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Technical Progress Report

Entitled

DEVELOPMENT OF RADIATION-HARDENED CERAMIC COMPOSITES
FOR FUSION APPLICATIONS

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Submitted on behalf of

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MASTER

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The attached document summarizes progress relative to the tasks identified for the second year (September 1, 1993 - August 31, 1994) for Grant No. DE-FG02-92ER54181.

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Tensile Behavior of Irradiated SiC Fibers

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The strength and toughness of continuous fiber reinforced ceramic composites(CFCC) are highly dependent on the fiber strength distribution. To first order, weaker fibers lead to low strength but higher toughness while stronger fibers lead to high strength composites of relatively low toughness. Toughness is associated with pullout of the fibers from the ceramic matrix. It has been shown previously that both strength and toughness of SiC/NicalonTM composites are drastically changed following irradiation.

This paper will present and discuss results for low oxygen Nicalon fibers irradiated at three damage levels; 0.013 dpa, 0.13 dpa and 0.32 dpa. Single fibers were tensile tested and analyzed, using Weibull statistics, for mean strength and distribution. Tensile modulus was also determined. Using a diffractometer, the fiber grain size and percent crystallinity were determined. The initial results of these low level neutron irradiations exhibit no substantial degradation of the properties investigated. Therefore, continued research at higher doses is recommended.

1. Introduction

Silicon carbide(SiC) has been considered as a low-activation fusion reactor structural material for about twenty years.[1-5] Since bulk SiC fractures easily, the bulk SiC is processed with SiC fibers to produce a continuous fiber reinforced ceramic composite(CFCC). The tensile behavior of SiC fibers needs to be studied to allow prediction of composite behavior and tailoring of composite properties.

Through the rule of mixtures, composite strength and stiffness can be estimated. The work of fracture(WOF) which is related to toughness due to pullout is dependent on the pullout length,h, as shown below in equation 1

$$WOF = \frac{V_f h^2 \tau}{3 r} \quad (1)$$

where h is the pullout length, r is the fiber radius and t is the frictional shear stress. The pullout length is dependent on the statistical distribution of the fiber strength.

Ceramic grade Nicalon has been studied extensively[6-10] and has adequate properties up to 1100-1200 C. However, studies of the neutron irradiation behavior of Nicalon[10] have shown that the fiber is unstable. Neutron irradiation densifies the fiber which increases strength and modulus but also increases the brittleness of the fiber. In the

densification process, the fiber diameter also decreases which causes the fiber to pull away from the interface thus significantly reducing the composite toughness.

A recently developed experimental fiber produced by the Nippon Carbon Company employs the same processing as Nicalon except that the fiber is crosslinked using electron irradiation and cured in an inert atmosphere.[11,12] This new processing technique removes most of the oxygen which is normally found in ceramic grade Nicalon. The reduction in oxygen content is from >10 wt% to <0.5 wt%. The oxygen removal allows a greater amount of the Si and C to combine with each other rather than with oxygen, resulting in very high crystallinity($>95\%$) for the low oxygen Nicalon compared to that of ceramic grade Nicalon($<80\%$).

The irradiation behavior of these newer fibers needs to be investigated to determine if they are stable in a neutron radiation field. A recent study[13] found that low oxygen Nicalon does not densify under low levels of neutron irradiation. Thus, this fiber shows promise for use in neutron environments but the irradiation behavior of this fiber needs to be investigated further before actual use. This paper will discuss the low level neutron irradiation properties of low oxygen Nicalon. The properties investigated are tensile strength, tensile modulus, grain size and percent crystallinity.

2 Experimental Setup and Data Reduction

The tensile testing was performed on an Instron Model 1130 per ASTM 3379-75[14]. The load was measured with a Entran 2#(4.4 N) load cell and the displacement was measured with a laser micrometer made by Keyence Corporation. The load and displacement were recorded and controlled by a computer using Instron Series IX software.

The fiber gauge length was set by cutting a rectangle into an index card with one of the dimensions 25 mm(gauge length) and epoxying the individual fibers across this rectangular hole. The fiber was vertically aligned in pneumatic grips and the edges of the index card carefully cut. The displacement speed was set at 0.5 mm/min.

