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High temperature exposure of low-oxygen SiC fibers (Hi-Nicalon) in CO-CO_2 gas mixtures

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The oxidation behavior and thermal stability of Si-C fibers (Hi-Nicalon) in CO-CO_2 gas mixtures were investigated at 1773 K, through mass change determination, XRD analysis, resistivity measurement, SEM observation and tensile test. Mass gain and cristobalite formation were observed at $p_{CO_2} \geqq 2 \times 10^3$ Pa, showing the occurrence of passive-oxidation of the fibers. The active-oxidation, which was characterized by the mass loss, involved the formation of carbon film at $p_{CO_2} \leqq 5 \times 10^2$ Pa. 65–90% of the strength in the as-received state was retained after the active-oxidation at $p_{CO_2} \leqq 10^2$ Pa and after the passive-oxidation at $p_{CO_2} \geqq 5 \times 10^4$ Pa. Surface imperfections produced very large decrease in tensile strength in the CO_2 partial pressure range of 5×10^2 to 10^4 Pa.
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1. Introduction

Since polycarbosilane-derived silicon carbide fibers have excellent high-temperature strength and oxidation resistance, their wide-spread applications at elevated temperatures may be expected, in addition to the use as reinforcing fibers of ceramic-matrix composites. However, such applications are confined under particular environments. When Si-C-O fibers (Nicalon, Nippon Carbon Co.) are exposed in inert gas above 1500 K, marked degradation of strength is caused by the thermal decomposition of amorphous silicon oxycarbide phase. This degradation could be prevented by introducing the electron-beam irradiation curing method of polycarbosilane fibers. The silicon carbide fibers have excellent oxidation resistance under higher oxygen potentials. This is because the SiO_2 film formed by passive-oxidation retards further oxidation of the fibers. The thermal stability and oxidation of silicon carbide fibers has been extensively investigated under inert and highly-oxidizing environments (Ar, N_2, O_2 and air). On the other hand, little reports were made on the oxidation behavior of the fibers under lower oxygen pressure and in CO and/or CO_2 gas. Under lower oxygen potentials, the active-oxidation allows to vaporize SiO gas from the silicon carbide fibers. Therefore, the active-oxidation does the most serious damage to fiber strength. The active-to-passive oxidation transitions and thermal stability for various types of silicon carbide fibers were studied in Ar-O_2 gas mixtures and under reduced pressures [1–5]. The strength degradation of Nicalon fibers was effectively reduced after exposure in Ar-CO gas mixtures at higher temperatures [6–8]. The exposure of S-C fibers (Hi-Nicalon, Nippon Carbon Co.) in CO gas at 1773 K caused large mass loss which is characteristic of active-oxidation, in addition to the formation of carbon film [9]. On the other hand, Nicalon and Hi-Nicalon fibers were oxidized in the passive-oxidation regime in CO_2 gas at 1773 K [10, 11]. Furthermore, the oxygen potential region of the active-to-passive oxidation transition for the oxidation of Hi-Nicalon fibers in Ar-CO_2 gas mixtures was found to be nearly identical to that in Ar-O_2 gas mixtures [12]. Thus, the oxidation behaviors of silicon carbide fibers in CO was quite different from that in CO_2 gas. Therefore, the oxidation in CO-CO_2 gas mixtures appears to give several interesting results. In the present work, the oxidation behavior and thermal stability of Hi-Nicalon fibers at 1773 K in a wide range of CO_2 partial pressures were studied through mass change determination, X-ray diffraction analysis, resistivity measurements, scanning electron microscopic observation and tensile tests. The CO_2 partial pressure for the active-to-passive oxidation transition was determined for Hi-Nicalon in CO-CO_2 gas mixtures. The experimental results were compared with those for the oxidation of Hi-Nicalon in Ar-O_2 and Ar-CO_2 gas mixtures [2, 12].

2. Experimental method

The sample employed in this study is Si-C fibers (Hi-Nicalon) manufactured by Nippon Carbon Co. (Tokyo, Japan). Hi-Nicalon fibers have a molar composition of $SiC_{1.39}O_{0.01}$ and a mean diameter of 14 μm. 500 mg of fibers, 3 cm in length, were charged in a high-purity alumina boat and then 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 100 cm^3/min. The partial pressure of carbon dioxide was changed over a range from 0 ($p_{CO} = 10^5$ Pa) to 10^5 Pa ($p_{CO} = 0$ Pa). The sample was heated at a rate of 300 K/min and after holding of 36 ks at 1773 K, it was cooled to room-temperature at 600 K/h.

The mass change of the fibers was determined by weighing before and after exposure in CO-CO_2 gas mixtures. The existing phases and β-SiC crystallite size of the fibers were determined by X-ray diffractometer (XRD). SiO_2 film was removed with NH_4OH + HF solution (molar ratio NH_4OH/HF = 1/5), in order to separate a single fiber from the bundles which adhered firmly to one another after passive-oxidation. Thus, the specific resistivity measurements and tensile tests were done with SiO_2-removed fibers (unoxidized cores). On the other hand, the carbon-coated fibers after active-oxidation, as it is, were subjected to resistivity measurement and tensile test.

3. Results

3.1. Mass change

Fig. 1 shows the relationship between the mass change and the partial pressure of carbon dioxide, p_{CO_2}, for fibers exposed for 36 ks at 1773 K and $p_{CO_2} = 0$–10^5 Pa. Here, W_0 is the initial mass of the fibers and ΔW is the mass change determined from the difference of the fiber mass before and after exposure. For comparison, the mass change for the fibers exposed for 36 ks at 1773 K in Ar-CO_2 gas mixtures are shown in this figure [12]. The exposure in CO-CO_2 gas mixtures yielded the mass gain at $p_{CO_2} \geqq 2 \times 10^3$ Pa and the mass loss at $p_{CO_2} \leqq 10^3$ Pa. The transition from mass gain to mass loss is slightly shifted in high p_{CO_2} value in comparison with that for fibers exposed in Ar-CO_2 gas mixtures. In addition, noteworthy is a large increase in the mass gain at $p_{CO_2} = 5 \times 10^3$ Pa. For the fibers exposed in Ar-CO_2 gas mixtures, such a increase was observed at $p_{CO_2} = 2 \times 10^3$ Pa.

