

EFFECTS OF NEUTRON IRRADIATION ON DIMENSIONAL STABILITY AND ON MECHANICAL PROPERTIES OF SiC/SiC COMPOSITES - G. E. Youngblood, C. H. Henager, Jr., D. J. Senior, and G. W. Hollenberg (Pacific Northwest Laboratory)^a

OBJECTIVE

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

SUMMARY

The dimensional stability and some mechanical properties of two similar 2D 0-90° weave SiC_f/SiC composites made with NicalonTM ceramic-grade (CG) fiber were characterized and compared after neutron irradiation to those properties for β-SiC. The major difference between these two composites was that one had a thin (150 nm) and the other a thick (1000 nm) graphite interface layer. The irradiation conditions consisted of relatively high doses (4.3 to 26 dpa-SiC) at high temperatures (430 to 1200°C).

Up to about 900°C, swelling of the irradiated SiC_f/SiC composites (< 0.5%) was slightly less than for irradiated monolithic SiC and was relatively independent of dose. The strengths and the modulus of these SiC_f/SiC composites were reduced by about 50% by the irradiation. During irradiation, the Nicalon CG fibers tended to densify and shrink, thus partially decoupling the fibers from the matrix. The decoupling of the fibers from the matrix led to loss of load transfer capability and effectively increased the porosity of the material. Considerable microcracking of the matrix also resulted due to the residual stresses between the shrinking fibers and the expanding matrix.

Synthesis of irradiation resistant SiC_f/SiC composites in the future will require fabrication using improved SiC fibers with better irradiation damage stability. Only then can the fiber/matrix interface thickness and perhaps type be optimized for better performance.

PROGRESS AND STATUS

Introduction

Silicon carbide (SiC) has been considered as a structural material for fusion reactor applications since the 1970s primarily because of its low residual activation and high temperature properties [1,2]. However, except for some special applications, the brittle fracture nature of monolithic SiC limits its use. In the last decade a new class of SiC materials has evolved from the space industry which exhibits a type of inelastic deformation and non brittle failure. These new SiC materials are SiC fiber-reinforced composites (SiC_f/SiC). They consist of continuous fibers, primarily SiC, in a chemically vapor infiltrated (CVI) matrix of β-SiC. The fibers are coated with a thin interfacial layer, generally graphite, which allows considerable debonding of the fibers from the matrix. Under stress the debonding and associated fiber sliding with strain energy absorption lead to high fracture toughness and high strain-to-failure in these composites, in contrast to the brittle fracture characteristics exhibited by monolithic SiC [3].

Recently, several technical issues were identified which would require further development before the successful application of SiC_f/SiC in a fusion reactor could be realized [4]. This investigation provides an initial effort to address two of these issues: namely, the effects of neutron irradiation on the

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dimensional stability and on the mechanical properties of SiC_f/SiC composite made with commercially available Nicalon CG fiber.

Experimental Description

A SiC_f/SiC composite, consisting of a Nicalon CG fiber layup in a 2D 0-90° weave pattern with a CVI β-SiC matrix (manufactured by Dupont Co., Wilmington DE) was examined as the reference material in this work. Nicalon CG is a polymer-derived Si-C-O fiber (12 ± 2 wt% O, C:Si = 1.3) that is produced as a textile-grade yarn by Nippon Carbon Co. of Japan. The unirradiated fiber had a mean diameter of 14 μm, a density of 2.54 g/cm³, and a reported tensile strength of 2.6 GPa and tensile modulus of 190 GPa at room temperature [5]. For comparison, the tested monolithic β-SiC had a four-point bend strength of 360 MPa and bend modulus of 390 GPa. The reported fiber microstructure consisted of small nanocrystalline (≈ 2 nm.) β-SiC grains within a somewhat amorphous Si-C-O matrix [6]. Prior to the CVI process, a uniform 150 nm coating of pyrolytic graphite was deposited onto the Nicalon fibers.

For comparison, data were acquired for a similar 2D 0-90° weave composite fabricated by Oak Ridge National Laboratory. This composite also was made with Nicalon CG fiber, but the graphite interface layer was much thicker (≈ 1000 nm). In the remainder of this paper the two composite types will be referred to as 2D-150 nm and 2D-1000 nm, respectively. For a more complete picture, some irradiation data from other work [7] for monolithic β-SiC and Nicalon CG fiber alone and for SiC_f/SiC composites will be combined with this new data.

