STABILITY OF 3-D CARBON FIBER COMPOSITE TO HIGH NEUTRON FLUENCE - L. L. Snead, Y. Katoh, and K. Ozawa. (*Oak Ridge National Laboratory)*

OBJECTIVE

This work addresses the temperature and dose limitation of carbon fiber composites for nuclear applications. Additionally, the importance of relative degree of graphitization, or crystalline perfection, on the irradiation-induced changes are discussed.

SUMMARY

The dimensional stability, elastic modulus, and flexural strength of a high quality, three-dimensional balanced weave carbon fiber composite has been evaluated over a range of neutron fluence to ~32 dpa at ~ 800°C. Results indicate that while the composite exhibits continuous strengthening over this dose range, this occurs with measurable loss of mass, increased volume, and for the highest dose studied, a large reduction in elastic modulus. While the balanced weave composite was orthogonally isotropic, a significant anisotropic dimensional change occurred under irradiation. Dimensional change was dominated by fiber dimensional change and the overall shrinkage or swelling in a direction was determined by the extent to which intrinsic the fiber shrinkage was capable of restraining swelling of matrix and fiber bundles.

PROGRESS AND STATUS

Introduction

Carbon fiber composites are currently being utilized as plasma facing materials in fusion reactors and will be used in the strike plates for the ITER. Such composites are also being considered for application in core structures of high-temperature gas-cooled reactors.[1] The effects of irradiation on stability and mechanical properties have been well studied for graphite,[2,3] and in some detail for carbon fiber composites, [4-9] with their irradiation effects generally explained using a simple description of irradiation damage in the perfect graphite crystal. In the basic model, the graphite crystal is assumed to be of infinite dimension with displaced atoms preferring to come to rest between the basal planes. New interstitial planes form between these original basal planes resulting in a large dimensional change perpendicular to the basal plane (<c> axis swelling.) At low temperature irradiation,[10] (below a few hundred degrees Celcius) where vacancy mobility is limited,[10] in-plane vacancies will to a limited extent be annihilated resulting in dilation in-plane (<a> axis shrinkage.) For pyrolytic graphite this anisotropic dimensional change occurs without conserving volume. As the crystal is irradiated at temperatures where significant vacancy mobility is present (>1000K) the same anisotopic dimensional change occurs, though proceeds in a volume-conserving manner.[10] Additionally, the crystallite size (perfection) has a significant effect on the crystalline dimensional change with more perfect, larger crystals, having lower dimensional change.

This mechanism for anisotropic swelling leads to the large irradiation-induced dimensional change of pyrolitic graphite (as much as 100%,) and results in the eventual destruction of the nuclear graphite structure due to the induced internal stresses. In previous work carbon fiber composite properties such as dimensional change, strength, and thermal conductivity have been studied, and have been shown to trend in a similar manner to graphite. Specifically, both graphite and composites undergo significant increases in strength and elastic modulus while thermal conductivity is drastically reduced. However, unlike graphite, the composite dimensional change is shown to be dominated by fibers and is dependent on the composite architecture (the fiber weave), and to the selection of fiber type.[11] Of note from Burchell's original work and work to follow[1,4] is that the behavior of the composite can be well described using the theory of anisotropic dimensional change of the pyrolitic graphite (discussed above) when considering that graphite fibers are essentially very high perfection forms of graphite with graphite planes preferentially oriented parallel to their fiber axis. In this model fibers would be expected to grow in diameter and shrink axially with irradiation as the new basal planes are formed. Such behavior has been previously shown[1,4,11] and it has been speculated that though appropriate balancing of the fiber architecture the large irradiation-induced anisotropic dimensional changes of the fiber can be balanced, minimizing the overall effect on dimensional change and extending the useful lifetime of carbon fiber composite.

The irradiation effects studies to date have been limited to relatively low doses. The purpose of this paper is to explore the performance of a high-quality, balanced-weave composite to a dose considered beyond a "lifetime" dose for nuclear graphite. In particular the dimensional change under irradiation as well as its effects on strength is studied.

