Oxidation behavior and thermal stability of Si-C-O fibers (Nicalon) in carbon dioxide

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The oxidation behavior and thermal stability of Si-C-O fibers (Nicalon) in CO_2 gas were examined at 1273 to 1773 K through mass change determination, XRD analysis, resistivity measurement, SEM observation and tensile test. Large mass gains and SiO_2 film formation show that Nicalon fibers are passively oxidized in CO_2, as well as Si-C fibers (Hi-Nicalon). The grain growth of β-SiC, the drop of resistivity and the crystallization of SiO_2 film were observed above 1573 K. On being oxidized at high temperature, the thermal decomposition of SiC_XO_Y and the formation of imperfections in SiO_2 film caused the degradation of the room-temperature tensile strength of both the as-oxidized fibers and unoxidized cores. It became evident that the oxygen partial pressure for the active-to-passive oxidation transition of Nicalon fibers is between 1.00×10^2 and 1.78×10^2 Pa at 1773 K.
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1. Introduction

Polycarbosilane-derived silicon carbide fibers such as Si-C-O, Si-C and SiC fibers (Nicalon, Hi-Nicalon and Hi-Nicalon S, Nippon carbon Co., Tokyo, Japan) have become of interest as a reinforcing material in ceramic-matrix composites for high-temperature applications. An understanding of the thermal stability and oxidation resistance of the fibers is of great importance, because they may be exposed to high-temperature environments during either fabrication and service. Therefore, the changes in microstructure and mechanical properties have been investigated in various environments including Ar, N_2, O_2, air and vacuum, etc and at different temperatures and pressures [1–20]. The silicon catbide fibers are necessarily exposed to CO_2-containing combustion environments in the applications to gas turbine, piston engine and heat-exchanger pipe etc. However, there have not been investigation into the oxidation of silicon carbide fibers in CO_2 gas. In the previous report, the authors examined further the oxidation behavior of Hi-Nicalon fibers in CO_2 gas [21]. A large mass gain and SiO_2-film formation were observed after the oxidation in CO_2 gas, showing the occurrence of passive-oxidation. Furthermore, they were highly oxidized compared to a bulk CVD-SiC [22]. This may be partially contributed to different microstructure: SiC + free carbon for Hi-Nicalon and pure SiC for CVD-SiC. Nicalon fibers contain a large amount of silicon oxycarbide (SiC_XO_Y), in addition to SiC crystallites and free carbon. From a comparison between the oxygen potential of CO_2 gas and the oxygen pressure of the active-to-passive oxidation transition for Nicalon fibers [18], they may be actively oxidized at high temperature. Therefore, it is possible that there is a large difference in oxidation behavior between Nicalon and

Hi-Nicalon fibers. However, the oxidation of Nicalon fibers in CO_2 gas has not yet been studied.

In this study, mass change determination, X-ray diffraction, specific resistivity measurement, SEM observation and tensile testing were carried out on Nicalon fibers after heat-treatment at 1273–1773 K in CO_2 gas. The possible oxidation mechanism was discussed in detail by correlating with the variations in fiber properties. Furthermore, the present results were compared with the results for the oxidation of Hi-Nicalon fibers [21].

2. Experimental method

The silicon carbide fibers employed in this study are Si-C-O fibers (Nicalon 202) manufactured by Nippon Carbon Co. (Tokyo, Japan). The properties of Nicalon fibers are given in Table I, together with those of Hi-Nicalon fibers (Si-C fibers).

500 mg of fibers, 3 cm in length, were placed in an alumina boat and subsequently it was set in the alumina tube of an SiC resistant furnace. After evacuation to 1 Pa, CO_2 gas was allowed to flow into the alumina tube at a flow rate of 100 cm^3/min. The sample was heated at a rate of 300 K/h and after holding of 36 ks at each temperature in the range of 1273 to 1773 K, it was cooled to room-temperature at 600 K/h.

The mass change of the fibers was measured by weighing before and after heat-treatment in CO_2 gas. The existing phases and apparent β-SiC crystallite size of the fibers were determined by X-ray diffractometry (XRD). The fibers, SiO_2 film of which was removed with $NH_4OH + HF$ solution, were subjected to the specific resistivity measurement. The resistivity was measured at room-temperature by applying a direct current to a single fiber. Both ends of a fiber were attached, with an electroconductive resin, to copper electrode plates

