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Evaluation of neutron irradiated silicon carbide and silicon carbide composites

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Abstract

The effects of fast neutron irradiation on SiC and SiC composites have been studied. The materials used were chemical vapor deposition (CVD) SiC and SiC/SiC composites reinforced with either Hi-Nicalon™ Type-S, Hi-Nicalon™ or Sylramic™ fibers fabricated by chemical vapor infiltration. A statistically significant population of flexural samples were irradiated up to 4.6×10^{25} n/m^2 ($E > 0.1$ MeV) at 300, 500, and 800 °C in the High Flux Isotope Reactor at Oak Ridge National Laboratory. Dimensions and weights of the flexural bars were measured before and after the neutron irradiation. Mechanical properties were evaluated by four point flexural testing. Volume increase was seen for all bend bars following neutron irradiation. The magnitude of swelling depended on irradiation temperature and material, while it was nearly independent of irradiation fluence over the fluence range studied. Flexural strength of CVD SiC increased following irradiation depending on irradiation temperature. Over the temperature range studied, no significant degradation in mechanical properties was seen for composites fabricated with Hi-Nicalon™ Type-S, while composites reinforced with Hi-Nicalon™ or Sylramic fibers showed significant degradation. The effects of irradiation on the Weibull failure statistics are also presented suggesting a reduction in the Weibull modulus upon irradiation. The cause of this potential reduction is not known.

1. Introduction

Silicon carbide has been considered for use in nuclear systems due to its excellent high-temperature properties, good corrosion resistance, low neutron absorption cross-section, and stability under neutron irradiation. Moreover, the low neutron induced radioactivity inherent to SiC offers economic (waste disposal) and potential maintenance benefits. For these reasons SiC composites, which offer flaw tolerance and more uniform failure as compared to monolithic SiC, are being considered for application in fusion power systems, the Gen IV gas fast reactors (GFR), and next generation nuclear power (NGNP) reactors. SiC is also the primary barrier material for TRISO coated fuel particles used in these high-temperature gas cooled reactors.

A fundamental hurdle to the application of SiC as a structural material for nuclear systems is the

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inherent brittle and erratic fracture mode of monolithic SiC. For over a decade nuclear programs have followed the research carried out under such programs as the DOE Continuous Fiber Ceramic Composite and Fossil Energy programs as well as the work by NASA and others toward the development of SiC fiber, SiC matrix composites. While the issues for nuclear application of SiC are somewhat different than these non-nuclear programs, the potential benefit of the composites are the same [1–6]. By incorporation of continuous fibers into SiC, cracks that would otherwise propagate and cause catastrophic failure are tied-up at the fiber/matrix interface. For this reason, well engineered SiC/SiC composites exhibit higher fracture toughness and less scatter in mechanical properties compared to monolithic SiC [7,8].

Despite these potential attributes, SiC/SiC composites are relatively new, and therefore, lack comprehensive data for both mechanical properties and irradiation-modified properties. This situation is compounded by the evolution of improved fibers (toward more stoichiometric microstructures), which further drives the need for continuing irradiation-effects programs. For this reason the effects of irradiation on fiber and composites are somewhat limited. Moreover, the irradiation-effects data on high purity SiC are also quite limited. The objective of this work is to quantitatively understand neutron irradiation effects on mechanical and physical properties of SiC and SiC/SiC composites, including composites reinforced with highly pure and fully crystalline fibers. Particular emphasis is placed on irradiation of materials in sufficient quantity, and with a unified geometry, such that the statistical nature of the mechanical property changes is understood.

2. Experimental

Materials used in this work were monolithic chemical vapor deposited (CVD) SiC (CVD silicon carbide®, Rohm and Haas Co.) and SiC/SiC composites with 2D plain-weave reinforcements of either Hi-Nicalon™ Type-S, Hi-Nicalon™ (Nippon Carbon Co., Ltd.), or Sylramic™ (Dow Corning Corp.) fibers. Composite plates were manufactured by hypertherm high temperature composites in a single batch process. The fiber–matrix interphase and composite matrix are therefore considered to be the same for all composite materials. Where the Hi-Nicalon™ fiber contains nominally 75% SiC, 21% C and ~1% SiO_2, the Hi-Nicalon™ Type-S fiber contains 99% SiC, ~1% C, and well under 0.1% SiO_2. The elastic modulus of the Hi-Nicalon™ Type-S fiber is considerably higher than that of the Hi-Nicalon™ fiber, 408 GPa as compared to 270 GPa. Moreover the density of the Hi-Nicalon™ Type-S is 3.08 g/cc as compared to 2.74 g/cc for the Hi-Nicalon™ fiber. The Sylramic fiber is similar to the Hi-Nicalon™ fiber in that it is significantly off stoichiometry with 28.5% C, 0.7% O, 2.1% Ti, 2.3% B, and 0.4% N, balance SiC. However, the density of 3.1 g/cc is closer to that of the Hi-Nicalon™ Type-S.

The SiC/SiC composites were fabricated by Hypertherm Inc. using an isothermal chemical vapor infiltration (ICVI) method with multilayer fiber coatings of C and SiC. In the multilayer C/SiC interphase, the first SiC layer of 100 nm thick was deposited following the deposition of a thin carbon (C) layer of 20 nm. Then, three SiC/C bi-layers were deposited as shown in Fig. 1. The materials were machined into flexural bars with dimensions 50.7 (long) $\times$ 6.28 (wide) $\times$ 2.84 (thick) mm. This thickness corresponds to ~14 fabric layers. As these samples were machined from thick plate all surfaces contain 'disrupted' fabrics with exposed fibers. It is expected that some of the statistical variability in flexural strength is due to the position of the outer fabrics and the amount of fiber machined from that surface fabric layer. Mean measured density of CVD SiC and composites reinforced with Hi-Nicalon™ Type-S, Hi-Nicalon™ or Sylramic before irradiation was 3.20, 2.52, 2.51 and 2.53 g/cc, respectively.

Flexural bars were irradiated in the target region of the high flux isotope reactor (HFIR) at Oak Ridge National Laboratory with total fluences of 0.6×10^{25} n/m^2–4.6×10^{25} n/m^2 ($E > 0.1$ MeV). Irradiation capsules were filled with static ultra high purity helium, neon, or argon depending on the target temperature. Each bend bar had a SiC temperature monitor pressed to its surface with a spring. Irradiation temperatures were ~300, 500, and 800 °C as measured by post-irradiation annealing of the SiC temperature monitors. The accuracy in temperature was ±20 °C. An equivalence of one displacement per atom (dpa) = 1×10^{25} n/m^2 ($E >$ 0.1 MeV) is assumed based on calculations using the HFIR neutron spectrum and an assumed displacement energy of 30 eV.

Dimensions and mass of all flexural bars were measured before and after neutron irradiation.