The composites and fibers were irradiated in either the FFTF or the EBR-II reactors, each a sodium-cooled reactor possessing a fast neutron spectrum with more than 50% of the flux greater than 0.1 MeV. Bend bar specimens and fiber bundles were irradiated at 430, 500, 800, 1000, 1200 and 1500°C to doses of from 4.3 to 26 dpa-SiC. Since it is the high energy neutrons that cause most of the irradiation damage in materials like SiC, the irradiation exposure is given in units of displacements per atom (dpa-SiC) for comparison to other reactor spectrums. The 430°C irradiation was for a weeper capsule at the liquid sodium coolant temperature; all other irradiation temperatures were established for gas-gapped TZM capsules with W ballast for gamma heating. Thermal expansion devices (TED), small vials containing sodium that respond to the sodium thermal expansion, indicated temperatures of 500-505°C and 780-820°C in capsules where the predicted temperatures were 500 and 800°C, respectively. The SiC specimens exhibited only limited activation after irradiation (10 to 200 mR/h at 15 cm), but were highly smearable (18 to 250 cpm/cm²). Continued precautions during subsequent handling and testing of these materials was necessary. The neutron activation was associated with background contaminants within the SiC ceramics, i.e., ⁵⁴Mn, ⁵⁸Co, etc.

All flexural bars, three or four bars for each experimental condition, were cut and diamond machined with 3.18 x 6.35 mm cross sections and 38.1 mm lengths. The 2D fiber weave directions were maintained parallel to the specimen length and width directions. Dimensional measurements of the bars were made before and after irradiation using a DR-25C optical gauge (Bausch and Lomb) with a rounded probe to ensure point contact. Due to a high degree of surface roughness and the tendency for some of the specimens to bow slightly after irradiation, only the length measurements, determined with an accuracy of ± 0.0025 mm, were used as the basis for the linear dimensional changes.

Four-point bend tests were carried out at the temperature of irradiation to measure strength, modulus and fracture energy. Fixtures conforming to MIL-STD-1942 (MR) were manufactured from polycrystalline SiC [8]. The test fixture was fully articulating with a lower universal joint and an upper crossed roller pin design for self alignment. Load was applied to the fixture using an Instron 1125 test machine with a 1000 pound load cell at a strain rate of 1.8x10⁻⁵ s⁻¹. The upper/lower spans were set at 30/15 mm for the 38.1 mm length bars. Midpoint displacements were monitored via alumina extension rods attached to a strain-gauge extensometer. The specimen deflection and load were corrected to account for the spring constant of the loading bellows and extensometers. Mechanical testing was conducted in flowing, high-purity argon (0.5 cc/hr) contained within a ceramic tube that was sealed by bellows at top and bottom. Test temperatures were monitored with a platinum-30% rhenium/platinum-6% rhenium (Type B)

thermocouple placed within 1.6 mm of the specimen centers. The specimens were held for 15 minutes at each test temperature ($\pm 5^\circ\text{C}$) prior to testing. Exhaust gas, measured with a Thermoxy oxygen meter, had less than 10 ppm oxygen. Because of the irradiated specimen's smearability, the entire testing apparatus was enclosed within a high air flow hood.

A data acquisition system collected, averaged and recorded 30 data points per second for load, time, displacement, oxygen partial pressure and temperature. Outer surface stresses and strains were calculated using elastic, flexural expressions. The modulus in bending was determined by applying a least squares fit to the linear portion of the stress-strain behavior.

Results and Discussion

Dimensional Stability

Averaged length changes of the irradiated SiC_f/SiC composites (2D-150 nm and 2D-1000 nm) and the monolithic SiC are shown in Figure 1 for the various irradiation temperatures regardless of fluence levels. Standard deviations for the length change measurements varied from 0.01% for the monolithic material up to 0.11% for the composites. For comparison, the swelling data for monolithic SiC determined by Palentine [9] and by Price [10] also are shown in Figure 1.