TABLE I Properties of polycarbosilane-derived SiC Fibers

	Nicalon	Hi-Nicalon
Chemical composition		
Si (mass%)	56.6	62.4
C (mass%)	31.7	37.1
O (mass%)	11.7	0.5
Si/C atomic ratio	1.31	1.39
Fiber diameter (μm)	15	14
Density (kg/m^3)	2550	2740

spaced 0.8 mm apart. Ten fibers were measured to determine the average resistivity. Room-temperature tensile strength tests were conducted on an as-oxidized fiber and an SiO_2-removed fiber (unoxidized core) using a 10 mm gauge length and a constant crosshead speed of 2 mm/min. The average of 10 tensile testing was taken as the strength under each oxidation condition. Morphologies of as-oxidized fibers and SiO_2-removed fibers were examined by field emission scanning electron microscopy.
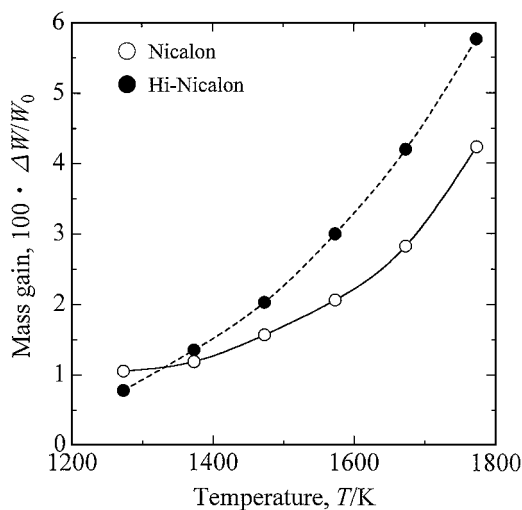

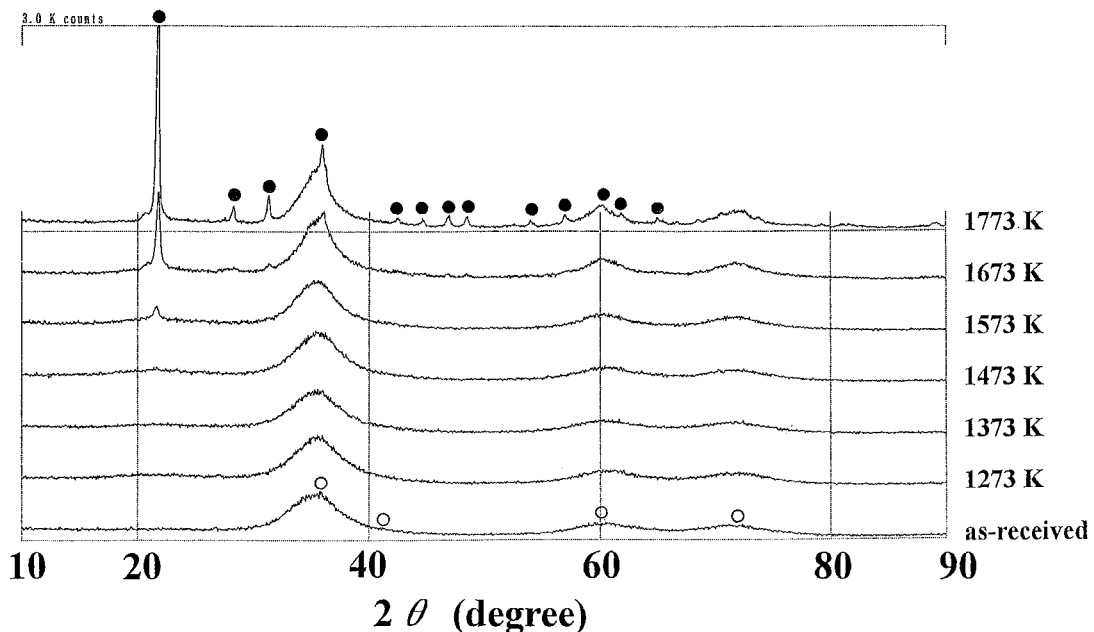*Figure 1* Mass gain of Nicalon fibers oxidized for 36 ks in CO_2 gas at different temperatures.

3. Results
3.1. Mass change
Fig. 1 shows that the heat-treatment of Nicalon fibers in CO_2 gas produces the mass gain. Here, W_0 is the initial mass of the fibers and ΔW is the mass gain determined from the difference of the fiber mass before and after heat-treatments. The observed mass gain exhibits that Nicalon fibers are passively oxidized as well as Hi-Nicalon fibers [21]. The mass gain is less for Nicalon than for Hi-Nicalon, being attributed to the different composition and microstructure.

3.2. X-ray diffraction analysis
Fig. 2 shows the X-ray diffraction patterns for Nicalon fibers oxidized in CO_2 gas. The SiO_2 film formed around the fibers was amorphous silica below 1473 K and cristobalite above 1573 K. Cristobalite peaks became significantly sharp at higher temperatures. A similar results were found in the oxidation of Hi-Nicalon fibers and CVD-SiC in CO_2 gas [21, 22]. β-SiC peaks became gradually sharp with increasing temperature. Using the Scherrer's formula, the β-SiC crystallite size was calculated from the half-value width of (111) peak. Prior to X-ray diffraction, the SiO_2 film was removed with $NH_4OH + HF$ solution. Fig. 3A shows the relationship between β-SiC crystal size and heat-treatment temperature. While the growth of β-SiC crystal was little observed below 1473 K, it became very rapid above 1573 K. This is consistent with the result for the heat-treatment in inert gas, implying the thermal decomposition of amorphous silicon oxycarbide (SiC_XO_Y) phase in CO_2 gas [10, 11].

