MICROSTRUCTURAL EFFECTS OF NEUTRON IRRADIATION ON SIC-BASED FIBERS -

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OBJECTIVE

The objective of this task is to examine the irradiation effects on advanced SiC-type fibers.

SUMMARY

For extreme irradiation conditions, 43 dpa at temperatures of ≈ 1000°C, Hi Nicalon SiC fiber exhibits a much higher degree of microstructural stability than Nicalon CG fiber.

Introduction

Monolithic silicon carbide (SiC), and more recently SiC fiber reinforced SiC composites (SiC_f/SiC), have been examined for fusion reactor applications because of their intrinsically low afterheat and residual activation as well as their promising high temperature performance [1-3]. In particular, SiC_f/SiC is attractive as a structural material because its strength, toughness and strain-to-failure properties can be improved over that of monolithic SiC. Monolithic SiC itself has exhibited attractive dimensional stability in a high energy neutron environment, especially in the high temperature range of 800 to 1000°C [4]. However, available commercial SiC-based fibers have exhibited serious degradation for these same irradiation conditions. For instance, the observed shrinkage of irradiated Nicalon CG™ fiber was thought to be primarily responsible for the concurrent mechanical property degradation in irradiated SiC_f/SiC composites made with this fiber [4].

To determine the reason for the dimensional instability of the irradiated Nicalon fiber and, in general, whether the irradiation performance of SiC-based fibers can be improved, a microstructural analysis by TEM was carried out for two different Nicalon SiC fiber types, CG and Hi Nicalon.

Although the production of both Nicalon fibers starts from a polycarbosilane precursor fiber, subsequent processing routes yield a much lower oxygen content in the Hi Nicalon (0.5 wt. %) as compared to the Nicalon CG (11.7 wt. %). The resulting microstructure of Nicalon CG was reported to consist of ß-SiC grains of about 2 nm size surrounded by an amorphous Si-C-O phase and some turbostratic free carbon [6]. Likewise, the microstructure of Hi Nicalon was more crystalline because the ß-SiC grains were closer to 5 nm size, the turbostratic carbon layers were more organized and the amorphous Si-C-O phase was no longer observable. The chemical composition and microstructures which result from the different fiber processing routes lead to the slightly higher density and tensile modulus exhibited by Hi Nicalon as compared to Nicalon CG, while the tensile strength and elongation are slightly lower.

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Fiber Characterization

Typical properties of the two examined Nicalon fiber types, both manufactured by Nippon Carbon Co., appear in Table 1.

Table 1. Typical Properties of Nicalon CG and Hi Nicalon [5].

Properties		**Nicalon CG**	**Hi Nicalon**
Fiber diameter	(um)	14	14
Density	(g/cm^3)	2.55	2.74
Tensile strength	(GPa)	3.0	2.8
Tensile modulus	(GPa)	220	270
Elongation	(%)	1.4	1.0
Chemical composition	Si (wt %)	56.6	62.4
	C	31.7	37.1
	O	11.7	0.5
	C/Si (atomic)	1.31	1.39
Crystallite grain size	(nm)	<2	5-10
Amorphous matrix		Si-C-O someurbostraticC	turbostratic C

Snead, et al, reported on the neutron radiation effects on these two SiC-based fibers for relatively low doses (1-3 dpa) at temperatures <500°C [7]. They attributed the observed structural degradation in Nicalon CG fibers to the presence of the Si-C-O amorphous phase, whereas the performance of Hi Nicalon fibers was much better, resembling somewhat the behavior of monolithic SiC. Youngblood, et al, also reported that the dimensional stability of a more crystalline SiC-type fiber was much improved compared to that of Nicalon CG after neutron irradiation at 430°C to a relatively high dose of 26 dpa [8]. They also observed that any shrinkage in SiC-based fibers due to the irradiation had occurred by the time doses less than 5 dpa had been attained. In contrast, axial shrinkage of carbon fibers, irradiated together with the SiC-based fibers, was much greater (up to 60%) and did not saturate as a function of dose, while in the diametral direction the carbon fibers continually swelled. The latter observation is connected to the fundamental nature of radiation damage in the anisotropic graphite structure, i.e., shrinkage in the crystallographic â direction with concurrent growth in the c direction [9]. Since both Nicalon CG and especially Hi Nicalon contain a significant turbostratic intergrain carbon phase, the irradiation performance of graphite fibers is relevant.

