

Thermal stability of low-oxygen silicon carbide fibers (Hi-Nicalon) in carbon monoxide

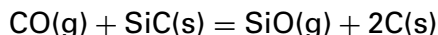
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The effect of CO treatments on thermal stability of low-oxygen SiC fibers (Hi-Nicalon) was examined at 1273–1773 K using mass change measurements, X-ray diffraction (XRD) analysis, Auger electron spectroscopy (AES) analysis, resistivity measurements, scanning electron microscopy (SEM) observation and tensile tests. The fiber properties remained unchanged by heating below 1573 K. In addition to the grain growth of SiC, reduction of resistivity and degradation of strength above 1573 K, mass loss was observed above 1673 K. AES analysis showed carbon film formation on fiber surfaces at high temperature. The carbon film was formed by the following reaction:



A Tensile strength of 1.83 GPa was retained even after exposure at 1773 K for 10 h, owing to the suppressing effect of the carbon film on the thermal decomposition of SiC_xO_y phase.

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1. Introduction

Polycarbosilane-derived silicon carbide fibers such as Nicalon, Hi-Nicalon and Hi-Nicalon S (Nippon Carbon Co., Tokyo, Japan) are the best reinforcing materials for ceramic matrix composites. Ceramic matrix composite materials are submitted to high-temperature applications of long duration under different environmental conditions. Therefore, the fibers require excellent mechanical properties, chemical and structural stability, and oxidation resistance at high temperatures.

Thus, structural and mechanical changes to the fibers have been mainly investigated after high-temperature exposure in inert gas (Ar and N_2), oxidizing gas (air, O_2 , Ar– O_2 and H_2O) and vacuum [1–22]. In particular, the oxidation in Ar– O_2 gas mixtures made clear the active-to-passive oxidation transition of SiC fibers. While fiber strength was retained to a high degree after passive-oxidation, it was practically lost after active-oxidation [18, 20, 22]. When SiC fibers are used as hot section components of gas turbines, piston engines and heat exchanger tubes, they were exposed to high-temperature combustion environments. The present authors investigated the oxidation behavior of SiC fibers in CO_2 gas, showing that Nicalon and Hi-Nicalon fibers were severely oxidized in the passive-oxidation regime [23, 24]. The combustion gases contain CO gas, as well as CO_2 gas. Therefore, the thermal stability of silicon carbide fibers in CO-containing environments must be investigated. However, very little work has reported on the high-temperature exposure of SiC fibers to CO gas.

CO treatments of Nicalon fibers were investigated to evaluate the suppression of the thermal decomposition of amorphous silicon oxycarbide (SiC_xO_y) phase [25–27]. Although the CO heat-treatments cause the formation of a carbon layer on the surface of fibers, there is as yet no generally accepted explanation of the mechanism for the carbon-film formation. In addition, the carbon film, as well as a SiO_2 film, may be expected to be effective in the suppression of the thermal decomposition of the SiC_xO_y phase.

In this study, Hi-Nicalon fibers were heat-treated at 1273 to 1773 K in flowing CO gas. The thermal stability of the fibers in CO gas was investigated through thermogravimetric (TG) analysis, X-ray diffraction, resistivity measurement, SEM observation and tensile testing. Furthermore, the results of these experiments are discussed in relation to the formation mechanism of a carbon film on the surface of the fibers and thermodynamical considerations.

2. Experimental method

The Hi-Nicalon fibers employed for this study have a composition of $\text{SiC}_{1.40}\text{O}_{0.05}$ and a mean diameter of 14 μm . Fibers weighing 500 mg and 3 cm long, were placed in an alumina boat and then set in an alumina reaction tube of a horizontal SiC resistance furnace. After evacuation, CO or Ar–CO gas was passed into the alumina reaction tube at a flow rate of 100 cm^3/min . The fibers were heated in flowing CO gas at a rate of

300 K/h and held for 1–10 h at each temperature in the range 1273–1773 K. Then, they were cooled to room temperature at a rate of 600 K/h.