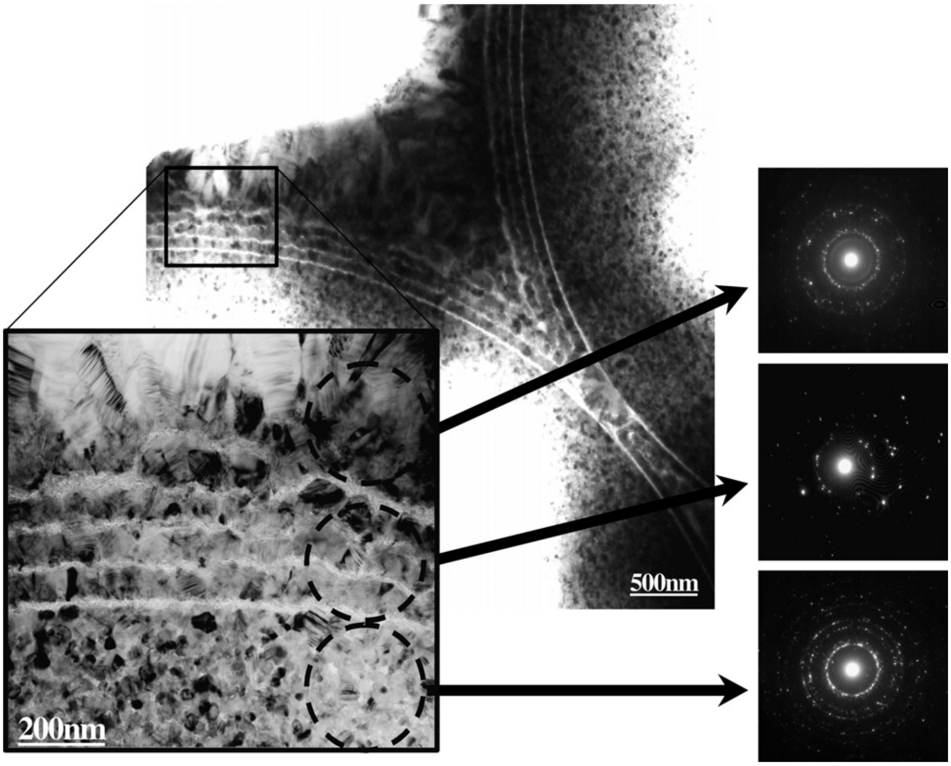

Fig. 1. TEM images of multilayer interphase of SiC/SiC composites.

Mechanical properties were evaluated by four-point flexural testing at ambient temperature for both irradiated and non-irradiated specimens according to ASTM C1341-00. The support span and the loading span were 40 and 20 mm, respectively. This span, along with the physical dimensions of the sample, resulted in a primary tensile surface failure as opposed to an interlaminar composite failure. The crosshead speed was 8.5 μm/s. The crosshead displacement was used to determine the specimen deflection. The compliance of the test set-up was measured using a thick block of rigid material (sintered α-SiC, Hexoloy® SA, 100 (long) × 25 (wide) × 15 (thick) mm), which is noncompliant relative to the load train. Elastic modulus, proportional limit stress (PLS) and flexural strength were obtained from evaluation of the compliance-corrected stress–strain curves. Elastic modulus was calculated by drawing a tangent to the steepest straight-line portion. Dynamic elastic modulus was also measured for non-irradiated specimens by impulse excitation and vibration method following ASTM C1259-01. The PLS was defined by the authors as the stress at which it deviates from linear fit to the proportional portion by 5%. Flexural strength was the maximum stress endured.

The majority of data presented in this paper assumed normal distribution and is presented as the mean value ±1 standard deviation. The reason for choosing this distribution is that for each condition of irradiation temperature and fluence between four and twelve bend bars were irradiated, which is less than the 15–30 data point recommended for Weibull analysis. In the discussion section, data are combined and a two-parameter Weibull analysis is performed.

3. Results

3.1. Volume change following neutron irradiation

Volumetric swelling of each bend bar was estimated from the dimensions of the flexural bars before and after neutron irradiation. Fig. 2 shows the dependence of swelling of CVD SiC on fluence and irradiation temperature. Error bars represent ±1 standard deviation. The magnitude of swelling for the CVD SiC depended on the irradiation

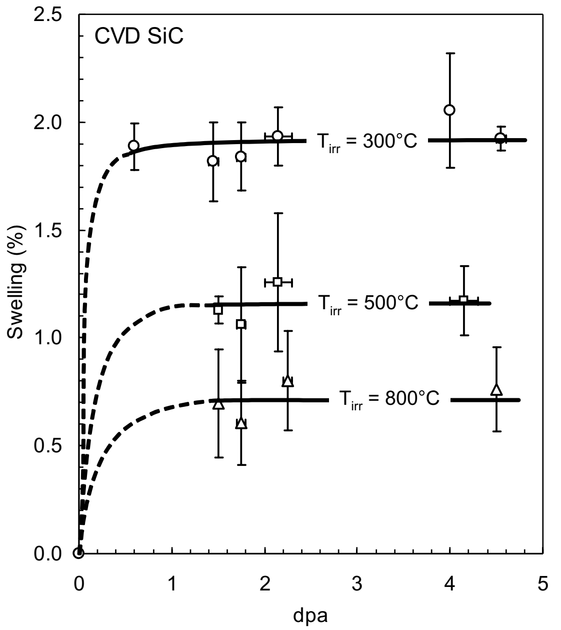

Fig. 2. Effect of irradiation fluence and temperature on volume change of CVD SiC.

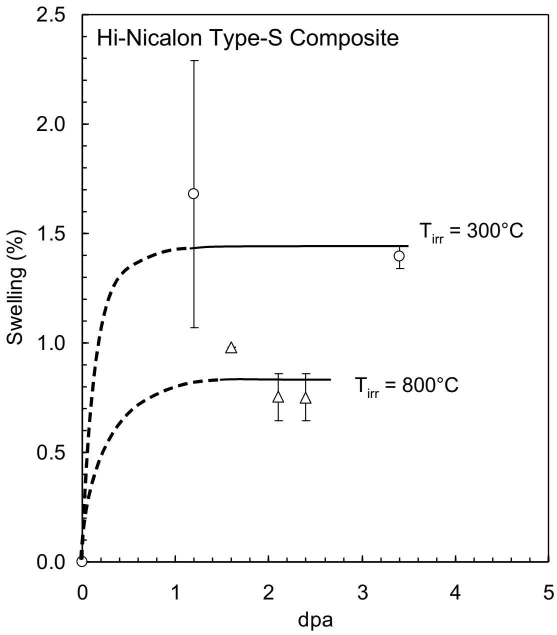

Fig. 3. Effect of irradiation fluence and temperature on volume change of composites reinforced with Hi-Nicalon™ Type-S fibers.

temperature, while it is nearly independent of irradiation fluence within the irradiated dose range. The magnitude of swelling decreased with increasing irradiation temperature. The magnitude of swelling saturated at approximately 1.9%, 1.1% and 0.7% at the irradiation temperature of 300 °C, 500 °C and 800 °C, respectively.

The same tendency for swelling, which depends on irradiation temperature and is independent of irradiation fluence after reaching saturation, was seen in composite materials used in this work. Figs. 3 and 4 show the effect of neutron irradiation on swelling of composites reinforced with Hi-Nicalon™ Type-S fibers and composites reinforced with Hi-Nicalon™ fibers, respectively. The magnitude of swelling of the composites reinforced with Hi-Nicalon™ Type-S fibers saturated at approximately 1.4% and 0.8% at the irradiation temperature of 300 °C and 800 °C, respectively. The magnitude of swelling of the composites reinforced with Hi-Nicalon™ fibers saturated at approximately 1.4%, 1.0%, and 0.6% at the irradiation temperature of 300 °C, 500 °C and 800 °C, respectively.

