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High Temperature Strength and Oxidation Resistance of Newly Developed SiC Fibers †

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Abstract

As a result of R & D efforts for silicon carbide (SiC) fibers, near-stoichiometric and highly crystalline SiC fiber (Hi-Nicalon type S) has been developed. In this research, to estimate the potential capability of Hi-Nicalon type S for reinforcement of ceramic matrix composites, fiber tensile tests at high temperature and fiber oxidation tests at 1373 K were carried out. Hi-Nicalon fibers were also tested to compare with Hi-Nicalon type S. From the results of research for effects of gauge length on fiber strength, the strength-gauge length relationship of Hi-Nicalon type S was found to follow the weakest-link rule. The results of tensile tests at high temperature indicated that the strength of Hi-Nicalon type S slightly increased with increasing test temperature. Finally, 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.

KEY WORDS: (SiC Fibers) (Ceramic Matrix Composites) (Ceramics) (High Temperature) (Oxidation) (Tensile Strength) (Composites)

1. 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 the 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 estimate the potential capability of 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.

2. 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

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%

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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) with a constant crosshead rate of 5.5 μm/s. Hi-Nicalon type S 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 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 also were examined. 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.

3. Results and Discussion

3.1 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 **Eq. (1)**,

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

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.

Eq. (1) 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 **Eq. (2)**, which was suggested by Watson and Smith[8] and Gutans and Tamuzs[9],

$$P(\sigma) \equiv 1 - F(\sigma) \equiv \exp\left[-\left(\frac{l}{l_0}\right)^\alpha \cdot \left(\frac{\sigma}{\sigma_0}\right)^m\right] \qquad (2)$$

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.* [10] suggested that α = 0.60 for Kevlar 49 fibers, and Watson and Smith[8] 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[11] reported that α = 1.0 for single Nicalon fibers. In contrast, recent data for ultra high-strength polyethylene fibers yield α near zero[12]. 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

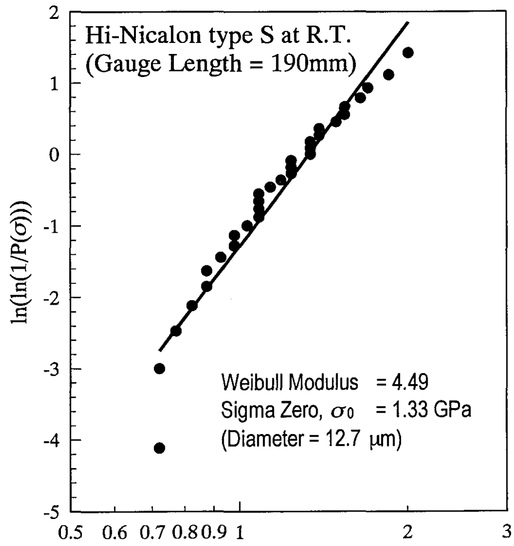

Fig. 1 Results of fiber tensile tests of Hi-Nicalon type S with 190 mm gauge length at R.T..

the analysis of the fiber tensile tests according to Eq. (2), 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%, the strength-gauge length relationship of Hi-Nicalon type S was found to follow the weakest-link rule.

3.2 Fiber tensile tests at high temperature

The results of fiber tensile tests at R.T. and high temperature are shown in **Table 2**. The diameters of fibers were decided 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 fibers did not change after heat treatment, annealing in argon for 2 hours or oxidation in air for 2 hours.

The effect 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 is probably due to microstructural development in the fiber, such as grain growth. Takeda *et*

Table 2 Results of fiber tensile tests at R.T. and high temperature.

	Hi-Nicalon type S			Hi-Nicalon		Hi-Nicalon annealed	Hi-Nicalon oxidized
Test Temperature	R.T.	1373 K	1673 K	R.T.	1373 K	1373 K	1373 K
Weibull Modulus, m	4.49	4.06	6.11	5.06	6.58	3.73	5.35
Tensile Strength, σ_0	1.33 GPa	1.60 GPa	1.74 GPa	2.88 GPa	2.94 GPa	2.20 GPa	2.16 GPa
Standard Deviation	0.32 GPa	0.39 GPa	0.28 GPa	0.60 GPa	0.49 GPa	0.55 GPa	0.43 GPa
Diameter of Fibers	12.7 μm	12.7 μm	12.7 μm	12.6 μm	12.6 μm	12.6 μm	12.6 μm
Number of Specimens	31	30	32	34	30	31	31

