# EFFECTS OF NEUTRON IRRADIATION ON THE STRENGTH OF CONTINUOUS FIBER REINFORCED SiC/SiC COMPOSITES

-- G. E. Youngblood, C. H. Henager, Jr., and R. H. Jones (Pacific Northwest National Laboratory)*

## OBJECTIVE

The objective of this work is to assess the development of continuous, fiber-reinforced $SiC_f$/SiC composites for structural applications in advanced fusion energy systems.

## SUMMARY

Flexural strength data as a function of irradiation temperature and dose for a $SiC_f$/SiC composite made with Nicalon-CG fiber suggest three major degradation mechanisms. Based on an analysis of tensile strength and microstructural data for irradiated Nicalon-CG and Hi-Nicalon fibers, it is anticipated that these degradation mechanisms will be alleviated in Hi-Nicalon reinforced composites.

## PROGRESS AND STATUS

### Introduction

This paper updates previously reported results [1, 2] on the mechanical properties of irradiated, continuous fiber-reinforced silicon carbide composite ($SiC_f$/SiC). In this composite, hereafter referred to as reference $SiC_f$/SiC, the Nicalon$^{TM}$-CG fibers were coated with a 150 nm thick pyrolytic carbon interphase prior to a chemical vapor infiltration (CVI) deposition of the matrix. Bend bar samples made from reference $SiC_f$/SiC were irradiated in four different experiments in either the FFTF or the EBR-II fast reactors at temperature and dose ranges covering 430°C to 1200°C and 4 to 80 dpa-SiC, respectively. Only after the accumulation of a considerable amount of mechanical property data obtained by using a consistent set of test procedures on this single type of irradiated material is it now possible to analyze in detail this material's irradiation performance and its degradation mechanisms.

A substantial degradation in mechanical and thermal properties at radiation damage levels as low as 1 dpa-SiC was reported for a type of $SiC_f$/SiC similar to reference $SiC_f$/SiC [3, 4]. However, irradiation experiments to higher doses have shown that the degradation tends to saturate at a relatively low dose and further degradation remains relatively small [2]. The degradation of reference $SiC_f$/SiC was shown to be primarily connected to the poor irradiation performance of the Nicalon-CG type fibers, although additional microcracking in the matrix also was observed. In separate studies of irradiated fiber bundles, it was shown that Nicalon-CG fibers shrink and densify [5] while their strengths decrease during irradiation [6]. As a result, the ultimate bend strength of irradiated reference $SiC_f$/SiC probably is degraded by both fiber strength loss and decoupling from the matrix. A modest reduction in the matrix cracking stress (defined here as the maximum stress where stress remains proportional to strain) and an overall reduction of the modulus, both of which depend upon the irradiation temperature and dose, also were observed. Notably, catastrophic brittle failure never was observed in the tested reference $SiC_f$/SiC bend bars. In spite of the fiber/matrix debonding and loss of fiber strength, the irradiated bend bars still exhibited a strength greater than the matrix cracking stress and a large strain-to-failure. Nevertheless, these high dose studies concur with several low dose studies that to achieve acceptable radiation performance in a $SiC_f$/SiC composite, a fiber more radiation tolerant than Nicalon-CG must be used.

---

* Pacific Northwest National Laboratory (PNNL) is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO-1830.

In a study comparing the irradiation performance of several types of SiC-based fibers, the Hi-Nicalon$^{TM}$ fiber was shown to exhibit a minimum density increase (+0.7 ± 0.4%) and a 40% increase in tensile strength after irradiation at 1000°C to a dose of 43 dpa-SiC [6]. Osborne, et al. [7, 8] noted similar trends for low temperature (100°C), low dose (<1 dpa-SiC) irradiations. Apparently, the Hi-Nicalon fiber behaves much differently than the Nicalon-CG fiber during low and high temperature irradiations. In either case, it exhibits a marked improvement in irradiation stability over that of Nicalon-CG fiber.

It is the goal of this report to combine and analyze all of the irradiation behavior data obtained at PNNL for the reference $SiC_f$/SiC. From this analysis, reasons why a composite reinforced with Hi-Nicalon fiber should exhibit enhanced mechanical properties as well as improved irradiation performance over that of the reference composite are given.