The magnitude of swelling for CVD SiC was larger than that of composites reinforced with Hi-Nicalon™ fibers at all irradiation temperatures. Moreover, CVD SiC swelling was larger than that of composites reinforced with Hi-Nicalon™ Type-S

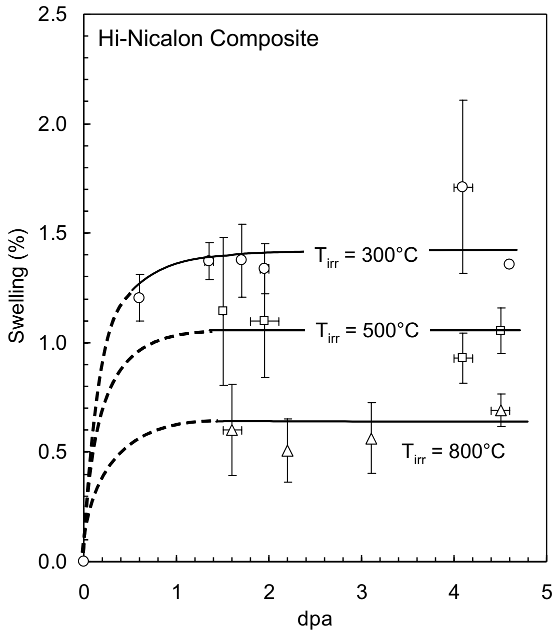

Fig. 4. Effect of irradiation fluence and temperature on volume change of composites reinforced with Hi-Nicalon™ fibers.

fibers at 300 °C irradiation, while it was about the same at 800 °C irradiation. Only 9 bars of Sylramic fiber composite were evaluated following irradiation at 1.1–1.4 dpa and 300 °C. The magnitude of the swelling of composites reinforced with Sylramic fibers was 3.2%, significantly higher than the other materials. Higher temperature irradiation led to physical destruction of the Sylramic composites, therefore swelling was not considered meaningful to report. There was no appreciable mass change in any materials studied.

3.2. Neutron irradiation effect on mechanical properties

Raw data for the mechanical property tests, including the statistics of testing, are provided in Tables 1–3. A typical flexural stress–strain curves of CVD SiC and composites reinforced with Hi-Nicalon™ Type-S and Hi-Nicalon™ fibers before and after irradiation at 800 °C is depicted in Fig. 5. The irradiation doses are 2.2, 2.1 and 2.2 dpa for CVD SiC, Hi-Nicalon™ Type-S composites and Hi-Nicalon™ composites, respectively. The CVD SiC exhibits brittle fracture behavior and the PLS corresponds to flexural strength. The elastic modulus of CVD SiC is somewhat greater than that of composite materials, as seen by the slope of the load–displacement curves. As will be seen later, the strength of irradiated CVD SiC undergoes a modest increase as depicted by the traces in Fig. 5. A slight decrease in the elastic modulus of CVD SiC would also be expected, though this is not apparent from the Fig. 5. Moreover, of the two composite systems the Hi-Nicalon™ Type-S has a statistically insignificant change in strength while the irradiated Hi-Nicalon™ composites undergoes substantial degradation.

In the non-irradiated state, composites reinforced with Hi-Nicalon™ Type-S fibers exhibit a more brittle fracture behavior as compared with the Hi-Nicalon™ fiber composites. For composites reinforced with Hi-Nicalon™ Type-S fibers, PLS was 15–30% lower than the flexural strength in both non-irradiated and irradiated states. As stated previously, no significant irradiation effect on the strength was observed in composites reinforced with Hi-Nicalon™ Type-S fibers. The same applies to the PLS for the Hi-Nicalon™ Type-S composites. However, a slight decrease in the slope near the stress maximum was observed for the neutron irradiated material. This was a consistent finding, though as seen by comparing the Hi-Nicalon™ Type-S composite traces of Fig. 5, was not a significant effect. In contrast, a large decrease of PLS, flexural strength, and elastic modulus was seen in composites reinforced

Table 1
CVD SiC

Irradiation temperature (°C)	DPA	Number of valid tests	Flexural strength (MPa)	
			Average	Std. dev.
N/A	0	25	426.1	53.1
300	0.6	2	512.9	36.1
	1.4–1.5	19	536.2	154.4
	1.7–1.8	8	553.5	127.0
	2.0–2.3	16	611.3	94.4
	4.0	8	598.0	89.7
	4.5–4.6	4	591.0	67.8
500	1.5	4	428.3	112.6
	1.7–1.8	14	515.2	113.6
	2.0–2.3	26	551.8	105.1
	4.0–4.3	11	555.8	127.5
800	1.5	6	513.1	67.0
	1.7–1.8	7	576.5	83.2
	2.2–2.3	19	565.4	71.2
	4.5	2	539.0	96.5

Table 2
Hi-Nicalon™ Type-S

Irradiation temperature (°C)	DPA	Number of valid tests	Prop. limit stress (MPa)		Flexural strength (MPa)	
			Average	Std. dev.	Average	Std. dev.
N/A	0	30	375.0	50.9	469.9	70.1
300	1.2	4	341.0	27.1	413.0	34.6
	3.4	2	332.4	4.5	420.4	29.8
500	1.8	2	355.3	44.3	444.0	7.2
800	0.7	2	342.6	22.6	475.2	20.7
	1.6	2	306.2	21.6	422.9	35.2
	2.1	4	344.5	7.8	450.0	22.4
	2.4	2	300.5	2.8	440.8	2.7

Table 3
Hi-Nicalon™

Irradiation temperature (°C)	DPA	Number of valid tests	Prop. limit stress (MPa)		Flexural strength (MPa)	
			Average	Std. dev.	Average	Std. dev.
N/A	0	37	326.2	35.5	508.9	62.4
300	0.6	2	239.2	13.6	348.9	31.6
	1.3–1.4	10	217.4	31.4	307.6	46.8
	1.7	4	220.7	17.0	328.8	27.0
	1.9–2.0	4	221.0	22.6	297.3	46.5
	4.0–4.2	6	206.7	30.3	279.0	37.4
	4.6	2	229.0	0.8	298.5	5.4
500	1.5	6	258.8	52.9	357.0	64.7
	1.8–2.1	10	238.3	27.6	327.6	42.3
	4.0–4.2	6	220.1	7.1	299.2	23.3
	4.5	2	247.6	10.8	340.0	35.2
800	1.5–1.7	6	264.3	29.6	346.2	42.8
	2.2	7	241.7	17.2	323.1	34.5
	3.1	2	205.4	34.2	281.9	52.3
	4.4–4.6	8	233.5	55.8	309.9	26.0

