JOURNAL OF MATERIALS SCIENCE **38** (2003) 4973–4979

Effect of reduced pressure on oxidation and thermal stability of polycarbosilane-derived SiC fibers

T. SHIMOO, K. OKAMURA
Department of Metallurgy and Materials Science, Graduate School of Engineering, Osaka Prefecture University, 1-1, Gakuen-cho, Sakai, Osaka 599-8531, Japan
H. TAKEUCHI
Sanyo Special Steel Co. Ltd., 3007 Nakashima, Shikama-ku, Himeji, Hyogo 672-8677, Japan

To clarify the effects of reduced pressure on the thermal stability of polycarbosilane-derived SiC fibers (Nicalon, Hi-Nicalon and Hi-Nicalon S), the heat-treatments were conducted at 1623 and 1723 K under total pressures (p_T) of 1–10^5 Pa. The oxidation behavior and thermal stability of the fibers were investigated through examinations of mass change, grain growth, specific resistivity, fiber morphology and tensile strength. All the fibers were definitely oxidized in the active-oxidation regime at $p_T \leq 10^2$ Pa and $T = 1723$ K. Nicalon and Hi-Nicalon S were subjected to serious degradation of fiber strength. Hi-Nicalon had a strength of 1.2 GPa even after heat-treatment at $p_T = 1$ Pa.

1. Introduction

Much attention has recently been paid to the continuous silicon carbide fibers as reinforcing material in ceramic-matrix composites [1, 2]. Three types of the polycarbosilane-derived SiC fibers are commercially available: Nicalon, Hi-Nicalon and Hi-Nicalon S (Nippon Carbon Co., Tokyo, Japan) [3]. Nicalon fibers prepared by the oxidation curing method contain a large amount of oxygen (12 mass%) as an amorphous silicon oxycarbide (SiC_XO_Y) phase in the microstructure. The SiC_XO_Y phase is thermally decomposed at elevated temperature, resulting in the significant degradation of fiber strength. It is Hi-Nicalon fibers that succeeded in lowering the oxygen content to 0.5 mass% by the electron-beam-irradiation curing method for the purpose of improving high-temperature thermability. Furthermore, nearly stoichiometric SiC fiber (i.e., Hi-Nicalon S) could be prepared by removal of carbon by heat-treatment in hydrogen. Such differences in oxygen content and microstructure may greatly affect the properties of the fibers exposed to high temperatures in different environments.

In previous report, the fibers were exposed at temperatures of 1573–1773 K under a reduced pressure of 1.3 Pa [4]. The SiC crystallites in the fiber were subjected to the active-oxidation by retained oxygen gas at ≥1673 K, resulting in serious damage to the fiber structure. While Nicalon and Hi-Nicalon S completely lost their strength, Hi-Nicalon had appreciable levels of strength: 1 GPa at 1673 K and 0.5 GPa at 1773 K [4]. On the other hand, under a reduced pressure of 10^{-3} Pa, only the SiC_XO_Y phase is completely decomposed, causing the mass loss value of 26–28% [5, 6]. In addition, the heat-treatment under high oxygen partial pressure causes the passive-oxidation which is characterized by the mass gain and the formation of SiO_2 film, leading to the high strength retention of fiber core [7–10]. Thus, the heat-treatments under different reduced pressures produce a definite difference in fiber properties. However, the effect of reduced pressures (i.e., total pressures) on the oxidation of the SiC fibers has not yet been satisfactorily clarified.

In this work, three types of SiC fibers were heat-treated at 1623 and 1723 K in the pressure range from 1 to 10^5 Pa. The oxidation behavior and the resultant thermal stability of SiC fibers were investigated through mass change determination, X-ray diffraction analysis, resistivity measurement, morphological examination and room-temperature tensile testing.

2. Experimental method

Three types of polycarbosilane-derived SiC fiber manufactured by Nippon Carbon Co. (Tokyo, Japan): Si—C—O fiber (Nicalon), SiC fiber (Hi-Nicalon) and stoichiometric SiC fiber (Hi-Nicalon S). The properties of fibers are shown in Table I [3].

The heat-treatment of the fibers were performed at 1623 and 1723 K under each total pressure of 1, 10, 10^2, 10^3 and 10^5 Pa in a horizontal SiC resistance furnace. The total pressure inside an alumina tube was maintained by controlling the air leak of vacuum system. Fibers, 0.5 g in mass and 30 mm in length, were put in an alumina boat and placed in an alumina tube. After controlling to a given total pressure, they were heated at a heating rate of 300 K/h. Then, they were held for

TABLE I Properties of polycarbosilane-derived SiC fibers [3]

	Nicalon	Hi-Nicalon	Hi-Nicalon S
Chemical composition			
Si (mass%)	56.6	62.4	68.9
C (mass%)	31.7	37.1	30.9
O (mass%)	11.7	0.5	0.2
Si/C atomic ratio	1.31	1.39	1.05
Fiber diameter (μm)	15	14	12
Density (kg/m^3)	2550	2740	3100

1 h at the chosen temperature and cooled at a rate of 300 K/h.

