EVALUATION OF ADVANCED SiC FIBERS FOR REINFORCEMENT OF CMC

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SUMMARY: As a result of R & D efforts for silicon carbide (SiC) fibers, a near-stoichiometric and highly crystalline SiC fiber (Hi-Nicalon type S) has been developed. In this research, to evaluate Hi-Nicalon type S for reinforcement of ceramic matrix composites, fiber tensile tests at high temperature, fiber oxidation tests and fiber bend stress relaxation tests were carried out. Hi-Nicalon fibers were also tested to compare with Hi-Nicalon type S. The strength-gauge length relationship of Hi-Nicalon type S was found to follow the weakest-link rule, described by a Weibull distribution. The results of tensile tests at high temperature indicated that the strength of oxidized Hi-Nicalon type S decreases at elevated temperature. From the SEM observation results of oxidized fibers, the oxidation behavior of Hi-Nicalon type S was found to fit the Deal/Grove linear-parabolic model. Finally, Hi-Nicalon type S fibers were more resistant to bend stress relaxation than Hi-Nicalon fibers.

KEYWORDS: SiC fiber, high temperature, fiber tensile strength, oxidation, creep, ceramic matrix composites

INTRODUCTION

SiC-based fibers, which have high tensile strength, high elastic modulus and good thermal stability, are one of the most promising candidates for the reinforcement of ceramic matrix composites (CMCs) [1-3]. Many types of SiC-based fibers have been produced industrially: for example Nicalon of Nippon Carbon Co., Ltd. and Tyranno Lox-M of UBE Co., Ltd.. At high temperature, however, microstructural changes in those SiC-based fibers occur because of surplus oxygen in the fibers [4-6], thus degrading the properties of CMCs. Therefore SiC-based fibers with a low oxygen content have been developed: Hi-Nicalon of Nippon Carbon Co., Ltd. and Tyranno Lox-E of UBE Co. Ltd.. Recently, based on research on the effect of C/Si on thermomechanical properties of fibers, the near-stoichiometric and highly crystalline SiC fiber, which was named Hi-Nicalon type S, has been developed by Nippon Carbon Co., Ltd. [7].

In this study, to evaluate Hi-Nicalon type S fibers for CMCs, fiber tensile tests at high temperature were carried out with 190 mm gauge length. In general, fiber strength is usually measured according to ASTM standards in USA or JIS standards in Japan where the gauge length is 1 inch or 25 mm, respectively. So the effects of gauge length on the fiber strength was examined. In addition, since fiber oxidation can seriously degrade the mechanical behavior of CMCs, oxidation studies were carried out. Furthermore, to evaluate creep resistance of the fibers, bend stress relaxation experiments for Hi-Nicalon type S and Hi-Nicalon were also applied.

EXPERIMENTAL

Materials used for the fiber tensile tests were Hi-Nicalon type S and Hi-Nicalon. Characteristic properties of these fibers, as reported by the manufacturer, are shown in Table 1 where the tensile strength at room temperature (R.T.) was measured with 25 mm gauge length according to JIS standards (JIS R 7601) by Nippon Carbon Co., Ltd.. In this study a 190 mm gauge length was used to ensure that the ends of the fibers, where the load was applied, were cool during high-temperature testing. The fiber tensile tests were carried out with a Micropull Tensile Test Machine (Micropull Science, Thousand Oaks, Ca.) with a constant crosshead rate of 5.5 μm/s. Hi-Nicalon type S fibers were tested at R.T., 1373 K, and 1673 K, in air. Hi-Nicalon fibers were tested at R.T. and 1373 K, in air. In addition, Hi-Nicalon type S that were oxidized at 1373 K in air for 10 hours were examined, and Hi-Nicalon fibers that were annealed at 1373 K in argon for 2 hours and fibers that were oxidized at 1373 K in air for 2 hours were also studied. To study the oxidation behavior of Hi-Nicalon type S fibers, fibers were oxidized at 1373 K for 10, 50, 100 and 210 hours, in air. The oxide layer thickness of fibers was measured directly with SEM observations.