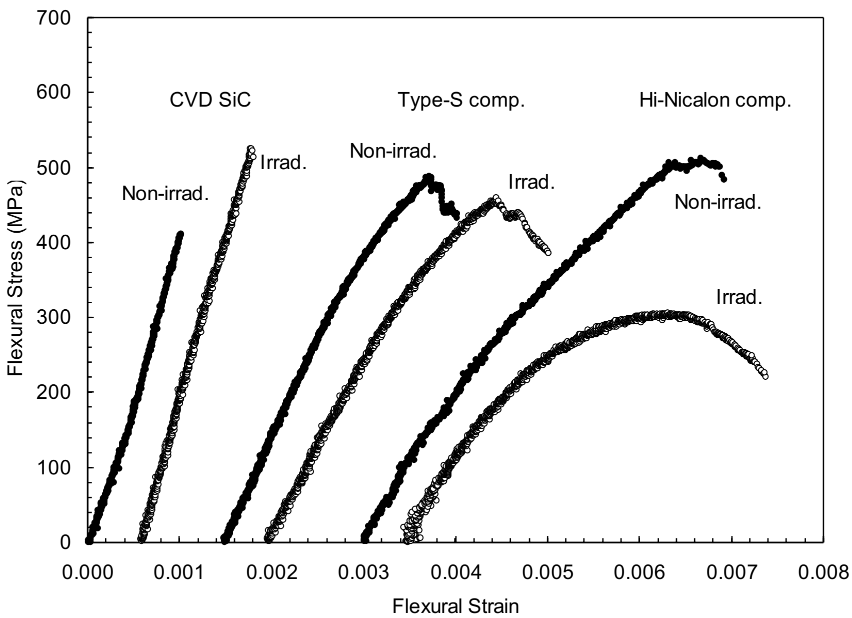

Fig. 5. Typical flexural stress-strain curves of non-irradiated and irradiated (at 800 °C) CVD SiC (2.2 dpa), Hi-Nicalon™ Type-S composites (2.1 dpa) and Hi-Nicalon™ composites (2.2 dpa). Curves offset from zero strain for clarity.

with Hi-Nicalon™ fibers following irradiation. More than 30% of flexural strength was lost upon irradiation.

Composites reinforced with Sylramic fibers showed a very brittle fracture behavior and a near complete absence of fiber pull-out. The proportional limit stress and flexural strength of these composites was much smaller than those of the Nicalon™ family fiber composites, though the elastic modulus was greater. In the irradiated state, the elastic modulus, PLS and flexural strength decreased to less than half the value of the non-irradiated material.

The effects of neutron fluence on elastic modulus of CVD SiC and Hi-Nicalon™ and Hi-Nicalon™ Type-S composites are shown in Fig. 6. The flexural

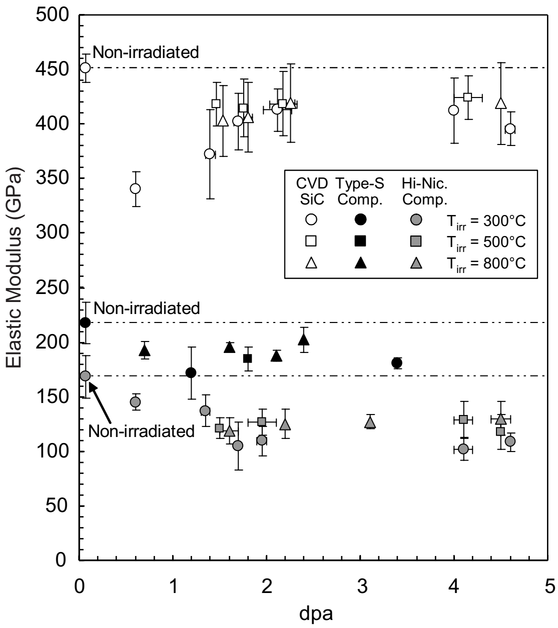

Fig. 6. Effect of fluence on elastic modulus of CVD SiC and tangential modulus of composites reinforced with Hi-Nicalon™ Type-S and Hi-Nicalon™ fibers.

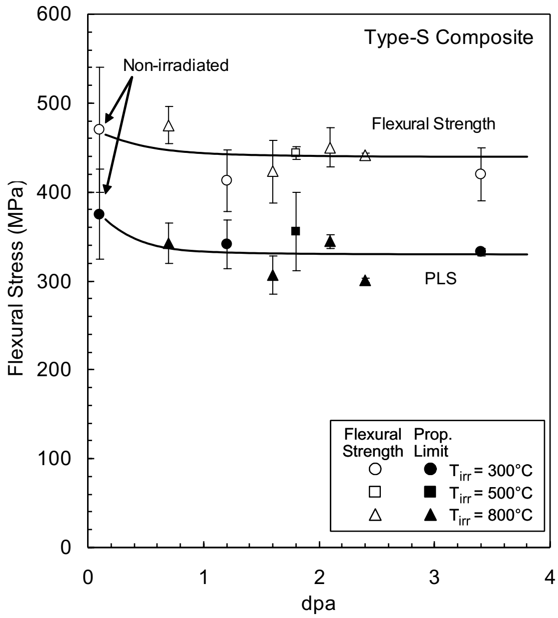

Fig. 8. Effect of fluence on proportional limit stress and ultimate flexural strength of composites reinforced with Hi-Nicalon™ Type-S fibers.

strength of the irradiated CVD SiC is given in Fig. 7 as a function of neutron fluence. The flexural strength and PLS are plotted against neutron damage for composites reinforced with Hi-Nicalon™ Type-S and Hi-Nicalon™ fibers in Figs. 8 and 9, respectively. Error bars represent ±1 standard deviation. As seen in the figures, the magnitude of PLS and flexural strength tends to saturate for doses >1 dpa.

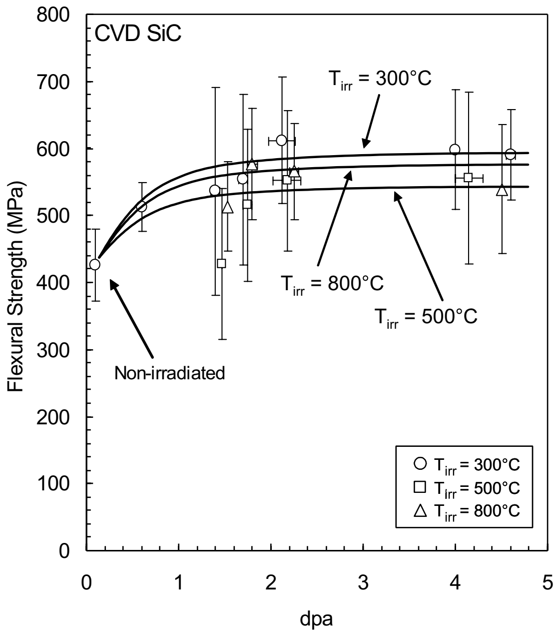

Fig. 7. Effect of fluence on flexural strength of CVD SiC.

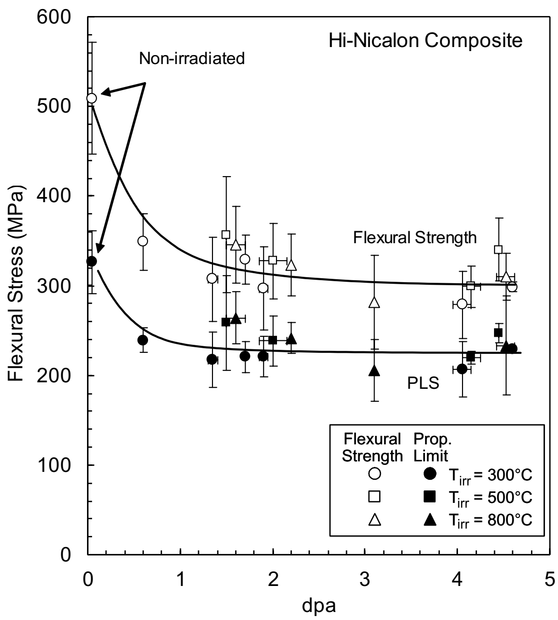

Fig. 9. Effect of fluence on proportional limit stress and flexural strength of composites reinforced with Hi-Nicalon™ fibers.

