DIMENSIONAL STABILITY OF SIC-TYPE FIBERS NEUTRON IRRADIATED TO HIGH DOSES

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OBJECTIVE

The objective of this study is to examine the dimensional stability after neutron irradiation of a selection of SiC fiber types.

SUMMARY

Silicon carbide based fibers with a range of stoichiometries and microstructures (Nicalon CG, Nicalon HVR, HPZ, Tyranno, and Dow/NASA Xstalline) were selected for evaluation of their dimensional stability after neutron irradiation to high doses. For comparison, carbon fibers with a range of graphitization also were evaluated.

The fibers were irradiated in the MOTA 2B cycle of the FFTF reactor. Two sets of the selected C and SiC fiber types were exposed at 430°C to a fluence of 5.5×10^{21} n/cm^2 or 2.5×10^{22} n/cm^2 (E≥0.1 MeV), equivalent to relatively high doses of 5.3 and 25 dpa-SiC. Dimensional stability was determined by measuring the length and density changes of the fibers after the irradiations.

For the SiC-based fibers above 5 dpa-SiC, little dose dependence was observed except for the Tyranno fiber. The HPZ, Tyranno and Nicalon HVR fibers, whose pre-irradiated densities were quite low, exhibited substantially more axial shrinkage than the Nicalon CG fiber. Even though the shrinkage of the Nicalon CG fiber was moderate (about 2% at 430°C), fiber shrinkage and debonding from the matrix previously had been observed to result in decreased strengths in Nicalon fiber SiC/SiC composites irradiated to the same fluence and at similar and at higher temperatures. The developmental fiber, Dow/NASA Xstalline, actually exhibited slight swelling rather than shrinkage. The composition of the Dow/NASA fiber was near stoichiometric SiC, the density was 90% of theoretical for SiC, and the microstructure was reported to be more crystalline than for the other SiC-based fibers.

For the C fibers, the amount of axial shrinkage was much greater than observed for the irradiated SiC-based fibers and generally was greater the lower the degree of initial graphitization. Also, in contrast to the irradiated SiC behavior, the radiation damage did not appear to saturate, but continuously increased with increasing dose. The axial shrinkage exceeded about 20% for the most graphitic C fiber and exceeded 60% for the less graphitic fiber at the higher dose. Independent of the initial degree of graphitization, the densities of all the C fibers increased and appeared to saturate at a common value by the 3 dpa-C dose. With increasing dose above 3 dpa-C, the densities decreased and returned almost to their unirradiated values by 15 dpa-C. The density change data indicated that C fibers will continuously shrink in the axial direction (i.e., the preferred alignment of the graphitic a-axis in C fibers) under irradiation. However, in the diametral direction, graphitic c-axis growth will be accommodated by porosity and/or amorphicity initially, but with continued irradiation diametral swelling will commence once the accommodation is over.

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Silicon carbide based fibers that are close to stoichiometric and crystalline appear to have the radiation damage tolerance necessary to make SiC/SiC composites suitable for further testing and development for fusion power system applications. Due to the fundamental nature of radiation damage in graphite, dimensional instability (extreme axial shrinkage and diametral swelling) of C fiber irradiated to high doses will prevent their use in C/C composites for long-term operations in a fusion power system.

PROGRESS AND STATUS

Introduction

Silicon carbide (SiC/SiC) and carbon (C/C) continuous fiber reinforced composites have been considered for fusion power system applications because they exhibit favorable physical and mechanical properties [1,2] as well as low residual neutron activation [3,4]. Furthermore, because of their design flexibility, such composites offer the possibility to be tailored for specific applications. For instance, the conceptual design of the ARIES I reactor, a first generation fusion electrical power plant, is based on the use of SiC/SiC composite for the diverter and first wall [5]. This design takes advantage of the high operating temperature capability (800 to 1000 °C), moderate structural toughness, and a low interaction with the contained plasma. One conceptual design of the International Thermonuclear Experimental Reactor (ITER) proposes the use of C/C composite tiles to protect the first wall against melting and fatigue [6]. Currently, the JT-60 tokamak test reactor in Japan uses these C/C composite tiles to line the first wall to provide protection against the tremendous heat generated during pulsed plasma tests [7].

