

THERMOCHEMICAL INSTABILITY EFFECTS IN SiC-BASED FIBERS AND SiC_f/SiC COMPOSITES -- G. E. Youngblood, C. H. Henager and R. H. Jones (Pacific Northwest National Laboratory)*

OBJECTIVE

The objective of this work is to assess the development and the performance of continuous fiber SiC_f/SiC composites as structural material for advanced fusion energy systems.

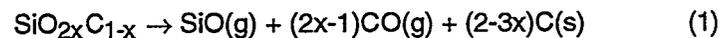
SUMMARY

Thermochemical instability in irradiated SiC-based fibers with an amorphous silicon oxycarbide phase leads to shrinkage and mass loss. SiC_f/SiC composites made with these fibers also exhibit mass loss as well as severe mechanical property degradation when irradiated at 800°C, a temperature much below the generally accepted 1100°C threshold for thermochemical degradation alone. The mass loss is due to an internal oxidation mechanism within these fibers which likely degrades the carbon interphase as well as the fibers in SiC_f/SiC composites even in so-called "inert" gas environments. Furthermore, the mechanism must be accelerated by the irradiation environment.

PROGRESS AND STATUS

Introduction

The thermochemical stability of continuous SiC fiber-reinforced/SiC matrix composites (SiC_f/SiC) can be compromised at high temperatures even in "inert" environments such as argon or helium. Usually composite degradation is related to the instability of the fibers, which for Nicalon™ CG fiber occurs when temperatures exceed about 1100°C and is primarily connected to the instability of the silicon oxycarbide phase (SiO_{2x}C_{1-x}) in this fiber [1]. According to Labrugere, et al, the mass of Nicalon CG fiber will decrease as the oxygen and free carbon in the bulk fiber decrease following primary and secondary processes [2]:



where CO is the main gaseous species formed during the fiber decomposition. Fiber shrinkage, SiC grain growth and tensile strength loss generally accompany such mass loss in Nicalon CG fiber. In a SiC_f/SiC composite, the carbon present in the left-hand side of Eq. (2) could also include carbon used as fiber coating [2]. Since the mechanical behavior of the composite is so dependent on the interphase performance, potential reactions at the fiber-carbon interface due to this secondary process will profoundly contribute to the degradation of the composite properties. Notably, this degradation mechanism does not depend directly upon the surrounding oxygen partial

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pressure, but depends on the local activities established by the constituents, usually the fiber and the fiber coating compositions, and perhaps upon structural diffusion restrictions.

Development efforts devoted to improving fiber stability and composite performance have met with considerable success with the recent commercial introduction of the low oxygen Hi Nicalon™ fiber. Likewise, the developmental fibers, S type Hi Nicalon™ and Sylramic™, have compositions very near stoichiometric SiC and should be considerably more stable than Nicalon CG. Nevertheless, for fusion or other applications involving an irradiation environment, experiments that test composite or fiber stability must be carefully planned and carried out because an irradiation environment will surely accelerate degradation mechanisms. Even though the operation temperature may be considered low enough to ensure thermal stability, proper consideration must be given to the effects of longer exposure times, enhanced kinetics, and the actual gaseous environment encountered in an irradiation experiment (or in service).

As an example, consider a typical irradiation subcapsule loaded with SiC_f/SiC bend bars made with Nicalon CG fiber. The fiber has the following composition in weight percent: Si (56.5), C (31.2), O (12.3) and a C/Si atomic ratio of 1.3. The samples usually will take up about 70% of the subcapsule volume, while the remaining space is back-filled with helium gas (at one atm.). Assuming that the bars contain 40 volume percent fiber, oxygen represents about 4.8% of the mass loading. Free carbon, carbon not associated with the SiC phase balance, also represents about 4.8% of the mass loading, while a 0.15 μm thick pyrocarbon fiber coating would contribute another 1.4%. If all of the oxygen were consumed via the internal oxidation process described by Eqs. (1) and (2), CO(g) would be generated and the composite mass loss would be about 8.4% due to mass loss in the fibers and of the carbon interphase. In a closed system, such as in an irradiation subcapsule, the CO gas pressure buildup would retard completion of the reactions and the mass loss would be less than the 8.4% for complete oxygen loss [3]. Nevertheless, fiber and probably coating mass loss could occur with attendant degradation of fiber and composite properties when the fibers (or matrix) contain unstable oxycarbide phases.

