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Low dose irradiation performance of SiC interphase SiC/SiC composites

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Abstract

Reduced oxygen Hi–Nicalon™ fiber reinforced composite SiC materials were densified with a chemically vapor infiltrated (CVI) silicon carbide (SiC) matrix and interphases of either 'porous' SiC or multilayer SiC and irradiated to a neutron fluence of 1.1×10^{25} n m^{-2} ($E > 0.1$ MeV) in the temperature range of 260 to 1060°C. The unirradiated properties of these composites are superior to previously studied ceramic grade Nicalon fiber reinforced/carbon interphase materials. Negligible reduction in the macroscopic matrix microcracking stress was observed after irradiation for the multilayer SiC interphase material and a slight reduction in matrix microcracking stress was observed for the composite with porous SiC interphase. The reduction in strength for the porous SiC interfacial material is greatest for the highest irradiation temperature. The ultimate fracture stress (in four point bending) following irradiation for the multilayer SiC and porous SiC interphase materials was reduced by 15% and 30%, respectively, which is an improvement over the 40% reduction suffered by irradiated ceramic grade Nicalon fiber materials fabricated in a similar fashion, though with a carbon interphase. The degradation of the mechanical properties of these composites is analyzed by comparison with the irradiation behavior of bare Hi–Nicalon fiber and Morton chemically vapor deposited (CVD) SiC. It is concluded that the degradation of these composites, as with the previous generation ceramic grade Nicalon fiber materials, is dominated by interfacial effects, though the overall degradation of fiber and hence composite is reduced for the newer low-oxygen fiber. © 1998 Elsevier Science B.V.

1. Introduction

The use of silicon carbide (SiC) composites as fusion system structural materials has recently been considered mainly due to the development of high strength, continuous SiC fibers. The incorporation of these fibers into the brittle SiC matrix of a composite material is the key to the improved toughness as compared to monolithic SiC. Such fibers can be woven in various architectures and the preforms infiltrated with a SiC matrix by various methods, yielding a composite with reported bending strengths as high as 600 MPa [1]. Another very attractive feature of these materials is that the degree of toughness can be designed into the composite by the application of a compliant interfacial layer between fiber and matrix. This layer, while being strong enough to transfer load from the stiff matrix to the high strength fibers (and vice versa), is also compliant enough to debond in the presence of a propagating matrix crack, thus promoting fiber pull out and enhanced toughness.

Silicon carbide fibers are commercially processed through many different routes. The most widely studied, developed and commercialized SiC fiber is derived from the polymer precursor process first introduced by Yajima et al. [2]. The fibers are commercially available under the

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trade name Nicalon fiber. The first stage of the Nicalon fiber process involves the low temperature melt-spinning of the polycarbosilane (PCS) polymer. These spun fibers, which are in the 'green state', are then stabilized by elevated temperature exposure to oxygen and successively ceramized in an inert atmosphere to a final temperature of 1300°C. Because of the relatively low price, good mechanical properties and excellent weavability of these fibers, they have found widespread use both in the laboratory as well as in industry.

It is important to note that due to the presence of excess oxygen and carbon, these fibers are more correctly classified as SiC-based fibers, rather than SiC fibers. The manufacturer's quoted composition for Nicalon NLM-202, which is close to figures given by Yajima et al. [3] for preproduction fibers, is 65% β-SiC with 23% SiO_2 and 11% free carbon. The actual elemental content and structure of Nicalon fiber has been widely debated [4–7]. Two comprehensive studies have found the elemental composition of the fiber to be close to that given by the manufacturer, though the structure itself is significantly more complex [8,9]. Both studies describe the system as a dispersal of β-SiC crystallites of a few nanometers in size embedded in a continuum glassy silicon oxycarbide matrix ($Si–O_x–C_y$, where $x + y$ is approximately 4).

Recently, the Nicalon fiber thermomechanical properties have been improved by altering the method of cross linking the spun polymer. Rather than curing the PCS in air, the polymer is subjected to ionizing radiation in a helium environment. Cross linking the PCS in this manner first used ultraviolet light [10,11], although the most successful demonstration is for the Nicalon pre-ceramic polymer and uses electron irradiation [12,13]. This process reduces the atomic oxygen content from greater than 15% (standard Nicalon fiber) to less than 0.5% and is the process with which Hi–Nicalon fiber is made [13]. The average SiC crystallite size for this product increases by more than a factor of two over the ceramic grade fiber, and the fiber elastic modulus undergoes a large increase while the strength decreases slightly. The density of the Hi–Nicalon fiber is also increased from 2.55 g/cm^3 (ceramic grade Nicalon fiber) to 2.74 g/cm^3, which is approximately 85% theoretical SiC density. Also of interest for nuclear applications, the Hi–Nicalon fiber density was seen not to undergo the dramatic densification seen in ceramic grade Nicalon fiber, at least for low dose neutron irradiations [14].

This paper presents results on composite materials which have been developed to be more radiation resistant than the standard ceramic grade Nicalon fiber reinforced composites previously studied. The previous, first generation SiC composites (Nicalon fiber/CVD SiC with a graphitic interphase) have been studied in some detail with the observation that the large irradiation-induced degradation in fracture strength was due to disruption of the interface between the fiber/matrix interphase [14–16]. This disruption has been attributed to densification of the Nicalon fiber. The composites developed for this irradiation study were chosen based on the following assumptions: (1) that the reduced oxygen Nicalon fiber would be more stable to neutron irradiation, and (2) that by replacing the carbon interphase with a silicon carbide-based interphase the swelling behavior of the fiber and matrix would be similar, thereby limiting the tendency for disruption of the fiber/matrix interface.

