SiC FIBER EVALUATIONS - G. E. Youngblood and R. H. Jones (Pacific Northwest National Laboratory)*

OBJECTIVE

The objective of this report is to evaluate the unirradiated properties of near stoichiometric β-SiC fibers which will be irradiated in the JUPITER/HFIR 14J experiment.

SUMMARY

The SiC fiber types selected for the JUPITER 14J irradiation experiment are presented together with the rationale for their selection. The fiber diameter variation from fiber-to-fiber within a tow and along single filament lengths was assessed by image analysis and SEM for four SiC-based fibers: Hi-Nicalon, Hi-Nicalon Type S, Tyranno SA and Dow Sylramic. Because of the apparently characteristic fiber diameter variations observed across tows (6-22 μm) as well as along single filaments (up to $\pm 1.0\mu$m/cm), it is not appropriate to use average fiber diameters to determine individual fiber strengths or fiber strength distributions. Generally, SiC fibers with larger diameters have lower tensile strengths. Therefore, a 3-parameter modified Weibull analysis which includes a diameter dependence parameter is preferred over the simple 2-parameter Weibull analysis to properly describe SiC fiber strength distributions. The newly introduced diameter dependence parameter may be a sensitive measure of fiber quality or performance.

PROGRESS AND STATUS

Introduction

The JUPITER HFIR/14J neutron irradiation experiment, scheduled to commence in March, 1999 and to be completed in March, 2000, is part of the U.S./Monbusho collaboration. The irradiations will be carried out at 300, 500 and 800°C to a dose of $\approx$10 dpa-SiC.

Better irradiation stability of SiC/SiC composites is expected if fiber properties are closely matched to that of the SiC matrix so that differential swelling or shrinkage between the fiber and matrix can be minimized [1]. Therefore, several advanced fibers with near stoichiometric β-SiC compositions and crystalline structures were selected for the HFIR/14J irradiation. This report will discuss ongoing evaluations of these fibers.

HFIR/14J Fiber Matrix

The selected fiber types for the HFIR/14J experiment are listed in Table 1. All of the listed fibers are polymer-derived with room temperature tensile strengths in excess of 2.5 GPa and have fine diameters which make them suitable for weaving into fabric for SiC/SiC composite fabrication. Except for the Hi-Nicalon fiber, these fibers have been given a final sintering treatment at 1600°C or greater to stabilize their crystalline structures. Therefore, their bulk density and elastic modulus values ($\approx$3.1 g/cc and $\approx$400 GPa, respectively) approach monolithic β-SiC values. The Hi-Nicalon fiber has lower density and modulus values (2.7 g/cc and 270 GPa, respectively), and has exhibited long-term radiation degradation [3].

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Table 1. Measured Properties* of Near Stoichiometric β-SiC Fibers to be Irradiated in 14J.

Measured Property	Hi-Nicalon (1)	Annealed Hi-Nic (2)	Hi-Nic Type S (1)	Tyranno SA (3)	Tyranno SA(2) (3)	Dow Sylramic(4)	Dow Syl. (2) (4)
Avg. Diameter (μm)	13.8/14	(14)	12.3/13	9.4/10	(10)	(10)	9.2/10
Density (g/cc)	2.69/ 2.74	2.82	3.08/3.1	(3.02)	(3.1)	(3.1)	(>3.1)
RT Tensile Strength (GPa)	3.4/2.8	nm	2.1/2.5	(2.8)	(2.8)	(3.2)	(3.2)
RT Modulus (GPa)	(270)	nm	(420)	(420)	(375)	(400)	(>400)
RT Elongation (%)	(1.0)	nm	(~0.6)	(0.7)	(~0.7)	(~0.8)	(<~0.8)
RT Therm. Cond. (W/mK)	4.8/5.3	nm	(18)	(65)	nm	(46)	(>46)
RT Elect. Cond. (Ω-cm)	3.0/1.4	1.1	30/0.1	nm	nm	nm	nm
Second Phases (wt. %)	Turbo C 18 v /%	nm	0.2 O	<2 Al 0.3 O	<2 Al 0.3 O	2.2 TiB_2 0.8 O	< B <0.8 O
XRD Crystallite-Size (nm)	4.0/4	nm	11/22	40/38	(150**)	85/90	(~100)
Continuous Use Temp (°C)#	1078	1215	1256	~1300 est.	nm	1261	nm

Manufacturer's values are listed second or in parenthesis
(1) Nippon Carbon Co., Ltd., Yokohama, Japan
(2) Annealed at 1500°C, Argon (1 hr.)
(3) Ube Industries, Ltd., Ube City, Japan
(4) Dow Corning Corp., Midland, Michigan, USA
** Determined from TEM microstructures
# Determined from the fiber BSR thermal creep when m = 0.5 for a 100 hr. test in argon [2].