In this report, results from two experiments will be explained by using this internal oxidation mechanism. In the first experiment, the irradiation temperature was 800°C, a low enough temperature where SiC_f/SiC composite mass loss was thought not to be a consideration. In a second experiment, an unusual fiber shrinkage behavior will be explained according to the mass loss mechanism. Since the composites in the first experiment were fabricated using the same fibers examined in the second experiment, the fiber shrinkage results and the composite property degradation are correlated through the mass loss mechanism.

Experimental

For the first experiment, composite SiC_f/SiC was obtained from three sources: Dupont, General Atomics (GA) and Ubekosansha (Ube, Japan). The material was cut into bend bars whose descriptions are given in Table 1. The Dupont material, so-called reference CVI SiC_f/SiC made with 0.15 μm pyrocarbon (PyC) coated Nicalon CG fiber, was described in detail in the previous Semiannual Report [4]. The composite made by GA was similar to the Dupont material, except that the PyC coating on the Nicalon CG fiber

was slightly thicker (0.2 μm). The Ube composite was made with Tyranno fiber, but the coating was unspecified. Both the Dupont and GA bend bars were cut orthogonal to the 2D-0/90° plain weave, while the Ube bend bars were a 2D-0/90° or -45/45° pattern.

Table 1. Composite SiC_f/SiC irradiated in COBRA 1A2

Source	Fiber	Coating (μm)	Weave (°)	L x W x H (mm)	Density (g/cc)	Number
Dupont	Nic CG	0.15 PyC	0/90	38x6.3x3.5	2.50	6
GA	Nic CG	0.2 PyC	0/90	38x6.1x3.0	2.60	7
GA	Nic CG	0.2 PyC	0/90	38x3.3x1.7	2.45	8
Ube	Tyranno	?	0/90	25x3.8x1.9	2.50	6
Ube	Tyranno	?	45/45	25x3.8x1.9	2.50	6

Half of the samples were inserted into a TZM subcapsule (D05) and irradiated in the EBR II reactor Runs 162-170 for 337 EFPD as part of the COBRA 1A2 test series. The other half were preserved for comparative purposes. Subcapsule D05 received a fast fluence of 6.58×10^{26} n/m² ($E > 0.1$ MeV), equivalent to a calculated dose of about 80 dpa-SiC [5]. The gas-gapped, but uninstrumented subcapsule was designed to operate at 800°C; however two passive SiC temperature monitors in subcapsule D05 indicated that the end of cycle (EOC) temperature actually was $550 \pm 50^\circ\text{C}$. Similar bars inserted into subcapsules F06 and G03 during the same test indicated EOC irradiation temperatures within 25°C of their design temperatures, 500 and 615°C, respectively. It is assumed that the beginning of cycle (BOC) irradiation temperature was 800°C, as designed. Because of possible gas-gap changes during the long-term reactor operation, it also is assumed that the EOC temperature truly was $550 \pm 50^\circ\text{C}$.

The samples were weighed and dimensioned before and after irradiation. Four-point flexure stress-strain curves were acquired for both the unirradiated and irradiated samples. The flexure tests were carried out at the BOC irradiation temperature of 800°C by a procedure described previously [6]. SiC fixtures with outer/inner spans of 30/15 or 20/10 mm were used with the 38 and 25 mm length bars, respectively. Fracture surfaces were examined by SEM for representative samples.

For the second experiment, Nicalon CG and Tyranno fibers also were irradiated in the EBR II reactor, but at 1000°C for 165 EFPD [7]. The effective dose was 43 dpa-SiC. The fiber properties are given in Table 2. The Tyranno fiber contains even more oxygen and free carbon in an amorphous oxycarbide phase than does the Nicalon CG fiber.

Table 2. Properties of SiC-based fibers selected for mass loss analysis.

Fiber Type	Composition (w/o)	Density (g/cc)	Strength (GPa)	Modulus (GPa)	Microstructure
Nicalon CG	Si-31C-12O	2.55	2.6	190	2 nm β -SiC grains, free C in amorphous Si-O-C matrix
Tyranno	Si-28C-17O-3Ti	2.37	2.5	190	2 nm β -SiC grains, free C in amorphous Si-O-C-Ti matrix

In the experiment, bare and coated fiber bundles (63 or 32 mm lengths, respectively) were irradiated and fiber bundle length and density changes were determined.