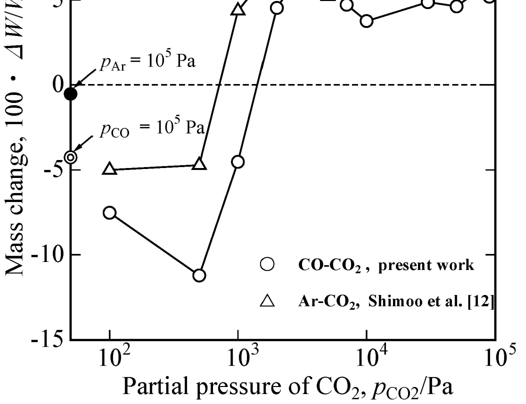

Figure 1 Mass change for Hi-Nicalon fibers exposed for 36 ks at 1773 K in CO-CO_2 and Ar-CO_2 gas mixtures.

3.2. X-ray diffraction analysis

Fig. 2 shows the X-ray diffraction patterns for the fibers exposed for 36 ks at 1773 K and $p_{CO_2} = 0$–10^5 Pa. Sharp cristobalite peaks were found at $p_{CO_2} \geqq 10^3$ Pa. The cristobalite formation implies the occurrence of passive-oxidation. In addition to the mass loss observed (Fig. 1), no cristobalite phase was detected at $p_{CO_2} \leqq 5 \times 10^2$ Pa. For the fibers exposed in Ar-CO_2 gas mixtures, the active-oxidation occurred at $p_{CO_2} \leqq 5 \times 10^2$ Pa [12]. A broad peak at $2\theta = 26°$ is attributable to the formation of carbon film, being confirmed by the exposure in CO gas [9]. Therefore, both the active-oxidation and the carbon formation appear to occur concurrently at $p_{CO_2} \leqq 5 \times 10^2$ Pa. The apparent crystal size of β-SiC, D_{SiC}, was calculated by using Scherrer' formula. Fig. 3 shows the relationship between D_{SiC} and p_{CO_2}. When Hi-Nicalon was exposed to 1773 K, the apparent crystal size of β-SiC increased by a factor of 3. However, the D_{SiC} value after exposure remained unchanged, independently on p_{CO_2}. Hi-Nicalon fibers are thought to be the micro-structure composite of noncrystallized Si-C phase, free carbon and amorphous SiC_XO_Y phase [13, 14]. The increase of D_{SiC} during high-temperature exposure is due to the crystallization of Si-C phase and the thermal decomposition of SiC_XO_Y phase.

3.3. Specific resistivity

Fig. 4 shows the specific resistivity of the fibers, ρ, as a function of CO_2 partial pressure. The resistivity of fibers is one of the properties which is quite sensitively to a minor change of microstructure. The exposure at 1773 K causes the crystallization of Si-C phase and the evolution of carbon aggregates, resulting in the decrease of resistivity [13, 14]. There was a significant decrease of about 80% in the resistivity of fibers throughout a range of cristobalite formation at $p_{CO_2} \geqq 10^3$ Pa (Fig. 2). The carbon formation at $p_{CO_2} \leqq 5 \times 10^2$ Pa caused a further reduction in resistivity: a decrease of ρ from 10^{-2} to $10^{-3}\Omega$m.

3.4. Fiber morphology

Fig. 5 shows the SEM photographs of the cross-section and surface for the fibers exposed for 36 ks in CO-CO_2 gas mixtures at 1773 K. As can be seen from Fig. 2, a film of smooth appearance is carbon at $p_{CO_2} \leqq 5 \times 10^2$ Pa. The exposure at $p_{CO_2} = 10^2$ Pa produced a very thin carbon film, as well as the exposure in pure CO gas (A, B) [9]. The carbon film was greatly advanced after exposure at $p_{CO_2} = 5 \times 10^2$ Pa, though its thickness scattered largely each fiber (C, D). XRD analysis indicates that the films formed at $p_{CO_2} \geqq 10^3$ Pa are cristobalite (E–J). The exposure at $p_{CO_2} = 5 \times 10^3$ Pa, as a consequence of severely exothermic oxidation, appears to cause the rise in temperature so as to allow cristobalite film to fuse (G, H). This is substantiated by a large mass gain, i.e., excessive passive-oxidation (Fig. 1). In spite of higher p_{CO_2} value, Hi-Nicalon was mildly oxidized at $p_{CO_2} = 10^4$ Pa, and its appearance was smooth and glassy.

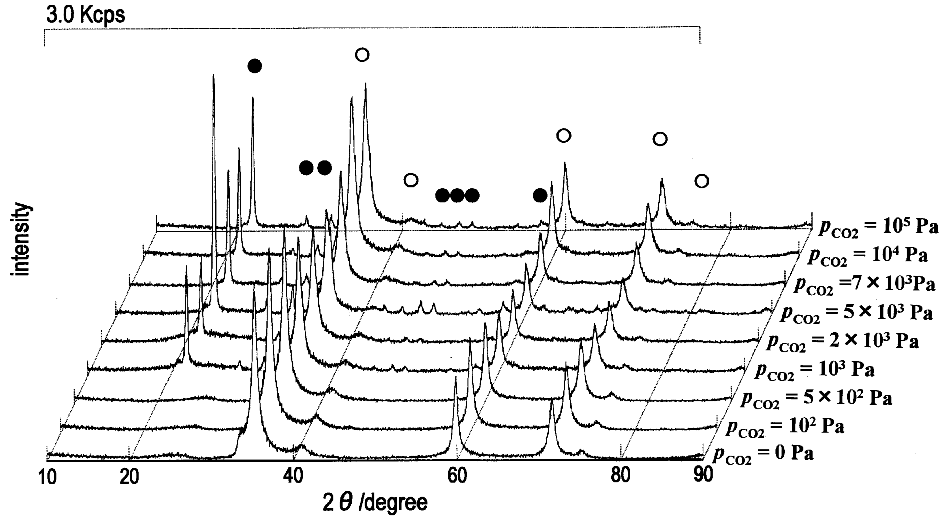

Figure 2 X-ray diffraction patterns for as-received fiber and fibers oxidized for 36 ks at 1773 K in CO-CO$_2$ gas mixtures with different CO$_2$ partial pressures. ○: β-SiC, ●: cristobalite.