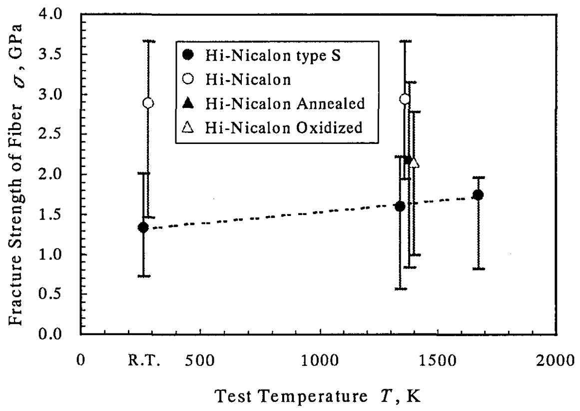

Fig. 2 Effects of test temperature on tensile strength of fiber.

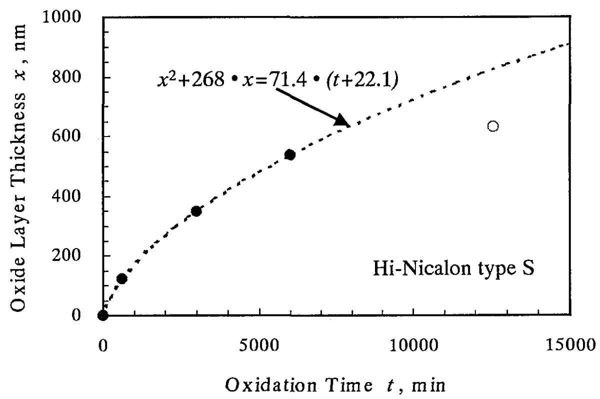

Fig. 3 Effects of oxidation time on oxide layer thickness.

al.[13] has also reported a decreasing strength with increasing temperature for Hi-Nicalon fibers annealed in argon. It is also possible that these results are due to damage to the fiber surfaces caused by removal of the protective sizing and additional handling steps. On the other hand, for Hi-Nicalon type S, the strength increased slightly with increasing test temperature up to 1673 K. One possible explanation for this apparent increase in strength is the formation of a thin layer of oxide that blunts, or heals, pre-existing flaws in the fibers. In addition, thermal expansion may close some of the pre-existing flaws on the fiber surface. Since Takeda *et al.*[13] has measured a decrease in the strength of Hi-Nicalon type S with increasing heat-treatment temperature, it is likely that simultaneous changes in the fiber microstructure occur during high temperature testing. Since the initial grain size of the Hi-Nicalon type S is larger than that of the Hi-Nicalon fibers, if grain growth occurred in both fibers at a similar rate (i.e., controlled by the same diffusional process) then the strength of the Hi-Nicalon type S fibers would decrease more slowly than the Hi-Nicalon fibers. If the decrease in strength occurred at a slow enough rate then another process, such as flaw healing due to the growth of a surface oxide, may be capable of mitigating the strength loss temporarily.

3.3 Oxidation tests

The effects of oxidation time on oxide layer thickness of Hi-Nicalon type S are shown in **Fig. 3**. 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.3, 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 result might be smaller than the true thickness.

To analyze the oxidation results the Deal/Grove linear-parabolic model[14], which describes the growth of silica (SiO_2) on silicon, was applied. 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,

Table 3 Rate constants for Deal/Grove model[15].

	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

$$x^2 + A \cdot x = B \cdot (t + \tau) \qquad (3)$$

where x and τ are oxide thickness and time, respectively. The time constant t allows the origin (x = 0) of the model to adjust 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.

The oxidation behavior of silicon and SiC has been well described by the Deal/Grove model[14]. Ramberg *et al.*[15] 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 3**. 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.*[15]. Thus the oxidation behavior of Hi-Nicalon type S was found to fit the Deal/Grove model.

4. Conclusions

To estimate the potential capability of newly developed advanced SiC fibers (Hi-Nicalon type S) for reinforcement of ceramic matrix composites, fiber tensile tests at high temperature with 190 mm gauge length and fiber oxidation tests at 1373 K were carried out. The conclusions can be summarized as follows.

(1) The relationship between the strength of Hi-Nicalon type S at room temperature and the gauge length was found to follow the weakest-link rule, described by the Weibull distribution.

(2) The strength of Hi-Nicalon type S slightly increased with increasing test temperature up to 1673 K. 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 at 1373 K.

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

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