3.3. Specific resistivity
The specific resistivity is very sensitive to a minor microstructural change of the silicon carbide fibers. Fig. 3B shows that the resistivity decreases rapidly with increasing temperature. The resistivity of the fibers oxidized at 1773 K is 2 orders of magnitude lower than that
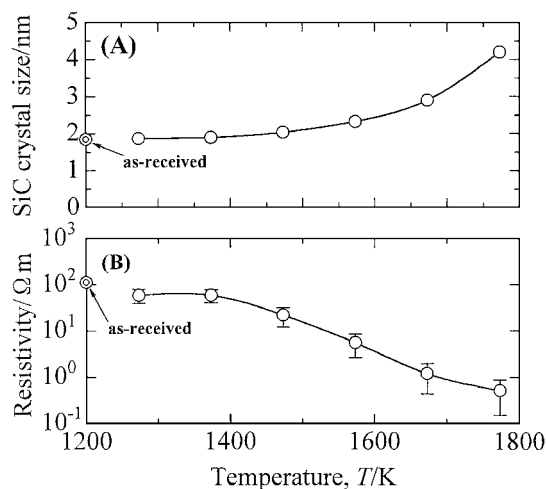

Figure 2 X-ray diffraction patterns of Nicalon fibers oxidized for 36 ks in CO_2 gas at different temperatures: ○ β-SiC, ● α-cristobalite.

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Figure 3 β-SiC crystallite size (A) and specific resistivity (B) of Nicalon fibers oxidized for 36 ks in CO_2 gas at different temperatures.

of the as-received fibers. In the addition to the crystal growth of β-SiC (Fig. 3A), the reduction of resistivity suggests that the thermal decomposition of SiC_XO_Y phase and the organization of free carbon phase occurred during heat-treatment in CO_2 gas [10, 11].

3.4. Morphology
Fig. 4 shows typical morphologies of the fibers oxidized in CO_2 gas. After oxidation of 36 ks at 1273 K, a thin glassy SiO_2 film was formed on the fiber surface, as shown in photos A and B. The surface of SiO_2-removed fiber (unoxidized core) also was smooth and dense (photo D). When the fibers were oxidized at 1773 K, a significant development of SiO_2 film was observed (photo E). The SiO_2 film crystallized into cristobalite and, as a consequence of β to α transformation at about 570 K, the cracking SiO_2 film of occurred during cooling (photo F). At all oxidation-temperatures, the fracture surface of the fibers display a glassy appearance, as well as in the as-received state (Photos A, C, E and G). Thus, the surface of the unoxidized core seemingly had a smooth appearance even after the oxidation at 1773 K, as shown in photo H. However, Fig. 5A (SEM photograph at high magnification) shows that a number of large pits were formed on the surface of the unoxidized core. On the other hand, Fig. 5B shows that only small pits were formed on the core surface for the low-oxygen silicon carbide fibers (Hi-Nicalon). Different pit size is probably attributed to the difference in oxygen content between Nicalon and Hi-Nicalon.

3.5. Tensile strength
Fig. 6 shows the room-temperature tensile strength for the as-oxidized fiber (SiO_2-coated fiber) and the unoxidized core (SiO_2-removed fiber). The change in strength as a function of temperature was well reflected in the surface morphologies of the fibers. The increased temperature led to a significant reduction in the strength of the as-oxidized fibers. While the fibers oxidized at 1273 K had a high strength, i.e., 86% of a strength (about 3 GPa) in the as-received state, the fibers oxidized at 1773 K were too fragile to subject to tensile testing. On the other hand, for the unoxidized core, a gradual

degradation of strength was observed below 1673 K, ranging from 80% to 60% of a strength in the as-received state. The oxidation at 1773 K caused a significant reduction of strength as well as a strength in the as-oxidized state, though 25% of a strength in the as-received state was retained.