Experimental

The carbon fiber composite selected for this study was the Fiber Materials Incorporated FMI-222 material, a balanced weave Amoco P-120 pitch-based fiber, pitch matrix composite. The non-irradiated density of the composite is approximately 1.96 g/cm^3. Materials were irradiated in the High Flux Isotope Reactor at the Oak Ridge National Laboratory in small "rabbit" capsules sealed in a high-purity helium environment. The capsules included a SiC temperature monitor used to determine the irradiation temperature, post-irradiation. Irradiation was carried out to fast neutron fluences of 4.1, 7.3, 9.5, and 32 x 10^{25} n/m^2 (E>0.1 MeV.) The irradiation temperature of all but the highest dose capsule was ~ 800°C. At the 32 x 10^{25} n/m^2 dose level the severe swelling of the capsule distorted the sample holder which effected the gas-gap used to achieve the target temperature. This irradiation condition is therefore a combination of 800°C and (later in the irradiation) an undefined lower temperature. The geometry of the samples irradiated were bars of dimension 3.2 x 6.4 x 50.8 mm where the orthogonal axes of the bar were oriented parallel to the balanced x, y, and z tows of the composite. Elastic modulus was determined by both sonic modulus using a Grindosonic and by application of strain gages to the tensile surface of the bend bar. Four-point bend testing was carried out at room temperature with a load and support span of 20 and 40 mm.

Results and Discussion

The gross mass and dimensional change resulted in the data plotted in Figure 1, which provides data for the irradiated material, a non-irradiated set of samples, and a set of samples which were baked at 800°C in a capsule-representative environment. It is noted that within statistical uncertainty (plotted as ± standard deviation throughout) the thermal control sample set resulted in the same values as the non-irradiated (as machined) sample set. Upon irradiation a clear, increase in the envelope volume to a value of 24.8% at the 32 dpa value is achieved. This volume increase is the largest contributor towards the plotted trend for density change (figure 1), though a small loss in mass occurred. This mass loss was attributed to dislodging of matrix graphite from the surface of the composite caused by the dimensional change in the fiber tows.

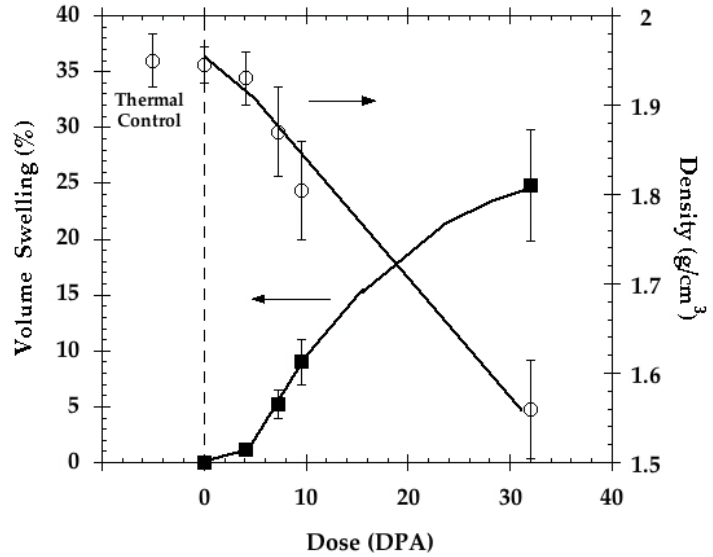

Figure 1 : Effect of irradiation on volume and density change of FMI-222 carbon fiber composite.

Discussion of volumetric change in composite materials is somewhat misleading in that the dimensional change is strongly dependent on both the architecture of the composite and the dimensions for which the change is measured.[4] This is clearly demonstrated by inspection of

Figure 2, which provides the percentage change along the bend bar axis. In this study, the composite weave was a balanced weave (same volume fraction of fibers in the x, y, and z direction) and the axis of the bend bar was aligned parallel to the axis of the fiber tows. The data of figure 2 can therefore be interpreted as the dimensional change in the longest fiber direction (Length-50.8 mm) which shows strong contraction for the entire irradiation exposure, and for the two much shorter fiber directions (Width-6.4mm, and Thickness-3.2mm) each of which exhibit expansion over the irradiation dose range studied. As mentioned in the introduction, the dimensional change behavior of fiber can be conveniently described with the classical description of the dimensional change behavior of pyrolytic graphite. However, in the case of graphite fibers, the graphene planes are oriented with their <a> axis parallel to the axis of the fibers such that the formation of inter-plane interstitial clusters will tend to cause fiber diametral (<c> axis) swelling. For the temperature of this irradiation, (800°C), significant interstitial and vacancy mobility exists such that annihilation of vacancies is expected leading to <a> contraction. For pyrolytic graphite, such contraction and expansion occurs in near volume conservation, and may be occurring in the highly crystalline fibers of this material.[10] As has been shown previously [1,4] for this material, the sample surface clearly shown evidence of the anisotopic dimensional change of the fibers, with fiber tows fattening and pulling into the free surface of the sample exposing (and liberating) the infiltrated pitch matrix. From figure 1 the contraction of the continuous fiber tow in the 50.8 mm length direction of the bend bar has had the effect of constraining any swelling that may have occurred in the matrix and dominates any aggregate effect of diametral swelling of fiber tows oriented orthogonally to the length axis. However, for the Width and Thickness direction the continuous fiber length are not able to restrain such swelling and the material swells in those directions, with the shorter fiber length (3.2 mm) having the larger swelling. The clear conclusion from this is that the swelling of such large unit cell carbon fiber composites must be viewed both in terms of the architecture, the direction through the architecture the swelling is being considered, and the thickness of the component in the direction.