Results

Composite average 4-pt. bend strengths (BStren), strains at maximum strength (BStrain), initial modulus (IMod) values, proportional limits (PropLim), and relative mass losses after irradiation are given in Table 3. For comparison, the unirradiated values are listed above the irradiated values for each composite type with the standard deviations given in parenthesis. Representative flexure stress-strain curves are given in Figure 1 for the unirradiated and irradiated composites. Representative SEM fracture surfaces are depicted for unirradiated and irradiated SiC_f/SiC composite in Figure 2.

Table 3. Composite mechanical properties before and after irradiation.*

Bar Type/ Fiber Type	BStren (MPa)	BStrain (%)	IMod (GPa)	PropLim (MPa)	Mass Loss (%)
Dupont/ Nic CG	369 (29) 207 (29)	0.43 (0.06) 0.38 (0.08)	102 (17) 111 (42)	210 (30) 117 (20)	0.15 (0.02)
GA-3.0/ Nic CG	329 (30) 129 (46)	0.94 (0.13) 0.57 (0.17)	146 (18) 130 (30)	120 (10) 67 (17)	0.37 (0.06)
GA-1.7/ Nic CG	374 (42) 88 (6)	0.76 (0.08) 0.10 (0.03)	150 (35) 140 (12)	163 (21) 82 (2)	0.74 (0.26)
Ube-0/90 Tyranno	120 (30) 148 (30)	0.13 (0.05) 0.12 (0.02)	97 (5) 117 (7)	120 (30) 148 (brittle)	0.75
Ube-45/45 Tyranno	215 (55)	0.31 (0.05)	102 (5)	150 (30) too brittle	0.63

* Calculated from flexure tests at 800°C in argon.

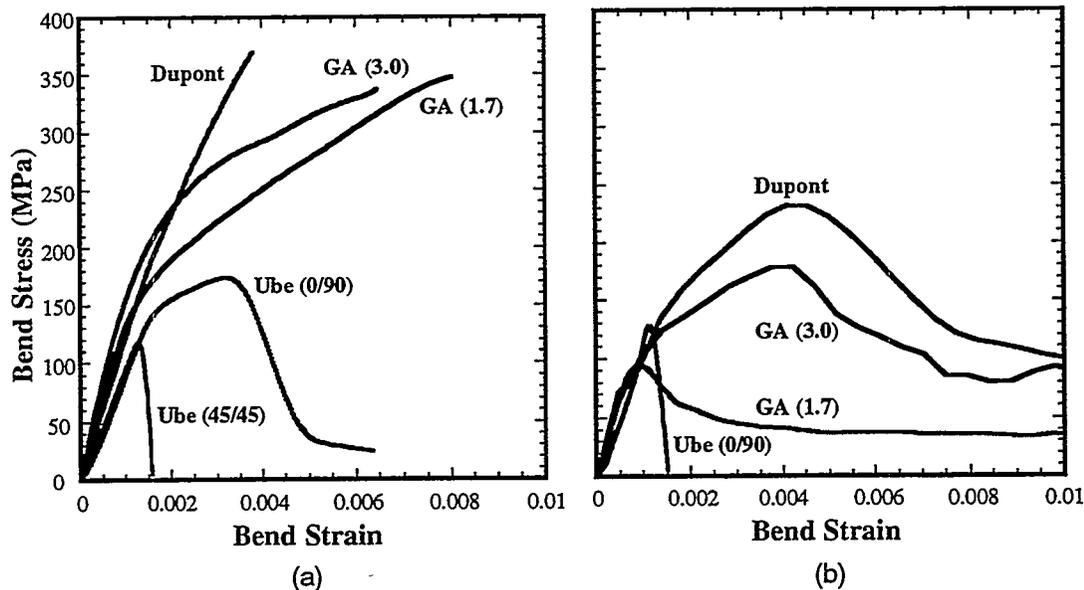


Figure 1. Representative 4-pt. bend stress-strain curves for (a) unirradiated and (b) irradiated SiC_f/SiC composites. The flexure tests were performed at 800°C in argon.