## Materials

Several plates of reference $SiC_f$/SiC composite were fabricated by Dupont using the isothermal CVI process and Nicalon-CG fabric with a 2D 0-90° plain weave pattern. The plates nominally contained 40 volume percent fiber which were laid up as eight fabric plys through the plate thickness. During the CVI process, the deposition layers grow outward from the individual fibers until they intersect and eventually seal off the gas flow, thus ending the process. A radial, columnar polycrystalline microstructure, essentially 100% ß-SiC, is formed; however the grains are expected to contain a high concentration of stacking faults [9]. Because of the fabric weave and the matrix growth patterns, a bimodal distribution of residual macroporosity develops. It consists of linear pores which lie within and parallel to the fiber yarns with dimensions similar to that of a single fiber and laminar-shaped pores which lie between the fabric plies with dimensions similar to the fabric unit cell (≈ 1 $mm^2$). The latter pores are responsible for the somewhat weaker shear strength for a 2D weave composite. The smaller linear pores within the fiber bundles are primarily responsible for the permeable nature of these composites. The total macroporosity typically represents 10-15% of the structure volume. In Reference 2 (Fig. 4), a complete set of optical micrographs which depict the micro- and macro-structures for both unirradiated and irradiated reference $SiC_f$/SiC are presented.

For comparison, a similar composite plate with Hi-Nicalon replacing the Nicalon-CG fabric also was obtained from Dupont. Another difference with this advanced material was a thicker graphite interface layer (≈ 1000 nm) was applied to the fibers. The plates were cut into a large number of rectangular flexure bars measuring 3.2 x 6.4 x 38 $mm^3$. All bars were cut normal to the weave pattern so that about 20% of the fiber yarns were parallel to the lengths of the flexure bars.

Both the Nicalon-CG and Hi-Nicalon fibers, produced as textile-grade yarns by Nippon Carbon Co. of Japan, are polymer-derived. Nicalon-CG is a Si-C-O fiber (12 ± 2 wt% O, C:Si = 1.3) whose microstructure consists of small, nanocrystalline (≈ 2 nm) ß-SiC grains within a somewhat amorphous Si-C-O matrix. Due to a different curing step in its manufacture, Hi-Nicalon has a significantly lower oxygen content (<0.5 wt% O) than Nicalon-CG and a somewhat higher carbon to silicon ratio (C:Si = 1.4). The Hi-Nicalon fiber microstructure consists of nanocrystalline (5-10 nm) ß-SiC grains separated by thin (1-2 nm) turbostratic graphite layers [10]. Each of the yarns contains 500 individual fibers and have an elliptical cross-section with about a 1.2 mm width and a 6/1 aspect ratio. Other relevant properties for both unirradiated and irradiated Nicalon-CG and Hi-Nicalon fibers are presented in Table 1 and will be discussed later.

## Irradiation and Test Conditions

The composites and fibers were irradiated in either the FFTF or the EBR-II reactors under conditions described previously [2]. Bend bar specimens were irradiated at 430, 500, 800, 1000 and 1200°C to doses of from 4 to 80 dpa-SiC. Four-point flexure stress-strain curves were used to determine the ultimate bend strengths, the matrix cracking stresses and the bend modulus of the reference $SiC_f$/SiC material for the given irradiation conditions. To simulate material properties expected under actual operating conditions in a fusion environment, these curves were acquired at the temperatures of the irradiations, again as reported previously [2]. Flexure data also have been obtained at ambient and 500°C for the unirradiated $SiC_f/SiC$ composite made with Hi-Nicalon fabric. This material will be irradiated in the HFIR reactor at 500°C to a dose of about 10 dpa-SiC. Tensile strength and modulus data, collected at ambient using a Micropul$^{TM}$ device described elsewhere [6], are given in Table 1 for both unirradiated and irradiated Nicalon-CG and Hi-Nicalon fibers.

