IRRADIATION-INDUCED STRUCTURE AND PROPERTY CHANGES IN TOKAMAK PLASMA-FACING, CARBON-CARBON COMPOSITES

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ABSTRACT

Carbon-carbon composites are an attractive choice for fusion reactor plasma-facing components because of their low atomic number, superior thermal shock resistance, and low neutron activation. Next generation plasma fusion reactors, such as the International Thermonuclear Experimental Reactor (ITER), will require advanced carbon-carbon composite materials possessing high thermal conductivity to manage the anticipated severe heat loads. Moreover, ignition machines such as ITER will produce large neutron fluxes. Consequently, the influence of neutron damage on the structure and properties of carbon-carbon composite materials must be evaluated. Data from two irradiation experiments are reported and discussed here. Carbon-carbon composite materials were irradiated in target capsules in the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL). A peak damage dose of 4.7 displacements per atom (dpa) at 600°C was attained. The carbon materials irradiated included unidirectional, two-directional, and three-directional carbon-carbon composites. Dimensional changes are reported for the composite materials and are related to single crystal dimensional changes through fiber and composite structural models. Moreover, the irradiation-induced dimensional changes are reported and discussed in terms of their architecture, fiber type, and graphitization temperature. The effect of neutron irradiation on thermal conductivity of two three-directional, carbon-carbon composites is reported and the recovery of thermal conductivity due to thermal annealing is discussed.

KEY WORDS: Radiation Damage; Property Changes; Carbon-Carbon Composites.

1. INTRODUCTION

Tokamak fusion devices such as the Tokamak Fusion Test Reactor (TFTR) and DIIID in the USA; the Joint European Torus (JET), Tore Supra, and TEXTOR in Europe; and JT-60U in Japan make extensive use of carbon-carbon composites and fine-grained graphites as plasma facing materials. Attributes such as low atomic number, high thermal

shock resistance, lack of a melting temperature (graphite sublimes at ~3600K), and high thermal conductivity make carbon-carbon composites the material of choice for tokamak first wall, limiter and divertor armor (Fig. 1).

Next generation tokamak fusion reactors such as the International Thermonuclear Experimental Reactor (ITER) will utilize carbon-carbon composite materials for their first wall and divertor armor [1]. Plasma-facing components in ITER must endure a severe environment with high surface operating temperatures, extremely high heat fluxes, and eddy-current induced stresses which arise when the plasma becomes unstable and collapses (a phenomenon referred to as "plasma disruption"). Moreover, ITER will be an ignition machine and will therefore produce a substantial neutron flux from the deuterium-tritium fusion reaction:

$$^{2}H + {}^{3}H \rightarrow {}^{4}He + n\ (14.1\ MeV) \qquad (1)$$

Plasma facing carbon-carbon composite materials will suffer substantial structure and property degradation as a result of carbon atom displacements and crystal lattice damage caused by impinging high energy fusion neutrons.

Neutron damage effects on graphite have been studied for over 40 years and the structure and property changes are well understood [2,3]. More recently the influence of neutron damage on the properties of the fusion relevant graphite "GraphNOL N3M" was reported [4] and efforts have been directed toward developing a model to describe the irradiation induced structure and property changes in nuclear graphites [5]. Neutron irradiation causes the displacement of carbon atoms from their equilibrium lattice positions into interstitial locations, leaving vacancies in the basal planes (Fig. 2). Interstitial carbon atoms become increasingly mobile at higher temperatures, forming clusters and eventually new planes. Vacancies, which are also mobile at higher temperatures, form vacancy loops which eventually collapse. A consequence of the neutron damage is a rapid increase in graphite strength and elastic moduli due to dislocation pinning. Subsequent changes in strength and elastic moduli occur due to changes in the polycrystalline structure of the graphite.

Neutron irradiation-induced defects act as phonon scattering centers and reduce the phonon mean free path. Consequently, the thermal conductivity will be significantly degraded by neutron damage. In addition to physical property changes, graphites undergo dimensional and volume changes when irradiated. Initially, there is a volume shrinkage, but the shrinkage rate decreases and a reversal to growth occurs at higher fluences. This effect is temperature dependent; above ~600°C as irradiation temperature increases, the reversal from shrinkage to growth occurs at lower fluences.

In contrast to graphite, little work has been performed on the effect of neutron damage on carbon-carbon composites [6,7]. Gray [8] and Price et al. [9] have reported the irradiation-induced dimensional changes of carbon fibers. The fibers were observed to shrink along their length whereas the fiber diameter initially shrank and subsequently swelled. Burchell et al. [10] have reported that two-directional, carbon-carbon composites discs exhibited an increase in thickness (perpendicular to the fabric layers) and a shrinkage in diameter (parallel to the fiber axis) on irradiation at 400°C to a damage dose or fluence of approximately 12 displacements per atom (dpa). The behavior of unidirectional, two-directional, and three-directional carbon-carbon composites at 600°C and to relatively low fluences (<1.5 dpa) have been reported recently [11]. Three-

directional carbon-carbon composites were shown to exhibit more isotropic dimensional changes than either unidirectional or two-directional composite materials. Pitch fiber composites were shown to be more dimensionally stable than PAN fiber composites and high final heat-treatment (graphitization) temperatures were found to be beneficial. The effect of neutron irradiation, at 600°C and damage doses up to approximately 2.5 dpa, on the brittle-ring strength of unidirectional, two-directional, and three-directional carbon-carbon composites have been reported [12]. For PAN fiber two-directional, and pitch fiber three-directional carbon-carbon composites, the strength increased with increasing dose, whereas the PAN fiber three-directional carbon-carbon composite showed an initial increase in strength up to ~0.7 dpa, followed by a strength decrease. Here, dimensional and thermal conductivity changes are reported for unidirectional, two-directional, and three-directional carbon-carbon composites after irradiation to a peak neutron damage dose of 4.7 dpa at an irradiation temperature of 600°C.

