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Suppression of active-oxidation of Si-C fibers (Hi-Nicalon) under reduced pressure by carbon or silica coating

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The suppression of the active-oxidation of Si-C fibers (Hi-Nicalon) by carbon or silica coating were investigated at 1773 K under a reduced pressure of 1.32 Pa, through mass change determination, XRD analysis, resistivity measurement, SEM observation and tensile test. The coating of carbon and silica were conducted by heat-treating at 1773 K in CO-CO_2 gas mixtures. After exposure under a reduced pressure, the carbon coating formed in pure CO gas remained almost perfect and the retained strength of 1.7 GPa was nearly identical to that in the as-heat treated state. On the other hand, the carbon coatings formed under other conditions and all the silica coatings were completely lost during vacuum exposure. The retained strengths were in the range of 0 to 1.6 GPa. The silica film was found to be ineffective for suppressing the active-oxidation during vacuum exposure.

1. Introduction

Silicon carbide has excellent oxidation resistance at elevated temperatures under high oxygen potentials. This is because a stable silica film is formed on the surface of silicon carbides and it retards further oxidation of the silicon carbides. On the other hand, under low oxygen potentials, silicon carbide gasifies into SiO and CO, leaving no residue. In the extreme case, silicon carbide is completely lost. The former and the latter oxidation of silicon carbide are called the passive-oxidation and the active-oxidation, respectively. Polycarbosilane-derived silicon carbide fibers such as Nicalon, Hi-Nicalon and Hi-Nicalon S (Nippon Carbon Co., Japan) also were subject to active-oxidation during high-temperature exposure under low oxygen potentials [1–5]. Particularly, under reduced pressures, the active-oxidation was severely caused by a very slight amount of retained oxygen [4, 5]. Nicalon and Hi-Nicalon S fibers, as a consequence of active-oxidation, were completely lost during exposure at 1773 K under a pressure of 1.32 Pa. On the other hand, Hi-Nicalon fiber was relatively resistant to the active-oxidation under a reduced pressure. Excess carbon present in Hi-Nicalon fiber appears to be effective for the retardation of active-oxidation. In addition, silica film suppressed completely the active-oxidation of silicon carbide fibers under one atmospheric pressure [6]. Therefore, there is the possibility that carbon and silica coatings are useful for suppressing the active-oxidation of silicon carbide fibers under reduced pressures.

In the previous paper, Hi-Nicalon fiber was heat-treated at 1773 K in CO-CO_2 gas mixtures [7]. While Hi-Nicalon fibers were coated with the carbon film of different thickness at $p_{CO_2} \leq 5 \times 10^2$ Pa, they were coated with the silica film of different thickness at $p_{CO_2} \geq 10^3$ Pa. In the present work, Hi-Nicalon fibers were heat-treated at 1773 K in CO-CO_2 gas mixtures with different CO_2 partial pressures, and subsequently they were exposed at 1773 K under a reduced pressure of 1.32 Pa. Suppression effects of carbon and silica film on the active-oxidation of Hi-Nicalon fibers were investigated through mass change determination, X-ray diffraction analysis, resistivity measurements, scanning electron microscopic observation and tensile tests. The suppression of the active-oxidation by silica film under a reduced pressure was compared with that under one atmospheric pressure [6].

2. Experimental procedure

The sample employed in this study is Si-C fibers (Hi-Nicalon) manufactured by Nippon Carbon Co. (Tokyo, Japan). Hi-Nicalon fiber has a molar composition of $SiC_{1.39}O_{0.01}$ and a mean diameter of 14 μm. The coatings of Hi-Nicalon fiber with carbon and silica were conducted by the following method:

500 mg of fibers, 30 mm in length, were charged in a high-purity alumina boat and then were placed in an alumina tube of an SiC resistance furnace. After evacuation, a CO-CO_2 gas mixture was allowed to flow into the tube at a flow rate of 10^{-4} m^3/min. The partial

pressure of carbon dioxide in CO-CO_2 gas mixtures was controlled to each value of 0 (pure CO), 10^2, 5×10^2, 5×10^3, 10^4 and 10^5 Pa (pure CO_2). The sample was heated at a rate of 300 K/h and after holding for 36 ks at 1773 K, it was cooled to room-temperature at 600 K/h.

Carbon- or silica-coated fibers were charged in a high-purity alumina boat and then were placed in an alumina tube of an SiC resistance furnace. After evacuation, the sample was heated at a rate of 300 K/h and after holding for 3.6 ks at 1773 K, it was cooled to room-temperature at 600 K/h. During exposure of the sample, a reduced pressure was kept through continuous evacuation.

The mass change was determined by weighing before and after vacuum exposure. The existing phases and β-SiC crystallite size of the fibers were determined by X-ray diffractometer (XRD). Morphologies of the fibers were examined by field-emission scanning microscopy (FE-SEM). The specific resistivity measurements were performed at room temperature by applying a direct current to a single fiber. Both ends of a fibers were attached, with an electroconductive resin, to copper electrode plates spaced 0.8 mm apart. Ten fibers were tested to determine the average resistivity. Room-temperature tensile tests were conducted using a 10 mm gauge length and a crosshead speed of 2 mm/min. The average of 10 tensile tests was taken as the tensile strength under each heat-treatment.