Table 1: Characteristic properties of fibers used

	Hi-Nicalon type S	Hi-Nicalon
Diameter	12 μm	14 μm
Density	3.20 Mg/m^3	2.73 Mg/m^3
Tensile Strength	2.45 GPa	3.02 GPa
Tensile Modulus	390 GPa	273 GPa
Oxygen	0.8 wt%	0.6 wt%

To evaluate the creep resistance of the fibers, the bend stress relaxation technique [8] was used. Fibers were wound around a silicon carbide rod that was placed inside a hollow silicon carbide cylinder with a slightly larger inner diameter than the outer diameter of the rod. The rod, fibers, and outer sleeve were then placed in a furnace and held at various temperatures for 1 and 100 hours in flowing argon. After these treatments, the fibers were removed and the residual curvature was measured. A parameter related to the amount of strain relaxation, presumably due to fiber creep, was calculated from the initial radius of the rod and fibers, r_0, and the radius of curvature of the fibers after heat-treatment, r_f,

$$m_{BSR} = 1 - \frac{r_0}{r_f} \tag{1}$$

Thus, a value of 1 for m_{BSR} represents no creep and a value of 0 for m_{BSR} represents complete relaxation.

RESULTS AND DISCUSSION

Effect of Gauge Length

The strength (σ) distribution of brittle fibers like SiC, glass or carbon fibers usually follows a classical Weibull distribution described by the following Eqn 2,

$$P(\sigma) \equiv 1 - F(\sigma) \equiv \exp\left[-\left(\frac{\sigma}{\sigma_0}\right)^m\right] \tag{2}$$

where $P(\sigma)$, $F(\sigma)$, m and σ_0 are probability of survival, probability of failure, shape parameter (Weibull modulus) and scale parameter (sigma zero), respectively. The results of fiber tensile tests of Hi-Nicalon type S with 190 mm gauge length at R.T. are shown in Fig. 1. The strength of the fiber was 1.33 GPa according to the classical Weibull distribution. The fiber diameter, 12.7 µm, was determined from SEM measurements of Hi-Nicalon type S fibers.

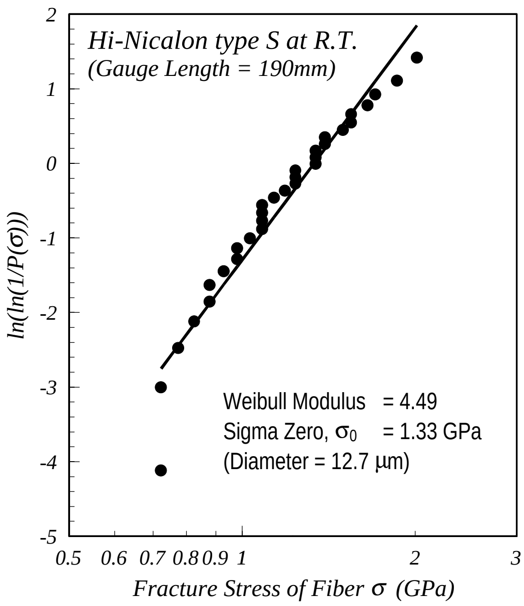

Fig. 1: Results of fiber tensile tests of Hi-Nicalon type S with 190 mm gauge length at R.T.

Equation (2) does not explicitly include the effects of gauge length. To predict the strength at a different gauge length, the results were analyzed by using the following modified equation, which was suggested by Watson and Smith [9] and Gutans and Tamuzs [10],

$$P(\sigma) \equiv 1 - F(\sigma) \equiv \exp\left[-\left(\frac{l}{l_0}\right)^\alpha \cdot \left(\frac{\sigma}{\sigma_0}\right)^m\right] \tag{3}$$