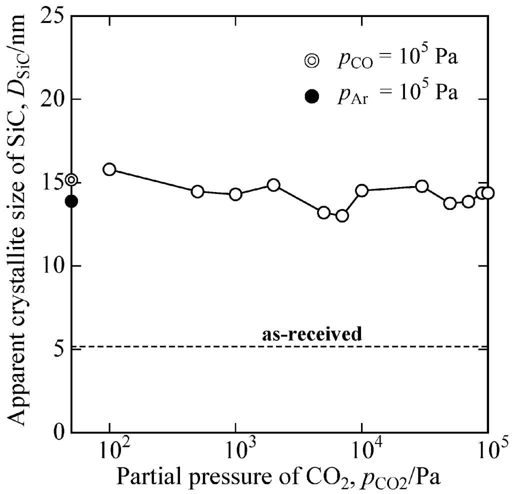

Figure 3 β-SiC crystallite size of fibers exposed for 36 ks at 1773 K in CO-CO$_2$ gas mixtures with different CO$_2$ partial pressures.

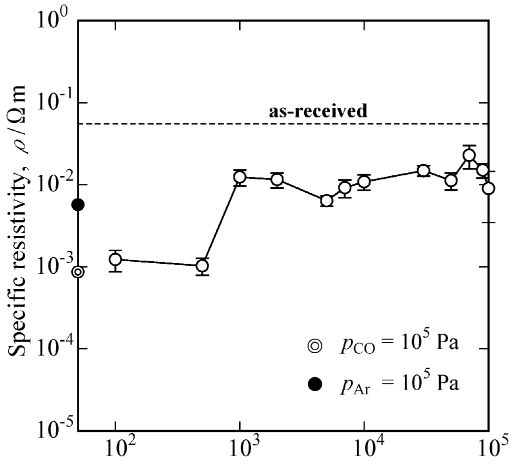

Figure 4 Specific resistivity of fibers exposed for 36 ks at 1773 K in CO-CO$_2$ gas mixtures with different CO$_2$ partial pressures.

Fig. 6 shows the surface morphologies of fiber cores, i.e., SiO$_2$-removed fibers after passive-oxidation. The fibers exposed at $p_{\mathrm{CO_2}} = 10^3$ and 5×10^3 Pa were irregularly oxidized, resulting in the formation of pits and grooves (B, C). On the other hand, the fiber core after oxidation in pure CO$_2$ gas (at $p_{\mathrm{CO_2}} = 10^5$ Pa) had a smooth surface (D), as well as the as-received fibers (A).

Fig. 7 shows the surface morphologies of carbon-coated fibers after active-oxidation at $T = 1773$ K and $p_{\mathrm{CO_2}} \leqq 5 \times 10^2$ Pa. The coarse grains were formed on a carbon film formed in pure CO gas: at $p_{\mathrm{CO_2}} = 0$ Pa (B). They are considered to be β-SiC crystals which were produced by the reaction of SiO gas (decomposition gas of SiC$_X$O$_y$ phase) with carbon film [15]. The surfaces of the carbon films formed at $p_{\mathrm{CO_2}} = 10^2$ and 5×10^2 Pa were relatively smooth (C, D), though they were a little rougher than the surface of as-received fibers (A).

Fig. 8 shows the magnified cross-section of carbon film formed on the fibers. The fiber exposed at $p_{\mathrm{CO_2}} = 0$ Pa (in pure CO gas) had a carbon film of 350 nm thickness (A). The carbon layer displays a rough and porous appearance, compared to the unreacted core. The carbon film developed to the greatest extent at $p_{\mathrm{CO_2}} = 5\times10^2$ Pa. All the cross section demonstrated in photo (B) is composed of carbon film. Photo (C) shows the interface between the carbon film and the unreacted core. Similarly, the carbon layer is rougher than the unreacted core. In addition, the carbon film formed at $p_{\mathrm{CO_2}} = 5 \times 10^2$ Pa displays porous morphology compared to that formed in pure CO gas.

3.5. Tensile strength

Fig. 9 shows the room-temperature tensile strength of the fibers exposed for 36 ks at 1773 K and $p_{\mathrm{CO_2}} =$ 0–10^5 Pa. The silica film was removed with NH$_4$F+HF solution, because the fibers adhered one to another after exposure at $p_{\mathrm{CO_2}} \geqq 10^3$ Pa. The fibers exposed at $p_{\mathrm{CO_2}} \leqq 5\times10^2$ Pa were subjected to tensile test in the as-carbon coated state, because a fiber could be separated from them. Marked degradation of strength was caused as the CO$_2$ partial pressure was lowered, and a minimum strength was attained at $p_{\mathrm{CO_2}} = 5 \times 10^3$ Pa. Then, further reduction decrease in CO$_2$ pressure at $p_{\mathrm{CO_2}} \leqq 5\times10^3$ Pa caused large increase in fiber strength.

