

Neutron Irradiation Damage in Graphite Foam and its Effect on Properties

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Abstract

The Solid State Reactor (SSR) is an advanced reactor concept that would take advantage of newly developed materials, with enhanced heat transfer characteristics, to provide an inherently safe, self-regulated heat source. High conductivity graphite foam, developed and produced at Oak Ridge National Laboratory (ORNL), is being evaluated as a candidate material for the core of basic heat source modules.

Irradiation studies at ORNL's High Flux Isotope Reactor (HFIR) facility were conducted to determine the effects of neutron flux on the thermal properties of the graphite foam as a function of neutron dose up to 2.6 displacements per atom (dpa). Samples were characterized for dimensional and structural changes, and thermal properties as a function of dose. Following the initial effects of the irradiation, the samples were annealed at 1000 and 1200°C and the thermal properties measured as a function of temperature.

Keywords: A: graphite, B: annealing, D: radiation damage, thermal diffusivity, thermal conductivity.

1. INTRODUCTION

The Solid State Reactor (SSR) is an advanced reactor concept that would take advantage of newly developed materials with enhanced heat transfer characteristics and superb high temperature mechanical properties to provide an inherently safe, self-regulated heat source. The concept achieves demand-driven heat generation without the need of moving parts or working fluids. The nature of the reactor design makes the concept inherently safe, proliferation resistant, and ideal as a long-term reliable source of power for harsh, remote, and/or inaccessible environments [1].

High conductivity graphite foam, developed and produced at Oak Ridge National Laboratory (ORNL), is being evaluated as a candidate material for the core of basic heat source modules. The graphite foam will act mainly as structural support and heat conduction material. Neutron moderation will primarily take place in the reflector yielding an energy spectrum peaked in the epithermal regime. The low density of the foam will result in a low carbon-uranium ratio. This is the key to attain a zero burn-up reactivity swing over long time periods.

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2. EXPERIMENTAL

2.1 Foam sample for irradiation studies

The graphite foam utilized in this project was produced using a process developed at ORNL in the Carbon Materials Technology Group [2]. Foam was produced from an AR mesophase pitch, produced by Mitsubishi Gas Chemical Co. Foamed samples were first carbonized to 1000°C in nitrogen atmosphere, and subsequently graphitized to ~2800°C in argon, to develop the graphitic structure of the foam thus enhancing their thermal properties.

The manufacturing process for graphite foam induces a preferred alignment of the ligaments of the foam in the Z-direction (see Figure 1). This alignment translates into an anisotropic behavior of the properties of the foam (i.e., the thermal conductivity in the Z-direction is 3-4 times that of the X- or Y-direction). To evaluate the effect of this texture, samples in both orientations (OP and IP) were studied.

Cylindrical samples of graphite foam were machined from a block of graphite foam produced from an AR mesophase pitch and graphitized at 2800°C. A total of 38 cylindrical samples (19 in-plane, IP, and 19 out-of-plane, OP) of approximately 6-mm diameter by 10-mm length were machined.

Four irradiation capsules were prepared for this project. Three foam samples plus a CVD SiC temperature monitor were fitted in each capsule. Two of the capsules were used for the IP samples and the other two were used for the OP samples; a total of twelve foam samples were irradiated at ORNL's HFIR. Table 1 lists the content of each capsule and the neutron irradiation dose received. The location of the capsules within the hydraulic tube (position 3-4) was such that the variation of the neutron flux was less than 15% from capsule to capsule.

2.2. Temperature monitor analysis

In order to determine the ultimate irradiation temperature, an isochronal annealing method was followed [3]. The temperature monitor was first sliced into three pieces to reduce its thickness (due to the low thermal conductivity of SiC, a thinner sample is required to perform the measurements). The thermal diffusivity of the sample was measured at 200°C and taken as the reference value. The sample was then heated to temperatures between 400 and 600°C in 50°C intervals. After each temperature increment, the sample was cooled down to 200°C and its thermal diffusivity measured. A similar procedure was repeated for temperatures from 610 up to 890°C but in 20°C intervals.

From a graph of thermal diffusivity at 200°C as a function of annealing temperature, it was determined that

the actual irradiation temperature of the temperature monitors was $770^{\circ}\text{C} \pm 25^{\circ}\text{C}$. With the type of capsules utilized for this project (vanadium holder), a temperature difference of about 30°C between the temperature monitor and the graphite foam was calculated. Therefore, we can say that the irradiation temperature of the graphite foam was $740^{\circ}\text{C} \pm 25^{\circ}\text{C}$. This temperature is significantly higher than the designed irradiation temperature of 600°C .

2.3 Sample characterization

Pre- and post-irradiation examination of the graphite foam samples included dimensional changes, microstructural examination, and thermal diffusivity.

