

STRENGTH OF NEUTRON IRRADIATED SILICON CARBIDE AND SILICON CARBIDE COMPOSITE - L. L. Snead and T. Hinoki (ORNL) and Y. Katoh (Kyoto University)

OBJECTIVE

The objective of this paper is to compare recently generated data on the effect of irradiation on stoichiometric SiC with previous results on stoichiometric and non-stoichiometric forms of SiC and SiC composites.

SUMMARY

Specimens of monolithic SiC and SiC composite have been irradiated with fission neutrons in the temperature and dose range of 90-1000°C and $1.1- 7.7 \times 10^{25} \text{ n/m}^2$ ($E > 0.1 \text{ dpa}$), respectively. Materials included stoichiometric chemically vapor deposited SiC and composites containing SiC-based fibers chemically vapor infiltrated with SiC. For the case of the monolithic SiC and the composite containing the near-zero oxygen content fibers, no degradation in bend strength was observed. Composite materials containing the higher oxygen content fibers exhibited significant degradation. These results are compared with data from the literature on the irradiation effects on the properties of stoichiometric and non-stoichiometric SiC-based materials.

PROGRESS AND STATUS

Introduction

Silicon carbide (SiC) has been widely used as a pressure vessel for fuel-particles in high-temperature gas cooled reactors. One design of such a pressure vessel is the TRISO system. The TRISO coating system contains internal gas pressures generated during fissioning of the fuel kernel material and acts as a diffusion barrier to metallic fission products. Figure 1 (left) gives a schematic representation of the TRISO fuel particle. The coating layer adjacent to the fuel kernel is a low density PyC (buffer layer) containing about 50% porosity. This layer absorbs fission product recoils from the kernel, provides a reservoir for fission product gases, and accommodates kernel swelling limiting forces transmitted to the outer coatings. The next layer is a high-density, isotropic PyC layer that protects the kernel from reactions with chlorine present during deposition of the SiC layer, provides structural support for the SiC layer, and protects the SiC from fission products and carbon monoxide during operation. The outermost layer is another high-density, isotropic PyC layer that protects the SiC during the remainder of the fabrication process and provides structural stability to the particle during irradiation. High Density PyC and SiC layers are impervious to fission gases at normal operating temperatures and the SiC layer is an effective barrier to both gaseous and metal fission products. A polished section of an actual fuel kernel, with SiC shown as the brightest ring, is shown in Figure 1(right). Typical high temperature gas cooled reactors employing this fuel would operate in a temperature range of 800-1300°C and be subjected to up to $\sim 5 \times 10^{25} \text{ n/m}^2$ ($E > 0.1 \text{ MeV}$.)

A more recent (proposed) application of SiC is as a structural material for fusion reactors. In this case, SiC would be used in the form of woven composites and formed into very large structures. An example of the scale and design for a SiC fusion reactor structure is described in the recent work of Giancarli [1]. In that design, concentric shells of SiC/SiC on the order of a few square meters are nested to form the first wall and blanket structure. Such structures are building blocks to surround the toroidal plasma. For such a fusion power system application, the SiC composite would receive as much as 100 dpa over its lifetime and be expected to operate at temperatures as high as 1000°C.

For both SiC coated nuclear fuels and structural applications, knowledge of the effects of irradiation on mechanical properties are critical. This paper will present new results on the effect of neutron irradiation on the strength of chemically vapor deposited SiC as applied for the TRISO system, and SiC/SiC composites as proposed for fusion structural materials. Particular emphasis is placed on the importance of stoichiometry of the SiC materials on the degradation in strength of these materials due to neutron irradiation.

