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Effect of CO_2 partial pressure on oxidation of low-oxygen SiC fibers (Hi-Nicalon) in Ar-CO_2 gas mixtures

T. SHIMOO, K. OKAMURA
Department of Metallurgy and Materials Science, Graduate School of Engineering, Osaka Prefecture University, 1-1, Gakuen-cho, Sakai, 599-8531 Osaka, Japan

T. MORITA
Osaka Gas Co., Ltd., 4-1-2, Hirano-machi, Chuo-ku, 541-0046 Osaka, Japan

The oxidation behavior and thermal stability of Si–C fibers (Hi-Nicalon) in Ar-CO_2 gas mixtures were investigated at 1773 K, through mass change determination, XRD analysis, resistivity measurement, SEM observation and tensile tests. Mass gain and cristobalite formation were observed at $p_{CO_2} \geqq 10^3$ Pa, showing the occurrence of passive-oxidation of the fibers. On the other hand, the active-oxidation was characterized by the mass loss, no formation of SiO_2 film and a marked increase in resistivity at $p_{CO_2} \leqq 5 \times 10^2$ Pa. The oxygen potential for the active-to-passive oxidation transition in Ar-CO_2 gas mixtures was nearly identical to that in Ar-O_2 gas mixtures. About 50% of the strength in the as-received state was retained after the active-oxidation in Ar-CO_2 gas mixtures.

1. Introduction

Polycarbosilane-derived silicon carbide fibers are of great importance as reinforcing materials of ceramic matrix composites (CMC) for high-temperature applications. The high-temperature stability and oxidation resistance are required for fabrication and service of such fiber-reinforced CMC. Therefore, the microstructure, microchemistry, mechanical properties and thermal stability have been extensively investigated for the silicon carbide fibers after high-temperature exposure in inert environments (Ar, N_2 and vacuum) and oxidizing environments (O_2 and air). The combustion environments have been changed over a wide range of oxygen potentials. As a result, silicon carbide fibers can be oxidized in either the passive-oxidation regime or the active-oxidation regime. Since the passive-oxidation allows the surface of silicon carbide fibers to be coated with a stable SiO_2 film under high oxygen potential, further oxidation can be retarded. On the other hand, the active-oxidation causes the evaporation of SiC in the fibers producing SiO gas under a low oxygen potential, resulting in a marked degradation of fiber strength. While there were numerous reports on the passive-oxidation of silicon carbide fibers [1–21], there was little information on the active-oxidation of silicon carbide fibers. The authors have investigated the oxidation behaviors for various types of polymer-derived silicon carbide fibers in Ar-O_2 gas mixtures ranging from active-oxidation to passive-oxidation region [22–24]. CO_2 gas is necessarily present in the combustion environments. Therefore, further investigations of the oxidation of silicon carbide fibers throughout a wide range of CO_2 concentrations are important. Therefore, the oxidation of Nicalon and Hi-Nicalon fibers (Nippon Carbon Co., Japan) has been studied in pure CO_2 gas [25, 26]. The exposure of the fibers at 1773 K in CO_2 gas showed the mass gain and silica formation which are characteristic of passive-oxidation. The reduction in CO_2 partial pressure appears to cause the transition from passive-oxidation to active-oxidation. In the present work, the CO_2 partial pressures were controlled by diluting CO_2 gas with Ar gas. The oxidation behavior of Hi-Nicalon fibers at 1773 K under CO_2 partial pressures from 10^2 to 10^5 Pa was 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 Ar-CO_2 gas mixtures. These results were compared with those for the oxidation of Hi-Nicalon in Ar-O_2 gas mixtures [23].

2. Experimental method

The samples employed in this study were 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 were placed in a alumina tube of an SiC resistance furnace. After evacuation, an Ar-CO_2 gas mixture was allowed to flow in to the tube at a flow rate of 100 cm^3/min. The partial pressure of carbon dioxide was changed over a range from

10^2 to 10^5 Pa ($p_{Ar} = 0$ 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 oxidation in Ar-CO_2 gas mixtures. The existing phases and β-SiC crystallite size of the fibers were determined by X-ray diffractometer (XRD). Before the specific resistivity measurements and tensile tests, SiO_2 film was removed with NH_4OH + HF solution. The fibers oxidized in the active-oxidation region, as it is, were subjected to resistivity measurement and tensile test. The 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 oxidation. Morphologies of as-oxidized fibers and SiO_2-removed fibers were examined by field-emission scanning microscopy (FE-SEM).

3. Results

3.1. Mass change

Fig. 1 shows the mass changes for Hi-Nicalon fibers oxidized for 36 ks at $T = 1773$ K and $p_{CO_2} = 10^2$–10^5 Pa. There were the mass gains of +5–+7% at $p_{CO_2} \geqq 10^3$ Pa. Hi-Nicalon fibers were oxidized in the passive-oxidation regime in pure CO_2 gas (at $p_{CO_2} = 10^5$ Pa) [25]. Therefore, the observed mass gains show the occurrence of passive-oxidation as well. On the other hand, the mass losses of about −5% were observed at $p_{CO_2} \leqq 5 \times 10^2$ Pa. These values are significantly lower than the mass loss of −0.5% after exposure of 36 ks at $T = 1773$ K and $p_{Ar} = 10^5$ Pa (in pure Ar gas). Furthermore, they were roughly double the mass loss of −2.3% for compete decomposition of amorphous silicon oxycarbide (SiC_XO_Y) phase in Hi-Nicalon fibers [13]. This result implies that the high-temperature exposure in Ar-CO_2 gas mixtures with low CO_2 partial pressures caused the thermal decomposition of SiC_XO_Y phase and the subsequent active-oxidation of SiC grains, as well as the exposure in Ar-O_2 gas mixtures of $p_{CO_2} \leqq 10$ Pa [23].