2. EXPERIMENTAL

The materials irradiated are summarized in Table 1. The composite materials were heat-treated at 2650 or 3100°C prior to irradiation. Pre-irradiation characterization included dimensional measurements and specimen mass. Thermal diffusivity was measured on unirradiated control specimens cut from adjacent locations in the carbon-carbon composite billets. Thermal conductivity was calculated from the thermal diffusivity measured by the thermal pulse techniques, using the formula

$$K = \alpha \cdot \rho \cdot C_v \ (W/m \cdot K) \qquad (2)$$

where α is the thermal diffusivity (m^2/s), ρ is the specimen density (kg/m^3), and C_v is the specific heat at constant volume ($J/kg \cdot K$). Thermal diffusivity measurements were made on irradiated and unirradiated specimens over the temperature range 100-1600°C.

TABLE 1 SUMMARY OF MATERIALS IRRADIATED IN HFIR CAPSULES HTFC-I AND II AND REPORTED HERE

Designation	Description	Heat Treatment Condition
UFC	Fiber Materials, Inc. 1D C/C composite. PAN Fibers.	3100°C
RFC	Fiber Materials, Inc. Random fiber composite. PAN Fibers (chopped).	2650 and 3100°C
223	Fiber Materials, Inc. 3D C/C composite. PAN Fibers.	2650 and 3100°C
222	Fiber Materials, Inc. 3D C/C composite. Pitch Fibers (P55).	2650 and 3100°C

Irradiations were performed in the target region of the High Flux Isotope Reactor (HFIR) at the Oak Ridge National Laboratory (ORNL). The irradiation capsules, designated HTFC-I and -II, were neon gas filled and the specimen temperature was controlled by sizing the annular gap between the specimen and the capsule. Silicon

carbide temperature monitors were placed at intervals throughout the capsule. The specimens were either hollow cylinders, 6.35-mm long with an inside diameter of 3.2 mm and an outside diameter of 12 mm (nominal), or solid cylinders of 12-mm outside diameter (nominal) and lengths ranging from 6 to 12 mm. A maximum neutron fluence of 2.44 x 10^{25}n/m^2 [E>50 keV] or 1.6 dpa, and 7.28 x 10^{25} n/m^2 [E>50 keV] or 4.7 dpa, was attained for HTFC-I and -II, respectively, at an irradiation temperature of 600°C.

3. RESULTS AND DISCUSSION

3.1 Dimensional Change

Neutron irradiation induced dimensional changes for three of the materials studied here are shown in Fig. 3 as a function of damage dose or fluence in dpa. Specimen length and directional changes are shown for a unidirectional, carbon-carbon composite (UFC), a two-directional carbon-carbon composite (RFC) and a three-directional, carbon-carbon composite (223). The unidirectional carbon-carbon composite exhibited extremely anisotropic dimensional changes, undergoing rapid shrinkage in the fiber-axis direction (length). In the direction perpendicular to the fiber axis (diameter) the composite first shrank up to a fluence of approximately 1 dpa, followed by a reversal to expansion, reaching the original diameter at about 2.5 dpa and continuing to expand at an increasing rate. Similar trends are observed for the two-directional, carbon-carbon composite (RFC), where the fiber axis is in the diametral direction. In the off-axis direction (length) the composite exhibited a slight contraction followed by expansion, returning to the original length at approximately 2 dpa. The diametral (fiber-axis) directions of the RFC specimen exhibited shrinkage, although the magnitude of the shrinkage was much less for the same fluence than in the case of the unidirectional composite. In contrast to the unidirectional and two-directional composites, the 3D PAN composite exhibited isotopic behavior at fluences up to approximately 2 dpa. At doses greater than 2 dpa the composite x direction (specimen length) continued to show shrinkage, whereas the fiber x-y (diameter) direction exhibited reversal and slight growth.

Interpretation of the irradiation-induced dimensional changes of carbon-carbon composite materials requires: (i) an understanding of the graphite single crystal dimensional changes; (ii) a microstructural model of the carbon fibers used in the composites (PAN fibers in all three materials in Fig. 3); and (iii) knowledge of the composite architecture and the interactions of the fiber, fiber bundle, matrix, and porosity in the composite. As described in the introduction, the mechanism of neutron damage in the graphite crystal is well understood. Figure 2 shows an illustration of the mechanism of neutron displacement damage. The graphite crystal lattice undergoes expansion in the <c> direction (perpendicular to the layer planes) and shrinkage in the two <a> directions (parallel to the layer planes). Several models for the microstructure of PAN fibers have been suggested [13]. Pennock et al. [14] have reported the structure of pitch-based carbon fibers, and typical pitch fiber structures are shown in Fig. 4. Figure 5 shows a "core-sheath" model similar to that described by Bennett and Johnson [15]. Previously we have explained the dimensional changes of PAN-based composites at lower fluence using this fiber microstructural model [11]. In the core sheath model, the graphitic layer planes are arranged circumferentially in the fiber periphery and radially at the core of the fiber. Therefore, in the sheath region the preferred crystallographic <c> direction is perpendicular to fiber axis (radial) and the two crystallographic <a> directions are circumferential and axial.