4. Discussion
### 4.1. Oxidation mechanism
The oxidizing gas used in present work was pure CO_2 gas. The mass gain and SiO_2 film formation show that Nicalon fibers were passively oxidized in CO_2 gas (Figs 1–3), as well as Hi-Nicalon fibers [21]. The overall reaction for the passive-oxidation of Nicalon fibers is given by the following equation.

$$SiC_{1.20}O_{0.41}(s) + 2.79CO_2(g) = SiO_2(s) + 3.99CO(g) \tag{1}$$
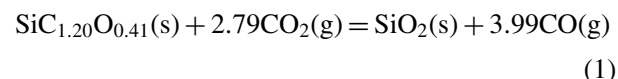
According to thermodynamic consideration, only a small amount of CO_2 gas can decompose at high temperatures:

$$CO_2(g) = CO(g) + 1/2O_2(g)$$
$$\Delta G°/cal \cdot mol^{-1} = 67150 - 20.37T \text{ [23]} \tag{2}$$
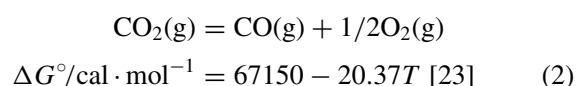
Nicalon fibers should be oxidized not by CO_2, but by O_2. Therefore, the oxidation reaction may be divided into two elementary steps. The adsorbed CO_2 molecules on the fiber surface dissociates into CO and O_2, and subsequently O_2 oxidizes the fibers:

$$SiC_{1.20}O_{0.41}(s) + 1.395O_2(g) = SiO_2(s) + 1.20CO(g) \tag{3}$$
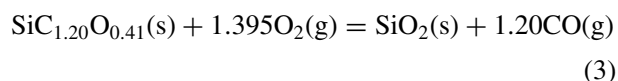
From the stoichiometry and standard free enthalpy change for reaction (2), the equilibrium partial pressure, p_{O_2}, for the dissociation of CO_2 gas was calculated to be in the range of 1.22 Pa at 1273 K to 1.78×10^2 Pa at 1773 K. Fig. 7 shows the relationship between p_{O_2} and temperature. The oxygen partial pressures for the active-to-passive oxidation transition of SiC, $p_{O_2}^*$, also are shown in Fig. 7. $p_{O_2}^*$ is strongly dependent upon the types of SiC [24]. In addition, there is a wide range of active-to-passive oxidation transition for SiC [25]. The oxygen potential of CO_2 gas at the experimental temperature (1.22 Pa at 1273 K to 1.78×10^2 Pa at 1773 K) definitely corresponds to the oxygen partial pressures for the passive-oxidation region below about 1400 K [24, 25] and the upper-limit of the active-to-passive oxidation transition region above 1490 K [25]. In Ar-O_2 gas mixtures and at 1773 K, Nicalon fibers were oxidized in the active-oxidation regime at $p_{O_2} = 10^2$ Pa and in the passive-oxidation regime at $p_{O_2} = 5 \times 10^2$ Pa [18]. From this result, the oxygen potential of CO_2 gas at 1773 K (1.78×10^2 Pa) is within the oxygen partial pressures for the active-to-passive oxidation transition for Nicalon fibers. However, a significant mass gain (Fig. 1) and cristobalite film formation at 1773 K (Figs 2 and 4) are evidently the results of the occurrence of the passive-oxidation. This result shows that Nicalon fibers are passively oxidized in CO_2 gas, as well as Hi-Nicalon fibers and the bulk CVD β-SiC [21, 22].
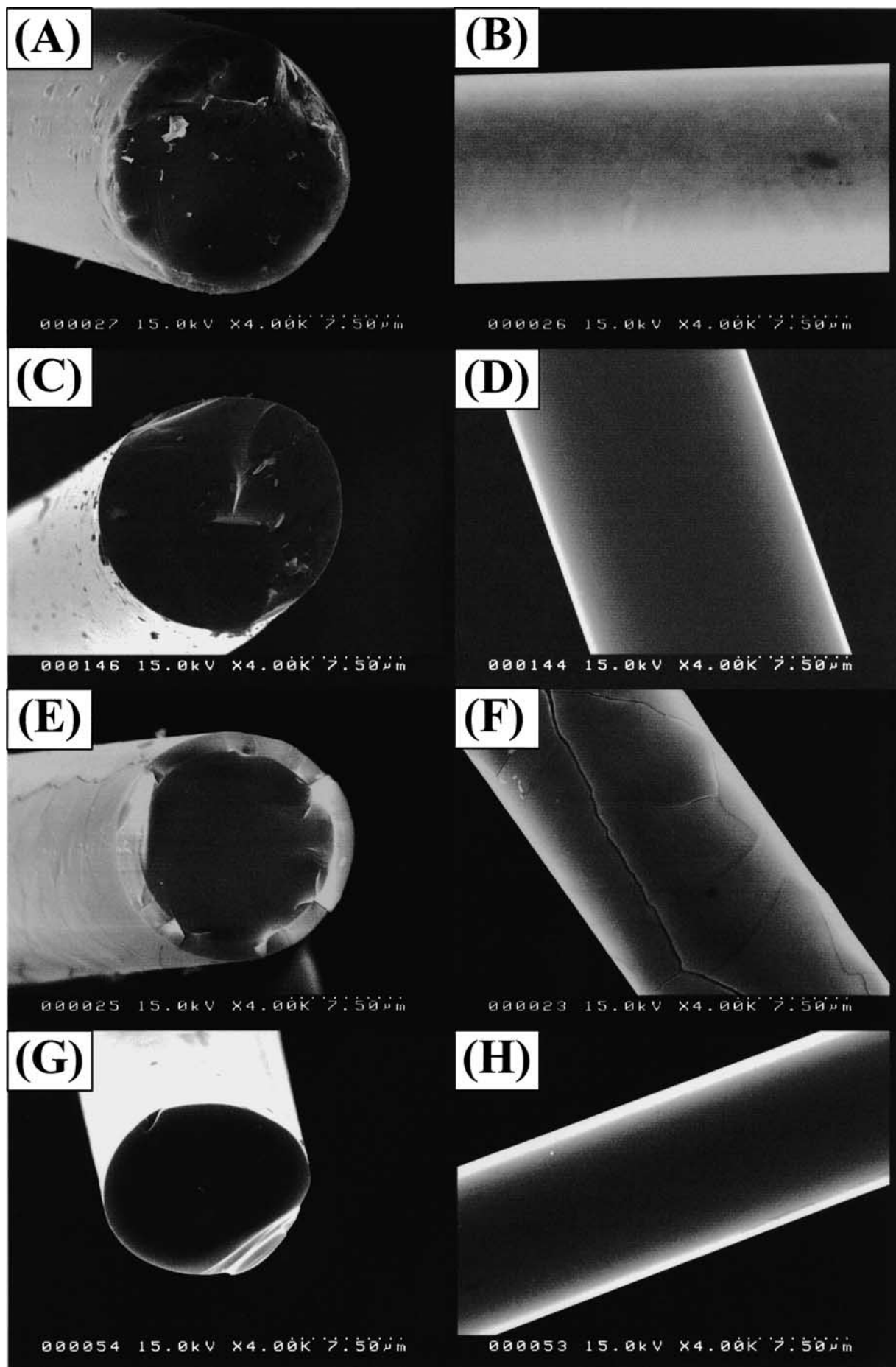
Figure 4 Morphologies of Nicalon fibers oxidized for 36 ks in CO_2 gas at 1273 K (photos A–D) and 1773 K (photos E–H). Photos C, D, G and H are morphologies of unoxidized cores (SiO_2 film was removed with $NH_4F + HF$ solution.)
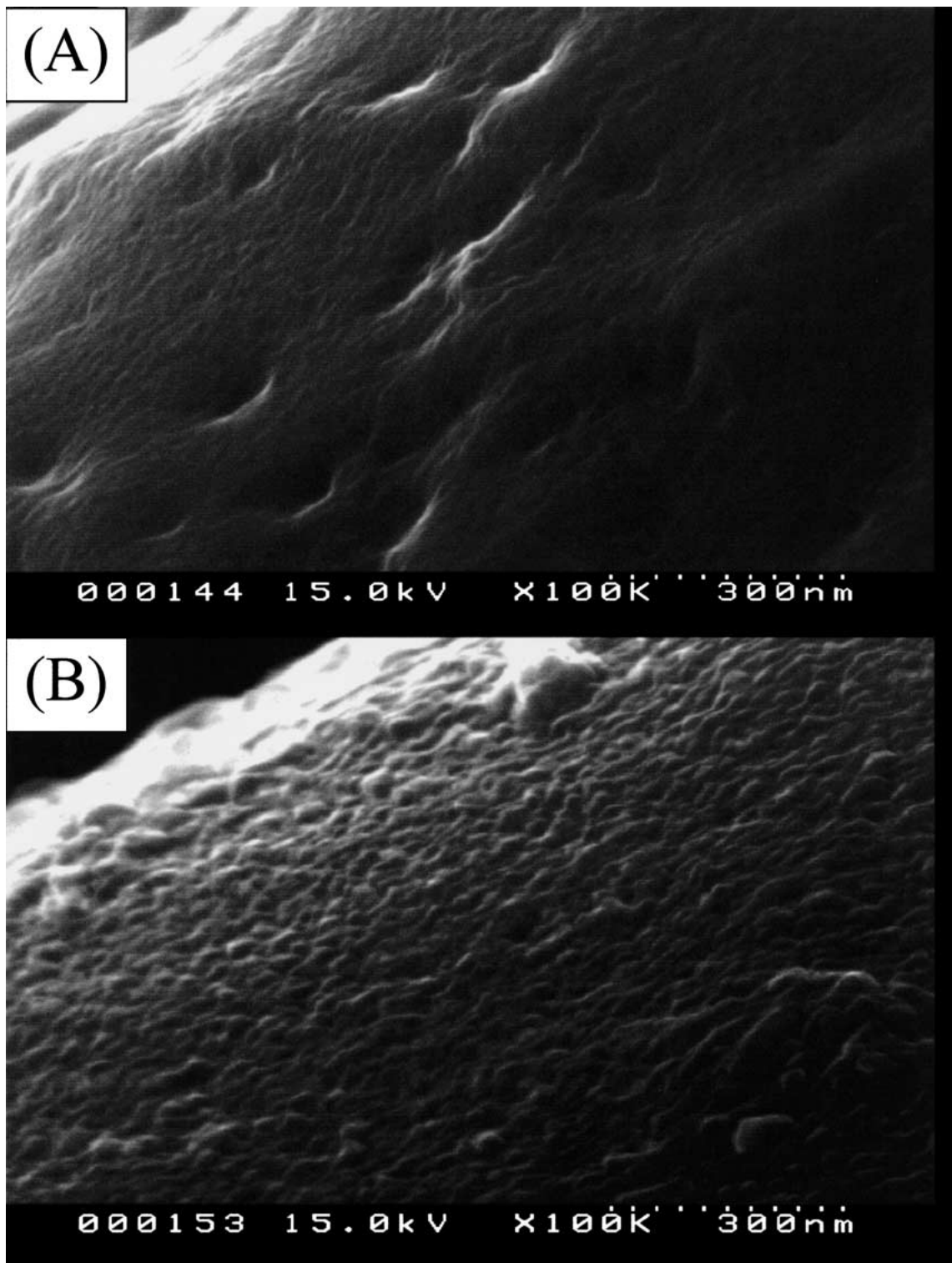
Figure 5 Surface morphologies of unoxidized core after oxidation for 36 ks in CO_2 gas at 1773 K (photo A: Nicalon, photo B: Hi-Nicalon).