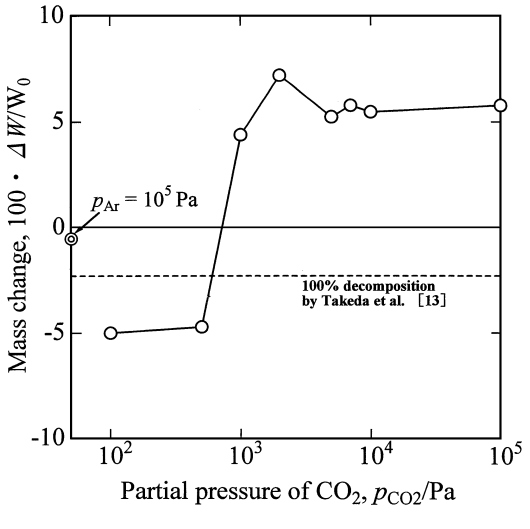

Figure 1 Mass changes for Hi-Nicalon fibers exposed for 36 ks at 1773 K in Ar-CO_2 gas mixtures.

3.2. X-ray diffraction analysis

Fig. 2 shows the X-ray diffraction patterns for the fibers oxidized for 36 ks at $T = 1773$ K and $p_{CO_2} = 0$–10^5 Pa. The sharp X-ray diffraction peak at $2\theta \doteqdot 22^\circ$ reveals that Hi-Nicalon fibers were passively oxidized at $p_{CO_2} \geqq 10^3$ Pa, resulting in the formation of a cristobalite film on the fiber surface. On the other hand, in view of the mass loss (Fig. 1), no detection of cristobalite phase implies the occurrence of active-oxidation at $p_{CO_2} \leqq 5 \times 10^2$ Pa.

The apparent crystallite size of β-SiC, D_{SiC} was calculated from the half-width value of (111) peak using Scherrer's formula. Fig. 3 shows the value D_{SiC} shows a function of p_{CO_2}. The fibers after oxidation at 1773 K have three times larger β-SiC crystallite size ($D_{SiC} \doteqdot 14$ nm) than the as-received fibers, independently on p_{CO_2}. The grain growth β-SiC is thought to be mainly caused by the crystallization of uncrystallized Si–C phase in Hi-Nicalon fibers ($T \geqq 1473$ K) [27]. Thus, Fig. 3 reveals that the oxidation temperature is a controlling factor in the grain growth of β-SiC.

3.3. Fiber morphology

Fig. 4 show the morphologies of the fibers oxidized for 36 ks at 1773 K. All the fibers oxidized in the passive-oxidation region were coated with thick cristobalite film (A–F). The cristobalite film is known to crack during cooling, owing to a large volume shrinkage associated to the cristobalite $\beta \rightarrow \alpha$ transition (A and C). Therefore, it is noted that no crack was observed in the cristobalite film formed at $p_{CO_2} = 10^3$ Pa (E). On the other hand, the fracture appearance of unoxidized cores is smooth and glassy (B, D and F). The fiber surface is slightly roughened after exposure at $p_{CO_2} = 5 \times 10^2$ Pa (G, H). A further reduction in p_{CO_2} value ($p_{CO_2} = 10^2$ Pa) results in a peculiar appearance on fiber surface. As a consequence of active-oxidation, the grooves are deeply scooped in the surface of fiber (I, J). The fiber core displays a glassy fracture surface, as well as that oxidized in the passive-oxidation region, showing that the active-oxidation advances from the surface to the interior.

SEM photos at high magnification are shown in Fig. 5, for the fibers in the as-received state and after active-oxidation. The irregularity of the surface is very weak in the as-received state (A). The active-oxidation, as a consequence of the gasification of SiC grains, causes serious unevenness of fiber surface (B, C).

3.4. Specific resistivity

Fig. 6 shows the specific resistivity of the fibers oxidized for 36 ks at $T = 1773$ K as a function of p_{CO_2}. For the fibers oxidized at $p_{CO_2} \geqq 10^3$ Pa, a cristobalite