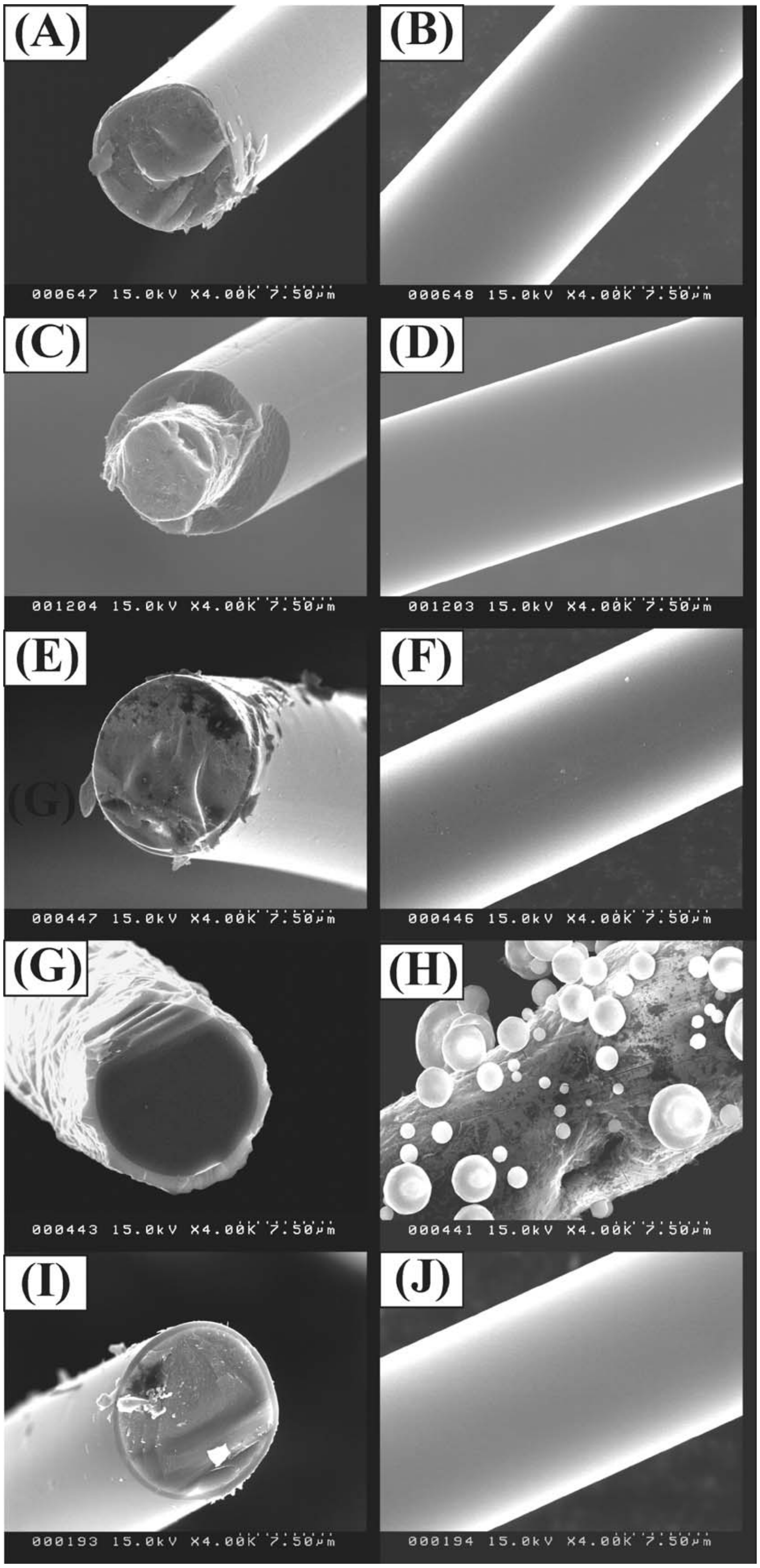

Figure 5 SEM photographs of fibers heat-treated for 36 ks at 1773 K in CO-CO$_2$ gas mixtures. (A, B): $p_{CO_2} = 10^2$ Pa, (C, D): $p_{CO_2} = 5 \times 10^2$ Pa, (E, F): $p_{CO_2} = 10^3$ Pa, (G, H): $p_{CO_2} = 5 \times 10^3$ Pa, (I, J): $p_{CO_2} = 10^4$ Pa.

4. Discussion

Figs 1 and 2 show that the mass gain and cristobalite formation are caused after exposure at $T = 1773$ K and $p_{CO_2} \geqq 2 \times 10^3$ Pa. It may be noted that the fibers exposed at $p_{CO_2} = 10^3$ Pa displayed the mass loss and formation of cristobalite. The same result was observed for the oxidation of Si-Ti-C-O fibers (Lox M, Ube Industries Co., Japan) in Ar-O$_2$ gas mixtures [3] and chemically vapor-deposited SiC in CO-CO$_2$ gas mixtures [16]. The oxidation of Hi-Nicalon fibers at $p_{CO_2} = 10^3$ Pa is thought to be within the active-to-passive transition oxidation transition domain. In addition to the mass

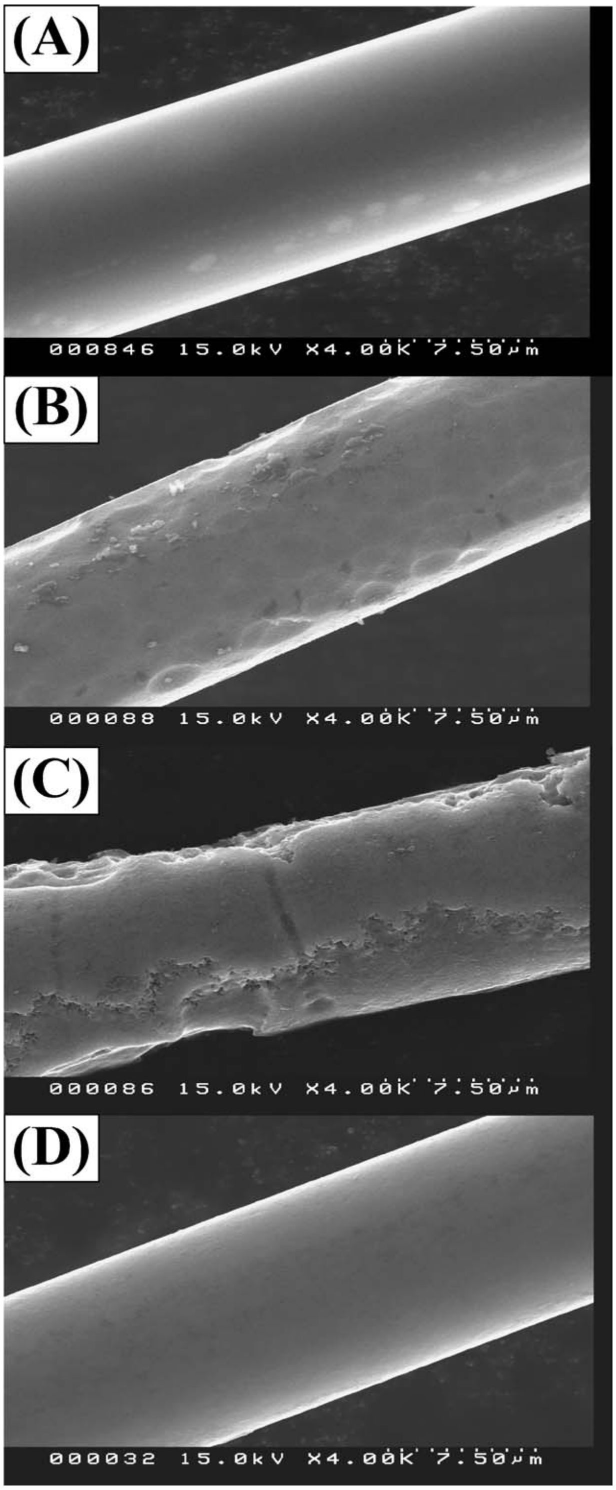

Figure 6 Surface morphologies of fiber core after passive-oxidation for 18 ks at 1773 K in CO-CO_2 gas mixtures. SiO_2 film was removed with NH_4F + HF solution. (A): as-received, (B): $p_{CO_2} = 10^3$ Pa, (C): $p_{CO_2} = 5 \times 10^3$ Pa, (D): $p_{CO_2} = 10^5$ Pa.