However, eventual longer term operation of a fusion test power system will require a material with an improved radiation damage tolerance. Previous tests at Pacific Northwest Laboratory of C/C composite coupons exhibited unacceptable performance after irradiations simulating fusion power system operating temperatures and neutron fluences. Extreme dimensional changes, warping and delamination occurred in the tested composites. Later tests of irradiated SiC/SiC composite exhibited much improved performance; however test coupons still indicated an unacceptable degree of degradation [8]. By far, the most important cause of degradation of C/C or SiC/SiC composites during irradiation was the dimensional instability of the fibers [8,9]. Until an irradiation tolerant fiber is developed and used in making composites, optimizing other composite design or fabrication parameters such as the type and thickness of interfacial fiber coatings, matrix processing conditions, and fiber weave architectures cannot be conducted.

The purpose of this study was to examine the dimensional stability after neutron irradiation of a selection of C and SiC fiber types. For this study, one developmental and four commercially available SiC-based fiber types were selected to cover a range of SiC stoichiometries and microstructures. Pitch-based C fibers were selected to cover a range of graphitization. Based on these results, desired fiber properties or promising fiber types may be recommended for inclusion in further testing for the composite development program for fusion power system applications.

Experimental Description

The fibers were irradiated in the MOTA 2B cycle of the FFTF reactor, a sodium-cooled reactor possessing a fast neutron spectrum with more than 60% of the flux greater than 0.1 MeV. Duplicate sets of representative fiber bundles, either
2.54 ± 0.01 or 3.05 ± 0.01 cm long and containing 500-1000 individual fibers, were cut from as-received fiber yarns and loaded into individual Poco graphite holders. Each set of graphite holders was loaded into one of two stainless steel weeper capsules which were out-gassed and heated overnight to 450 °C, back-filled with helium to approximately atmospheric pressure and welded closed. The two sets of encapsulated fiber samples were irradiated at 430 °C, but at different core locations. One set was exposed to a fluence

of 5.5 x 10^{21} n/cm2, the other to 2.5 x 10^{22} n/cm2 (E ≥ 0.1 MeV). Since the high energy neutrons cause most of the irradiation damage in SiC and carbon, irradiation dose is reported in units of displacements per atom (dpa-SiC or dpa-C, respectively).

After irradiation, the graphite holders were opened in a glove box and the fiber bundles were removed and photographed. The irradiated fiber lengths were measured directly from photographs of each bundle using a traversing microscope. The accuracy of the fiber length measurements was dominated by the alignment of the fiber bundle ends. After making length measurements, the bundles were cut in half. One of the half-bundles was mounted in resin for optical microscopy of the fiber cross-sections; the other half was used for density measurements. Average fiber diameters and associated variances were determined by digital image analysis of the fiber cross-sections.

The fiber densities were determined before and after irradiation using a liquid density gradient column technique with appropriate mixtures of carbon tetrachloride (CCl_4), bromoform ($CHBr_3$) and methylene iodide (CH_2I_2). A single column covered a 0.4 g/cm^3 density range over a 100 cm length; therefore a number of columns with different liquid ratios were necessary to cover the fiber density range 2.0 to 3.1 g/cm^3. Even though the fiber bundles sometimes separated and spread over ≈ 1 cm along the column, the precision of the density measurements was estimated to be ≤0.002 g/cm^3.

Results and Discussion

Tables 1 and 2 list the unirradiated properties for the tested SiC-based and C fibers, respectively. The compositions, room temperature tensile strengths and moduli were taken from the literature [10,11]. The Dow Xstalline fiber is a developmental SiC product, whereas the other SiC-based fibers are commercially available. The HPZ and Nicalon HVR fiber microstructures are rather amorphous; the Nicalon CG and Tyranno microstructures contain a considerable amount of ≈2 nm β-SiC crystallites in a Si-O-C or Si-O-C-Ti matrix with excess C; and the Dow Xstalline microstructure is primarily 100 nm β-SiC grains. The degree of graphitization of the C fibers depends on their final heat treatment temperature (HTT); as the HTT increases, the degree of graphitization and the tensile modulus increase [12]. The tensile modulus values ranged from 179 to 894 GPa for these C fibers.

Table 1. Unirradiated properties of tested SiC-based fibers.