where l and l_0 are the different gauge lengths ($l \geq l_0$), and α is a parameter between 0 and 1. Phoenix *et al*. [11] suggested that α = 0.60 for Kevlar 49 fibers, and Watson and Smith [9] obtained α = 0.90 for carbon fibers. In the case of fibers that obey the weakest-link rule, α becomes 1.0 and Wu and Netravali [12] reported that α = 1.0 for single Nicalon fibers. In contrast, recent data for ultra high-strength polyethylene fibers yield α near zero [13]. To compare with Nippon Carbon's results shown in Table 1, 190 and 25 mm were used for l and l_0, respectively, and α was assumed to be 1.0. Then, from the analysis of the fiber tensile tests according to Eqn 3, the strength of Hi-Nicalon type S with 25 mm gauge length was calculated to be 2.09 GPa. If the fiber diameter was assumed to be 12.0 μm according to Table 1 as reported by the manufacturer, the strength of Hi-Nicalon type S with 25 mm gauge length was calculated to be 2.35 GPa, which is in agreement with Nippon Carbon's results considering that the typical value for the standard deviation is 0.36 GPa and the Weibull modulus is relatively low. Since the standard deviation of the fiber diameter was 0.78 μm and the accuracy of SEM observation was considered to be 10%, these results indicate that the strength-gauge length relationship of Hi-Nicalon type S was found to follow the weakest-link rule.

Fiber Strength at High Temperature

The results of fiber tensile tests at R.T. and high temperature are shown in Table 2 and 3 for Hi-Nicalon type S and Hi-Nicalon, respectively. The diameters of fibers were obtained from SEM observations of the tested fibers. The strength of fibers was calculated from the classical Weibull distribution analysis, where at least 30 fibers were tested. The diameter of Hi-Nicalon fibers did not change after heat treatment, annealing in argon for 2 hours or oxidation in air for 2 hours.

Table 2: Results of fiber tensile tests of Hi-Nicalon type S

	Hi-Nicalon type S			Hi-Nicalon type S oxidized in Air	
Test Temperature	R.T.	1373 K	1673 K	R.T.	1373 K
Weibull Modulus, m	4.49	4.06	6.11	3.18	4.52
Tensile Strength, σ_0	1.33 GPa	1.60 GPa	1.74 GPa	1.40 GPa	1.40 GPa
Standard Deviation	0.32 GPa	0.39 GPa	0.28 GPa	0.43 GPa	0.32 GPa
Diameter of Fibers	12.7 μm	12.7 μm	12.7 μm	13.15 μm	13.15 μm
Number of Specimens	31	30	32	34	31

Table 3: Results of fiber tensile tests of Hi-Nicalon

	Hi-Nicalon		Hi-Nicalon annealed in Ar	Hi-Nicalon oxidized in Air
Test Temperature	R.T.	1373 K	1373 K	1373 K
Weibull Modulus, m	5.06	6.58	3.73	5.35
Tensile Strength, σ_0	2.88 GPa	2.94 GPa	2.20 GPa	2.16 GPa
Standard Deviation	0.60 GPa	0.49 GPa	0.55 GPa	0.43 GPa
Diameter of Fibers	12.6 μm	12.6 μm	12.6 μm	12.6 μm
Number of Specimens	34	30	31	31

The effects of test temperature on the tensile strength values of the fibers are shown in Fig. 2. In the case of Hi-Nicalon, the strength of the fibers scarcely changed with increasing test temperature. After fibers were annealed or oxidized, the strength decreased significantly although the diameter did not change. This decrease in strength may be due to microstructural development in the fiber, such as grain growth, or due to damage caused by the additional handling steps. Takeda *et al*. [14] has also reported a decreasing strength with increasing temperature for Hi-Nicalon fibers annealed in argon. On the other hand, for Hi-Nicalon type

S, the apparent strength increased slightly with increasing test temperature up to 1673 K, and after the fibers were oxidized, the strength slightly decreased. For the oxidized fibers, although the strength at R.T. appeared stronger than the strength of the unoxidized fibers at R.T., there seemed to be no difference between them considering the typical values for the standard deviation and the low Weibull modulus shown in Table 2. In addition, the strength of the oxidized fibers did not change with increasing test temperature.