However, SiC/SiC composite with Hi-Nicalon reinforcement is commercially available. Since considerable irradiation performance data has been accumulated for this fiber, it is retained in the experimental matrix as a reference. To examine if the irradiation performance of the Hi-Nicalon fiber could be improved without degrading its other properties, a high temperature anneal (1500°C, 1 hour in argon) was given to a fiber bundle prior to insertion into 14J. The remaining stoichiometric SiC fibers listed in Table 1 currently are being evaluated for advanced aerospace applications because of their improved creep and rupture strength properties as well as improved oxidation resistance [4]. The Hi-Nicalon Type S and Dow Sylramic fibers just recently have become commercially available, although in limited amounts. Both of these fiber types have been given additional treatments to improve their creep and rupture strength properties even more.

These treated fibers, listed as Tyranno SA(2) and Dow Sylramic(2) in Table 1, are developmental and are available only on special request at this time.

Recently, the thermal diffusivity of the Hi-Nicalon fiber was determined as a function of temperature from RT to 200°C [5]. Similar measurements are planned for the other selected fibers and the upper temperature limit for the difusivity measurements will be extended to 1000°C. Other characterization measurements include crystallite size determinations by XRD and field emission SEM and RT electrical conductivity determinations. Irradiation effects on these fiber properties will be assessed after the 14J irradiations. The fiber continuous use temperature was estimated from a 100 hr. thermal creep bend stress relaxation (BSR) test as discussed previously [2]. A similar fiber BSR test to examine the potential for irradiation-enhanced creep will be carried out in HFIR/14J. To more closely simulate the time-temperature conditions expected in the HFIR/14J irradiation, a 1000 hr. fiber thermal creep BSR test will be carried out. Of particular interest is the effect of the added aluminum in the Tyranno SA fiber and the reduced boron in the Sylramic fiber. The aluninum (as Al_2O_3) stabilizes grain growth in the Tyranno fiber while reduced boron in the Sylramic should alleviate the expected helium generation problem in a neutron irradiation environment.

Effects of Diameter Variation on Fiber Tensile Strength

Initial characterization of the Hi-Nicalon, Hi-Nicalon Type S, Tyranno SA and Dow Sylramic fibers has indicated that they typically exhibit a large variation in their effective diameters (6-22 μm) as well as strength dependence on their diameters. A simple 2-parameter Weibull analysis, as recommended by ASTM D3379 [6], may not be adequate to describe fiber strength distributions before and after irradiation treatments [7]. Therefore, a study to assess the influence of diameter variation on fiber tensile strengths and strength distributions was carried out. A 3-parameter "modified" Weibull analysis method, recently developed by Zhu et al. [8], was examined as a better way to describe fiber strength distributions.

Typical fiber diameter (cross-sectional shape) variations across a tow were examined by image analysis of approximately 200 fiber cross sections per fiber. The fiber diameter sizes exhibited near normal distributions with the Hi-Nicalon and Tyranno SA fibers having 1σ standard deviations near 13%, and the Hi-Nicalon S and Dow Sylramic having standard deviations <10%. Surprisingly, the measured average aspect ratios (fiber maximum diameter/breadth) were about 1.1 for each of the four examined fibers. To investigate typical fiber diameter variation along a filament length, three neighboring 30 cm long filaments were pulled from a tow and cut sequentially into 1 cm segments. The equivalent fiber diameter was determined from multiple measurements made directly from SEM micrographs of the individual segments. Diameter variations of up to $\pm 1\mu$m/cm length were observed for each of the four fiber types.

Because of the apparently characteristic fiber diameter variations observed across tows as well as along single filaments for SiC fibers, it is not appropriate to use average fiber diameters to determine individual fiber strengths. Particularly, fiber strength distributions are affected, as a 10% error in diameter results in about a 20% error in the calculated breaking stress. Such errors show up as additional scatter in the Weibull strength distribution. Therefore, it is necessary to measure/determine the fiber cross-sectional area (equivalent diameter) at the point of the original fracture to properly assess the fiber strength distribution.

