

Carbon elimination by heat-treatment in hydrogen and its effect on thermal stability of polycarbosilane-derived silicon carbide fibers

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Carbon elimination from EB-cured PCS fibers by H₂-treatment and the thermal stability of resultant SiC fibers were examined through TG, chemical analysis, AES analysis, XRD analysis, resistivity measurements, SEM observation and tensile tests. The C/Si mole ratio from 1.50 to 1.05 could be achieved by H₂-heat treatment at $t \geq 4$ h and $T = 773$ – 1173 K. There was no difference in XRD patterns, fiber morphology and tensile strength of the fibers in the as-H₂-treated state. H₂-treatment at higher temperature caused the reduction in residue and the increase in resistivity of the fibers. An oxygen-rich layer was formed on the fiber surface after H₂-treatment, resulting in the mass loss, the coarsening of β -SiC grains and a marked degradation of fiber strength after exposure to higher temperature. Prevention of oxygen uptake after H₂-treatment is essential to improve the thermal stability of SiC fibers. © 2004 Kluwer Academic Publishers

1. Introduction

Most of polycarbosilane-derived silicon carbide fibers which are commercially available have C/Si mole ratios larger than stoichiometric ratio of SiC. Typically, the C/Si mole ratio is 1.31 for Si–C–O fibers (Nicalon, Nippon Carbon) prepared by oxygen-curing method and it is 1.39 for Si–C fibers (Hi-Nicalon, Nippon Carbon) prepared by electron-beam irradiation curing method. Such excess carbon is attributable to the C/Si ratio of 2 for polycarbosilane precursor as a starting material. In order to improve the high-temperature stability and oxidation resistance of silicon carbide fibers, many attempts have been made to eliminate excess carbon and to manufacture the stoichiometric SiC fibers [1–16]. Two types of stoichiometric silicon carbide fibers are on the market today:

Syrramic fiber (Dow Corning) [1, 9, 10], UF-HM fiber (3M) [6, 7] and Tyranno SA fiber (Ube Industries) [15] are prepared by sintering and carbothermic reduction at 1873 K and higher. On the other hand, Hi-Nicalon S is (Nippon Carbon) [3, 8] is prepared by heat-treatment in Ar-H₂ gas mixture. While excess carbon can be eliminated as CO gas by the former method, it can be eliminated as CH₄ gas by the latter method.

Carbon elimination from polycarbosilane fibers by the heat-treatment under H₂ atmosphere has been studied [11, 12, 16]. Further investigation is thought to be required to reveal the mechanism of carbon elimination by H₂-treatment. In the present work, electron-beam irradiation cured polycarbosilane (EB-cured PCS) fibers were heat-treated in flowing H₂ gas at 623 to 1173 K.

In particular, a detailed study was made on the effect of H₂-treatment time on the carbon elimination from the EB-cured PCS fibers. Furthermore, in order to evaluate the thermal stability of the carbon-eliminated fibers, they were subjected to the exposure test at 1473–1873 K in flowing argon. In order to acquire a deeper understanding of the effect of carbon elimination, the fibers in the H₂-treated state and after high-temperature exposure were characterized through mass change determination, chemical analysis, Auger electron spectroscopic analysis, X-ray diffraction examination, scanning electron microscopic observation, resistivity measurements and tensile tests.

2. Experimental method

The sample employed in this work is the electron-beam-irradiation cured polycarbosilane (EB-cured PCS) fibers manufactured by Nippon Carbon Co. (Tokyo, Japan). It has a molar composition of SiC_{1.93}O_{0.035}H_{3.78} and mean diameter of 23.5 μ m.

When heated EB-cured PCS fibers in H₂ gas, carbon is probably eliminated through the generation of CH₄ gas [11, 16]. EB-cured PCS fibers were heated in a evacuated alumina tube, and then the gases accumulated in a sample tube were analyzed by gas chromatography. Fig. 1 shows the change in pressure accompanying the gas evolution during heat-treatment in a vacuum. For comparison, the pressure change for the fibers after heat-treatment in H₂ gas at 1173 K (C/Si = 1.05) also is shown in this figure. The analysis of gases reveals that a peak at $T = 800$ – 1200 K is attributable

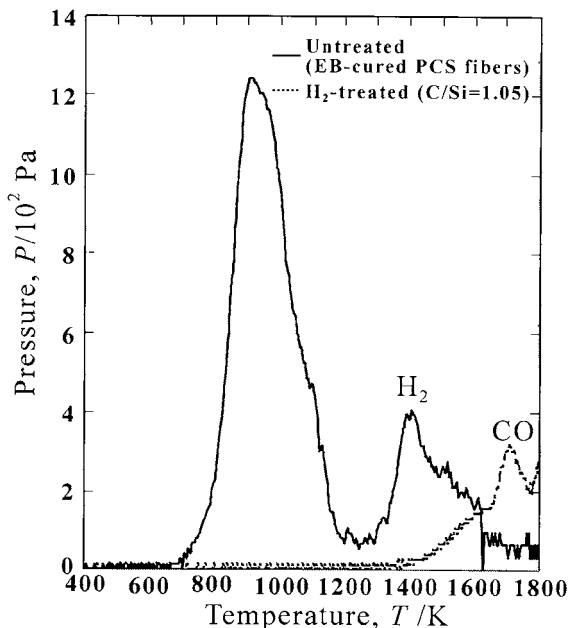


Figure 1 Gas evolution during heat-treatment of EB-cured PCS fibers and H₂-treated fibers.

to the CH₄ evolution. From this result, H₂-treatment of the EB-cured PCS fibers was conducted at $T = 773$ – 1173 K.

EB-cured PCS fibers of 100 mm in length were placed in a quartz crucible and subsequently it was set in an alumina tube of a vertical SiC resistant furnace. In H₂ gas stream of 2×10^{-4} m³/min, the EB-cured PCS fibers were heated at heating rate of 10 K/min, and were held for $t = 0$ – 10 h at each temperature of $T = 773$ – 1173 K. After H₂-treatment, H₂ gas in a reaction tube was flushed by flowing Ar at 2×10^{-4} m³/min. Subsequently, the fibers were heated to 1473 K in Ar and after holding of 1 h, they were slowly cooled to room-temperature. This successive process is called H₂-treatment in later.