The amount of gas evolved was determined from the difference in the mass of the fibers before and after exposure. Phase detection and the estimation of β -SiC crystallite size were conducted using X-ray diffraction (XRD) analysis. The grain growth of β -SiC above around 10 nm causes the development of twins and polytype domains, inducing considerable errors in the SiC crystallite size measurement by XRD. Therefore, the measured values (apparent β -SiC crystallite sizes) were used only as an aid in the relative evaluation of the grain growth of SiC. The composition of the fiber surfaces was analyzed using Auger electron spectroscopy (AES), and the fiber morphology was examined using a field-emission-type scanning electron microscope (FE-SEM). The specific resistivity of the fibers was determined at room temperature by applying a direct current. Electroconductive resin was applied to both ends of a fiber to attach them to copper electrode plates that were 0.8 mm apart. The average of ten measurements was used as the specific resistivity for each exposure condition. The room-temperature tensile strength of a fiber of 10 mm gauge length was measured with a tensile testing machine (Orientec Co., TENSILON UTM-20, Tokyo, Japan) using a 100 g load cell and a constant crosshead speed of 2 mm/min. An average from 20 fibers was used for each exposed fiber.

3. Results

3.1. Mass change

Fig. 1 shows the mass change of Hi-Nicalon fibers exposed for 10 h to Ar–CO gas mixtures at 1773 K as a function of the partial pressure of carbon monoxide (p_{CO}). Here, ΔW and W_0 are the mass change caused by the exposure and the initial mass of the fibers, respectively. The mass loss of $100 \cdot \Delta W/W_0 = -0.54$ was observed after exposure in argon, being attributed to the thermal decomposition of an amorphous silicon oxycarbide (SiC_xO_y) phase. The addition of CO to argon enhanced the mass loss of the fibers. There was little further mass change at $p_{\text{CO}} \geq 5 \times 10^{-4}$ Pa. Finally, the exposure in pure carbon monoxide gas produced a mass loss of $100 \cdot \Delta W/W_0 = -4.27$. This value

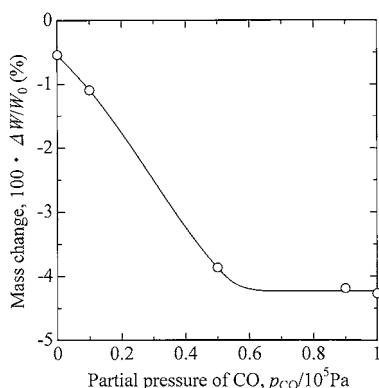


Figure 1 Relation between mass change and CO partial pressure for Hi-Nicalon fibers exposed for 10 h at 1773 K in Ar–CO gas mixtures.

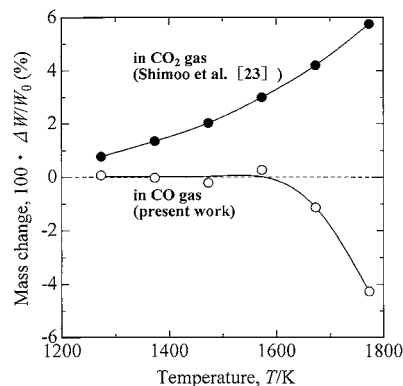


Figure 2 Relation between mass change and temperature for Hi-Nicalon fibers exposed for 10 h in CO gas.

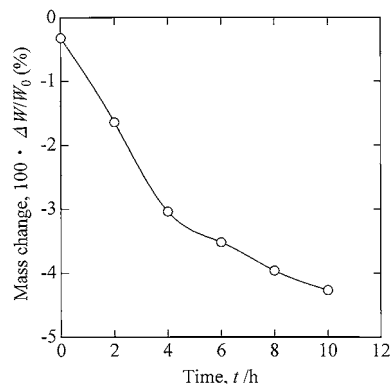


Figure 3 Relation between mass change and keeping time for Hi-Nicalon fibers exposed at 1773 K in CO gas.

is much larger than the mass loss after the complete decomposition of SiC_xO_y phase (about 1%).

Fig. 2 shows the mass change of Hi-Nicalon fibers exposed for 10 h to CO gas at different temperatures. The mass change of the fibers heat-treated in CO_2 gas is shown for comparison [23]. The exposure in CO_2 gas, as a consequence of the passive-oxidation, caused a large increase in fiber mass. In contrast, the mass of the fibers after exposure in CO gas was almost unchanged at $T \leq 1573$ K and decreased significantly at $T \geq 1673$ K.

Fig. 3 shows the change in mass with time for Hi-Nicalon fibers exposed to CO gas at 1773 K. When heated from room-temperature to 1773 K ($t = 0$ h), a mass loss of $100 \cdot \Delta W/W_0 = -0.32$ had already occurred. The mass loss exceeded the value for the complete decomposition of SiC_xO_y phase at $t = 2$ h. The mass loss continued until $100 \cdot \Delta W/W_0 = -4.27$ was attained at $t = 10$ h. The large mass loss suggests that a reaction other than the thermal decomposition of SiC_xO_y phase occurred during exposure to CO gas.