3. Results

3.1. Mass change and gas evolution

Hi-Nicalon fibers, which were previously heat-treated for 36 ks at 1773 K in CO-CO_2 gas mixtures and were coated with carbon or silica film, were exposed for 3.6 ks at 1773 K under a pressure of 1.32 Pa. Fig. 1 shows the mass change, $100 \cdot \Delta W/W_0$, of the fibers after exposure under a reduced pressure (vacuum exposure) as a function of CO_2 partial pressure in heat treatment atmospheres. Here, ΔW and W_0 are the difference in fiber mass before and after vacuum exposure and the initial mass of the fibers, respectively. The calculated values for the mass change are considered in the post paragraph. Hi-Nicalon fiber, in the as-received state, produced a large mass loss of 59.32% after vacuum exposure. The mass loss was attributable to the thermal decomposition of amorphous silicon oxycarbide (SiC_XO_Y) phase and the subsequent active-oxidation of β-SiC grains [1, 2]. The complete decomposition of SiC_XO_Y phase yields a mass loss of about 2.3% for Hi-Nicalon fiber [8]. The retained oxygen in an evacuated alumina tube ($p_{O_2} = 0.27$ Pa) is thought to cause the active-oxidation of Hi-Nicalon fiber. For example, under one atmospheric pressure of Ar-O_2 gas mixtures, Hi-Nicalon fiber was actively oxidized at $p_{O_2} \leq 10$ Pa [2]. While the carbon coating of Hi-Nicalon fiber was conducted by heat-treatment in CO-CO_2 gas mixtures of $p_{CO_2} \leq 5 \times 10^2$ Pa, the silica coating of Hi-Nicalon fiber was conducted by heat-treatment at $p_{O_2} \geq 5 \times 10^3$ Pa [4]. There was only slight mass loss of $\Delta W/W_0 = -0.70\%$ for the fibers heat-treated at $p_{CO_2} = 0$ Pa (in pure CO gas). It was found that the thermal decomposition of the SiC_XO_Y phase was well suppressed by the carbon film, because the measured mass loss was much smaller than a mass loss produced by complete decomposition, $\Delta W/W_0 = -2.3\%$ [8]. Large mass loss of $\Delta W/W_0 \fallingdotseq -50\%$ observed in the fibers heat-treated at $p_{CO_2} = 10^2$ and 5×10^2 Pa demonstrates that the active-oxidation, as well as 100% decomposition of the SiC_XO_Y phase, occurred during vacuum exposure. The fibers heat-treatedd at $p_{CO_2} = 5 \times 10^3$, 10^4 and 10^5 Pa produced still larger mass loss ($\Delta W/W_0 = -73$ to 87%). Thus the silica coating was found to be less effective in retarding the active-oxidation of Hi-Nicalon fiber during vacuum exposure.

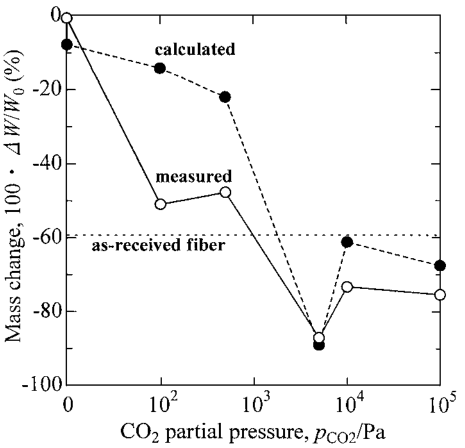

Figure 1 Mass change of Hi-Nicalon fibers after vacuum exposure of 3.6 ks at 1773 K as function of CO_2 partial pressure in heat treatment atmosphere.

Fig. 2 shows the pressure change in the reaction tube during heating from room temperature to 1773 K and then holding at 1773 K for 3.6 ks under a reduced pressure. When the as-received fiber was exposed under a reduced pressure, an increase in pressure began at

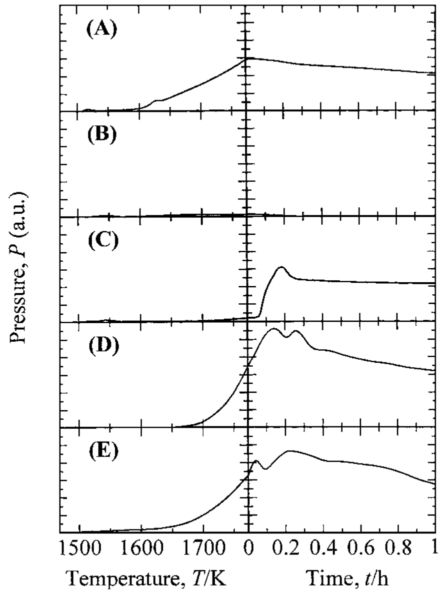

Figure 2 Change in pressure in reaction tube during exposure at 1773 K under pressure of 1.32 Pa: as-received fiber (A), fiber heat-treated for 36 ks at 1773 K in CO-CO_2 gas mixtures of $p_{CO_2} = 0$ Pa (B), 5×10^2 Pa (C), 5×10^3 Pa (D) and 10^5 Pa (E).

about 1600 K and the pressure reached to a maximum at 1773 K. No change in pressure was observed for the fiber heat-treated at $p_{CO_2} = 0$ Pa (in pure CO gas), being consistent with the mass change data (Fig. 1). For the fiber heat-treated at $p_{CO_2} = 5 \times 10^2$ Pa, there was little increase in pressure during heating to 1773 K and there was an abrupt increase in pressure after holding for about 10 min at 1773 K. On the other hand, for the fibers coated with silica film at $p_{CO_2} = 5 \times 10^3$ and 10^5 Pa, the pressure was gradually increased at about 1600 K to 1773 K and a high pressure was allowed to continue during holding at 1773 K. This, together with the mass change data (Fig. 1), reveals that the silica (cristobalite) film is ineffective in retarding the active-oxidation of Hi-Nicalon fiber during vacuum exposure.