The amount of gas evolved was determined from the difference in the fiber mass before and after heat-treatment. The crystal phases of the fibers were identified with an X-ray diffractometer (Rigaku Co., Type RINT 1100, Tokyo, Japan) using Cu K_α radiation, and the apparent size of β-SiC crystallite (D_{SiC}) was calculated from the half-value width of (111) peak using Scherrer's formula. The fiber morphologies after heat-treatment were examined using a field emission scanning electron microscope (Hitachi Ltd., Type S5400, Tokyo, Japan). 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 heat-treatment condition. The room-temperature strength of a fiber of 10 mm in length was measured with a tensile tester (Model TENSILON UTM-20, Orientec Co., Tokyo, Japan), using a load cell of 100 g and a crosshead speed of 2 mm/min. The mean value of twenty tensile strengths was used for each fiber.

3. Results

3.1. Mass change

Fig. 1 shows the mass change of SiC fibers heat-treated at 1623 and 1723 K under different total-pressures. The heat-treatment at total pressure (p_{T}) of 10^5 Pa (i.e., at atmospheric pressure of air) yielded a small mass gain in all types of fibers, exhibiting the occurrence of passive-oxidation. At $p_{\mathrm{T}} \leq 10^3$ Pa, the mass loss was observed. This is attributable to the decomposition of an amorphous $\mathrm{SiC}_X\mathrm{O}_Y$ phase in fibers and the generation of both SiO and CO gases. The 100% decomposition of $\mathrm{SiC}_X\mathrm{O}_Y$ phase in the fibers under argon atmosphere gives the following mass loss: $100\cdot\Delta W/W_0 \fallingdotseq 26\%$ for Nicalon, 3% for Hi-Nicalon and 1% for Hi-Nicalon S, respectively [3]. Here, W_0 and ΔW are the initial mass of fibers and the mass change caused by heat-treatment, respectively. The largest mass loss was produced in Nicalon fibers, but it was kept within 26% at 1623 K. For Hi-Nicalon and Hi-Nicalon S fibers, the mass loss at $p_{\mathrm{T}} \leq 10^2$ Pa was above 3 and 1% at 1623 K, respectively. On the other hand, after the heat-treatment at 1723 K and at $p_{\mathrm{T}} \leq 10^2$ Pa, Nicalon fibers showed the mass loss greater than 100% decomposition value, i.e., $100\cdot\Delta\ W/W_0 \fallingdotseq 26\%$. In particular, the heat-treatment at $p_{\mathrm{T}} = 1$ Pa caused great mass loss; $100\cdot\Delta W/W_0 = 87.5\%$ for Nicalon, 47.3% for Hi-Nicalon and 62.7% for Hi-Nicalon S, respectively. Such significant gas generation shows that the thermal decomposition of $\mathrm{SiC}_X\mathrm{O}_Y$ phase was followed by the active-oxidation of SiC crystallites [4].

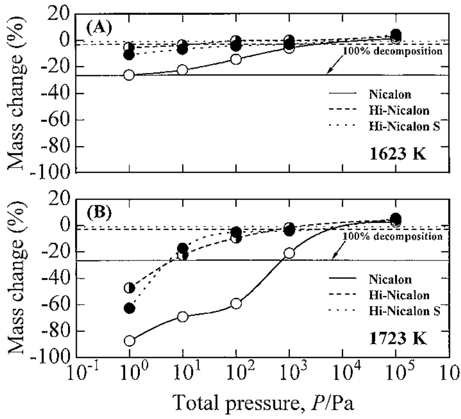

Figure 1 Mass change from SiC fibers heat-treated for 1 h at 1623 and 1723 K under different total pressures. "100% decomposition" lines show mass losses due to complete decomposition of $\mathrm{SiC}_X\mathrm{O}_Y$ phase in fibers.

3.2. X-ray diffraction

Fig. 2 shows the X-ray diffraction patterns of the fibers heat-treated at 1723 K. At $p_{\mathrm{T}} \leq 10^3$ Pa, cristobalite peak at $2\theta \fallingdotseq 22°$ was not detected and only β-SiC peaks were observed in all the fibers. The effect of total pressure, p_{T} on the β-SiC grain growth for the fibers heat-treated at 1623 and 1723 K is shown in Fig. 3. Nicalon, in the as-received state, has a microcrystalline structure with a grain size of 3 nm. When Nicalon was heat-treated under lower total pressures, a significant coarsening of β-SiC crystal was observed. Hi-Nicalon exhibited slight crystal growth after heat-treatment and the SiC crystal size was almost constant with the p_{T} value; the mean sizes were 6 nm at 1623 K and 8 nm