3.2. Surface composition of fibers

Fig. 4 shows the composition profile, determined by AES analysis, for the as-received fiber and the fibers exposed for 10 h at 1773 K to CO gas. Although there was a 50 nm thick carbon-enriched layer on the surface of the as-received fiber, the distribution of silicon and carbon was uniform in the interior. Exposure to CO gas

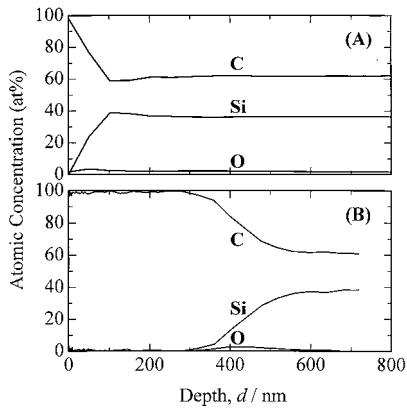


Figure 4 AES depth profiles of Hi-Nicalon fibers in as-received state (A) and after exposure of 10 h at 1773 K in CO gas (B).

produced a 300 nm thick carbon film on the fiber surface. There was a carbon gradient between the carbon film and the fiber core, and the C/Si ratio decreased over a depth range from 300 to 550 nm. The existence of a concentration gradient implies the interaction of the fiber surface with CO gas.

3.3. XRD analysis

Fig. 5 shows the XRD patterns for the fibers exposed for 10 h to CO at different temperatures. A broad diffraction peak of carbon at $2\theta = 26^\circ$ was detected for the fibers exposed at 1773 K. The peak was observed even after heat-treatment at 1773 K in Ar gas, implying the organization of free carbon in the fiber core. Therefore, the formation of the carbon film could not be shown by XRD analysis. The diffraction pattern of β -SiC became gradually sharper with increasing temperature. The apparent crystallite size of β -SiC, D_{SiC} was calculated from the half-width value of (111) peak using Scherrer's formula. Fig. 6 shows the value D_{SiC} as a function of exposure temperature. β -SiC crystallite size was held at 5–6 nm at $T \leq 1473$ K and grain growth began at $T \geq 1573$ K. The variation in crystallite size was almost identical to that for Hi-Nicalon fibers exposed to CO₂ gas [23]. On being exposed to high temperatures, the grain growth β -SiC is caused by the crystallization

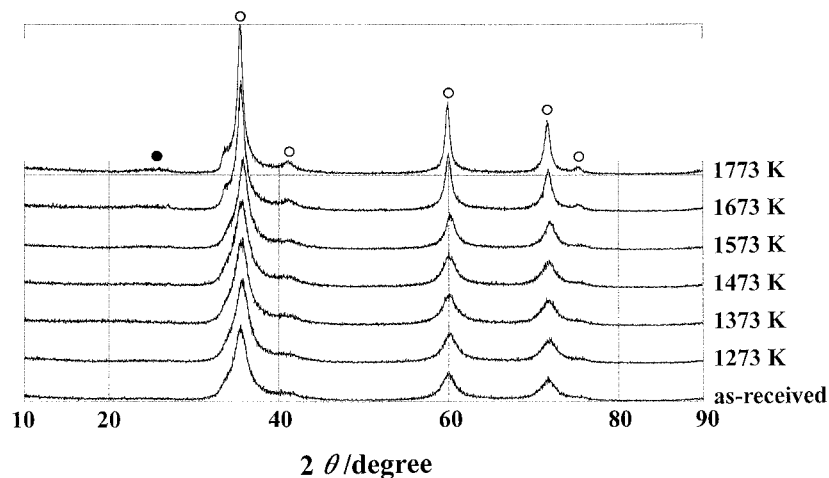


Figure 5 XRD patterns for Hi-Nicalon fibers in as-received state and after exposure of 10 h at 1273–1773 K in CO gas. ○ β -SiC; ● carbon.

of Si–C phase ($T \geq 1473$ K) and the thermal decomposition of SiC_xO_y phase ($T \geq 1673$ K) [28, 29]. The grain growth β -SiC in Nicalon fibers is principally attributed to the decomposition of SiC_xO_y phase. On the other hand, the crystallization of Si–C phase seems to be critical for the grain growth in Hi-Nicalon fibers on account of the relatively low oxygen content [28].