Table 1. Nicalon-CG and Hi-Nicalon Fiber Properties.

| Property | Nicalon-CG (unirrad.) | Nicalon-CG (irrad.) | Hi-Nicalon (unirrad.) | Hi-Nicalon (irrad.) | Ref. |
|---|---|---|---|---|---|
| **Density** | 2.58 g/cc | +5.8 ± 0.2% | | not in | (a) |
| | " " | +5.3 ± 0.2% | | not in | (b) |
| | 2.54 g/cc | 14.7 ± 0.9% | | not in | (c) |
| | 2.57 g/cc | +9.5 ± 1.0% | 2.76 g/cc | +0.7 ± 0.3% | (d) |
| | " " | to be measured | 2.74 g/cc | to be measured | (e) |
| **Crystallite Size (nm)** | <2 | 5+ | 5-10 | 5-10 | (d) |
| | | not in | 3.1 | 2.8 | (e) |
| **Strength (GPa)** | 3.0 ± 1.6 | 1.9 ± 0.6 | 2.4 ± 0.8 | 3.4 ± 0.7 | (d) |
| | " " | to be measured | " " | to be measured | (f) |
| | | not in | 2.9 ± 0.8 | 3.7 | (e) |
| **Elastic Mod. (GPa)** | 160 | 180 | 210 | 260 | (d) |
| | | | 280 | 300 | (f) |

(a) FFTF at 430°C, 5.3 dpa-SiC [5]; (b) FFTF at 430°C, 26 dpa-SiC [5];
(c) EBR-II at 850°C, 25 dpa-SiC [1]; (d) EBR-II at 1000°C, 43 dpa-SiC [6];
(f) EBR-II at 800°C, 80 dpa-SiC [new data]; (e) HIFR at 100°C, 2.5 dpa-SiC [8];

## Results and Discussion

From Table 1, it is noted that the Nicalon-CG fiber density increases significantly for a broad range of radiation conditions. Also, the tensile strength of the fiber decreased from 3.0 GPa to 1.9 GPa while the elastic modulus increased slightly from 160 to 180 GPa for the unirradiated and irradiated condition of 1000°C/43 dpa-SiC, respectively. Osborne, et al. [7], presented evidence that Nicalon-CG contains an amorphous $SiO_xC_y$ phase that is unstable under irradiation. This phase converts to crystalline SiC and CO gas, which causes Nicalon-CG fiber to densify (and shrink) and to become weaker. Observations by TEM [10] showed that the Nicalon-CG crystallite size increased from about 2 nm (unirradiated) to 5 nm (irradiated at 1000°C, 43 dpa-SiC), which supports Osborne's findings.

In contrast, the Hi-Nicalon density slightly increased while little change in the crystallite size was observed for the 1000°C/43 dpa-SiC irradiation. Surprisingly, the tensile strength increased by 40% from 2.4 to 3.4 GPa while the elastic modulus increased slightly from 210 to 260 GPa for the unirradiated and irradiated conditions, respectively. Osborne, et al. [8], also observed a strength increase for Hi-Nicalon from 2.9 GPa to 3.6 GPa for quite different irradiation conditions (100°C/2.5 dpa-SiC). Apparently, the Hi-Nicalon fiber exhibits much more radiation tolerance than Nicalon-CG fiber for a broad range of irradiation conditions.

In Figure 1, the 4-pt flexure strengths of unirradiated and irradiated reference $SiC_f/SiC$ are presented in a 3D plot. The independent irradiation/test temperature and dose variables form the horizontal axes and the dependent flexure strength variable forms the elevation axis. Qualitative strength contours and constant dose