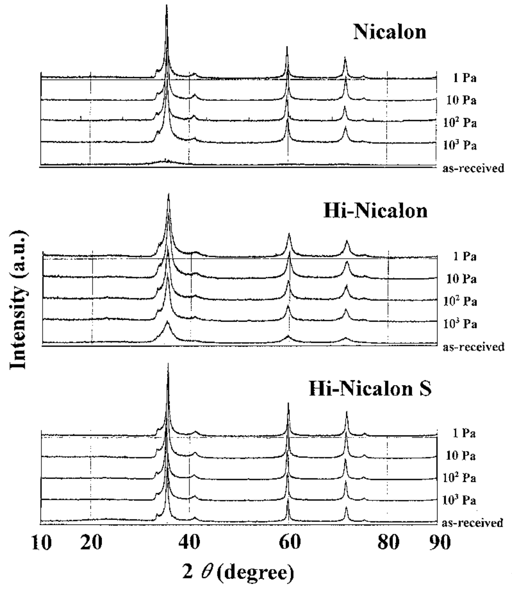

Figure 2 X-ray diffraction patterns for SiC fibers heat-treated for 1 h at 1723 K under different total pressures.

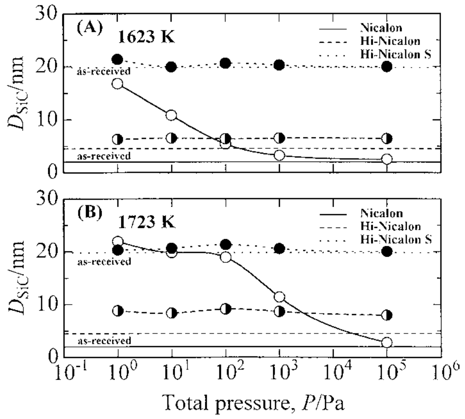

Figure 3 SiC crystallite size (D_{SiC}) of SiC fibers heat-treated for 1 h at 1623 and 1723 K under different total pressures.

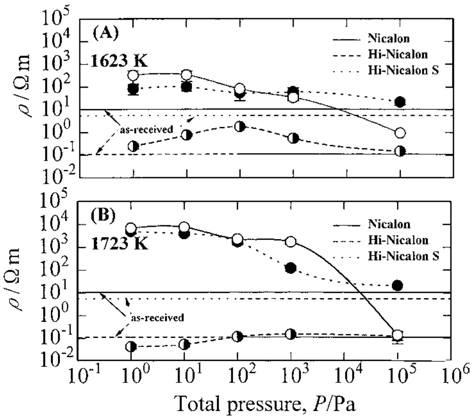

Figure 4 Specific resistivity (ρ) of SiC fibers heat-treated for 1 h at 1623 and 1723 K under different total pressures.

at 1723 K respectively, compared with 4.5 nm in the as-received fiber. On the other hand, Hi-Nicalon S having a coarse-grained structure in the as-received state did not cause at all the grain growth of SiC after the heat-treatment.

3.3. Specific resistivity

Fig. 4 shows the specific resistivity for the fibers heat-treated at 1623 and 1723 K as a function of the p_T value. It may be noted that the decreased p_T value led to significant increase in the resistivities of Nicalon and Hi-Nicalon. This tendency was enhanced at lower pressure and higher temperature. The heat-treatment at $p_T = 1$ Pa and 1723 K caused a increase in resistivity over five orders of magnitude for Nicalon and three orders of magnitude for Hi-Nicalon. The resistivity of Hi-Nicalon S after heat-treatment varied within one order of magnitude compared to the as-received value, regardless of the p_T value.

3.4. Fiber morphology

Fig. 5 shows the morphologies of Nicalon fibers heat-treated at 1723 K. The fiber heat-treated at $p_T = 10^3$ Pa (B) had a smooth and pore-free appearance as well as the as-received fiber (A). The heat-treatment at $p_T = 10^2$ and 1 Pa produced a porous and coarse-grained structure throughout the entire area of the fiber surface (C and D). In addition, the reduction of fiber diameter was found for the fibers heat-treated at $p_T = 1$ Pa. Fig. 6 shows the morphologies of Hi-Nicalon fibers heat-treated at 1723 K. Even after heat-treatment at $p_T = 10^2$ Pa, Hi-Nicalon retained a relatively smooth and fine-grained structure (C). Hi-Nicalon ultimately exhibited an increase in grain size and porosity only at the fiber surface after heat-treatment at $p_T = 1$ Pa (D). Morphologies of Hi-Nicalon S fibers heat-treated at 1723 K is shown in Fig. 7. In the as-received state, fine grains are deposited on the smooth surface (A). The deposited grains disappeared after heat-treatment. Particularly noteworthy is the formation of large pits on the coarse-grained surface of Hi-Nicalon S fiber heat-treated at $p_T = 10^2$ Pa (C), Further reduction of the p_T value resulted in significantly increased cavity (D).

3.5. Tensile strength

Room-temperature tensile strength of the fibers heat-treated at different total pressures is shown in Fig. 8. While the heat-treatment at $p_T = 10^5$ Pa (atmospheric exposure) slightly degraded the strength of Hi-Nicalon and Hi-Nicalon S, it significantly degraded that of Nicalon. A decrease in p_T value produced a very large decrease in the strength of Nicalon and Hi-Nicalon S. In particular, the strength of Nicalon was completely lost after the heat-treatment at $p_T \leq 10^2$ Pa. On the other hand, even after heat-treatment at 1723 K and $p_T = 1$ Pa, Hi-Nicalon had a relatively high strength: 1.2 GPa, i.e., 43% of as-received strength.