The bend strengths, strains and proportional limits (an indicator of the matrix cracking strengths) decreased roughly 50% or more after the irradiation for the Dupont and GA

composites made with Nicalon CG fiber. The mechanical property degradation was greater for the GA composites compared to the Dupont composite, and for the thin (1.7 mm) GA bars compared to the thick (3.0 mm) GA bars. A similar trend is observed when the composite mass losses are compared, i.e., the mass loss for the GA composites were larger than for the Dupont composite, and the thin GA bars exhibited a

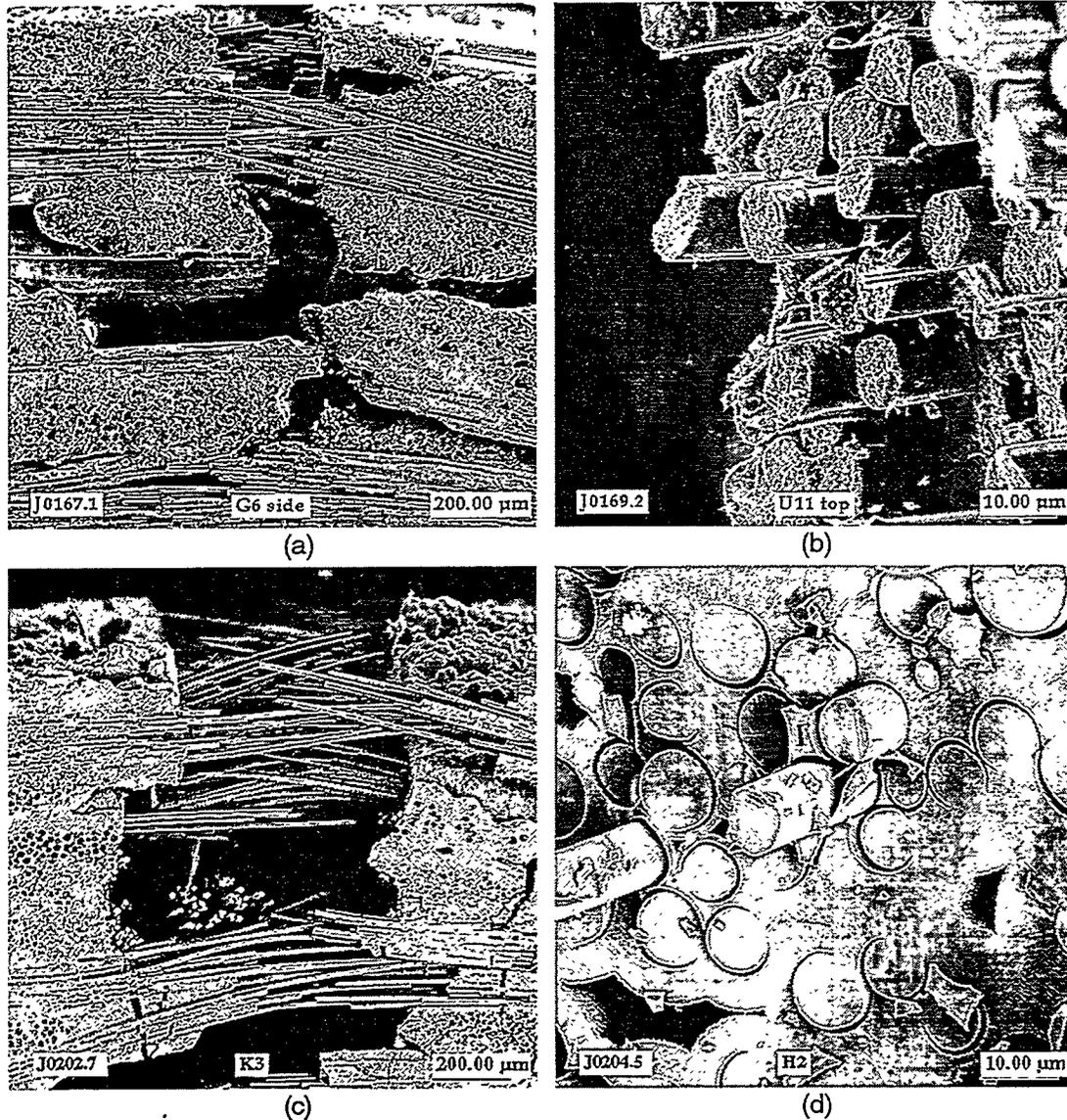


Figure 2. Representative SEM fracture surfaces near the tensile surface for unirradiated (a) GA/Nic CG and (b) Ube/Tyranno composites and for irradiated (c) Dupont/Nic CG and (d) GA/Nic CG composites. Fig. 2(a) illustrates desirable random fiber pull-out for the GA/Nic CG material, while Fig. 2(b) illustrates limited fiber bundle pull-out characteristic of brittle fracture for the Ube/Tyranno material. Fig. 2(c) illustrates more extensive fiber pull-out for the irradiated Dupont/Nic CG material, while Fig. 2(d) illustrates a brittle fracture surface for the irradiated GA/Nic CG material with limited fiber pull-out and large gaps around the individual fibers.

larger mass loss than the thick GA bars. For example, the thin irradiated GA bars, with an average mass loss of 0.74%, exhibited a severely degraded stress-strain curve (see Fig. 1b). The curves for all of the irradiated composites indicate greatly reduced toughness. The mechanical properties for the unirradiated Ube composites were characteristic of brittle fracture, however, the irradiated Ube composites also exhibited significant mass loss.