The H₂-treated fibers were subjected to high-temperature exposure test after standing for 24 h in air. The fibers were heated at 10 K/min in flowing argon. Then, they were held for 1 h at a given temperature in the range of 1473–1873 K and cooled at a rate of 10 K/min.

The fibers were subjected to chemical analysis for carbon and silicon, and surface analysis by Auger electron spectroscopy (AES). The existing phases in the fibers were identified by X-ray diffractometry (XRD), and the morphologies of fibers were examined by field-emission scanning electron microscope (FE-SEM). The SiC crystallite size was calculated from the half-value width of (111) peak using a Scherrer's formula. The specific resistivity measurements were conducted at room-temperature by applying a direct current to a single fiber. Room-temperature tensile tests were carried out using a 10 mm gauge length and a constant crosshead speed of 2 mm/min.

3. Results and discussion

3.1. Heat-treatment of EB-cured PCS fibers in hydrogen

Fig. 2 shows the change in the C/Si mole ratio of fibers during heat-treatment at each temperature of $T = 773$ –

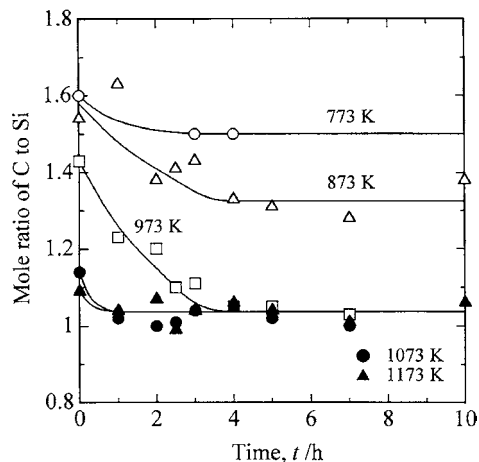


Figure 2 Change in C/Si mole ratio of fibers during heat-treatment at $T = 773$ – 1173 K in H₂ gas stream.

1173 K in H₂ gas stream. The original EB-cured PCS fibers have a C/Si mole ratio of 1.97. The C/Si ratio was reduced to 1.60–1.09 immediately after heating to $T = 773$ – 1173 K and further reduction of C/Si ratio was caused during holding at each temperature. Fig. 1 shows that the H₂-treated fibers evolve only CO gas during vacuum heating. From this result, no hydrogen is picked up by the fibers during heat-treatment in H₂ gas. Therefore, the H₂-treatment of PCS fibers causes the elimination of carbon alone. Hydrogen attack appears to proceed towards the center of PCS fibers, leaving behind a carbon-eliminated layer. Immediately after heating to 973 K in flowing H₂ gas ($t = 0$ h), the limiting C/Si mole ratio of 1.05 seems to be already achieved at the outermost of the fiber. The C/Si ratio of the core will be kept at 1.97 without undergoing the elimination of carbon. Consequently, the chemical analysis indicates that a mean C/Si ratio is 1.42 at $t = 0$ h. Further reduction in C/Si ratio could not be caused by H₂-treatment at $t = 4$ – 10 h. Therefore, the C/Si mole ratio was uniformly 1.05 throughout the cross section of the fibers after H₂-treatment of 4 h. Since carbon was no longer eliminated at $t \geq 4$ h, the duration of H₂-treatment was set at $t = 4$ h. Although the elimination of carbon was greatly accelerated by raising H₂-treatment temperature, the C/Si ratio smaller than 1.05 could not be achieved even at 1173 K.

Fig. 3 shows the C/Si mole ratio of the fibers after H₂-treatment of $t = 4$ h as a function of H₂-treatment

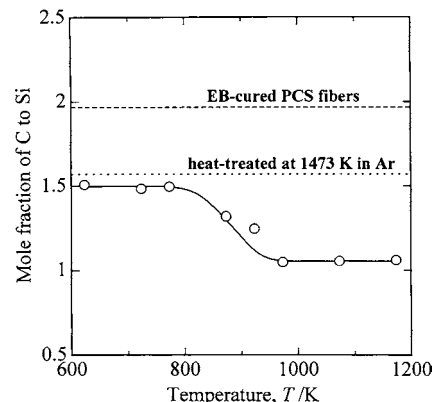
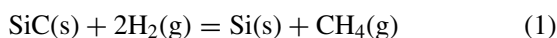


Figure 3 Relationship between C/Si mole ratio of fibers after H₂-treatment of $t = 4$ h and H₂-treatment temperature.

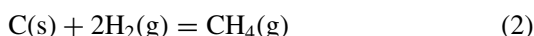
temperature. Compared with stoichiometric SiC, the EB-cured PCS fibers contain a large excess of carbon ($C/Si = 1.97$). Despite of very high heat-treatment temperature ($T = 1473$ K), carbon was insufficiently eliminated by the heat-treatment in Ar gas and hence the C/Si mole ratio was 1.57. On the other hand, the H_2 -treatment resulted in the reduction of C/Si ratio to 1.60 even at 773 K. Although the C/Si mole ratio was reduced by increasing the H_2 -treatment temperature, it was unchanged by varying the H_2 -treatment temperature at $T \geq 973$ K. This indicates a limit of carbon elimination by H_2 -treatment. Consequently, it was impossible to manufacture the SiC fibers with the C/Si mole ratio smaller than 1.05.

For the heat-treatment in Ar gas, the reduction of C/Si ratio to 1.57 is attributed to CH_4 evolution that is caused by the decomposition of Si-CH₃ bonds (methyl branch) [17, 18]. H_2 -treatment at $T \leq 773$ K appears to decompose only the Si-CH₃ bonds, because the C/Si mole ratio of 1.50 is almost identical to that of the fibers after-treatment in Ar. At $T \geq 973$ K, CH₂-Si-CH₂ cross-linking between PCS chains is attacked by hydrogen and the CH_4 evolution by the decomposition of C-H bonds leads to further reduction of C/Si ratio.

