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Radiation response of SiC-based fibers

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Abstract

Loss of strength in irradiated fiber-reinforced SiC/SiC composite generally is related to degradation in the reinforcing fiber. To assess fiber degradation, the density and length changes were determined for four types of SiC-based fibers (Tyranno, Nicalon CG, Hi Nicalon and Dow X) after high temperature (up to 1000°C) and high dose (up to 80 dpa-SiC) irradiations. For the fibers with nonstoichiometric compositions (the first three types in the list), the fiber densities increased from 6% to 12%. In contrast, a slight decrease in density (<1%) was observed for the Dow X fiber with a quasi-stoichiometric composition. Fiber length changes (0–5.6% shrinkage) suggested small mass losses (1–6%) had occurred for irradiated uncoated fibers. In contrast, excessive linear shrinkage of the pyrocarbon-coated Nicalon CG and Tyranno fibers (7–9% and 16–32%, respectively) indicated that much larger mass losses (11–84%) had occurred for these coated fibers. Crystallization and crystal growth were observed to have taken place at fiber surfaces by SEM and in the bulk by XRD, moreso for irradiated Nicalon CG than for Hi Nicalon fiber. The radiation response of the quasi-stoichiometric Dow X fiber was the most promising. Further testing of this type fiber is recommended.

1. Introduction

Silicon carbide (SiC) exhibits remarkable dimensional stability in a neutron irradiation environment with linear swelling <0.2% independent of dose in the 800–1000°C temperature range [1]. It also exhibits very low induced activity and afterheat; however, it is a brittle ceramic. As compared to monolithic SiC, continuous fiber-reinforced silicon carbide composite (SiC_f/SiC) exhibits improved toughness with a noncatastrophic high strain-to-failure of about 0.5% versus about 0.1% for monolithic SiC. For these reasons, SiC_f/SiC has been considered as a structural material for first wall or breeder blanket applications in advanced fusion power plant concepts [2,3].

The radiation stability of SiC_f/SiC primarily depends on the dimensional, thermochemical and thermomechanical stability of the fiber [4]. Therefore, the purpose of this paper is to assess the performance of several types of irradiated SiC-based fibers to provide guidance for future fiber and composite development for fusion applications.

2. Experimental methods

Selected properties and compositions for the four fiber types evaluated are given in Table 1. The examined fibers can be grouped into three categories: (1) nanocrystalline SiC fibers with excess carbon and oxygen – Tyranno and Nicalon CG, (2) nanocrystalline SiC fibers with excess carbon (residual oxygen <1%) – Hi Nicalon, and (3) quasi-stoichiometric crystalline SiC fibers – Dow X (an early version of now available Sylramic™ fiber). All of these fibers are polymer-derived, have small diameters and are suitable for weaving as yarns into fabric for composite reinforcement.

In Table 1, measured lot specific data are indicated with normal type, while manufacturer's data are indicated in parentheses. The tensile strengths for 25 mm

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Table 1
Compositions and selected properties of tested SiC-based fibers

Fiber properties [a]	Tyranno [b]	Nicalon CG [c]	Hi Nicalon [c]	Dow X [d]
Diameter(μm)	10 (9)	14 (14)	13 (14)	9 (10)
Density (g/cc)	2.35 (2.35)	2.55 (2.55)	2.75 (2.74)	3.03 (3.1)
RT tensile strength (GPa)	2.5 (3.5)	2.8 (3.0)	2.4 (2.8)	3.1 (3.2)
RT elastic modulus (GPa)	(170)	(220)	(270)	(380)
Composition (wt%)				
Si	(51.4)	(56.6)	(62.4)	(67)
C	(29.6)	(31.7)	(37.1)	(29)
O	(18)	(11.7)	(0.5)	(0.8)
Other	(1.0, Ti)			(3, TiB_2)
C/Si (atomic)	(1.3)	(1.31)	(1.39)	(1.0)
Crystallite size (nm)	1.3 (1.0)	2.0 (2.5)	4.0 (5)	85
Maximum use temp. (°C)	1035	1110	1230	1440

[a] Measured lot specific data, manufacturer's data shown in parentheses.
[b] Ube Industries, Ltd., Ube City, Yamaguchi 755, Japan.
[c] Nippon Carbon Co., Ltd., Yokohama 221, Japan.
[d] Dow Corning Corp., Midland, MI, USA.

gauge lengths were measured using a constant displacement Micropull device (Micropull Science, Thousand Oaks, CA); the average diameters were determined from SEM views of the fiber cross-sections after tensile strength testing; the densities were determined for representative fiber bundles by a liquid gradient column technique; the crystallite sizes were determined by using the Scherrer equation for the β-SiC $\langle 1\ 1\ 1\rangle$ XRD peak; and the maximum use temperatures were estimated from bend stress relaxation (BSR) creep tests of single fibers [5]. The maximum use temperature is defined here as the transition temperature where the BSR parameter m is equal to 0.5 for 1 h exposure in argon [6]. Since the fiber strength is known to degrade above this transition temperature, it is an effective measure of the high temperature thermochemical stability of the fiber [7].