In Table 4, the measured irradiation-induced relative density ($\Delta\rho/\rho_0$) and length ($\Delta L/L_0$) changes reported for coated and uncoated Nicalon CG and Tyranno fibers are presented along with relative mass loss ($\Delta m/m_0$) predictions. The ratios of the carbon coating mass to the fiber mass (m_c/m_f) also are listed for each fiber. This ratio was estimated using the expression $m_c/m_f = 4t\rho_c/\rho_f D_f$ where t , ρ_c , ρ_f and D_f are the carbon coating thickness and density and the fiber density and mean diameter, respectively.

Table 4. Irradiated fiber mass loss predicted from measured length and density changes.

Fiber	PyC Coat (μm)	$\Delta\rho/\rho_0$ (%) [*]	$\Delta L/L_0$ (%) [*]	$\Delta m/m_0$ (%) [^]	m_c/m_f (%)
Nic CG1	bare	+8.5 (0.4)	-2.9 (0.5)	-0.2	0
Nic CG2	bare	+10.3 (1.3)	-3.8 (0.4)	-1.1	0
Nic CG1	0.15	+10.1 (0.4)	-7.1 (0.8)	-11	3.2
Nic CG2	0.15	+9.4 (0.5)	-7.1 (0.5)	-12	3.2
Nic CG2	0.15 (BN)	+12.4 (0.4)	-3.0 (2.4)	+3	0
Tyranno	bare	+12.7 (0.7)	-5.6 (1.3)	-4	0
Tyranno	0.15	+12.9 (0.5)	-16.6 (0.5)	-37	3.4

* Measured values from Ref. [7], standard deviations given in parenthesis.

^ Calculated using Eq. (3)

The irradiated Nicalon CG and Tyranno fibers both exhibited significant instability with density increases near 9 and 13% and linear shrinkage from 3-7% and 6-17%, respectively. The irradiated fibers that were coated with 0.15 μm PyC shrunk significantly more than the uncoated fibers. The same trend was noted for uncoated and coated HPZ type fibers which also have a high oxygen content. In contrast, Hi Nicalon fiber with a low 0.5% oxygen content exhibited only a 0.7% density increase (data reported in Ref. [7]).

DISCUSSION

It is proposed that the thermochemical instability of the oxycarbide phase in Nicalon CG and Tyranno fibers, which apparently is enhanced by irradiation even at 800°C or below, leads to mass loss and mechanical property degradation in the composites made with these fibers.

For fibers, a good approximation for $\Delta m/m_0$ is given in terms of $\Delta\rho/\rho_0$ and $\Delta L/L_0$ by:

$$\Delta m/m_0 = 3(\Delta L/L_0) + \Delta\rho/\rho_0 \quad (3)$$

In deriving Eq. (3), differentials of the mass density ($\rho = 4m/\pi D^2 L$) were taken and isotropic shrinkage ($\Delta D/D = \Delta L/L_0$) was assumed.

Equation (3) was used to predict the $\Delta m/m_0$ values from the measured density and length change measurements in Table 4. The $\Delta L/L_0$ measurements sometimes have rather large uncertainties due to the difficulty in demarcating the ends of a fiber bundle. Nevertheless, the predictions listed in Table 4 consistently indicate mass losses for all cases except for the BN-coated Nicalon fiber. The predicted mass losses for the uncoated and coated Nicalon CG fibers average about -0.6% and -12%, respectively. The predicted mass losses for the uncoated and coated Tyranno fibers are much larger, -4% and -37%, respectively. Apparently, the carbon coating enhances the mass loss mechanism in these two irradiated fibers.