Under inert gas atmosphere, complete ceramization of EB-cured PCS fibers yields the ceramic fibers which are composed of β -SiC and free carbon [19]. During heat-treatment in flowing H_2 gas, SiC and/or carbon in the fibers may react with hydrogen to produce CH_4 gas:



$$\Delta G^\circ(\text{J/mol}) = -17990 + 103.01T [20]$$



$$\Delta G^\circ(\text{cal/mol}) = -91040 + 110.67T [20]$$

Fig. 4 shows the relationship between the equilibrium partial pressure of CH_4 and temperature. The p_{CH_4} values for SiC is 3 orders of magnitude lower than that for carbon in the temperature range for the H_2 -treatment of EB-cured PCS fibers. Very low p_{CH_4} value may lead to difficulty in hydrogen attack of SiC in the fibers. Pure silicon carbide is stable in H_2 gas at $T \leq 1700$ K [21].

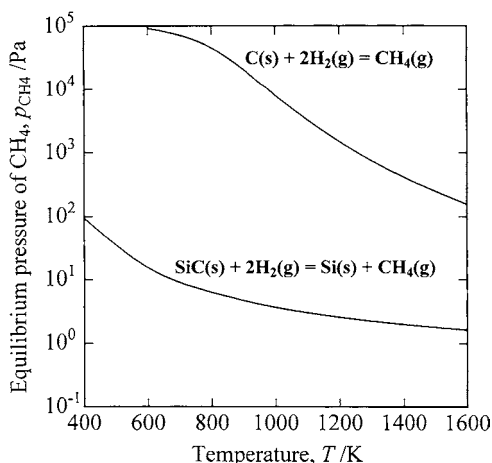


Figure 4 Relationship between equilibrium partial pressure of CH_4 and temperature.

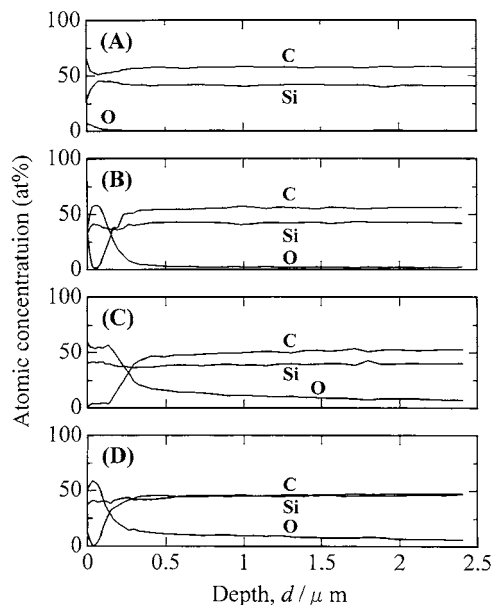


Figure 5 Composition profiles of heat-treated fibers (AES analysis): (A) heat-treatment in Ar at 1473 K ($C/Si = 1.57$), (B) H_2 -treatment at 773 K ($C/Si = 1.50$), (C) H_2 -treatment at 873 K ($C/Si = 1.33$), and (D) H_2 -treatment at 1073 K ($C/Si = 1.05$).

Therefore, as can be seen from Figs 2 and 3, the C/Si mole ratio of the silicon carbide fibers could not be reduced to a value of less than unit (stoichiometric ratio of SiC) by H_2 -treatment at $T \leq 1173$ K. However, a C/Si mole ratio of 1.05, which was much lower than the value for heat-treatment in Ar ($C/Si = 1.57$), could be achieved by H_2 -treatment at $973 \text{ K} \leq T \leq 1173$ K.

Fig. 5 shows the composition profiles, determined by AES analysis, for the fibers heat-treated in flowing argon and hydrogen gases. Although a very thin carbon-enriched film is present on the surface of the fibers heat-treated at 1473 K in argon, the distribution of silicon and carbon is uniform in its core (A). On the other hand, all the H_2 -treated fibers contain considerable amounts of oxygen (B, C and D). An oxygen-enriched and carbon-depleted layer of about $0.3 \mu\text{m}$ in thickness is formed, and oxygen penetrates deeply into the interior of the fibers. However, the C/Si mol ratio is uniform in the fiber core, and it decreases with increasing temperature. The AES depth profiles also indicate that that H_2 -treatment of 4 h caused the uniform elimination of carbon throughout the cross section of the fibers.

Fig. 6 shows that the morphology of the fibers is independent on both the temperature and the duration of H_2 -treatment. All the fibers had a smooth surface and a glassy cross section, as well as the fibers heat-treated in flowing argon. In addition, the H_2 -treated fibers showed almost identical X-ray diffraction patterns, irrespective of the conditions of H_2 -treatment.

3.2. High-temperature exposure of SiC fibers

Figs 7 and 8 show the X-ray diffraction patterns for the SiC fibers in the as H_2 -treated state and after exposure to 1473–1873 K in flowing argon. The XRD pattern of the fiber after heat-treatment at 1473 K in