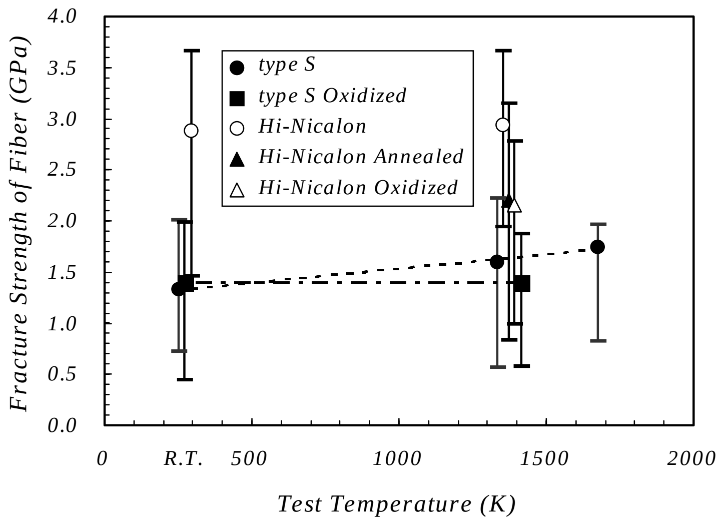

Fig. 2: Effects of test temperature on tensile strength of fiber

A schematic illustration of the tensile test apparatus used for high temperature experiments is shown in Fig. 3. In many of the experiments conducted at high temperature the entire length of the fiber inside the furnace remained intact after failure. During these tests, a part of the fiber is heated by the furnace directly and another part is heated by heat transfer indirectly. On these parts of the fiber, a thin layer of oxide that can blunt or heal pre-existing flaws on the surface of the fiber may be formed. Hence, failure is more likely to occur in the cooler sections of the fiber, as observed. This effect can be described by defining an effective gauge length of the fibers at each temperature. The effective, or real, gauge length is the length of the fiber over which failure initiates. In order to determine the effective gauge length it was assumed that the upper bound of the fiber strength values at high temperature were those measured at R.T.; i.e., there was no decrease in the strength of the fibers due to temperature. Equation (3), with $\alpha = 1.0$, was used to calculate effective gauge lengths of 84 and 57 mm at 1373 K and 1673 K, respectively. These values are smaller than 105 mm, which is the length of the fiber that is not heated by the furnace directly.

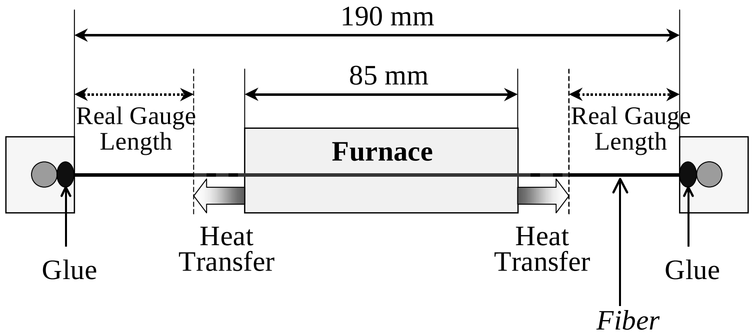

Fig. 3: Schematic illustration of fiber tensile test at high temperature

Although the primary fracture surfaces were not always recovered, the fracture surfaces of fibers tested at R.T., 1373 K, and 1673 K were indistinguishable. Hence, it is likely that the fibers tested at elevated temperature failed from pre-existing flaws in the cooler regions of the fiber as shown in Fig. 4. The effect of temperature was to heal some flaws on the fiber surface and reduce the probability of a strength-limiting flaw occurring on the fiber surface, leading to higher observed strength values. Unfortunately, these results demonstrate that, due to fiber oxidation during testing, this apparatus was not capable of measuring the true high temperature strength of the fibers. Nevertheless, it appears that the room temperature strength values are the upper bound of the high-temperature strength also.