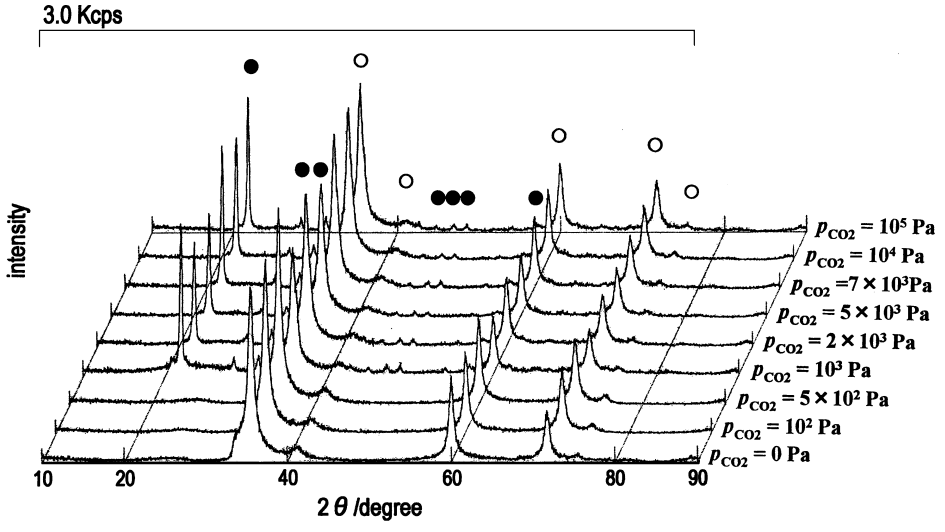

Figure 2 X-ray diffraction patterns for as-received fiber and fibers oxidized for 36 ks at 1773 K in Ar-CO_2 gas mixtures with different CO_2 partial pressures.

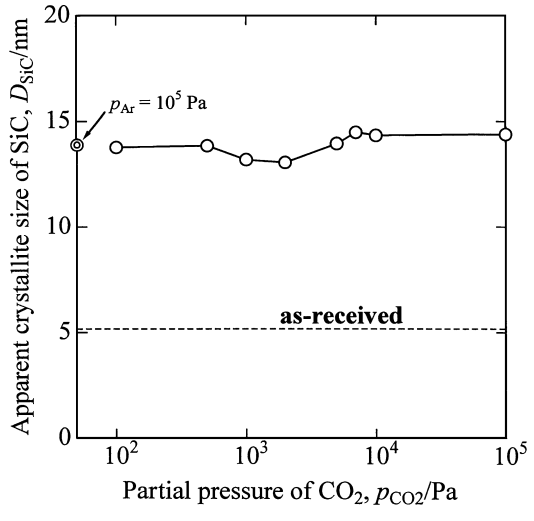

Figure 3 β-SiC crystallite size of fibers heated for 36 ks at 1773 K in Ar-CO_2 gas mixtures with different CO_2 partial pressures.

film was removed with NH_4F + HF solution before resistivity measurement. The resistivity of unoxidized core after passive-oxidation at $p_{CO_2} \geqq 10^3$ Pa is lowered to about half of that for the as-received fibers. This appears to be responsible for the organization of free carbon and the crystallization of Si–C phase in the fibers at $T = 1773$ K [9, 27]. On the other hand, after active-oxidation region at $p_{CO_2} \leqq 5 \times 10^2$ Pa, the resistivity was larger than that in the as-received state. This is because the activation-oxidation renders the fiber structure highly porous, resulting in hindrance to the electrical conduction in a fiber. In addition, such high porosity of the fibers leads to a marked reduction of cross-sectional area controlling the conductivity. Therefore, the net resistivity of the fibers oxidized in the active-oxidation regime is thought to be overestimated by the use of apparent cross-sectional area calculated from the fiber diameter.

3.5. Tensile strength

Fig. 7 shows the room-temperature tensile strength for the fibers after oxidation of 36 ks at 1773 K, as a function of p_{CO_2} value. The fibers oxidized in the passive-oxidation region (at $p_{CO_2} \geqq 10^3$ Pa) were subjected to tensile tests after removal of a cristobalite film. About 90% of the strength in the as-received state (2.4 GPa) is retained after oxidation at $p_{CO_2} \geqq 7 \times 10^3$ Pa. This strength is much larger than that of the fibers exposed in Ar gas (1.7 GPa). The reduction of p_{CO_2} in the passive-oxidation region causes a marked degradation of strength from 2.4 GPa at at $p_{CO_2} = 7 \times 10^3$ Pa to 0.7 GPa at $p_{CO_2} = 10^3$ Pa. After oxidation in Ar-CO_2 gas mixtures, about 50% of the strength in the as-received state is retained even in the active-oxidation region.

4. Discussion

The passive-oxidation rate of high-purity stoichiometric CVD-SiC in CO_2 gas was negligibly small and independent of temperature [28]. On the other hand, Hi-Nicalon fibers employed in this work were subjected to a severe passive-oxidation and showed strong temperature-dependence of oxidation rate [25]. At $T = 1773$ K and $p_{CO_2} \geqq 10^3$ Pa, Hi-Nicalon fibers were passively oxidized in Ar-CO_2 gas mixtures, as well as pure CO_2 gas. A further reduction in CO_2 partial pressure to $p_{CO_2} \leqq 5 \times 10^2$ Pa caused the active-oxidation of Hi-Nicalon fibers. The oxidation of silicon carbide in CO_2 gas are given as follows [29]:

passive-oxidation,

$$SiC(s) + CO_2(g) = SiO_2(s) + 2C(s) \quad (1)$$

active-oxidation,

$$2SiC(s) + CO_2(g) = 2SiO(g) + 3C(s) \quad (2)$$

The heat-treatment of Hi-Nicalon fibers in CO gas caused the formation of carbon film [30]. However, Auger electron spectroscopic analysis and X-ray diffraction show that no carbon film was formed on the surface of Hi-Nicalon fibers after oxidation in Ar-CO_2 gas mixtures. Therefore, it is necessary to consider alternative mechanism for the oxidation of Hi-Nicalon by CO_2 gas.