The relationship between D_{SiC} and exposure time is shown in Fig. 7A. When the temperature of the fibers was raised from room-temperature to 1773 K at 300 K/h ($t = 0$ h), SiC crystal grew from 5 nm (in as-received state) to 10 nm. Although further coarsening of SiC crystal was observed during holding at 1773 K, there was little the grain growth at $t \geq 4$ h.

3.4. Specific resistivity

The temperature dependence of specific resistivity is shown in Fig. 8. After exposure to CO gas, the fibers coated with carbon film were submitted for resistivity measurements. Whereas, the resistivity measurements for the fibers exposed to CO₂ gas were conducted after having removed the SiO₂-film [23]. The resistivity at $T \leq 1473$ K was the same as that of the as-received fibers, suggesting no variation in the microstructure of the fibers. As a result of the crystallization of the Si–C phase and the percolation of carbon networks, the resistivity decreased at $T \geq 1573$ K [28, 29]. There was a larger drop of resistivity after exposure to CO gas than to CO₂ gas. This is because an electrically-conductive carbon film was formed on the fiber surface in CO gas. Changes in resistivity with time at 1773 K are shown in Fig. 7B. A considerable drop in resistivity was observed at $t = 0$ h. The reduction of resistivity continued even at $t = 10$ h, being inconsistent with the grain growth of SiC crystals. The resistivity drop at $t \geq 4$ h is considered to be mainly due to the formation of the carbon film.

3.5. Fiber morphology

Fig. 9 shows the morphologies of the as-received fibers and the fibers exposed at 1573–1773 K to CO gas. The as-received fiber had a smooth surface and a glassy

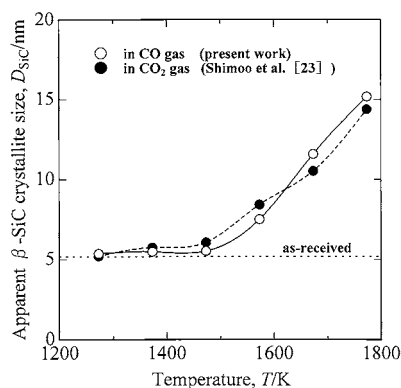


Figure 6 Apparent β -SiC crystallite size of Hi-Nicalon fibers exposed for 10 h at different temperatures in CO gas.

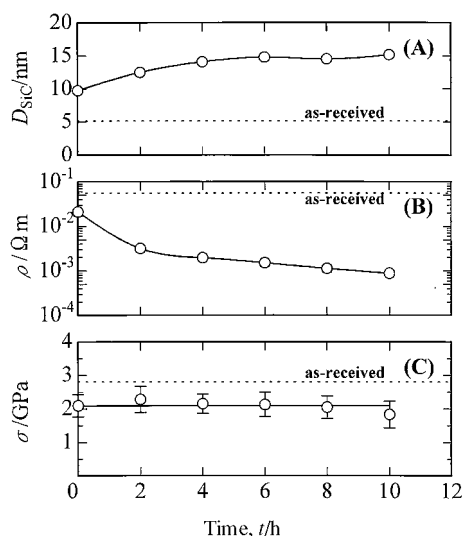


Figure 7 Apparent β -SiC crystallite size (A), specific resistivity (B) and room-temperature tensile strength (C) of Hi-Nicalon fibers exposed at 1773 K in CO gas as function of keeping time.

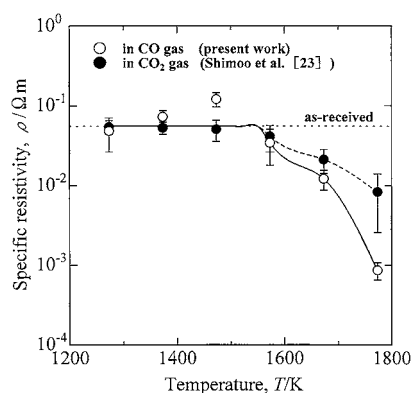


Figure 8 Specific resistivity of Hi-Nicalon fibers exposed for 10 h at different temperatures in CO gas.

cross-section (photos (A) and (B)). The fracture surface shows that the fibers failed in a brittle manner. No carbon film was formed at 1573 K (photos (C) and (D)). Exposure at higher temperatures caused the development of the carbon film on the fiber surface (photos (F) and (H)). Seemingly, the fracture appearance of the fiber core after exposure, like that of the as-received fibers, was glassy (photos (D), (F) and (H)).