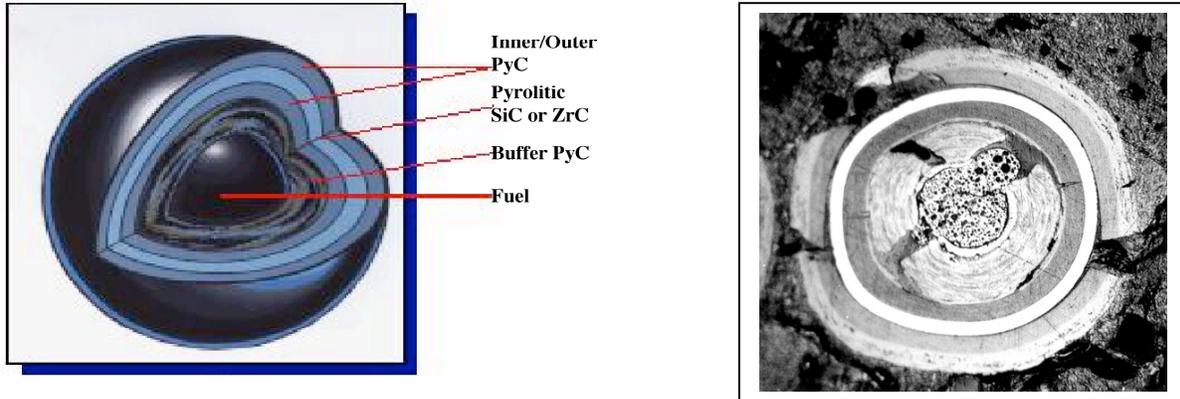


Figure 1: Schematic and polished section of TRISO fuel particle.

Experimental

The chemically vapor deposited (CVD) SiC was obtained from Morton Advanced Ceramics (now Rohm Haas) in plate form. Impurities in this material are at or less than the ppm level. Grain size varies from 5-10 μ m with a 100% theoretical density (3.21 g/cc.) The crystal structure is highly faulted FCC β -SiC. The strength as provided by the manufacturer is 470 MPa at ambient, and 575 MPa at 1400°C using a four-point fixture and a 0.5 nm RMS surface finish. The Weibull parameters as provided by the manufacturer are modulus of 11.45 and scale factor of 460 MPa. Bend bars were machined into 1 x 1 x 25 mm and tested at room temperature in four-point bending with a load and support span of 6.25 and 19.05 mm, respectively. The cross-head displacement rate was 0.0085 mm/s. Data was analyzed using a two-parameter Weibull treatment. Density was measured using a density gradient column technique [2] utilizing a mixture of methylene iodide and ethylene bromide. Density samples were soaked in hydrofluoric acid for period of 1 hour to remove any surface silica.

Composite materials were fabricated in the High Temperature Materials Laboratory at the Oak Ridge National Laboratory. Fabric was layed-up in a 0/90° pattern and infiltrated by forced flow chemical vapor infiltration [3]. Fibers chosen were from the Nicalon™ family: Hi and Type-S. Properties are listed in Table 1. For each case a carbon interphase was applied between the fiber and the matrix. Composite bend bars were machined in the as-received condition (2.3 x 6 x 30 mm) and baked at 200°C in air prior to loading into graphite holders for irradiation. Bend testing was carried out at room temperature at a cross-head displacement of 0.0085 mm/s. Load and support spans were 6.45 and 19.05 mm, respectively. Due to a lack of materials the use of thermal control specimens was not possible. However, previous work which included limited thermal control samples for CVD SiC/C interphase/Hi-Nicalon composite fabricated with the identical process to the composites in this study and held for 30 days at ~300 and 1000°C in an inert cover gas. No significant effect of the thermal treatment was seen in that work.

Nicalon™ Fiber Type	C/Si Atomic Ratio	Oxygen Content (wt/%)	Tensile Strength (GPa)	Tensile Modulus (GPa)	Density (g/cm ³)	Diameter (μ m)
Ceramic Grade	1.31	11.7	3.0	220	2.97	2.55
Hi	1.39	0.5	2.8	270	7.77	2.74
Type-S	1.05	0.8	2.6	410	24.1	3.1

Table 1: Properties of Nicalon™ family fibers.

Irradiation was carried out in both the flux trap of the High Flux Isotope Reactor (HFIR) at ORNL and the V-15 core position of High Flux Beam Reactor (HFBR). The High Flux Beam Reactor irradiation of the CVD SiC material was a thermocouple-monitored experiment with a static helium fill gas surrounding samples inserted into vanadium holders. The calculated neutron fluence was 1.1 dpa. A conversion of 1×10^{25} n/m² (E>0.1 MeV) is assumed equivalent to 1 dpa in both reactors. The high fluence (14J experiment, 6 and 7.7 dpa) HFIR irradiation was carried out for 8 cycles in a thermocouple-controlled capsule with 300, 500 and 800°C zones. Heaters and sweep gas was used to maintain target irradiation temperature.