The thermal diffusivity (α) was measured using an Anter system. Thermal conductivity (K) values were then estimated utilizing the following relation:

$$K = \alpha \cdot \rho \cdot C,$$

where C is the specific heat and ρ the density of the foam. Density was measured using the Euclidian method and the specific heat for a given temperature was calculated using Kelly's relationship [4].

Irradiated samples were annealed in a vacuum furnace to temperatures of 1000 and 1200°C .

3. RESULTS AND DISCUSSION

3.1 Dimensional changes

Figure 2 reports the volume change of the irradiation samples as a function of neutron dose expressed as displacements per atom (i.e., the average number of times each carbon atom is displaced from its equilibrium lattice position). The volume change was determined from the pre- and post-irradiation specimen dimensions. As indicated by the data in Figure 2, the volume change behavior is dominated by a rapid swelling of the graphite foam at relatively low doses, followed by a turnaround to shrinkage. The data indicates that the shrinkage continues into net volume shrinkage, i.e., $\Delta V/V = 0$, at ~ 3 dpa.

The dimensional changes are reported in Figure 3. Similarly, the dimensional change (as represented by the change in specimen length) is dominated by initial low dose (ϕ) expansion, followed by a turnaround to shrinkage. Significant anisotropy in the neutron irradiation-induced dimensional change is seen in Figure 3, with the OP-type specimens reaching $dL/d\phi = 0$ (turnaround) at smaller length changes than the IP-type specimens, and the return to original length ($\Delta L/L = 0$) occurring at lower dose for the OP specimens. While these observations are based upon very limited data, it is evident that a reversal from growth to shrinkage occurs in graphite foam at the temperature of this irradiation study.

3.2 Thermal properties of irradiate graphite foam

So far, two irradiated samples have been evaluated for thermal properties after irradiation. Annealing studies were also conducted on these samples. The selected samples were OP-9 and OP-17, irradiated to 2.6 and 0.3 dpa, respectively.

The lower curves of Figures 4 and 5 show the temperature dependence of the graphite foam thermal conductivity after irradiation. For this irradiation temperature ($\sim 740^{\circ}\text{C}$), the room temperature thermal conductivity decreased from an average of ~ 70 W/m \cdot K

(for nonirradiated foam) to ~ 30 W/m \cdot K for a dose of 0.3 dpa and to ~ 15 W/m \cdot K for a dose of 2.6 dpa. Some fraction of the irradiation-induced damage was annealed from the material by heating it above its irradiation temperature (1000°C). The annealing effect may be seen in the "cooling" curves of Figures 4 and 5. More substantial recovery of thermal conductivity can be expected as the annealing temperature is increased, as observed in the curves for samples annealed at 1200°C .

The mechanism of thermal conductivity and the degradation of thermal conductivity of graphite materials have been extensively reviewed [4,5,6,7,8,9]. The increase of thermal resistance due to irradiation damage has been ascribed to the formation of the following: (i) submicroscopic interstitial clusters containing 4 ± 2 carbon atoms; (ii) vacant lattice sites, existing as singles, pairs, or small groups; and (iii) vacancy loops, which exist in the basal plane of the graphite crystal and are too small to have collapsed parallel to the hexagonal axis [5].

For graphite materials, the reduction in thermal conductivity due to irradiation damage is temperature and dose sensitive. At any irradiation temperature, the decreasing thermal conductivity will reach a "saturation" limit. This limit is not exceeded until the graphite undergoes gross structural changes (caused by pore generation and cracking) at high fluences. The saturated thermal conductivity will be attained more rapidly and will be at lower conductivity level at lower temperatures.

Thermal conductivity measurements and annealing studies of irradiated samples showed that thermal conductivity decreased as the irradiation dose increased. This effect is consistent with typical results for graphite samples as it is shown in Figure 6, where the variation of room temperature thermal conductivity as a function of irradiation dose is shown for graphite foam samples and for nuclear grade graphite H 451.

4. CONCLUSION

It has been shown that the foam's thermal properties decrease with both temperature and radiation dose. However, it has also been shown that the foam recovers a significant portion of the decrease when annealed. This behavior of reduced thermal properties is not unique to the graphite foam, a similar trend is found with highly ordered pyrolytic graphite. Although significant knowledge of this material and its behavior under irradiation has been gained, the need for further work on irradiation effects is clearly indicated.

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Table 1. Capsule's content and neutron irradiation dose.

Capsule	Foam Samples	Monitor	Dose ¹ (dpa)	Planned Irradiation Temperature
NERI-1	IP-1, IP-3, IP-4,	CVD SiC TM 600	2.6	600°C
NERI-2	OP-2, OP-3, OP-9	CVD SiC TM 601	2.6	600°C
NERI-3	IP-7, IP-14, IP-15	CVD SiC TM 602	0.3	600°C
NERI-4	OP-15, OP-16, OP-17	CVD SiC TM 603	0.3	600°C

¹ A conversion of $0.7 \times 10^{25} \text{ n/m}^2 (E > 0.1 \text{ MeV}) = 1 \text{ dpa}$ is assumed

* Note: IP and OP refer to the orientation of the sample within the block of graphite foam (see Figure 1).

