CREEP BEHAVIOR FOR ADVANCED POLYCRYSTALLINE SiC FIBERS - G. E. Youngblood and R. H. Jones (Pacific Northwest National Laboratory),* G. N. Morscher (Case Western Reserve University) and Akira Kohyama (Institute of Advanced Energy, Kyoto University, Japan)

OBJECTIVE

The objective of this work is to examine irradiation enhanced creep behavior in advanced polycrystalline SiC fibers.

SUMMARY

A bend stress relaxation (BSR) test is planned to examine irradiation enhanced creep in polycrystalline SiC fibers which are under development for use as fiber reinforcement in SiC/SiC composite. Baseline 1 hr and 100 hr BSR thermal creep "m" curves have been obtained for five selected advanced SiC fiber types and for standard Nicalon CG fiber. The transition temperature, that temperature where the S-shaped m-curve has a value 0.5, is a measure of fiber creep resistance. In order of decreasing thermal creep resistance, with the 100 hr BSR transition temperature given in parenthesis, the fibers ranked: Sylramic (1261°C), Nicalon S (1256°C), annealed Hi Nicalon (1215°C), Hi Nicalon (1078°C), Nicalon CG (1003°C) and Tyranno E (932°C). The thermal creep for Sylramic, Nicalon S, Hi Nicalon and Nicalon CG fibers in a 5000 hr irradiation creep BSR test is projected from the temperature dependence of the m-curves determined during 1 and 100 hr BSR control tests.

PROGRESS AND STATUS

Introduction

As part of the Joint DOE/Monbusho Program to support materials development for fusion energy, PNNL has initiated a systematic study of the potential effects of irradiation creep in SiC/SiC composites and SiC fibers. A previous report described a simple bend stress relaxation test designed to examine the creep behavior of irradiated and unirradiated SiC fibers [1]. A second report presented 1 hr BSR thermal creep results for selected advanced fibers, namely Nicalon S™ and Hi Nicalon™ manufactured by Nippon Carbon Co. and Sylramic™ manufactured by Dow Corning Corp [2]. This report presents 100 hr BSR thermal creep results for these same fibers plus results for annealed Hi Nicalon and Hi Nicalon S fibers and the newly introduced Tyranno™ Lox E fiber, the latter fiber being manufactured by Ubekosansha, Japan. The properties for the selected fibers are given in Table 1. Measured lot specific properties are italicized; otherwise manufacturer's values are given.

All the fibers listed in Table 1 are polymer-derived, small diameter fibers suitable for weaving into fabric for composite fabrication. They were received as fiber tows from which single fiber strands were selected for the BSR and tensile strength tests. The measured tensile strengths were made at ambient using a Micropul™ device designed for this purpose. They represent the average strength values from a Weibull analysis for 20-25 individual

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Table 1. Properties of SiC Fibers Selected for the Irradiation Creep Tests.

Property	Nic CG	Hi Nic	Nic S	Sylramic	Hi Nic*	Nic S*	Tyranno E
Diam, µm	*14*	*12*	*11*	10	*12*	*11*	*11*
Density, g/cm^3	*2.55*	*2.74*	*2.98*	3.0	2.8	3.1	*2.40*
Tens. Stren., GPa	*2.6*	*3.4*	2.6	2.8	*2.4*	*1.0*	3.3
Tens. Mod., GPa	190	270	420	400	320	440	220
Composition-Si (wt %) -C -O (atomic) - C/Si	56 32 12 1.31	62 37 0.5 1.39	69 31 0.2 1.05	66 28 0.9 +2 (B) 1.0			55 37 6 + 2 (Ti) 1.6
Xstallite G. S., nm	*<2*	*5*	10	75	8	10	18
Transition Temp.,°C (1 hr, m = 0.5)	*1110*	*1230*	*1450*	*1420*			

*Annealed one hour in argon at 1500°C.