Results

CVD SiC Data

Table 2 gives the reduced data for the CVD SiC including the Weibull parameters and density change. The quoted temperatures for the 14J experiment have an uncertainty of less than 10°C, while those from the SiC-1 experiment have a larger range (as listed.) The temperature for this experiment tended to increase throughout the irradiation. It is important to note that the plates from which the bend bars were taken for the 14J and SiC-1 experiments were different, and the machining was conducted at different times. This may explain the difference in non-irradiated strengths between the two experimental batches, though the difference is still within the standard deviation listed.

ID	T _{irr} (°C)	Dose dpa, or $\times 10^{25}$ n/m ² (E>0.1MeV)	Density Change (%)	Weibull Mean (MPa)	Weibull Standard Deviation (MPa)	Weibull Modulus	Size Parameter (MPa)	Number of Samples
HFIR-14J								
Non-irr	-	-	-	353	72	13	368	29
14J	300±10	7.7	2.0	399	117	5	434	10
	500±10	6	1.65	576	133	10	607	20
	800±10	7.7	.82	540	138	8	588	31
HFBR SiC-1								
Non-irr	-	-	-	416	109	7	444	30
	80-90	1.1	3.09	424	114	7	455	17
	250-270	1.1	1.8	407	109	7	437	25
	385	1.1	1.37	392	112	6	485	23
	960-1150	1.1	.45	448	145	4	495	23

Table 2: Reduced data for CVD SiC.

The normalized strength data ($\sigma_{irr}/\sigma_{non-irr}$) for the CVD SiC as a function of irradiation temperature are given in Figure 2. The error bars represent ± 1 Weibull's standard deviation while the temperature uncertainty is the measured range in temperature during irradiation. For the ~1000°C data point, the temperature band is weighted towards the lower temperature end reflecting the greater exposure time at this lower (~1000°C) temperature.

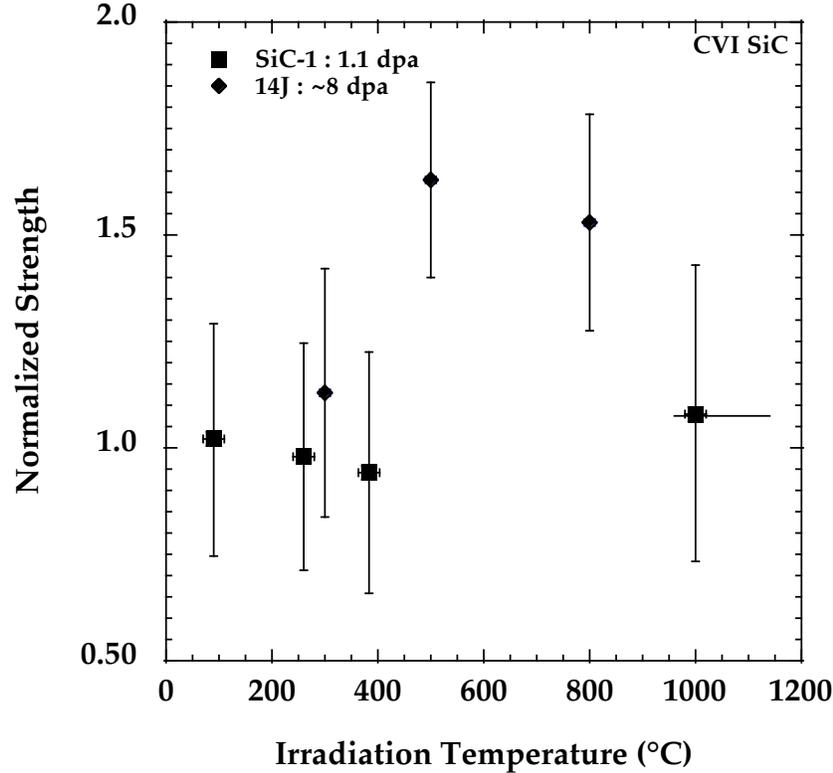


Figure 2: Effect of temperature on normalized strength ($\sigma_{irr}/\sigma_{non-irr}$) of neutron irradiated CVD SiC.