By inspection, the relative mass loss is a factor of 4 to 10 larger than the m_c/m_f ratio for the coated Nicalon CG or Tyranno fibers, respectively. For the Nicalon fibers with 0.15 μm thick PyC coating, the ratio of the bulk free carbon mass to the carbon coating mass also is about four. This implies that nearly all of the free carbon in the Nicalon fiber as well as the fiber coating was oxidized and lost as $\text{CO}(\text{g})$ via the internal oxidation mechanism. Likewise, for the Tyranno fiber with a factor of 10 larger all the bulk free carbon and the carbon coating must have been oxidized.

Since the irradiation temperature was 1000°C in the fiber experiment, a larger fiber mass loss and more severe degradation would be expected than if the temperature were 800°C, the BOC irradiation temperature of the SiC_f/SiC composites containing these same fibers. The irradiated SiC_f/SiC composite mechanical property degradation follows the behavior expected for composite made with fiber exhibiting thermochemical instability, except that the degradation occurs even at 800°C or lower due to the irradiation. For the irradiated Dupont and GA composites, the larger mass loss correlates with more severe degradation. The flexural strengths for the irradiated GA composites were lower than for the irradiated Dupont composites. Apparently, the fiber mass loss mechanism is retarded somewhat by the composite structure as the thinner GA samples lost significantly more mass than the thicker GA samples. All the observed composite mass losses were lower than 0.75%, much below the 8.4% limit which is possible only if all the oxygen were to react. The diminished composite mass losses probably occurred as a result of temperatures lower than 1000°C, buildup of a retarding CO partial pressure in the subcapsule and the CVI matrix structure acting as a gas diffusion barrier. Nevertheless, the mechanical property degradation exhibited by these two types of SiC_f/SiC composites was severe and would be unacceptable for fusion structural components.

CONCLUSIONS

1. SiC_f/SiC composite made with SiC-based fibers that contain an amorphous silicon oxycarbide phase may exhibit mass loss due to an internal oxidation mechanism.
2. The mass loss is correlated to fiber and interphase degradation, and perhaps to severe composite mechanical property degradation.
3. The internal oxidation mass loss mechanism can occur at temperatures of 800°C or lower in an irradiation environment, much below the 1100°C thermal stability threshold generally accepted for these materials.

4. The internal oxidation mechanism can be retarded in a closed system due to buildup of CO gas. However in an open or large gas volume system, the reactions could proceed unrestricted and the mass loss and mechanical property degradation probably would be worse than observed in a closed system.

FUTURE WORK

Future work will emphasize testing composites made with low oxygen content fibers to avoid the internal oxidation mass loss mechanism. Careful attention will be given to assessing mass loss behavior in fibers or in composites in future irradiation experiments.

REFERENCES

1. P. Greil, "Thermodynamic Calculations of Si-C-O Fiber Stability in Ceramic Matrix Composites," *J. of the European Ceram. Soc.*, 6, 53-64 (1990).
2. C. Labrugere, A. Guette and R. Naslain, "Effect of Ageing Treatments at High Temperatures on the Microstructure and Mechanical Behavior of 2D Nicalon/C/SiC Composites. 1: Ageing under Vacuum or Argon," *J. of the European Ceramic Soc.*, 17, 623-640 (1997).
3. M. H. Jaskowiak and J. A. DiCarlo, "Pressure Effects on the Thermal Stability of Silicon Carbide Fibers," *J. Am. Ceram. Soc.*, 72 (2), 192-97 (1989).
4. G. E. Youngblood, C. H. Henager, Jr., and R. H. Jones, "Effects of Neutron Irradiation on the Strength of Continuous Fiber Reinforced SiC/SiC Composites," p. 117 in *Fusion Materials Semiannual Progress Report*, DOE/ER-0313/21, 1996.
5. L. R. Greenwood and R. T. Ratner, "Neutron Dosimetry and Damage Calculations for the EBR-II COBRA-1A Irradiations." *ibid.*, p. 225.
6. G. E. Youngblood, C. H. Henager, Jr., D. J. Senior and G. W. Hollenberg, "Effects of Neutron Irradiation on Dimensional Stability and on Mechanical Properties of SiC/SiC Composites," p. 321 in *Fusion Materials Semiannual Progress Report*, DOE/ER-0313/17.
7. D. J. Senior, G. E. Youngblood, J. L. Brimhall, D. J. Trimble, G. A. Newsome and J. J. Woods, "Dimensional Stability and Strength of Neutron-Irradiated SiC-Based Fibers," *Fusion Technol.*, 30 (3), 956-68 (1996).