4. Discussion

4.1. Swelling

The effect of neutron irradiation on SiC swelling behavior has been widely studied. In the lowest temperature regime (<150 °C) amorphization of the SiC crystal has been demonstrated under neutron irradiation by Snead and Hay [9]. Significant changes in thermophysical properties occur upon amorphization, including an ~11% volume expansion. Above the critical temperature for amorphization (~150 °C) the crystal retains its identity, though significant strain due to the formation of interstitials occurs. This is generally referred to as the point-defect dominated regime and has a strong temperature dependence and exhibits saturation swelling at relatively low damage levels (a few dpa.) The temperature dependence for swelling in this regime is driven by the temperature-dependent mobility and stability of silicon and carbon interstitials and clusters reducing the surviving defects following cascade events, thereby reducing crystal lattice strain. As the mobility of both interstitial types is significant for temperatures approaching 1000 °C, the surviving defect fraction is quite small and the associated swelling approaches zero. However, with the enhancement of diffusion, extended defect formation becomes important. Early work by Price [10] reported loop or void formation for irradiation above 1000 °C. Later work by Yano and Iseki [11] identified interstitial Frank loop formation for heavily irradiated α and β SiC at 840 °C. However, for temperatures less than 1000 °C significant swelling apparently does not occur [12] due to these defects. For temperature above 1000 °C [12] Price has shown significant swelling, though the magnitude and temperature and fluence dependence of this swelling is not well understood due to the limitations of the previous experiments. Moreover, this high-temperature swelling will likely not saturate with dose [12], and as irradiation temperature increases, the amount of swelling may decrease due to thermal emission of vacancies.

The irradiations carried out in this work were in the intermediate temperature regime (~150 °C–1000 °C) where point defect swelling is dominant. The magnitude of swelling for the CVD SiC saturated at low fluence and decreased with increasing temperature. Specifically, for 300, 500, and 800 °C irradiations, the saturation swelling was 1.9, 1.1, and 0.7%, respectively. Swelling estimated from the work of Price et al. [12] including α and β-SiC of several types (i.e. CVD, single crystal and self-bonded), was approximately 2.2%, 1.5% and 0.5% at these temperatures of interest. Although the swelling results in the present work are somewhat lower than this previous work, results are in general agreement with the results for CVD SiC alone obtained by Price [13], Snead et al. [14,15] and Katoh et al. [16] elsewhere. The reason for the discrepancy with the earlier Price work could be due to a number of factors including the purity of material and issues dealing with the irradiation itself (i.e., temperature).

Composites reinforced with Hi-Nicalon™ Type-S fibers showed similar swelling behavior to that of CVD SiC, although the trend is not as clear as that of CVD SiC due in part to the limited amount of data. However, the swelling behavior of high purity fibers is known to be similar to that of CVD SiC [17]. The slight difference in the magnitude of swelling for the composites reinforced with Hi-Nicalon™ Type-S from that of CVD SiC might be attributed to the presence of the fiber/matrix interphase and the slight difference in swelling between the fiber and CVD SiC. Moreover, the swelling behavior is complicated for composites due to intrinsic cracking which may initially accommodate swelling. Further investigations into the interplay of the irradiation effects on fiber, matrix, interphase, and intrinsic cracking are required in particular to understand the swelling saturation behavior for the composite.

Composites reinforced with Hi-Nicalon™ fibers also showed similar swelling behavior to that of CVD SiC, although the magnitude was less. It was reported that Hi-Nicalon™ fibers underwent shrinkage of approximately 1.8% following neutron irradiation at 500–550 °C [18], while identically irradiated CVD SiC underwent swelling of approximately 1.1% [18] in agreement with the 500 °C irradiation of this work. The magnitude of swelling of the composites reinforced with Hi-Nicalon™ fibers seems high considering the shrinkage of the fiber, if fiber/matrix interfacial bonding was rigid. However, interfacial debonding following irradiation was reported by Snead in composites reinforced with Nicalon™ [19] and Hi-Nicalon™ [20] fibers. For this reason the macroscopic swelling for the Hi-Nicalon™ composites is considered independent of the fiber.

Composites reinforced with Sylramic fibers showed the largest swelling following 300 °C irradiation. It was reported that the magnitude of swelling of Sylramic fiber was approximately 3.2% following neutron irradiation at 500–550 °C [21], while 1.1% in CVD SiC for the same irradiation condition. It is speculated that the reason for the gross swelling in the Sylramic fibers is due to the boron impurity present in the Sylramic fibers. Without elimination of the B-10 present by isotopically tailoring or Sylramic fiber processing changes, use of this fiber for nuclear systems appears problematic.

4.2. Elastic modulus

The reduction of elastic modulus has not been previously reported by flexural evaluation, although some decrease of elastic modulus has been reported by application of indentation techniques [18,22,23] to neutron irradiated materials. As discussed by Katoh elsewhere [15] the slight reduction in elastic modulus is consistent with and a result of the lattice expansion. From the CVD SiC data of Fig. 6 a clear, immediate, decrease in elastic modulus is observed followed by a statistically supportable recovery, though for the irradiation condition of this study the elastic modulus does not fully recover. This observation supports similar observations done on the more limited datasets [18,22,23] of the previous work. Moreover, the present data samples much larger volumes as compared to the previous nano-indentation techniques and is therefore more representative of this materials use as a structure.

4.3. Flexural strength

4.3.1. Monolithic SiC

There have been several studies of the effect of irradiation on the mechanical properties of monolithic SiC [12,13,15,24–34]. When considering the irradiation effects on the strength of SiC, it is important to differentiate between the stoichiometric and non-stoichiometric ceramics. Forms of SiC include reaction bonded, sintered, pressureless sintered, SiC converted from reaction of graphite with molten Si or silicon monoxide, SiC derived from polymer precursors, and materials formed from the decomposition of gasses such as methyl or ethyltrichlorosilane (MTS or ETS.) In each case, chemical impurities are present at some levels within the SiC grains. The highest purity materials tend to be those manufactured from gas phase decomposition. As example, the Rohm & Haas CVD material used in this study has a manufacturer quoted chemistry of less than a part per million for metallic impurities. However, examples of CVD SiC deposited from MTS with as much as 6.3 wt% free silicon have been studied and results indicate that both high-temperature and irradiation performance suffers [35]. In some forms studied, such as the commercial reaction-bonded Norton NC-430, molten silicon is added to SiC and graphite powder resulting in 8–10% free silicon which resides at crystallite boundaries. Sintered materials have been made with either B (~0.4 wt% Carborundum α-SiC), Si, Al or rare earth oxide as sintering aids, with the sintering-aid primarily residing at the grain boundary in the final form.

Fig. 7 clearly indicates an increase in flexural strength for the CVD SiC irradiated in the study. While the increased flexural strength is statistically significant, the effect of temperature, if any, is obscured by statistical variation. Fig. 10 shows a comparison of the normalized flexural strength data from the present work and of Price [12,24], Dienst [27] and Snead et al. [36] on pyrolitic (CVD) SiC. For all cases, the values are for Weibull's mean with error bars indicating ±1 Weibull's standard deviation. However, while the work of Dienst [27,32] references the use of ten samples per condition and gives Weibull's mean and modulus, no standard deviation was given. The dotted lines of the figure are approximations of this standard deviation as calculated using Weibull data provided by Dienst [27,32]. From the compilation data of Fig. 10 it appears that a real increase in flexural strength occurs for CVD SiC for doses of less than 10 dpa. For doses greater than 10 dpa the effect of irradiation on flexural strength is less clear in that the data of Price [24] and Dienst [27] are contradictory. Unfortunately, the stoichiometry and density of the material used are not given, so the presence of free silicon cannot be dismissed as the mechanism responsible for the strength reduction. Higher dose irradiations are required to determine if the strength reduction for doses greater than 10 dpa is real.