SiC/SiC Composite

The effect of irradiation on the composite materials tested in this study is given in Table 3. For the Type-S Nicalon™ composite both plain and satin weave fabrics were employed. For the FCVI process employed in this work, the satin weave composites had lower fiber volume fractions and higher resulting porosity. This was typical of Results for Type-S satin weave composite include interphase thickness of 150 and 500 nm. It was observed that composites fabricated from the satin weave fabric tended to have a higher porosity and correspondingly larger scatter in mechanical properties. The mean strength and standard deviation values given in Table 3 assume a normal distribution as the number of samples was limited. The mean strength given is the ultimate bend strength.

Fiber	Weave	C thickness (nm)	Fiber Fraction (%)	Void (%)	Irr. temp. (°C)	Length Change* (%)	Mean strength (MPa)	Standard deviation	Number of samples
Type-S	Plane	150	36	14	Non-irrad.	-	425	12.2	2
					300	.64	469	22.9	2
					800	.25	474	12.9	3
Type-S	Satin	150	29	20	Non-irrad.	-	271	-	3
					300	.72	314	22.1	3
					800	.30	267	58.1	4
Type-S	Satin	500	30	19	Non-irrad.	-	344	23.4	4
					300		406	36.7	2
Hi-Nicalon	Plane	150	37	11	Non-irrad.		442	18.1	4
					800		278	18.2	2

* In-plane length change.

Table 3: Reduced data for high-dose irradiated SiC composites

Discussion

Monolithic SiC

Due to the lack of data available on irradiation effects for the CVI SiC shells, and more generally, monolithic pyrolytic SiC in the temperature ranges of interest for gas cooled reactors, a number of assumptions have been made with respect to material performance of SiC. These assumptions have been outlined in the CEGA(Combustion Engineering-General Atomics) report, which summarizes properties of interest for modeling TRISO fuel particles [4]. As described by CEGA, the non-irradiated room temperature strength of CVD SiC in the literature ranges from 60 Mpa [5] to over 3100 Mpa [6]. This variability is due to many factors, including both material and test dependent parameters. Strength was obtained using several techniques including three and four-point bending and ring compression testing.

Based on the review of the original papers on the subject Yavuz [5,6], it appears that the presence of free silicon (as much as 6%), which becomes molten at the high temperatures, would serve to seriously degrade strength. The presence of free silicon in the TRISO fuel particles SiC was known [8], though its importance not fully recognized. Such degradation in non-irradiated strength at high temperatures due to the presence of free silicon has also been studied in detail by Lara-Curzio [9]. As will be mentioned later, previous work on powder processed SiC [10-13] clearly indicates that the presence of free silicon causes anisotropic dimensional change under irradiation resulting in strength reduction. Additionally, it is clear for all ceramics that factors such as surface condition, machining, and test orientation with respect to grinding can have and influence on strength. As example, Cockeram [14] has measured the four point bend strength for both Morton and Coors stoichiometric CVD SiC and found a significant difference in strength between the two materials and a dependence of strength on orientation with respect to the grinding direction. He also reports small or insignificant effect of orientation with respect to the CVD growth direction. The Morton material of Cockeram's work is equivalent to the CVD SiC of the present study.

The effect of irradiation on SiC strength is similarly limited by sparse data. CEGA discusses the use of two experimental studies and the model proposed by Allelein [15] for TRISO shell evaluation. The data used in Allelein's empirical model were based on a single irradiation at 1165°C to a fluence of 2.88×10^{25} n/m² (E>0.18 MeV.) With this data a Weibull's mean strength reduction from 834 to 687 MPa was found. However, as CEGA points out, the model does not compare well with the earlier work by Price[16] which shows no affect for irradiation at 630°C and 1020°C. CEGA goes on to show the unfavorable comparison of the model with the Price data and concludes: "These inconsistencies need resolution before any recommendation on correction for the irradiation effect. For the interim, we assume that there is no effect of irradiation on strength."