2. Materials

2.1. Porous SiC interphase material

A series of composites were fabricated to deposit a 'porous' SiC interphase first on ceramic grade Nicalon fiber to optimize the process and then on low oxygen content Hi–Nicalon fiber for the irradiation study. Deposition variables were the relative mixture of methyltrichlorosilane, argon, methane and hydrogen flow gases as well as the infiltration temperature. The porous SiC interfacial composites were processed at the High Temperature Materials Laboratory at the Oak Ridge National Laboratory using the forced chemical vapor infiltration (FCVI) method [17,18]. The infiltrated silicon carbide matrix was deposited from methyltrichlorosilane with a typical infiltration time of 18 h. The dimensions of the as fabricated discs were 4.45 cm diameter and 1.25 cm thickness.

The composite architecture was a 1800 denier (500 filament yarn) plain weave fabric and was laid-up inside a graphite holder with a fiber volume fraction of approximately 40%. The fabricated composite void fraction was 10–12%. Hi–Nicalon fiber, from lot number NC9302, was obtained in fabric form from the Dow Corning corporation, and was manufactured by Nippon Carbon in February of 1993. The fabric lay-up was constructed by rotating each layer 30° with respect to its neighbor. Sizing of both fiber systems was removed with an acetone wash following fiber lay-up.

A substantial degradation of the standard Nicalon fiber was seen due to interaction with the (porous SiC) reactant gases leading to very low composite strengths, especially on the higher temperature surface of the preform, presumably due to accelerated kinetics. For this reason, a thin (0.1 μm) coating of carbon from a propylene precursor was deposited on fibers prior to the porous SiC deposition as a reaction barrier. The results of the process development led to a composite infiltrated at 900°C. Testing a series of bend bars through the thickness of the composites yielded constant strengths for this Hi–Nicalon fiber composite. Two composites were fabricated under identical conditions and yielded nearly identical matrix microcracking and ultimate fracture stresses. Specifically, the matrix microcracking and ultimate fracture stress were 250 ± 32 and 507 ± 75 MPa, respectively. These values exceed those for

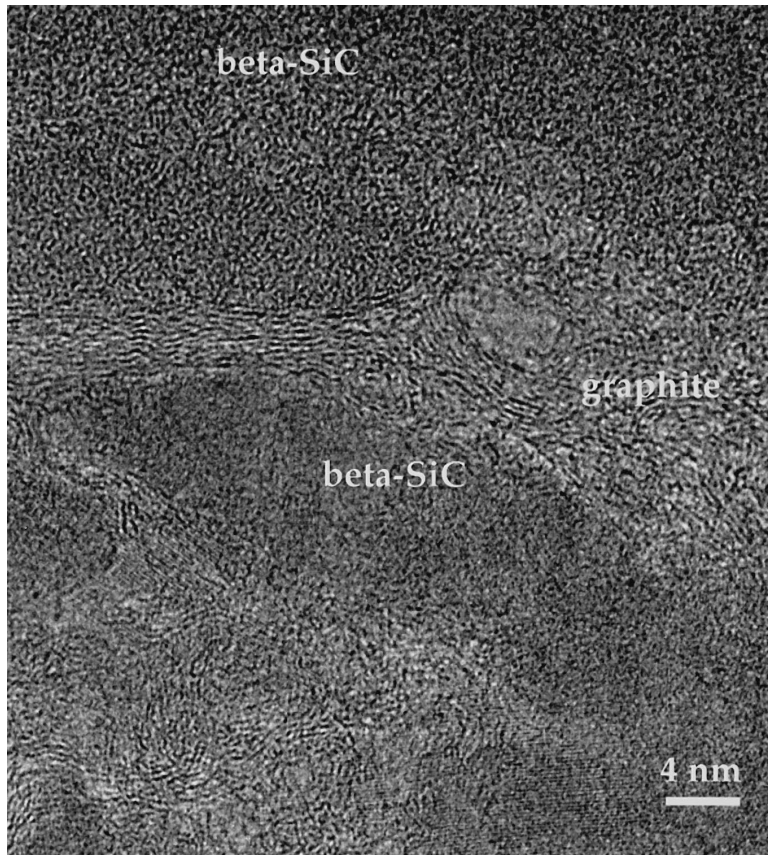

Fig. 1. High resolution TEM image of the porous SiC interphase.

($\simeq 0.15$ μm) carbon interfacial materials fabricated with either regular Nicalon fiber (40% higher) or Hi–Nicalon fiber (10% higher). Fig. 1 shows a high resolution TEM image of the 'porous' SiC interphase. This micrograph shows interconnected β-SiC surrounding islands of 'poorly' graphitized carbon. The interphase is best described as a two component mixture of carbon and β-SiC, where the SiC is the predominant phase.

2.2. Multilayer SiC interphase material

Composites containing a multilayer SiC fiber coating were fabricated for evaluation in the irradiation using chemical vapor infiltration of Hi–Nicalon fiber preforms by Hyper-Therm High-Temperature Composites, Inc. Plain weave Hi–Nicalon fiber fabric containing 16 fiber pics/inch produced by Nippon Carbon was obtained from Dow Corning Corporation. The fabric was cut into individual plies 150 mm × 300 mm in planform and laid-up in a $(0,90)_s$ fiber architecture containing 8 plies per preform. The preform was compacted to $\simeq$ 35% fiber volume within a graphite holding tool during deposition of the fiber coating and subsequent SiC matrix densification. This process results in a material with a density of 2.83 g/cm^3, which corresponds to less than 10% residual closed porosity.

An initial layer of pyrolytic carbon 20 nm thick was deposited on the fiber preform to prevent the previously discussed interaction with the SiC processing phases. The first SiC layer of the multilayer fiber coating is then deposited followed by a 20 nm interrupted layer of pyrolytic carbon. This process is then repeated until the desired number of SiC layers are fabricated within the fiber coating. For the material irradiated under the present study, two unbonded SiC layers of slightly less than 100 nm were utilized for the multilayer SiC fiber coating. Fig. 2 shows a high magnification, back-scattered electron image of the multilayer SiC fiber coating obtained from field-emission scanning electron microscopy. The entire fiber coating is observed to be 0.2 μm in thickness, and the atomic number contrast of the back-scattered image shows that the composition of the fiber coating is similar to the CVD SiC matrix.