From the experimental data of the oxidation in CO_2 and Ar-O_2 gas, it became evident that the active-to-passive oxidation transition for Nicalon fibers existed between 1.00×10^2 and 1.78×10^2 Pa.

4.2. Oxidation kinetics

Fig. 8 shows the oxidized fraction (X) of the fibers heat-treated for 36 ks at different temperatures. For comparison, the X values are shown for Nicalon fibers oxidized in Ar-25%O_2 gas mixture and Hi-Nicalon fibers oxidized in CO_2 gas and Ar-25%O_2 gas mixture

[13, 16, 21]. The oxidized fraction (X) of fibers can be calculated from the stoichiometry of reactions

$$X = 4.435 \cdot (\Delta W/W_0) \quad \text{for Nicalon} \tag{4}$$

$$X = 3.167 \cdot (\Delta W/W_0) \quad \text{for Hi-Nicalon} \tag{5}$$

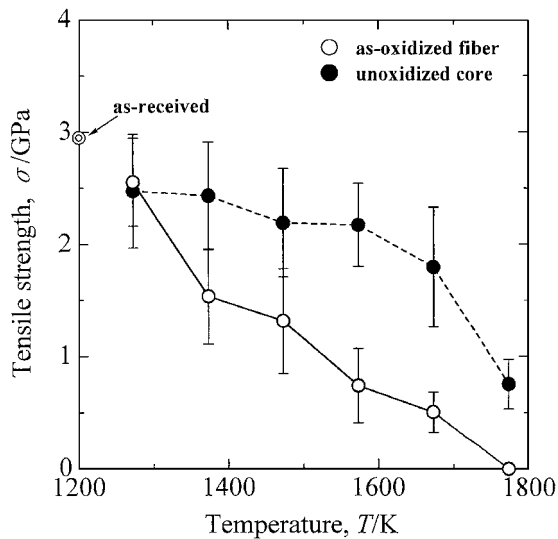Here the overall reactions for the oxidation of Hi-Nicalon is represented by:

$$SiC_{1.39}O_{0.01}(s) + 3.38CO_2(g) = SiO_2(s) + 4.77CO(g) \tag{6}$$

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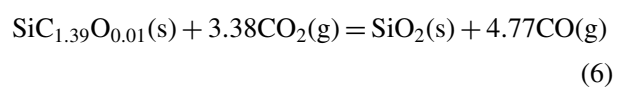
Figure 6 Tensile strength of Nicalon fibers oxidized for 36 ks in CO_2 gas at different temperatures.
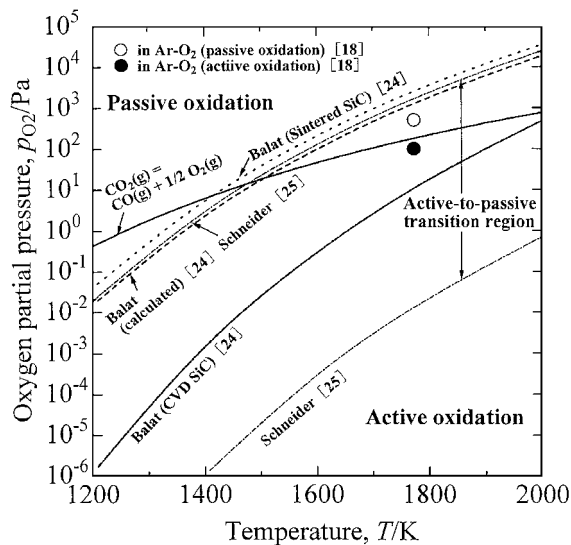