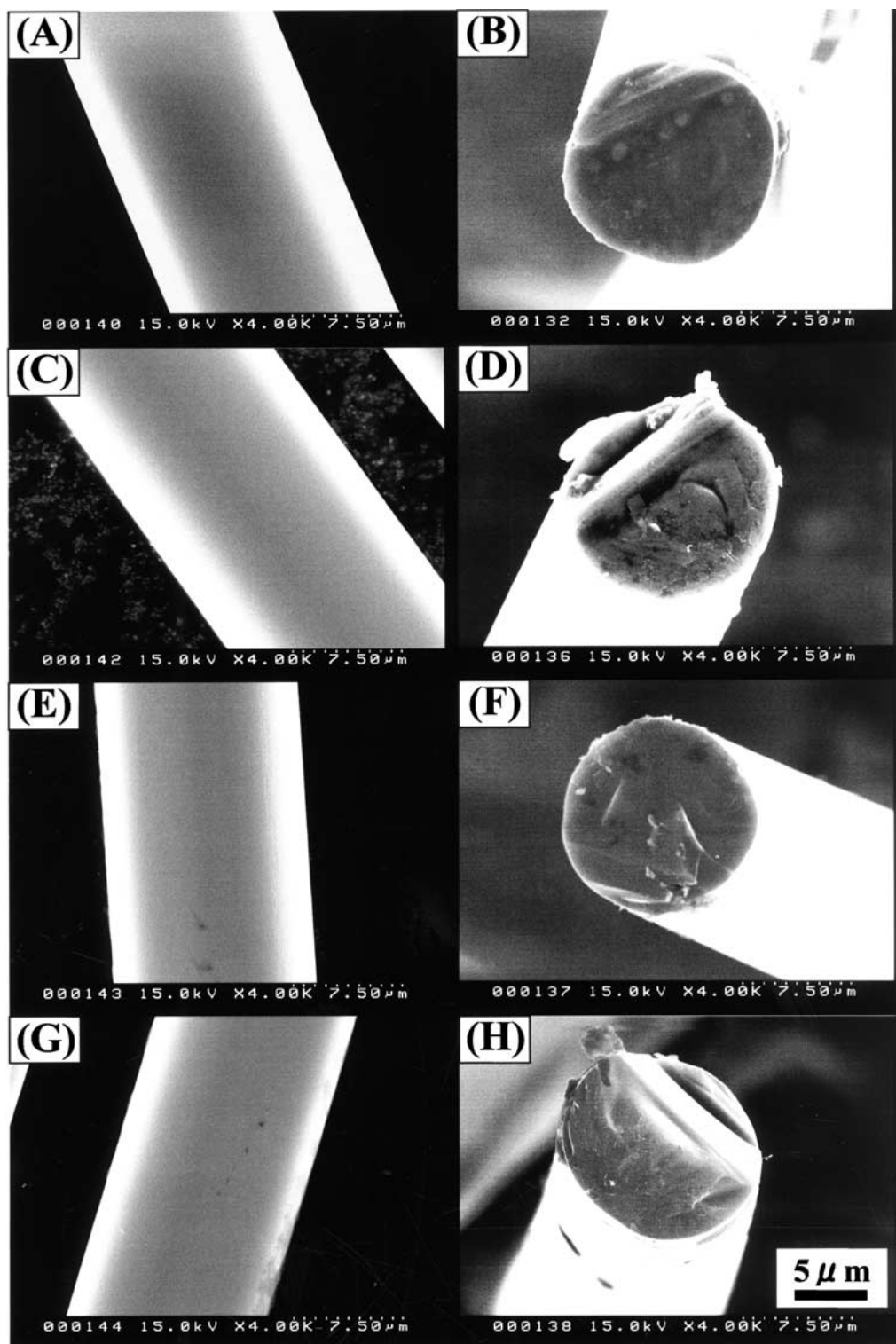


Figure 6 SEM photographs of fibers heat-treated in H_2 gas: (A, B): $T = 773$ K, $t = 0$ h, (C, D): $T = 773$ K, $t = 5$ h, (E, F): $T = 973$ K, $t = 0$ h and (G, H): $T = 973$ K, $t = 5$ h.

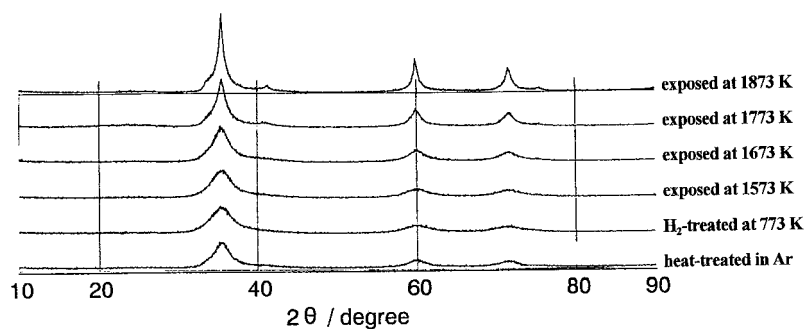


Figure 7 XRD patterns for fibers heat-treated at 1473 K in Ar, heat-treated at 773 K in H_2 and exposed to 1573–1873 K in Ar.

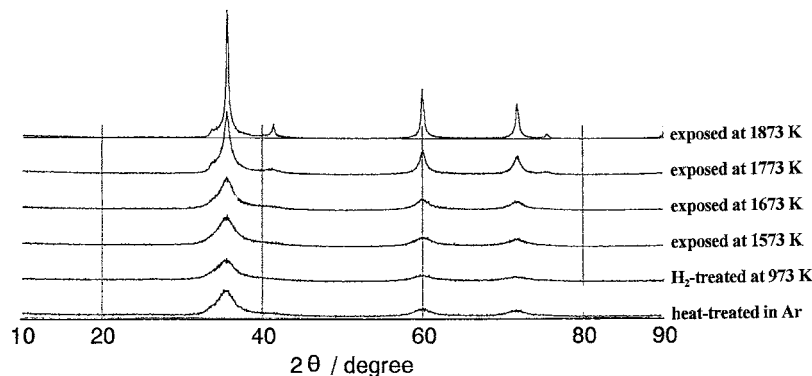


Figure 8 XRD patterns for fibers heat-treated at 1473 K in Ar, heat-treated at 973 K in H₂ and exposed to 1573–1873 K in Ar.

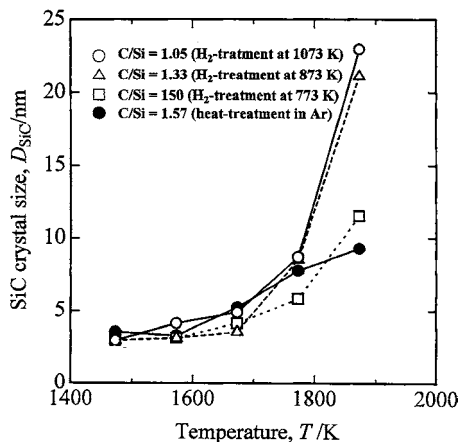


Figure 9 Relationship between apparent crystallite size of β -SiC and exposure temperature.

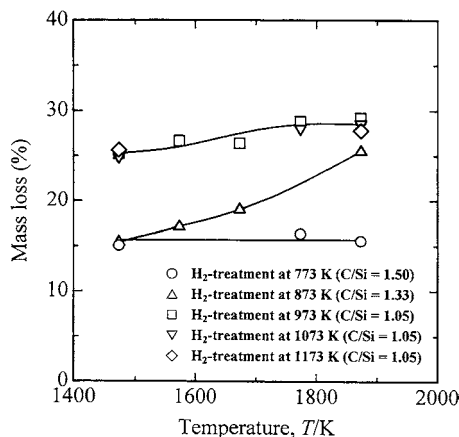


Figure 10 Relationship between mass loss of fibers and exposure temperature.