measurements for each fiber type. Two of the fibers, Hi Nicalon and Nicalon S, were annealed simultaneously at 1500°C in argon to improve their creep resistance. For these two fibers, the strengths were determined using a "bit" strength test in which single strands were bent around drill bit shanks of diminishing diameters until the fiber failed. By this test, the strengths of annealed Hi Nicalon (Hi Nic*) and Nicalon S (Nic S*) were determined to have decreased to values of 2.4 ± 0.5 and 1.0 ± 0.3 GPa, respectively. The Hi Nic* strength decrease was similar to that observed by Ichikawa, et al. [7] for annealed Hi Nicalon. On the other hand, the Nic S* strength decreased by an amount much larger than expected. SEM inspection of the Nic S* fiber surface revealed numerous, but unexplained pore "blowout" type flaws. For this reason, the Nic S* fibers were eliminated from further consideration in this BSR test series. The 1 hr BSR transition temperatures were taken from the one hour BSR creep results given in Ref. [2].

Theoretical and Experimental Review

Theoretical and experimental details of the BSR test were presented previously [1,2]. Briefly, an initial elastic bend strain is applied to a single fiber by wrapping several coiled loops onto a SiC mandrel of radius R_o. The loops are captured by a SiC sleeve that slips over the fiber-wrapped mandrel. For the test designed to examine the potential effects of irradiation enhanced creep, the fiber loops will be subjected to a specific time (t), temperature (T), and irradiation dose (ϕ) at the fixture imposed strain ($\varepsilon_o = r_f/R_o$), where ε_o represents the maximum strain at the outer edge of the coiled fibers and r_f is the fiber radius. The BSR parameter "m" quantifies the stress relaxation that occurs during treatment and is determined from:

$$m = 1 - R_o/R_a \qquad (1)$$

where R_a is the arc radius of the relaxed fiber measured after treatment. In BSR tests, values of m range from 1 to 0 with m = 1 or 0 indicating the occurrence of no relaxation or complete relaxation by creep, respectively. Intermediate values of m indicate partial relaxation. To separate thermal from irradiation creep effects, the irradiation dependent strain increment $\Delta\varepsilon$ can be defined as

$$\Delta\varepsilon = \varepsilon_o\{1/m(\phi,T,t,\varepsilon_o) - 1/m(T,t,\varepsilon_o)\} \quad (2)$$

The term in brackets is the difference in reciprocal m-values for the irradiation and the thermal control BSR tests, respectively. Results for the 1 hr thermal control BSR tests were given in Ref. [2]; the results for the 100 hr control tests are given in this report.

A good approximation for the tensile creep strain (ε_c) that would result from a constant stress creep test for equivalent BSR test temperatures and times can be estimated from measured m-values via [2]:

$$\varepsilon_c/\varepsilon_o \approx m^{-1} - 1 \quad (3)$$

In particular, ε_c predicted by Eq. (3) has been shown to approximately give the same time and temperature dependence as conventional tensile creep data [5].

Primary creep in fibers can be modelled by the semi-empirical creep equation [6]:

$$\varepsilon_c = A_o\sigma^n[t\,exp(-Q/RT)]^p \quad (4)$$

In this expression A_o, n and p are empirically determined creep parameters, σ is stress in GPa, t is time in hours, Q is the controlling creep energy in kJ/mol, R is the gas constant (8.31 J/mol-K) and T is temperature in Kelvin. Using Eqs. (3) and (4), for Nicalon fiber DiCarlo obtained close agreement between converted BSR m-data and actual tensile creep data. From DiCarlo's analysis the creep parameters for Nicalon fiber were: $A_o = 2.2 \times 10^5$, n = 1.2, p = 0.40, and Q = 500 ± 65 kJ/mol.

The effective creep energy Q can be estimated directly from m-data by the cross-cut method using the expression $Q = 2.3R/\Delta(1/T)$ where $\Delta(1/T)$ is the spacing between one order of magnitude change in time at a constant m-value [3]. The numerical factor 2.3 must be replaced by 4.6 for two orders of magnitude time change. Alternately, Eq. (3) can be employed to convert measured m-data to normalized creep strains which are then used with Eq. (4) to calculate the best-fit empirical parameters and the Q-values by linear regression. The latter approach is fairly accurate for the condition 0.9 > m > 0.1. Once the Q-value is obtained, normalized thermal creep strains (or m-values) can be estimated for any stress, time and temperature assuming that Eq. (4) continues to describe the creep process.

