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Effect of heat treatment on the tensile strength and creep resistance of advanced SiC fibers

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Abstract

SiC-based fibers, Hi-Niclaon™, Hi-Nicalon™ type S and Tyranno™-SA, were heat treated at 1300–1900 °C in Ar for 1 h. After heat treatment, room temperature tensile strength and 1-h bend stress relaxation (BSR) at 1400 °C in Ar were evaluated for these fibers. As a result, excellent strength retention was exhibited after heat treatment at temperature up to 1780 °C for the Hi-Nicalon™ type S fiber and up to 1900 °C for the Tyranno™-SA fiber. In contrast, relatively low strength retention was observed for Hi-Nicalon™ fiber heat-treated above 1600 °C. Creep resistance of the as-received fibers was improved by high-temperature heat treatments, especially at temperatures above the fiber's processing temperature. The microstructure analysis by means of X-ray diffractometer (XRD) and scanning electron microscopy (SEM) indicated that properties of SiC fibers at elevated temperatures are controlled by crystallite size as well as by other factors.

1. Introduction

Several fusion reactor concepts have been proposed that use SiC/SiC composite as the primary structural materials for the first wall/blanket because of its high irradiation stability and low after-heat [1–4]. Acceptable performance of high temperature ceramic matrix composites (CMCs) depends upon judicious selection and incorporation of ceramic fiber reinforcement with the proper chemical, physical and mechanical properties. For high temperature operation, the most desired critical fiber properties are high strength and stiffness and the reliable retention of these properties throughout the service life of the application. Creep of fibers could cause the matrix cracks and accelerate sub-critical crack growth in CMCs [5].

Recently developed SiC-based fibers with highly crystallized structure and near stoichiometric composition (such as Hi-Nicalon™ type S [6] and Tyranno™-SA [7]), are promising reinforcement for CMCs fabrication. These fibers experienced a pyrolysis/sintering process during fabrication and their microstructure and mechanical properties depend on the heat treatment temperature (HTT). On the other hand, the CMCs may be fabricated above the fiber's processing temperature [8,9], in which case, the performance of fibers could be changed by high temperature heat treatment. However, the effect of heat treatment effect on the fiber's properties in the CMCs requires further investigation to identify the factors which affect the high temperature properties of fiber. Thus, for exploring the optimum condition for high performance CMCs fabrication and application, the present investigation was designed to characterize the creep and tensile behavior of advanced SiC fibers before and after heat treatment at elevated temperatures. Fracture behavior and microstructure also were examined.

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2. Experimental procedure

2.1. Materials and heat treatment condition

The fibers examined in this study were Hi-Nicalon™ (HNL), Hi-Nicalon™ Type-S (HNLS) and Tyranno™ SA (TySA). Table 1 lists fibers properties provided by the manufacturers. The fibers were heat treated in Ar under a pressure of 10^4 Pa at a flow rate of 2 l/min at 20 °C/min and held for 1 h at desired temperature from 1300 to 1900 °C. After heat treatment, the apparent crystalline size of β-SiC was estimated from the half-value width of the (1 1 1) peak (d_{111}) by employing the Scherrer formulation.

2.2. Measurement of fiber tensile properties and BSR creep resistance

Tensile strength of the individual filaments was measured at room temperature in ambient atmosphere with an Instron test machine (model 5581). The load was applied at a constant strain rate of 2×10^{-4}/s and measured by a load-cell of 2.5 N. The individual filaments had a gage length of 25.4 mm and were mounted and aligned on cardboard fixture as illustrated in previous study [10]. The cardboard fixture was cut on both sides prior to test. The fiber diameters were determined by SEM examination of the fiber fragment protruding from one of the glued ends. The total number of tests for each fiber type varied from 20 to 30. The tensile test generally followed ASTM-recommended procedures [11]. After tensile test, FE-SEM was used to characterize the fracture surface of fiber fragment by a technique similar to that developed by Youngblood [10]. Weibull analysis was performed. The two-parameter Weibull theory was applied to characterize the fracture behavior of brittle SiC fibers [12]. The frequency of fiber failure, F_i, at the nth ranked sample from a total of N specimens, is obtained from the mean rank method as $F_i = n/(N+1)$.

The creep behavior of fibers was assessed by bend stress relaxation (BSR) method developed by Morscher and Dicarlo [13]. In the BSR test, the filament is bent around a mandrel with fixed radius and hold at constant strain. The BSR test on the as-received fibers was carried out at temperatures in the range of 1000–1500 °C in argon atmosphere for 1 h. In addition, 1-h BSR test at 1400 °C was performed on the heat-treated fibers. The BSR parameter m is the average for 3–7 fibers for each condition.

