.

The exposure to 1773 K in air caused the decomposition of SiC_xO_y phase at the earliest stage of oxidation, resulting in the grain growth of β-SiC and the reduction of specific resistivity (Figs 6 and 7). The strength degradation after oxidation appears to be partly attributed to the coarsening of SiC grains. After oxidation of 72 ks in air, almost identical values of β-SiC grain size and specific resistivity were observed, independently on the heat-treatment temperature. From this result, it seems that the core of oxidized fibers had a similar structure. However, Fig. 11 shows that the strength after oxidation was affected by the fiber structure in the as-heat treated state. The oxidation introduced new defects on the core surface (photo D in Fig. 8), and caused further degradation of the strength. Since the active-oxidation made the fiber structure highly porous, the fibers were already fragile in the as-heat treated state [4]. The subsequent oxidation did not cause the structural change of fiber core, and consequently further degradation of fiber strength was not caused after oxidation at 1773 K (Figs 10 and 11). Finally, the fibers heat-treated at 1573 K had high oxidation resistance and good strength after oxidation.

5. Conclusions

The fibers heat-treated at lower temperatures rapidly liberated H_2 gas at early stage of oxidation. The porous structure of the fibers caused the degradation of strength and poor oxidation resistance. The presence of water vapor also appears to accelerated the passive-oxidation of the fibers. The fibers were subjected to the thermal decomposition of SiC_xO_y phase and the active-oxidation of SiC grains during heat-treatment at 1673 K. The strength of such fibers was significantly low in the as-heat treated state. Subsequently, the fibers were subjected to severe passive-oxidation in air because of high permeability to oxygen gas. As a consequence of development and densification of SiO_2 film, the oxidation was retarded at the later stage of oxidation. From high strength and oxidation resistance, the most suitable temperature for heat-treatment was 1573 K.

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