Ar ($C/Si = 1.57$) is nearly identical to that of the fibers the fibers after H₂-treated at 773 and 973 K ($C/Si = 1.50$ and 1.05). This is because the H₂-treated fibers were subsequently heat-treated at 1473 K in Ar gas. The sharpness of β -SiC peaks increased with rising exposure temperature. It may be noted that the β -SiC peaks for the fiber with low C/Si mole ratio was sharp after high-temperature exposure. Fig 9 shows the relationship between the apparent crystallite size of β -SiC, D_{SiC} and exposure temperature, T_E . At $T_E \leq 1773$ K, the D_{SiC} value was almost independent on the C/Si ratio of the fibers. It is noteworthy that the reduction of the C/Si ratio caused a marked grain growth of β -SiC at $T_E = 1873$ K. Excess carbon is present as free carbon surrounding β -SiC grains, resulting in preventing the coalescence of β -SiC grains. Thus, for the fibers with high C/Si ratio, the grain growth is thought to be retarded during exposure to 1873 K in Ar gas.

Fig. 10 shows the mass loss of the fibers during exposure at 1473–1873 K. The mass loss was determined from the difference of the fiber mass before and after high-temperature exposure. The fibers with $C/Si = 1.50$ shows a small mass loss (about 16%), independently to exposure temperature. For the fiber with $C/Si = 1.33$, the mass loss increased with increasing exposure temperature; from 16% at $T_E = 1473$ K to 25% at $T_E = 1873$ K. Large mass loss (25–28%) was caused for the fibers with $C/Si = 1.05$. The mass loss during exposing to high temperatures is responsible for oxy-

gen picked up after H₂-treatment (Fig. 5). Oxygen in the fibers is present as amorphous silicon oxycarbide (SiC_xO_y) phase. At high temperatures, SiC_xO_y phase is crystallizes into β -SiC, accompanying the generation of SiO and CO gases.

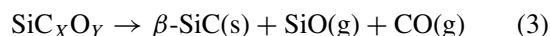


Fig. 11 shows the specific resistivity of the fibers in the heat-treated state and after exposure at $T = 1473$ –1773 K in Ar. The fibers exposed to 1873 K were too fragile to be submitted to resistivity measurements.

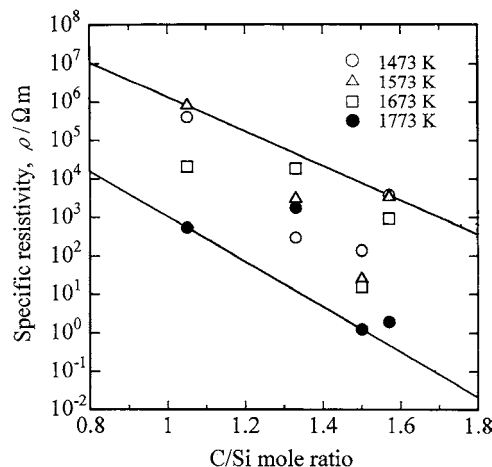


Figure 11 Relationship between specific resistivity and C/Si mole ratio of fibers after exposure at $T = 1473$ –1773 K in Ar.

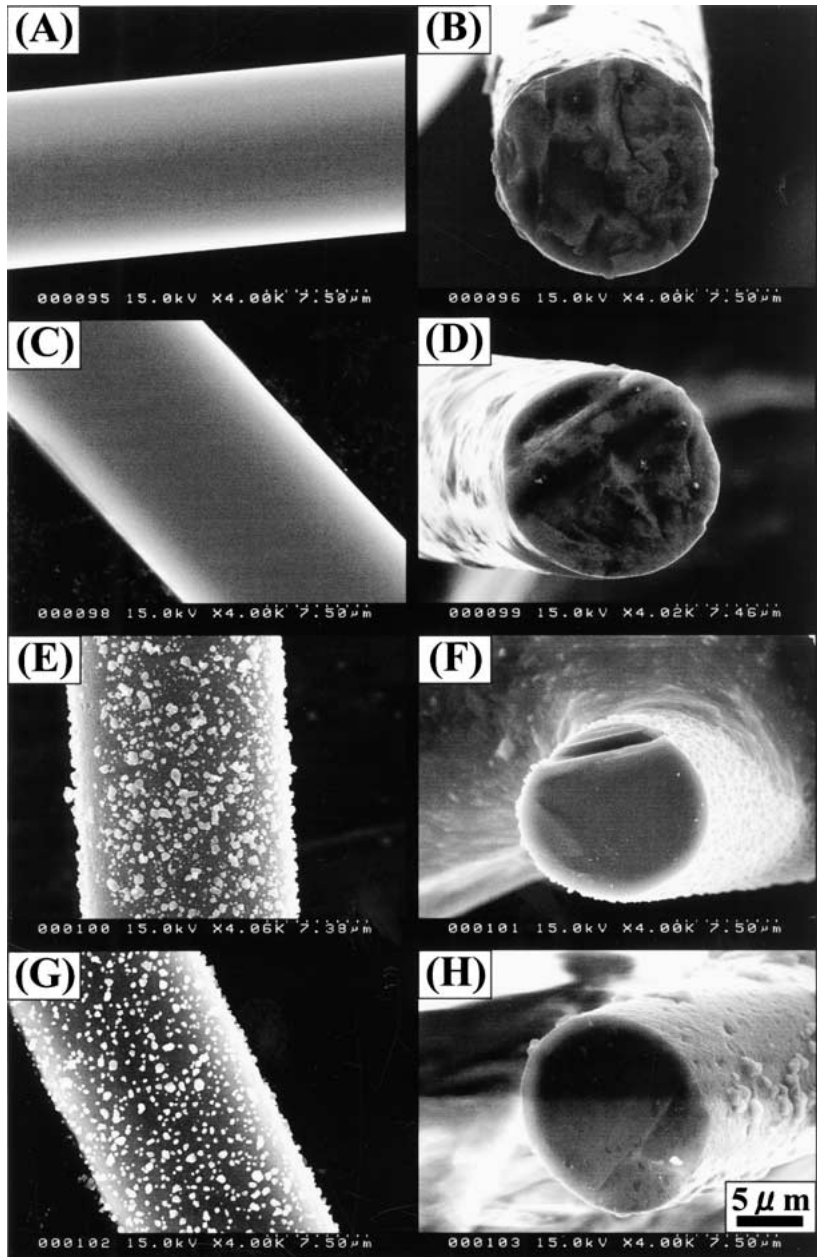


Figure 12 SEM photographs of fibers (C/Si = 1.50) heat-treated for 4 h at 773 K in H₂ gas and subsequently exposed for 1 h at 1573 K (A, B), 1673 K (C, D), 1773 K (E, F) and 1873 K (G, H) in Ar gas.