3.2. X-ray diffraction and β-SiC crystal size

Fig. 3 shows the X-ray diffraction patterns for the fibers after vacuum exposure. Although a broad pattern of amorphous carbon at $2\theta \fallingdotseq 26°$ was retained for the fibers heat-treated state at $p_{CO_2} = 0$ Pa (in pure CO gas), it became obscure for the fibers heat-treated at $p_{CO_2} = 10^2$ and 5×10^2 Pa [7]. During vacuum exposure, the carbon film produced by the heat-treatment at $p_{CO_2} = 0$ Pa was little oxidized by the retained oxygen in the reaction tube, whereas the carbon films formed at $p_{CO_2} = 10^2$ and 5×10^2 Pa were completely oxidized. The cristobalite peaks observed after heat treating at $p_{CO_2} \geq 5 \times 10^3$ Pa [7] disappeared after vacuum exposure. This implies that the cristobalite film reacted with the unoxidized core during vacuum exposure.

The apparent β-SiC crystal size, D_{SiC}, was calculated from the (111) peak of β-SiC, using Scherrer's formula. The relationship between D_{SiC} and p_{CO_2} of heat-treatment atmosphere is shown in Fig. 4. The heat-treatment for 36 ks at 1773 K in CO-CO_2 gas mixtures increased the D_{SiC} value by a factor of 2.5 to 3. The subsequent exposure for 3.6 ks at 1773 K under a reduced pressure caused only a slight increase in the D_{SiC} value. The coarsening of β-SiC crystals, which is responsible for the thermal decomposition of SiC_XO_Y phase and the crystallization of noncrystallized Si-C phase [9, 10], is strongly dependent on heating temperature and holding time. Therefore, the same thermal history of Hi-Nicalon fiber allowed β-SiC crystals to grow to nearly identical size.

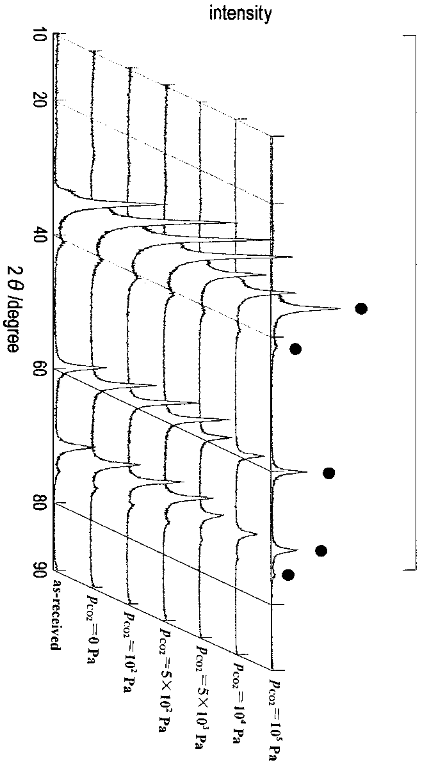

Figure 3 X-ray diffraction patterns for fibers exposed for 36 ks at 1773 K under reduced pressure after heat-treatment of 36 ks at 1773 K in CO-CO_2 gas mixtures with different CO_2 partial pressures. ●: β-SiC.

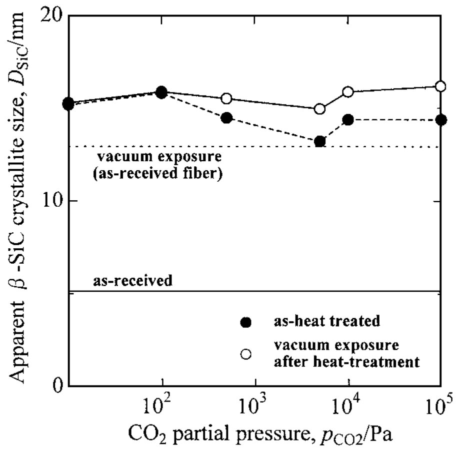

Figure 4 Relationship between apparent SiC crystal size after vacuum exposure for 3.6 ks at 1773 K and CO_2 partial pressure of heat-treatment atmosphere.

3.3. Specific resistivity of fibers

Fig. 5 shows the specific resistivity, ρ, of the fibers in the as-heat-treated state and after exposure under a reduced pressure of 1.32 Pa (vacuum exposure). The heat-treatment at 1773 K in CO-CO_2 gas mixtures caused the decrease in the resistivity of Hi-Nicalon fiber. In particular, the formation of carbon film at $p_{CO_2} \leq 5 \times 10^2$ Pa caused 2 orders of magnitude drop of resistivity. The vacuum exposure led to large increase in specific

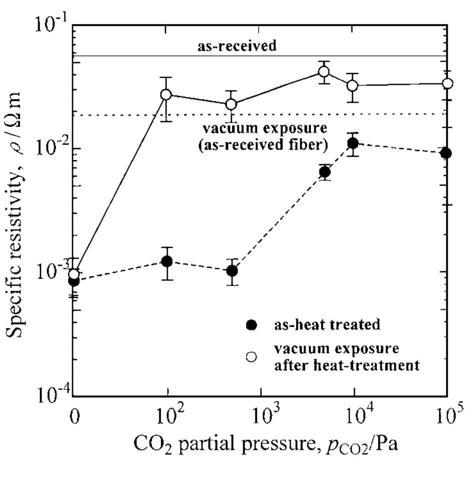

Figure 5 Relationship between specific resistivity of Hi-Nicalon fibers after vacuum exposure for 3.6 ks at 1773 K and CO_2 partial pressure of heat-treatment atmosphere.

resistivity for the fibers heat-treated at $p_{\mathrm{CO_2}} \geq 10^2$ Pa. This seems to be attributable to the disappearance of carbon film and the subsequent breakdown of fiber structure by the active-oxidation. Since the carbon film of the fiber heat-treated at $p_{\mathrm{CO_2}} = 0$ Pa (in pure CO gas) was hardly oxidized during vacuum exposure, resulting in keeping of a low resistivity of about 10^{-3} Ω m.