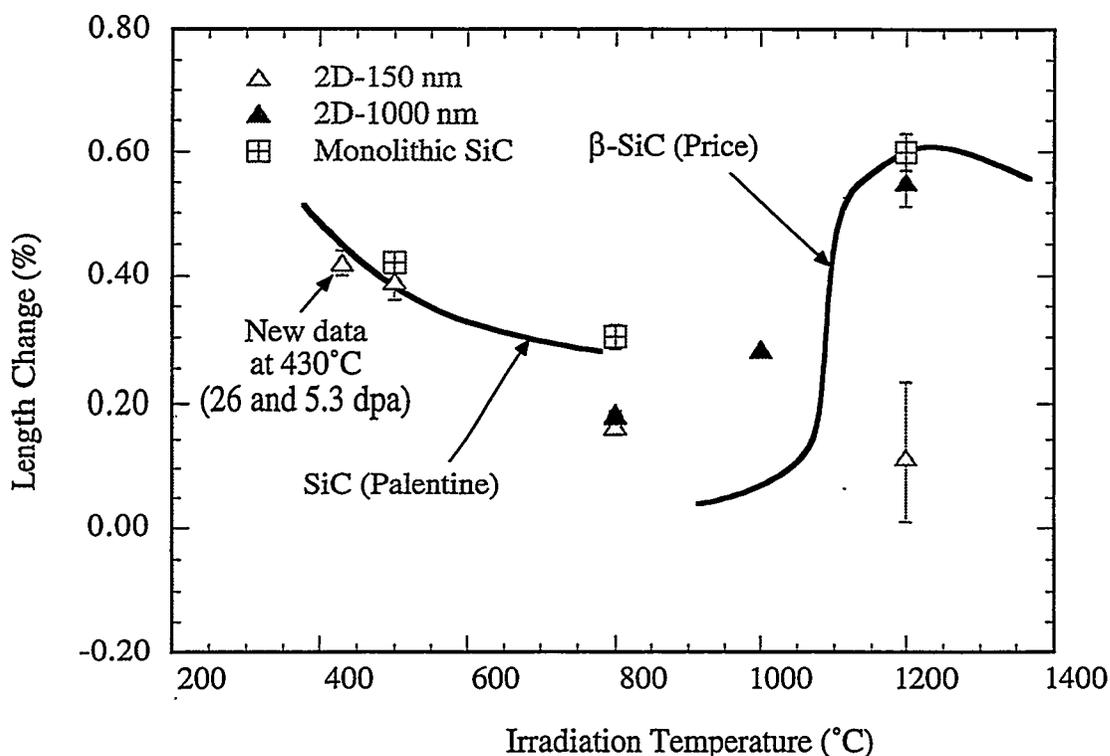


Fig. 1. Macroscopic length change vs. irradiation temperature for monolithic SiC and 2D SiC_f/SiC (2D-150 nm and 2D-1000 nm) composites. The solid lines represent similar measurements for monolithic SiC made by Palentine [7] and by Price [8].

At 430, 500 and 800°C, the swelling of both the monolithic and the 2D-150 nm composite were in close agreement with Palentine's data [7]. At 800°C, the 2D-1000 nm composite exhibited somewhat lower swelling. This new data appears to reflect the steady decline in the swelling with irradiation temperature

for SiC-based materials and, as observed by Palentine [7], is relatively independent of dose over this temperature range. Swelling of SiC in this lower temperature range can be attributed to an increase in the lattice constants due to a higher degree of metamictization in the SiC crystal structure [11]. As the temperature increases, the thermal annealing rate increases and the pseudo-equilibrium level of defects decreases. Consequently, the amount of swelling is reduced in the crystalline SiC material.

In contrast, the length of a bundle of Nicalon CG fibers irradiated at 850°C to a dose of 26 dpa contracted and the fiber density increased. The measured relative length change was $-4.4 \pm 1.1\%$ and the density change, determined by a liquid gradient column technique, was $+14.7 \pm 0.8\%$. By assuming isotropic contraction, the length change calculated from the density change is $-4.7 \pm 0.8\%$, which is in good agreement with the measured length change value. The Nicalon fiber density change determined here is consistent with density change trends with irradiation dose reported by Okamura et al [12]. During irradiation, the fibers actually shrink as the somewhat amorphous nano-crystalline microstructure of the Nicalon CG fiber becomes more ordered [12].

For irradiation temperatures above about 900°C, the monolithic SiC and the 2D-1000 nm SiC composite exhibited enhanced swelling, in agreement with the data of Price for β -SiC for comparable doses. However, at 1200°C the swelling of the 2D-150 nm composite was in line with its swelling trend observed at lower temperatures. Price proposed that void formation rather than lattice expansion dominates the swelling mechanism at irradiation temperatures above 1200°C. Consequently, the swelling would be expected to be almost proportional to fluence rather than fluence independent, as was observed for the irradiations at temperatures lower than 900°C.