Fiber diameters are measured after the fiber is broken to reduce any possibility of surface damage. This is allowable since the fibers fail without any plastic deformation so the "before" and "after" diameters are the same. A picture is taken of the broken fiber in an optical microscope and magnified to 400X. The fiber diameter on the magnified picture can be measured using vernier calipers to an accuracy of 0.001"(0.025 mm). The true fiber diameter is calculated by dividing the measured value by 400.

Strength was calculated as load divided by area and modulus was calculated as stress divided by strain where the strain is displacement divided by gauge length. Weibull

statistics (the two parameter model)[15-17] were used to reduce the raw strength data. The average tensile modulus was calculated as the simple average of the moduli which assumes a Gaussian distribution.

X-ray diffraction data was obtained by placing a powder sample in a diffractometer and measuring the intensities at various angles. This is accomplished automatically on a Norelco Diffractometer. The diffraction is performed at 35 kV and 15 mA using Cu K_{α} radiation.

To mount a sample, a pulverized fiber is mixed with toluene in a mortar to give it some viscosity. The mixture is poured onto a Si wafer which has low background signal and has been cut just off the (111) plane so there will be no peaks due to the Si. The chamber is flooded with He to lower the background scattering which would occur in air. This background reduction is necessary when investigating the crystallinity of the fibers. Scattering of non-crystalline material(glass) produces a halo which peaks at about 20° . Scattering from air will mask this effect and make the amorphous peak indistinguishable from the scattering due to air..

The range of scattering angle, 2θ , is 10° to 110° to include the amorphous halo and several low intensity SiC peaks at 100° and 105° . The data is reduced using Scintagg software which de-convolutes the peaks from background and from one another. The software will give peak intensity, full width at half maximum, 2θ and the integrated intensities. The crystal size was calculated using the Sherrer formula[18] and also including the effect of lattice strain. Percent crystallinity is calculated by dividing the integrated intensity for the peaks due to diffraction of SiC by the total integrated intensity which includes the amorphous halo.

The fibers were irradiated in the High Flux Isotope Reactor(HFIR) at ORNL. The fibers were enclosed in an aluminum tube which was welded shut in an argon atmosphere. The neutron flux ($E > 0.1$ MeV) was 7.8×10^{14} n/(cm² s). The rule of thumb for conversion of fluence to dpa for SiC is 1×10^{25} n/m² per 1 dpa. Low oxygen fibers were tested prior to irradiation and also for various irradiation conditions which included 1.28×10^{23} n/m²(0.013 dpa), 12.8×10^{23} n/m²(0.13 dpa) and 32.2×10^{23} n/m²(0.32 dpa). The test temperature was estimated to be 100 C which is the coolant temperature. There is some uncertainty in the irradiation temperature of the fibers. If the fibers had good contact with the walls of the capsule, there would be sufficient heat transfer to keep the fibers at 100 C to offset any heating due to the irradiation. There was some evidence that the fibers were at a higher temperature which include the fusing of the fibers' sizing and the slight blackening of the aluminum foil which wrapped the fibers.

3 Results and Discussion

Table 1 presents the reduced data from the tensile tests. The mean strength and modulus are plotted versus dose in Figure 1. The experimental error for the strength and modulus calculations is 1.6% for the strength and 3.5% for the modulus. The majority of the modulus error is from the displacement measurement (about 2%). Figure 2 presents a sample load-displacement curve and Figures 3-6 present Weibull plots for the various conditions. Note that Figure 2, a typical load-displacement curve for a fiber tensile test, is linear showing that the fibers do not exhibit plastic deformation.

The standard deviations may appear high for mean strength but this behavior is typical of materials with low Weibull moduli. The standard deviation signifies the range around the mean which contains 67% of the data (Gaussian) and has the same significance as the Weibull moduli. Low Weibull moduli correspond to standard deviations which are a higher percentage of the mean. Therefore, the standard deviations serve as a check on the Weibull data. With the higher Weibull moduli, the fibers are considered more reliable. This means that the fiber strengths are in a tighter (narrower) distribution so they have a higher probability of failing at the same strength which is similar to most metals.