Name	Source	Composition (w/o)	RT Tensile Strength (GPa)	RT Tensile Modulus (GPa)	Density (g/cc)	Diameter (μm)
Nicalon CG	Nippon Carbon	Si-31C-12O	2.6	190	*2.582*	*13.7 ± 1.4*
Nicalon HVR	Nippon Carbon	Si-31C-12O	2.9	190	*2.308*	*15.4 ± 2.3*
Tyranno	Ube	Si-28C-17O-3Ti	2.5	190	*2.350*	*6.9 ± 0.5*
HPZ	Dow Corning	Si-28N-10C-4O	2.3	180	*2.242*	*5.9 x 13.2*
Dow Xstalline	Dow/NASA	Si-(30-35)C		420	*2.872*	*7.1 ± 0.2*

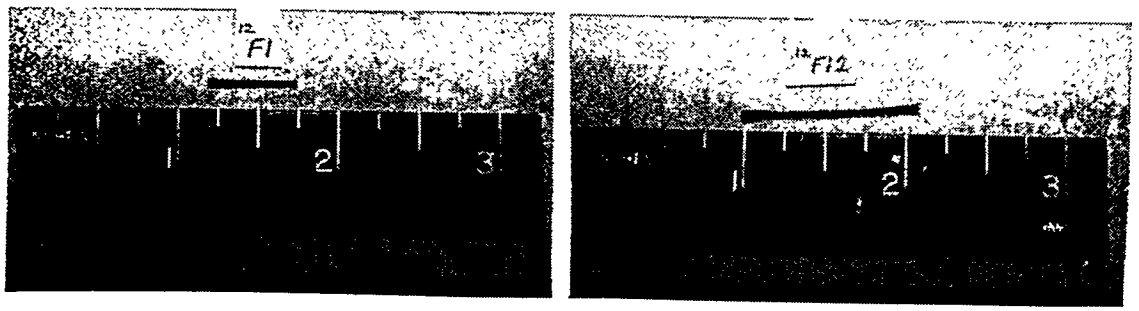
NOTES:
1. Values from references [9,10] indicated by normal type.
2. Values measured in this study indicated by italic type.
3. HPZ fiber has a non-circular cross-section.

Table 2. Unirradiated properties of tested C Fibers.

Name	Source	RT Tensile Strength (GPa)	RT Tensile Modulus (GPa)	Density (g/cc)	Diameter (μm)
E35	DuPont	2.8	241	*2.030*	*9.3 + 0.9*
E55	DuPont	3.2	378	*2.083*	*8.2 + 0.8*
E75	DuPont	3.1	516	*2.100*	*9.3 + 0.7*
E105	DuPont	3.3	724	*2.119*	*9.6 + 0.6*
E120	DuPont	3.4	827	*2.127*	*8.9 + 0.8*
E130	DuPont	3.9	894	*2.132*	*9.2 + 0.8*
- K139	Mitsubishi		738	*2.132*	*9.1 + 0.5*
- K321	Mitsubishi		179	*2.030*	*9.6 + 0.4*

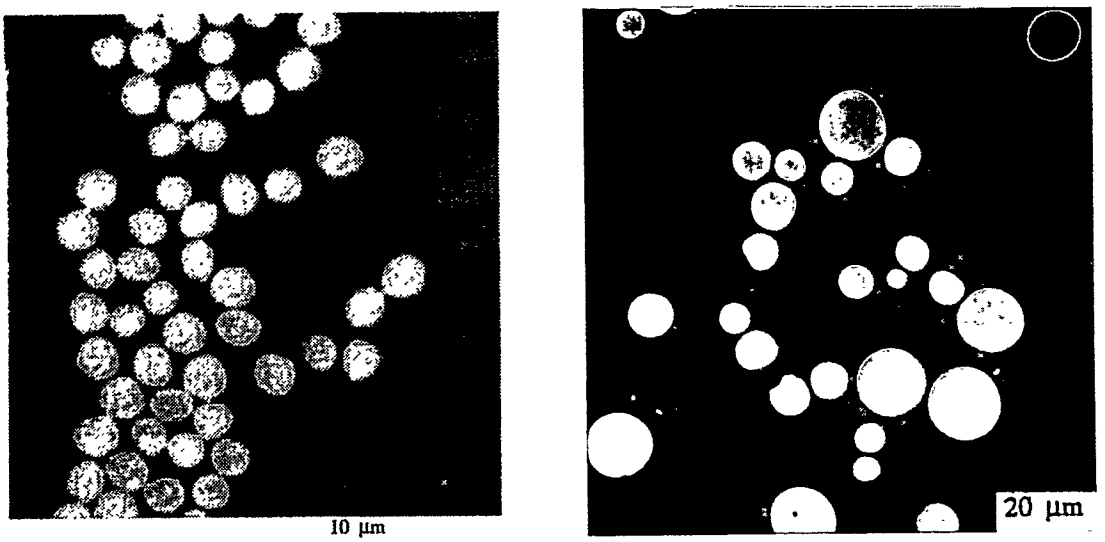
NOTES: 1. Values from the manufacturer indicated by normal type.
2. Values measured in this study indicated by italic type.

