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Microstructure and oxidative degradation behavior of silicon carbide fiber Hi-Nicalon type S

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Abstract

Polycarbosilane-derived SiC fibers, Nicalon, Hi-Nicalon, and Hi-Nicalon type S were exposed for 1 to 100 h at 1273–1773 K in air. Oxide layer growth and tensile strength change of these fibers were examined after the oxidation test. As a result, three types of SiC fibers decreased their strength as oxide layer thickness increased. Fracture origins were determined at near the oxide layer-fiber interface. Adhered fibers arised from softening of silicon oxide at high temperature were also observed. In this study, Hi-Nicalon type S showed better oxidation resistance than other polycarbosilane-derived SiC fibers after 1673 K or higher temperature exposure in air for 10 h. This result was explained by the poreless silicon oxide layer structure of Hi-Nicalon type S.

1. Introduction

SiC-based fibers which have high tensile strength, high elastic modulus, and good thermal stability are one of the candidate materials for the reinforcement fibers of ceramic matrix composites (CMCs). Especially SiC fibers produced via polymer pyrolysis have an advantage of flexible, fine diameter form over those from CVD or sintering processes [1]. The Si–C–O fiber, Nicalon, synthesized from polycarbosilane (PCS) has been produced industrially and provided widely to heat-resistant materials and reinforcement for CMCs [2,3].

Recently, the SiC fiber with a low oxygen content, Hi-Nicalon, has been developed. Fig. 1 shows the schematic diagram of Nippon Carbon's SiC fiber development history. Hi-Nicalon fiber has a higher elastic modulus and creep resistance, and much improved thermal stability than that of Nicalon fiber [4–6]. Hi-Nicalon has been provided to improve the mechanical properties of CMCs [7]. Based on the study of thermo-mechanical properties with various C/Si fibers, the fiber with C/Si atomic ratio of 1.05 was selected as a new grade of Hi-Nicalon. This fiber is pyrolyzed at high temperature with special conditions, and SiC crystals grew without decreasing the fiber strength. The near-stoichiometric, highly crystalline SiC fiber, which was named "Hi- Nicalon type S", has been successfully developed [8].

In this work, the effect of fiber structure on oxidation resistance in air at high temperature, which is supposed to be most actual use for CMCs. With difference with oxide ceramics, silicon carbide is not stable because of its oxidation [9–12]. As regard to oxidation kinetics and degradation of fiber strength should depend on the microstructure of the fiber, that is chemical composition and β-SiC crystallite size, etc. Three types of SiC-based fibers derived from polycarbosilane were examined their oxidation degradation behavior as a function of its microstructure.

2. Experimental procedure

Three types of SiC-based fibers, Nicalon, Hi-Nicalon, and Hi-Nicalon type S, were treated in humid air (dew point is ca. 20°C) at 1273 to 1773 K for 1 to 100 h treatment. For comparison, these fibers were exposed in dry air (H_2O:<2.6 ppm). The thickness of oxidized layer was estimated by calculation of oxygen content of the fiber. As a result of oxidation from SiC to SiO_2, the oxygen content increases in the fiber as following formula.

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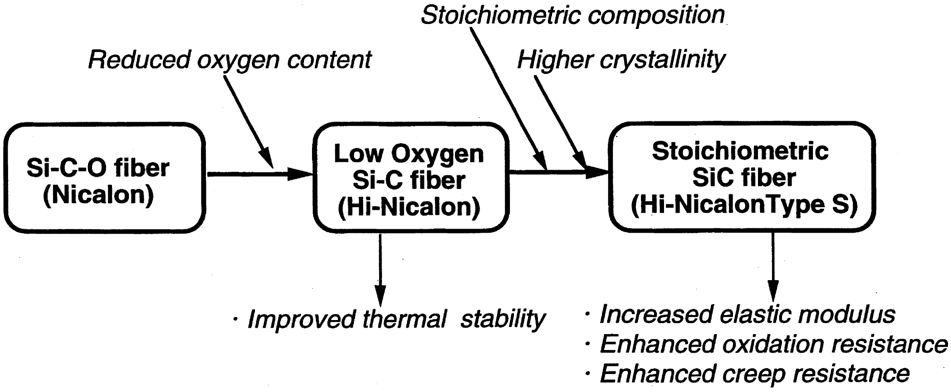