For the tensile modulus, the standard deviation relates to the differences in fiber structure. If all the fibers had the same structure then the moduli would be the same for each batch tested. With high standard deviations the internal structure of the fibers vary and the numbers presented in Table 1 represent an average property. The reason for averaging the bulk properties is that the x-ray diffraction data yields property averages. The x-ray diffraction data represents information on grains of differing size and orientation and for fibers of differing composition. Thus, this data gives an average of the bulk structure.

Table 2 presents the reduced results of the diffraction data. The family of planes investigated was {111}. The 0.13 dpa fibers had noisy data (not enough material to get significant diffraction) so it was not analyzed. Crystal sizes are in angstroms and the lengths correspond to the [111] direction. Strain is not reported in this table but it was calculated to increase with higher dose.

Crystallite sizes were calculated as described in Section 2 and the ranges in size correspond to the difference between the Gaussian and Cauchy fits to the peaks. Percent crystallinity was not reported for the low dose fibers due to problems with the experimental setup, i.e., the amorphous halo around 20-25 degrees was masked by some residue of scotch tape on the Si wafer. This problem was corrected for the higher doses, but due to the limited amount of material available, the low dose irradiation could not be repeated.

The tensile data shows a decrease in mean strength and increase in embrittlement (lower Weibull parameter) at low doses but at higher doses the strength increases and the fibers become less brittle. At the highest dose tested, the strength and reliability were higher than for the unirradiated condition. The change in reliability, shown by the different Weibull moduli, suggests that there is a different controlling mechanism for failure and this failure mechanism will be discussed later. The strength increase of the fibers is consistent with observations by other authors for irradiated ceramic grade Nicalon.[19-21] Ceramic grade Nicalon strength increase is due to densification while the strength increase for the low oxygen Nicalon is not fully understood but a possible explanation is presented below.

The strength increase with irradiation is normal for most materials. Metals considered for fusion show embrittlement and strength increases as dose increases.[22-24] Embrittlement is different for metals than for ceramics. Metal embrittlement is due to increasing the number of interstitials and vacancies which will pin dislocations or act as barriers to dislocation movement, resulting in a reduction of plastic deformation and an increase in strength. In most ceramics, especially SiC, there is little or no macroscopic plastic deformation, so the dislocation mechanism is not valid.

From the x-ray data, the unstrained average crystal size was calculated and shown to have decreased slightly at the highest dose but to have no significant change at the lowest dose. Since the fibers are nearly all crystalline, the cause of failure could be due to changes in crystal size which would change the internal flaw population. This assumes that the flaw population is limited by the grain size. This would be the case if the surface flaws are insignificant compared to the flaws due to the grains and if there are no large inclusions in the bulk of the fiber which could cause stress concentration.

Orowan and Petch[25] have shown that strength will vary with $d^{-1/2}$, where d is the average grain size. Figure 7 shows a plot of mean strength versus one over the square root of the crystal size. The plot follows linearity for the three points involved which suggests that change in crystal size is a mechanism for strength increase in the irradiated fibers. The data would be more convincing if there were more points, however, it does appear that crystal size has an effect on the strength of the fibers.

The decrease in crystal size and corresponding crystallinity decrease at the highest dose can be partially explained via the fact that the neutrons cause atom displacements which result in a reduction of the effective size of the crystal lattice of each individual crystal. Thus, the point defect population is constantly increasing due to the irradiation and the ordered arrangement of atoms constantly decreases as more Si or C atoms are put in interstitial positions or are put in vacancies previously occupied by other atoms.

The change in crystallinity would affect the tensile modulus. The initial decrease in modulus corresponds to the decrease in crystallinity. The reason for the modulus increase at 0.32 dpa is not completely understood. The modulus is a measure of the average bond strength but it is not linear with atomic spacing.[26] A possible explanation for the modulus increase is that at the low dpa levels, the bond length increases due to the creation of vacancies and interstitials as discussed above. As the damage increases the vacancies are filled in, but not necessarily with the original occupant of the lattice site and therefore, the modulus would increase again but crystallinity would continue to decrease.

Another cause of microstructural changes which would affect the modulus is possible variations in the irradiation temperature. The temperature in the irradiation capsule must be known and controlled to a reasonable accuracy (within 20 degrees) so that there are no microstructural changes due to temperature. The temperature for this study was not measured directly but was estimated to be at about the coolant temperature of 100 C.