4. Discussion

The microstructure of polycarbosilane-derived SiC fibers is composed of β-SiC crystallites, free carbon and amorphous silicon oxycarbide (SiC_XO_Y) phase. At high temperatures, the SiC_XO_Y phase crystallizes into β-SiC and generates both SiO and CO gases:

$$SiC_XO_Y(s) \rightarrow \beta\text{-}SiC(s) + SiO(g) + CO(g) \quad (1)$$

The complete decomposition of the SiC_XO_Y phase leads to the mass losses of about 26% for Nicalon, 3% for Hi-Nicalon and 1% for Hi-Nicalon S. The thermal decomposition of the SiC_XO_Y phase have a tendency to occur even in oxidizing environments. When the SiC fibers are exposed to the atmospheres with sufficiently high oxygen partial pressure, the SiO_2 film is formed on the fiber surface by the passive-oxidation of β-SiC crystallites

$$SiC(s) + O_2(g) = SiO_2(s) + C(s) \quad (2)$$

$$SiC(s) + 3/2O_2(g) = SiO_2(s) + CO(g) \quad (3)$$

$$SiC(s) + 2O_2(g) = SiO_2(s) + CO_2(g) \quad (4)$$

The exposure to air ($p_T = 10^5$ Pa) caused the formation of SiO_2 film on the fiber surface, resulting in the mass gain (Fig. 1). The SiO_2 film suppressed the

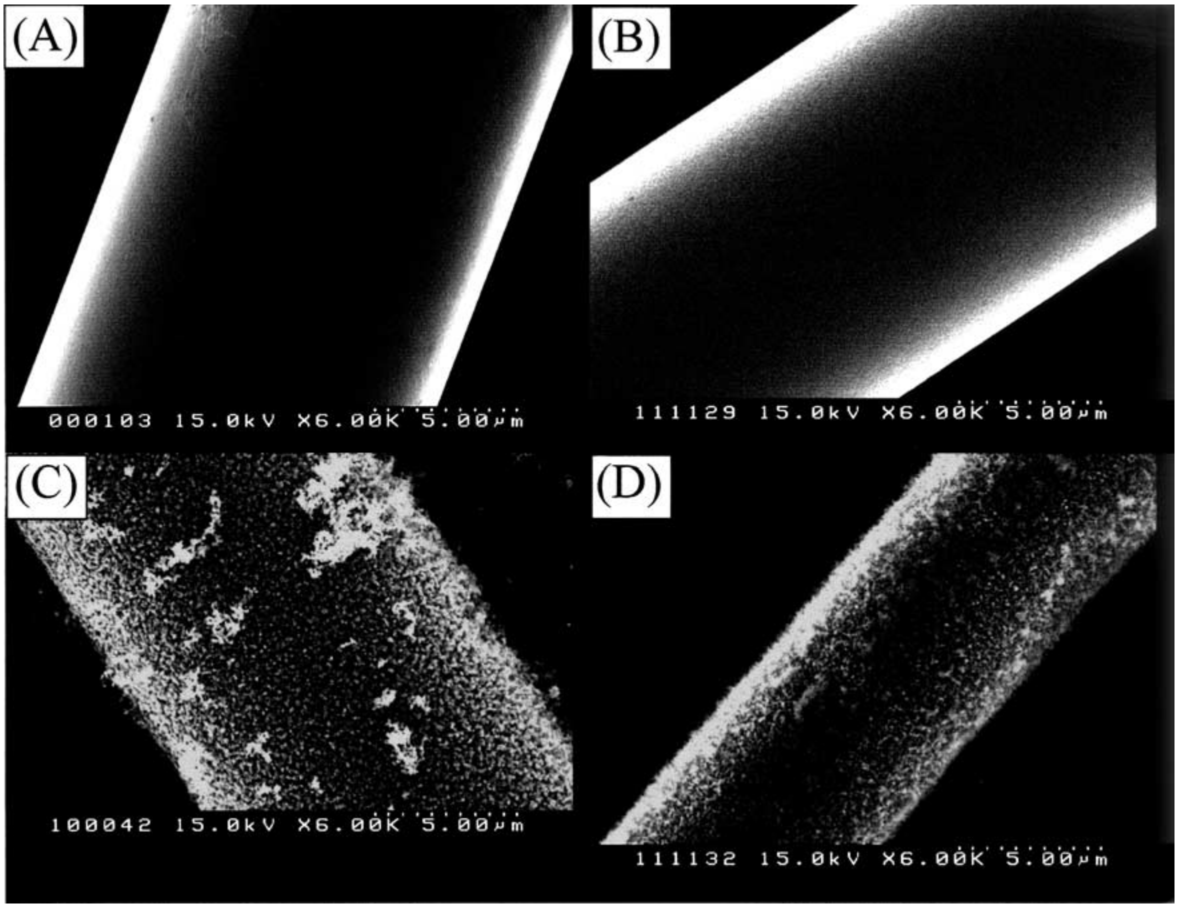

Figure 5 Morphologies of Nicalon fibers in as-received state (A) and after heat-treatment for 1 h at 1723 K under total pressures of 10^3 Pa (B), 10^2 Pa (C) and 1 Pa (D).