Room temperature mechanical properties of the materials were extensively evaluated before irradiation. Tensile tests were performed on 100 mm straight-sided samples

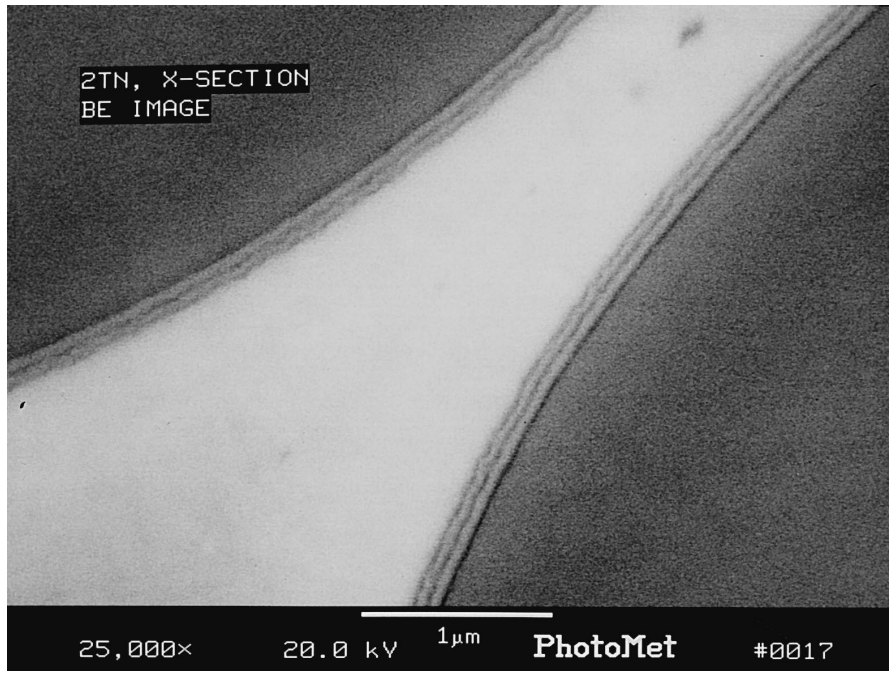

Fig. 2. Back-scattered electron image of multilayer SiC fiber coating on Hi–Nicalon fibers. SiC layers are ≃ 100 nm thick and interrupted pyrolytic carbon layers are ≃ 20 nm.

utilizing adhesively-bonded resistive strain gauges. Table 1 presents a comparison of the materials produced for this study with a Hi–Nicalon fiber/CVI SiC containing a pyrolytic carbon fiber coating. A comparison of the two materials shows that the multilayer SiC fiber coating possesses strength and strain capabilities similar to the optimized pyrolytic carbon fiber coating system. Due to the known dimensional instability of pyrolitic graphite under neutron irradiation, the multilayer interphase system alone was carried into the irradiation study. Additionally, three-point flexural tests with a 63 mm span were performed on the material. The failure stress and strain were, respectively, 666 ± 91 MPa and $0.53 \pm 0.11\%$. Pre-irradiated flexural properties were also measured on the materials in the smaller geometry (25 mm span) necessary for the irradiation study. Lower failure stresses of ≃ 506 MPa were obtained, and were attributed to the presence of a shear component in the failure of the composite due to the short span required for the irradiation tests.

2.3. Chemically vapor deposited material

Samples were prepared from CVD SiC purchased in May 1994 from Morton. Samples were machined from a single plate of as-deposited material. The density as measured by the density gradient column method (cf. Section 3.2) was 3.203 g/cm^3.

3. Experimental procedures and results

3.1. Irradiation

Hi–Nicalon fiber reinforced CVI SiC materials with multilayer and porous SiC interfacial materials were machined to dimensions of $2.5 \times 3 \times 25$ mm for the irradiation study. The porous SiC material surfaces were machined such that the top and bottom surfaces had exposed

Table 1
As-fabricated tensile properties of Hi–Nicalon fiber/SiC with multilayer SiC fiber coating as compared to Hi–Nicalon fiber/SiC with pyrolytic carbon fiber coating

Material system	Elastic modulus (GPa)	Matrix microcracking (MPa)	Tensile failure stress (MPa)	Tensile failure strain (%)
Hi–Nicalon fiber/SiC with multilayer SiC fiber coating	352 ± 55	102 ± 18	290 ± 14	0.42 ± 0.06
Hi–Nicalon fiber/SiC with pyrolytic carbon fiber coating	285 ± 16	81 ± 6	325 ± 12	0.67 ± 0.04

fabric where the surface layer had been ground flat. The multilayer SiC material had a thin CVD SiC overcoat ($\simeq 100$ μm) so that the top and bottom fabric layer were not exposed. The fabric orientation was such that the fabric was in the plane of the width and length axes of the bend bar. All edges of the bend bars were ground flat, thus some of the fibers were machined away for the porous SiC interfacial materials. The Morton CVD SiC was machined into $1 \times 1 \times 25$ mm bars. All materials were cleaned in acetone and isopropyl alcohol prior to the irradiation capsule assembly.

A single irradiation capsule, SiC-1, was assembled consisting of subcapsules which contained the samples. The bend bar samples had at least one side in flush contact with the inside of a subcapsule to allow for heat transfer. Subcapsules were either 6061 aluminum alloy or V–4Cr–4Ti alloy. The sample temperature was achieved by machining gas gaps into the subcapsule so that the nuclear heating was conducted through the helium cover gas. A single type-K thermocouple was embedded in each subcapsule and the temperature was continuously recorded. Following welding of the aluminum capsule exterior the capsule was evacuated using a turbomolecular pump and backfilled with ultra-high purity helium. This procedure was repeated three times with a final backfill to a helium over pressure of 15 psi. The positive pressure of helium was monitored during the irradiation period.

