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Evaluation of neutron irradiated near-stoichiometric silicon carbide fiber composites

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Abstract

Composites have been fabricated by chemical vapor infiltration of silicon carbide (SiC) into SiC-based fiber preforms. Fibers were Ceramic Grade Nicalon™, Hi-Nicalon™ and Hi-Nicalon™ Type-S. Results are presented for two parallel studies on the effects of neutron irradiation on these materials. In the first study, neutron irradiation induced changes in mechanical properties, as measured by bend testing, for Hi-Nicalon™ fiber materials of varied interphase structures is measured. Results indicate that both the Ceramic Grade Nicalon™ and Hi-Nicalon™ materials degrade substantially under irradiation, though the higher oxygen content Ceramic Grade fiber degrades more rapidly and more substantially. Of the three interfaces studied in the Hi-Nicalon™ system, the multilayer SiC is the most radiation resistant. At a dose of ~1 dpa the mechanical property degradation of the Hi-Nicalon™ composite is consistent with a fiber densification-induced debonding. At a dose of 10 dpa the properties continue to degrade raising the question of degradation in the CVD SiC matrix as well. Low-dose results on the Hi-Nicalon™ Type-S fabricated material are encouraging, as they appear to not lose, and perhaps slightly increase, in ultimate bend strength. This result is consistent with the supposition that as the oxygen content in SiC-based fibers is reduced, the irradiation stability and hence composite performance under irradiation will improve.

1. Introduction

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 [1]. The fibers are commercially available under the trade name of Nicalon™. 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.

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 [2] for pre-production 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 [3–5]. 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 [6,7]. Both studies describe the system as a dispersion 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

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in a helium environment. Cross-linking the PCS in this manner first used ultraviolet light [8,9], although the most successful demonstration is for the Nicalon preceramic polymer and uses electron irradiation [10,11]. 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 [11]. 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 irradiation [12]. It is the densification of these fibers that was identified early on as the source of the poor irradiation performance of SiC composites [13]. Recently, a further improvement in the Nicalon™ system has been achieved (Type-S Nicalon™). Essentially, the Hi-Nicalon™ process has been taken a step further with the result of a near theoretical density fiber with very low excess carbon and oxygen (<0.1%). A comparison of the physical properties of the three Nicalon™ SiC-based fibers taken from manufacturer's information is given in Table 1.

The following is a synopsis of two parallel studies on the effects of neutron irradiation on chemically vapor infiltrated SiC composites fabricated from the Nicalon™ family of fibers. In the first study, the neutron irradiation-induced mechanical properties of Hi-Nicalon™ fiber composites of varied interphase structures is presented. The three interphases chosen are pyrolytic carbon, pseudo porous SiC and multilayer SiC. In the second study, the mechanical properties of neutron irradiated composites fabricated from all three fiber types are presented including the first reported data on the irradiation performance of Nicalon™ Type-S composites.

2. Experimental

All composites, with the exception of the multilayer SiC interphase materials were processed at the High Temperature Materials Laboratory at the Oak Ridge National Laboratory using the forced chemical vapor infiltration (FCVI) method [14]. The infiltrated silicon carbide matrix was deposited from methyltrichlorosilane with a typical infiltration time of ~18 h. Carbon interphases for both the varied interphase and varied fiber studies were deposited by decomposition of propylene. The carbon interphase thickness was ~0.12 μm for the varied fiber studied and varied at ~0.1, 0.2 and 0.3 μm for the varied interphase study. The porous SiC interphase was deposited from a mixture of methyltrichlorosilane, argon, methane and hydrogen glow gases. The thickness of the porous SiC interphase was ~0.1 μm. For the case of the multilayer SiC interphase, there were four SiC multilayers applied with a thin (~20 nm) layer of pyrolitic carbon in between. The dimensions of the fabricated discs were 4.45 cm diameter and 1.25 cm thickness. Composites containing a multilayer SiC fiber coating were fabricated using isothermal chemical vapor infiltration of Hi-Nicalon™ fiber preforms by Hyper-Therm High-Temperature Composites, Inc. Further information on the manufacture of these composites is found elsewhere [15].

Two bend bar geometries were used. This first, consistent with previous work, was $2.5 \times 3 \times 25$ mm^3 with the axis normal to the weave being parallel to the 3×25 mm^2 plane. This geometry was used for the plain weave Hi-Nicalon™ fiber-varied interphase samples. Load and support spans were 5 and 20 mm, respectively The second geometry, selected as the new standard geometry, was $2.3 \times 6 \times 30$ mm^3 with the axis normal to the weave being normal to the 6×30 mm^2 plane. This geometry was used for the fiber comparison study. Load and support spans were 10 and 20 mm, respectively Bend testing was carried out under ambient conditions with a cross-head speed of 8.5×10^{-3} mm/s.