Fig. 1. Schematic drawing of Nippon Carbon's SiC fibers development.

$$Si_xC_yO_z + (x + (y - z)/2)O_2 \rightarrow xSiO_2 + yCO. \qquad (1)$$

In the case of thicker oxidation layer than about 0.5 μm, the thickness of oxidation layer was measured directly by SEM micrographs. The two methods gave almost good agreement as regard to measure the thickness. However, in the case of Nicalon fiber after higher temperature or long time exposure, they did not agree because of its thermal decomposition. In this case, SEM result was adopted to measure the thickness of oxide layer.

The structure of oxide layer was examined by XRD (model: Geigerflex, Rigaku). It was found that the oxide layer was amorphous silica or cristobalite, and the mixture of them in some case. Tensile strength of the fibers before and after the oxidation test was measured by single filament method (JIS R 7601) with 25 mm gage length (model: UTM-2, Orientec Co.). Fracture origin was detected by fracture surface observation with SEM (model: JSM-5310, JEOL), which was caught at the test in the glycerine.

3. Results and discussion

(1) *Structure and mechanical properties of SiC fibers.* Table 1 shows the typical properties of Hi-Nicalon type S as compared to other PCS-derived SiC fibers. The baseline properties of type S are preliminary ones. Fiber diameter and tex (weight/yarn length) of type S are rather smaller than other two types of fibers. Tensile strength of Hi-Nicalon type S is 2.6 GPa, which is sufficiently high for the reinforcement of CMCs. Type S shows the highest modulus of 420 GPa and the highest density, 3.1 g/cm^3. Specific resistivity of type S is much smaller, which will be explained by the existence of a carbon layer at the fiber surface.

(2) *Thermal stability at high temperature in argon or air atmosphere.* Fig. 2 shows the tensile strength of the fibers after the thermal exposure test for 10 h in argon. Nicalon fiber exhibited low strength after exposure at 1673 K, substantially degraded after exposure at 1773 K. On the other hand, Hi-Nicalon and type S retained a good strength even after 1873 K exposure. Hi-Nicalon

Table 1
Typical properties of polycarbosilane-derived SiC fibers

Properties	Nicalon NL-200	Hi-Nicalon	Hi-Nicalon type S
Fiber diameter (μm)	14	14	12
Number of filaments (fil./yarn)	500	500	500
Tex (g/1000 m)	210	200	180
Tensile strength (GPa)	3.0	2.8	2.6
Tensile modulus (GPa)	220	270	420
Elongation (%)	1.4	1.0	0.6
Density (g/cm^3)	2.55	2.74	3.10
Specific resistivity (ohm cm)	10^3–10^4	1.4	0.1
Chemical composition Si (wt%)	56.6	62.4	68.9
C	31.7	37.1	30.9
O	11.7	0.5	0.2
C/Si (atomic)	1.31	1.39	1.05

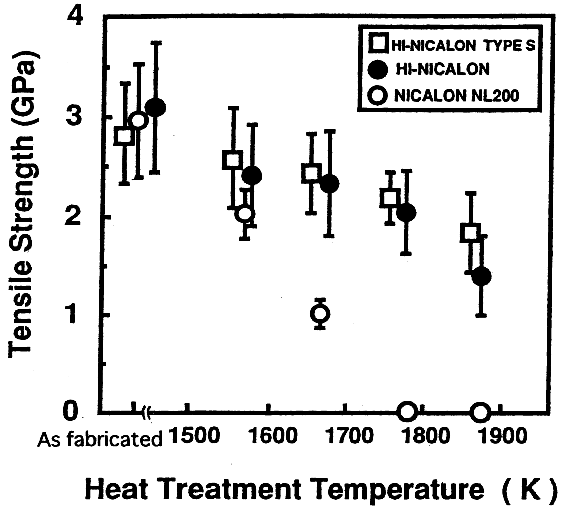

Fig. 2. Tensile strength of SiC fibers after 10 h exposure at elevated temperature in argon.