3.4. Fiber morphologies

Fig. 6 shows the SEM photographs of the as-received fiber and the carbon-coated fibers after vacuum exposure. When the as-received fiber was subjected to vacuum exposure, many pores were produced on the surface as though they were circular indentations (A). However, its fractured surface, like that in the as-received state, was pore-free and glassy (B). The shrinkage in the mean diameter from 14.0 to 11.1 μm was caused by the active-oxidation during vacuum exposure. Almost all of the carbon film on the fiber heat-treated at $p_{\mathrm{CO_2}} = 0$ Pa (in CO gas) remained after vacuum exposure. In addition, it had a smooth surface and a glassy cross-section (C and D). Vacuum exposure of the fibers heat-treated at $p_{\mathrm{CO_2}} = 10^2$ and 5×10^2 Pa led to the complete loss of carbon films (E–H). Although the surface was porous or rugged, the fractured surface was still glassy. In particular, for the fibers heat-treated at $p_{\mathrm{CO_2}} = 5 \times 10^2$ Pa, a marked shrinkage in fiber diameter was caused by the oxidation of thick carbon film and the subsequent active-oxidation, resulting in the reduction of mean fiber diameter from 14.4 to 10.1 μm (G, H).

Fig. 7 shows the morphologies of the silica-coated fibers after vacuum exposure. The silica (cristobalite) film of all the fibers was completely lost after vacuum exposure, being consistent with the XRD data (Fig. 3). The vacuum exposure of Hi-Nicalon fiber heat treated at $p_{\mathrm{CO_2}} = 10^5$ Pa (in pure $\mathrm{CO_2}$ gas) resulted in the formation of deep grooves on the surface (A). This implies that part of the cracking of cristobalite film was produced during passive-oxidation [7]. Yet, most of the cracks are produced by α-to-β cristobalite transformation during cooling from the oxidation temperature to room temperature. The fiber heat-treated at $p_{\mathrm{CO_2}} = 10^4$ Pa, as a consequence of active-oxidation, has a highly porous surface after vacuum exposure (C). Hi-Nicalon fibers were subjected to serious damage during heat-treating at $p_{\mathrm{CO_2}} = 5 \times 10^3$ Pa [7], leaving large recesses on the surface after vacuum exposure (E). The loss of cristobalite film permitted the mean diameter of fibers to reduce from 13.8 to 11.5 μm. The cross section of the fibers was pore-free after vacuum exposure, implying that the active-oxidation proceeded from the surface towards the center of fibers (B, D and F).

Fig. 8 shows the magnified SEM photos of the fiber surface after vacuum exposure. After active-oxidation, all the fibers coated with carbon and silica (D–H) have a similar surface structure as well as the as-received fiber (B). The active-oxidation renders the surface porous and undulating. The outermost surface of the carbon film was partly oxidized during vacuum exposure of the fiber heat-treated in CO gas. However, the fiber surface remained relatively smooth, owing to the absence of active-oxidation (C).

3.5. Room temperature tensile strength

Fig. 9 shows the room-temperature tensile strength, σ, of the fibers in the as-heat treated state and after vacuum exposure. The tensile strength of the fiber heat-treated in pure CO gas remained almost unchanged before and after vacuum exposure ($\sigma = 1.7$ GPa). This result is consistent with resistivity measurement and SEM observation, suggesting that the active-oxidation of the fiber core was suppressed by the carbon film. The carbon films produced at $p_{\mathrm{CO_2}} = 10^2$ and 5×10^2 Pa were ineffective for the retardation of active-oxidation, resulting in almost same strength as the as-received fiber without a carbon film ($\sigma \fallingdotseq 1.2$ GPa). On the other hand, the silica-coated fibers show further degradation of strength after vacuum exposure. Particularly, it may be noted that the fiber heat-treated at $p_{\mathrm{CO_2}} = 5 \times 10^3$ Pa lost strength completely.

4. Discussion

Hi-Nicalon fibers were coated with a carbon film during heat treating in CO-$\mathrm{CO_2}$ gas mixtures of $p_{\mathrm{CO_2}} \leq 5 \times 10^2$ Pa [7]. Thin carbon film formed in pure CO gas was found to be very efficient in suppressing the thermal decomposition of the $\mathrm{SiC}_X\mathrm{O}_Y$ phase and the active-oxidation of β-SiC grains during exposure under a reduced pressure (vacuum exposure). On the other hand, there was a large mass loss ($\Delta W/W_0 \fallingdotseq -50\%$) for the fibers the heat-treatment at $p_{\mathrm{CO_2}} = 10^2$ and 5×10^2 Pa, despite of the presence of a thick carbon film. Yet, it was smaller than the mass loss of the as-received fibers after vacuum exposure ($\Delta W/W_0 \fallingdotseq -59\%$). This shows that such carbon films were ineffective in suppressing the active-oxidation of fiber core. The removal of the carbon film and subsequent active-oxidation of the β-SiC grains are thought to be caused by the retained oxygen in the alumina tube. The removal of carbon is expressed by the following oxidation reaction:

$$\begin{gathered}\mathrm{C(s)} + 1/2\mathrm{O_2(g)} = \mathrm{CO(g)} \\ \Delta G^\circ\ (\mathrm{J/mol}) = -114390 - 85.77\,T\ [11]\end{gathered} \tag{1}$$