As mentioned earlier, the presence of free silicon in some pyrolitic SiC, or the presence of Si or other sintering aids in powder processed SiC has a great influence on strength and other mechanical properties of irradiated SiC. This point can be illustrated by inspection of Fig. 11, which contains a compilation of data on powder-processed forms of SiC. In this plot error bars refer to ±1 standard deviation for normally distributed data. Insufficient data was available for Weibull analysis. Clearly, normalized flexural strength is substantially degraded at relatively low

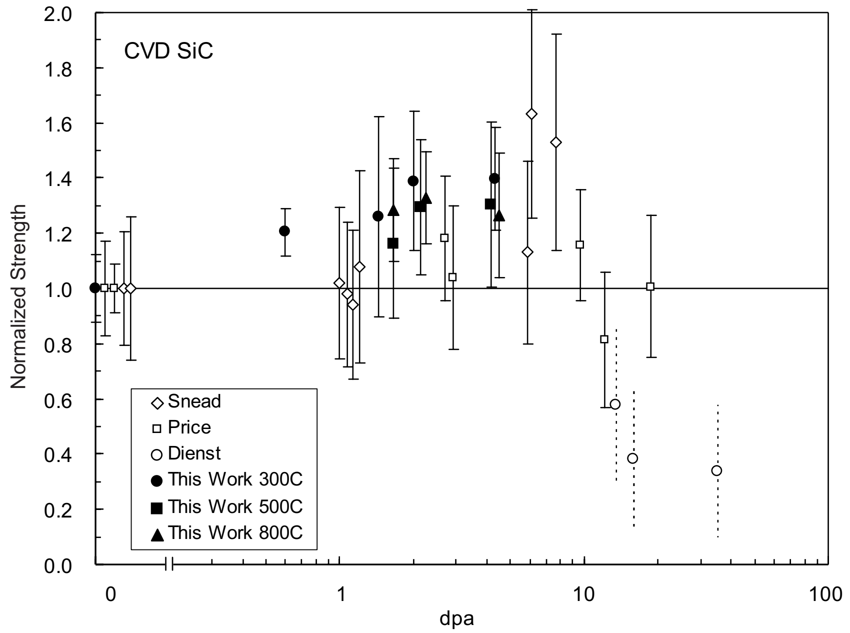

Fig. 10. Fluence dependence of irradiated flexural strength of CVD SiC normalized to unirradiated strength.

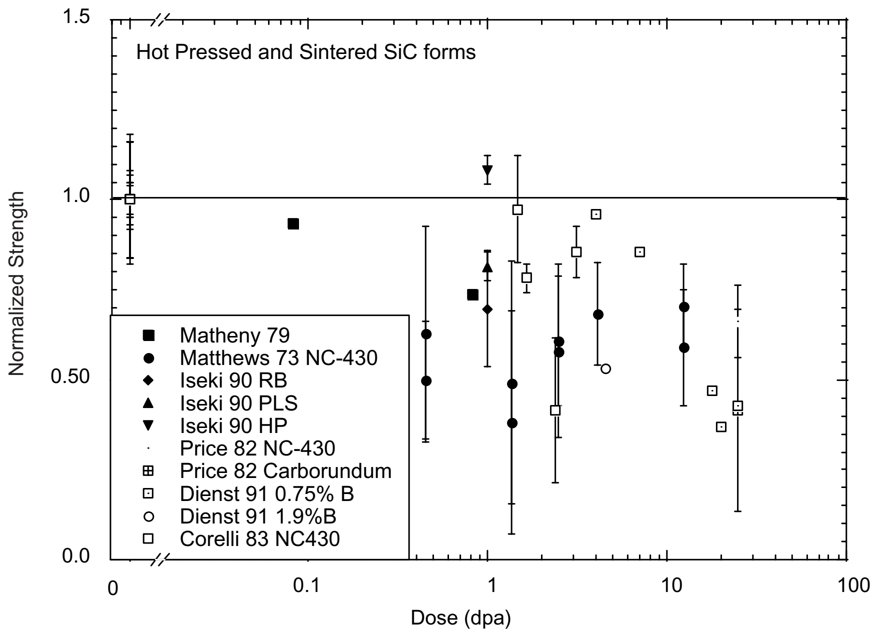

Fig. 11. Fluence dependence of irradiated flexural strength of hot-pressed and sintered SiC normalized to unirradiated strength.

fluence. For the case of materials (such as Norton NC-430) with free silicon at the grain boundary, anisotropic swelling between the Si and SiC causes disruption at the grain boundary reducing mechanical properties of strength, elastic and Weibull's modulus [26,30]. Other materials that contain boron as sintering aids further suffered from the additional recoil damage due to the (n, α) reaction and the corresponding presence of helium bubbles near the grain boundaries [25]. Clearly, stoichiometric materials such as pyrolitic (CVD) SiC offer the greatest resistance to irradiation-induced strength reduction.

4.3.2. SiC composite

The effect of neutron irradiation on SiC matrix/SiC fiber composites have been studied for more than ten years with early Nicalon™ fiber composites exhibiting significant degradation in mechanical properties following neutron irradiation [19]. It was recognized that the cause of this degradation was debonding between the fiber and the chemically vapor infiltrated matrix [19]. This disruption of the carbon interphase layer compromised the load transfer between the high-stiffness matrix and the high-strength fibers. 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 [37] for pre-production fibers, is 65% β-SiC with 23% SiO_2 and 11% free carbon. The microstructure of these fibers are of dispersed 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). Second generation Nicalon™ fibers were then produced by improving the method of cross-linking the spun polymer, though there was still substantial excess oxygen (0.5%) and a C/Si imbalance (1.31). The density of the second-generation (Hi-Nicalon™) fiber was increased from 2.55 g/cc (ceramic grade Nicalon™ fiber) to 2.74 g/cc, which is approximately 85% theoretical SiC density. Of interest for nuclear applications, the Hi-Nicalon™ fiber density did not to undergo the dramatic densification seen in ceramic grade Nicalon™ fiber, at least for low-dose neutron irradiation [38]. It is the densification of these fibers that was identified early on as the source of the poor irradiation performance of SiC composites [19]. However, results on the Hi-Nicalon™ fiber composite of this study clearly indicate (Fig. 9) that a significant reduction in both flexural and proportional limit stress occurs. Moreover the effect appears to be temperature insensitive over the range studied and saturates by a few dpa.