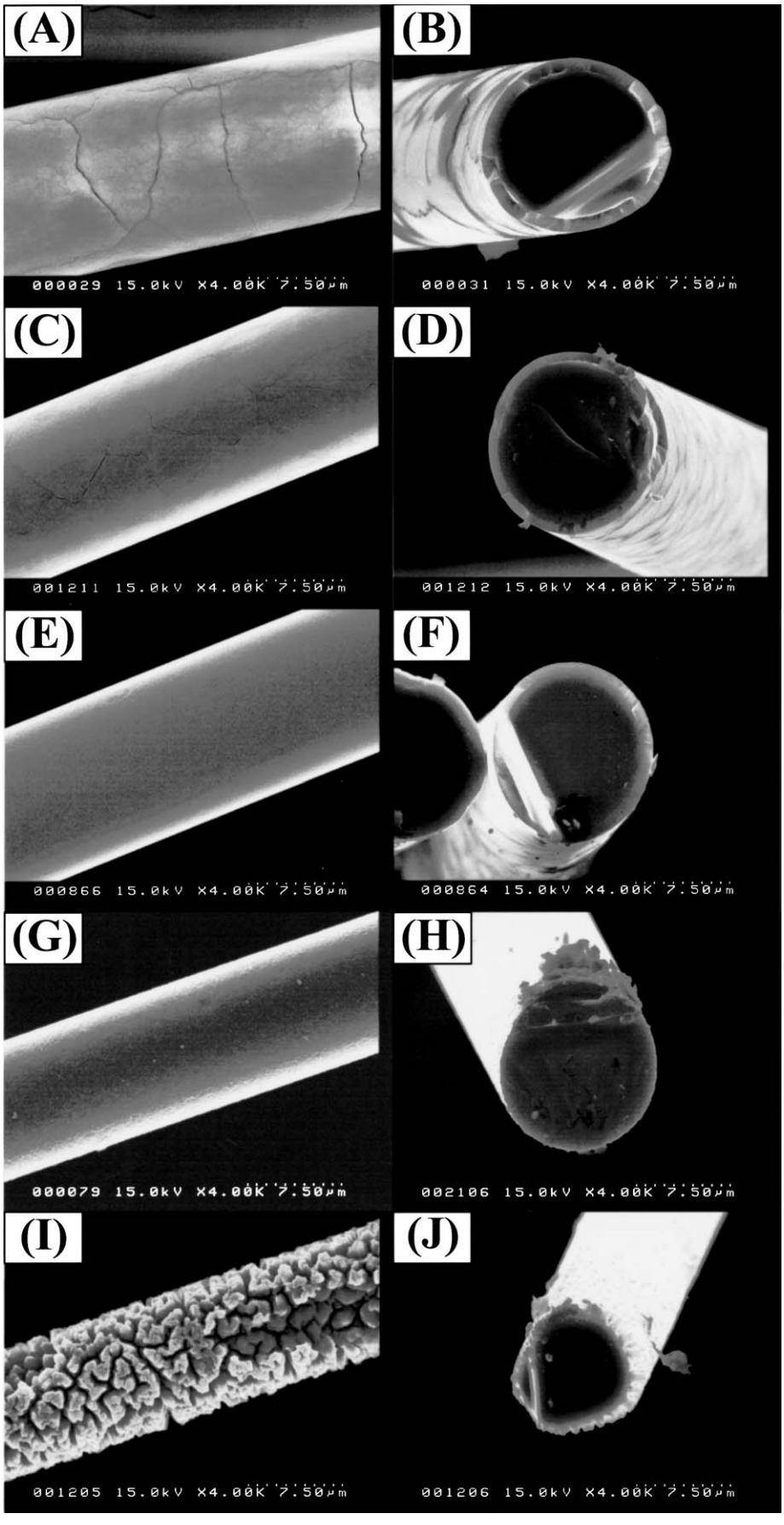

Figure 4 SEM photographs of fibres oxidized for 36 ks in Ar-CO_2 gas mixtures. (A), (B): $p_{CO_2} = 10^5$ Pa, (C), (D): $p_{CO_2} = 10^4$ Pa, (E), (F): $p_{CO_2} = 10^3$ Pa, (G), (H): $p_{CO_2} = 5 \times 10^2$ Pa, (I), (J): $p_{CO_2} = 10^2$ Pa.