Figures 1a and 1b present post-irradiation photographs of a low modulus C fiber (E35) and a Nicalon CG fiber bundle, respectively. The pre-irradiated bundle lengths were each 3.05 cm (1.20 in). As for the E35 fiber in Fig. 1a, axial shrinkage of all the irradiated C fibers was visually apparent. Shrinkage (or swelling) of the irradiated SiC fibers could only be discerned by length measurements with a traversing microscope.



Figures 1a and 1b. Representative post irradiation photographs of E35 C (left) and Nicalon CG SiC (right) fiber bundles. Each fiber bundle, originally cut to lengths of 1.20 inches, had been irradiated to the same fluence (2.5×10^{22} n/cm^2, $E \geq 0.1$ MeV) at 430 °C.

Figures 2a and 2b present typical cross-sectional views of SiC and C fiber bundles after they were mounted and polished. From digital image analysis of such views, the average diameters and associated standard deviations listed in Tables 1 and 2 for each fiber type were determined. Unfortunately, the large cross-sectional area variation within each fiber type precluded the possibility of making diametral dimensional change measurements for the irradiated fibers.



Figures 2a and 2b. Cross-sectional views of the resin mounted and polished E35 C (left) and Nicalon CG SiC (right) fiber bundles.

Table 3 presents a comparison of length changes for the irradiated SiC-based fibers determined by two methods.

Table 3. Comparison of two methods for determining length changes of SiC-based fibers due to neutron irradiation.

Name	5.3 dpa-SiC		26 dpa-SiC	
	Direct (%)	Density Change (%)	Direct (%)	Density Change (%)
Nicalon CG	-2.4 + 0.8	-1.9 + 0.2	-3.5 + 0.7	-1.8 + 0.2
Nicalon CG (a)			-4.4 + 0.7	-4.9 + 0.3
Nicalon HVR	-5.2 + 0.8	-5.6 + 0.2	-5.8 + 0.8	-5.5 + 0.2
Tyranno	-0.9 + 0.6	-3.1 + 0.4	-1.6 + 2.0	-6.0 + 0.4
HPZ	-7.3 + 0.9		-8.3 + 0.7	-8.0 + 0.2
Dow Xstalline	1.5 + 1.5		2.0 + 2.0	0.5 + 0.2

NOTES: a. Irradiation temperature was 430 °C except for (a) where it was 850 °C.

In the direct method, the fractional length change was determined from the difference between the unirradiated and irradiated fiber bundle lengths as measured by using the traversing microscope. The density change method relates the measured density change before and after irradiation to the expected length change. If the fiber mass is unchanged during irradiation, the fractional change in density, $\Delta\rho/\rho$, for a circular fiber of diameter D and length L is given by:

$$\Delta\rho/\rho \approx -(\Delta L/L) - 2(\Delta D/D) \quad (1)$$

Then if the volumetric fiber shrinkage (or swelling) is isotropic:

$$\Delta L/L \approx -1/3(\Delta\rho/\rho) \quad (2)$$

One would expect isotropic shrinkage (swelling) in the SiC-based fibers due to the cubic structure of the ß-SiC crystallites which comprise much of the fiber micro-structure. Except for the Tyranno fiber, which contains a high concentration of O and some Ti as well as excess C, general agreement between the length changes determined by the direct and density change methods justifies using Eq. (2) for estimating the SiC-based fiber length change. By comparison of the estimated variations listed in Table 3, it also is apparent that the density change method is more precise than the direct method for estimating the length changes if the change is isotropic.