The observed dependencies of the fiber tensile strengths on diameter for the Hi-Nicalon, Hi-Nicalon Type S and Dow Sylramic fibers are illustrated in Figure 1(a-d). In Figure 1(a-d), the fiber tensile strengths exhibit significant scatter. Nevertheless, the general trend that fibers with larger diameters have lower strengths is consistent. The tensile strength (σ) versus

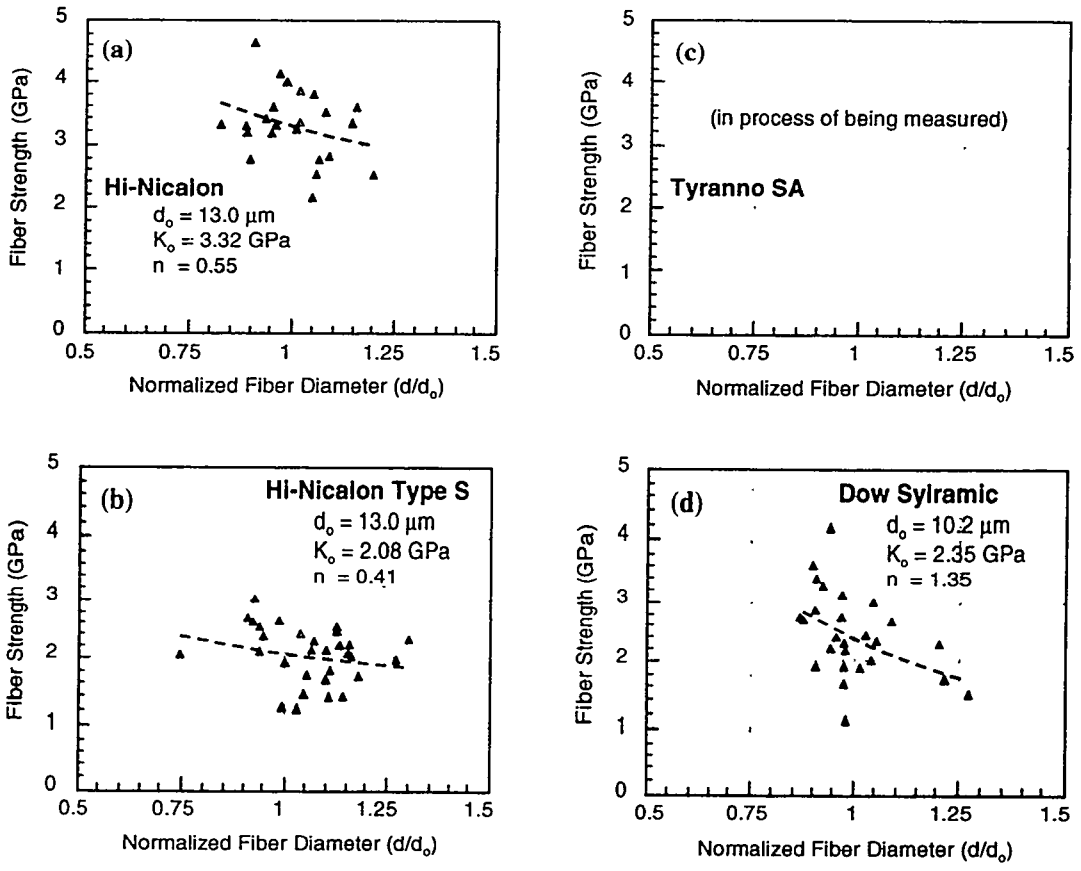

Figure 1(a-d). Tensile strength dependence on the normalized diameter for (a) Hi-Nicalon, (b) Hi-Nicalon Type S, (c) Tyranno SA and (d) Dow Sylramic fiber types.

normalized diameter (d/d_o) data were fit with a power law dependence of the form

$$\sigma = K_o(d/d_o)^{-n} \qquad (1)$$

where d_o is the average diameter of the data set, n is the power law exponent and K_o is the average strength expected for a fiber with diameter d_o. The values of d_o, K_o and n are included in the plots for each fiber type. The strongest strength dependence on diameter (n=1.35) was exhibited by the Dow Sylramic fiber, while the weakest (n=0.41) was exhibited by the Hi-Nicalon Type S fiber.