The specific resistivity is quite sensible to the microstructural change of the fibers, particularly to the removal of free carbon and the crystal growth of β -SiC. The high-temperature exposure caused a drop of 3–4 orders magnitude for the resistivities of the fibers with C/Si = 1.05–1.59. This is attributable to the crystallization of amorphous SiC_xO_y phase into β -SiC and the organization of free carbon during high-temperature exposure [22]. Naturally, carbon elimination by H₂-treatment resulted in a marked increase of resistivity. There is about 3 orders magnitude increase between C/SiC = 1.57 (heat-treatment in Ar at 1473 K) and 1.05 (heat-treatment in H₂ at 973 K).

Fig. 12 shows the SEM photographs for the fibers heat-treated for 4 h in H₂ gas at 773 K (C/Si = 1.50) and subsequently exposed to 1573–1873 K in Ar gas. The surface of the fibers exposed at $T \leq 1673$ K shows a smooth appearance (A–D). When exposed at $T \geq 1773$ K, coarsened β -SiC grains are sparsely dis-

tributed on the fiber surface (E–H). Such grain growth of SiC is thought to be produced by the gaseous reaction between the decomposition gases, SiO and CO [23].



Fig. 13 shows the morphologies of the fibers heat-treated for 4 h in H₂ gas at 973 K (C/Si = 1.05) and subsequently exposed to 1573–1873 K in Ar gas. The fibers exposed at $T \leq 1673$ K hold a smooth surface, as well as the fibers with C/Si = 1.50 (A–D). The exposure to 1773 K renders the surface porous, while it does not cause the coarsening of β -SiC crystals (E, F). A marked coarsening of β -SiC crystals was observed after exposure to 1873 K (G, H). Thus, the morphologies of fiber surface after exposure above 1773 K are greatly different between the fibers with C/Si = 1.50 and those with C/Si = 1.05. The coarsened SiC grains is responsible

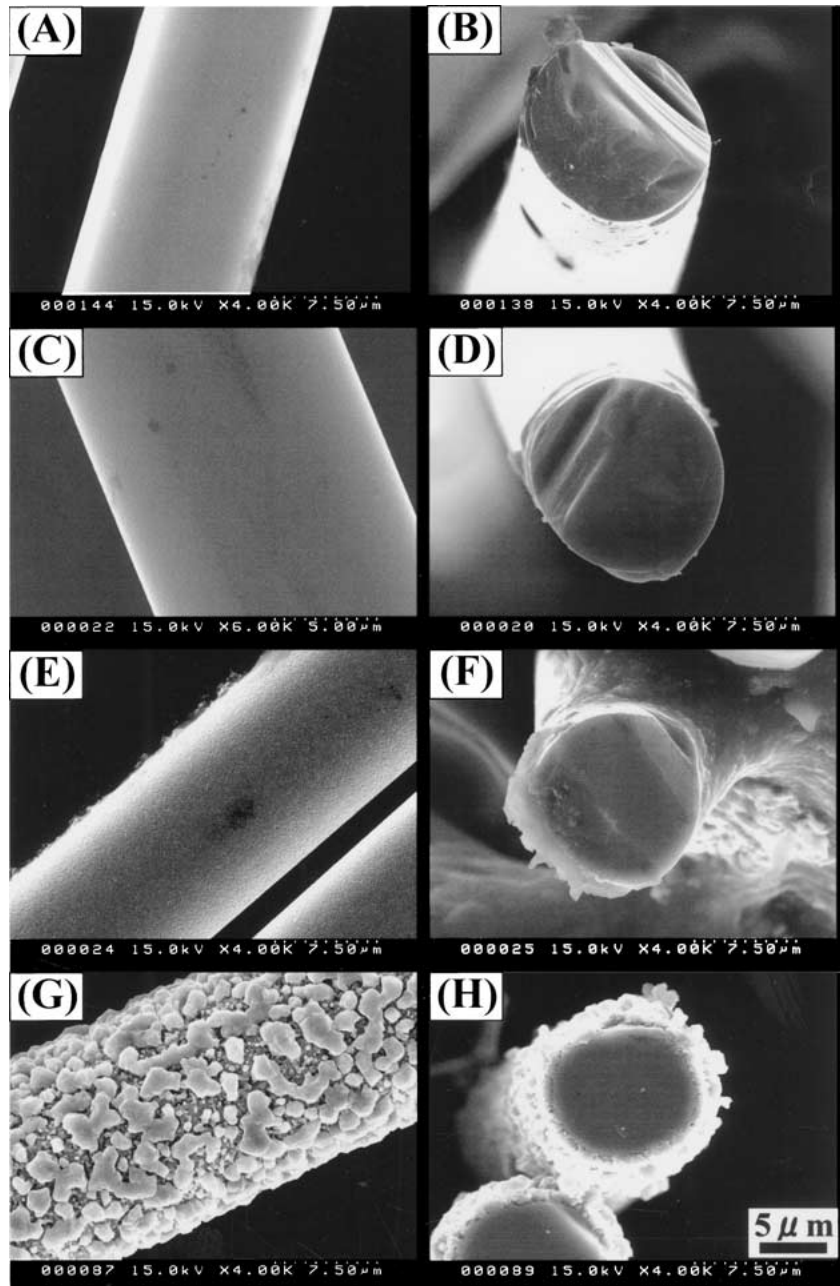


Figure 13 SEM photographs of fibers ($C/Si = 1.05$) heat-treated for 4 h at 773 K in H_2 gas and subsequently exposed for 1 h at 1573 K (A, B), 1673 K (C, D), 1773 K (E, F) and 1873 K (G, H) in Ar gas.

for the thermal decomposition of SiC_xO_y phase, Equation 3. Figs 12 and 13 exhibit that the cross-sections of all the fibers display a glassy appearance. The grain coarsening is restricted to the surface of fibers even after exposure to 1873 K (Fig. 13(H)). This is because SiC_xO_y phase is present at the surface of the H_2 -treated fibers (Fig. 5).