The SiC-1 capsule was inserted into the V-16 in-core thimble of the high flux beam reactor at the Brookhaven National Laboratory. The duration of the irradiation was one reactor cycle which corresponds to an approximate fast neutron fluence of 1.1×10^{25} n m^{-2} ($E > 0.1$ MeV). This corresponds to $\simeq 1.1$ displacements per atom (dpa) in SiC, assuming a sublattice-averaged displacement energy of 40 eV. The irradiation temperature for the multilayer-SiC interfacial composite was 385°C and was constant within 5°C throughout the irradiation. Two subcapsules were used for the porous-SiC interfacial composite. The lower temperature subcapsule which was made of type 6061 aluminum alloy had a constant irradiation temperature of 260°C, constant within 5°C throughout the irradiation. The higher temperature subcapsule, which was fabricated from vanadium, initially achieved a temperature of 1060°C and then decreased in temperature linearly with time to a final temperature of 910°C. It is believed that this decrease in temperature may be due to swelling of the vanadium subcapsule (associated with interstitial pickup from the capsule gas) which narrowed the gas gap thus reducing the temperature. Other factors such as increased emissivity of the vanadium subcapsule surface would also cause a reduction of the subcapsule temperature. Post-irradiation examination of the SiC samples did not show any evidence of reaction with the subcapsules.

Irradiation of Hi–Nicalon fiber to several different doses was carried out in the hydraulic tube facility of the high flux isotope reactor at the Oak Ridge National Laboratory. The dose equivalent of 1.0×10^{25} n m^{-2} ($E > 0.1$ MeV) = 1 dpa was also used. Fiber samples were held in either a type 6061 aluminum alloy or graphite subcapsules and sealed inside a 'rabbit' capsule with either a ultra-high purity helium or argon environment. Sample temperature was again achieved by gas gap conduction of the nuclear heating. These capsules were uninstrumented. Irradiation temperatures were estimated from density vs. annealing temperature plots generated by isochronal annealing of SiC temperature monitors. Further discussion of these irradiations is given in a separate paper in these proceedings [19].

3.2. Testing

The density change of CVD SiC was measured using the density gradient column technique [20] utilizing mixtures of methylene iodide and *tetra*-bromethane. The estimated accuracy for this procedure is $\simeq 0.003$ g/cm^3. The Hi–Nicalon fiber density was determined by placing small fiber loops into a column of methylene iodide and bromoform. All samples which were measured using the density gradient column were first placed in a bath of hydrofluoric acid for at least four hours followed by an acetone and isopropyl alcohol rinse. The samples were then air dried and placed in a solution consisting of the lighter column fluid prior to being put in the column.

All bend testing was conducted at room temperature using a four point bend fixture with load and support spans of 0.5 and 2.0 cm, respectively. The cross head displacement speed was 8.5×10^{-4} cm s^{-1}. The gage length and cross head speed for the single fiber testing was 25 mm and 8.5×10^{-4} cm s^{-1}, respectively. Bare fiber testing at room temperature was carried out using laser extensometry. Other specifics related to the measurement of the Hi–Nicalon fiber strength and elastic modulus are given elsewhere [19]. HRTEM images were taken using the Hitachi HF-2000 field emission microscope in the Materials Analysis User Center at ORNL.

3.3. Results

Table 2 gives the results of the room temperature bend testing and the material dimensional changes. For the multilayer SiC interfacial material the irradiation temperature was 385°C while the porous SiC interfacial material was irradiated at 260°C and 1042 → 910°C. The matrix microcracking and ultimate fracture stress are reported in both the unirradiated and irradiated condition. The matrix microcracking stress was taken from the load-displacement curve as the departure from linearity and is, therefore, a macroscopic matrix stress. Undoubtedly matrix microcracking occurred at stresses below this value. In the unirradiated condition several bend tests were conducted for each material, while only two samples were tested in the irradiated condition. The last three columns of Table 2

Table 2
Mechanical and dimensional stability of materials following neutron irradiation

Sample	Matrix microcrack stress (MPa)	Ultimate fracture stress (MPa)	$\Delta thick_{comp.}$ (%)	$\Delta length_{comp.}$ (%)	Linear swelling (%) Morton CVD
Hypertherm multilayer SiC composite					
Unirradiated	250 ± 32 (6 tests)	507 ± 75 (6 tests)			
Irradiated at 385°C	290	462	$0.51 \rightarrow 1.56$	$0.3 \rightarrow 0.61$	0.46
	244	371	1.0 ave (5 tests)	0.46 ave (6 tests)	
ORNL porous SiC composite					
Unirradiated	298 ± 22 (8 tests)	515 ± 19 (8 tests)			
Irradiated at 260°C	268	347	$0.5 \rightarrow 1.37$	$0.43 \rightarrow 0.52$	0.56
	251	344	0.95 ave (3 tests)	0.49 ave (4 tests)	
Irradiated at $1042 \rightarrow 910$°C	210	332	$0.38 \rightarrow 1.32$	$-0.17 \rightarrow 0.0$	
	201	304	0.75 ave (3 tests)	-0.06 ave (3 tests)	1.18

give the percent change in thickness and length for the composites and the percent dimensional change for the CVD SiC. The thickness quoted is in the direction normal to the plane of the fabric.

4. Discussion

It is difficult to make quantitative assessment of the effect of irradiation from the bend strength data given in Table 2. It is obviously difficult to analyze bend strength data for laminated composites and the small samples typically used for irradiation studies. However, on a qualitative basis the load-displacement curves in Figs. 3 and 4 for the porous and multilayer SiC materials can be used along with fractographic analysis and the tabulated results to make some observations.