To assess the dimensional and thermochemical stability of the irradiated fibers, length and density changes were determined for representative fiber bundles after irradiation. The Tyranno and Nicalon CG fibers were tested uncoated or coated with a thin (≈150 nm) pyrocarbon (PyC) layer. For the irradiations, a single fiber bundle was cut to a specified length (3.00 ± 0.02 cm) and carefully slid into a protective SiC tube (Hexoloy SA™ sintered SiC (Carborundum, Niagara Falls, NY)). After irradiation, the fiber bundle was pushed out from its protection tube with a small diameter rod and its length was immediately measured using a digital imaging technique with ×12 magnification. Then the irradiated fiber bundles were separated into smaller bundles for SEM and XRD analysis and strength measurements of individual fibers. A 1 cm bundle was used for density measurements. Although the residual activity of the SiC fibers and their tube holders was low (<10 mR/h on contact), the work was performed in a modified glove box or a hood to satisfy safety requirements.

In this study, the radiation response for the four SiC fiber types after high temperature, high dose exposures (43 dpa-SiC at 1000°C and 80 dpa-SiC at 800°C) is emphasized. The data for the 43 dpa-SiC dose, taken from Ref. [8], were combined with recently obtained 80 dpa-SiC data. Both irradiations took place in the EBR II fast reactor. The tests were uninstrumented, so the irradiation temperatures were achieved by designing a gas gap around the subcapsules and adjusting the coolant gas flows. The sealed subcapsules only contained the SiC fibers inside their SiC protection tubes and other SiC/SiC bar samples, and were back-filled with helium at approximately one atmosphere pressure. Apparent end-of-cycle (EOC) irradiation temperatures were measured with passive CVD β-SiC temperature monitors. For the 1000°C and 800°C irradiations, the fluences and exposure times were 34.0×10^{25} n/m^2 ($E > 0.11$ MeV) for 185 EFPD and 68.5×10^{25} n/m^2 ($E > 0.11$ MeV) for 337 EFPD, respectively. Due to long-term swelling of the subcapsule and consequent additional cooling, the sample irradiation temperature decreased from 800°C to 550°C near EOC for the 80 dpa irradiation. However, for analysis it was assumed that most of this irradiation took place at the design temperature of 800°C.

3. Results

As an example of the fiber bundle length measuring technique, magnified images of irradiated (a) Nicalon CG and (b) PyC-coated Tyranno fiber bundles are

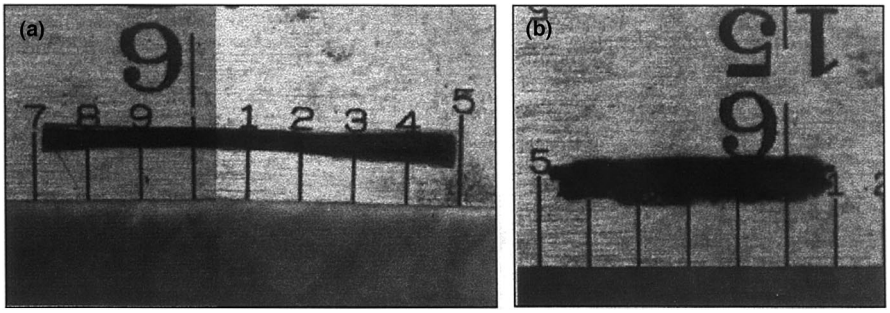

Fig. 1. Two examples of fiber bundle shrinkage due to irradiation. The unirradiated bundle lengths were 0.80 ± 0.01 in. The uncoated Nicalon CG bundle (a) shrunk 3.9 ± 0.3%; the PyC-coated Tyranno bundle, (b) shrunk 32 ± 1%.

shown in Fig. 1. Both of these fiber bundles initially were 0.8 in. long in the unirradiated condition. After irradiation at 800°C to 80 dpa-SiC, it is evident from the images that axial fiber shrinkage occurred. Careful measurement from these images revealed that the uncoated Nicalon CG fiber shrunk 3.9 ± 0.3% while the PyC-coated Tyranno fiber shrunk 32 ± 1%. The uneven bundle ends contribute to a larger uncertainty for the irradiated Tyranno fiber shrinkage.