The macroscopic length change of the irradiated SiC_f/SiC composites can be explained by considering that the fibers were mechanically decoupled from the matrix. The higher composite swelling values near the monolithic swelling values indicate full decoupling while the lower values, observed for the 2D-150 nm composite for instance, suggest only a partial decoupling. It is reasonable to expect some degree of decoupling in these composites as the fiber shrinks away from the matrix during irradiation. The density change data for the Nicalon CG fibers at 850°C indicates that there was considerable diametral shrinkage as well as length shrinkage.

Mechanical Properties

Typical four-point bend stress-strain curves at 430 and 800°C for the SiC_f/SiC composites before and after neutron irradiation are shown in Figure 2. At 800°C, the strengths or maximum stress achieved for the unirradiated 2D-150 nm and 2D-1000 nm SiC_f/SiC composites were about 600 and 300 MPa, respectively. At 430°C for the unirradiated 2D-150 nm specimen, the strength decreased to about 400 MPa. Dupont literature strength values for the 2D-150 nm material also indicate such a temperature dependence with a possible maximum strength near 800°C (quoted values are 300, 400 and 270 MPa at 23, 1000 and 1400°C, respectively [5]). For comparison, similar curves are presented for unirradiated (and irradiated) monolithic SiC at 800°C. At this temperature, the strength of the unirradiated 2D-150 nm composite was greater while the strength of the 2D-1000 nm composite was slightly less than that of the monolithic material. Also, the brittle stress-strain behavior of the monolithic SiC is contrasted with the inelastic-type deformation displayed by the SiC_f/SiC composites in Figure 2. The unirradiated SiC_f/SiC composites achieved strains greater than 1.5% with residual toughness beyond the uniform elongation point (not shown in Figure 2) during bend testing. After bend testing, most of the composite bar specimens were removed from the flexural fixture in one piece.

The effect of irradiation damage on the mechanical properties for both these two composites with different interface thicknesses also is demonstrated by the stress-strain curves in Figure 2. The strengths were reduced by 50% or more at both test temperatures. Nevertheless, the general feature of inelastic deformation with a large strain-to-failure is retained for the irradiated composites.

The explicit dose dependencies of the four-point bend strengths and bend modulus for the SiC_f/SiC composites irradiated at 430, 500, 800 and 1200°C are shown in Figure 3, upper and lower, respectively.