Applying graphite crystal dimensional changes to the fiber microstructural models in Figs. 4 and 5, we would predict the fiber behavior to be dominated by shrinkage in the <a> direction, resulting in both fiber axial and diametral shrinkages. Expansion of the fiber in the <c> direction, and diametral <a> shrinkage, may be initially accommodated by the fiber interplanar voids or pores in the fiber, or by the extensive network of cracks known to exist within the carbon-carbon composite, such as those within fiber bundles or at fiber bundle matrix interfaces.

The influence of composite architecture is evident from a comparison of the irradiation-induced dimensional behavior of unidirectional and two-directional PAN-fiber, carbon-carbon composite materials (Fig. 3). In the unidirectional material the PAN fibers are aligned along the specimen axis (Fig. 6). The composite would thus be expected to shrink along the fiber axis (length) direction upon irradiation due to fiber axial shrinkage. In the diametral direction (perpendicular to fiber-axis) we would predict an initial shrinkage followed by a reversal to growth as the internal porosity is filled by the fiber <c> direction growth. Behavior of this nature is clearly displayed by the unidirectional, carbon-carbon composite (Fig. 6). In the two-directional, random-fiber composite (RFC) material, the PAN fibers are oriented randomly in one plane but are all perpendicular to the axis of the irradiation specimen (Fig. 7). The dominant <a> axis shrinkage of the fiber under neutron irradiation will thus cause shrinkage in the specimen diametral direction; whereas in the axial direction, the specimen should mimic the fiber diametral behavior, initially shrinking, followed by a turnaround to growth as indicated by our results (Fig. 3).

In a three-directional, carbon-carbon composite, irradiation-induced shrinkage in both diametral and length directions would be predicted due to x, y, and z fiber axial shrinkage. This is indeed what was observed experimentally up to relatively low fluences (Fig. 3). At higher fluences the complex interaction between fiber axial shrinkage, diametral growth, porosity, and matrix behavior will cause a turnaround to growth. The fluence at which the turnaround occurs will be influenced by several factors, such as the distribution of fiber, i.e., the fiber-volume fraction in each of the three directions, the amount and distribution of porosity in the material, the fiber type, structure, crystallinity, and the matrix structure, crystallinity, and irradiation-dimensional behavior. In the three-directional PAN fiber composite material (223) reported here, the turnaround to growth began in the x-y (diametral) direction at approximately 2-3 dpa, whereas in the z (length) direction turnaround clearly did not occur at fluences up to 5 dpa. It is postulated that this anisotropy is the result of an unbalanced fiber distribution, and/or presence of more accommodating porosity along the x- or y-fiber-matrix interfaces than along the z-fiber-matrix interface. Additional studies of fiber matrix interface porosity in unirradiated and irradiated specimens of three-directional, carbon-carbon composite are planned to elucidate more fully the fiber-matrix interaction.

The influence of fiber structure and crystallinity on the irradiation-induced dimensional change of two three-directional, carbon-carbon composite materials is shown in Fig. 8. In Fig. 8(a), the dimensional changes of a pitch fiber (222) and a PAN fiber (223) three-directional composite in the z-fiber direction are shown. The pitch fiber composite exhibited less shrinkage for the same fluence than the PAN fiber composite. The superior behavior of the pitch-fiber composite is attributed to the greater degree of crystallinity in pitch fibers [16]. The data in Fig. 8(b) indicate that increasing the final graphitization temperature reduces magnitude of dimensional change in a three-directional PAN-fiber composite. The relationship between increased crystallinity or

increased final heat treatment temperature and reductions in the magnitude of neutron irradiation-induced dimensional change has been clearly demonstrated in studies of the irradiation behavior of pyrolytic graphites [17]. In this and previous studies of irradiation damage [11], we have shown that composites manufactured from more crystalline pitch fibers, or that are graphitized at high temperatures (>3000°C), exhibit less dimensional change at a given fluence than carbon-carbon composites manufactured from less crystalline PAN fibers or graphitized at lower temperatures (<2700°C).