From a design standpoint, both the matrix microcracking and ultimate fracture stress are important. One can think of designing a component for routine use to some fraction of the matrix microcracking stress while allowing accidental events to go above this stress into the permanent damage regime. By inspection of Table 2 it is seen that the matrix microcracking stress is only moderately affected by irradiation for the multilayer SiC interfacial composite. In this case the average matrix microcracking stress increases from 250 to 267 MPa, though this increase is not statistically significant. In the case of the porous SiC interfacial material there appears to be a real decrease in the matrix microcracking stress from 298 ± 22 MPa in the unirradiated case to $\simeq 260$ MPa for the 260°C irradiation and 210 MPa for the $1042 \rightarrow 910$°C irradiation. From inspection of Figs. 3 and 4, the stiffness of the multilayer SiC interfacial

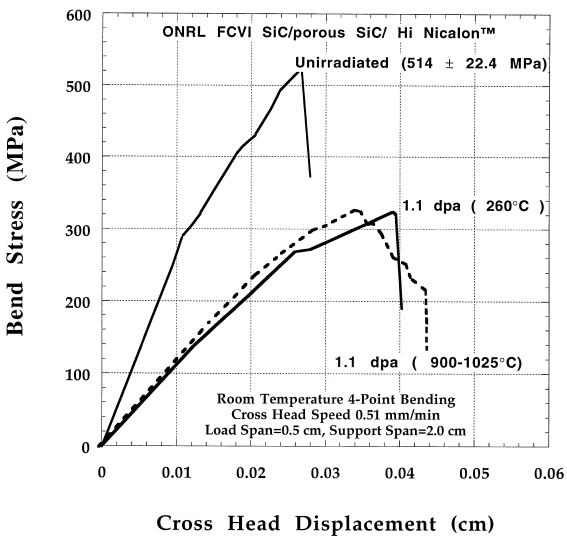

Fig. 3. Load–displacement curves for porous SiC interphase composite in unirradiated and neutron irradiated conditions.

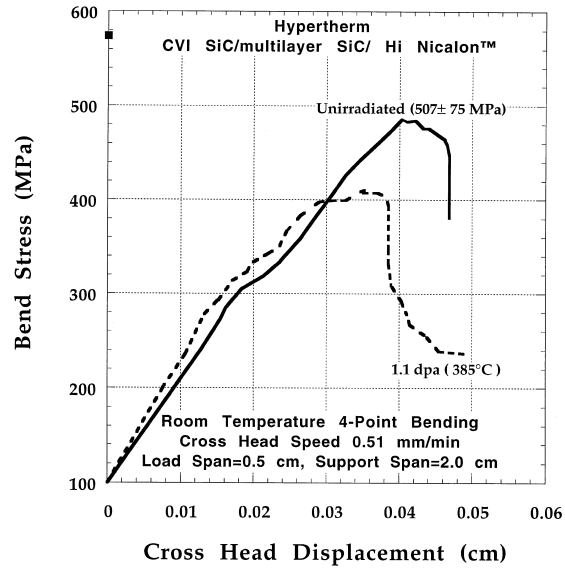

Fig. 4. Load–displacement curves for multilayer SiC interphase composite in unirradiated and neutron irradiated conditions.

composite did not change with irradiation while the stiffness of the porous SiC material significantly decreased. The retention of stiffness up to the matrix microcracking stress for the multilayer SiC interphase can be attributed to the thin (100 μm) overcoat on the bend bars. At the irradiation temperatures and fluence levels studied there should be practically no change in the overcoat structure and properties. However, the stiffness is retained above the matrix microcracking stress and is therefore associated with the stiffness of the composite. There is likely a distinct difference between the behavior of the irradiated multilayer and porous SiC composites. One possibility, which will be discussed later, is that a partial or full disruption of the fiber/matrix interphase has occurred for the porous SiC interphase, while the multilayer SiC interphase is still intact and able to transfer load to the fibers. The simplest explanation for the difference is that the mechanical or chemical bond between the interphase and matrix for the multilayer interphase is stronger, or more resistant to neutron irradiation.

The ultimate fracture strength, which gives an indication of the ability to resist catastrophic failure in the permanent damage regime, is reduced for both the multilayer and porous SiC interfacial materials. Both materials have an average ultimate fracture strength in bending of approximately 500 MPa with a standard deviation of 75 MPa for the multilayer material and 19 MPa for the porous SiC interphase material. Irradiation at 385°C reduced the average strength of the multilayer material to 416 MPa. The porous SiC material was substantially degraded in ultimate strength to 345 MPa at the 260°C irradiation temperature and to 315 MPa for the 1042–910°C irradiation. Due to the limited availability of material it was not possible to compare these high temperature irradiation results with similar, unirradiated material which was annealed at the irradiation temperatures. From the reported temperature/time degradation of the Hi–Nicalon fiber no change is expected [13], though such a composite degradation is possible.

The matrix microcracking and ultimate fracture strength in bending can be compared to ceramic grade Nicalon fiber composites previously irradiated to 1 dpa at 300°C in the high flux isotope reactor [15]. These ceramic grade Nicalon fiber composites also yielded negligible reduction in matrix microcracking, though they underwent a large reduction in load carrying capacity above the matrix microcracking stress. Specifically, the ultimate fracture strength of the standard Nicalon fiber composite was reduced to approximately 60% of the unirradiated value as compared with the $\simeq$ 85% retention in strength for the multilayer SiC interphase material presented here. The porous SiC interfacial composite retained approximately 70% of its initial fracture strength. The reduction in the ultimate fracture strength of the ceramic grade Nicalon fiber materials has been attributed to a decoupling of the fiber and matrix caused by the densification of the fiber [15,16,21]. This has been verified by TEM observation of crack surfaces and indirectly through measurements of the interfacial shear and sliding stress of the fiber [15,16,22]. It has also been indirectly confirmed by inspection of the exaggerated fiber pull-out lengths from SEM micrographs [15,16]. Another indirect confirmation of the decoupling is the significant reduction in the load carrying capability of these materials above the matrix microcracking stress. In essence, when the fiber shrinks the chemical bond responsible for the interfacial shear strength is broken and the