type S showed the highest strength, 1.8 GPa, after 10 h exposure in argon at 1873 K. It is evident that SiC-based fibers with reduced oxygen content exhibits superior thermal stability.

On the other hand, thermal degradation behavior of the SiC fibers in air has different aspect. Fig. 3 shows the tensile strength of SiC fibres after 10 h exposure at 1673 K in dry or wet air. The moisture in the air accelerates the oxidation. This fact is also known in oxidation of monolithic SiC [13]. Tensile strength of SiC fibers after the oxidation for 10 h exposure in air is shown in Fig. 4. Tensile strength also decreased with higher temperature. The strength of three fibers is similar up to 1473 K. However at 1673 K or higher temperature, Hi-Nicalon type S showed the highest strength, Hi-Nicalon is stronger than Nicalon. Fig. 5 shows the effect of temperature on silicon oxide layer thickness of three types of SiC based fibers after 10 h exposure in air. Oxide layer thickness increased in accordance with temperature, no significant difference among three SiC fibers was observed. The oxidation reaction of these three SiC-based fibers is almost the same in spite of different fiber structure.

In order to investigate the reason of fiber strength degradation, structural change of the fibers were examined. Figs. 6–8 shows the SEM micrographs of fracture surfaces of SiC fibers after the oxidation test. Many pores on the fracture surface in Nicalon after 1673 K exposure for 10 h in air was observed. The crack of the fiber propagated around the oxide layer with the pores. On the other hand, Hi-Nicalon showed very few pores, and Hi-Nicalon type S had no pores in the fracture surfaces. The pores should arise from CO gas enclosed in viscous oxide at high temperature. Two possible reason to evolve CO gas are proposed, one is oxidation of carbon and another is fiber decomposition, as following formulas:

Oxidation of SiC-based fiber (for SiC and excess C)

$$\mathrm{Si}_x\mathrm{C}_y\mathrm{O}_z + (x + (y - z))\mathrm{O}_2 \rightarrow x\mathrm{SiO}_2 + y\mathrm{CO}. \qquad (2)$$

Since all C elements in the fiber can be oxidized into CO, C content in the fiber is proportional to formed CO gas volume. Nicalon and Hi-Nicalon contains excess C, but Hi-Nicalon type S is near stoichiometric composition of SiC. Thus Hi-Nicalon type S exhibits the least CO gas generation. On the other hand, Nicalon contains significant oxygen in the fiber. Because Si–C–O ceramics are thermodynamically unstable, fiber decomposition occurs at high temperature as follows.

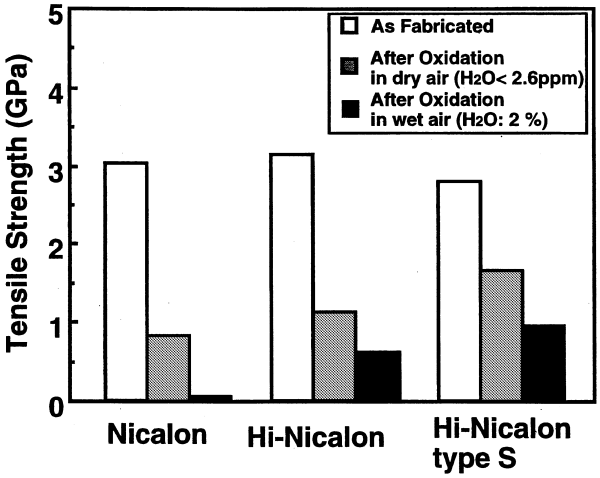

Fig. 3. Tensile strength of SiC fibers after 10 h exposure at 1673 K in day (<2.6 ppm) or wet (2% H_2O) air.