The partial pressure of retained oxygen in the tube is estimated to be $p_{\mathrm{O_2}} = 0.27$ Pa under a reduced pressure of 1.32 Pa. From Equation 1, the equilibrium CO pressure, p_{CO}, was thermodynamically calculated to be 1.17×10^{10} Pa. This demonstrates that the oxidation reaction (1) can proceed at a reduced pressure of 1.32 Pa. The heat-treatment in CO-$\mathrm{CO_2}$ gas mixtures produces the carbon film on the fibers according to the following overall reaction [12]:

$$\mathrm{SiC_{1.39}O_{0.01}(s)} + 0.99\mathrm{CO(g)} = \mathrm{SiO(g)} + 2.38\mathrm{C(s)} \tag{2}$$

The above reaction caused the mass loss of the fibers at $p_{\mathrm{CO_2}} \leq 5 \times 10^2$ Pa. Using the stoichiometry of

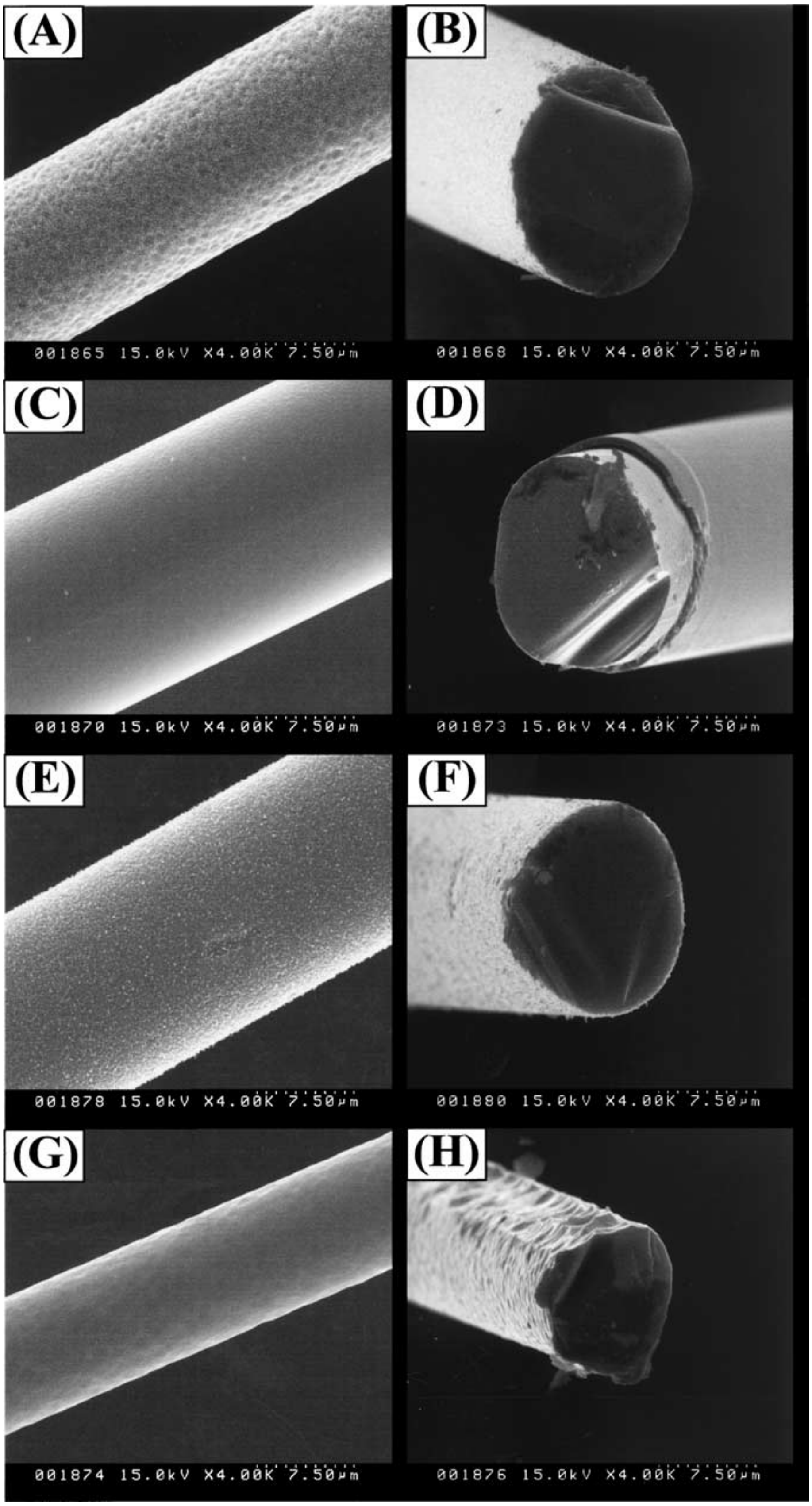

Figure 6 SEM photographs of as-received fiber (A, B) and fibers exposed for 3.6 ks at 1773 K under pressure of 1.32 Pa (C–H): heat-treatment of 36 ks at 1773 K in CO-CO$_2$ gas mixtures of $p_{\mathrm{CO}_2} = 0$ Pa (C, D), 10^2 Pa (E, F) and 5×10^2 Pa (G, H).