3.2 Thermal Conductivity

Thermal conductivity is a key physical property for plasma facing materials. Degradation of thermal conductivity due to neutron damage will result in higher surface armor temperatures and hence greater surface losses due to sputtering and erosion processes. The effect of neutron damage on high temperature thermal conductivity is therefore of considerable interest. Here, we shall limit our discussion to the two three-directional, carbon-carbon composite (223 PAN fiber and 222 pitch fiber) materials. The temperature dependence of thermal conductivity is shown for 223 (PAN) and 222 (pitch) composites in Figs. 9 and 10, respectively. For each composite, three conductivity data sets are shown: (i) unirradiated conditions (closed triangles), (ii) irradiated condition (open circles), and (iii) irradiated and annealed to 1600°C condition (open squares). For both composites, the thermal conductivity is measured in the z-fiber bundle direction. A comparison of Figs. 9 and 10 indicates that the 222 (pitch fiber) composite has a greater thermal conductivity prior to irradiation. This is attributed to the higher crystallinity and consequent longer phonon mean free path in the pitch fiber (222) material. Both the 222 and 223 composites suffer severe degradation of thermal conductivity after irradiation to <4 dpa. At the temperature of irradiation (~600°C) the reduction is between 50 and 60%. The thermal conductivity of the irradiated samples increases with temperature which is in direct contrast to the unirradiated specimens. The increase was attributed to thermal annealing of irradiation-induced defects which act as phonon-phonon scattering centers. At higher measurement temperatures the irradiated and unirradiated specimen data sets therefore tend to converge as increasing amounts of the displacement damage are annealed. Post-annealing (cooldown) thermal conductivity curves are also shown in Figs. 9 and 10, revealing the extent of recovery of thermal conductivity. At the irradiation temperature, the post-annealing thermal conductivity was reduced by as little as 20%. The effect of irradiation and post-irradiation annealing on the thermal conductivity as a function of neutron fluence (dpa) is shown for the 222 (pitch fiber) carbon-carbon composite in Fig. 11. The thermal conductivity at the irradiation temperature is reduced to approximately 60% of the unirradiated value at fluences as low as ~1 dpa, but the reduction saturates and is relatively constant over the fluence range 1 to 4.5 dpa. At larger neutron damage doses than shown in Fig. 11, the thermal conductivity would be expected to eventually degrade due to irradiation-induced structural changes (break-up) of the composite material. The extent to which thermal conductivity is recovered after thermal annealing at 1600°C is also shown in Fig. 11, where the post-annealing thermal conductivity is only 20-30% less than the unirradiated thermal conductivity at irradiation temperature. The degree to which irradiation induced losses of thermal conductivity may be recovered in carbon-carbon composites is particularly significant to the design of next generation tokamaks such as ITER, where plasma disruptions may cause high plasma-facing component surface temperatures and hence beneficial thermal annealing and recovery of thermal conductivity.

4. CONCLUSIONS

A series of carbon-carbon composite materials have been irradiated in the HFIR at 600°C to a peak fluence of 4.7 dpa. Dimensional changes have been analyzed in terms of architecture, reinforcing fiber precursor, and final graphitizing temperature. The dimensional change behavior can be interpreted through a fiber microstructural model and the expected graphite single crystal dimensional changes. The data reported show that three-directional composites behave more isotropically than two-directional or unidirectional composites. Pitch fiber composites are more dimensionally stable than PAN fiber carbon-carbon composites and a higher final graphitization temperature is beneficial.

The thermal conductivity of carbon-carbon composites is severely degraded by neutron irradiation in the damage dose range 1 to 4.6 dpa to approximately 50-60% of the unirradiated value. However, post-irradiation annealing to 1600°C causes a recovery of thermal conductivity to approximately 80% of the unirradiated value at the irradiation temperature. The extent to which thermal conductivity can be recovered is of great significance to the design of plasma facing components for next generation fusion devices.

5. ACKNOWLEDGEMENTS

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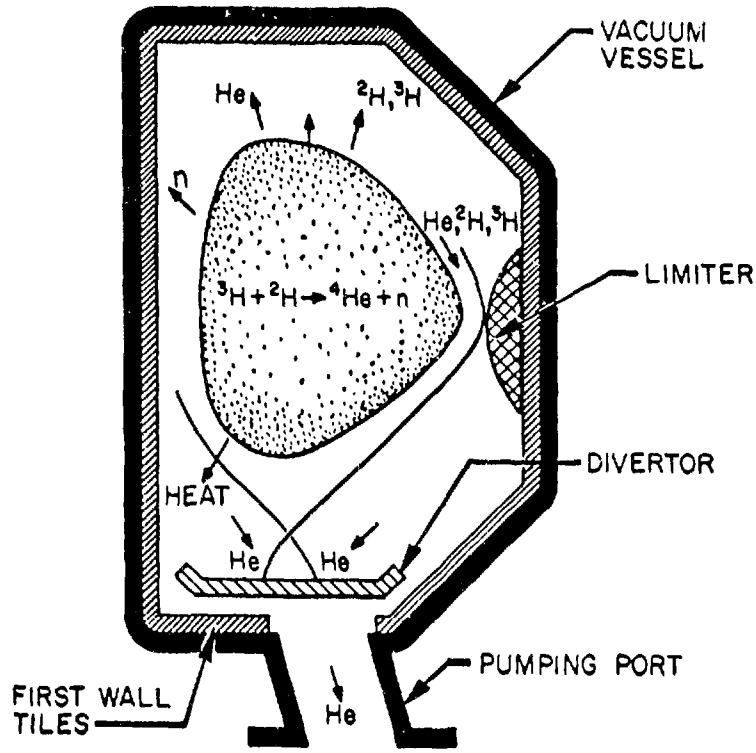

FIGURE 1. The major plasma facing components of a tokamak fusion device.