Experimental

Small bundles (6.35 cm long) of Nicalon CG and Hi Nicalon fibers were irradiated at 1000°C in the EBR-II reactor to a high dose of 43 dpa. These irradiation conditions represent a most severe exposure expected for a fusion reactor design; exposure conditions for which SiC structures would be preferable to metal structures. Both Nicalon fiber types were expected to be thermally stable at temperatures around 1000°C based on short term exposures during strength retention [5], grain growth [9], and creep resistance [10] tests. However, to separate from irradiation effects the possible effects of long term exposure of the fibers to high temperature alone, control samples of each fiber type were held at 1000°C in a helium atmosphere for 165 days, which approximately duplicated the thermal exposure of the irradiated fibers.

Changes in fiber length, density and tensile strength will be analyzed at a later time. The emphasis of this report is the analysis of the microstructural changes induced by either (1) the thermal heat treatment without irradiation (HT) or (2) the high temperature, high dose neutron irradiation (HTHD).

Microstructural observations of the as received (AR), the HT and the HTHD fibers were carried out by TEM (JEOL-2000FX) at 200 kV. Specimen preparation consisted of fixing a few individual fibers to a thin molybdenum washer and ion milling the fibers with 5 keV argon ions to perforation through their centers. The remaining sides of the perforated fiber retained the fiber shape.

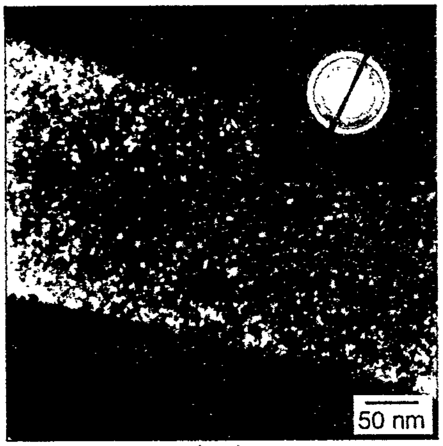
Results and Discussion

Representative TEM micrographs of both unirradiated and irradiated Nicalon CG and Hi Nicalon fibers are shown in Figures 1 (a-c) and 2 (a-c), respectively. Figure 1-a is a dark field image of the HT Nicalon CG fiber. The TEM micrograph shows an extremely fine grain structure with crystallite sizes below 2 nm. The accompanying selected area diffraction (SAD) pattern is a series of fuzzy concentric rings which indicates an amorphous state. The SAD pattern for the AR fiber was identical. The micrograph, which was taken along the first bright inner ring of the SAD, is representative of both unirradiated cases. The corresponding bright field image (not shown) indicated no apparent diffraction contrast. The microstructure of the HT Nicalon CG appeared to be stable for the long time exposure of 165 days at 1000°C in an inert atmosphere. Microstructural changes observed are due to the irradiation conditions, not to the thermal conditions alone.

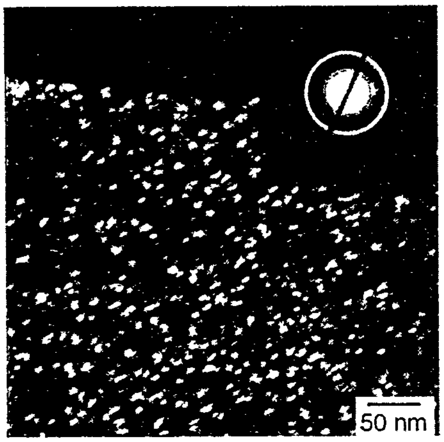
Figures 1-b and 1-c are images of a HTHD Nicalon CG specimen in dark and bright field, respectively. Some small bright spots are now observed superimposed on the diffraction rings of the accompanying SAD. The micrographs show grain growth with some grains exceeding 5 nm. Small black spots also are now observed in Figure 1-c. These black spots are attributed to the same grains seen as bright spots in Figure 1-b. It is readily apparent that the irradiation conditions (43 dpa at 1000°C) induced considerable grain growth and crystallization in Nicalon CG.