There have been several studies of the effect of irradiation on the mechanical properties of monolithic SiC [10-13,16-24]. When considering the irradiation effects on strength of SiC it is important to differentiate between the stoichiometric and non-stoichiometric ceramics. Forms 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 transition. As example, the Morton CVD material used in this study has a manufacturer quoted chemistry of less than a part per million for metallic impurities (<http://www.cvdmaterials.com/sicprop1.htm>). 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 [5]. In some forms, 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 boron (eg ~0.4 wt% Carborundum □-SiC), Si or Al as sintering aids, with the sintering-aid primarily residing at the grain boundary in the final form.

Figure 3 shows a comparison of the normalized bend strength data from the present work and of Price [10,16] and Dienst [23] on pyrolytic, CVI 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 [22,23] 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 [22,23]. From the

compilation data of figure 3 it is clear that for doses less than ~10 dpa no degradation, and possibly a slight increase, in mean strength has occurred. In all cases (cf Table 2) irradiation reduces the Weibull's modulus. For doses greater than 10 dpa the effect of irradiation on strength is less clear in that the data of Price[10] and Dienst[23] 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.

Recent work has been carried out on samples taken from the same CVD SiC samples in this work. Nogami[25] reports Vicker's hardness increasing for all dose levels and temperatures for the samples. For the 7.7 dpa, 800°C irradiation a hardness increase of ~ 20% was reported. Also of interest is that the indentation fracture toughness is increased at this level supporting the apparent increase in strength given in this work.

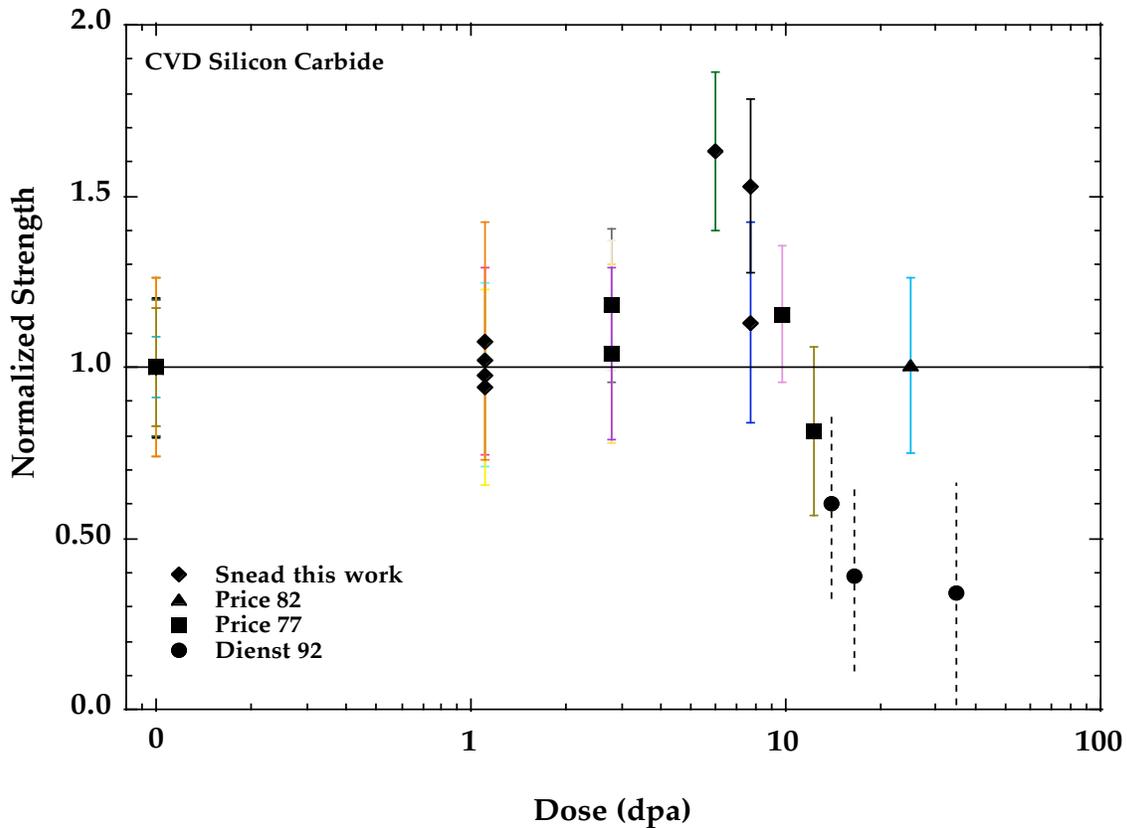


Figure 3: Normalized strength ($\sigma_{irr}/\sigma_{non-irr}$) of CVD SiC data as a function of dose for this study and literature data.