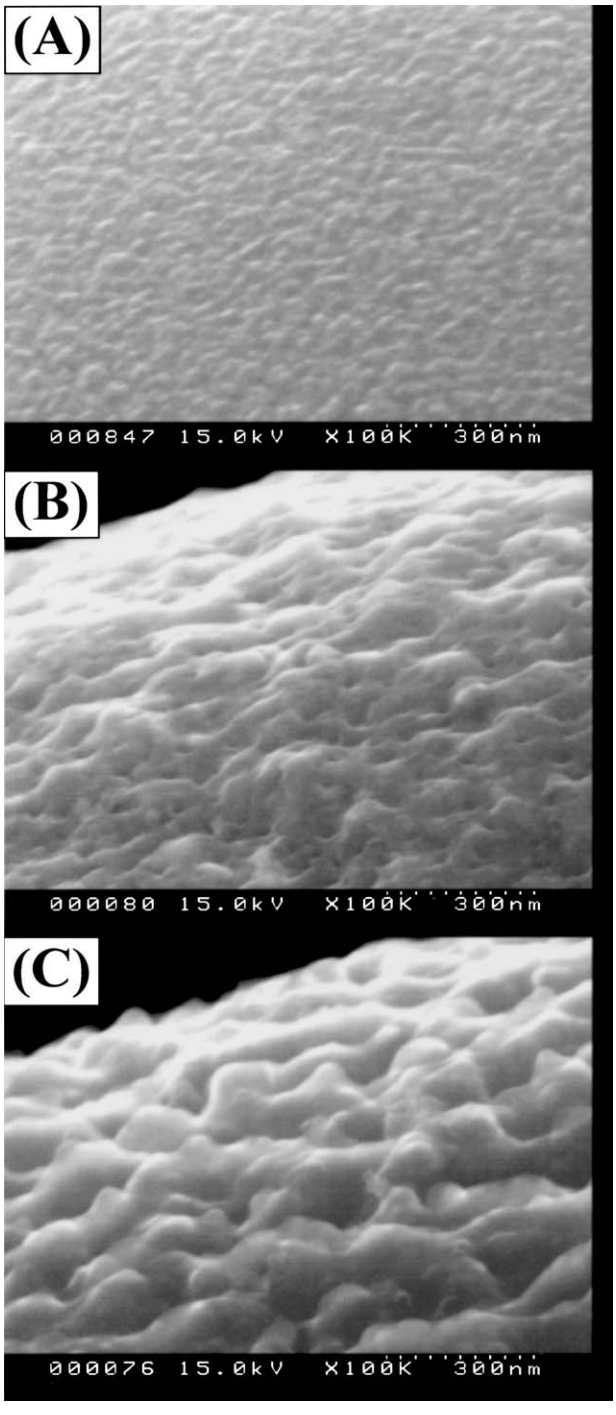

Figure 5 SEM photographs of as-received fiber (A) and fibers oxidized for 36 ks in Ar-CO_2 gas mixtures of $p_{CO_2} = 5 \times 10^2$ Pa (B) and 10^2 Pa (C).

CO_2 gas dissociates to CO and O_2 gases at high temperatures.

$$CO_2(g) = CO(g) + 1/2O_2(g) \quad (3)$$

$$\Delta G^\circ(\text{J/mol}) = 280960 - 85.23T/\text{K [31]}$$

Subsequently, Hi-Nicalon fibers are oxidized by dissociated oxygen:

in the passive-oxidation region:

$$SiC_{1.39}O_{0.01}(s) + 1.69O_2(g) = SiO_2(s) + 1.39CO(g) \quad (4)$$

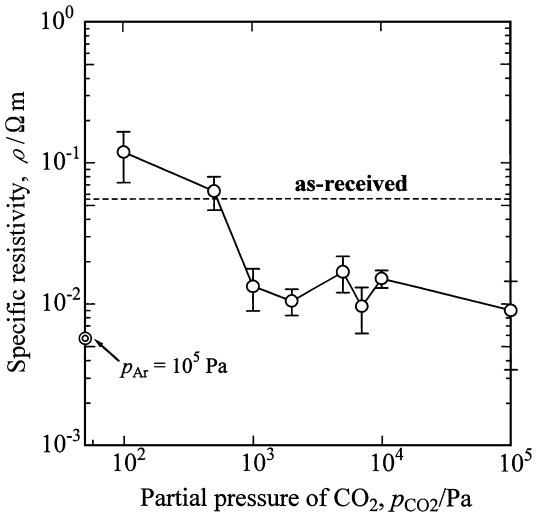

Figure 6 Specific resistivity of fibers heated for 36 ks at 1773 K in Ar-CO_2 gas mixtures with different CO_2 partial pressures.

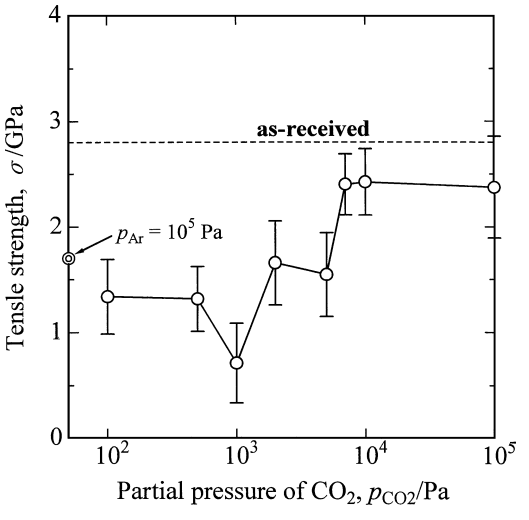

Figure 7 Room temperature tensile strength of fibers heated for 36 ks at 1773 K in Ar-CO_2 gas mixtures with different CO_2 partial pressures.

in the active-oxidation region:

$$SiC_{1.39}O_{0.01}(s) + 1.19O_2(g) = SiO(g) + 1.39CO(g). \quad (5)$$

The oxygen potentials of Ar-CO_2 gas mixtures, p_{O_2}, can be calculated from the standard free energy change, ΔG°, for the dissociation of CO_2 gas, i.e., reaction (1). Thus, on the basis of p_{O_2} values in gas mixtures, the properties of Hi-Nicalon fibers oxidized in Ar-CO_2 gas mixtures were compared with those of Hi-Nicalon fibers oxidized in Ar-O_2 gas mixtures [25].