Recently, a further improvement in the Nicalon™ system has been achieved (Type-S Hi-Nicalon™). Essentially, the Hi-Nicalon™ process has been taken a step further with the resulting in a near theoretical density fiber with very low excess oxygen (<0.1%). However, even for the recent, highly crystalline SiC fibers, significant free carbon exists as turbostratic pockets within the fiber. In spite of the existence of C pockets, limited study seems to indicate that these bare fibers as well as their composites possess favorable irradiation behavior [17,39]. Essentially fibers as-irradiated swelling, elastic modulus, and strength behave in a similar fashion to CVD SiC. Such behavior should lead to superior as-irradiated composite performance. Within the statistical limitation of this study, this is found for the Hi-Nicalon™ Type-S/multilayer SiC interphase/CVD SiC matrix composite (Fig. 8). Specifically, the flexural strength does not show significant degradation. However, the proportional limit is somewhat reduced. Typically, the proportional limit stress is closely related to the matrix cracking stress. For model continuous fiber-reinforced ceramic composites, matrix cracking stress is determined by a combination of fiber/matrix interfacial frictional stress, matrix fracture energy, fiber radius, fiber volume fraction and elastic moduli of fiber, matrix and composite [40]. As mentioned earlier, the post-irradiation elastic modulus of CVD SiC slightly decreased in this work. Following the work of Nozawa et al. [39], for the irradiation dose and temperature range typical of this study, the elastic modulus of the fiber will follow the similar trend. Considering the small flexural strength increase of CVD SiC seen here and elsewhere [15] it is most likely that matrix fracture energy increased following irradiation. Therefore, the degradation of fiber/matrix interphase and/or the slight decrease of elastic moduli of the constituents following irradiation is thought to be responsible for the slight degradation of PLS in composites reinforced with Hi-Nicalon™ Type-S. Recent work by Nozawa et al. [41] confirms that the multi-layer SiC interphase of this study, in the radiation-tolerant Hi-Nicalon™ Type-S composite, does undergo a changed interfacial state.

The data generated for the Sylramic composite was in large part compromised by the extensive microcracking and swelling of the material following irradiation. This was seen by SEM fracture surface comparison of irradiated and non-irradiated composites. As mentioned earlier, this is attributed to the presence of boron in the fiber which would rapidly transmute to helium under neutron irradiation. As discussed earlier, the swelling at 300 °C was substantially higher than all other materials. Proportional limit strength for the 300 °C irradiation underwent a decrease from about 200 MPa to about 75 MPa at a dose level of ∼1.4 dpa. This degradation was the largest observed and is also attributed to degradation in the fiber. Data on flexural strength and volume change for the higher temperature irradiations is considered unreliable due to gross deterioration of the composite.

4.4. Statistical scatter

A change in the Weibull statistics, indicating a higher scatter in as-irradiated flexural strength has been observed by previous authors, though the point could not be made convincingly due to limitations in the number of tests observed. In the earliest work known to the authors, Sheldon [42] noted a 14% decrease in crushing strength of highly irradiated CVD SiC shells with an increase of the coefficient of variation from 8% to 14%. Price [24] went on to 4-point bend test relatively thin (~0.6 mm) strips of CVD SiC deposited onto a graphite substrate. In his work the flexural strength following an $\sim 9.4 \times 10^{25}$ n/m^2 ($E > 0.1$ MeV) irradiation was unchanged within the statistical scatter, but the scatter itself increased from about 10–30% of the mean flexural strength. Unfortunately, there were not sufficient samples in Price's work to infer Weibull parameters. In more recent work by Dienst [27] the Weibull modulus was decreased from about 10 to less than 5 for irradiation of $\sim 1 \times 10^{26}$ n/m^2 ($E > 0.1$ MeV.) However, it is worth noting that the Dienst work used a rather limited sample size (about 10 bars.) In work by Snead et al. [15], which used the same materials and test method as the present study, but with relatively small bars ($1 \times 1 \times 25$ mm,) the sample population was within the 15–30 sample guideline for applying Weibull statistics. In that work the Weibull modulus decreased from a non-irradiated value of about 13–10 for 500 °C irradiation, and 8 for 800 °C irradiation. For a separate set of samples of similar size, but with different machining and lower fluence irradiation, the Weibull modulus decreased from about 7 to about 4 for the highest temperature irradiation (about 1050 °C).

Fig. 12 shows a compilation Weibull plot of flexural strength of non-irradiated and irradiated CVD SiC taken in the present study. The sample population is included in Table 1. For all three irradiation temperatures the population size was in excess of 30, typically recommended for adequate Weibull statistics. The data was arranged by irradiation temperature including data for non-irradiated and 1.5–4.6 dpa dose range. It is clear that Weibull modulus decreased by irradiation and appears dependent on irradiation temperature. This is not easily visualized through inspection of Fig. 12 unless one notes that there are significantly more low stress fractures populating the 300 °C population. Comparing the 300–800 °C data sets it is clear that about 15 samples (greater than 30%) failed at a load less than that of the lowest strength 800 °C sample. Additionally, the 300 °C data set also had several samples which failed at a load higher than the highest strength 800 °C specimen. This resulted in a significant different in the 300 °C and 800 °C Weibull moduli. For the cases of irradiation at 300 and 500 °C, the Weibull modulus exhibited a pronounced decreased upon irradiation. For the 800 °C irradiation case, the Weibull modulus remained nearly unchanged. The scale parameters of flexural strength of non-irradiated materials and materials irradiated at 300, 500, and 800 °C were 450, 618, 578 and 592 MPa, respectively. The Weibull modulus of flexural strength of non-irradiated materials and materials irradiated at 300, 500, and 800 °C were 9.6, 6.2, 5.5 and 8.7, respectively.

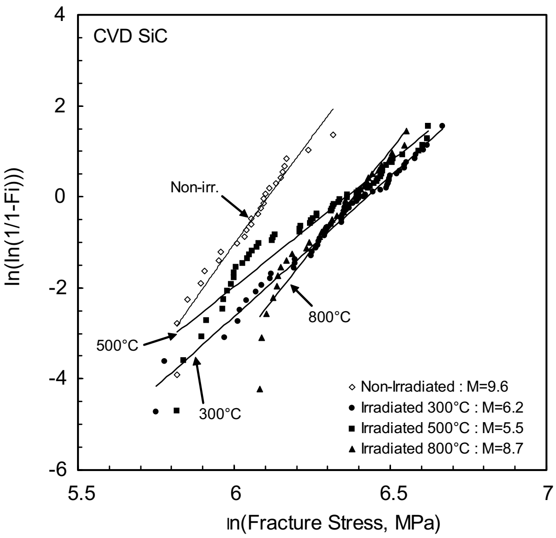

Fig. 12. Weibull plot of flexural strength of non-irradiated and irradiated CVD SiC in the dose range of 1.5–4.6 dpa.

The reason for the reduction in Weibull modulus and the increase in mean flexural strength for these materials is unknown, but is of considerable interest both from a fundamental irradiation materials science and practical application standpoint. It is speculated that crack blunting may occur in the irradiated material due to the compressive force developing in the material due to interstitial cluster formation. However, it is also possible that radiation-enhanced-diffusion may alter the stress state at intrinsic and machining-induced flaws in the material, requiring greater applied stress for crack propagation. An interesting area of future work would be to specifically investigate the effect of neutron irradiation on the stress state around induced flaws and compare the statistics of failure for such samples before and after irradiation.

Finally it is noted use of standard deviation for the small population of composite samples (c.f. Tables 2 and 3) are problematic. A large, non-sensored population was used for the non-irradiated condition. Specifically, 30 samples for the Hi-Nicalon™ Type S and 37 samples for the Hi-Nicalon™ samples. By inspection of Tables 1 and 2 the standard deviation for the non-irradiated composites was quite large (10–20% of the average.) For the case of the irradiation specimens as many as a few specimens per condition were tested. Obviously, application of the standard deviation for so few specimens is problematic. However, the fact that the deviation for these small populations is low indicates that the values are similar.