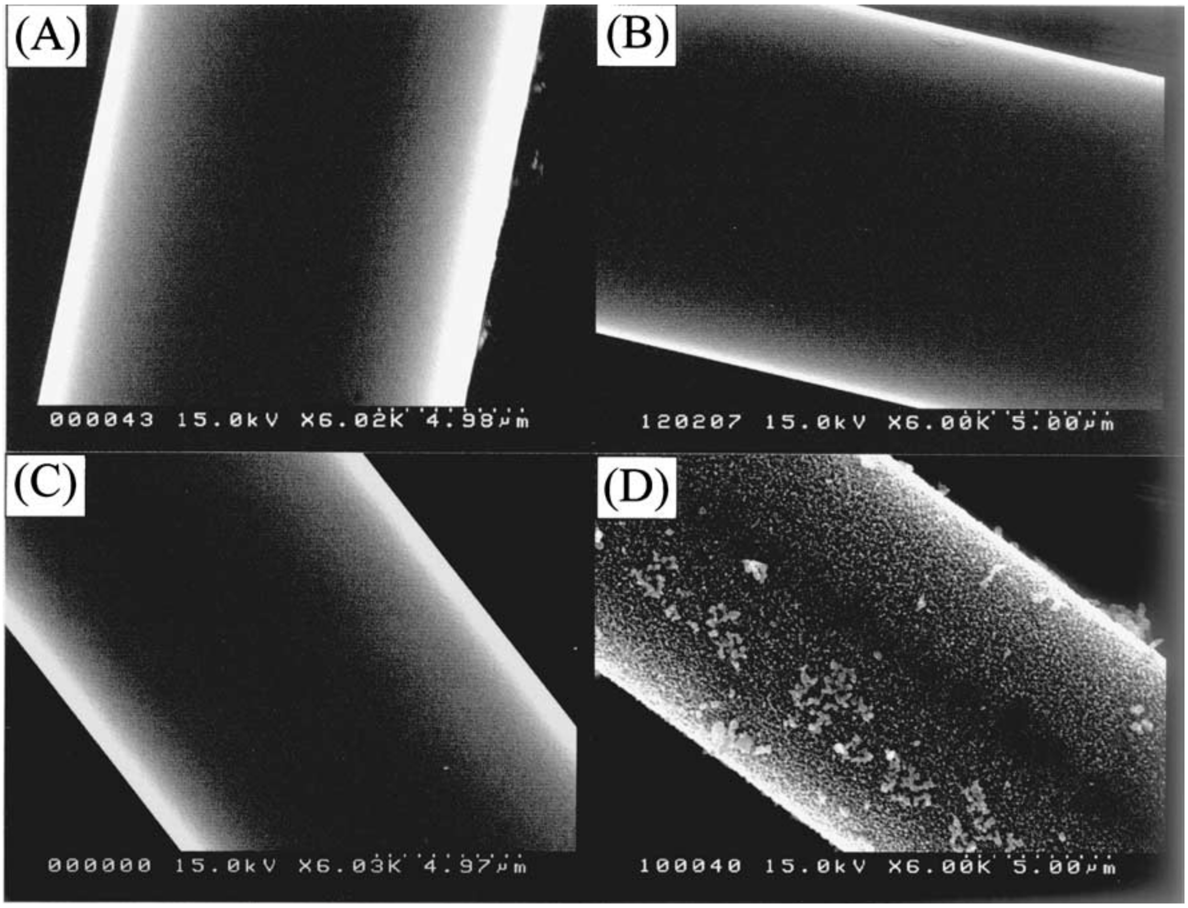

Figure 6 Morphologies of Hi-Nicalon fibers in as-received state (A) and after heat-treatment for 1 h at 1723 K under total pressures of 10^3 Pa (B), 10^2 Pa (C) and 1 Pa (D).