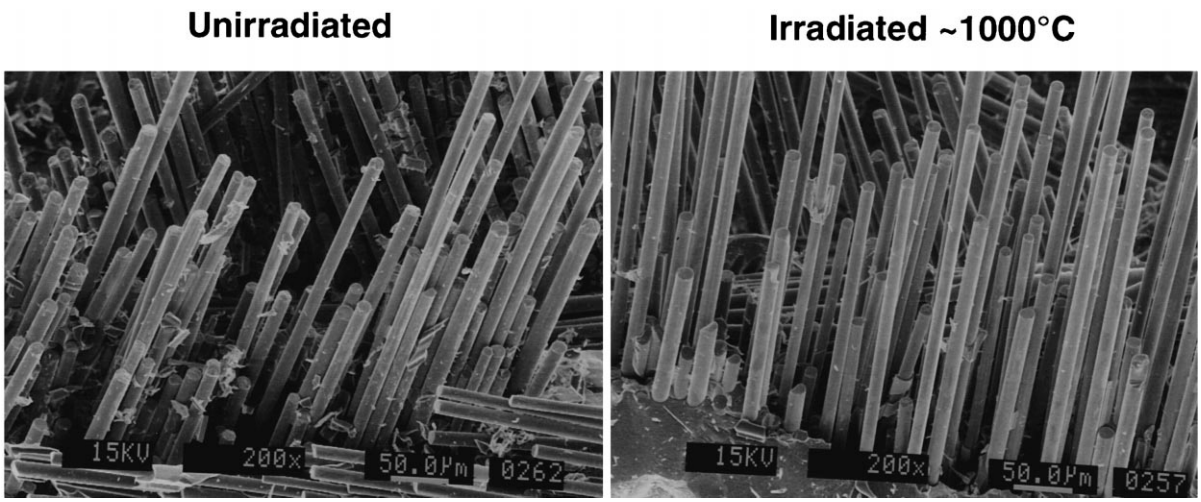

Fig. 5. SEM images of the fracture surfaces of unirradiated and irradiated porous SiC interphase composites.

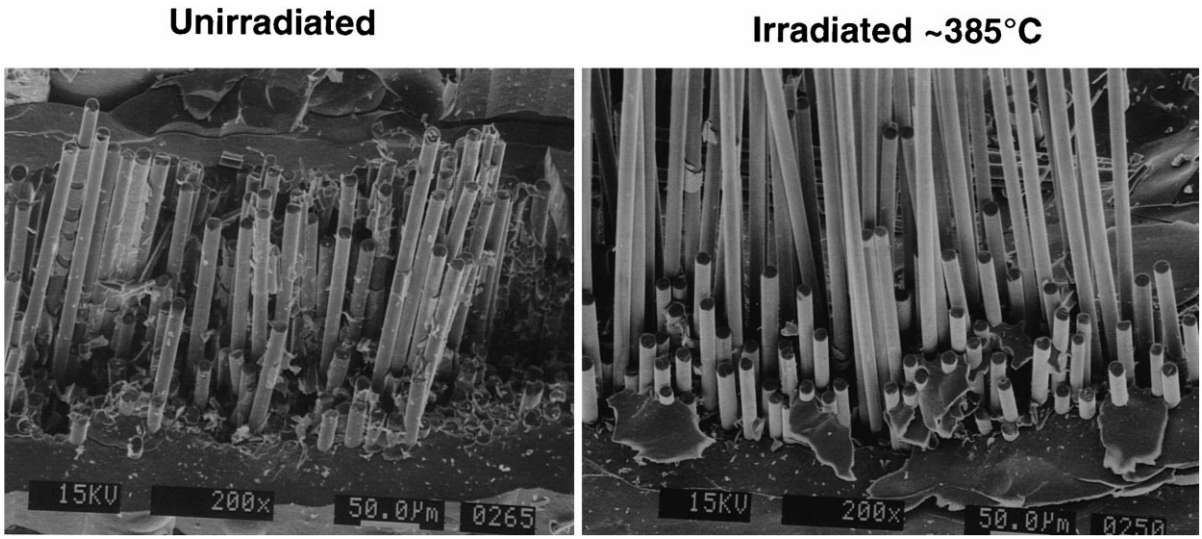

Fig. 6. SEM images of the fracture surfaces of unirradiated and irradiated multilayer SiC interphase composites.

ability of the matrix to transfer load across this interphase to the fiber is compromised. There is, however, an interfacial friction sliding stress which, while reduced [15], still allows some load to be transferred to the fibers with the overall effect of a weaker composite.

Figs. 5 and 6 are SEM micrographs for the Hi–Nicalon fiber reinforced materials irradiated in this study. Fig. 5 shows a comparison of the fiber pull-out length of the porous SiC interphase material for the unirradiated and irradiated cases. A comparison of these fracture surfaces indicates that the fiber pull-out length is greater for the irradiated composite. The same is true for the multilayer SiC interphase materials shown in Fig. 6. This enhanced pull-out is most likely due to a reduction in the interfacial shear stress. In comparison with the standard Nicalon fiber composite materials mentioned in the previous paragraph, this radiation-induced increase in pull-out length was far less substantial.

As mentioned in the introduction, the significant reduction in strength of earlier, ceramic grade Nicalon fiber composites was attributed to densification of the fiber. This behavior is in contrast to the usual radiation-induced lattice strain and swelling expected in SiC, which is given in Fig. 7 for fully dense, CVD SiC. Fig. 7 includes data on pyrolitic SiC published by Blackstone and Voice [23], Price [24–26], Snead et al. [27] and the present data on the Morton high purity CVD SiC. The assumption implicit in this data is that saturation expansion has occurred which, at least in the 100–900°C range, should be achieved by a few dpa [23]. This assumption is invalid at both the temperature extremes of the data in Fig. 7. Recent data [27] indicate that for temperatures of approximately 100°C amorphization of the crystal, with corresponding $\simeq 10\%$ swelling, occurs at less than 2.6 dpa. There also seems to be a discrepancy between the elevated temperature irradiations of this and the earlier literature data. Specifically, volumetric swelling occurred to 3.53% in the $1047 \rightarrow 960$°C irradiation and 4.4% in the $1060 \rightarrow 910$°C irradiation. The volumetric swelling at the high temperatures (> 800°C) is no longer dominated by defect strain but by the formation of interstitial Frank loops [28] and tetrahedral voids [26] and therefore will not saturate at low fluences. The high dose swelling behavior in this temperature range is not known. The intermediate temperature data for Morton CVD SiC of this study at 260°C and 385°C should be in the saturation regime for point defect swelling and agrees with the published data given in Fig. 7.