Fig. 14 shows the room-temperature tensile strength of the fibers with $C/Si = 1.05$ –1.57 as a function of exposure temperature (T_E). The tensile strength of the fibers in the as- H_2 -treated state and after high temperature exposure was almost independent upon the C/Si mole ratio. A degradation of fiber strength was little caused by the exposure at $T_E \leq 1673$ K. On the other hand, marked degradation was observed after exposure to $T_E \geq 1773$ K. By comparing Fig. 14 with Figs 12 and 13, it is clear that the change in strength accompanying the exposure test is attributable to the variation in the

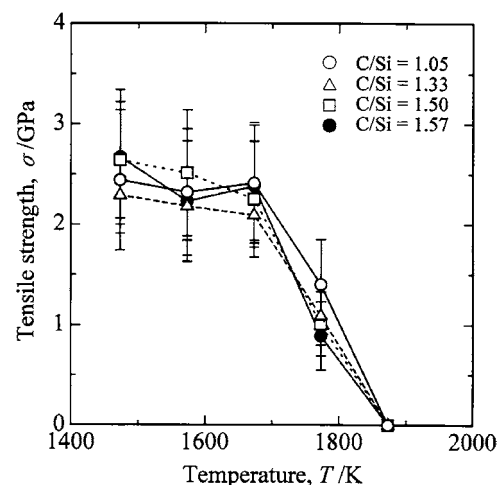


Figure 14 Relationship between room-temperature tensile strength of fibers with $C/Si = 1.05$ –1.57 and exposure temperature.

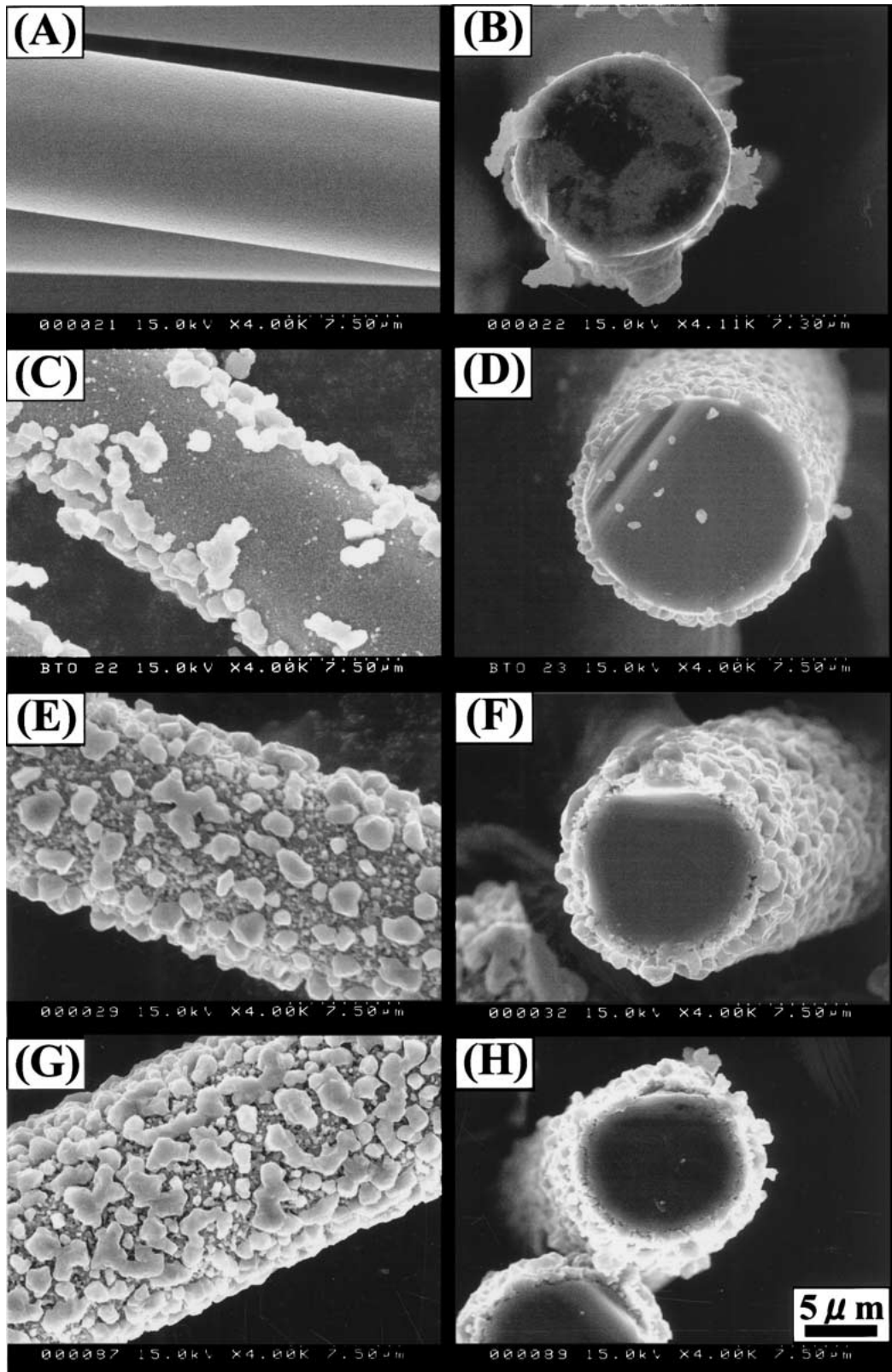


Figure 15 SEM photographs of fiber exposed for 1 h at 1873 K in Ar gas after H₂-treatment for 4 h at 973 K and standing for 5 min (A, B), 15 min (C, D), 1 h (E, F) and 24 h (G, H) at room-temperature in air.

morphologies of the fibers during exposing at high-temperatures.