In Fig. 2, the measured densities for the four types of SiC-based fibers irradiated in EBR II (solid symbols) are combined with the literature data (open symbols) to present the change in fiber density over four decades of fluence [9,10]. As a rough rule, 1×10^{25} n/m^2 can be taken equivalent to a 1 dpa-SiC dose. The guidance lines indicate continuously increasing densities with fluence up to 68.5×10^{25} n/m^2 (equivalent to an 80 dpa-SiC dose for the EBR II spectrum) for the three non-stoichiometric SiC fiber types. In contrast, the Dow X stoichiometric SiC fiber exhibits slightly decreasing densities with dose. The irradiation temperatures, ranging from 100°C to 650°C for the lower dose literature data, apparently have only a secondary effect on the density changes exhibited by irradiated SiC fibers.

In Table 2, the calculated relative density and length changes for the four irradiated SiC fiber types after doses of 43 or 80 dpa-SiC are compared. All three nonstoichiometric fiber types, coated or uncoated, exhibited a roughly 10% density increase and a length decrease which varied from 3% to 32%. In contrast, within the limits of measurement uncertainties, the stoichiometric Dow X fiber exhibited relatively small changes in either its density or length. The final two columns in Table 2 list the estimated mass loss for all of the irradiated fibers which will be discussed in Section 4. For clarity the uncertainties in the density and length

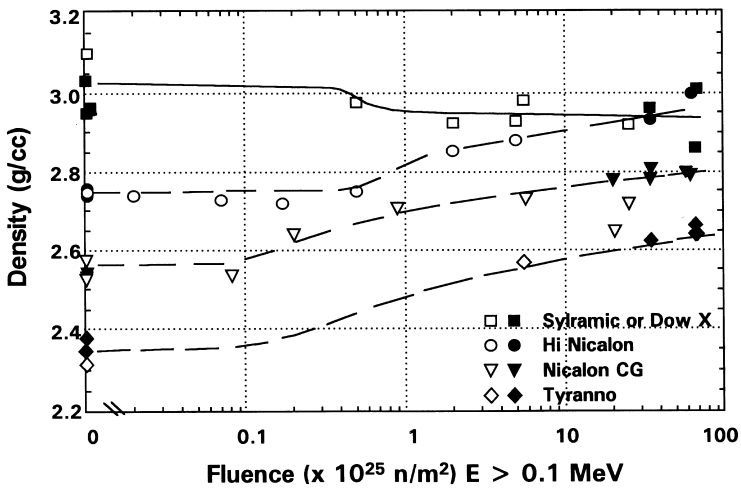

Fig. 2. Density as a function of fast neutron fluence for four SiC-based fibers. The literature data from Refs. [9,10] (open symbols); high temperature (800°C and 1000°C), high dose data from this work (solid symbols).

Table 2
Relative fiber mass changes calculated from measured relative density and length changes for irradiated uncoated and PyC-coated SiC-based fibers [a]

Fiber type	$\Delta\rho/\rho_0$		$\Delta L/L_0$		$\Delta m/m_0$	
	43 dpa (%)	80 dpa (%)	43 dpa (%)	80 dpa (%)	43 dpa (%)	80 dpa (%)
Tyranno	+11.7	+13.3	−5.6	−5.4	−5.1 (0.8)	−2.7 (2.4)
Tyranno + PyC [b]	+12.0	+12.5	−16.6	−32 (1)	−38 (2)	−84 (2)
Nicalon CG-1	+9.1	+9.8	−3.1	−4.6	−0.7 (1.3)	−4 (2)
Nicalon CG-2	+10.3	+9.6	−3.5	−4.4	−1.1 (1.0)	−3.6 (0.5)
Nicalon CG-3	+9.6	+9.8	−2.9	−4.6	−1.0 (1.3)	−4.0 (2.2)
Nic CG + PyC [b]	+10.1	+11.3	−7.1	−9 (1.3)	−11 (2.3)	−16 (4)
Hi Nicalon	+6.3	+9.8	−4 (2)	−4.1	−5.7 (5)	−2.7 (2.3)
Dow X	−0.2	−0.8 (2)	−1.5	+2 (4)	−4.7 (2.6)	+5 (8)