The modified 3-parameter Weibull analysis, as presented by Zhu [8], was used to analyze the fiber tensile strength data. In this method, the strength data are fit by linear regression to the modified Weibull expression

$$\mathrm{Ln}\{\mathrm{Ln}[(N+1)/(N+1-i)]\} - h\mathrm{Ln}(d_i/d_o) = \beta\mathrm{Ln}(\sigma_i) - \beta\mathrm{Ln}(\sigma_o) \qquad (2)$$

where i is the rank of the fiber tensile strengths arranged in descending order; N is the total number of tensile tests; σ_i and d_i are the corresponding measured tensile strength and diameter

values, respectively; and β and σ_0 are the Weibull shape and strength parameters, respectively. In the left-hand side of Eqn (2), the second term appears as a correction factor to the first term, which is the standard Weibull failure probability ranking term. The new parameter (h) represents the fiber strength dependence on the fiber diameter. Since the Weibull mean strength (σ_{WM}) is given by

$$\sigma_{WM} = \sigma_0\Gamma(1 + 1/\beta)(d/d_0)^{-h/\beta} \qquad (3)$$

where Γ is the gamma function with argument $(1 + 1/\beta)$, the identities

$$n = h/\beta \qquad \text{and} \qquad K_0 = \sigma_0\Gamma(1 + 1/\beta) \qquad (4)$$

are required to make Eqns (1) and (3) equivalent [8].

Iteration is necessary to derive the three parameters β, σ_0 and h. To do this, conventional 2-parameter Weibull analysis yields an initial β value (β_0). A fixed n value is obtained by linear regression fitting the fiber tensile strength-diameter data to Eqn (1). An initial h value ($h_1 = n\beta_0$) is inserted into Eqn (2), and new values for β and σ_0 are obtained. This cycle is repeated until the β, σ_0 and h values converge which usually only requires five or six iterations. The modified Weibull analysis results for the three fiber types for which the tensile tests have been completed are given in Table 2.

Table 2. Summary of 3-Parameter Modified Weibull Analysis for SiC-Fibers

Fiber Type	β	σ_0 (GPa)	h	σ_{WM} (GPa)	$\Delta\ \sigma_{WM}$ (GPa)
Hi-Nicalon	6.99	3.58	3.87	3.35	±0.56
Hi-Nicalon S	5.18	2.29	2.11	2.11	±0.47
Dow Sylramic	4.77	2.63	6.43	2.40	±0.57

The σ_0 and β values derived from the simple 2-parameter Weibull analysis of the Hi-Nicalon, Hi-Nicalon Type S and Dow Sylramic fiber tensile strength data were 3.61, 2.31 and 2.72 GPa and 6.37, 4.93 and 3.80, respectively. The 2-parameter σ_0 values were only slightly higher than the corresponding 3-parameter values listed in Table 2. However, the 3-parameter β values were significantly larger than the corresponding 2-parameter β values. The degree of difference in either value becomes larger as the fiber strength dependence on diameter becomes stronger (larger n or h values). The σ_{WM} values (Table 2) agree closely with the K_0 values (Fig. 1) derived from fitting the tensile strength and normalized diameter data for each fiber type.

The scatter in the strength versus diameter data shown in Fig. 1 primarily is due to the statistical variation of flaw sizes and is the dominant mechanism responsible for the Weibull strength distribution. If h = 2.0 in Eqn (2), the modified Weibull analysis reduces to the single modal Weibull distribution that includes the fiber strength dependence on test volume (proportional to d^2 for fibers with the same length). If the fiber strength is primarily determined by surface flaws, a strength dependence on fiber surface area (proportional to d^1) is expected and h = 1.0. The tensile strength distribution for the Hi-Nicalon Type S fiber with h = 2.11 nearly falls into the former category. However, when h > 2, as appears to be the case for the Hi-Nicalon and Dow Sylramic fibers with h = 3.87 and 6.43, respectively, flaw location and type also influence the fracture mechanics [9]. In this respect, the parameter h should be sensitive to processing variables, and

also may be valuable as an indicator of the effects of fiber treatments as well as the effects of irradiation.

FUTURE WORK

The characterization of the properties for the unirradiated SiC fiber specimens will be continued through 1999.

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