A marked uptake of oxygen at the surface of the fibers caused significant coarsening of β -SiC grains during high-temperature exposure, resulting in serious degradation of room-temperature strength of the fibers. The uptake of oxygen appears to occur while the H₂-treated

fibers are allowed to stand for 24 h in air before high-temperature exposure test. To confirm this estimation, the fibers heat-treated at 973 K in H₂ gas were submitted to exposure test (at $T = 1873$ K and $t = 1$ h) after standing for $t = 5$ min–24 h in air. Fig. 15 shows the SEM photographs of the fibers after exposure test. No grain growth of SiC was observed for the fiber after

standing for 5 min in air (A, B). The fiber surface was smooth as well as the fibers in the as-H₂-treated state (Fig. 6). For the fiber after standing of 15 min in air, the coarsened SiC grains were sparsely distributed on the surface of the fibers (C, D). Further elongation of the standing time resulted in the development of coarsened grains throughout entire surface of the fibers (E–H). This result implies that the as-H₂-treated fibers picked up oxygen during standing in air. In addition, the coarse-grained film of β -SiC is verified by the result that the uptake of oxygen was limited solely to the surface of the fibers, being consistent with AES results (Fig. 5). The attack of hydrogen against CH₂–Si–CH₂ cross-linking between PCS chains appears to cause the CH₄ evolution and the formation of Si radicals. Since the Si radicals are highly reactive to oxygen, the as-H₂-treated fibers could pick up a large amount of oxygen during standing in air. Therefore, the inactivation of Si radicals is required in order to improve the thermal stability of the H₂-treated SiC fibers.

4. Conclusion

Excess carbon in EB-cured PCS fibers is thought to be eliminated as CH₄ gas by reacting with H₂ gas. After H₂-treatment of 4 h, the homogeneity of C/Si ratio was well established throughout the cross-section of fibers. H₂-treatment at $T = 773$ K, 873 K and 973–1173 K could achieved the C/Si mole ratios of 1.50, 1.33 and 1.50, respectively. While the SiC crystal size, morphology and strength of the fibers were not independent on H₂-treatment temperature, the reduction in residue and increase in resistivity of the fibers were caused by the rise in H₂-treatment temperature. The surface layer of H₂-treated fibers took up a large amount of oxygen during standing in air. The fibers with smaller C/Si ratio showed larger mass loss and coarsened SiC grains after high-temperature exposure. As a consequence of thermal decomposition of SiC_xO_y phase, marked degradation of room-temperature strength was to be avoided after exposure in Ar gas at $T \geq 1773$ K. Prevention of the oxygen pick-up after H₂-treatment is essential to effectuate the reduction of C/Si ratio of the fibers.

References

1. J. LIPOWITZ, *Amer. Ceram. Bull.* **70** (1991) 1888.
2. M. LAINE and F. BABONNEAU, *Chem. Mater.* **5** (1993) 260.
3. M. TAKEDA, J. SAKAMOTO, Y. IMAI, H. ICHIKAWA and T. ISHIKAWA, *Ceram. Eng. Sci. Proc.* **15** (1994) 133.
4. Z. F. ZHANG, C. S. SCOTTO and R. M. LAINE, *ibid.* **15** (1994) 152.
5. *Idem.*, *Mater. Res. Soc. Symp. Proc.* **327** (1994) 207.
6. M. D. SACKS, G. W. SCHEIFFELE, M. SALEEM, G. A. STAAB, A. A. MORRONE and T. J. WILLIAMS, *ibid.* **365** (1995) 3.
7. M. D. SACKS, A. A. MORRONE, G. W. SCHEIFFELE and M. SALEEM, *Ceram. Eng. Sci. Proc.* **16** (1995) 25.
8. M. TAKEDA, J. SAKAMOTO, A. SAEKI, Y. IMAI and H. ICHIKAWA, *ibid.* **16** (1995) 37.
9. J. LIPOWITZ, J. A. LABE, K. T. NGUEN, L. D. ORR and R. R. ANDROL, *ibid.* **16** (1995) 55.
10. J. LIPOWITZ, J. A. LABE, K. A. ZANGVIL and Y. XU, *ibid.* **18** (1997) 145.
11. A. T. HEMIDA, R. PAILLER and R. NASLAIN, *J. Mater. Sci.* **32** (1997) 2359.
12. A. T. HEMIDA, R. PAILLER, R. NASLAIN, J. P. PILLOT, M. BIROT and J. DUNOGUES, *ibid.* **32** (1997) 2367.
13. A. T. HEMIDA, M. BIROT, J. P. PILLOT, J. DUNOGUES and R. PAILLER, *ibid.* **32** (1997) 3475.
14. *Idem.*, *ibid.* **32** (1997) 3485.
15. T. ISHIKAWA, Y. KOHTOKU, K. KUMAGAWA, T. YAMAMURA and T. NAGASAWA, *Nature (London)* **391** (1998) 773.
16. M. TAKEDA, A. SAEKI, J. SAKAMOTO, Y. IMAI and H. ICHIKAWA, *J. Amer. Ceram. Sci.* **83** (2000) 1063.
17. M. SUGIMOTO, T. SHIMOO, K. OKAMURA and T. SEGUCHI, *ibid.* **78** (1995) 1013.
18. *Idem.*, *ibid.* **78** (1995) 1849.
19. G. CHOLLON, R. PAILLER, R. NASLAIN, F. LAANANI, M. MONTHIOUX and P. OLRÉ, *J. Mater. Sci.* **32** (1997) 327.
20. E. T. TURKDOGAN, "Physical Chemistry of High Temperature Technology" (Academic Press, New York, 1980) p. 1.
21. L. A. LAY, "Corrosion Resistance of Technical Ceramics" (The Stationery Office Books, London, 1991) p. 116.
22. 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.
23. T. SHIMOO, I. TSUKADA, T. SEGUCHI and K. OKAMURA, *J. Amer. Ceram. Sci.* **81** (1998) 2109.

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