Fig. 10 shows the magnified images of the morphology of the fibers exposed at 1773 K to CO gas. The

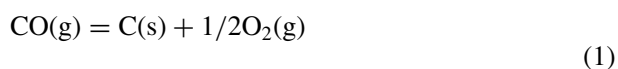
surface morphology of the fibers was significantly irregular (photo (A)). In addition, a continuous cavity was observed between the carbon film and the fiber core (photo (B)). The carbon-gradient layer observed by AES analysis was probably crushed on breaking the fibers (Fig. 4).

3.6. Tensile strength

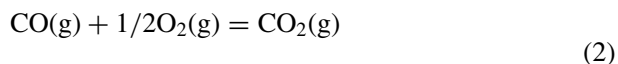
Fig. 11 shows the room-temperature strength of the fibers after an exposure of 10 h at 1273–1773 K to CO gas. The strength of the fibers heat-treated in CO₂ gas under the same exposure condition is shown in this figure [23]. The tensile strength of the fibers gradually decreased with an increase in exposure temperature. The degradation of fiber strength may be partly attributed to the thermal decomposition of SiC_xO_y phase. The strength of the fibers coated with carbon film during exposure to CO gas was lower than that of fiber core (the fiber after SiO₂-removal) after exposure to CO₂ gas. This implies that the carbon film has the strength-controlling imperfections, as well as SiO₂ film. After exposure at elevated temperature, the strength of carbon-film coated fibers was considerably higher than that SiO₂-film coated fibers. Fig. 7C shows the change with time of the strength of the fibers exposed at 1773 K to CO gas. When the fibers were heated from room-temperature to 1773 K (at $t = 0$ h), there was a decrease of about 25% in tensile strength. It is noted that no further degradation of fiber strength occurred during holding times of $t = 0$ –10 h.

4. Discussion

At high temperatures, CO gas dissociates into C and O₂, and then CO₂ gas also is produced. Finally the following equilibria are established:



$$\Delta G^\circ \text{ (J/mol)} = 114390 + 85.77T \text{ [30]}$$

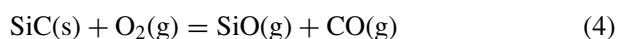


$$\Delta G^\circ \text{ (J/mol)} = -280960 + 85.23T \text{ [30]}$$



$$\Delta G^\circ \text{ (J/mol)} = 395350 + 1.26T \text{ [30]}$$

The oxidation in Ar–O₂ gas mixtures shows that the active-to-passive oxidation transition occurs at an oxygen partial pressure between 10 and 25 Pa at 1773 K for Hi-Nicalon fibers [20]. The above equilibria yield an oxygen potential (equilibrium oxygen partial pressure), $p_{\text{O}_2} = 2.01 \times 10^{-11}$ Pa at 1773 K. Therefore, it is possible that SiC grains in Hi-Nicalon fibers could be oxidized in the active-oxidation regime under a CO atmosphere, according to the relationship:



Hi-Nicalon fibers exposed to Ar–O₂ gas mixtures showed the following characteristics of active-oxidation: a large mass loss, an increase in specific