The irradiation conditions were 43 dpa-SiC at 1000°C and 80 dpa-SiC at 800°C.
[a] Uncertainties exceeding 1% are given in parentheses.
[b] The pyrocarbon (PyC) coating nominally was 150 nm thick.

changes are not given except when they exceeded 1% (indicated with parentheses). The large uncertainty for the Dow X density change resulted because the fiber bundle dispersed into a cloud of individual fibers in the liquid gradient column. The large uncertainties that occurred for four of the length changes resulted because during irradiation or handling the fiber bundle ends became misaligned, as depicted for the Tyranno fiber bundle in Fig. 1(b). Since the relative mass change requires taking the difference between two similar values, the resulting uncertainty (also given in parentheses) can become relatively large.

4. Discussion

The similarity between the observed density and length changes for the nonstoichiometric fiber types suggests a common form of irradiation induced degradation in these fibers. From Table 1, the XRD crystallite

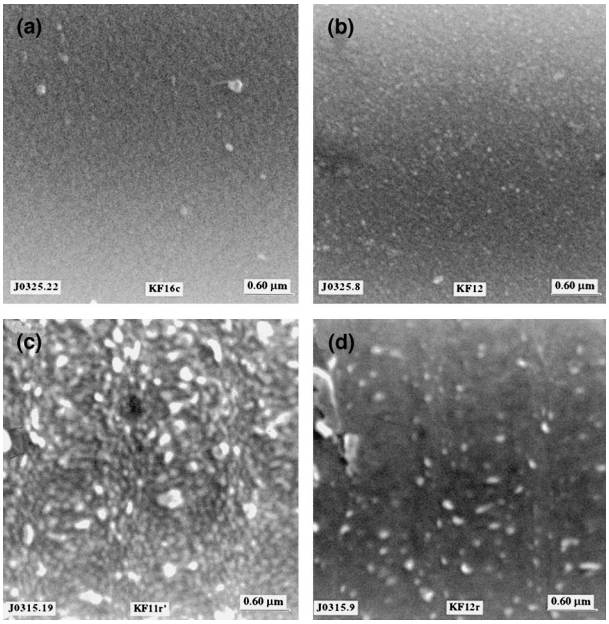

Fig. 3. SEM views of fiber surfaces for unirradiated and irradiated Nicalon CG and Hi Nicalon (a/c and b/d, respectively). The Nicalon CG fiber had been irradiated at 1000°C to 43 dpa-SiC and the Hi Nicalon fiber had been irradiated at 800°C to 80 dpa-SiC. Crystallization and crystal growth are evident at the fiber surfaces, moreso for the Nicalon CG fiber.

sizes were 1.3 and 4.0 nm for the unirradiated Nicalon CG and Hi Nicalon fibers, respectively. After the 80 dpa-SiC (800°C) irradiation, their XRD crystallite sizes had increased to 6.0 and 11 nm, respectively. In Fig. 3(a)–(d), typical SEM views of the Nicalon CG and Hi Nicalon fiber surfaces before (a and b, respectively) and after (c and d, respectively) high dose, high temperature irradiations indicate that extensive crystal growth had taken place, especially at the Nicalon CG fiber surface after the 1000°C irradiation. These observations confirm that crystallization and crystal growth can be induced by the irradiation at lower temperatures than that expected for these processes in unirradiated fibers, and is a degradation mechanism in common for these two fiber types.

The relative mass change entries in Table 2 were estimated from the relative density and length change values in the following way. By taking differentials of the density $\rho = m/V$, and substituting $\Delta V/V_0 \approx 3\Delta L/L_0$ (the isotropic shrinkage assumption for cubic β-SiC), the relative mass change ($\Delta m/m_0$) is given by

$$\Delta m/m_0 \approx 3\Delta L/L_0 + \Delta\rho/\rho_0, \quad (1)$$

where the Δ's indicate differences between irradiated and unirradiated values and the subscripted terms indicate the original unirradiated values for the mass, length and density, respectively.