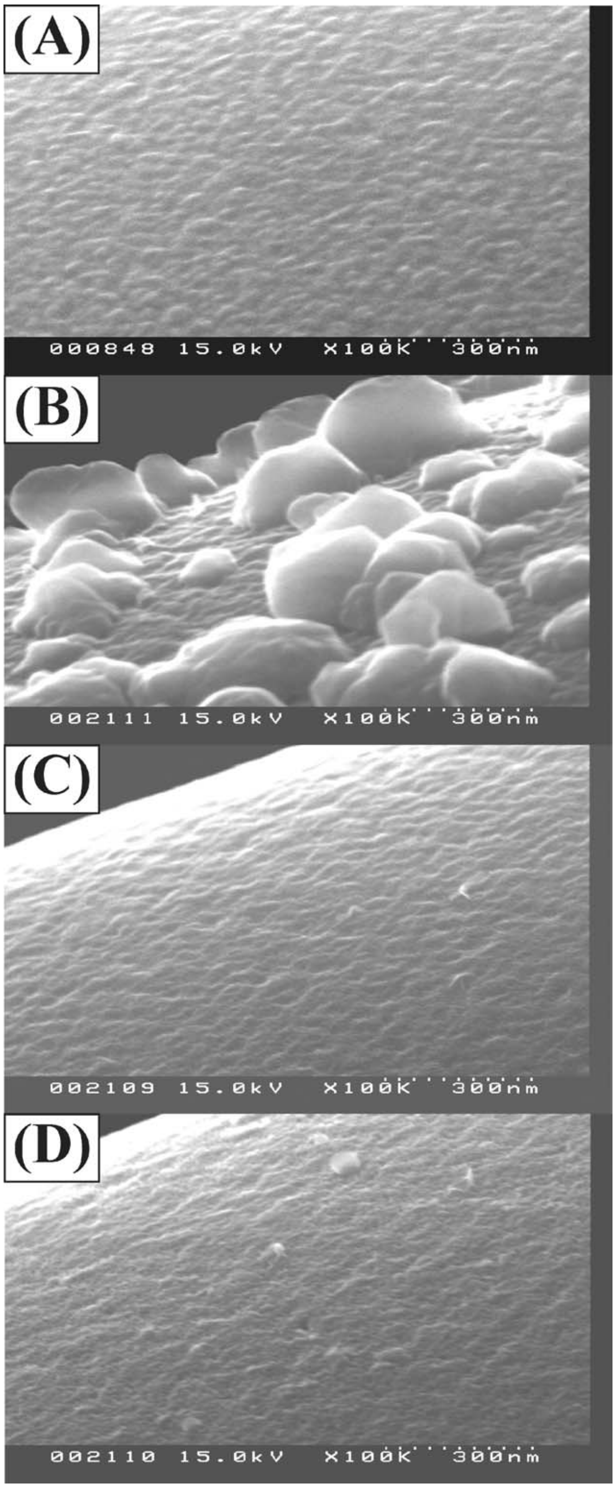

Figure 7 Surface morphologies of carbon-coated fiber after active-oxidation for 18 ks at 1773 K in CO-CO_2 gas mixtures. (A): as-received, (B): $p_{CO_2} = 0$ Pa, (C): $p_{CO_2} = 10^2$ Pa, (D): $p_{CO_2} = 5 \times 10^2$ Pa.

loss, no formation of cristobalite demonstrates that Hi-Nicalon fibers were oxidized in the active-oxidation regime at $p_{CO_2} \leqq 5 \times 10^2$ Pa. Therefore, for the exposure to 1773 K in CO-CO_2 gas mixtures, the p_{CO_2} value for the active-to-passive oxidation transition should be in the range of 5×10^2 to 2×10^3 Pa. This result is consistent with the p_{CO_2} value for the active-to-passive oxidation transition for Hi-Nicalon fibers during exposure in Ar-CO_2 gas mixtures [12].

The oxidation mechanism of silicon carbide fibers in CO-CO_2 gas mixtures is not yet clear. In the first place, the oxidation by associated oxygen is to be considered [17]. CO_2 dissociates into O_2 on the fiber surface:

$$\begin{aligned} CO_2(g) &= CO(g) + 1/2O_2(g) \\ \Delta G^\circ(\text{J/mol}) &= 280960 - 85.23T \text{ [18]} \end{aligned} \tag{1}$$

The dissociated oxygen may subsequently oxidize the fibers, according to the following overall