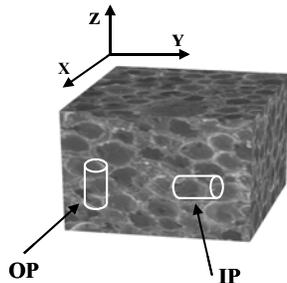


Figure 1. Orientation of machined samples within the block of carbon foam.

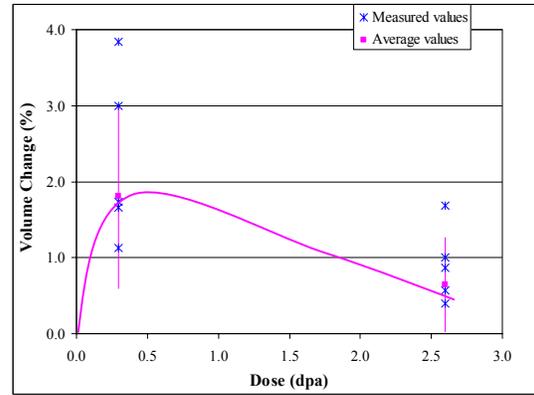


Figure 2. Volume changes ($\Delta V/V$) as a function of irradiation dose for graphite foam samples.

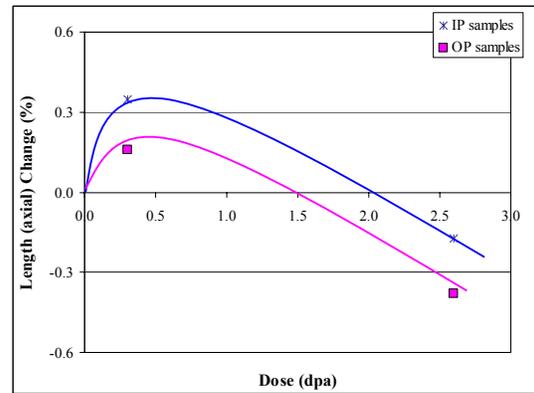


Figure 3. Dimensional changes ($\Delta l/l$) as a function of irradiation dose for graphite foam samples.

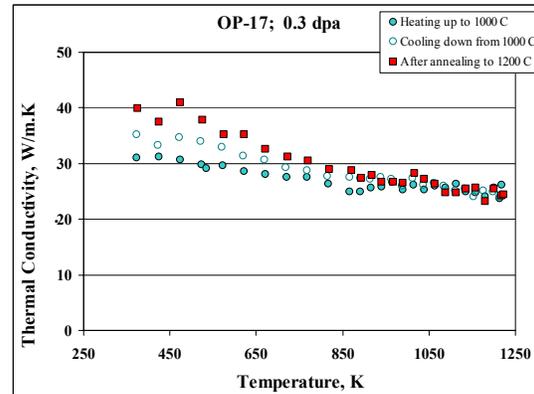


Figure 4. Thermal conductivity measurements of samples OP-17 after irradiation and after annealing to 1000 and 1200°C.

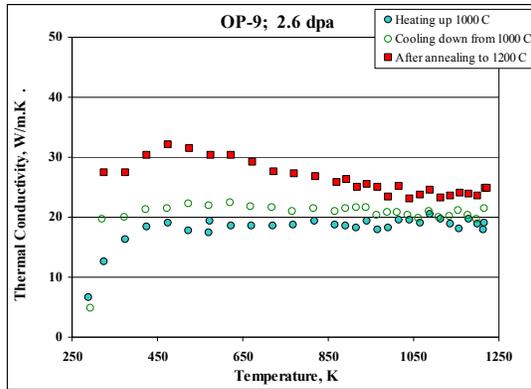


Figure 5. Thermal conductivity measurements of samples OP-9 after irradiation and after annealing to 1000 and 1200°C.

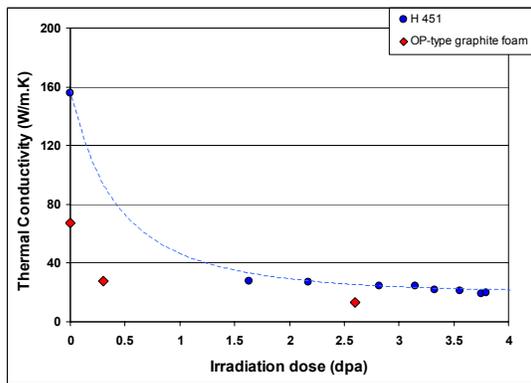


Figure 6. Room temperature conductivity versus irradiation dose for (i) nuclear grade graphite H 451, and (ii) graphite foam (OP-type samples).