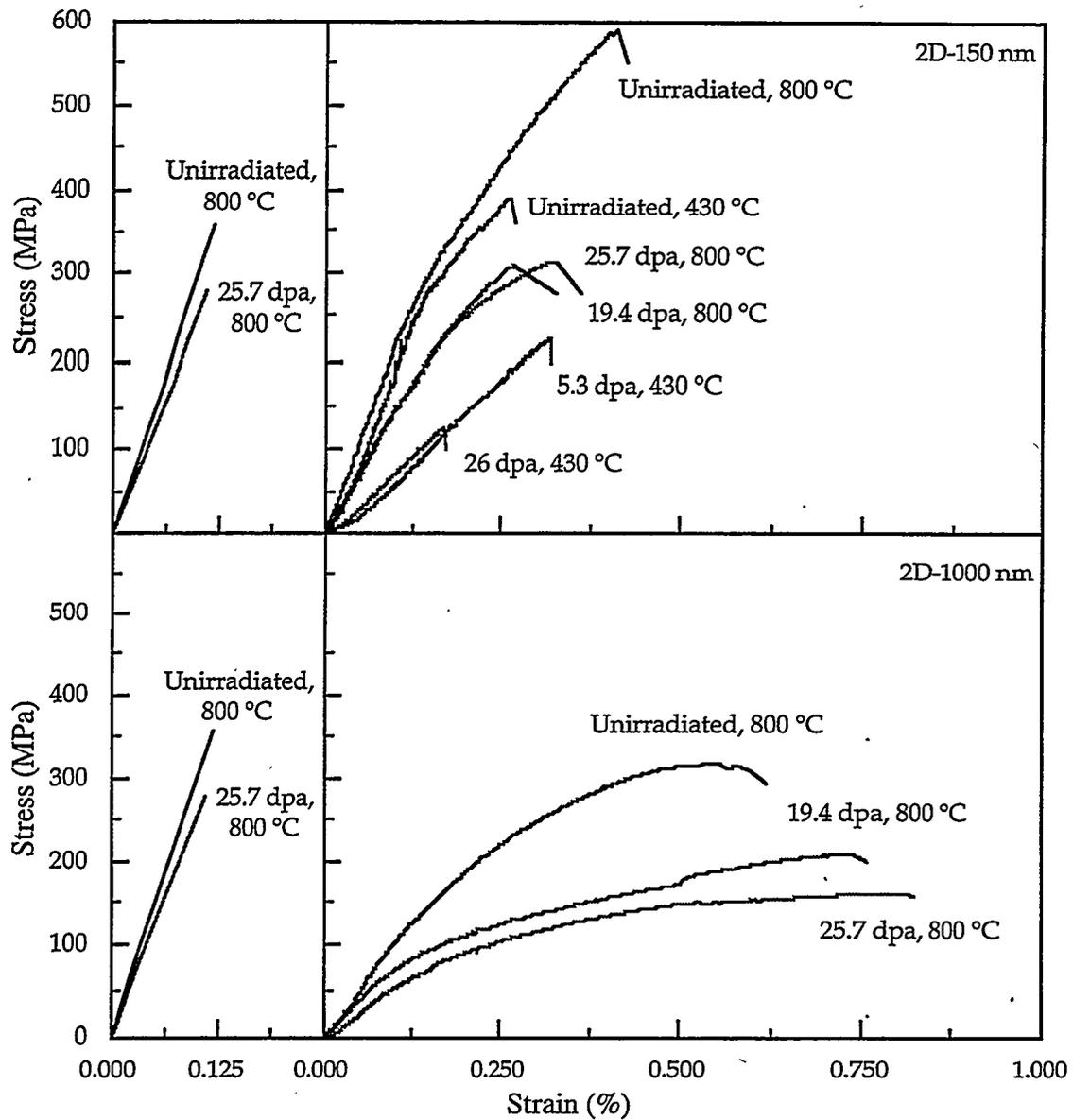


Fig. 2. Typical four-point bend stress-strain curves for SiC_f/SiC composites (2D-150 nm at 430 and 800°C and 2D-1000 nm at 800°C) before and after neutron irradiation. For comparison, similar curves determined for monolithic SiC are shown on the left. Note the improved strength and strain-to-failure (toughness) for the SiC composites compared to monolithic SiC.