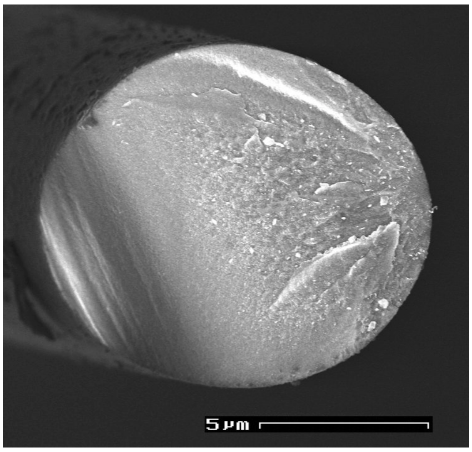

Fig. 4: Fracture surface of Hi-Nicalon type S tested at R.T.

For the high temperature tests of the oxidized Hi-Nicalon type S fibers, there was presumably the same temperature gradient in the fiber that would change the effective gauge length. So, at high temperature, the effective or real gauge length would be smaller than that at R.T. and the apparent strength would be higher than that at R.T.. Since the apparent strength of the fibers tested at elevated temperatures was actually the same as that measured at R.T., these results suggest that the strength of the oxidized fibers is lower at elevated temperatures. Unfortunately, the temperature at which the fibers are weakest can not be determined from these experiments.

Oxidation Resistance

The effects of oxidation time on oxide layer thickness of Hi-Nicalon type S are shown in Fig. 5. The thickness was measured from SEM observation of the cross section of the fibers normal to their axis. The thickness gradually increased with increasing oxidation time. In the case of 210 hours oxidation, which is indicated by an open circle in Fig. 5, the thickness was not clearly observed by SEM because not only the edges of fibers but also the surface of fibers were oxidized. So this value might be smaller than the true thickness.

The Deal/Grove linear-parabolic model [15], which describes the growth of silica (SiO_2) on silicon, was applied to analyze the oxidation results. This model describes the oxidation of silicon using a mixed-control model, in which the diffusion of oxygen through the oxide layer and the chemical reaction at the Si/SiO_2 interface act in series. These two processes are coupled by the concentration of the diffusing species at the interface. The Deal/Grove model predicts that, for thin oxide layers, the chemical reaction at the Si/SiO_2 interface is rate controlling. As the oxide thickens, the growth rate is limited by the coupled control between the interfacial reaction and the diffusion of oxygen through the SiO_2. Finally, for thick oxides, the growth rate is diffusion controlled. For fast gaseous diffusion, their model is,

$$x^2 + A \cdot x = B \cdot (t + \tau) \tag{4}$$

where x and t are oxide thickness and time, respectively. The time constant τ allows the origin ($x = 0$) of the model to allow for an initial oxide layer or regime not described by the model. B is the parabolic rate constant. B/A is the linear rate constant.

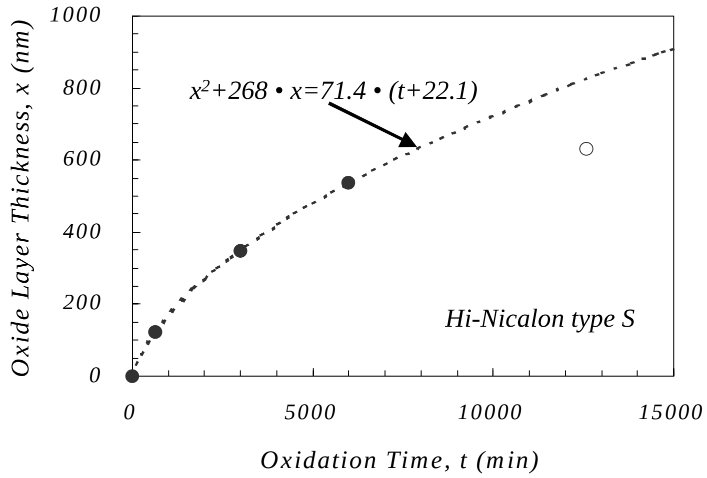

Fig. 5: Effects of oxidation time on oxide layer thickness

The oxidation behavior of silicon and SiC has been well described by the Deal/Grove model [15]. Ramberg *et al*. [16] examined the oxidation behavior of single-crystal SiC (α-SiC) and CVD-SiC (β-SiC), and reported the results of these rate constants as shown in Table 4. In this research, the Deal/Grove model was applied to the oxidation results for 0, 10, 50 and 100 hours. The results fitted this model very well, and the parabolic constant, B, was calculated to be 71.4 nm^2/min. This value is within the range reported by Ramberg *et al*. [16]. Thus the oxidation behavior of Hi-Nicalon type S was found to fit the Deal/Grove model.