Materials were irradiated in three separate campaigns. The varied fiber study was irradiated in the peripheral target tube position of High Flux Isoptope Reactor (HFIR) in sealed 'rabbit' capsules in a static argon environment. The two fluences for these irradiations were ~0.6 or $1.03–1.18 \times 10^{25}$ n/m^2 ($E > 0.1$ MeV). The irradiation temperature was ~400°C for the $1.03–1.18 \times 10^{25}$ n/m^2 ($E > 0.1$ MeV) rabbits and ~300°C for the 0.6×10^{25} n/m^2 ($E > 0.1$ MeV) rabbit. These irradiation temperatures were determined by isochronal annealing of SiC temperature monitors. For

Table 1
Physical properties of Nicalon™ SiC-based fibers

	SiC (%)	C (%)	SiO_2 (%)	Density (g/cm^3)	Strength (GPa)	Modulus (GPa)	Grain size (μm)
Nicalon™	65	11	23	2.55	3	220	~3
Hi-Nicalon™	75	21	<1	2.74	2.8	270	~10
Hi-Nicalon™ Type-S	99+	<0.1	<0.1	3.08	2.4	408	>100

the varied interphase study, irradiations were carried out both in the High Flux Beam Reactor (RIP) in experiment SiC-1 and the HFIR in the MFE-12J experiment. The SiC-1 capsule was inserted into the V-16 in-core thimble of HFBR for a duration of one reactor cycle which corresponds to an approximate fast neutron fluence of 1.1×10^{25} n/m^2 ($E > 0.1$ MeV). Irradiation temperature was measured by thermocouple inserted into the vanadium sample holder. The MFE-12J experiment was a HFIR RB 500°C temperature controlled capsule which was irradiated for five cycles for a nominal dose of 1×10^{26} n/m^2 ($E > 0.1$ MeV). It is assumed an equivalence of one displacement per atom (dpa) $= 1 \times 10^{25}$ n/m^2 ($E > 0.1$ MeV).

3. Results

Table 2 gives the bend test results for the varied interphase study. The matrix micro-cracking and ultimate fracture stress are reported in both the non-irradiated and irradiated condition. The matrix micro-cracking stress was taken from the load–displacement curve as the departure from linearity and is therefore a macroscopic matrix cracking stress. Undoubtedly, the matrix micro-cracking had occurred at stresses below this value. In the non-irradiated condition several bend tests were conducted for each material, while only a few samples were tested in the irradiated condition.

Figs. 1–4 give the results for the varied fiber study in the form of sample flexure curves. Fig. 1 shows the flexure curves for non-irradiated and irradiated composites fabricated from Ceramic Grade Nicalon™. In this case, four non-irradiated flexure curves are shown exhibiting considerably different behavior among materials. Fig. 2 shows the flexure curves for the Hi-Nicalon™ Type-S fibers. Due to a limited amount of material, only two non-irradiated samples were tested. For this reason statistical limitations must be taken into account for the Type-S fiber composites. Figs. 3 and 4 give the normalized flexure curves for plane and 8H Satin weave composites produced from each fiber. In each case the stress has been normalized to its non-irradiated mean value (average value inset into graph).

4. Discussion

As previously reported [15] the low-dose (1.1 dpa) irradiation of the Hi-Nicalon™ fiber composites (Table 2) shows a significant reduction in bend strength. This has been attributed to a partial debonding between the interphase and the fiber (or matrix) [15,16]. As the dose