For values of $\Delta m/m_0$ near zero, the relative fiber length change should be about one-third the magnitude of the relative fiber density change and opposite in sign, which is what was expected for the SiC fibers irradiated in an inert atmosphere at or below 1000°C. However, due to suspected mass loss, small negative values of mass change occurred for all the nonstoichiometric uncoated fibers, and large negative values occurred for the PyC-coated Nicalon CG and Tyranno fibers. For the PyC-coated Nicalon CG fiber, the mass losses calculated from Eq. (1) were 11 ± 2.3% and 16 ± 4% for the 43 and 80 dpa-SiC doses, respectively. The calculated mass losses for the PyC-coated Tyranno fiber were even larger, 38 ± 2% and 84 ± 2% for the 43 and 80 dpa-SiC doses, respectively. The 32% shrinkage in length for the irradiated PyC-coated Tyranno fiber listed in Table 2, which dominates the relative mass change calculation, is clearly evident in its bundle image shown in Fig. 2(b). The PyC-coating must have been responsible for enhancing the mass loss of these two fibers, which in common contain a significant amount of amorphous-like Si–C–O phase. The larger mass loss calculated for the PyC-coated Tyranno fiber correlates with its larger oxygen content (18% versus 12% for Nicalon CG) and its more noncrystalline phase content (1 nm XRD crystallite size versus 2.5 nm for Nicalon CG). This mass loss mechanism together with fiber densification explains the diametral shrinkage observed in the PyC-coated Nicalon CG reinforcement fibers and the subsequent loss in the SiC/SiC composite strength after irradiation to 26 dpa-SiC at 800°C [4]. A mass loss during the 80 dpa-SiC (800°C) irradiation also was reported for SiC_f/SiC bend bars made with the PyC-coated Nicalon CG fiber [11]. This composite mass loss and significant fiber shrinkage within the CVI matrix were attributed to the thermochemical instability of the fiber's amorphous silicon oxycarbide phase which apparently was induced by the irradiation even at the 800°C irradiation temperature. It was suggested that the bar mass losses occurred because oxygen contained within the Nicalon CG fibers combined with the free carbon in the fibers as well as with the carbon at the fiber surface and was exsolved primarily as carbonmonoxide. The observed 60% strength loss of the bend bars was attributed primarily to the degradation of the PyC-coated Nicalon CG fiber strength due to this internal carbothermal reduction.

Unfortunately, PyC-coated Hi Nicalon fiber by itself was not tested. However, due to the low oxygen content of Hi Nicalon, the internal carbothermal reduction degradation should not be as important. Nevertheless, long-term degradation of irradiated Hi Nicalon fiber through densification, crystallization and crystal growth indicates that composite made with this fiber also may not exhibit acceptable radiation tolerance, although further testing of this fiber and composite made with this fiber is warranted.

The radiation response of the stoichiometric, crystalline SiC fiber (Dow X) was much different. The slight, rather abrupt density decrease at about 1 dpa-SiC with no further density change, inferred by the guidance line in Fig. 2, suggests fiber swelling due to accumulation and saturation of irradiation defects somewhat similar to the radiation response of monolithic β-SiC. Thus, in a composite, this type of fiber should not exhibit debonding due to fiber shrinkage and matrix swelling. However, composite performance and effects of irradiation on strength of the crystalline, stoichiometric type fibers still needs to be tested. Also, possible adverse effects due to helium formation in neutron irradiated fibers (or composites) that contain boron as an additive need to be examined.

5. Conclusions

1. Consideration of SiC_f/SiC composites for use in advanced fusion power plant concepts is limited by the demonstrated dimensional and thermochemical instability of the reinforcing fibers during irradiation. The combination of high temperature and irradiation can enhance degradation in these fibers beyond that normally expected in a high temperature environment alone, especially if the fibers contain oxygen.

2. Pyrocarbon coatings enhance the dimensional and thermochemical instability of SiC fibers with excess

oxygen (e.g., Tyranno and Nicalon CG fibers). An internal carbothermal reduction mechanism is responsible for predicted coating and fiber mass loss and subsequent fiber shrinkage and debonding in a SiC/SiC composite made with these fibers.

3. Only slight improvement in radiation dimensional stability was exhibited by Hi Nicalon over bare Nicalon CG fibers after high temperature, high dose exposures. However, when PyC-coated in a composite, low oxygen Hi Nicalon fiber should not exhibit the carbothermal reduction degradation mechanism.

4. Microcrystalline, stoichiometric SiC fibers appear to exhibit acceptable dimensional stability after high temperature, high dose irradiation, and in a composite should behave somewhat similarly to a β-SiC matrix. For use in such environments, a more vigorous test and development program for this group of SiC fibers and composites is recommended.

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