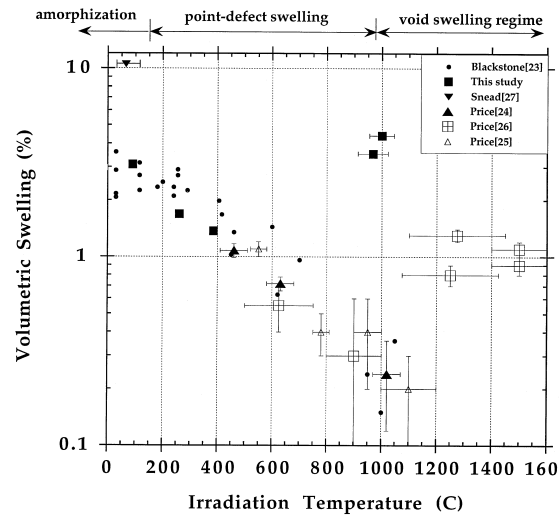

Fig. 7. Neutron-induced swelling of pyrolytic (CVD) SiC.

The volumetric swelling of the Morton CVD SiC should be analogous to the swelling which occurs in the matrix of the composites. While the composite consists of approximately 10% void fraction, these voids are primarily large ($\simeq 100$ μm) pores left by the infiltration process. As seen in Table 2, the length change of the composite materials irradiated at 385°C and 260°C generally agrees with the Morton CVD SiC linear swelling. It needs to be noted that due to surface roughness and machining non-uniformity it was difficult to accurately measure the composite thickness which is evident by the wide scatter in measured thickness values. The length measurements were more accurate and give a closer match to the CVD SiC swelling and are in general agreement with previous data on ceramic grade Nicalon fiber composites [16]. For the case of the composite material irradiated at 1060 → 910°C there is a poor match between the Morton CVD SiC and the length change of the composite. The experimental error in the density measurement of the Morton CVD material is $<$ 0.1% and it is unlikely that the experimental error in the length change of the three bend bars exceeded 0.2% (note the insignificant scatter of the measurements). This apparent discrepancy remains unanswered. Also of interest is that the change in the composite thickness, which corresponds to the direction normal to the fabric lay-up, for all three irradiation temperatures give comparatively large swelling. While there is admittedly larger measurement error in this direction, the lower end of the scatter in the values is consistently above the average length change for the composite and the volumetric change for the Morton CVD SiC. As will be discussed below, this apparent anisotropic composite swelling cannot be attributed to the fiber.

At the $\simeq 1.1$ dpa irradiation dose and the irradiation temperatures experienced by the composites of this study, the mechanical stability of the matrix material will be largely unaffected. Two studies on CVD SiC have indicated the bend strength is either unchanged [29] or undergoes a moderate reduction [30–33] at damage levels above about 10 dpa. As with the regular Nicalon fiber examined in previous studies [34], the low oxygen Hi–Nicalon fiber from which the composites of this study were fabricated undergoes significant physical property changes during irradiation. Specifically, the mean failure strength and Young's modulus are shown in Figs. 8 and 9, respectively. The error bars represent the 90% confidence limits for the Weibull distributed data. Data for two irradiation temperatures are given which bracket the lower temperature irradiations for the Hi–Nicalon fiber composite. A general trend towards increasing fiber strength is seen with an initial decrease in Young's modulus followed by a recovery to the unirradiated modulus values at >3 dpa. From the results in these two graphs it can be inferred that the fibers in the 1.1 dpa irradiated composites of this study would have undergone a slight ($\simeq 12\%$) increase in strength and decrease ($\simeq 7\%$) in Young's modulus. These tensile property changes, while significant, cannot explain the degradation in the irradiated composite strength summarized in Table 2.

As with the ceramic grade Nicalon fiber composites, the irradiation-induced degradation of the ultimate fracture strength of these Hi–Nicalon fiber materials appears to be dominated by the fiber/matrix interface. Similar to the ceramic grade Nicalon fiber behavior, the low oxygen Hi–Nicalon fiber undergoes radiation-induced densification. Fig. 10 gives a comparison of the normalized density change versus irradiation dose for the two fiber types and Morton CVD SiC. It is clear that the onset of densification occurs at a higher dose for the low oxygen fiber as compared with the ceramic grade Nicalon fiber and that

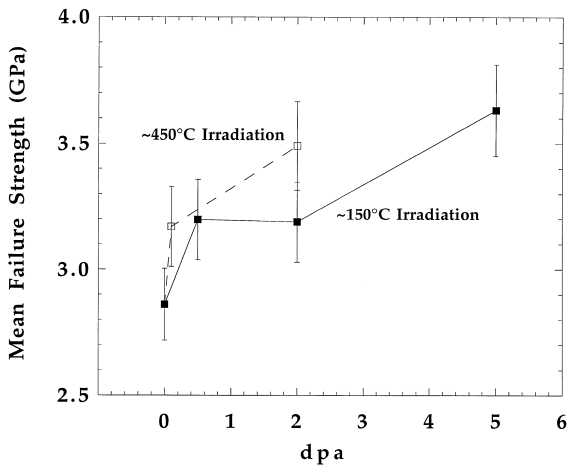

Fig. 8. The effect of irradiation on the tensile strength of bare Hi–Nicalon fiber.