Table 4: Rate constants for Deal/Grove model [16]

	B (nm^2/min)	B/A (nm^2/min)	τ
Single-crystal SiC $(000\bar{1})$	239.10	0.1678	4.573
Single-crystal SiC (0001)	11.15	0.0199	86.85
CVD SiC $(\bar{1}\bar{1}\bar{1})$	225.50	0.1841	0
CVD SiC (111)	12.98	2.807	0
Hi-Nicalon type S	71.4	0.266	22.1

Fiber Bend Stress Relaxation

To evaluate the resistance of the newly developed Hi-Nicalon type S fibers to creep, bend stress relaxation tests were performed. An illustration of the bend stress relaxation parameter,

m_{BSR}, is shown in Fig. 6. At a given temperature, a higher value of m_{BSR}, indicates a greater resistance to creep. As can be seen from the results shown in Fig. 6, Hi-Nicalon type S fibers were more creep resistant than Hi-Nicalon fibers. Although the intrinsic strength of the Hi-Nicalon type S fibers is slightly lower than that of the Hi-Nicalon fibers, as shown in Fig. 2, their ability to retain their strength and creep resistance to higher temperatures may be beneficial to their use in CMCs.

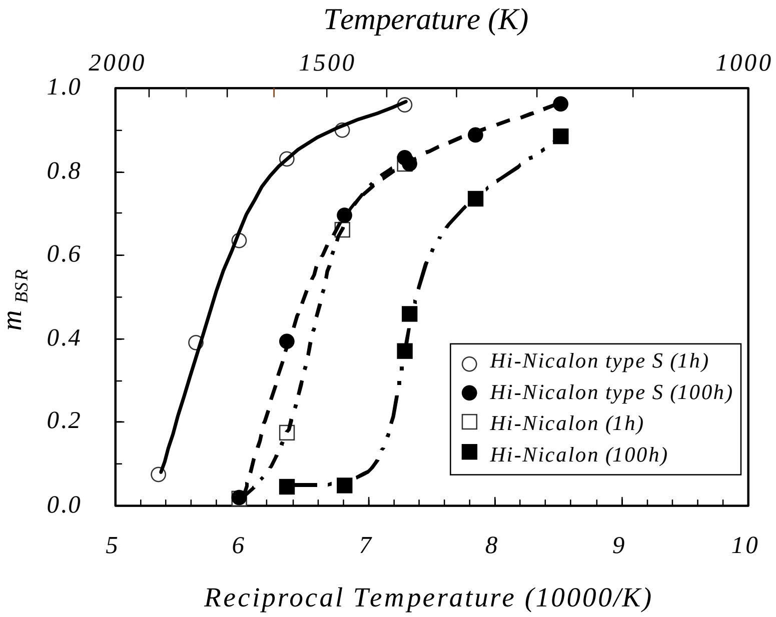

Fig. 6: Bend stress relaxation of Hi-Nicalon type S and Hi-Nicalon as a function of temperature

CONCLUSIONS

To estimate the suitability of near-stoichiometric and highly crystalline SiC fiber (Hi-Nicalon type S) for reinforcement of ceramic matrix composites, fiber tensile tests at high temperature with 190 mm gauge length, fiber oxidation tests at 1373 K and fiber bend stress relaxation tests were carried out. The conclusions can be summarized as follows.

(1) The strength-gauge length relationship of Hi-Nicalon type S at room temperature was found to follow the weakest-link rule, described by the Weibull distribution. This relationship can be used as an interpolation or extrapolation to the single fiber strength.