As mentioned earlier, the presence of free silicon in pyrolytic SiC, or the presence of Si or other sintering aids has a great influence on strength and other mechanical properties of irradiated SiC.[10-13,16-24] This point can be illustrated by inspection of Figure 5, which contains a compilation of data on powder processed forms of SiC. Clearly, normalized strength is substantially degraded at relatively low 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.[12,20] Other materials which 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.

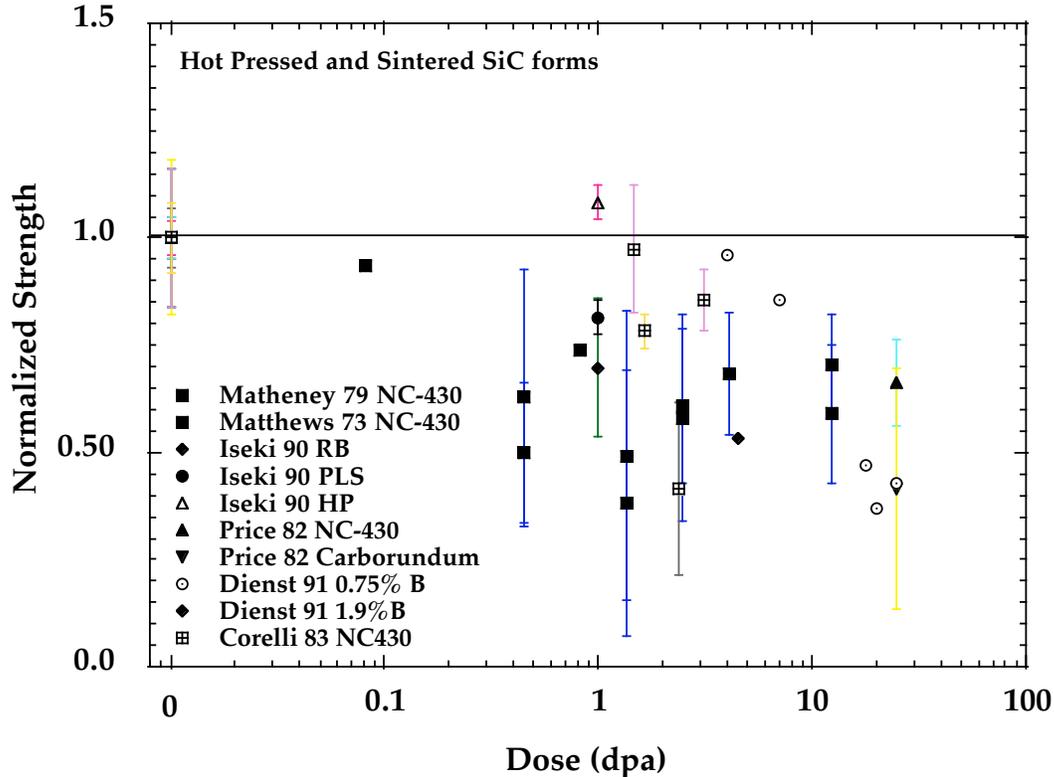


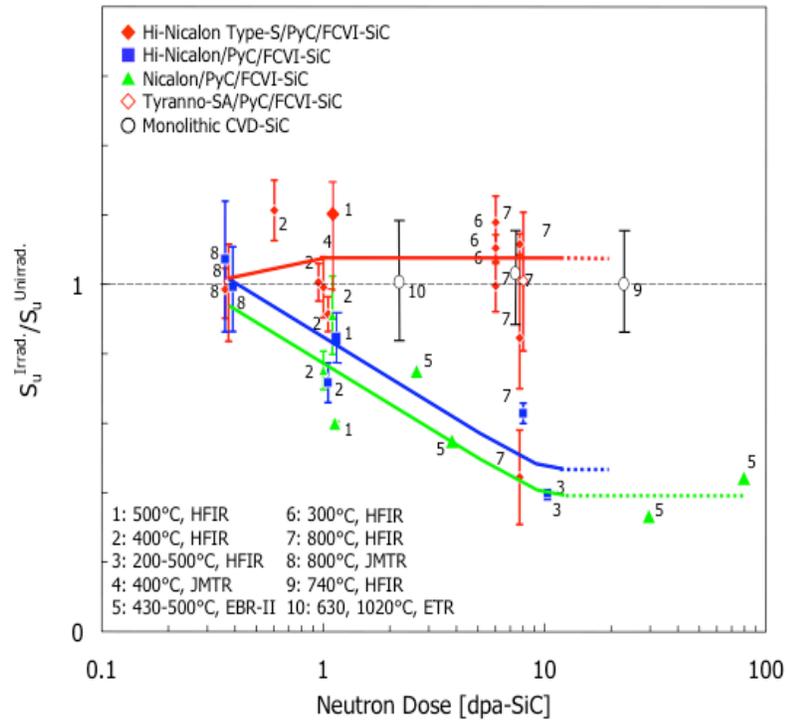
Figure 4: Effect of irradiation on powder processed monolithic SiC.

Silicon Carbide Composites

The effect of neutron irradiation on SiC matrix SiC fiber composites have been studied for more than ten years with early materials exhibiting significant degradation in mechanical properties following neutron irradiation.[26] It was recognized that the cause of this degradation was debonding between the fiber and the chemically vapor infiltrated matrix.[26] This disruption of the carbon interphase layer compromised the load transfer between the high-stiffness matrix and the high-strength fibers. It is an important 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[27] for pre-production fibers, is 65 % β -SiC with 23 % SiO₂ 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 was seen not to undergo the dramatic densification seen in ceramic grade Nicalon™ fiber, at least for low-dose neutron irradiation[28]. It is the densification of these fibers that was identified early on as the source of the poor irradiation performance of SiC composites.[26] 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%). Table 1 gives a chemical comparison of the Nicalon™ family fibers.

The impact of the evolution from SiC-based fibers with high oxygen content and excess silicon to near stoichiometric fibers on the performance following neutron irradiation is given in Figure 5. It is seen that the earliest fibers exhibited ~ 40% loss in ultimate bend strength at irradiation doses of a few dpa, which corresponds to