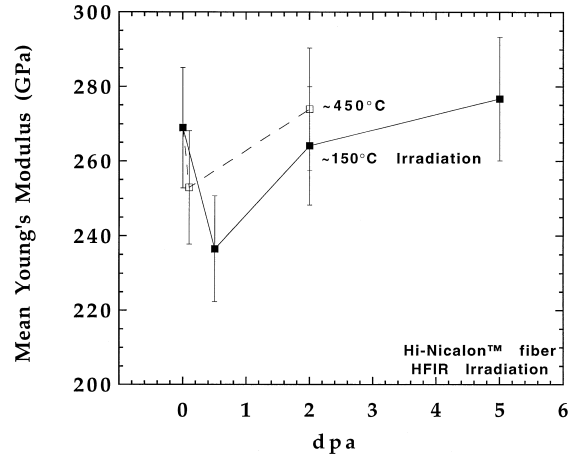

Fig. 9. The effect of irradiation on the Young's modulus of bare Hi–Nicalon fiber.

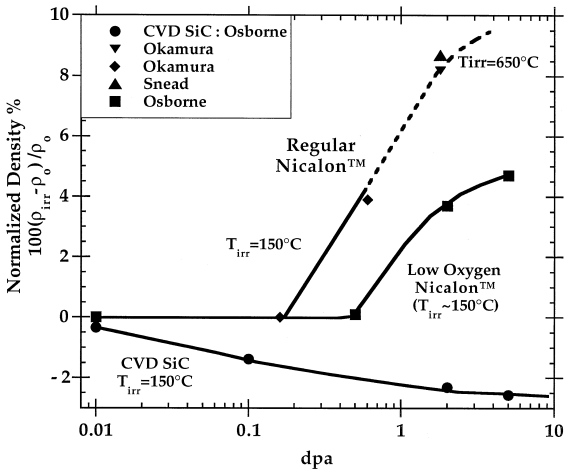

Fig. 10. Comparison of the effect of irradiation on the relative density change for regular and Hi–Nicalon fiber and CVD SiC.

the absolute increase in density is less for the reduced oxygen material. It should be noted that the highest dose data points for the regular Nicalon fiber are for 650°C irradiated material and are shown as an extrapolation of the 150°C, lower fluence data points. It is clear from the data in Fig. 10 that the behavior of both grades of Nicalon fiber is opposite to the point defect strain induced expansion expected for ceramics, and in particular CVD SiC irradiated at $\simeq$ 150°C.

If it is assumed that fiber in the composite densifies similarly to the bare fiber of Fig. 10, the Hi–Nicalon fiber irradiated to 1.1 dpa should undergo an approximately 2% increase in fiber density. This corresponds to $\simeq$ 50 nm decrease in (free) diameter as compared to the $\simeq$ 150 nm decrease which would be expected in ceramic grade Nicalon fiber materials. For both cases the result of the material irradiation is to develop a tensile stress at the interface between the fiber and the interphase. In the case of the irradiated ceramic grade Nicalon fiber materials this stress resulted in disruption of the interface between the carbon interphase and the fiber [15]. The Hi–Nicalon fiber composites irradiated in the current study, due to their reduced densification, should have significantly less induced tensile stress at the interphase. Whether partial or full disruption at the interphase has occurred is not known and will be resolved through direct TEM observation at a later date. However, a partial disruption of the porous SiC interphase would be consistent with the reduction in both the matrix microcracking and ultimate fracture strength observed. By the same reasoning it is also likely that the interphase of the multilayer SiC material has a higher retained interfacial shear stress, possibly due to the chemical bonding at the fiber/interphase interface, making a more radiation resistant structure. As a final note, there has been no measurement of the dimensional stability of the interphase itself. Both interfacial structures are primarily SiC with additional graphite in the form of dispersed islands in the case of the porous SiC and very thin ($\simeq$ 1–3 nm) graphite layers between the multilayer SiC. It is conceivable that the dimensional changes of the interphases themselves, along with the dimensional changes of the fiber and matrix, are combining to create the observed degradation in composite performance.

5. Conclusions

Reduced oxygen Hi–Nicalon fiber composite materials were fabricated with a CVI SiC matrix with interphases of either 'porous' SiC or multilayer SiC and irradiated to a neutron fluence of 1.1×10^{25} n m^{-2} ($E > 0.1$ MeV) in the temperature range of 260°C to 1025°C. Negligible reduction in the macroscopic matrix microcracking stress was seen for the multilayer SiC interphase material and a slight reduction in matrix microcracking stress was observed for the porous SiC material. The reduction for the porous SiC interfacial material is greatest for the higher temperature irradiation. The ultimate fracture stress for the multilayer SiC and porous SiC interphase materials was reduced by 15% and 30%, respectively, which is an improvement over the 40% reduction suffered by previously irradiated ceramic grade Nicalon fiber materials fabricated in a similar fashion, though with a carbon interphase. The absolute strength comparison is even more favorable for the irradiated Hi–Nicalon fiber composite due to the higher unirradiated matrix microcracking and ultimate fracture stresses of this material as compared to ceramic grade Nicalon fiber composites.

The irradiation-induced degradation of the ultimate fracture strength cannot be explained by a change in the mechanical properties of the fibers alone. At the 1.1 dpa dose level, the Hi–Nicalon fibers undergo a slight ($\simeq$ 10%) reduction in elastic modulus. The strength increase seen for the Hi–Nicalon fiber would have the effect of a slight increase in composite strength. The degradation of the Hi–Nicalon fiber composite material is consistent with a change in the stress state of the interphase, possibly caused by a mismatch in the swelling/densification behavior of the fiber, matrix or interphase. As with regular, ceramic grade Nicalon fiber, the reduced oxygen Hi–Nicalon fiber densifies during irradiation (in contrast to the swelling that occurs in pure SiC), though to a lower level.

It appears that the multilayer SiC interphase is more resistant to neutron damage than the porous SiC interphase applied in this study. The reason for this is unclear, though it is speculated that the interphase/fiber bond is stronger and therefore more resistant to tensile disruption caused by fiber densification. TEM examination of the irradiated composites will be required to clearly identify the failure mechanisms of these interphases.

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