Table 2
Irradiation performance of Hi-Nicalon™ fiber, CVI SiC matrix composites

Sample	Matrix micro-crack stress (MPa)	Ultimate fracture stress (MPa)
Hypertherm multilayer SiC		
Unirradiated	250 ± 32 (6 tests)	507 ± 75 (6 tests)
Unirradiated, anneal 385°C (30 day)	264 ± 17 (5 tests)	438 ± 21 (5 tests)
Irradiated at 385°C ~1.1 dpa	290, 244	371, 462
Irradiated at 300°C ~10 dpa	240, 250, 275	326, 329, 331
Irradiated at 500°C ~10 dpa	220, 240	254, 278
ORNL pyrolitic SiC composite		
~0.1 μm interface (CVI-917)		
Unirradiated	261 ± 21 (4 tests)	369 ± 48 (4 tests)
Irradiated 300°C, 10 dpa	225, 250, 255	297, 307, 335
Irradiated 500°C, 10 dpa	175 ± 40 (4 tests)	132, 178, 211, 250
~0.2 μm interface (CVI-918)		
Unirradiated	214 ± 38 (4 tests)	375 ± 51 (4 tests)
Irradiated at 385°C ~1.1 dpa	172, 285	235, 347
~0.3 μm interface (CVI-919)		
Unirradiated	151 ± 26 (4 tests)	267 ± 70 (4 tests)
Irradiated at 260°C ~1.1 dpa	151, 206	203, 246
Irradiated 300°C, 10 dpa	190, 190, 240	202, 214, 275
ORNL porous SiC composite		
Unirradiated	298 ± 22 (8 tests)	515 ± 19 (8 tests)
Unirradiated, anneal 260°C (30 day)	335, 332	507, 510
Irradiated at 260°C ~1.1 dpa	268, 251	347, 344
Unirradiated, anneal 1000°C (30 day)	287, 415	457, 507
Irradiated at 1042–>910°C ~1.1 dpa	210, 201	332, 304

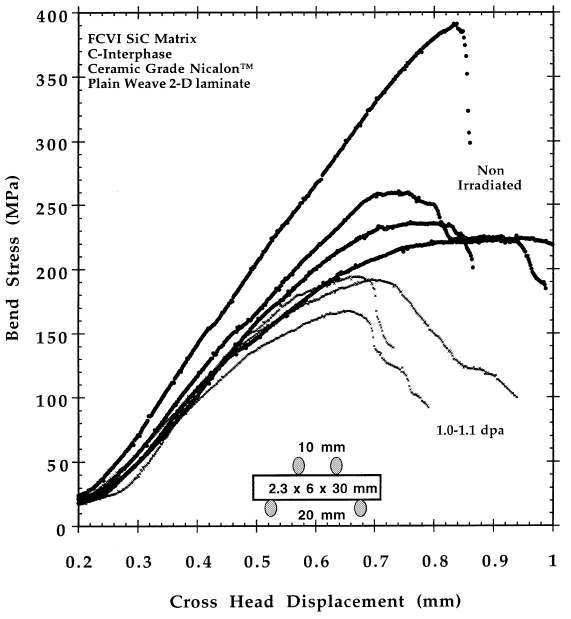

Fig. 1. Effect of ~1 dpa neutron irradiation on Ceramic Grade Nicalon™ fiber, CVI SiC matrix composite.

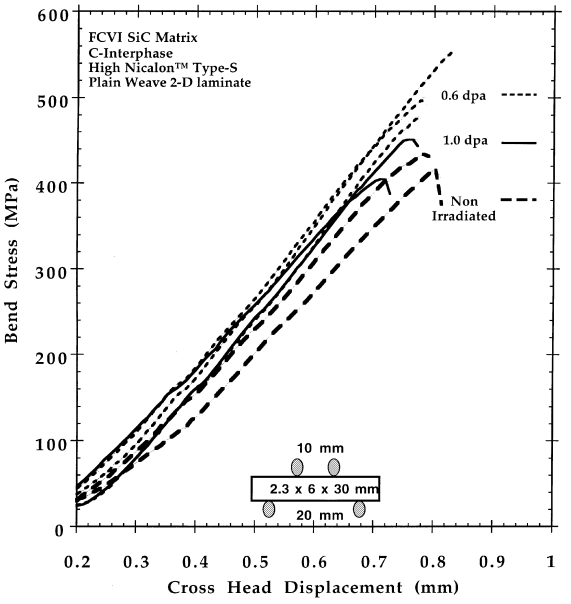

Fig. 2. Effect of ~1 dpa neutron irradiation on Hi-Nicalon™ Type-S fiber, CVI SiC matrix composite.

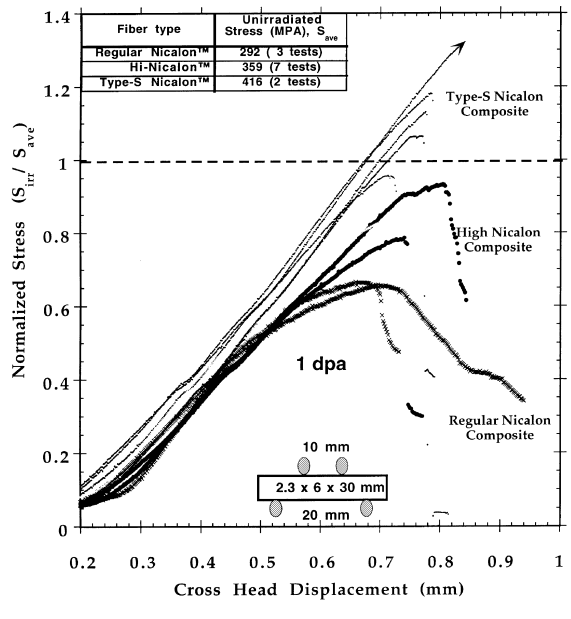

Fig. 3. Comparison of neutron irradiated plain weave CVI SiC composites with standard and reduced oxygen fibers.