3. Results and discussion

3.1. Fiber tensile strength

The Weibull average strength (σ_{avg}) was calculated from the relation $\sigma_{avg} = \sigma_0\Gamma(1+1/m)$, where $\Gamma(1+1/m)$ is a gamma function. The tensile results for three fiber types are depicted in Fig. 1(a)–(c). Hi-Nicalon™ fibers exhibited degradation in strength at all test temperatures as indicated in Fig. 1(a). In contrast, both near-stoichiometric fibers (Hi-Nicalon™ Type S and Tyranno™-SA), retained most of their initial strength up to 1780 and 1900 °C as shown in Fig. 1(b) and (c), respectively. Also, the Weibull modulus decreased with increasing the HTT for the Hi-Nicalon™ fibers suggests changes in flaw population and flaw size by gas evolution from the decomposition of amorphous SiCO phase. A high Weibull modulus implies better repeatability in strength and more uniform fracture behavior.

Fig. 2 shows average room temperature tensile strengths and apparent crystallite sizes for three types of fibers after heat treatment in Ar for 1 h at temperatures in the range of 1300–1900 °C. The grain growth has a significant effect on the strength of SiC-based fibers. For the Hi-Nicalon™ fiber, crystallization degraded its strength at all HTT. In both near stoichiometric fibers, strength degradations occurred at the temperatures where crystallite size began to increase.

The grain coarsening could be attributed to the coalescence of β-SiC nano-crystal during exposure at high temperatures [14]. Fibers with larger grain size generally have relatively lower strengths. But it should be noted that Hi-Nicalon™ showed more rapid strength degradation than Hi-Niclaon™ Type S above 1400 °C heat treatment as shown in Fig. (2). Hi-Nicalon™ has smaller crystal sizes comparing to that of HiNicalon™ Type S. Fiber strength is controlled by critical flaw size. Also, the residual stresses, which were generated from gas evolution during heat treatment at elevated temperatures and the mismatch in thermal expansion coefficient between excess carbon and SiC grain, could cause strength loss, and the contribution of residual stresses

Table 1
Nominal properties of SiC fibers provided by manufacturers

SiC fiber	C/Si	Oxygen (wt%)	Strength (GPa)	Modulus (GPa)	Density (g/cm^3)	Diameter (μm)
HNL	1.39	0.5	2.8	270	2.74	14
HNLS	1.05	0.2	2.6	420	3.1	12
TySA	1.07	<0.5	2.6	400	3.0	7

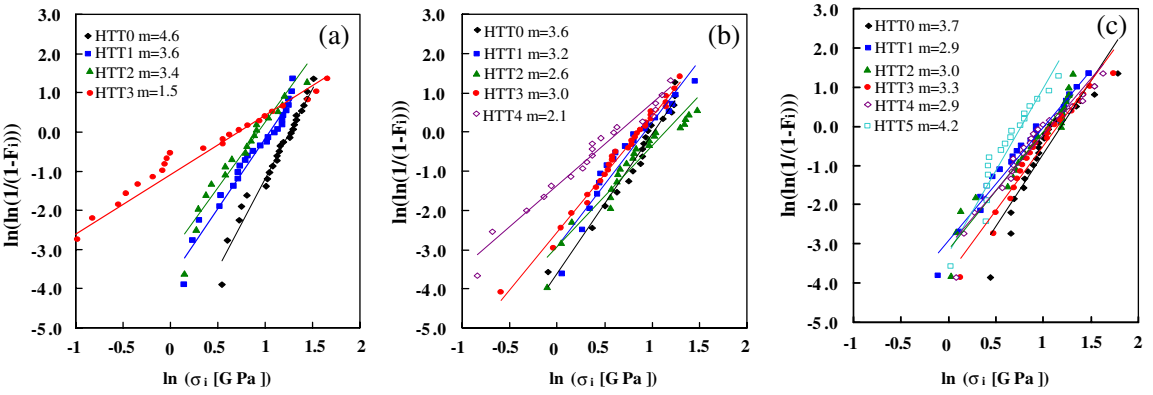

Fig. 1. Frequency of fiber failures as function of applied stress and fiber condition for: (a) Hi-Nicalon™; (b) Hi-Nicalon™ type S; (c) Tyranno™-SA, (HTT0-as received, HTT1 = 1300 °C, HTT2 = 1400 °C, HTT3 = 1600 °C, HTT4 = 1780 °C, HTT5 = 1900 °C).