only a few months operation in a fusion power reactor. While the Hi-Nicalon™ fiber composites showed slightly better performance mechanical properties still sharply degraded and debonding was still clearly seen through direct TEM observation of the interphase region.[29] Results from the current work are also provided in this plot and clearly indicate that degradation in strength does not occur. Moreover, it appears that a moderate increase in composite strength has occurred, though this observation is tempered by the statistical limitations.



1,2: L.L. Snead, et al., J. Nucl. Mater., 283-287 (2000) 551-555. 8: T. Nozawa, et al., J. Nucl. Mater., (2002) to be published.
 3,4: T. Hinoki, et al., Mater. Trans., JIM, 43 [4] (2002) to be published. 9: R.J. Price, et al., J. Nucl. Mater., 108-109 (1982) 732-738.
 5: R.H. Jones, et al., 1st IEA-SiC/SiC (1996). 10: R.J. Price, J. Nucl. Mater. 33 (1969) 17-22.
 6,7: T. Hinoki, et al., J. Nucl. Mater., (2002) to be published.

Figure 5: Effect of irradiation on Nicalon™ family SiC composites.

Conclusions

Over the neutron dose range of this study of (1.1 to 7.7 x 10²⁵ n/m² (E>0.1 MeV)) Weibull mean bend strength of stoichiometric pyrolytic silicon carbide remains unchanged or exhibits slight strengthening. Data is consistent with hardening and increased indentation fracture toughness measurements made previously on identical materials. A point of ambiguity exists at high doses because of an apparent contradiction in the literature between two high-dose studies. Another, high-dose experiment is called for on the newest, stoichiometric CVD SiC to address this discrepancy. As with the CVD SiC, composites fabricated from stoichiometric fibers and matrix undergo no change in proportional limit or ultimate bend strength, and may undergo a slight increase in strength. For both cases it is clearly important that elements in the form of impurities or second phases occurring at grain boundaries or within the crystallites. be minimized to retain as-irradiated strength of silicon carbide.

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