Results and Discussion

In Figure 1, the 100 hr BSR m-values for the SiC fibers listed in Table 1 (except for Nic S*) are plotted as a function of reciprocal temperature.

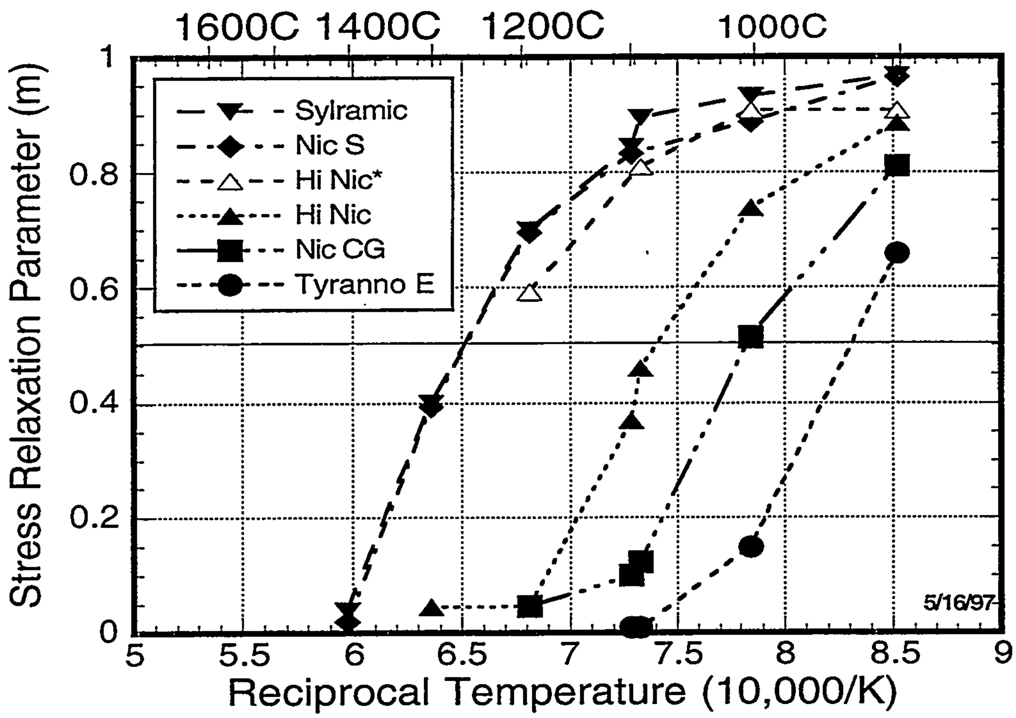

Fig. 1. Comparison of 100 hour BSR thermal creep results for advanced SiC and Nicalon CG fibers (ε_o = 0.1 to 0.3%).

In order of decreasing 100 hr transition temperatures (in parenthesis) or thermal creep resistance, the fibers ranked: Sylramic (1261°C), Nicalon S (1256°C), annealed Hi Nicalon (1215°C), Hi Nicalon (1078°C), Nicalon CG (1003°C) and Tyranno E (932°C). By comparison with the 1 hr BSR thermal creep results given in Ref. [2], the S-shaped curves have shifted right for the Nicalon S, Sylramic, Hi Nicalon and Nicalon CG fibers. The controlling creep "activation" energies were calculated for these four fiber types by the temperature shift cross-cut method and by linear regression using Eqs. (3) and (4). The results are given in Table 2.

Table 2. Thermal creep energy and projected m-values for 5000 hr , 800 or 1000°C tests.

Fiber Type	Q* (kJ/mol)	Q^ (kJ/mol)	m(800°C)#	m(1000°C)#
Nicalon CG	607	500 ± 65	0.88	0.18
Hi Nicalon	503	505 ± 40	0.95	0.37
Nicalon S	517	530 ± 60	0.99	0.65
Sylramic	622	650 ± 40	0.99	0.74

*Estimated using the temperature shift cross-cut method.
^Estimated using linear regression and Eqs. (3) and (4).
#Based on projections from the 100 hr m-values and using Eqs. (3) and (4).