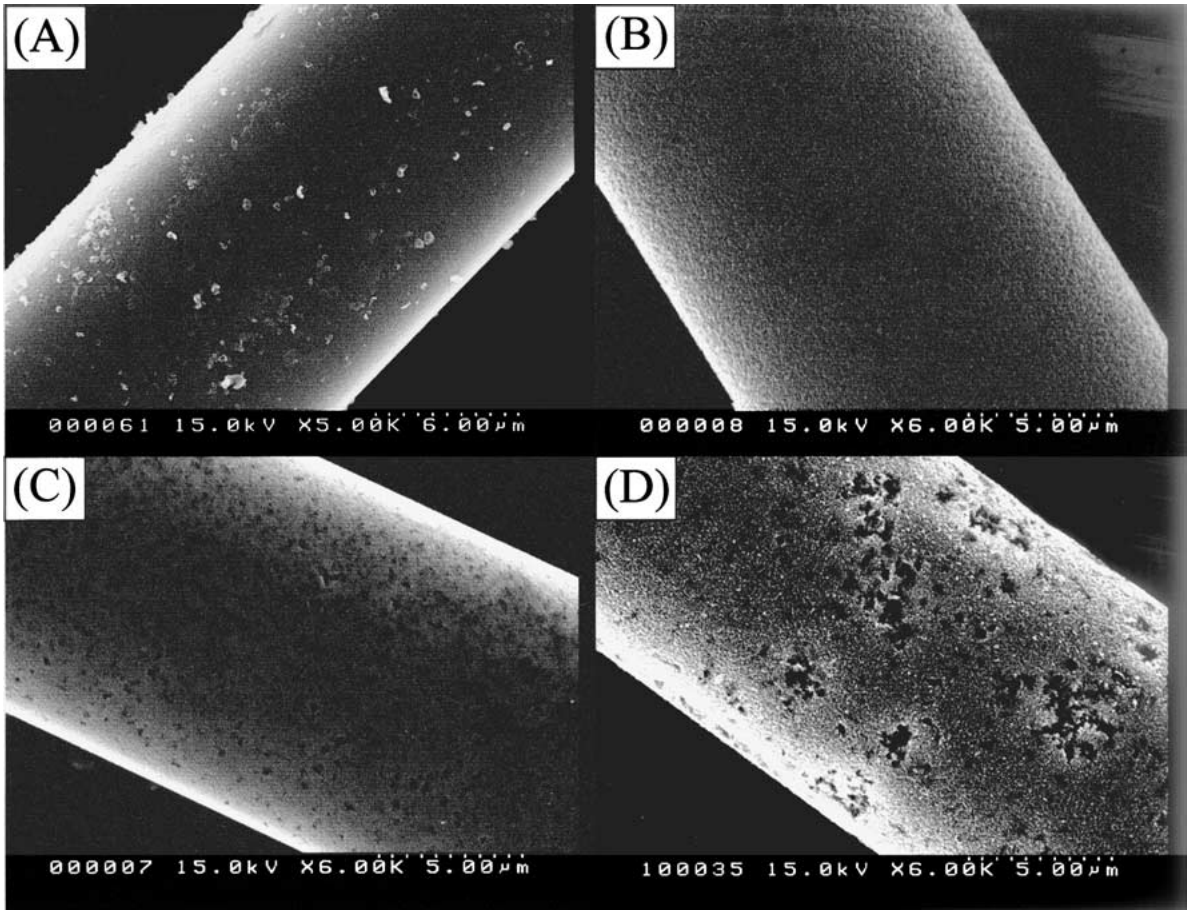

Figure 7 Morphologies of Hi-Nicalon S fibers in as-received state (A) and after heat-treatment for 1 h at 1723 K under total pressures of 10^3 Pa (B), 10^2 Pa (C) and 1 Pa (D).

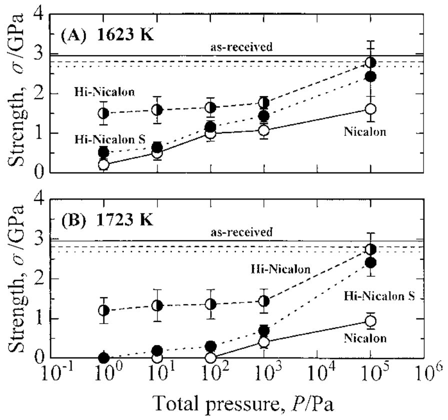

Figure 8 Room-temperature tensile strength (σ) of SiC fibers heat-treated for 1 h at 1623 and 1723 K under different total pressures.

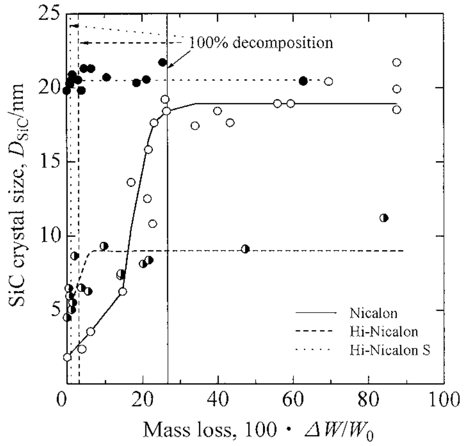

Figure 9 Relationship between SiC crystallite size and mass loss for SiC fibers heat-treated for 1 h at 1623 and 1723 K under different total pressures. "100% decomposition" lines show mass losses due to complete decomposition of SiC_XO_Y phase in fibers.