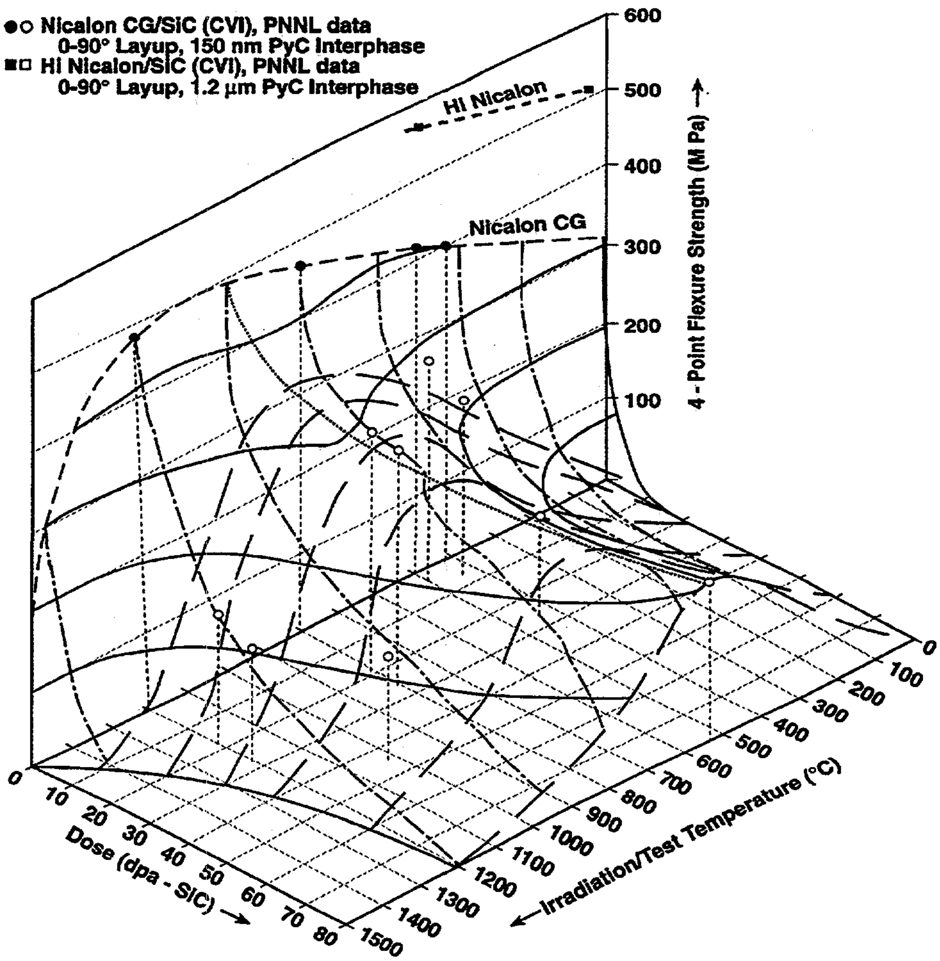


Figure 1. Proposed Strength-Irradiation Dose-Temperature Surface for Reference $SiC_f/SiC$ Composite

and temperature lines have been added to suggest a hypothetical 3D surface which represents the strength dependence on irradiation dose and temperature for the reference $SiC_f/SiC$ material.

Guided by a limited amount of data, this hypothetical surface nevertheless depicts three topological features which are characteristic of the irradiated reference $SiC_f/SiC$ strength behavior. In particular, these major features are suggested to be due to the following three different types of degradation mechanisms: (1) For the unirradiated reference $SiC_f/SiC$, the strength gradually increases with temperature from 300 MPa at ambient up to a maximum value of 510 MPa at about 1000-1200°C, then it steeply drops off with further temperature increase. This temperature dependence closely follows the bend strength-temperature curve for similar $SiC_f/SiC$ composite presented by Lamicq, et al. [11]. The strength for monolithic SiC also increases with temperature at about the same rate; but in contrast, it continues to increase up to and above 1500°C [1]. Therefore, the steep drop-off must be related to the characteristic loss in tensile strength of the Nicalon-CG fiber for temperatures exceeding about 1100°C. From the 3D plot, as the irradiation dose increases the temperature where the strength drop-off commences gradually diminishes. A dotted "optimum composite strength" ridge-line is shown starting at 500 MPa (1000°C/0 dpa-SiC) and gradually dropping but proceeding out to 210 MPa (550°C/80 dpa-SiC). This ridge-line behavior reflects a combination of the irradiation instability and the loss in strength at high temperature of the Nicalon-CG fiber. (2) For low irradiation doses, the strength drop-off initially is rather steep for all irradiation temperatures. While depending somewhat on the irradiation temperature, the rate of drop-off slows considerably for doses above about 1-2 dpa-SiC. This initial steep drop-off with dose appears to reflect the characteristic defect accumulation which saturates at doses below about 1 dpa-SiC for irradiated SiC. For instance, irradiated monolithic SiC exhibits roughly an initial 25% loss in flexural strength by 4.3 dpa-SiC, but retains its strength with further irradiation [1]. Also, the Nicalon-CG fiber itself probably continues to slowly lose strength with increasing irradiation time (proportional to dose) as it recrystallizes. The composite strength dose dependence also reflects this slower form of fiber strength degradation. (3) The difference between the SiC matrix swelling due to irradiation and the shrinkage of the irradiated Nicalon-CG fiber is greater for lower irradiation temperatures. Therefore, considerable debonding of the fiber from the matrix is expected at lower irradiation temperatures at fairly low doses. This causes the composite strength drop-off with dose to be much steeper. A strength "depression" in the 3D surface is expected at higher doses and lower temperatures. There is no data for reference $SiC_f/SiC$ irradiated to high doses at temperatures below 550°C, so the magnitude of the low temperature depression is speculative.