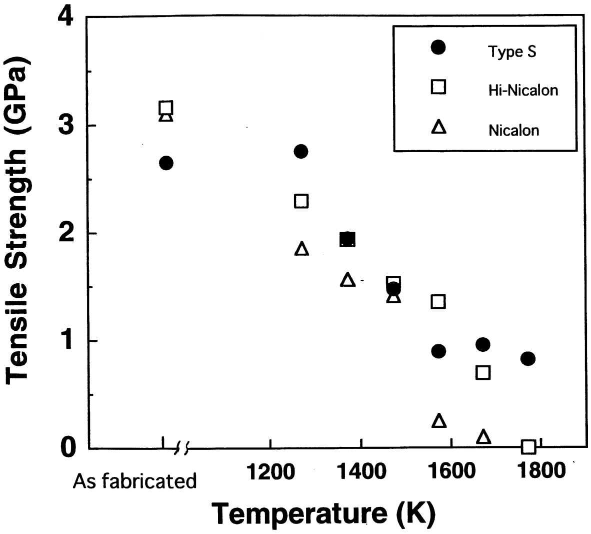

Fig. 4. Tensile strength of SiC fibers after 10 h exposure at elevated temperature in air (2% H_2O).

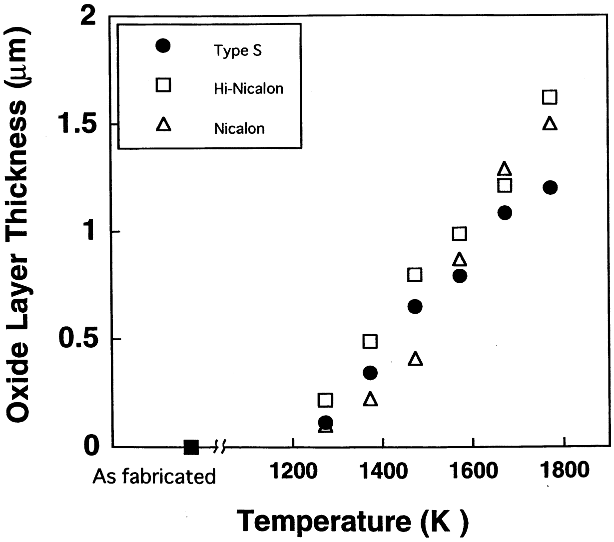

Fig. 5. Oxide layer thickness of SiC fibers after 10 h exposure at elevated temperature in air (2% H_2O).

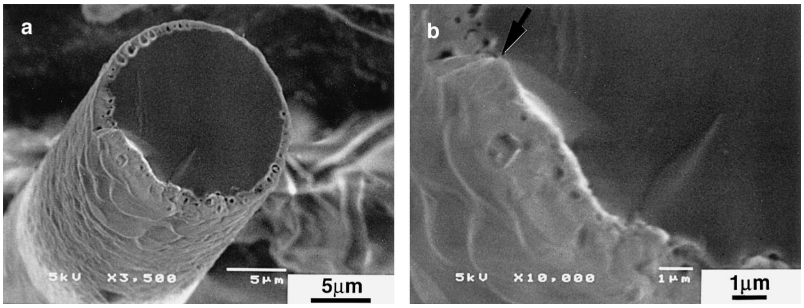

Fig. 6. SEM micrographs of Si–C–O fibers (Nicalon) after 1673 K–10 h treatment in air (2% H_2O). (A) fracture surface (0.2 GPa), and (B) magnified view, showing many pores and fracture origin (arrow) near the fiber surface.