Fair agreement was obtained using either the temperature shift cross-cut method or using Eqs. (3) and (4) to estimate the controlling thermal creep energy. The thermal creep energies for these polymer-derived SiC fibers lie in the 500-650 kJ/mol range. Creep energies in this range appear to correspond to the activation energies for carbon and silicon diffusion in SiC grain boundaries which have been reported as 563 and 550-611 kJ/mol, respectively [4]. For comparison, activation energies for C or Si lattice diffusion in ß-SiC are 840 and 912 kJ/mol, respectively. By inference then, thermal creep in the polymer-derived SiC fibers probably is controlled by a grain boundary mechanism, presumably grain boundary sliding.

To be able to discern any enhancement of creep by irradiation, it is desirable for the thermal creep contribution to be relatively small, i.e., $m(T,t,\varepsilon_o) \geq 0.8$ in Eq. (2). Using Eqs. (3) and (4), example thermal 5000 hr m-values were projected from the 100 hr m-values. The 5000 hr time period is typical of an irradiation cycle, and the 800 and 1000°C temperatures are fusion relevant. The thermal BSR m-value projections for these conditions also are given in Table 2.

For a BSR fiber creep test at 1000°C during a 5000 hr irradiation cycle, thermal creep would probably dominate any irradiation enhanced creep and make it unobservable except possibly for the Nicalon S and Sylramic fibers. However, for an irradiation temperature of 800°C the m-value projections for all the fibers are > 0.8. Therefore, a temperature of 800°C or lower is recommended for a 5000 hr (208 EFPD) fiber BSR irradiation creep test.

CONCLUSIONS

1. The thermal creep behavior for five advanced SiC fiber types and Nicalon CG was examined by using a 100 hr BSR fiber creep test. In order of decreasing creep resistance, the fibers ranked as follows: Sylramic, Nicalon S, annealed Hi Nicalon, Hi Nicalon, Nicalon CG and Tyranno E.

2. A methodology for predicting the thermal creep contribution during a BSR test of irradiated fibers was developed. To be able to separate thermal from irradiation creep, a temperature of 800°C or lower is recommended for a typical 5000 hr irradiation test cycle.

FUTURE WORK

Due to a scheduling conflict in the ATR reactor, the startup of the first BSR test on irradiated fibers has been delayed from January to August, 1997. This test will be carried out at 260°C to a 5 dpa dose. Expected completion of the irradiation cycle is May, 1998. A second test at 800°C is planned for the HFIR reactor as part of the Jupiter P3-4 experiment tentatively scheduled to commence mid-1998.

REFERENCES

1. G. E. Youngblood, M. L. Hamilton and R. H. Jones, "Technique for Measuring Irradiation Creep in Polycrystalline SiC Fibers," p. 146 in Fusion Materials Semiannual Progress Report for Period Ending June 30, 1996. DOE/ER--0313/20.

2. G. E. Youngblood, R. H. Jones, G. N. Morscher and Akira Kohyama, "Creep Behavior for Advanced Polycrystalline SiC fibers," p. 89 in Fusion Materials Semiannual Progress Report for Period Ending December 31, 1996. DOE/ER--0313/21.

3. Gregory N. Morscher and James A. DiCarlo, "A Simple Test for Thermomechanical Evaluation of Ceramic Fibers," J. Amer. Ceram. Soc.,75(1),136-40 (1992).

4. G. N. Morscher, J. A. DiCarlo, X. J. Ning and P. Pirouz, "Effect of Heat Treatment on the Stress Relaxation and Microstructure of CVD SiC Fibers," Advances in Ceramic-Matrix Composites, 679-90 (1995).

5. Gregory N. Morscher, Hee Man Yun and Jon C. Goldsby, "Viscoelastic Analysis of Bend Stress Relaxation and Tensile Creep of a Polycrystalline α-SiC Fiber," Plastic Deformation of Ceramics III (1995).

6. James A. DiCarlo, "Creep Limitations of Current Polycrystalline Ceramic Fibers," Composites Science and Technology 51, 213-222 (1994).

7. Hiroshi Ichikawa, Kiyohito Okamura and Tadao Seguchi, "Oxygen-Free Ceramic Fibers from Organosilicon Precursors and E-Beam Curing," p. 65 in High-Temperature Ceramic-Matrix Composites II, edited by A. G. Evans and R. Naslain, Ceramic Transactions, 58 (1995).