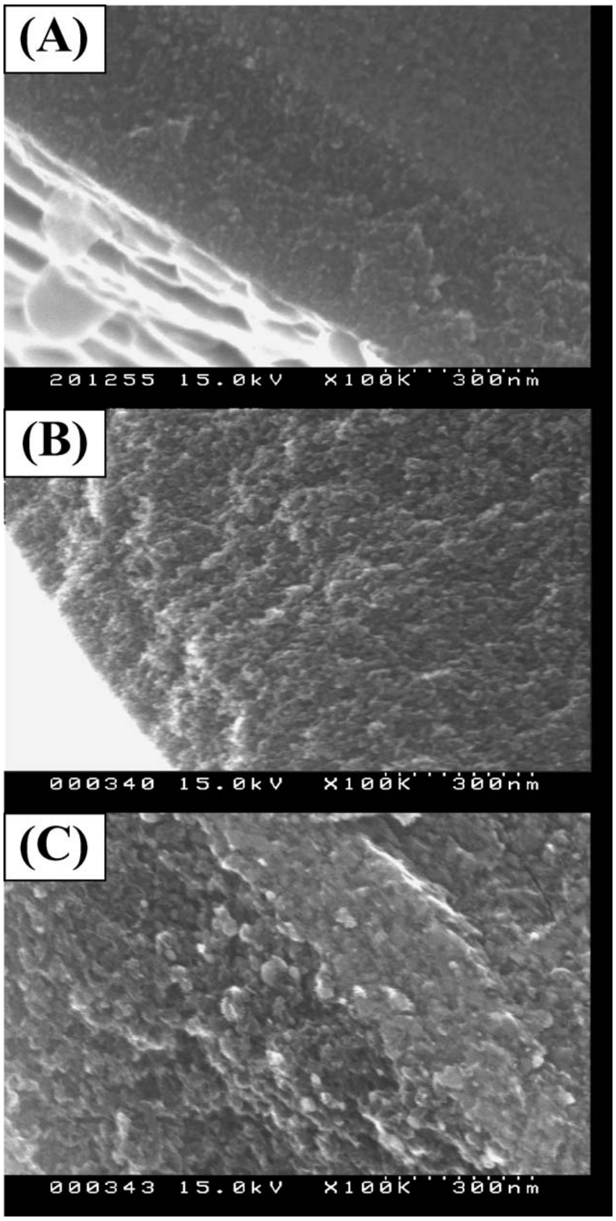

Figure 8 Cross-section morphologies of carbon-coated fibers after active-oxidation for 18 ks at 1773 K in CO-CO$_2$ gas mixtures. (A): $p_{CO_2} = 0$ Pa, carbon layer + fiber core, (B): $p_{CO_2} = 5 \times 10^2$ Pa, carbon layer, (C): $p_{CO_2} = 5 \times 10^2$ Pa, carbon layer + fiber core.

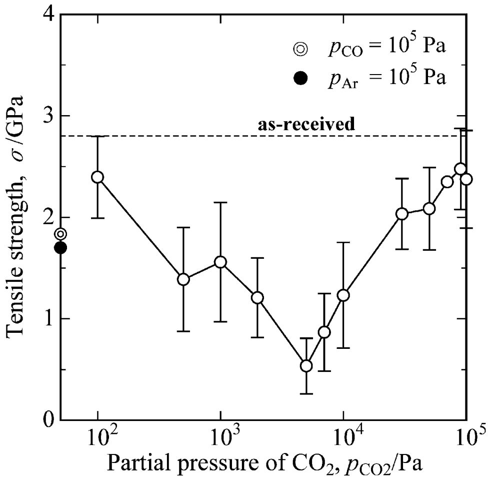

Figure 9 Room-temperature tensile strength of fibers exposed for 36 ks at 1773 K in CO-CO$_2$ gas mixtures with different CO$_2$ partial pressures.

reaction:

$$\text{passive-oxidation:}\quad SiC_{1.39}O_{0.01}(s) + 1.69O_2(g) = SiO_2(s) + 1.39CO(g) \quad (2)$$

$$\text{active-oxidation:}\quad SiC_{1.39}O_{0.01}(s) + 0.695O_2(g) = SiO(g) + 1.39CO(g) \quad (3)$$

From thermodynamic calculation of Equation 1, the oxygen potential, p_{O_2}, of Ar-CO$_2$ and CO-CO$_2$ gas mixture with $p_{CO_2} = 5 \times 10^2$ Pa is estimated to be 5.17 Pa and 5.68×10^{-8} Pa at $T = 1773$ K, respectively. Despite such a marked difference in the p_{O_2} value, the p_{CO_2} value for the active-to-passive oxidation transition was nearly identical in Ar-CO$_2$ and CO-CO$_2$ gas mixture. Therefore, the interaction of Hi-Nicalon fibers with CO$_2$ or CO gases should be brought into consideration.

The condensed phases in the Si-C-O system are SiC(s), SiO$_2$(s), Si(l) and C(s) at 1773 K. The phase equilibria under CO-CO$_2$ atmosphere can be established from the following equations:

$$SiC(s) + 3CO_2(g) = SiO_2(s) + 4CO(g) \qquad \Delta G^\circ\,(J/mol) = -28090 - 173.59T\ [18] \quad (4)$$

$$SiC(s) + CO_2(g) = Si(l) + 2CO(g) \qquad \Delta G^\circ\,(J/mol) = 290160 - 208.66T\ [18] \quad (5)$$

$$Si(l) + 2CO_2(g) = SiO_2(s) + 2CO(g) \qquad \Delta G^\circ\,(J/mol) = -394470 + 35.06T\ [18] \quad (6)$$

$$C(s) + CO_2(g) = 2CO(g) \qquad \Delta G^\circ\,(J/mol) = 166570 - 171.00T\ [18] \quad (7)$$

Fig. 10 shows the equilibrium state diagram of Si-C-O system at 1773 K. The compositions of CO-CO$_2$ gas mixtures used in the present work were plotted in this figure. SiO$_2$(s) is a stable phase, except for the exposure in pure CO gas ($p_{CO} = 10^5$ Pa). During exposure at elevated temperature, the SiO$_2$ film may interact with the unoxidized core (SiC phase) according to the following

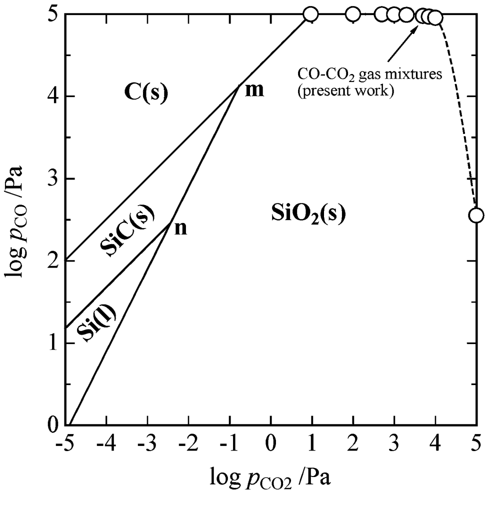

Figure 10 Phase diagram of Si-C-O system at 1773 K.

reaction:

$$2SiO_2(s) + SiC(s) = 3SiO(g) + CO(g) \tag{8}$$

Consequently, the gas bubbles is produced at the interface between the SiO_2 film and the unoxidized core. When the SiO_2 film is resistant to the pressure of gas bubbles, SiC is subjected to the passive-oxidation. On the other hand, the disappearance of SiO_2 film, as a consequence of the progress of reaction (8), leads to the active-oxidation of SiC. In addition to the observed mass loss and detected cristobalite phase at $p_{CO_2} = 10^3$ Pa (Figs 1 and 2), the irregularity of core surface (Fig. 6) implies the occurrence of above reaction during oxidation of Hi-Nicalon fibers. The pressures of the gas bubbles are determined by the equilibrium pressures of SiO and CO at the two-phase field of SiO_2-SiC from point "m" to point "n", as shown in Fig. 10.