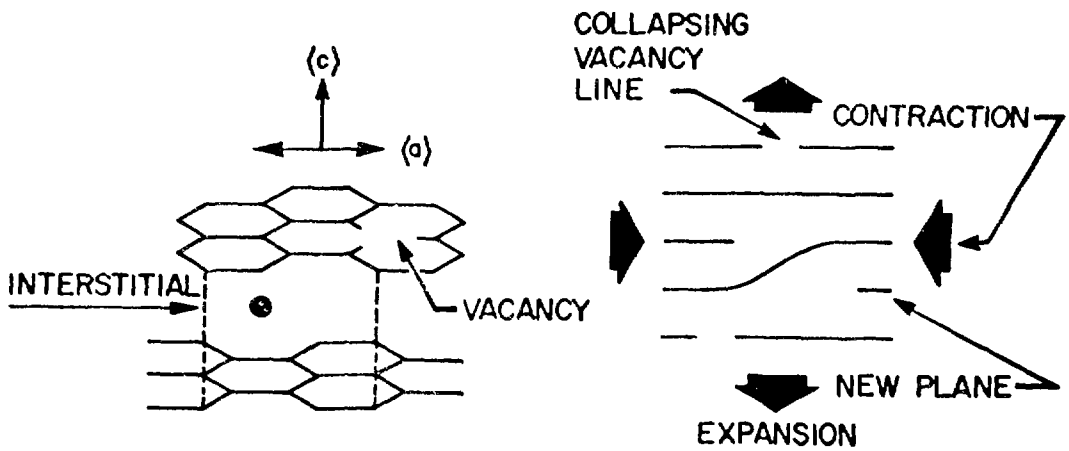

FIGURE 2. The mechanism of irradiation damage in the graphite crystal lattice.

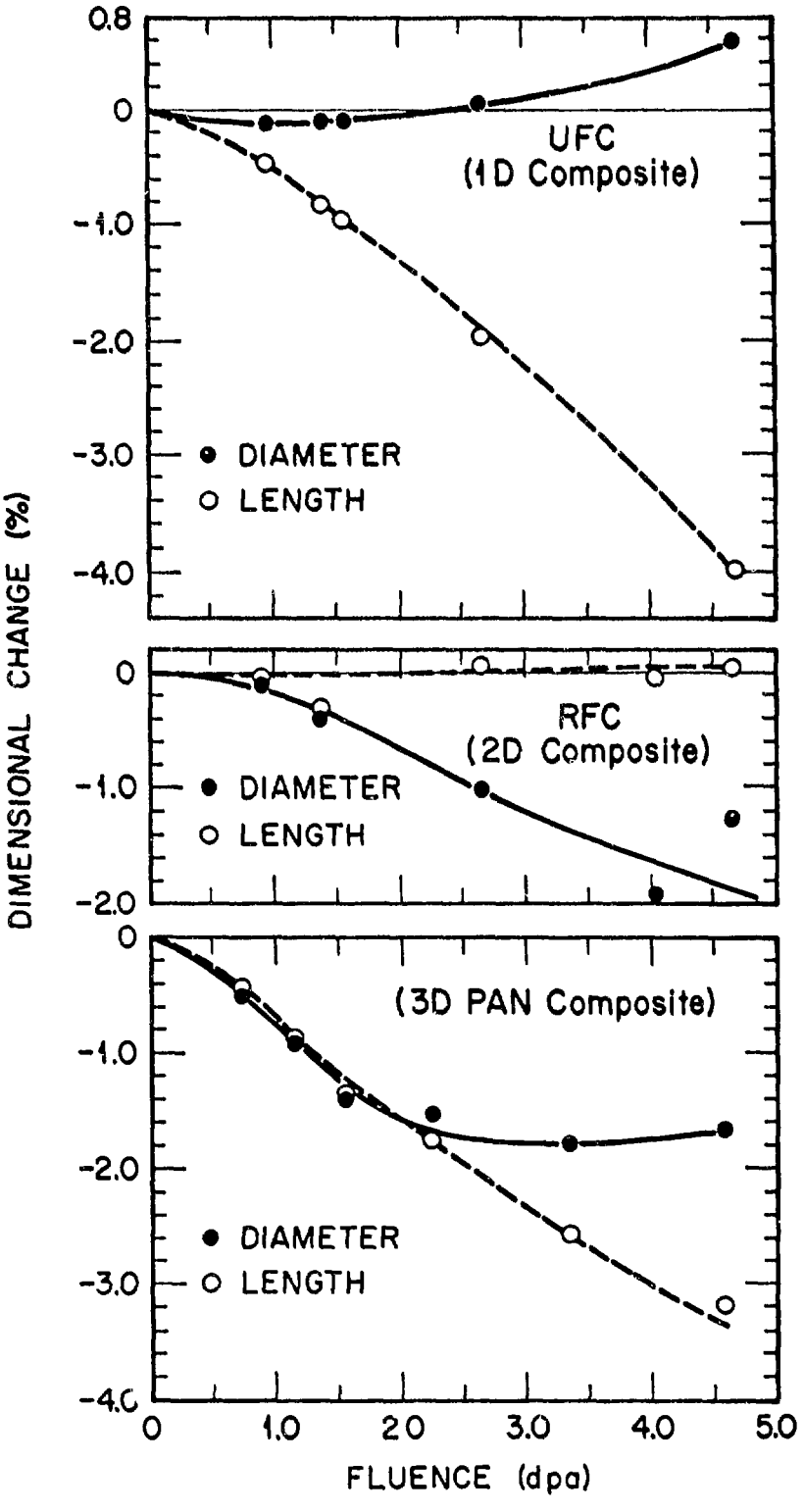

FIGURE 3. Neutron irradiation induced dimensional changes of several carbon-carbon composites irradiated at 600°C.