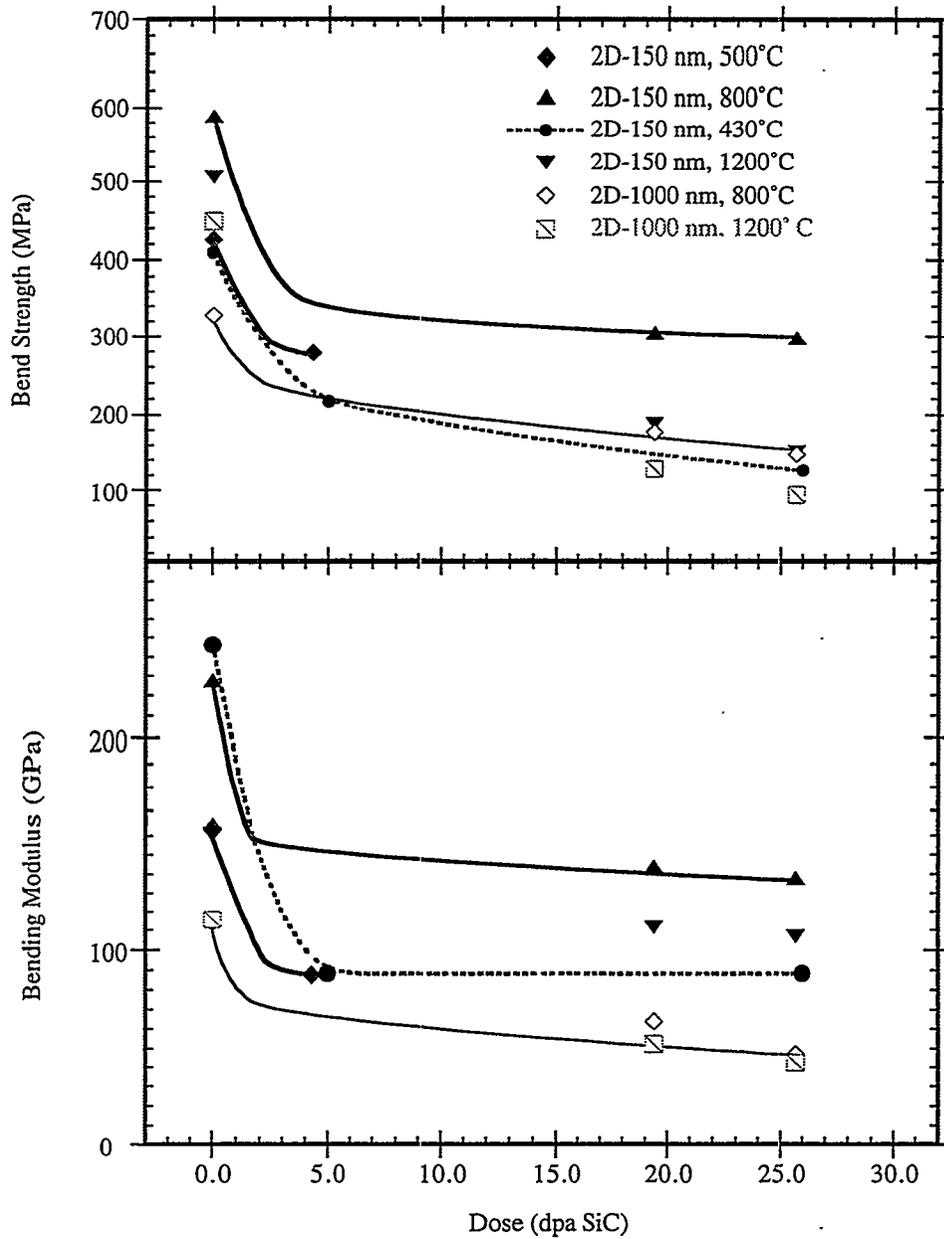


Fig. 3. Dose dependence of the four-point bend strength and modulus for SiC_f/SiC composites (2D-150 nm and 2D-1000 nm) neutron irradiated and tested at 430, 500, 800 and 1200°C. The lines indicate saturation of the irradiation effects at relatively low fluence levels [13].

In Figure 3, the dose dependence of these mechanical properties as indicated by solid or dashed lines, which infers an initial transient period followed by saturation with little further effect of exposure. Others have observed low fluence effects in SiC that saturate and then remain relatively unchanged up to higher fluence levels [13]. Likewise, a similar temperature dependence, noted previously for the strengths where optimum performance occurs at about 800°C, is followed for the 2D-150 nm material modulus. The generally lower values of strength and modulus for the 2D-1000 nm material appear to indicate that no such optimum temperature performance exists for the thicker interlayer composite.

In Figure 4, optical micrographs of the unirradiated 2D-150 nm composite and of the same composite irradiated at 500, 800 and 1200°C to doses of 4.3, 25.7 and 25.7 dpa, respectively, depict the microstructural changes after neutron irradiation. In particular, the gap formation around the fibers as well as the gap linking and crack formation, features responsible for the mechanical property changes, are already observed at 4.3 dpa (500°C). These same features appear to be relatively unchanged for further dose to 25.7 dpa (800°C).

By comparing the composite and fiber length change (and fiber density change) data and the microstructural data, the feature that appears to have the most bearing on the mechanical property degradation in irradiated SiC_f/SiC composites (as depicted in Figure 3) is the apparent partial decoupling of the Nicalon CG fibers from the β-SiC matrix. Fortunately, the decoupling is only partial, and the fibers still contribute to some load bearing (more so in the 2D-150 nm material than in the 2D-1000 nm material) and preservation of the inelastic-type deformation in these irradiated SiC_f/SiC composites as desired.

Typical fracture surfaces of the unirradiated and irradiated 2D-150 nm SiC_f/SiC composite are shown in Figure 5. For the unirradiated fracture (upper views), a singularly directed crack front with limited fiber pullout is observed. In contrast, for this composite irradiated at 800°C (lower views), the crack spreads and propagates in different directions and is accompanied by a significant amount of fiber pullout. Fiber pullout for the unirradiated composite was only ten's of microns, while for the irradiated materials it was millimeters in length. Crack bridging occurred in all these irradiated composites on a macroscopic scale; on a scale much larger than observed for the unirradiated materials. This observation is consistent with the partially decoupled fiber model for these irradiated SiC_f/SiC composites. With the weakened interfacial bonding, the fibers become loaded at distances approaching the weave spacing (millimeters) and fiber fractures occur at varied distances between the weave spacing. Note the crack tracing the weave pattern across the tensile surface view of the irradiated sample in Figure 5.

Fiber shrinkage and decoupling from the matrix during irradiation is an area of concern, but potentially is an area where marked improvement in irradiation performance can be attained. As a more irradiation tolerant fiber is developed, these SiC_f/SiC composites can be optimized for the nuclear application. It appears that the most pressing enabling technology for fabrication of successful composites for the space effort matches that for fusion reactor applications, i.e., the production and use of high-purity (no excess O or C), thermally stable, very fine grain β-SiC fiber for reinforcement in composites with a β-SiC matrix.