reaction (2), the mass of carbon film formed around the fibers was estimated from the measured value of mass loss. Then, the mass loss by complete oxidation of the carbon film, $100 \cdot \Delta W / W_0$, was calculated from the mass of carbon film. The calculated values are shown in Fig. 1. The carbon film on the fiber heat-treated at $p_{\mathrm{CO}_2} = 0$ Pa (in pure CO gas) was hardly oxidized during vacuum exposure. As shown in Fig. 6, the carbon film was distinctly retained after vacuum exposure (photo (D)). Since only the outermost surface of the

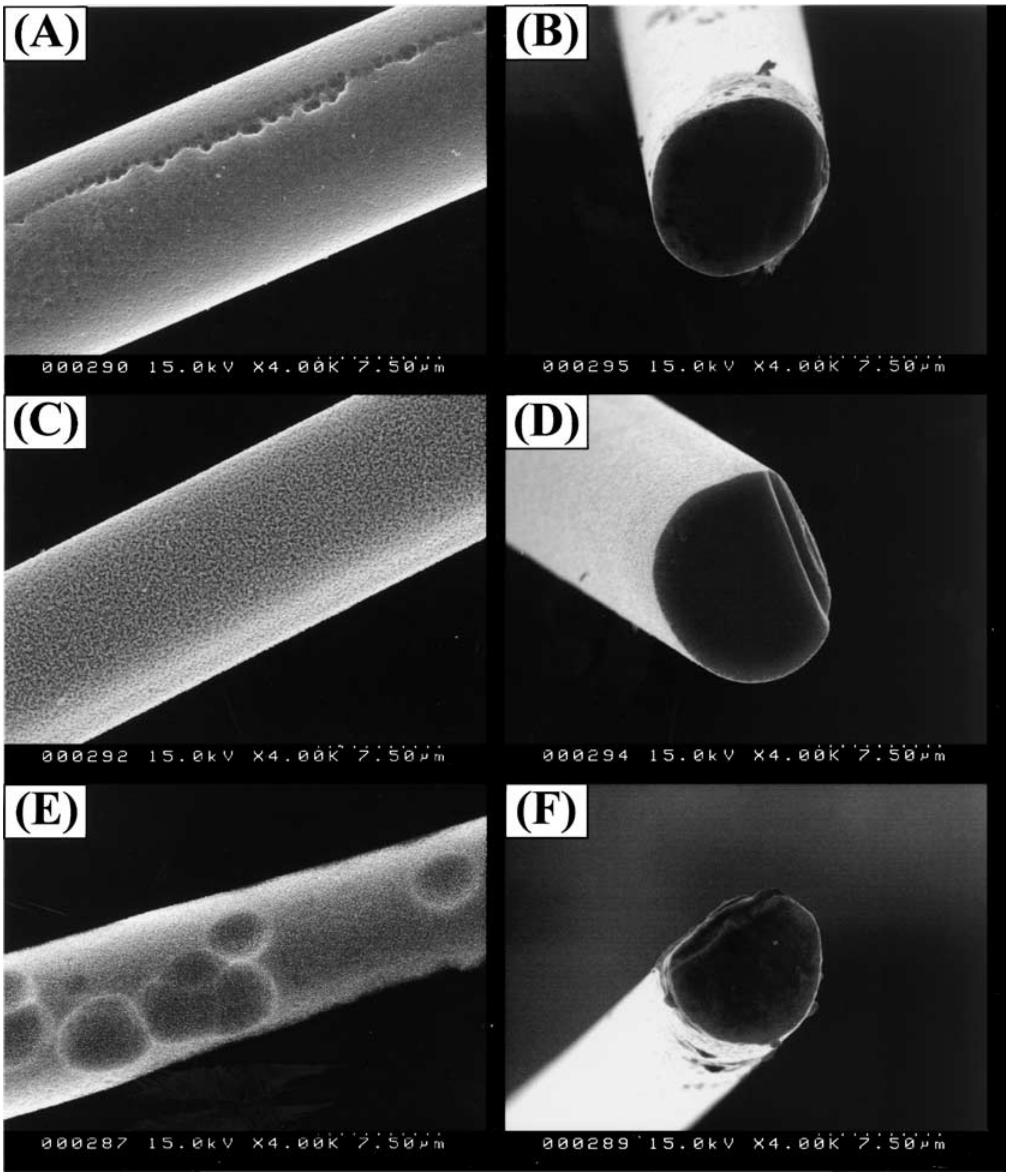

Figure 7 SEM photographs of fibers exposed for 3.6 ks at 1773 K under pressure of 1.32 Pa after heat-treatment for 36 ks at 1773 K in CO-CO_2 gas mixtures of $p_{CO_2} = 10^5$ Pa (A, B), 10^4 Pa (C, D) and 5×10^3 Pa (E, F).

carbon film was partly oxidized, there was a slight mass loss $\Delta W/W_0 = -0.70\%$ and a very small increase of pressure in the tube (Figs 1 and 2). In addition, Fig. 9 reveals that hardly any degradation of fiber strength was caused during the vacuum exposure. On the other hand, the calculated mass losses were smaller by about 40 and 30% than the measured one for the fibers heat-treated at $p_{CO_2} = 10^2$ and 5×10^2 Pa, respectively. This implies that the vacuum exposure caused the thermal decomposition of the SiC_XO_Y phase ($\Delta W/W_0 = -2.3\%$) and the subsequent active-oxidation of β-SiC grains after complete combustion of the carbon film. Complete removal of the carbon film was verified by a large increase of the specific resistivity after vacuum exposure (Fig. 5). Fig. 8 shows that the surface morphology of the fibers was rugged and porous after active-oxidation (D and E). The removal of carbon film seems to be strongly dependent upon the porosity of the carbon film. While the carbon film produced by heat-treating in pure CO gas was relatively dense owing to a slow rate of carbon formation, the carbon films produced at $p_{CO_2} = 10^2$ and 5×10^2 Pa were porous probably due to simultaneous oxidation of carbon by CO_2 gas [7]. Therefore, a porous carbon film, as a consequence of fast gaseous diffusion through pores, grew rapidly, resulting in the formation of thick carbon films at $p_{CO_2} = 10^2$ and 5×10^2 Pa. Naturally, such carbon films were easily oxidized during vacuum exposure.