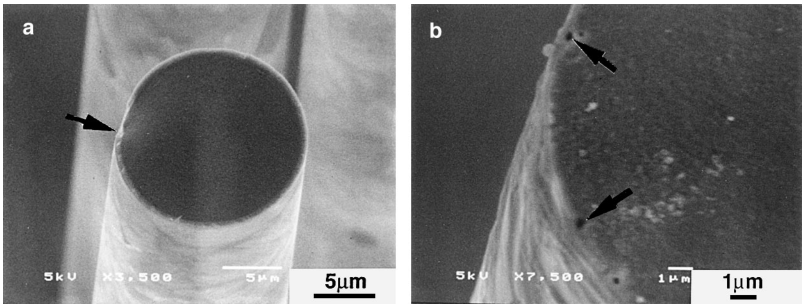

Fig. 7. SEM micrographs of Si–C fiber (Hi-Nicalon) after 1673 K–10 h exposure in air (2% H_2O). (A) fracture surface (0.7 GPa), showing fracture origin (arrow) near the fiber surface, (B) some pores (arrow) exist near the fiber surface (0.3 GPa).

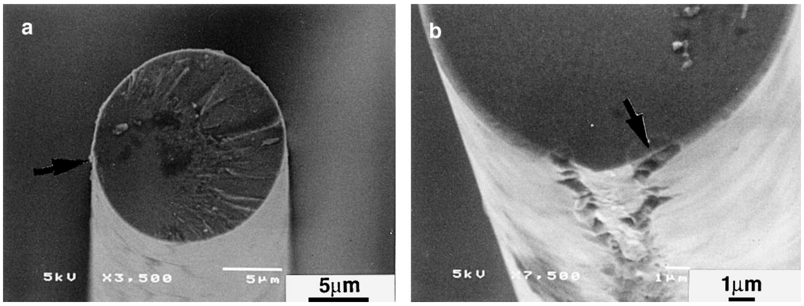

Fig. 8. SEM micrographs of stoichiometric SiC fiber (Hi-Nicalon type S) after 1673 K–10 h exposure in air (2% H_2O). (A) fracture surface (1.6 GPa), showing fracture origin at the fiber surface (arrow) and mirror, mist, and hackle zone, (B) fracture origin (arrow) is peeled oxide layer-fiber interface (0.6 GPa). Note that no visible pores exist near the fiber surface.

Decomposition of SiC-based fiber (O containing fiber)

$$\mathrm{Si}_x\mathrm{C}_y\mathrm{O}_z \rightarrow x\mathrm{SiO}_2 + (z-2x)\mathrm{CO} + (y-z+2x)\mathrm{C}.$$

In the case of Nicalon fiber, which contains 11.2wt% oxygen, decreased oxygen content to 2.9wt% after 1673 K for 10 h exposure in argon. However, Hi-Nicalon and Hi-Nicalon type S have no composition change because of very little oxygen content (<0.5 wt%). As a result of less CO generation for Hi-Nicalon type S, there were no pores at the fracture surface and the highest strength retention after oxidation.

At 1573 K or higher temperature not only crack formation at the fiber surface but also adhesion of filaments to each other was observed due to softening of silicon oxide. The silicon oxide would also acts as fracture origin in fiber strength test.

4. Conclusions

SiC-based fiber derived from polycarbosilane, Nicalon, Hi-Nicalon, and Hi-Nicalon type S were examined their oxidation behavior. As a result of oxidation test, oxidized SiC fibers decreased their strength as oxide layer thickness increased. The crack formation of oxide layer and adhesion of fibers to each other cause serious fiber degradation on tensile strength. Fracture origins were determined to exist at near the oxide layer-fiber interface. Though Nicalon had many pores from CO gas bubbles at the fracture surfaces, Hi-Nicalon type S has no pores at the fracture surface. In this study, Hi-Nicalon type S showed better oxidation resistance than other polycarbosilane-derived SiC fibers after 1673 K or higher temperature exposure in air for 10 h.

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