Figure 3 presents the fractional length change, determined by the density change method where possible, as a function of dose for the SiC-based fibers. Above 5 dpa-SiC, little dose dependence is observed except for the Tyranno fiber. However, this may be an artifact due to using the density change method for determining the Tyranno fiber length change. From Table 3, it is apparent that the assumption of isotropic shrinkage may not be valid for the Tyranno fiber. At 430 °C, the HPZ and the Nicalon HVR fibers, whose pre-irradiated densities were quite low, exhibited substantially more axial shrinkage than the Nicalon CG fiber. Even though the shrinkage of the Nicalon CG fiber was moderate (about 2% at 430 °C and 4.9% at 850 °C), such shrinkage has been observed to cause complete debonding from the matrix resulting in decreased strengths in continuous fiber reinforced SiC/SiC composites irradiated under similar conditions [8]. The developmental fiber, Dow/NASA Xstalline, actually exhibited slight swelling rather than shrinkage. The composition of the Dow/NASA fiber was near stoichiometric SiC, the unirradiated density was 90% of theoretical for SiC, and the microstructure was reported to be more crystalline than for the other SiC-based fibers [11]. The swelling observed for the irradiated Dow/NASA fiber is reasonably consistent with trends previously observed for irradiated crystalline SiC [8,12].

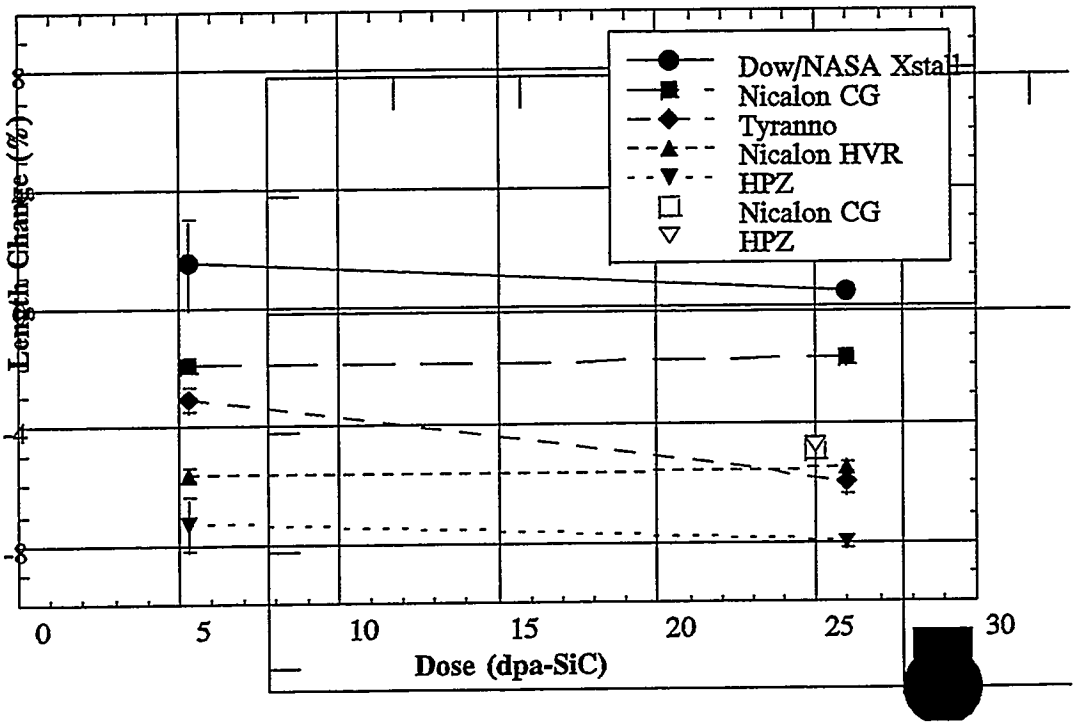


Figure 3. Shrinkage (Swelling) of SiC-based fibers after irradiation to 5.3 and 26 dpa-SiC at 430 °C. Single data points (open symbols) for Nicalon CG and HPZ fibers were irradiated at 850 °C to 25 dpa-SiC.