Figure 2-a is a dark field image of the heat treated (HT) Hi Nicalon fiber. Again, no differences were observable between the micrographs or their SAD patterns for the AR and HT fibers, thus the HT micrographs as presented are representative of the AR state as well. As expected, the microstructure of the Hi Nicalon fiber was stable at the 1000°C thermal exposure alone. However, in Hi Nicalon some of the ß-SiC grain sizes are 10 nm in size, which is much larger than observed for any of the SiC grains in Nicalon CG. Also, the accompanying SAD ring pattern now shows the appearance of some well defined spots due to a somewhat greater degree of crystallinity in Hi Nicalon as compared to Nicalon CG. These microstructural observations are in line with observations by others for unirradiated fibers of each type [5,6,9] and support the physical property differences reported for Nicalon CG and Hi Nicalon as given in Table 1.

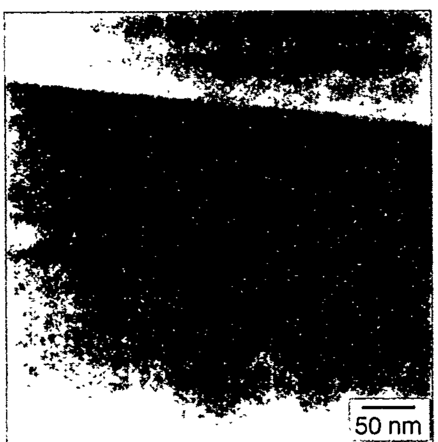
Dark and bright field images of a HTHD Hi Nicalon specimen are shown in Figures 2-b and 2-c, respectively. In contrast to the microstructural effects observed for HTHD Nicalon CG, relatively little change in the grain size was observed for HTHD Hi Nicalon. This observation is supported by the accompanying SAD pattern for the irradiated fiber shown in Figure 2-b, which is very similar to the SAD pattern shown in Figure 2-a for the unirradiated fiber. Nevertheless, the ring patterns indicate the existence of an amorphous or nanocrystalline structure as well.



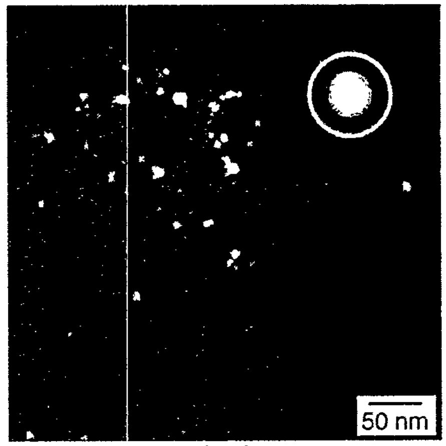
(1a)



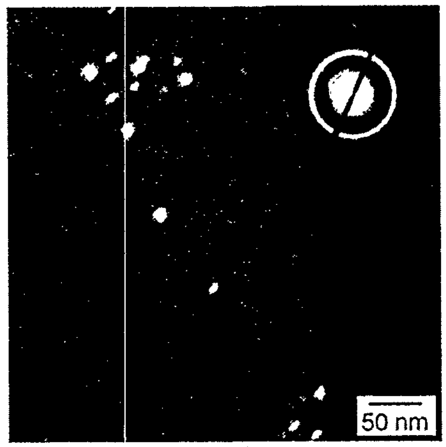
(1b)



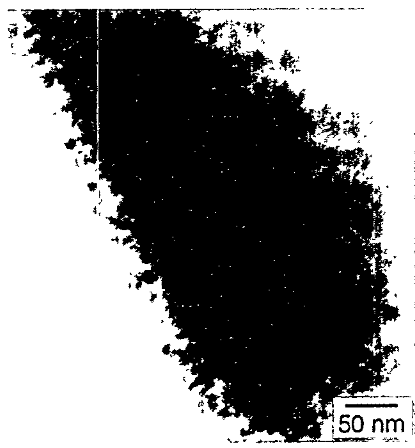
(1c)



(2a)



(2b)



(2c)

Figure 1(a-c) Nicalon CG. **(a)** TEM dark field and SAD of heat-treated (1010°C, 4000 hr in He) fiber, **(b)** dark field and SAD and **(c)** bright field of irradiated (43 dpa, 1000°C) fiber.