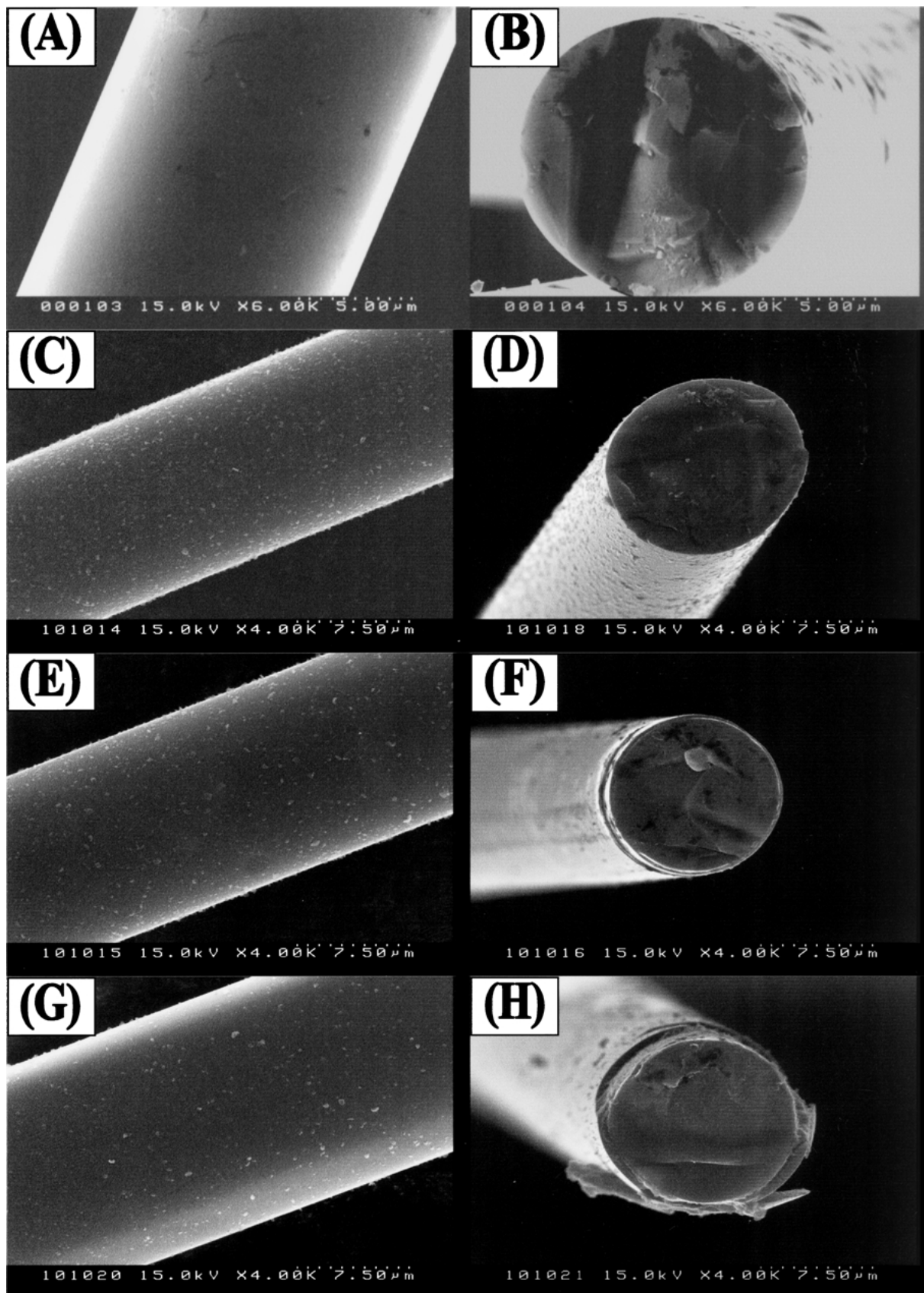


Figure 9 SEM photographs of Hi-Nicalon fibers in as received state (A, B) and after exposure of 10 h at 1573 K (C, D), 1673 K (E, F) and 1773 K (G, H) in CO gas.

resistivity, a dual fiber structure (coarsened surface and dense core) and the degradation of fiber strength to 0 GPa. The mass loss of the fibers after exposure in CO gas ($100 \cdot \Delta W/W_0 = -4.27$) is comparable with that of the fibers after active-oxidation in Ar-O₂ gas mixtures with an oxygen partial pressure

of 5 Pa. ($100 \cdot \Delta W/W_0 = -4.92$). However, a decrease in resistivity, a smooth film on the fiber surface and a retained strength of about 2 GPa were observed after exposure to CO gas. These results are not compatible with the characteristics of active-oxidation. The active-oxidation rate of the fibers appears to be