CONCLUSIONS

Swelling for irradiated SiC_f/SiC composites was only slightly less than for irradiated monolithic SiC. Up to about 900°C, the swelling appeared to be relatively independent of fluence. It is postulated that decoupling of the Nicalon fibers from the SiC matrix occurs during irradiation as these Nicalon CG fibers shrink and densify. The strengths and the modulus of the irradiated SiC_f/SiC composites were reduced by about 50%, which appears to be related to mechanically decoupling of the fibers from the matrix. After initial reductions, the mechanical properties become relatively independent of further neutron dose. Photographic evidence of crack propagation and fiber pull-out for the irradiated composites further support the concept of the Nicalon CG fibers being at least partially mechanically decoupled from the matrix.

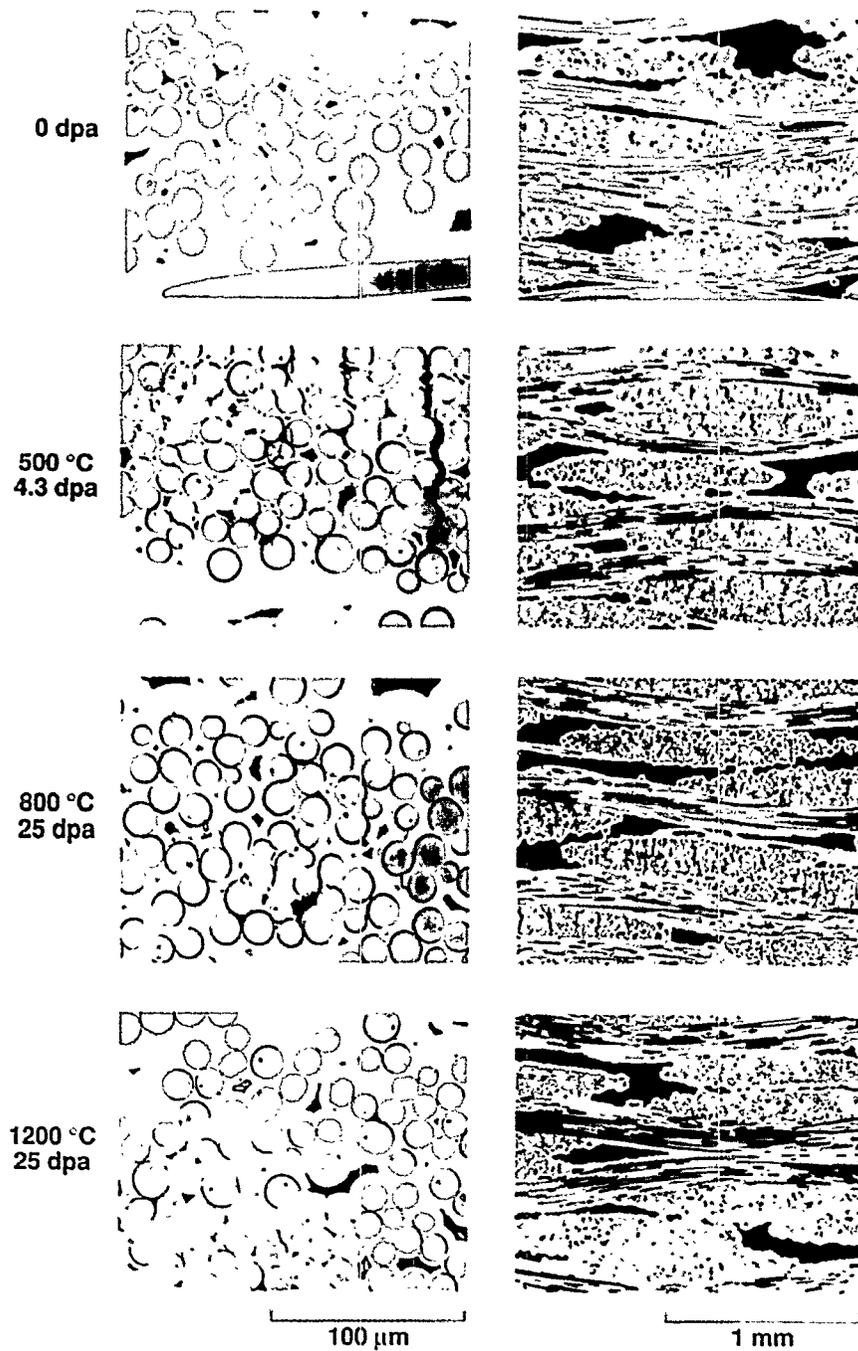


Fig. 4. Optical micrographs of the 2D-150 nm SiC_f/SiC composite depicting microstructural changes due to neutron irradiation at 500, 800 and 1200°C to doses of 4.3, 26 and 26 dpa, respectively. Note the residual macroscopic porosity as a result of the CVI processing in the right-hand views. Also note the gap formation about the fiber cross-sections for all irradiation doses and temperatures as well as the crack formation for the samples irradiated at 500 and 800°C, but not for the sample irradiated at 1200°C.