The fibers were passively oxidized during heat-treating at $p_{CO_2} \geq 5 \times 10^3$ Pa, allowing the fibers to coat with a cristobalite film. The formation of cristobalite film is expressed by the following overall equation:

$$SiC_{1.39}O_{0.01}(s) + 3.38CO_2(g) = SiO_2(s) + 4.77CO(g) \tag{3}$$

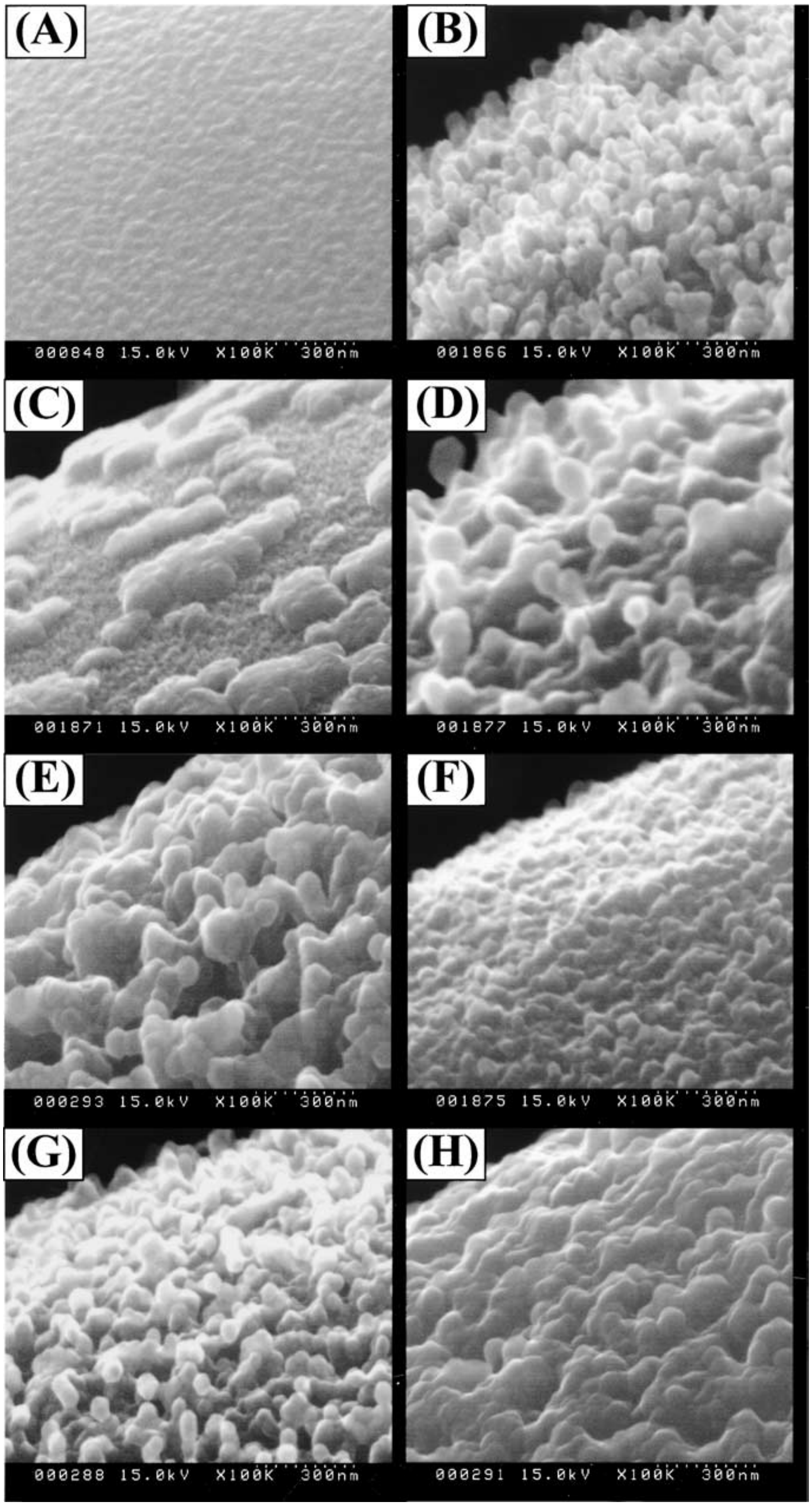

Figure 8 Surface morphologies of as-received fiber (A) and fibers exposed for 3.6 ks at 1773 K under pressure of 1.32 Pa (B–H): in as-received state (B) and after heat-treatment for 36 ks at 1773 K in CO-CO$_2$ gas mixtures of $p_{CO_2} = 0$ Pa (C), 10^2 Pa (D), 5×10^2 Pa (E), 5×10^3 Pa (F), 10^4 Pa (G) and 10^5 Pa (H).