5. Conclusion

Statistically significant results for the irradiation effects on mechanical and physical properties of SiC and SiC/SiC composites were obtained. Swelling was seen for both monolithic CVD SiC and composites fabricated from SiC-based fibers. The magnitude of swelling for CVD SiC depended on irradiation temperature, while it was independent of irradiation fluence within the irradiated range. Moreover, the magnitude of swelling decreased with increased irradiation temperature. The magnitude of swelling saturated at approximately 1.9%, 1.1%, and 0.7% at the irradiation temperature of 300, 500, and 800 °C, respectively. This is in full agreement with previous work on high-purity CVD SiC, though somewhat lower than seen for less pure forms of SiC.

The elastic modulus as measured by interpretation of flexural curves for CVD SiC is not greatly influenced for the irradiation conditions studied. However, a small change in modulus is observed in agreement with previous work applying indentation techniques to neutron and ion irradiated SiC.

Neutron irradiation increases the flexure strength of CVD SiC, which is dependent on temperature and appears to saturate at relatively low fluence. However, the breadth of scatter in flexure strength values for a large population of samples, as described by the Weibull modulus, is likely to decrease with irradiation and is also a function of temperature. The reason for this reduction, or which flaws are controlling the failure in CVD SiC is not currently known.

Composites reinforced with Hi-Nicalon™ Type-S fibers showed similar swelling behavior to that of CVD SiC. This is attributed to the similar microstructure of the fiber and matrix to that of CVD SiC. Significant irradiation effects on mechanical properties were not seen in composites reinforced with Hi-Nicalon™ Type-S. However slight degradation of PLS was observed and attributed to fiber/matrix interphase degradation and/or elastic modulus reduction following irradiation.

It was found that composites reinforced with Hi-Nicalon™ fibers also showed similar swelling behavior to that of CVD SiC, although the magnitude of the swelling is less than that of CVD SiC. Due to decoupling of the matrix and fiber of these composites, the magnitude of the swelling was determined by matrix swelling alone. The degradation of mechanical properties for the Hi-Nicalon™ composites, and in particular PLS, is consistent considering the fiber/matrix interfacial degradation.

Composites reinforced with Sylramic fibers showed the largest swelling and significant degradation of mechanical properties following irradiation. This has been attributed to the significant effect of the boron sintering aid in the Sylramic fiber. It can be concluded that composites reinforced with presently formulated Sylramic fibers are not suitable for nuclear application.

References

[1] L.L. Snead, Fusion Technol. 24 (1993) 65.
[2] L.L. Snead, R.H. Jones, A. Kohyama, P. Fenici, J. Nucl. Mater. 233–237 (1996) 26.
[3] Y. Katoh, A. Kohyama, T. Hinoki, L.L. Snead, Fusion Sci. Technol. 44 (2003) 155.
[4] P. Fenici et al., J. Nucl. Mater. 258–263 (1998) 215.
[5] R.H. Jones et al., J. Nucl. Mater. 307–311 (2002) 1057.
[6] A. Hasegawa et al., J. Nucl. Mater. 283–287 (2000) 128.
[7] T. Hinoki, E. Lara-Curzio, L.L. Snead, Fusion Sci. Technol. 44 (2003) 211.
[8] E. Lara-Curzio, Comprehensive Composites Encyclopedia 4–21 (2000) 533.
[9] L.L. Snead, J.C. Hay, J. Nucl. Mater. 273 (1999) 213.
[10] R.J. Price, J. Nucl. Mater. 48 (1973) 47.
[11] T. Yano, T. Iseki, Philos. Mag. A 62 (1990) 421.
[12] R. Price, Nucl. Technol. 35 (1977) 320.

[13] R.J. Price, J. Nucl. Mater. 33 (1969) 17.
[14] L.L. Snead et al., J. Nucl. Mater. 253 (1998) 20.
[15] Y. Katoh, L.L. Snead, J. ASTM Int. 2 (2005), 12377-1-13.
[16] Y. Katoh, H. Kishimoto, A. Kohyama, J. Nucl. Mater. 307–311 (2002) 1221.
[17] T. Hinoki et al., J. Nucl. Mater. 307–311 (2003) 1157.
[18] M.C. Osborne, J.C. Hay, L.L. Snead, D. Steiner, J. Am. Ceram. Soc. 82 (1999) 1141.
[19] L.L. Snead, D. Steiner, S.J. Zinkle, J. Nucl. Mater. 191–194 (1992) 566.
[20] L.L. Snead, E. LaraCurzio, Microstructure of irradiated materials, in: G.E. Lucas, R.C. Ewing, J.S. Williams (Eds.), MRS Warrendale PA, Boston MA, 540, 1999, p. 273.
[21] M.C. Osborne, C.R. Hubbard, L.L. Snead, D. Steiner, J. Nucl. Mater. 253 (1998) 67.
[22] L.L. Snead, S.J. Zinkle, D. Steiner, J. Nucl. Mater. 191–194 (1992) 560.
[23] S. Nogami, A. Hasegawa, L.L. Snead, J. Nucl. Mater. 307–311 (2002) 1163.
[24] R.J. Price, G.R. Hopkins, J. Nucl. Mater. 108&109 (1982) 732.
[25] J.C. Corelli, J. Hoole, J. Lazzaro, C.W. Lee, J. Am. Ceram. Soc. 66 (1983) 529.
[26] R. Matthews, J. Nucl. Mater. 51 (1974) 203.
[27] W. Dienst, J. Nucl. Mater. 191–194 (1992) 555.
[28] A.M. Carey, F.J. Pineau, C.W. Lee, J.C. Corelli, J. Nucl. Mater. 103&104 (1981) 789.
[29] S.D. Harrison, J.C. Corelli, J. Nucl. Mater. 99 (1981) 203.
[30] R.A. Matheny, J.C. Corelli, J. Nucl. Mater. 83 (1979) 313.
[31] T. Iseki et al., J. Nucl. Mater. 170 (1990) 95.
[32] W. Dienst et al., J. Nucl. Mater. 174 (1990) 102.
[33] F. Porz, G. Grathwohl, T. Thummler, Mater. Sci. Eng. 71 (1985) 273.
[34] G.W. Hollenberg et al., J. Nucl. Mater. 219 (1995) 70.
[35] B.O. Yavuz, R.E. Tressler, Ceram. Int. 8 (1992) 19.
[36] L.L. Snead, T. Hinoki, Y. Katoh, Report DOE/ER-0313/33 (2002).
[37] S. Yajima et al., Nature 279 (1979) 706.
[38] L.L. Snead, M. Osborne, K.L. More, J. Mater. Res. 10 (1995) 736.
[39] T. Nozawa, L.L. Snead, Y. Katoh, A. Kohyama, J. Nucl. Mater. 329–333 (1994) 544.
[40] W.A. Curtin, J. Am. Ceram. Soc. 74 (1991) 2837.
[41] T. Nozawa, Y. Katoh, K. Ozawa, L.L. Snead, A. Kohyama, J. Nucl. Mater., in press.
[42] B.E. Sheldon, Report UKAEA Report AERE-R8025 (1975).