(2) The results of tensile tests at high temperature indicated that the strength of oxidized Hi-Nicalon type S decreases at elevated temperature. On the other hand, the strength of Hi-Nicalon scarcely changed and decreased after annealing in argon for 2 hours or oxidation in air for 2 hours.

(3) The oxidation behavior of Hi-Nicalon type S was found to fit the Deal/Grove linear-parabolic model.

(4) Hi-Nicalon type S fibers were more resistant to bend stress relaxation than Hi-Nicalon fibers.

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REFERENCES

1. Lamicq, P.J., Bernhart, G.A., Dauchier, M.M. and Mace, J.G., “SiC/SiC Composite Ceramics”, *American Ceramic Society Bulletin*, Vol. 65, No. 2, 1986, pp.336-338.

2. Strife, J.R., Brennan, J.J. and Prewo, K.M., “Status of Continuous Fiber-Reinforced Ceramic Matrix Composite Processing Technology”, *Ceramic Engineering and Science Proceedings*, Vol. 11, No. 7-8, 1990, pp.871-919.

3. Jones, R.H. and Henager Jr., C.H., “High-temperature properties of SiC/SiC for fusion applications”, *Journal of Nuclear Materials*, Vol. 212-215, 1994, pp.830-834.

4. Okamura, K., Sato, M., Ishikawa, T. and Yamamura, T., *Sintering ’87*, Vol. 1, 1987, p.61.

5. Yamamura, T., Ishikawa, T., Shibuya, M., Hisayuki, T. and Okamura, K., “Development of a New Continuous Si-Ti-C-O Fibre Using an Organometallic Polymer Precursor”, *Journal of Materials Science*, Vol. 23, 1988, pp.2589-2594.

6. Hasegawa, Y., “Synthesis of Continuous Silicon Carbide Fiber Part 6 Pyrolysis Process of Cured Polycarbosilane Fibre and Structure of SiC Fibre”, *Journal of Materials Science*, Vol. 24, 1989, pp.1177-1190.

7. Takeda, M., Sakamoto, J., Saeki, A., Imai, Y. and Ichikawa, H., “High Performance Silicon Carbide Fiber Hi-Nicalon for Ceramic Matrix Composites”, *Ceramic Engineering and Science Proceedings*, Vol. 16, No. 4-5, 1995, pp.37-44.

8. Morscher, G.N. and DiCarlo, J.A., “A Simple Test for Thermomechanical Evaluation of Ceramic Fibers”, *Journal of American Ceramic Society*, Vol. 75, No. 1, 1992, pp.136-140.

9. Watson, A.S. and Smith, R.L., *Journal of Materials Science*, Vol. 20, 1985, p.3260.

10. Gutans, J. and Tamuzs, V., *Mechanics of Composite Materials*, Vol. 20, 1984, p.1107.

11. Phoenix, S.L., Schwartz, P. and Robinson IV, H.H., “Statistics for the Strength and Lifetime in Creep-Rupture of Model Carbon/Epoxy Composites”, *Composite Science Technology*, Vol. 32, No. 2, 1988, pp.81-120.

12. Wu, H.F. and Netravali, A.N., “Weibull Analysis of Strength-Length Relationship in Single Nicalon SiC Fibres”, *Journal of Materials Science*, Vol. 27, 1992, pp.3318-3324.

13. Schwartz, P., Netravali, A.N. and Sembach, S., *Textile Research Journal*, Vol. 56, 1986, p.502.

14. Takeda, M., Urano, A., Sakamoto, J. and Imai, Y., "Microstructure and Oxidative Degradation Behavior of Silicon Carbide Fiber Hi-Nicalon Type S", *Journal of Nuclear Materials*, in press.

15. Deal, B.E. and Grove, A.S., *Journal of Applied Physics*, Vol. 36, No. 12, 1965, p.3770.

16. Ramberg, C.E., Cruciani, G., Spear, K.E., Tressler, R.E. and Ramberg Jr., C.F., "Passive-Oxidation Kinetics of High-Purity Silicon Carbide from 800^o to 1100^{o}C", *Journal of American Ceramic Society*, Vol. 79, No. 11, 1996, pp.2897-2911.