Figure 4 presents the axial shrinkage for the C fibers with a range of graphitization for two relatively high irradiation doses, 3 and 15 dpa-C. Irradiation effects in C fibers have been examined by others [13], but only to doses less than 1 dpa-C. For these high dose irradiations, the amount of axial shrinkage for the C fibers was greater at low degrees of initial graphitization (as represented by initial values of tensile modulus) and generally was much greater than observed for the irradiated SiC-based fibers. Also, in contrast to the irradiated SiC fiber behavior, the radiation damage did not appear to saturate, but continuously increased with increasing dose. The axial shrinkage exceeded 20% for the most graphitic C fiber and exceeded 60% for the less graphitic fiber at the higher dose. It is the fundamental nature of radiation damage in graphite that leads to severe fiber dimensional instability at higher neutron doses, and thus to the unacceptable performance observed in irradiated continuous fiber reinforced C/C composites mentioned earlier.

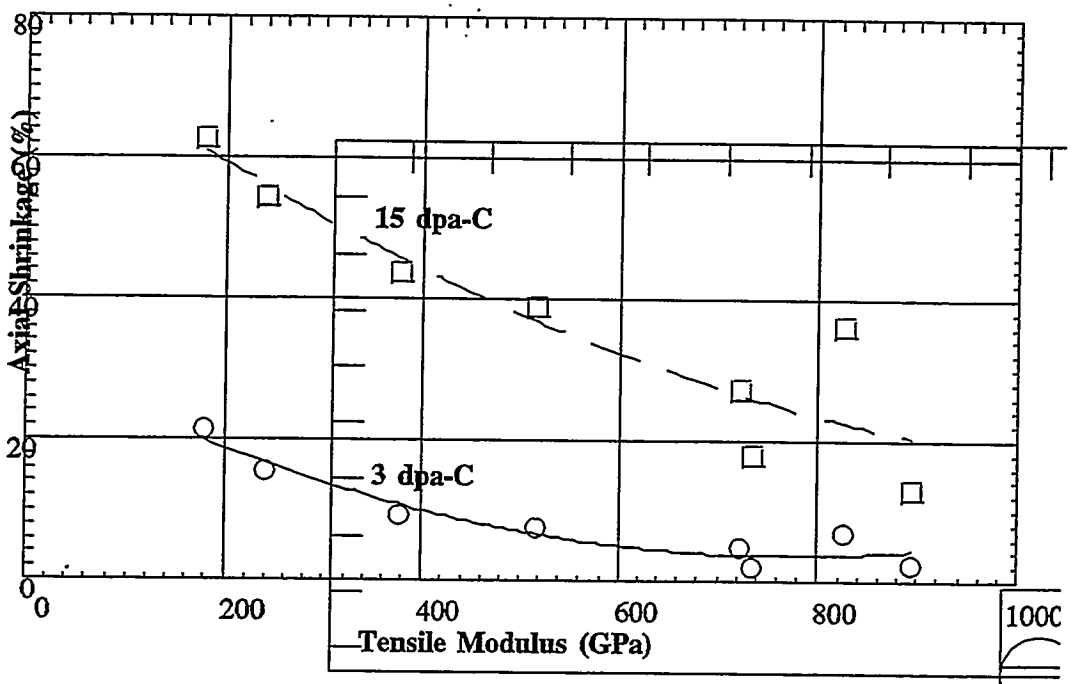


Figure 4. Dependence of the axial shrinkage of C fiber on the degree of graphitization (as indicated by the initial tensile modulus) for fibers irradiated at 430 °C to relatively high doses, 3 and 15 dpa-C. The curves are for guidance only.