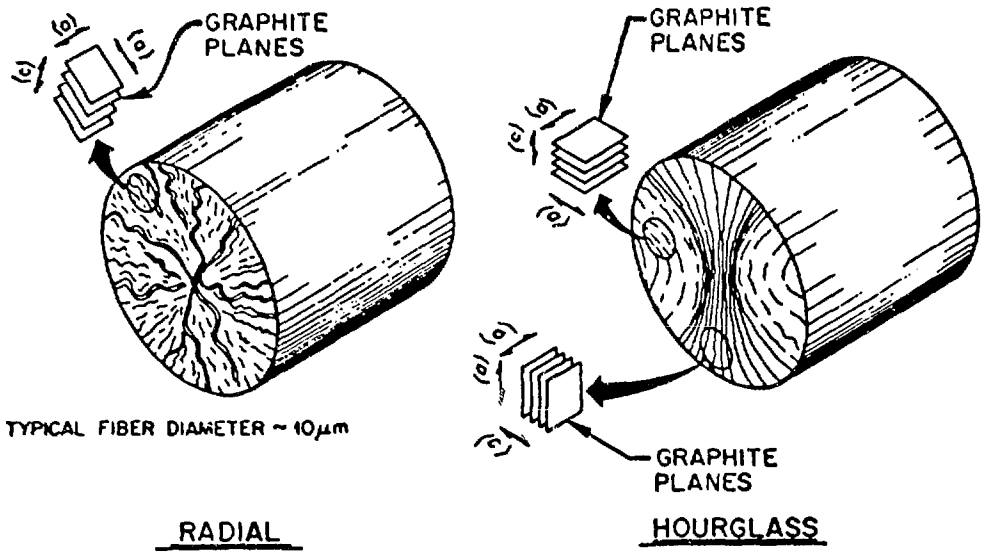

FIGURE 4. Pitch carbon fiber structural models and orientation of crystalographic basal planes.

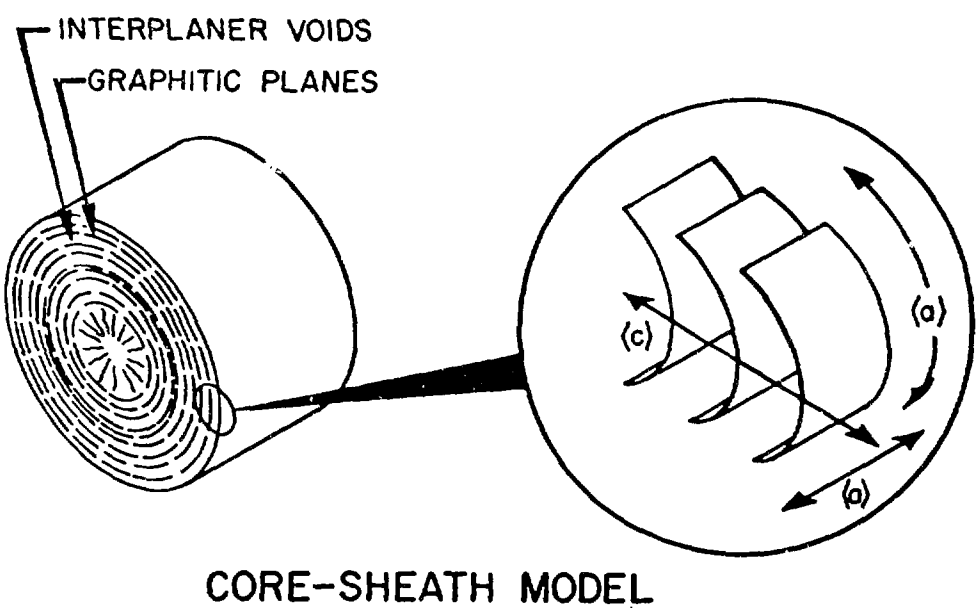

FIGURE 5. PAN carbon fiber structural model and orientation of graphite crystallographic basal planes [15].