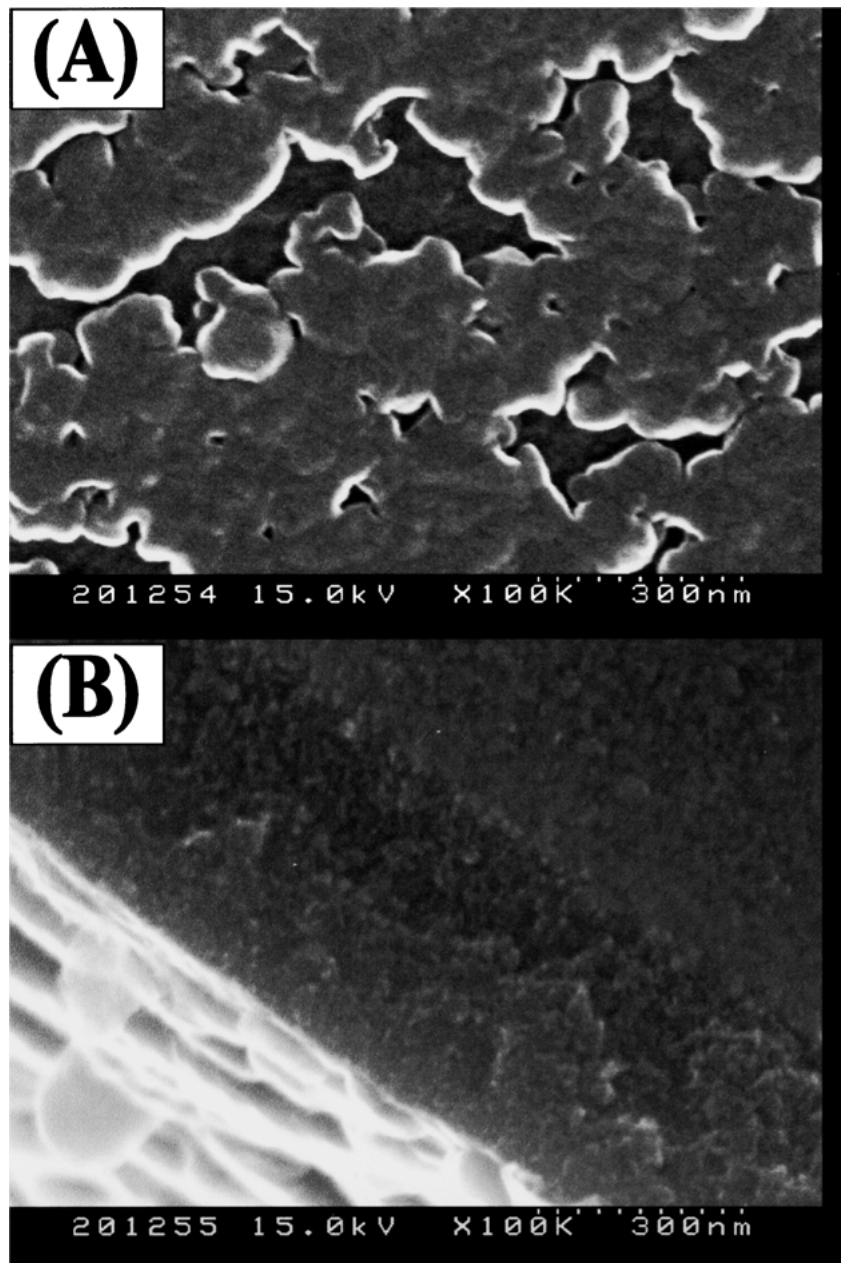
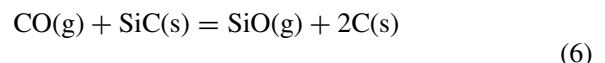
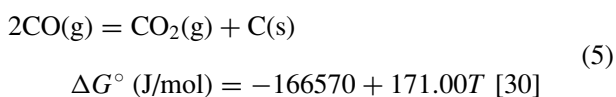


Figure 10 Magnified images for surface (A) and cross section (B) of Hi-Nicalon fibers exposed for 10 h at 1773 K in CO gas.

infinitesimal in CO gas, because of the extremely low oxygen partial pressures of 2.01×10^{-11} Pa. For example, Nicalon fibers were severely oxidized in the active-oxidation regime under a reduced pressure of 1.3 Pa ($p_{O_2} = 0.27$ Pa), but they were not oxidized in the active-oxidation regime under a reduced pressure of 10^{-4} Pa ($p_{O_2} = 2.1 \times 10^{-5}$ Pa) [3]. Therefore, the mass loss observed after exposure to CO must be attributed to another cause.