decomposition of the SiC_XO_Y phase through inhibiting the escape of decomposed gases, SiO and CO [7–10]. On the other hand, the heat-treatment at $p_T \leq 10^3$ Pa produced the mass loss and SiC crystal growth (Figs 1 and 3). In addition, X-ray diffraction and SEM observation showed no formation of SiO_2 film on the surface of all the fibers (Figs 2, 5, 6 and 7). These results suggest the occurrence of the decomposition reaction (1). The retained gas in an alumina tube is air (79%N_2-21%O_2). The low p_T value is favorable for the generation of decomposed gases and the low oxygen partial pressures ($p_{O2} \leq 2.1 \times 10^2$ Pa) retards the passive-oxidation of SiC crystals in the fibers. Thus, only the thermal decomposition of the SiC_XO_Y phase seems to occur at $p_{O2} \leq 10^3$ Pa. At further lower p_{O2} value and particularly at 1723 K, the masses loss exceeded the value derived from the complete decomposition of the SiC_XO_Y phase: 26% for Nicalon, 3% for Hi-Nicalon and 1% for Hi-Nicalon S (Fig. 1). This result demonstrates the occurrence of reactions other than the thermal decomposition of the SiC_XO_Y phase. At elevated temperature and low oxygen pressures, SiC is oxidized in the active-oxidation regime by the following reactions:

$$\mathrm{SiC(s)} + 1/2\mathrm{O_2(g)} = \mathrm{SiO(g)} + \mathrm{C(s)} \quad (5)$$

$$\mathrm{SiC(s)} + \mathrm{O_2(g)} = \mathrm{SiO(g)} + \mathrm{CO(g)} \quad (6)$$

$$\mathrm{SiC(s)} + 3/2\mathrm{O_2(g)} = \mathrm{SiO(g)} + \mathrm{CO_2(g)} \quad (7)$$

Since the oxidation product, SiO, is volatile material, the active-oxidation of SiC leads to a significant mass loss and no formation of oxide film. The mass loss data prove that the fibers were actively oxidized by the retained oxygen gas in an alumina tube (Fig. 1). Unquestionably the active-oxidation may take place at 1723 K and $p_T \le 10^2$ Pa ($p_{O_2} \le 2.1 \times 10$ Pa). Thus, the thermal decomposition of the SiC_XO_Y phase is thought to be followed by the active-oxidation of SiC crystallites. The thermal decomposition can be interpreted to be the active oxidation of SiC crystallites by oxygen contained in the fibers. Therefore, the active-oxidation of SiC crystallites by retained oxygen gas is thought to begin after consumption of the oxygen in the fibers. As seen from SEM observations, the active-oxidation caused the increase in porosity and the formation of pits (Figs 5, 6 and 7). For Nicalon and Hi-Nicalon S, the serious damage to the fiber structure is thought to cause the breakdown of the circuit and the reduction of the effective cross-sectional area for the electric conduction, resulting in a marked increase in the resistivity of the fibers (Fig. 4). In addition, the active-oxidation produced a significant degradation of fiber strength; particularly the strength of Nicalon was completely lost at 1723 K and $p_T \le 10^2$ Pa (Fig. 8). On the other hand, for Hi-Nicalon fiber, the fractured surface was relatively smooth after active-oxidation, implying a small damage to core structure. As a result, the resistivity was almost unchanged and appreciable strength was retained; $\sigma \fallingdotseq 1.2$ GPa even at 1723 K and $p_T = 1$ Pa. The AES analysis shows that Hi-Nicalon is coated with a thin carbon layer [11] . The presence of the carbon layer seems to be effective for the retardation of the active-oxidation under reduced pressures. This is consistent with the result that the carbon-coating of Nicalon NL200 by CVD method (Nicalon NL600, Nippon Carbon Co., Tokyo, Japan) was capable of retarding the active-oxidation. For example, the mass loss after heat-treatment for 1 h at 1723 K and $p_T = 1$ Pa were 31.2% for Nicalon NL600 and 88.2% for Nicalon NL200, respectively. It is not possible at present to predict the reason why the active-oxidation was hindered by the presence of carbon layer. Thus, the fiber were oxidized in the active-oxidation regime at $p_T \le 10^2$ Pa. However, a further reduction in p_T value causes no longer the active-oxidation. When exposed at $T = 1673$ K and $p_T = 10^{-3}$ Pa, Nicalon is merely subjected to the complete decomposition involving the mass loss of 26–28% [5, 6].

The thermal decomposition of the SiC_XO_Y phase results in the grain growth of β-SiC and gas generation. Therefore, β-SiC crystallite size (D_{SiC}) appears to be related to the mass loss of the heat-treated fibers ($100 \cdot \Delta W/W_0$). Fig. 9 shows the relationship between D_{SiC} and $100 \cdot \Delta W/W_0$. The crystal growth of SiC before complete decomposition is primarily responsible for thermal decomposition of the SiC_XO_Y phase. Therefore, Nicalon with high oxygen content (12%O) was markedly subjected to grain growth compared to Hi-Nicalon with low oxygen content (0.5%O). For Hi-Nicalon S having a nearly stoichiometric composition, SiC grain was coarse in the as-received state (about 20 nm) and it grew only slightly after thermal decomposition ($100 \cdot \Delta W/W_0 \le 1$). When the mass loss exceeds the value after complete decomposition of the SiC_XO_Y phase, no further increase in SiC crystallite size was observed in all the fibers. This result shows that no growth of SiC grain is caused by the active-oxidation.