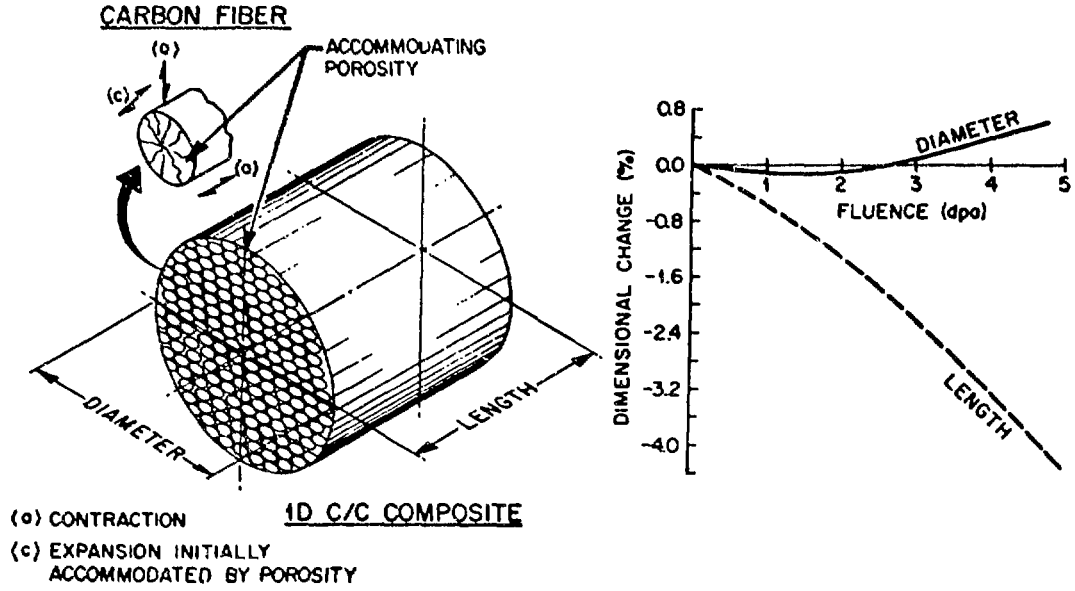

FIGURE 6. A microstructural interpretation of irradiation induced dimensional changes in a unidirectional carbon-carbon composite.

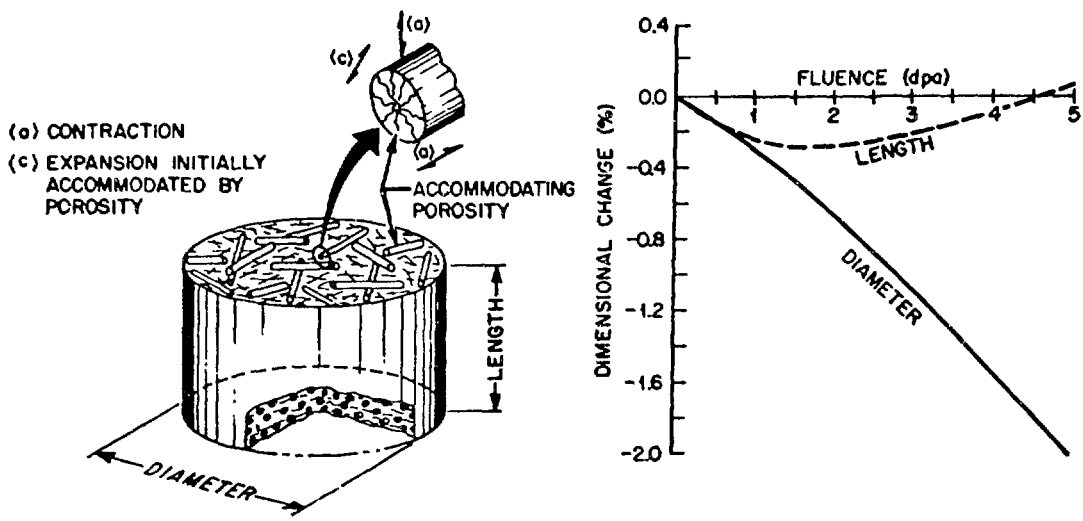

FIGURE 7. A microstructural interpretation of irradiation induced dimensional changes in a two-directional carbon-carbon composite.

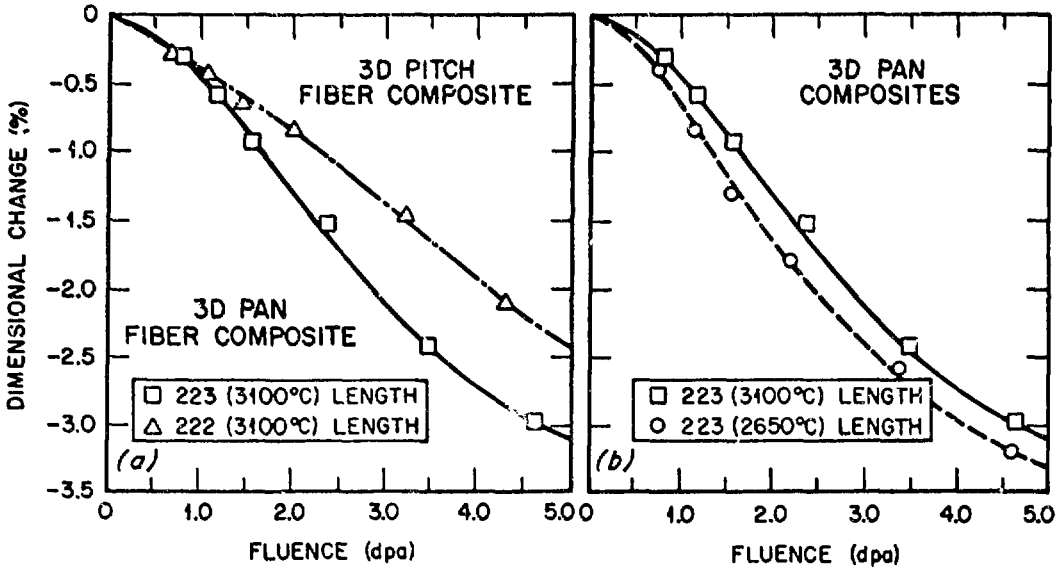

FIGURE 8. Irradiation dimensional change in two 3D, C/C composites: (a) a comparison of pitch and PAN fiber composite behavior, and (b) the effect of heat treatment temperature on the dimensional change of a PAN (223) C/C composite.