at point "m" (three-phase field of SiO_2-SiC-C);

$$2SiO_2(s) + 3C(s) = SiC(s) + 2CO(g) \tag{9}$$

$$SiO_2(s) + SiC(s) = 2SiO(g) + C(s) \tag{10}$$

$$\Delta G^\circ\,(\mathrm{J/mol}) = 779447 - 451T + 31T\log T \quad [19]$$

at point "n" (three-phase field of SiO_2-SiC-Si);

$$SiO_2(s) + Si(l) = 2SiO(g) \tag{11}$$

$$SiO_2(s) + 2SiC(s) = 3Si(l) + 2CO(g) \tag{12}$$

$$\Delta G^\circ\,(\mathrm{J/mol}) = 232980 - 108.12T \quad [18]$$

Gulbransen *et al.* showed that the equilibrium CO pressure of reaction (12), p_{CO}^{eq} gives an indication for the active-to-passive oxidation transition of SiC [20]. While the oxygen potential (p_{O_2}), which is lower than p_{CO}^{eq} reaction, causes the active-oxidation, reverse conditions ($p_{O_2} \geqq p_{CO}^{eq}$) causes the passive-oxidation. The calculated value was in good agreement with experimental value of the oxygen potential for the active-to-passive oxidation transition, $p_{O_2}^{tr}$. Gulbransen's approach can be considered applicable to the oxidation of SiC by CO_2 gas, as well. Therefore, it may be thought that the CO_2 potential for the active-to-passive oxidation transition ($p_{CO_2}^{tr}$) is equal to the p_{CO}^{eq} value for reaction (12). On the other hand, Wang *et al.* calculated the transition CO_2 pressure for the oxidation of SiC by using a different approach [19]. The transition for the oxidation of SiC is governed by reaction (10), and the $p_{CO_2}^{tr}$ value can be calculated by the following equation:

$$p_{CO_2}^{tr} = 0.39 p_{SiO}^{eq} \tag{13}$$

where p_{SiO}^{eq} is determined from Equation 10, corresponding to the equilibrium SiO pressure at point "m" in Fig. 10.

Fig. 11 shows the CO_2 pressure for the active-to-passive oxidation transition as a function of temperature. The transition CO_2 pressure also is shown for Hi-Nicalon fibers oxidized in CO-CO_2 and Ar-CO_2 gas mixtures at 1773 K. The type of oxidation for Hi-Nicalon fibers was evaluated on the basis of the mass change; the mass loss for active-oxidation and the mass gain for passive-oxidation. It may be noted that the $p_{CO_2}^{tr}$ value from Gulbransen's approach is almost identical to that from Wang's approach. In addition, there is the order-of-magnitude agreement between the experimental value for the oxidation of Hi-Nicalon fibers and the calculated values from both approaches. This appears to be principally responsible for the differences in the type of silicon carbide and the oxidation conditions such as gas flow rate and gas species. For example, reported values vary over five orders of magnitude for $p_{O_2}^{tr}$ of the oxidation of SiC by O_2 gas, depending on the oxidation conditions [21].

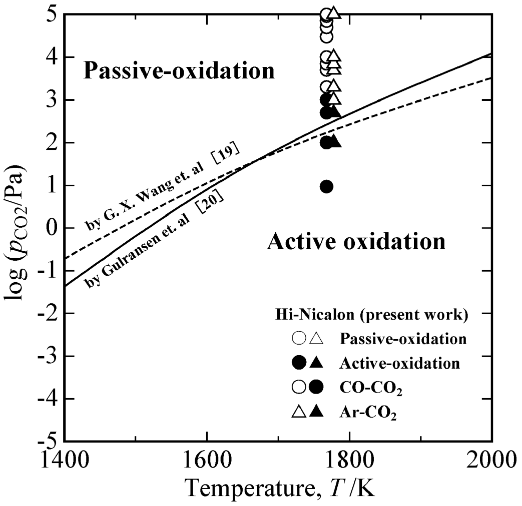

Figure 11 CO_2 partial pressure for active-to-passive oxidation transition of SiC as function of temperature.

Two types of oxidants must be considered for the oxidation in CO-CO_2 gas mixtures. When SiC is oxidized by CO_2 gas, the passive-oxidation can occur by the following reaction [17]:

$$SiC(s) + 3CO_2(g) = SiO_2(s) + 4CO(g) \tag{14}$$

On the other hand, the active-oxidation of SiC by CO_2 gas may be expressed by the following reactions [19]:

$$SiC(s) + 1/2CO_2(g) = SiO(g) + 3/2C(s) \tag{15}$$

$$SiC(s) + CO_2(g) = SiO(g) + CO(g) + C(s) \tag{16}$$

After exposure in Ar-CO_2 gas mixtures at 1773 K, the observed mass loss demonstrates the active-oxidation of Hi-Nicalon fibers at $p_{CO_2} \leqq 5\times10^2$ Pa [12]. However, AES determination and XRD analysis show that no carbon film was formed on the surface of the fibers. Therefore, reactions (15) and (16) are improbable for the active-oxidation of Hi-Nicalon fibers in CO-CO_2 gas mixtures. On the other hand, not only in Ar-CO_2 gas mixtures [12] but also in CO-CO_2 gas mixtures, the following active-oxidation is probable, even if the carbon film was produced at $p_{CO_2} \leqq 5\times10^2$ Pa:

$$SiC(s) + 2CO_2(g) = SiO(g) + 3CO(g), \tag{17}$$

The exposure of Hi-Nicalon fibers in pure CO gas at 1773 K caused the formation of carbon layer, in addition to the mass loss which is characteristic of active-oxidation [12]. The exposure of Si-C-O fibers (Nicalon, Nippon Carbon Co., Japan) and Si-Ti-C-O fibers (Tyranno, Ube Industries Co., Japan) in CO gas led to the formation of carbon layer as well [6–8]. Therefore, it is reasonable that silicon carbides is oxidized in the active-oxidation regime according to the following reaction [12, 19]:

$$\mathrm{SiC(s) + CO(g) = SiO(g) + 2C(s)} \tag{18}$$

Finally, Hi-Nicalon fibers are thougt to be oxidized in CO-CO_2 gas mixtures by the following overall reaction:

passive-oxidation

$$(p_{\mathrm{CO_2}} \geqq 2\times10^3\ \mathrm{Pa})\colon \mathrm{SiC_{1.39}O_{0.01}(s) + 3.38CO_2(g) = SiO_2(s) + 4.77CO(g)} \tag{19}$$

active-oxidation

$$(p_{\mathrm{CO_2}} \leqq 5\times10^2\ \mathrm{Pa})\colon \mathrm{SiC_{1.39}O_{0.01}(s) + 0.99CO(g) = SiO(g) + 2.38C(s)} \tag{20}$$