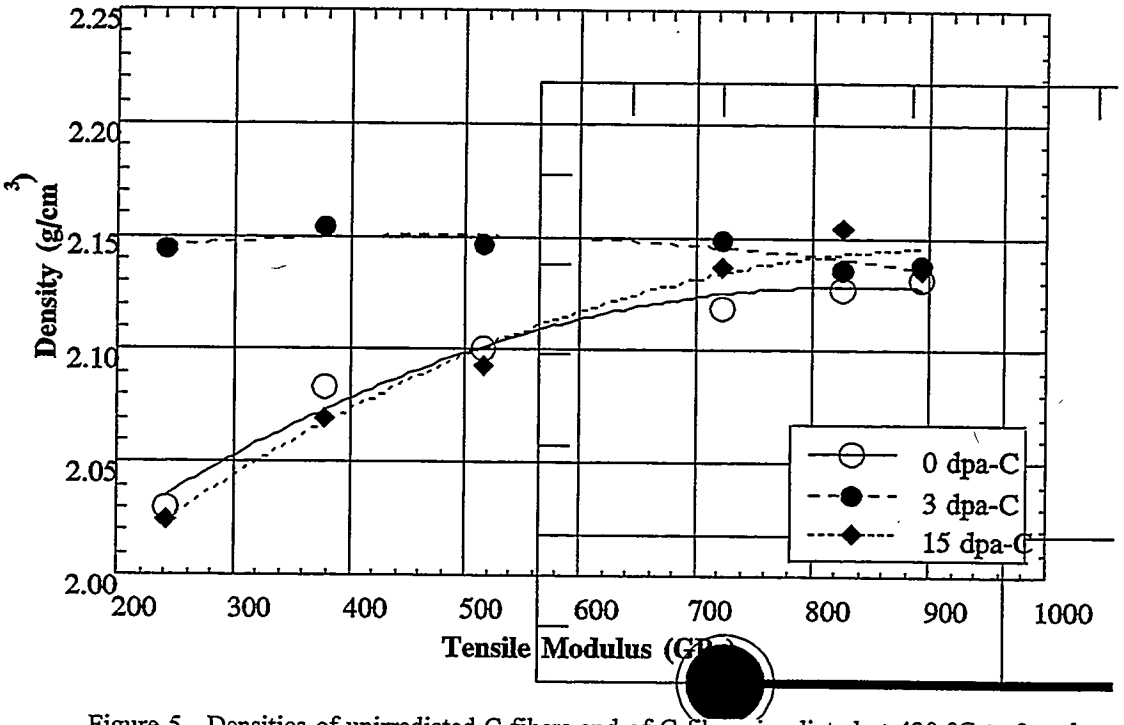


Figure 5. Densities of unirradiated C fibers and of C fibers irradiated at 430 °C to 3 and 15dpa-C as a function of their initial tensile modulus. The curves are for guidance only.

Figure 5 (shown on the preceding page) presents the densities of the unirradiated C fibers as a function of their degree of initial graphitization (again as represented by the tensile modulus) together with the densities of the same fibers irradiated at 430 °C to 3 and 15 dpa-C. As expected, the density of unirradiated C fiber increases continuously as the degree of graphitization increases. However, independent of the initial degree of graphitization, the densities of all the C fibers appeared to saturate at about 2.15 g/cm^3 by the 3 dpa-C dose. With increasing dose above 3 dpa-C, the densities appeared to decrease and returned almost to their unirradiated values by 15 dpa-C for each of the C fiber types. This observation coincides with the character of the dimensional changes of irradiated C fiber and the extreme amount of anisotropy in the hexagonal graphitic structure. X-ray analysis has indicated a preferential alignment of the hexagonal graphitic basal planes parallel to the fiber axis [14]. The data indicate that C fibers will continuously shrink in the axial direction (graphitic a-axis) under irradiation. Initially, diametral (graphitic c-axis) swelling will be accommodated by porosity and/or amorphicity until the saturation density of about 2.15 g/cm^3 has been reached. Continued irradiation damage will lead to additional c-axis growth and expected diametral swelling of the C fibers. This effect appears to be much more severe for the C fibers with a lower degree of initial graphitization.

CONCLUSIONS

- Due to the fundamental nature of radiation damage in graphite, dimensional instability (extreme axial shrinkage and diametral swelling) of C fiber irradiated to high doses will prevent their use in C/C composites for long-term operations in a fusion power system.

- Silicon carbide based fibers that are close to stoichiometric and crystalline appear to have the radiation damage tolerance necessary to make SiC/SiC composites suitable for further testing for fusion power system applications.

FUTURE WORK

Emphasis will be focused on examining the irradiation effects on additional alternate commercial and developmental SiC-based fibers. Irradiation exposures also will include a broader range of conditions. For instance, in the COBRA series of irradiations recently completed in the EBR II reactor, nine SiC-based fiber types were irradiated to a very high dose (≈80 dpa-SiC) at 800°C. Post-irradiation analysis of these fibers will be carried out during the next reporting period. The primary goal will be to identify other more radiation tolerant fibers, then use the best fibers to ultimately fabricate a high performance SiC_f/SiC composite suitable for advanced fusion power system applications.

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