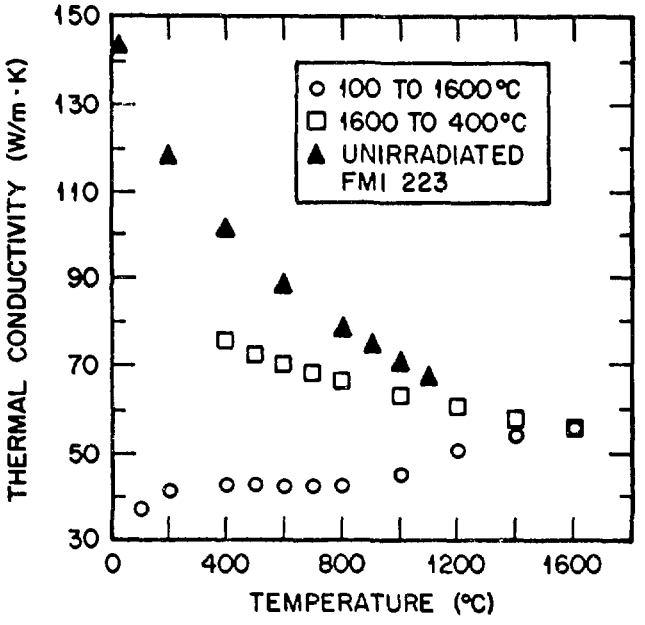

FIGURE 9. The temperature dependence of thermal conductivity for a three-directional carbon-carbon composite manufactured with PAN carbon fibers (FM1-223).

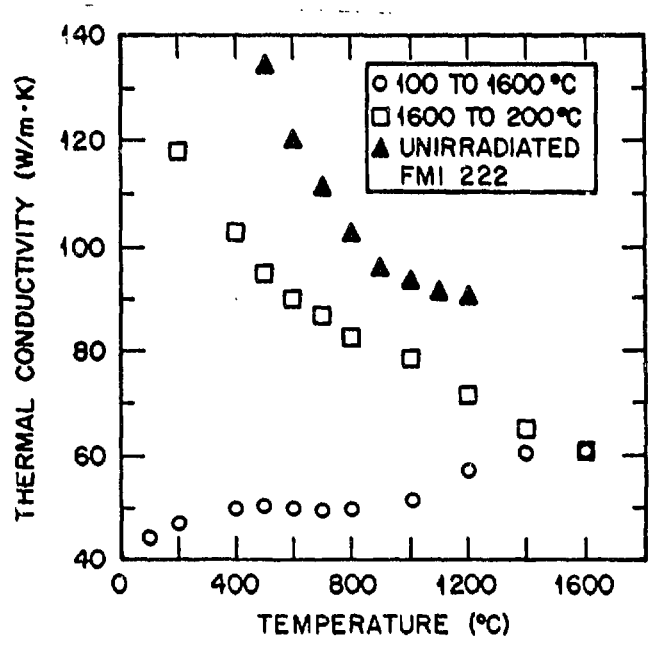

FIGURE 10. The temperature dependence of thermal conductivity for a three-directional carbon-carbon composite manufactured with pitch carbon fibers (FM1-222).

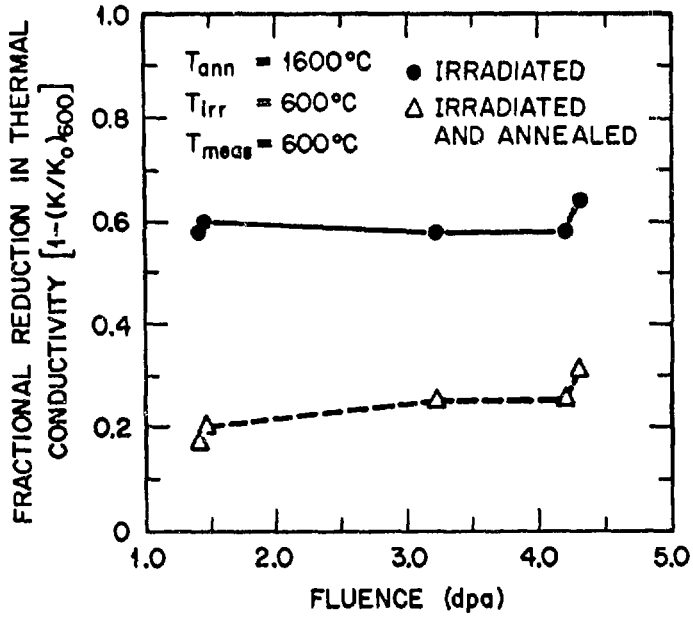

FIGURE 11. The fractional reduction in thermal conductivity as a function of neutron fluence (dpa) for a three-dimensional pitch fiber composite (FM1-222).

BIOGRAPHY

Dr. Tim Burchell is the Leader of the Carbon Materials Technology Group of the Oak Ridge National Laboratory, which is engaged in carbon materials development and characterization for the U.S. Department of Energy's Space Power Program, Nuclear Programs, and Fossil Materials Program. Dr. Burchell received his B.Sc. in Materials Science from the University of Bath, U.K. in 1981 and his Ph.D. in Materials Science from the University of Bath in 1986. He is the author of numerous papers on the subject of graphite fracture behavior and modelling, and the effects of neutron damage on carbon materials structure, properties, and fracture behavior. In 1987 he and two co-authors received the Pergamon Prize for the best paper published in CARBON Vol. 24.