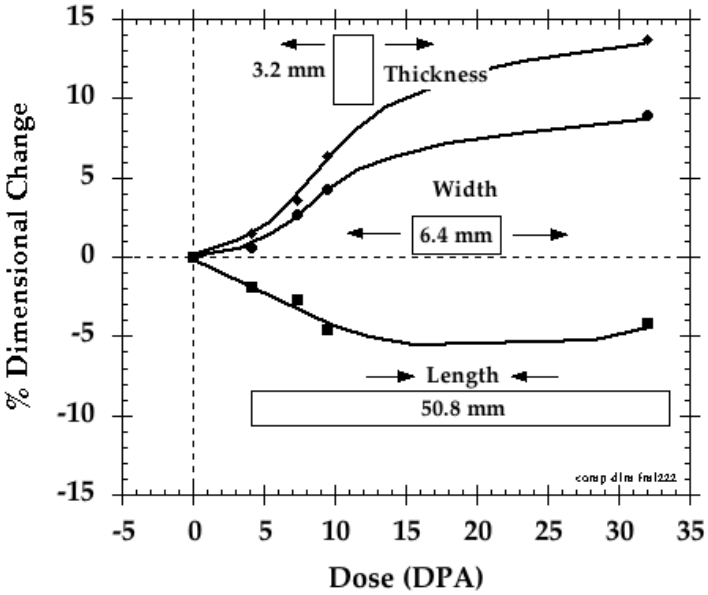

Figure 2 : Effect of Irradiation on the Dimensional Change of FMI-222 Carbon Fiber Composite.

The effects of irradiation on the mechanical properties for this material is presented in Figures 3 and 4. As seen in figure 3, the FMI-222 elastic modulus clearly shows an initial increase with irradiation with good agreement between the sonic modulus and strain gage measurement techniques. Several authors [5,8,12-14] have studied the effect of neutron irradiation on carbon fiber elastic modulus. The work of Sato [12] is the most relevant irradiation temperature to this study, reporting an increase in modulus following neutron irradiation to 1.2 x 10^{25} n/m^2, E>0.18 MeV in the temperature range of 750-810°C. Sato's irradiation, which is comparable in temperature though at about a quarter of the dose of the lowest dose point of the current study, is consistent with the findings of figure 3. He found an ~ 32 and 40% increase in elastic modulus for his composites, which is significantly higher than the interpolated data seen in figure 3. However, the larger relative increase for Sato's composite would be expected, as his PAN-based fiber composites possess much lower initial elastic modulus. The

maximum increase for the materials of this study was ~14%. In the dose range between 9.5 and 32 dpa the elastic modulus has clearly degraded for this material. However, it is not clear where the as-irradiated peak elastic modulus occurred.

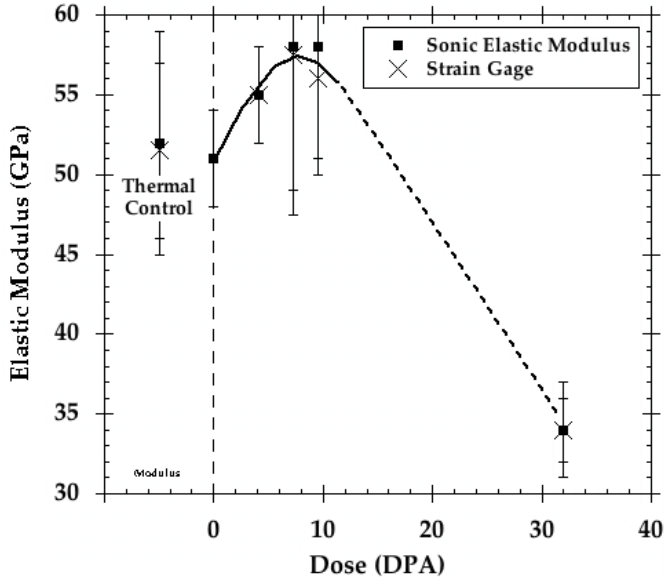

Figure 3 : Effect of Irradiation on the Elastic Modulus of FMI-222 Carbon Fiber Composite.