The cristobalite film has a tendency to react with the unoxidized core during high-temperature exposure:

$$SiC_{1.39}O_{0.01}(s) + 2.38SiO_2(s) = 3.38SiO(g) + 1.39CO(g) \quad (4)$$

The above reaction (4) proceeded gradually from 1600 to 1773 K under a reduced pressure of 1.32 Pa, whereas the oxidation of carbon film occurred suddenly during holding at 1773 K (Fig. 2). XRD analysis and SEM observation show that the cristobalite film was completely

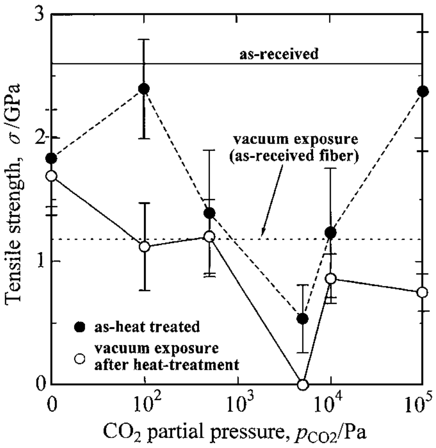

Figure 9 Room-temperature tensile strength of Hi-Nicalon fibers after vacuum exposure for 3.6 ks at 1773 K as function of CO_2 partial pressure of heat-treatment atmosphere.

lost after vacuum exposure (Figs 3 and 6). Using the stoichiometry of the passive-oxidation of Hi-Nicalon fiber (3), the amount of cristobalite formed was evaluated from the measured mass gain and then the mass loss after completion of reaction (4) was calculated from its amount. As can be seen from Fig. 1, the measured mass losses were larger than the calculated ones for the fibers heat-treated at $p_{CO_2} = 10^4$ and 10^5 Pa. Such a difference is responsible for the thermal decomposition of SiC_XO_Y phase ($\Delta W/W_0 = -2.3\%$) and the active-oxidation of β-SiC grains. Therefore, Fig. 8 shows that these fibers had similar surface morphologies to the carbon-coated fibers which were subjected to active-oxidation during vacuum exposure. In addition, Fig. 1 shows that most of the mass loss was due to reaction (4). In particular, for the fiber heat-treated at $p_{CO_2} = 5 \times 10^3$ Pa, the mass loss appears to be principally attributable to the occurrence of reaction (4), because of the presence of the very thick silica film. In such case, little active-oxidation occurred during vacuum exposure, resulting in the surface morphology distinct from that after active-oxidation (Fig. 8F).

Gas bubbles consisting of SiO and CO may be produced at the interface between the cristobalite film and the unoxidized core during exposure at elevated temperature. The equilibrium pressures of SiO and CO were approximately estimated by the following equation:

$$\begin{gathered} 2SiO_2(s) + SiC(s) = 3SiO(g) + CO(g)(5) \\ \Delta G^\circ\,(\mathrm{J/mol}) = 1457790 - 691.99T\ [11] \end{gathered} \tag{5}$$

The equilibrium pressures of SiO and CO were calculated to be 8.74×10^2 and 2.62×10^3 Pa at 1773 K, respectively. Therefore, the pressure of bubble formed at the interface between the cristobalite film and the unoxidized core was estimated to be 3.50×10^3 Pa at 1773 K. The active-to-passive oxidation transition is dependent upon whether the silica film is destroyed by the gas bubbles or not [12, 13]. The cristobalite film was destroyed by the bubble during vacuum exposure, because its pressure (3.50×10^3 Pa) was much higher than the pressure in the alumina tube (1.32 Pa). Then the core surface exposed by the removal of silica film was actively oxidized by the retained oxygen in the tube ($p_{O_2} = 0.27$ Pa). Under one atmospheric pressure of Ar-O_2 gas mixture and at 1773 K, Hi-Nicalon fiber with very thin silica film of 0.013 μm was passively oxidized even in the active-oxidation region ($p_{O_2} = 1$ Pa) [6]. Gas bubbles are probably produced at the interface between the silica film and the fiber core as well. However, the silica film can endure well the pressure of bubble (3.50×10^3 Pa) which is much smaller than one atmospheric pressure (10^5 Pa). Therefore, the active-oxidation of the unoxidized core could be perfectly suppressed by the very thin silica film, and moreover passive-oxidation took place despite the active-oxidation region of Hi-Nicalon fiber [2, 6]. Yet, under reduced pressures, no silica film can suppress the active-oxidation even if it is sufficiently thick.

5. Conclusion

The thermal stability of Hi-Nicalon fiber at 1773 K under a reduced pressure of 1.32 Pa was strongly dependent upon the physical properties of carbon film. The dense carbon film formed in pure CO gas suppressed nearly completely the thermal decomposition of the SiC_XO_Y phase and the subsequent active-oxidation of β-SiC grains. The porous carbon films formed in CO-CO_2 gas mixtures of $p_{CO_2} \geq 10^2$ Pa were completely oxidized and they could no longer suppress the active-oxidation of the fiber core. The silica coating was ineffective in improving the thermal stability of Hi-Nicalon fibers under a reduced pressure of 1.32 Pa. The interaction of silica film with unoxidized core begun at about 1600 K. Then the silica film was completely lost during holding at 1773 K, resulting in the active-oxidation of the fiber core. The occurrence of active-oxidation, as a consequence of the disappearance of carbon and silica film, caused a large degradation of fiber strength after vacuum exposure. Finally, only the carbon-coated fiber, which was produced by the heat-treatment in pure CO gas, was stable at 1773 K under a reduced pressure of 1.32 Pa and retained a strength of 1.7 GPa.

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