Figure 7 Oxygen potential of CO_2 gas and oxygen partial pressure for active-to-passive transition of SiC as function of temperature.
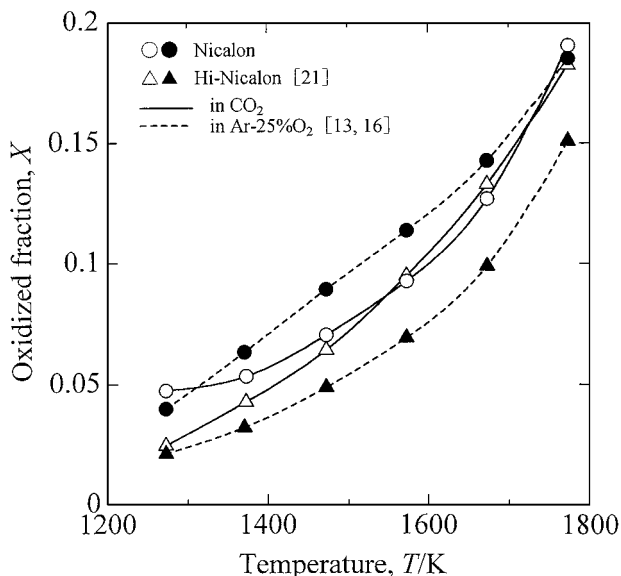

Figure 8 Oxidized fraction of Nicalon and Hi-Nicalon fibers oxidized for 36 ks in CO_2 gas at different temperatures.

Nicalon and Hi-Nicalon were oxidized to nearly identical X values for the oxidation in CO_2 gas, though Nicalon was more highly oxidized than Hi-Nicalon in Ar-25%O_2 gas mixture. There is less-definite difference between the X values for the oxidation in CO_2 gas and those for the oxidation in Ar-25%O_2 gas mixture, regardless of a significant difference in oxygen partial pressure. A possible cause for the rapid oxidation of Nicalon fibers in CO_2 gas is that the fibers are oxidized by the dissociated oxygen from CO_2 gas. Since the dissociated oxygen is in the highly activated state, it may cause the serious attack to the silicon carbide fibers. Furthermore, such rapid oxidation in CO_2 gas seems to be corresponding to the result that the reduction of p_{O_2} enhanced the passive-oxidation of Nicalon fibers in Ar-O_2 gas mixtures at $p_{O_2} \leqq 10^3$ Pa [18].

It was reported that the passive-oxidation of bulk β-CVD SiC in CO_2 gas was negligible compared to that in other oxidizing environments and was independent on temperature [22]. On the other hand, Nicalon fibers showed severe passive-oxidation, in addition to a strong temperature dependence of the oxidation rate. This seems to be because Nicalon fibers have significantly large specific surface area compared to bulk CVD SiC.

4.3. Degradation of fiber strength by oxidation

The fiber strength is strongly influenced by the development of SiO_2 film [26]. The b value can be estimated from the following relation:

$$b = r_0 \cdot \{1 - (1 - X)^{1/2}\} \qquad (7)$$

where r_0 is the initial mean radius of the fibers.

Fig. 9 shows the room-temperature strength of the SiO_2-removed fibers (unoxidized cores). The strengths of the unoxidized cores were roughly same between Nicalon and Hi-Nicalon fibers independently on oxidizing environments; CO_2 and Ar-25%O_2 gas. The development of SiO_2 film produced a significant reduction of strength for Nicalon fibers, though it produced a gradual
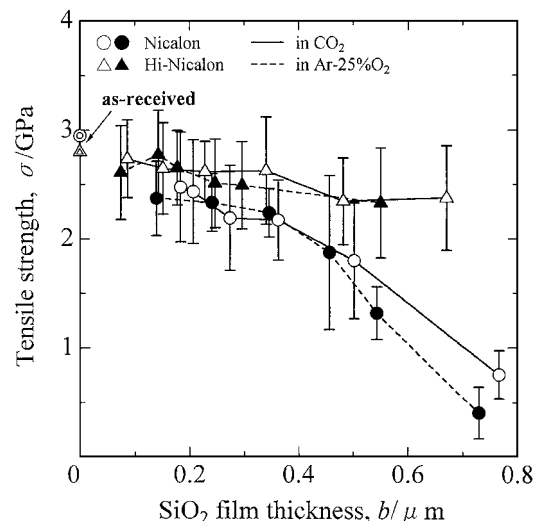