Synthesis of irradiation resistant SiC_f/SiC composites in the future will require: (1) improved SiC fibers with better irradiation damage stability, and then (2) optimization of the fiber/matrix interface layer thickness and perhaps interface type.

FUTURE WORK

Emphasis will be focused on examining the irradiation effects on alternate commercial and developmental SiC -based fibers to identify specific characteristics that might lead to a more radiation tolerant fiber and ultimately to a high performance SiC_f/SiC composite suitable for advanced fusion reactor applications..

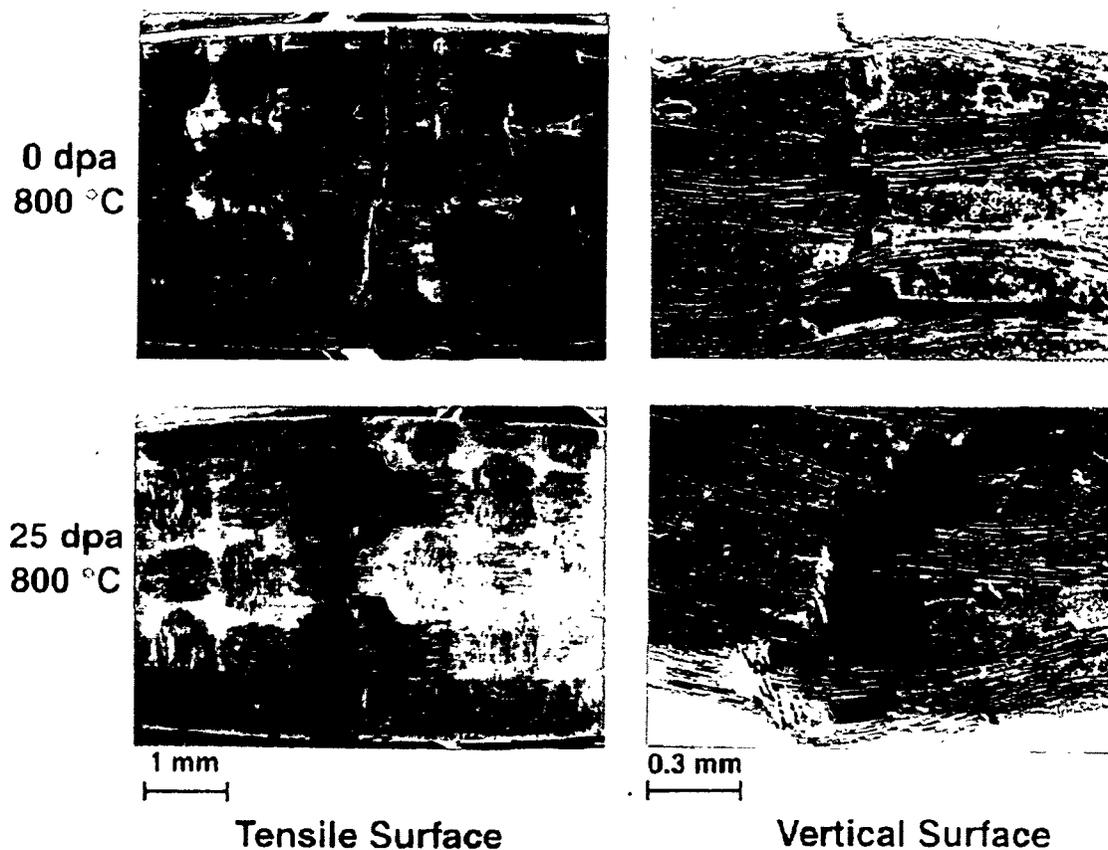


Fig. 5. Crack propagation in unirradiated (upper) and irradiated (lower) 2D-150 nm SiC_f/SiC composite after flexure testing at 800°C. Note the extensive amount of fiber pull-out after irradiation.

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