Figure 2(a-c) Hi Nicalon. **(a)** TEM dark field and SAD of heat-treated (1010°C, 4000 hr in He) fiber, **(b)** dark field and SAD and **(c)** bright field of irradiated (43 dpa, 1000°C) fiber. Bright ring in the SADs indicates the SiC {III} reflection ring.

Unfortunately, microstructural evidence for the presence of the turbostratic carbon intergrain layers, known to occur in both of these SiC fiber types with excess carbon, was not observed in this work. However, as observed previously for graphitic fiber [8], the effect of irradiation on the carbon intergrain layers would be expected to be detrimental.

Conclusions

Even for the extreme irradiation conditions examined in this work (43 dpa at ≈ 1000°C), the Hi Nicalon fiber shows a much higher degree of microstructural stability than the Nicalon CG fiber. It is expected that the physical properties of the Hi Nicalon also should exhibit enhanced irradiation performance, and if used in SiC_f/SiC composite, should lead to improved irradiation performance of the composite. Future development of a more stoichiometric SiC fiber without the carbon intergrain layers holds even more promise for producing a radiation tolerant fiber and, therefore, should be more appropriate for use in the fabrication of SiC_f/SiC composite for fusion applications.

Future Work

The length, density and strength change analysis of unirradiated and irradiated Nicalon CG and Hi Nicalon SiC fibers will be completed. These same two fiber types, as well as six other advanced SiC fiber types, have been irradiated in the COBRA 1A2 series (EBR II, 80 dpa at 800°C). Postirradiation analysis of all these fibers will soon commence. Future irradiations of Hi Nicalon fiber and Super Nicalon, a near stoichiometric SiC fiber type, will take place in HFIR (Jupiter P3-3, 10 dpa at 500°C) commencing in April, 1996, and analysis should be completed in early 1997.

Acknowledgments

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References

1. L. H. Rovner and G. R. Hopkins, "Ceramic Materials for Fusion," *Nucl. Technol.* **29(3)**, 274-302 (1976).

2. G. R. Hopkins and J. Chin, "SiC Matrix/SiC fiber Composite: A High-Heat Flux, Low Activation, Structural Material," *J. Nucl. Mater.* **141-143**, 148-151 (1986).

3. Russell H. Jones, Charles H. Henager, Jr. and Glenn W. Hollenberg, "Composites for Fusion Applications," *J. Nucl. Mater.* **191-194**, 75-83 (1992).

4. G. W. Hollenberg, C. H. Henager, Jr., G. E. Youngblood, D. J. Trimble, S. A. Simonson, G. A. Newsome and E. Lewis, "The Effect of Irradiation on the Stability and Properties of Monolithic SiC and SiC_f/SiC Composites up to 25 dpa," *J. Nucl. Mater.* **219**, 70-86 (1995).

5. Hiroshi Ichikawa, Kiyohito Okamura and Tadao Seguchi, "Oxygen-Free Ceramic Fibers from Organosilicon Precursors and E-Beam Curing," pp. 65-74 in High-Temperature Ceramic-Matrix Composites II, Ceramic Transactions vol. 58, edited by A. G. Evans and R. Naslain, The American Ceramic Society, Westerville, Ohio (1995).

6. A. R. Bunsell, M. H. Berger and N. Hochet, "Structural and Mechanical Characterisation of Some Alumina and SiC Based Fibres," pp. 85-94 in Ref. 5.

7. L. L. Snead, M. Osborne and K. L. More, "Effects of Radiation on SiC-Based Nicalon Fibers," *J. Mater. Res.* **10(3)**, 736-747 (1995).

8. G. E. Youngblood, D. J. Senor and G. W. Hollenberg, "Dimensional Stability of Neutron Irradiated Carbon and SiC-Based Fibers at High Doses," Fusion Materials Semiannual Progress Report for Period Ending March 31, 1995, U. S. Department of Energy publication DOE/ER-0313/18.

9. Ya. I. Shtrombakh, B. A. Gurovich, P. A. Platonov and V. M. Alekseev, "Radiation damage of Graphite and Carbon-Graphite Materials," J. Nucl. Mater. 225, 273-301 (1995).

10. G. Chollon, R. Bodet, R. Pailler and X. Bourrat, "Structure and Thermal Evolution of SiC-Based fibers with Low Oxygen Content," pp. 305-310 in Ref. 5.