Fig. 8 shows the mass change of Hi-Nicalon fibers oxidized for 36 ks at $T = 1773$ K as a function of oxygen potential (p_{O_2}) of Ar-CO_2 and Ar-O_2 gas mixtures. The mass gain caused by the passive-oxidation is smaller in Ar-CO_2 than in Ar-O_2 gas mixtures. This is partly due to different oxidation times; 36 ks for the oxidation in Ar-CO_2 gas mixtures, 72 Ks for that in Ar-O_2 gas mixtures. The mass change data displays that the transition from the mass gain to the mass loss occurred at $p_{O_2} = 5$–8 Pa in Ar-CO_2 gas mixtures and at $p_{O_2} = 10$–25 Pa in Ar-O_2 gas mixtures. Thus, the oxygen potential for the

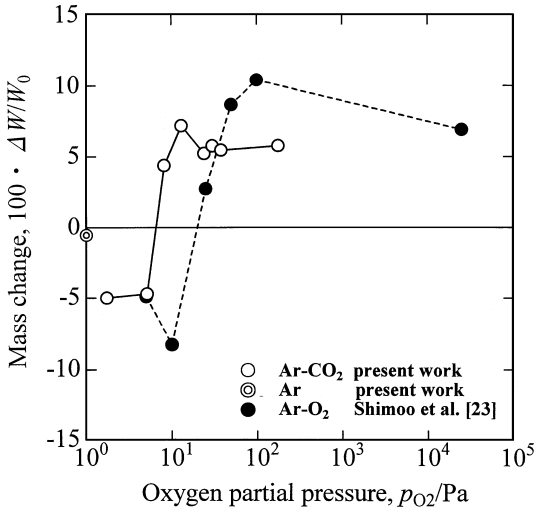

Figure 8 Mass change of Hi-Nicalon fibers heat-treated at 1773 K as function of oxygen potential of Ar-CO_2 and Ar-O_2 gas mixtures.

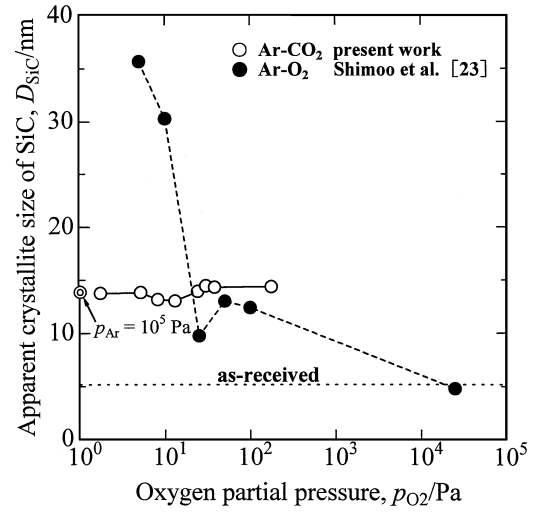

Figure 10 Relationship between apparent crystal size of β-SiC of Hi-Nicalon fibers oxidized at 1773 K and oxygen potential of gas mixtures.

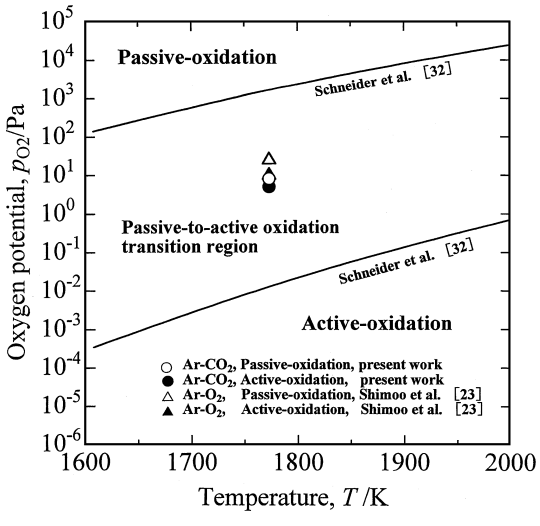

Figure 9 Oxygen potential of active-to-passive oxidation transition for different types of silicon carbide oxidized under various oxidation conditions [32] and for Hi-Nicalon fibers oxidized under Ar-CO_2 and Ar-O_2 gas mixtures.