Figure 9 Relationship between room-temperature tensile strength of unoxidized cores (SiO_2-removed fibers) and SiO_2 film thickness.

decrease in strength for Hi-Nicalon fibers. This is because Nicalon fibers having large amounts of SiC_XO_Y are thermally decomposed at the earliest stage of oxidation at higher temperatures. The serious strength degradation of Nicalon fibers is thought to be caused by the combination of the grain growth of β-SiC and the pit formation on the core surface (Figs 3 and 5). In particular, the pits formed on the core surface is most critical of all controlling factor in fiber strength. The pit is probably derived from the gas bubbles formed at the SiO_2 film/core interface. The generation of SiO and CO gases are caused by both the thermal decomposition of SiC_XO_Y phase in the unoxidized core and the reaction between the SiO_2 film and unoxidized core. Under conditions of passive-oxidation, SiO gas in bubbles is easily oxidized to SiO_2. The disappearance of bubbles leaves pits on the core surface. Consequently, the core strength was reduced to 0.74 GPa after oxidation at 1773 K ($b = 0.77\,\mu$m). The fibers oxidized at lower temperatures is virtually free from the thermal decomposition of SiC_XO_Y phase and the SiO_2 film/core reaction. Consequently, 83% of the strength in the as-received state, i.e., 2.5 GPa, was retained after oxidation at 1273 K ($b = 0.18\,\mu$m). On the other hand, for Hi-Nicalon fibers, because of low oxygen content, the pits were little formed on the core surface even at high temperature, as shown in Fig. 5B. Therefore, a high strength of 2.4 GPa was retained in the fiber oxidized at 1773 K ($b = 0.67\,\mu$m).

The room-temperature strengths of the as-oxidized (SiO_2-coated) fibers are summarized as a function of the SiO_2 film thickness (b) in Fig. 10. Nicalon fibers show nearly identical strengths after oxidation in CO_2 and Ar-25%O_2 gas, though Hi-Nicalon fibers show higher strengths after oxidation in CO_2 gas than after oxidation in Ar-25%O_2 gas mixture. For Nicalon fibers after oxidation at 1273 K ($b = 0.18\,\mu$m), a strength of 2.5 GPa, i.e., 86% of the strength in the as-received state was retained. When oxidized at higher temperatures, the development of SiO_2 film, as a consequence of increased imperfections, produced a very large decrease in strength. Ultimately after oxidation at 1773 K ($b = 0.77\,\mu$m), Nicalon fibers became too fragile to

subject to tensile testing, owing to the formation of deleterious cracks and pits (Figs 4 and 5). Comparing Fig. 9 with 10 shows that the imperfections in SiO_2 film is an important factor influencing the strength of the as-oxidized fibers.

5. Summary
The mass gain and SiO_2 formation were observed after heat-treatment of Nicalon fibers in CO_2 gas. Nicalon fibers are oxidized in the passive-oxidation regime, as well as Hi-Nicalon fibers. This is verified by the combination of thermodynamic consideration and the previous data of the oxidation in Ar-O_2 gas mixtures. In addition, the oxygen partial pressure of the active-to-passive oxidation transition for Nicalon fibers is in the range of 1.00×10^2 to 1.78×10^2 Pa. The grain growth of β-SiC, drop of resistivity and crystallization of SiO_2 film above 1573 K show the thermal decomposition of SiC_XO_Y resulting in the degradation of tensile strength of the unoxidized core. Compared to the funoxidized cores, the as-oxidized fibers showed a large degradation of tensile strength, owing to the imperfections of SiO_2 film.

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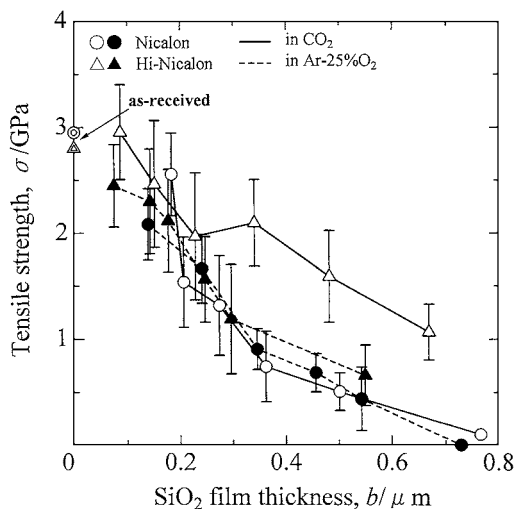
Figure 10 Relationship between room-temperature tensile strength of as-oxidized fibers (SiO_2-coated fibers) and SiO_2 film thickness.

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