In a previous report [12], it was recommended that at least six flexure samples be tested for each condition to achieve reliable and reproducible ( ± 10%) average strength values for $SiC_f/SiC$ composite. Much of the data used in this analysis were taken from earlier studies where only 2-4 bar samples for each condition were used, so the strength values must be considered qualitative. Importantly, test conditions themselves were always the same, thus the temperature- and dose-dependent trends depicted by the 3D strength surface are expected to be reliable for the $SiC_f/SiC$ material.

With reference to these three degradation features and the relevant properties of unirradiated and irradiated Nicalon-CG and Hi-Nicalon fibers already presented in Table 1, the strength behavior of $SiC_f/SiC$ composite should be improved by replacing Nicalon-CG with Hi-Nicalon fiber. In fact, for unirradiated $SiC_f/SiC$ made with Hi-Nicalon fiber this is the case (See Fig. 1). Between ambient and 500°C, the strengths of the Hi-Nicalon composite increased with temperature from 505 to 560 MPa, which represents about a 40% strength increase over that of reference $SiC_f/SiC$. Based on the improved thermal creep stability of Hi-Nicalon over that of Nicalon-CG fiber [13], the related composite strength "drop-off" temperature is expected to be increased by about 120°C for the Hi-Nicalon composite. The steep strength drop-off with irradiation dose exhibited by reference $SiC_f/SiC$, primarily due to the loss of strength of the Nicalon-CG fiber (especially at higher temperatures), also should not be observed for the Hi-Nicalon composite since the Hi-Nicalon fiber actually exhibited an increase in strength with irradiation. Finally, the low temperature strength depression, caused by larger differential swelling and debonding between the composite matrix and fiber during irradiation, should not be as severe for the Hi-Nicalon composite since the Hi-Nicalon fibers shrink very little with dose. Furthermore, other properties of the more crystalline Hi-Nicalon fiber, such as elastic modulus and thermal expansion, more closely match those of the ß-SiC matrix; so load transfer between the fiber and matrix should remain more uniform over a range of temperature and load conditions. Thus, the optimum "ridge-line" should be broader, have higher strength values and be shifted to higher temperatures for all doses for the Hi-Nicalon composite.

It has been shown that each of the three degradation mechanisms responsible for the topological features depicted by the 3D strength-temperature-dose surface for reference $SiC_f/SiC$ should be alleviated by replacing the Nicalon-CG with Hi-Nicalon fiber. Other advanced fibers with more crystalline microstructures made up of pure ß-SiC, such as Nicalon-S or Sylramic$^{TM}$ fiber, should promote similar improvements in irradiated $SiC_f/SiC$ composite.