Thus, CO_2-rich gas mixtures oxidize the fibers in the passive-oxidation regime, whereas CO-rich gas mixtures oxidize them in the active-oxidation regime. The active-to-passive oxidation transition occurs at 5×10^2 Pa $\leqq p_{\mathrm{CO_2}} \leqq 2\times10^2$ Pa.

Heat-treating in flowing CO gas led to dramatic improvements in the thermochemical stability of Nicalon and Tyranno fibers [6–8]. The reason seems to be that the presence of CO inhibits the evolution of decomposition gases (SiO and CO) from the fibers [22]. In particular, Nicalon fibers retained 37% of the as-received strength after exposure in CO gas at 1873 K [7]. Fig. 9 shows that Hi-Nicalon fibers retained 49–86% of the as-received strength (2.8 GPa) after exposure at $T = 1773$ K and $p_{\mathrm{CO_2}} \leqq 5\times10^2$ Pa. Since 61% of the as-received strength was retained even after exposure at 1773 K in Ar gas, the heat-treatment in CO-CO_2 gas mixtures is not necessarily effective in preventing the strength degradation of Hi-Nicalon fibers. This is because an amorphous carbon film formed on the fiber surface is essentially weak, because of its high porosity (Fig. 8). Yet, the strength of Hi-Nicalon fibers after active-oxidation was much higher in CO-CO_2 gas mixtures ($\sigma = 1.4$–2.4 GPa) than in Ar-O_2 gas mixtures ($\sigma \fallingdotseq 0$ GPa) [2]. In addition, the retained strength was 1.4 GPa even after active-oxidation in Ar-CO_2 gas mixtures [12]. This seems to be principally due to the different degree of the growth of SiC crystals. Marked coarsening of SiC grains (35 nm) is probably responsible for the complete loss of fiber strength after the active-oxidation in Ar-O_2 gas mixtures [2]. On the other hand, the grain growth of SiC was mild during exposure in CO-CO_2 and Ar-CO_2 gas mixtures, and its size was almost identical throughout the passive-oxidation and active-oxidation region (14–15 nm) [12]. Very high porosity and the resulting breakage of electrically conductive circuit led to a marked increase of specific resistivity of the fibers after active-oxidation in Ar-O_2 and Ar-CO_2 gas mixtures over that of the as-received fibers [2, 12]. On the other hand, the fibers oxidized actively in CO-CO_2 gas mixtures show very low resistivity, owing to the formation of carbon film and relatively low porosity of fiber core (Fig. 8).

The SiO_2 film was found to be effective for preventing the strength degradation of Hi-Nicalon fibers during high-temperature exposure [23, 24]. Therefore, the unoxidized core of the fibers retained very high strength after passive-oxidation in Ar-O_2 and Ar-CO_2 gas mixtures [2, 12]. Fig. 9 displays that Hi-Nicalon fibers oxidized passively at $p_{\mathrm{CO_2}} \geqq 5\times10^4$ Pa retained 65–80% of the as-received strength. On the other hand, the retained strengths after oxidation at $p_{\mathrm{CO_2}} = 2\times10^3$–$10^4$ Pa were 19–43% of the as-received strength, in spite of passive-oxidation region. It may be noted that these values are much smaller than the strengths of the fibers after active-oxidation at $p_{\mathrm{CO_2}} \leqq 5\times10^2$ Pa. The fibers were subjected to tensile test after removal of SiO_2 film with NH_4+HF solution. The SiO_2-removed fibers (unoxidized core) after oxidation at $p_{\mathrm{CO_2}} = 5\times10^3$ Pa have drastically irregular surface, being responsible for a marked reduction in strength (Fig. 6, photo (C)). While the transformation of β-to-α cristobalite on cooling resulted in the formation of cracks of SiO_2 film after oxidation at $p_{\mathrm{CO_2}} = 10^5$ Pa [10], the surface of the unoxidized core is very smooth (Fig. 6D). Consequently, a high tensile strength of 2.4 GPa was obtained (Fig. 9). On the other hand, the SiO_2 film was smooth after oxidation at $p_{\mathrm{CO_2}} = 10^3$ Pa, whereas the surface of the unoxidized core was significantly irregular (Figs 5E, F and 6B). The irregularity implies that reaction (8) occurred at the interface between SiO_2-film and unoxidized core. In such case, marked degradation. of strength was not to be avoid even in the passive-oxidation region.

5. Conclusion

The exposure of Hi-Nicalon fibers at 1773 K in CO-CO_2 gas mixtures caused the passive-oxidation which was characterized by the mass gain and cristobalite formation at $p_{\mathrm{CO_2}} \geqq 2\times10^3$ Pa and the active-oxidation which was characterized by the mass loss and carbon formation at $p_{\mathrm{CO_2}} \leqq 5\times10^2$ Pa. The carbon formation resulted in a drop of one order of magnitude for specific resistivity in the active-oxidation region. The active-to-passive oxidation transition is in the CO_2 partial pressure range of 5×10^2 Pa to 2×10^3 Pa. β-SiC grain size was almost identical throughout the active- and passive-oxidation region (about 14 nm). High strength of 2–2.5 GPa was retained after active-oxidation at $p_{\mathrm{CO_2}} \leqq 10^2$ Pa and passive-oxidation at $p_{\mathrm{CO_2}} \geqq 5\times10^4$ Pa. Porous carbon film produced considerable decrease in strength of the fiber after active-oxidation at $p_{\mathrm{CO_2}} = 5\times10^2$ Pa. Very irregular surface caused a marked strength degradation after passive-oxidation at $p_{\mathrm{CO_2}} = 5\times10^3$ Pa.

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