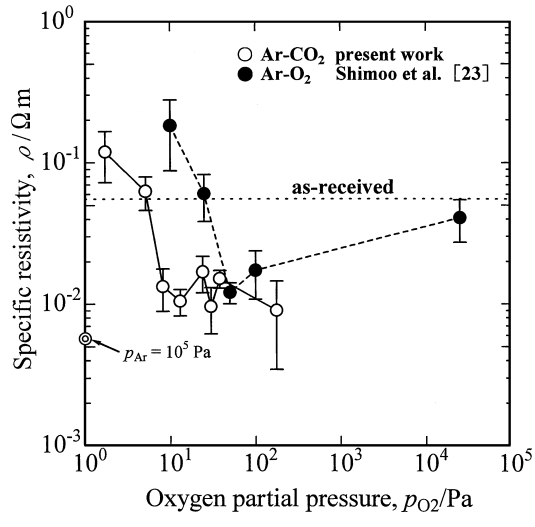

Figure 11 Relationship between specific resistivity of Hi-Nicalon fibers oxidized at 1773 K and oxygen potential of gas mixtures.

active-to-passive oxidation transition is slightly lower in Ar-CO_2 than in Ar-O_2 gas mixtures. The active-to-passive oxidation transition is probably dependent not only on the oxidation temperature and oxygen partial pressure but also on the gas flow rate, physical properties of SiO_2 film and diffusivity of oxygen through the film. Therefore, the different oxygen potential for the active-to-passive oxidation transition between Ar-CO_2 than Ar-O_2 gas mixtures appears to be attributable to the difference in the experimental conditions. In addition, it is possible that CO_2 gas, as well as the dissociated oxygen, oxidizes Hi-Nicalon fibers in Ar-CO_2 gas mixtures.

Fig. 9 shows the active-to-passive oxidation transition region for different types of silicon carbide oxidized under various oxidation conditions [32]. The transition region is in the wide range of $p_{O_2} = 10^{-2}$ to 10^3 Pa at 1773 K. The active-to-passive oxidation transition for Hi-Nicalon fibers oxidized in both Ar-CO_2 and Ar-O_2 gas mixtures are within this transition region for silicon carbides.

Fig. 10 shows the relationship between the apparent crystal size of β-SiC, D_{SiC}, and the oxygen potential (p_{O_2}) of gas mixtures [23]. After oxidation in Ar-CO_2 and Ar-O_2 gas mixtures at 1773 K, the growth of SiC crystals was caused by the crystallization of noncrystallized Si–C phase and thermal decomposition of amorphous Si–C–O phase [27]. In particular, it may be noted that a marked coarsening of SiC grains (D_{SiC} = 30–36 nm) after the active-oxidation in Ar-O_2 gas mixtures of $p_{O_2} \leqq 10$ Pa. On the other hand, in Ar-CO_2 gas mixture, the D_{SiC} value after active-oxidation ($p_{O_2} = 5$ Pa) was nearly identical to that after passive-oxidation.

Fig. 11 shows the relationship between the specific resistivity of Hi-Nicalon fibers, ρ, and the oxygen potential (p_{O_2}) of gas mixtures [23]. The ρ value in the passive-oxidation region was lower than that in the as-received state, owing to the crystallization of SiC phase and the organization of carbon aggregates at 1773 K [9, 27]. The active-oxidation in both Ar-CO_2 and Ar-O_2 gas mixtures at 1773 K caused severe breakdown of fibrous structure, resulting in a 10-fold increase in specific resistivity.

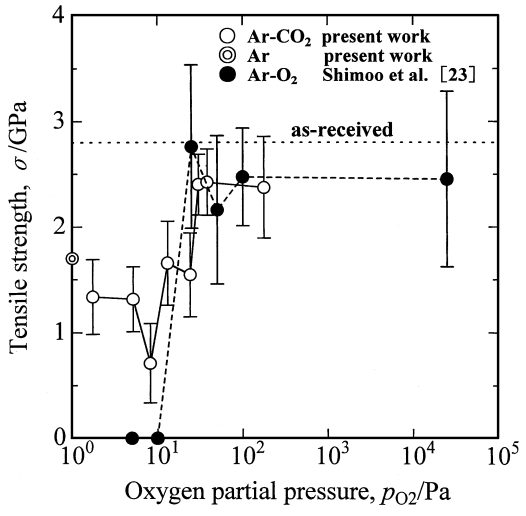

Figure 12 Relationship between room-temperature tensile strength of Hi-Nicalon fibers oxidized at 1773 K and oxygen potential of gas mixtures.

Fig. 12 shows the relationship between the room-temperature tensile strength of Hi-Nicalon fibers, σ, and the oxygen potential (p_{O_2}) of gas mixtures [23]. 80–90% of the strength in the as-received state was retained after oxidation at $p_{O_2} \geqq 50$ Pa. There was a marked degradation of fiber strength after oxidation at $p_{O_2} < 50$ Pa. The fiber strength was nearly completely lost after active-oxidation in Ar-O_2 gas mixtures ($p_{O_2} \leqq 10$ Pa). A drastic coarsening of SiC crystals during active-oxidation appears to be critical in the degradation of fiber strength. On the other hand, it may be noted that the fibers oxidized in Ar-CO_2 gas mixtures retained 48% of initial strength even after active-oxidation ($p_{O_2} = 1.7$ Pa). As can be seen from Fig. 10, this is because the coarsening of SiC grains during active-oxidation was retarded in Ar-CO_2 gas mixtures.