An important issue not discussed to this point is the effect of the composite interphase type and thickness. To attain the overall strength improvement in these Hi-Nicalon composites, a 1.2 μm thick carbon interphase was used. Potentially, the thicker interphase could be a problem due to the dimensional instability of graphite in an irradiation environment. This potential problem will be closely analyzed after the upcoming HFIR irradiations of this material. Other interface strategies, for instance utilizing porous SiC or multiple C/SiC/C layers in place of the graphite layer, currently are being developed by others [14].

## CONCLUSIONS

The irradiation performance of reference $SiC_f$/SiC is characterized by a 3D strength-temperature-dose surface that exhibits three types of degradation mechanisms. Each of the three proposed degradation mechanisms for irradiated reference $SiC_f$/SiC composite should be alleviated by replacing Nicalon-CG with Hi-Nicalon fiber.

## FUTURE WORK

The irradiation effects on a Hi-Nicalon $SiC_f$/SiC composite will be reported at the conclusion of the Jupiter P3-3 test cycle (February to December 1997, 500°C/10 dpa-SiC, in the HFIR reactor) in early 1998.

## REFERENCES


1. G. W. Hollenberg, C. H. Henager, Jr., G. E. Youngblood, D. J. Trimble, S. A. Simonson, G. A. Newsome and E. Lewis, "The Effect of Irradiation on the Stability and Properties of Monolithic Silicon Carbide and $SiC_f$/SiC Composites up to 25 dpa," *J. Nucl. Mater.*, 219, 70-86 (1995).

2. G. E. Youngblood, C. H. Henager, Jr., D. J. Senor 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 for Period ending September 31, 1994, DOE/ER-0313/17.

3. L. L. Snead and O. J. Schwarz, "Advanced SiC Composites for Fusion Applications," *J. Nucl. Mater.*, 219, 3-14 (1995). Also p.274 in Fusion Materials, Semiannual Progress Report for Period ending September 30, 1994, DOE/ER-0313/17.

4. L. L. Snead, D. Steiner and S. J. Zinkle, "Measurement of the Effect of Radiation Damage to Ceramic Composite Interfacial Strength," *J. Nucl. Mater.*, 191-194, 566-570 (1992).

5. G. E. Youngblood, D. J. Senor and G. W. Hollenberg, "Dimensional Stability of SiC-Type Fibers Neutron Irradiated to High Doses," p. 417 in Fusion Materials, Semiannual Progress Report for Period ending March 31, 1995, DOE/ER-0313/18.

6. D. J. Senor, 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," accepted for publication in *Fusion Technology* and based on a Poster presentation at the 12th Topical Meeting of Fusion Energy at the 1996 American Nuclear Society Annual Meeting, 16-20 June, Reno, NV.

7. M. C. Osborne, L. L. Snead and D. Steiner, "Tensile Behavior of Irradiated SiC Fibers," *J. Nucl. Mater.*, 219, 63-69 (1995).

8. M. C. Osborne, D. Steiner and L. L. Snead, "Neutron Irradiation Effects on Hi- Nicalon Silicon Carbide Fibers," p. 136 in Fusion Materials, Semiannual Progress Report for Period ending June 30, 1996, DOE/ER-0313/20.

9. G. E. Youngblood and W. Kowbel, "Improvement of the Thermal Conductivity of $SiC_f$/SiC

Composite," p.107 in Fusion Materials, Semiannual Progress Report for Period ending December 31, 1995, DOE/ER-0313/19.

10. G. E. Youngblood, R. H. Jones and A. Hasegawa, "Microstructural Effects of Neutron Irradiation on SiC-Based Fibers, p. 101, ibid.

11. Pierre J. Lamicq, Gerald A. Bernhart, M. M. Dauchier and Jean G. Mace, "SiC/SiC Composites," *Am. Ceram. Soc. Bull.*, 65 (2), 336-38 (1986).

12. G. E. Youngblood, C. H. Henager, Jr. and R. H. Jones, "Specimen Size Effect Considerations for Irradiation Studies of SiC/SiC, p. 140 in Fusion Materials, Semiannual Progress Report for Period ending June 30, 1996, DOE/ER-0313/20.

13. G. E. Youngblood and R. H. Jones, "Status of Measuring Irradiation Creep in SiC Fibers," this Report.

14. L. L. Snead, private communication.