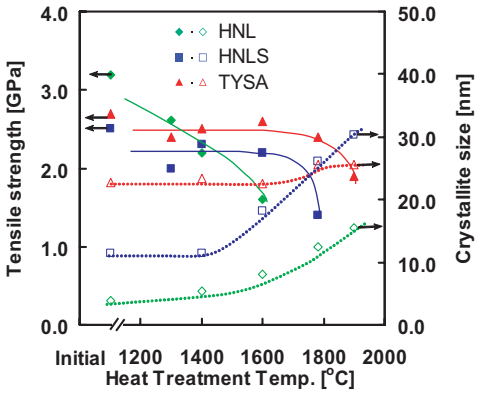

Fig. 2. Average room temperature tensile strength of fibers and apparent crystallite size of β-SiC under heat treatment at elevated temperatures in Ar for 1 h.

from the gas evolution to strength loss could increase with increasing the β-SiC grain size.

The typical fracture surfaces for as-received the three fiber types are shown in Fig. 3(a)–(c). For both as-received Hi-Nicalon™ and Hi-Nicalon™ Type S fibers, the fracture mainly originated from the inner critical flaws as shown in Fig. 3(a) and (b). The strength of fiber depends on the flaw sizes and distribution. The fracture mirror zone is formed during slow crack propagation. Occasionally, no obvious mirror zone was identified on the fracture surface in either type of Nicalon™ fibers. The fracture surfaces for the Tyranno-SA fiber showed a trans-crystallite fracture behavior (Fig. 3(c)).

3.2. BSR creep resistance

Fig. 4 shows dependence of 1-h BSR creep resistance m on testing temperature for as-received fibers. The stress relaxation occurred at temperature as low as 1000 °C. Hi-Nicalon™ type S and Tyranno™ SA exhibited much better creep resistance than Hi-Nicalon™ fiber as shown in Fig. 4. Fig. 5 shows dependence of 1-h BSR creep resistance m on HTT, which was tested at 1400 °C. Heat treatments of the fibers above the processing temperature resulted in improved creep resistance as shown in Fig. 5. The creep resistance of heat treated Hi-Nicalon™ fiber above 1400 °C was significantly improved. However, a relatively low tensile strength above 1400 °C heat treatment was observed as shown in Fig. 2.

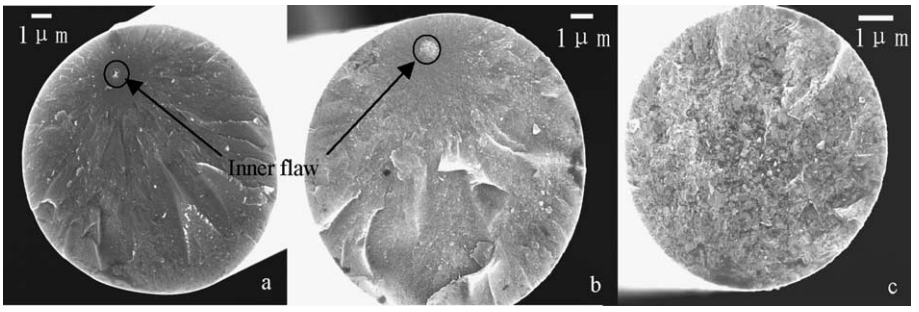

Fig. 3. Typical fracture surface observation in as-received: (a) Hi-Nicalon™; (b) Hi-Nicalon™ Type S; (c) Tyranno™-SA.

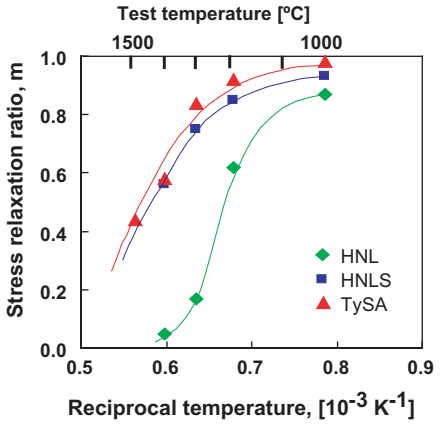

Fig. 4. 1-h stress relaxation ratio in Ar for as received fibers tested at elevated temperatures.

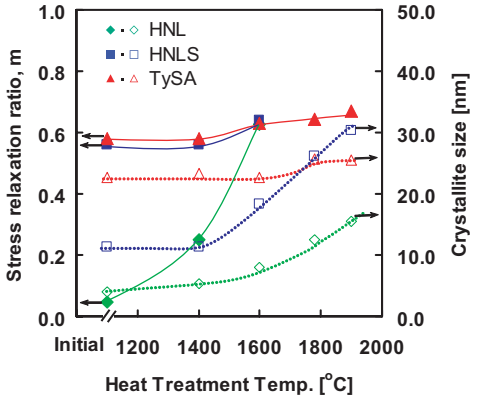

Fig. 5. 1-h stress relaxation ratio for heat treated Hi-Nicalon™, Hi-Nicalon™ type S and Tyranno™-SA fibers tested at 1400 °C in Ar.