In CO environments at high temperature, carbon may be deposited because of very high carbon potential. From Auger analysis and SEM observation (Fig. 4 and 8), a carbon film was formed on the fiber surface. Two probable reactions for the formation of the carbon film are



$$\Delta G^\circ (\text{J/mol}) = 83260 - 4.39T \quad [30]$$

Fig. 12 shows the equilibrium partial pressure of CO gas for reactions (5) and (6). Reaction (5) may occur at $T \leq 1425$ K and reaction (6) would be favoured at $T \geq 1425$ K. While reaction (5) yields a mass gain, reaction (6) yields a mass loss. The mass loss observed at $T \geq 1623$ K (Fig. 1) suggests that reaction (6) is valid for the formation of carbon film. In addition, the presence of a carbon gradient between the carbon film and the core shows the interaction of CO gas with SiC in the fibers. If the carbon deposition on the fiber surface is merely caused by reaction (5), a concentration gradient would not be formed beneath the carbon layer. The formation of the carbon film appears to cause the drop of resistivity. The specific resistivity of the fibers heat-treated below 1573 K was nearly identical to that of the as-received fibers (Fig. 8), implying that reaction

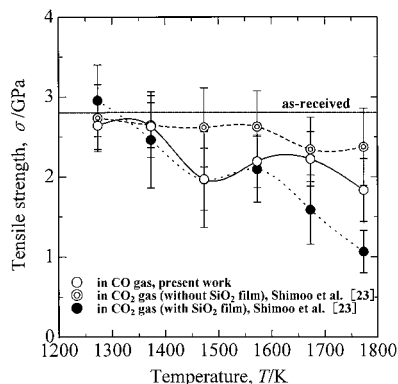


Figure 11 Room-temperature tensile strength of Hi-Nicalon fibers exposed for 10 h at different temperatures in CO gas.

(5) did not occur. Thus, the mass change and carbon-film formation were not observed in Figs 1 and 9. CO treatments above 1673 K are required in order to coat the fibers with carbon.

As can be seen from Fig. 6, SiC crystals coarsened markedly above 1573 K. This is caused by the thermal decomposition of the amorphous SiC_xO_y phase and the crystallization of the Si—C phase. The thermal decomposition of SiC_xO_y phase entails the generation of SiO and CO gases. Similar grain growth of SiC in both CO and CO_2 gas implies that the carbon film, as well as silica film, retarded the generation of decomposition gases. The room-temperature tensile strength of the fibers oxidized passively in CO_2 gas is shown in Fig. 11 [23]. The tensile strength of the fibers heat-treated in CO gas is lower than that of the core of the fibers heat-treated in CO_2 gas. This result appears to be attributed to the imperfections of the carbon film. Fig. 10 shows that the carbon film was not uniform in microstructure and that a porous layer was formed between the carbon film and the fiber core. However, the carbon film is less critical in relation to the degradation of fiber strength than the silica film. This is because the cristobalite film formed by oxidation in CO_2 above 1573 K cracked on cooling to room-temperature [23]. In flowing argon gas, the strength of Hi-Nicalon fibers was completely lost after an exposure of 5 h at 1773 K [31, 32]. On the other hand, in CO gas, the tensile strength of 1.83 GPa was retained even after an exposure of 10 h at 1773 K. This is due to the suppression effect of CO on the

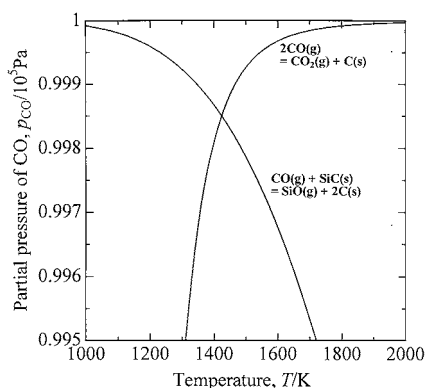


Figure 12 Equilibrium CO pressure of reactions for formation of carbon-film on Hi-Nicalon fibers.

thermal decomposition of an amorphous SiC_xO_y phase [25–27].

5. Summary

Low-oxygen SiC fibers (Hi-Nicalon) were exposed at 1273–1773 K to flowing CO gas. The properties of the fibers remained almost unchanged after exposure at temperatures below 1473 K. There was a grain growth of SiC, a reduction in resistivity and a degradation of strength after CO-treatment above 1573 K. The CO treatment above 1673 K caused the mass loss of the fibers. AES analysis and SEM observation showed the formation of carbon film on the surface of fibers. The carbon film is thought to be formed by the interaction of SiC crystals and CO gas. Even after an exposure of 10 h at 1773 K, a strength of 1.83 GPa was retained due to the suppressing effect of CO gas on the thermal decomposition of SiC_xO_y phase.

Acknowledgement

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