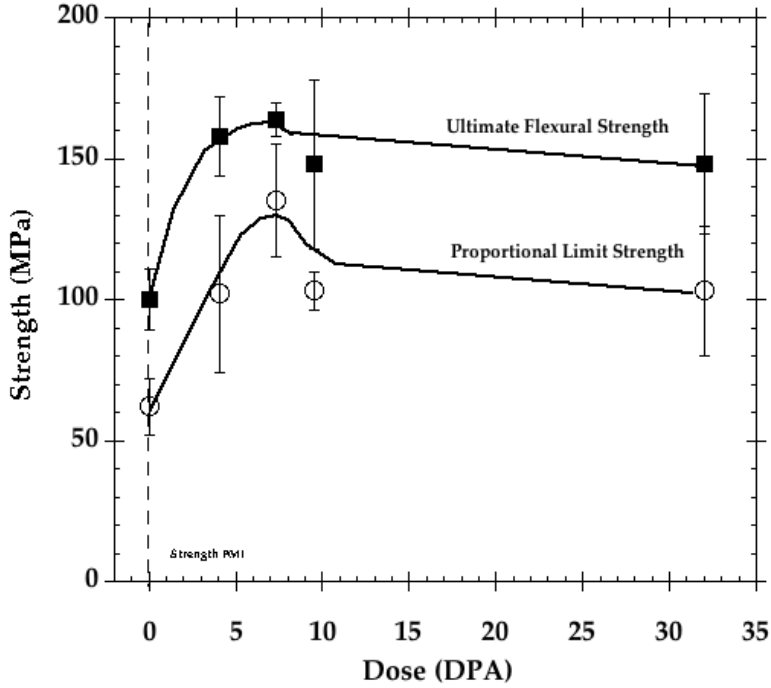

Figure 4 : Effect of Irradiation on the Strength of FMI-222 Carbon Fiber Composite.

The effect of irradiation on the mechanical properties of carbon fiber composites [5,8,12-15] has received less attention than nuclear graphite, though similar trends to graphite occur. As with graphite, CFC undergoes significantly increased strength at moderate neutron dose. For example, for identical material to the composite of this study, Burchell [15] demonstrated a 64% increase in brittle-ring strength following an intermediate irradiation dose at 600°C for the high quality, balanced weave FMI-222 composite. For identical composite, Snead et al[4] publish a nearly 100% increase in bend strength for irradiation to ~ $8x10^{25}$ n/m^2 (E>0.1 MeV.) It is noted that for nuclear graphites such as ASR-1R, TSX, and H451, irradiation in the 575-800°C temperature range results in a return to “nil swelling” and loss of mechanical properties in the dose range of 20-30 dpa (less than the dose of this study.)

Results of flexural testing is given in figure 4, which shows a significant increase in strength over the entire range of fluence studied. As seen in the figure, the 32 dpa level the composite material the FMI-222 composite has increased in ultimate bend flexural strength by approximately 50%, even though the elastic modulus has undergone significant reduction and the sample has been visibly degraded.

Conclusions

A high-quality pitch-based carbon fiber composite has been irradiated in a dose range up to 32 dpa. Resulting dimensional change is well described by the conventional description of irradiation damage in pyrolytic graphite, considering the particular morphology of the graphite fibers. For the balanced-weave composite tested volumetric change is positive over the dose range studied and quite large (24.8%) at the 32 dpa level. However, the dimensional swelling for this orthogonally isotropic composite was far from isotropic. It was seen and is speculated that for directions of long continuous fiber length (greater than 55 unit cells), the irradiation-induced fiber contraction restrains the composite in a dimensional shrinkage leading to overall shrinkage of the composite. However, when such constraint is not available (in shorter dimensions, in the case of this study ~ 3 and 6 unit cells) large expansions occur. Irradiation up to a dose of 9.5 dpa resulted in a significant increase in elastic modulus, as would be expected from previous, lower dose work on composites, and the general graphite literature. However, by the 32 dpa dose the elastic modulus showed significant degradation compared to the non-irradiated value. However, over the entire dose range of this study the bend strength of this composite increased. Such an increase occurred even though the material has undergone visible degradation, large swelling, and was well beyond the fluence from which typical nuclear graphite's would have entered into their micro-cracking and stage of severe loss of strength. Clearly the fibers, while undergoing very large dimensional changes that resulted in severe consequences on the composite matrix, including loss of mass, were able to maintain their load carrying capability.

References

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