Likely, this could be attributed to the increased grain sizes, high crystallization of β-SiC and more highly crystallized graphitic carbon. Such microstructural changes are expected to inhibit diffusion-controlled creep processes.

For the 1600 °C heat treated Hi-Niclaon™ fiber, the creep resistance was better than those of as-received near stoichiometric fibers although the fact that the grain sizes were much smaller than those of the latter fibers. This result indicated that the improved creep resistance depended on the crystallization and grain growth. The excess carbon distributed at the grain boundary for the Hi-Nicalon™ fiber inhibits the coalescence of β-SiC, which results in a stable grain boundary structure. This implies that stability of Grain boundaries (GB) plays an important role on the creep resistance of SiC fiber. This assumption was also demonstrated by Tyranno™-SA fiber. The enhanced creep resistance of the Tyranno™-SA fiber was obtained prior to increase its crystallite size. As a result of Al addition to Tyranno™-SA fiber, the complex oxide would be formed at GB by heat treatment and they can stabilize the grain boundary to improve the creep resistance. The stability of GB could be affected by GB composition.

4. Conclusions

(1) Most of initial tensile strength for both near stoichiometric fibers (Hi-Niclaon™ Type S and Tyranno™-SA) was retained after heat treatment up to 1780 °C. In fact, Tyranno™-SA fiber had excellent strength retention after heat treatment at 1900 °C. The tensile strength of fibers is extremely sensitive to the critical flaw size and distribution. The mechanism for the strength degradation is attributed to a combination of crystal growth of β-SiC and critical flaw/residual stress.

(2) The improved creep resistance was obtained for all of fiber types after high temperature heat treatment above 1400 °C, and is likely attributed to the crystallization and grain growth. It appears more likely that improved creep resistance occurs when HTT exceeds fiber fabrication temperature. In addition, the creep resistance is associated with GB composition. The GB composition could affect the stability of GB boundaries.

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References

[1] A.R. Raffray, L. El-Guebaly, S. Gordeev, S. Malang, E. Mogahed, F. Najmabadi, I. Sviatoslavsky, D.K. Sze, M.S. Tillack, X. Wang, Fus. Eng. Des. 58&59 (2001) 549.
[2] L. Giancarli, J.P. Bonal, A. Caso, G. Le Marois, N.B. Morley, J.F. Salavy, Fus. Eng. Des. 411 (1998) 165.
[3] B. Riccardi, P. Fenici, A. Frias Rebelo, L. Giancarli, G. Le Marois, E. Philippe, Fus. Eng. Des. 51&52 (2000) 11.
[4] S. Ueda, S. Nishio, Y. Seki, R. Kurihara, J. Adachi, S. Yamazaki, J. Nucl. Mater. 258–263 (1998) 1589.
[5] C.A. Lewinsohn, R.H. Jones, G.E. Youngblood, C.H. Henager Jr., in: R.H. Jones, A. Kohyama (Eds.), The Third IEA Workshop on SiC–SiC Ceramic Composites for Fusion Structural Applications, Cocoa Beach, FL, 29&30 January 1999, p. 76.
[6] H. Ichikawa, Ann. Chim. Sci. Mater. 25 (2000) 523.

[7] T. Ishikawa, Y. Kohtoku, K. Kumagawa, T. Yamamura, T. Nagasawa, Nature 391 (1998) 773.
[8] S. Dong, Y. Katoh, A. Kohyama, J. Am. Ceram. Soc. 86 (1) (2003) 26.
[9] S.P. Lee, Y. Katoh, J.S. Park, S. Dong, A. Kohyama, S. Suyama, H.K. Yoon, J. Nucl. Mater. 289 (2001) 30.
[10] G.E. Yougnblood, C. Lewinsohn, R.H. Jones, A. Kohyama, J. Nucl. Mater. 289 (2001) 1.
[11] ASTM D3379-75 (reapproved 1989) Standard test method for tensile strength and Young's modulus for high-modulus single-filament materials.
[12] W. Weibull, J. Appl. Mech. 18 (1951) 293.
[13] G.N. Morscher, J.A. Dicarlo, J. Am. Ceram. Soc. 75 (1) (1992) 136.
[14] T. Shimoo, I. Tsukada, M. Narisawa, T. Seguchi, K. Okamura, J. Ceram. Soc. Jpn. 105 (1997) 559.