5. Conclusion

The exposure of Hi-Nicalon fibers at 1773 K in Ar-CO_2 gas mixtures caused passive-oxidation which was characterized by mass gain and cristobalite formation at $p_{CO_2} \geqq 10^3$ Pa and the active-oxidation which was characterized by the mass loss and a marked increase in resistivity at $p_{CO_2} \leqq 5 \times 10^3$ Pa. The oxygen potential for the active-to-passive oxidation transition in Ar-CO_2 gas mixtures ($p_{O_2} = 5$–10 Pa) was slightly lower than that in Ar-O_2 gas mixtures ($p_{O_2} = 10$–25 Pa). While a marked coarsening of β-SiC grains was caused by the active-oxidation in Ar-O_2 gas mixtures ($D_{SiC} = 30$–36 nm), β-SiC grain size was almost identical throughout the active- and passive-oxidation region in Ar-CO_2 gas mixtures ($D_{SiC} = 13$–14 nm). Consequently, the fiber strength was completely lost after active-oxidation in Ar-O_2 gas mixtures but about 50% of the strength in the as-received state was retained after active-oxidation in Ar-CO_2 gas mixtures.

References

1. T. MAH, N. L. HECHT, D. E. MCCULLUM, J. R. HOENIGMAN, H. M. KIM, A. P. KATZ and H. A. LIPSITT, *J. Mater. Sci.* **19** (1984) 1191.
2. Y. MANIETTE and A. OBERLIN, *ibid.* **24** (1989) 3361.
3. L. FILIPUZZI and R. NASLAIN, in Proceedings of 7th CIMTEC, Mater. Sci. Monograph 68 Adv. Structural Inorg. Composites, edited by P. Voncenzini (Elsevier, Amsterdam, 1991) p. 35.
4. H.-E. KIM and A. J. MOORHEAD, *J. Amer. Ceram. Soc.* **74** (1991) 666.
5. Y. GOGOTSI and M. YOSHIMURA, *J. Mater. Sci. Lett.* **13** (1994) 680.
6. M. H. BERGER, N. HOCHET and A. R. BUNSELL, *J. Microsc.* **177** (1995) 230.
7. P. LE. COUSTUMER, M. MONTHIOUX and A. OBERLIN, *Br. Ceram. Trans.* **94** (1995) 177.
8. C. VIX-GUTERL and P. EHRBURGER, *J. Mater. Sci.* **31** (1996) 5363.
9. G. CHOLLON, R. R. PAILLER, R. NASLAIN, F. LAANANI, M. MONTHIOUX and P. PLRY, *ibid.* **32** (1997) 327.
10. G. CHOLLON, M. CZERNIAK, R. PAILLER, X. BOURRAT, R. NASLAIN, J. P. PILLOT and R. CANNET, *ibid.* **32** (1997) 893.
11. M. H. BERGER, N. HOCHE and A. R. BUNSELL, *J. Microsc.* **185** (1997) 243.
12. Y. T. ZHU, S. T. TAYLOR, M. G. STOUT, D. P. BUTT and T. C. LOWE, *J. Amer. Ceram.* **81** (1998) 655.
13. M. TAKEDA, J. SAKAMOTO, Y. IMAI and H. ICHIKAWA, *Comp. Sci. Tech.* **59** (1999) 813.
14. T. SHIMOO, H. CHEN and K. OKAMURA, *J. Ceram. Soc. Jpn.* **100** (1992) 929.
15. T. SHIMOO, T. HAYATSU, M. TAKEDA, H. ICHIKAWA, T. SEGUCHI and K. OKAMURA, *ibid.* **102** (1994) 617.
16. T. SHIMOO, F. TOYODA and K. OKAMURA, *ibid.* **106** (1998) 447.
17. *Idem.*, *ibid.* **107** (1999) 263.
18. *Idem.*, *J. Mater. Sci.* **35** (2000) 3301.
19. *Idem.*, *J. Amer. Ceram. Soc.* **83** (2000) 1450.
20. *Idem.*, *J. Mater. Sci.* **35** (2000) 3811.
21. T. SHIMOO, H. TAKEUCHI, M. TAKEDA and K. OKAMURA, *J. Ceram. Soc. Jpn.* **108** (2000) 1096.
22. T. SHIMOO, Y. MORISADA and K. OKAMURA, *J. Amer. Ceram. Soc.* **83** (2000) 3049.
23. *Idem.*, *J. Mater. Sci.* **37** (2002) 1793.
24. *Idem.*, *ibid.* **37** (2002) 4361.
25. T. SHIMOO, T. MORITA and K. OKAMURA, *J. Amer. Ceram. Soc.* **84** (2001) 2975.
26. *Idem.*, *J. Mater. Sci.* **37** (2002) 3181.
27. M.-H. BERGER, N. HOCHET and A. R. BUNSELL, "Properties and Microstructures of Small-Diameter SiC-Based Fibers," in "Fine Ceramic Fibers," edited by A. R. Bunsell and M.-H. Berger (Marcel Dekker, New York, 1999) p. 246.
28. E. J. OPILA, *J. Amer. Ceram. Soc.* **81** (1998) 1949.
29. G. X. WANG, G. Q. LU and A. B. YU, *J. Mater. Sci.* **33** (1998) 1309.
30. T. SHIMOO, T. MORITA and K. OKAMURA, *ibid.* **38** (2003) in printing.
31. E. T. TURKDOGAN, "Physical Chemistry of High Temperature Technology" (Academic Publishers, New York, 1980) p. 1.
32. B. SCHNEIDER, A. GUETTE, R. NASLAIN, M. CATALDI and A. COSTECALDE, *J. Mater. Sci.* **33** (1998) 535.

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