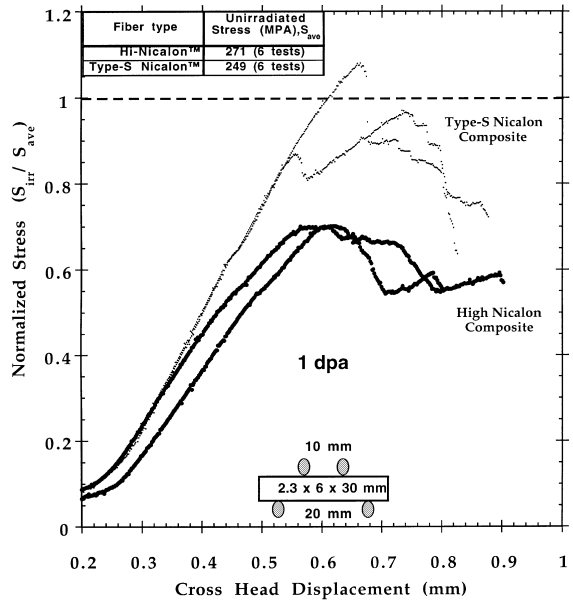

Fig. 4. Comparison of neutron irradiated 8H Satin weave CVI SiC composites with standard and reduced oxygen fibers.

is increased to 10 dpa (Table 2) the ultimate bend strength is further reduced, presumably caused by complete interfacial debonding. The matrix micro-cracking appears to be unaffected by the low-dose irradiation (Table 2). However, for the 10 dpa irradiation an apparent degradation in matrix micro-cracking occurs. While it is difficult to make any conclusions due to the limited number of tests, the matrix micro-cracking reduction is more pronounced for the 500°C irradiation as compared with the 300°C irradiation. Such degradation may be explained by a reduction in fracture strength of the CVD SiC. Decreasing fracture strength in CVD SiC

has been measured in one study by Dienst [17] at approximately 10 dpa.

Figs. 1–4 give clear evidence of the benefit to irradiation performance of reducing the oxygen content in the Nicalon™ fibers. By inspection of Figs. 1 and 2 it is apparent that a ~30% reduction of bend strength in the Ceramic Grade Nicalon™ composite occurs while the Type-S fiber composite exhibits no reduction. In fact, though adequate statistics are a limitation, it appears that a small initial increase in strength has occurred at the 0.6 dpa level. It should also be noted that there is a qualitative difference in the flexure curves of the Ceramic Grade and Type-S Nicalon™ composites. The Type-S fiber exhibits higher strength and essentially no post-ultimate load drop-off. However, the Type-S does sustain stresses well above its matrix micro-cracking stress and is therefore exhibiting composite toughness. The difference in behavior is likely due to the stiffer Type-S fiber (see Table 1) and possibly a difference in optimal carbon interphase thickness. However, the interphase thickness should be quite similar in all the three fiber composites for the fiber comparison study as the deposition conditions were identical. The absolute benefit of reducing the oxygen content in the Nicalon™ family fibers is shown in Figs. 3 and 4 for the plain and satin weave composite materials. For the low-dose irradiation (1 dpa) an approximately 40% reduction in bend strength occurs for the Ceramic Grade Nicalon™ composite, ~20% for the Hi-Nicalon™ composite and no reduction for the Type-S Nicalon™. The satin weave composite of Fig. 4 shows similar results.

5. Conclusions

1. Hi-Nicalon™ composites undergo significant reduction in bend strength due to fiber shrinkage and interfacial debonding similar to that experienced by Ceramic Grade Nicalon™ composites.
2. For the Hi-Nicalon™ system, the multilayer SiC interphase offers the most radiation resistance in ultimate bend strength.
3. Reducing the oxygen content in the Nicalon™ family fibers has a beneficial effect on the irradiated flexural properties. For the case of the very low oxygen content Type-S fiber (<0.1% SiO_2), no degradation in bend strength was observed. Higher dose irradiation will be necessary to determine when composite degradation may occur.

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