An issue unresolved in this study is the appearance of the fracture surfaces of the broken fibers. The fiber fracture surfaces would have given information on where the flaw which caused failure occurred. This information determines the mode of failure(surface or bulk) of the fiber. The authors investigating ceramic grade Nicalon suggested that there was a changing flaw population in the fibers with increasing irradiation.[19,20] A change in failure mode was seen in the data at the highest dose for this study. A failure mode change is detected in two ways: (1) by observing a bend in the Weibull plot; and (2) by tensile testing the fibers at different lengths to see if there is a surface effect on the strength. The bends in the Weibull plots on Figure 3 at 0.9 on the x-axis, on Figure 5 at 0.8, and on Figure 6 at 1.2, suggest that there is a varying mechanism for fiber failure. The actual flaws would also have been picked up by SEM of the fiber fracture surfaces. If there is no observable flaw when viewing the fracture surface, then the failure could be due to the change in crystal size which would justify the above theory on crystal size and mean strength.

The change in the Weibull moduli suggests initial embrittlement of the fibers. At the highest damage level, 0.32 dpa, the Weibull modulus was higher. Using the two parameter model for data analysis may not be appropriate due to the bends in the plots as discussed above. The overall increase in Weibull modulus at the highest damage level may indicate that neutron irradiation reduces the spread in the controlling flaw population so that the fibers will fail closer to the same mean stress.

4 Conclusions and Future Work

Neutron irradiation of low oxygen Nicalon at low doses(< 0.3 dpa) show initial embrittlement of the fibers. The mean strength and modulus decrease and then increase with increasing damage. X-ray diffraction data shows that the crystallinity and crystal size of the fibers decreased with increasing dose but as the percent crystallinity decreases the reliability increased. Overall, the irradiated data do not exhibit drastic changes in properties but rather represent small variations around the unirradiated values.

The absence of significant degradation of properties with irradiation suggests that the low oxygen Nicalon SiC fiber has potential for use in a neutron radiation environment. The effects of higher neutron doses need to be investigated before employment in CFCC's. Besides higher dose testing, future studies would include the same tests discussed in this paper. The future studies would also need additional information to develop a complete picture of the fiber's behavior. The additional information desired would include SEM of fracture surfaces, TEM of the fibers, testing fibers at different gauge lengths, Raman spectroscopy or EXAFS(Extended X-ray Absorption Fine Structure) and control of the irradiation temperature.

5 Acknowledgements

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New York pp. 15 1991.

Fiber Designation	Wiebull Modulus for Strength	Mean Strength (GPa)	Tensile Modulus (GPa)
Unirradiated	3.00	2.41 (0.764)	238.2 (62.8)
0.013 dpa	2.69	2.26 (0.903)	208.1 (47.6)
0.13 dpa	2.58	2.03 (0.844)	167.9 (47.3)
0.32 dpa	3.99	2.79 (0.623)	222.7 (61.0)

Table 1 Reduced Tensile Data for Low Oxygen Nicalon Fibers
(Standard Dievations are in parenthesis)

Fiber Designation	Crystal size(A)	Percent Crystallinity
Unirradiated	30.4 - 31.6	97.5
0.013 dpa	30.9 - 32.0	
0.32 dpa	27.1 - 28.1	93.6

Table 2 Reduced X-Ray Data for Low Oxygen Nicalon Fibers

Figure 1 Mean Strength and Modulus versus Damage Level

Figure 2 Sample Load-Displacement Curve

Figure 3 Unirradiated Low Oxygen Nicalon Wiebull Plot("R" is goodness of fit)

Figure 4 Irradiated Low Oxygen Nicalon(0.013 dpa) Wiebull Plot("R" is goodness of fit)

Figure 5 Irradiated Low Oxygen Nicalon(0.13 dpa) Weibull Plot("R" is goodness of fit)

Figure 6 Irradiated Low Oxygen Nicalon(0.32 dpa) Wiebull Plot("R" is goodness of fit)

Figure 7 Mean Strength versus $d^{-1/2}$ ("d" is the crystal size in Angstroms and "R" is goodness of fit)

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