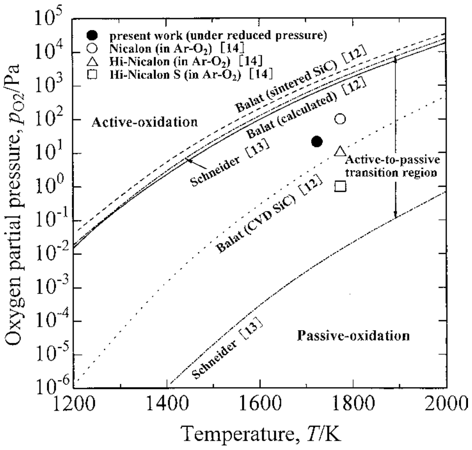

Figure 10 Oxygen partial pressure for active-to-passive oxidation transition of silicon carbide as function of temperature.

Fig. 10 shows the oxygen partial pressure of the active-to-passive oxidation transition (p_{O_2}) for SiC. The active-to-passive oxidation transition is greatly affect by the types of SiC [12, 13] . In present work, all types of SiC fibers were actively oxidized at 1723 K and $p_{O_2} = 2.1 \times 10$ Pa. Schneider's data shows that this p_{O_2} value is in the active-to-passive oxidation region. According to the oxidation at one atmospheric pressure of Ar-O_2 gas mixtures and 1773 K, the p_{O_2} values were 10^2 Pa for Nicalon, 10 Pa for Hi-Nicalon and 1 Pa for Hi-Nicalon S, respectively [14, 15] . It is possible that Nicalon alone is actively oxidized at $p_{O_2} = 2.1 \times 10$ Pa and 1723 K. However, mass change data, resistivity values and SEM observation show that Hi-Nicalon and Hi-Nicalon S were oxidized in the active-oxidation regime. The active-oxidation occurred at higher p_{O_2} value under reduced pressures than one atmospheric pressure.

5. Conclusions

The heat-treatment at total pressures $p_T \le 10^3$ Pa caused the thermal decomposition of SiC_XO_Y phase for three types of polycarbosilane-derived SiC fibers: Nicalon, Hi-Nicalon and Hi-Nicalon S. At 1723 K and $p_T \le 10^2$ Pa, the thermal decomposition of SiC_XO_Y phase was followed by the active-oxidation of SiC crystallites in the fibers. The grain growth of SiC was caused by the former, rather than the latter. The specific resistivities of Nicalon and Hi-Nicalon S were significantly raised by the active-oxidation. The active-oxidation of

Nicalon and Hi-Nicalon S rendered the fiber structure porous, resulting in the significant degradation of strength. The core of Hi-Nicalon remained dense after the active-oxidation and a strength of 1.2 GPa was retained even at $p_{\mathrm{T}} = 1$ Pa.

Acknowledgment

This study was partly supported by a grant from the Ministry of Education, Science, Sports and Culture under Grant No. 11450255.

References

1. R. R. NASLAIN, *Adv. Comp. Mater*. **8** (1999) 3.
2. *Idem., Key Engin. Mater.* **164/165** (1999) 3.
3. M. TAKEDA, J. SAKAMOTO, A. SAEKI, Y. IMAI and H. ICHIKAWA, *Ceram. Eng. Sci. Proc.* **16** (1998) 535.
4. T. SHIMOO, H. TAKEUCHI and K. OKAMURA, *J. Amer. Ceram. Soc.* **84** (2001) 566.
5. M. H. JASKOWIAK and J. A. DICARLO, *ibid.* **72** (1989) 192.
6. C. VIX-GUTERL and P. EHRBURGER, *J. Mater. Sci.* **31** (1996) 5363.
7. T. SHIMOO, F. TOYODA and K. OKAMURA, *J. Ceram. Soc. Jpn*. **107** (1999) 263.
8. *Idem., J. Amer. Ceram*. **83** (2000) 1450.
9. *Idem., J. Mater. Sci*. **35** (2000) 3811.
10. T. SHIMOO, H. TAKEUCH and K. OKAMURA, *J. Ceram. Soc. Jpn*. **108** (2000) 1096.
11. H. ICHIKAWA, K. OKAMURA and T. SEGUCHI, *Ceram. Trans*. **58** (1995) 65.
12. M. J. H. BALAT, *J. Europ. Ceram. Soc*. **16** (1996) 55.
13. B. SCHNEIDER, A. GUETTE, R. NASLAIN, M. CATALDI and COSTECALDE, *J. Mater. Sci.* **33** (1998) 535.
14. T. SHIMOO, Y. MORISADA and K. OKAMURA, *J. Amer. Ceram. Soc*. **83** (2000) 3049.
15. *Idem., J. Mater. Sci*. **37** (2002) 1793.

Received 29 May
and accepted 17 December 2001