THERMAL CONDUCTIVITY DEGRADATION OF GRAPHITES IRRADIATED AT LOW TEMPERATURE – L. L. Snead and T. D. Burchell (Oak Ridge National Laboratory)

OBJECTIVE

The objective of this work is to study the thermal conductivity degradation of new, high thermal conductivity graphites and to compare these results to more standard graphites irradiated at low temperatures.

SUMMARY

Several graphites and graphite composites (C/C's) have been irradiated near 150°C and at fluences up to a displacement level of 0.24 dpa. The materials ranged in unirradiated room temperature thermal conductivity of these materials varied from 114 W/m-K for H-451 isotropic graphite, to 670 W/m-K for unidirectional FMI-1D C/C composite. At the irradiation temperature a saturation reduction in thermal conductivity was seen to occur at displacement levels of approximately 0.1 dpa. All materials were seen to degrade to approximately 10 to 14 % of their original thermal conductivity after irradiation. The effect of post irradiation annealing on the thermal conductivity was also studied.

PROGRESS AND STATUS

Introduction

In recent years graphite has been used in every major tokamak reactor primarily due to its low atomic number, good strength, and high sublimation temperature. Because of the significant advances in C/C processing and fiber development, very high thermal conductivity materials have been recently demonstrated and become attractive for high heat flux applications. The most striking thermal conductivities have been demonstrated for the C/C's made from highly aligned graphite fibers which have intrinsic conductivity approaching that of pyrolitic graphite. One example of such fibers is the vapor grown carbon fibers,[1] which have thermal conductivity of 1950 W/m-K. Along with advances in fiber properties, there have been improvements in both the monolithic graphite and C/C matrix processing areas have occurred which have additionally enhanced thermal conductivities.

Figure 1 gives the thermal conductivity temperature dependence of some C/C composites and two graphites. Inset into the graph are the thermal conductivity of the fibers from which the C/C's were manufactured. The thermal conductivity of copper is included for reference. It is seen that generally the highest thermal conductivity fibers yield composites with the best thermal conductivities. However, in some cases (MKC-1PH), a composite of extremely high conductivity has been fabricated from moderate conductivity fibers. This is attributed to processing improvements which enhance the matrix contribution to the composite conductivity. It has been shown[2] for the MKC-1PH material that matrix graphite planes have aligned themselves radially around the fiber increasing thermal conductivity for the composite. The thermal conductivity in

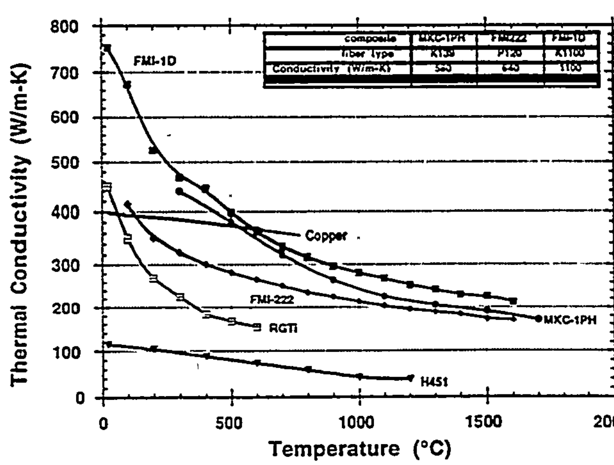

Fig. 1. Thermal conductivity-vs-temperature for some high conductivity graphite materials.

directions normal to the fiber, and thus normal to the matrix graphitic planes, have a correspondingly lower thermal conductivity. For this composite, and others of similar quality, the matrix contribution to thermal conductivity in the high conductivity direction is on the order of the fiber's contribution.

The H451 graphite of Figure 1 represents a standard, high quality, extruded, near isotropic, medium grain graphite which has been in service in the nuclear industry for many years. The second monolithic graphite (RGTi) is one which has been recently developed in Russia. RGTi graphite is prepared from starting materials similar to the H451 material, but includes ~7 weight percent titanium as a recrystallizing agent, yielding large graphitic islands with a preferred orientation perpendicular to the direction of hot pressing. Though the process of metal-induced recrystallization was first observed over twenty five years ago,[3] the demonstration of its effect on the thermal conductivity has been a more recent development.

The irradiation induced degradation in thermal conductivity of graphites is a serious problem for the use of these materials in fusion systems. As with ceramics, graphite thermal conductivity is dominated by phonon transport and is therefore greatly affected by neutron induced defects, such as lattice vacancies and interstitials. For this reason, the extent of the thermal conductivity reduction is directly related to the efficiency of creating and annealing lattice defects and is therefore strongly tied to the irradiation temperature.

The effect of neutron irradiation on the thermal conductivity of graphite has been widely studied. The majority of the literature[4-6] in this area has been in support of the gas cooled reactor program in the U.S. and United Kingdom and has focused on "nuclear" graphites as well as more fundamental work on pyrolitic graphite.[7-8] Over the past several years, the emphasis for radiation effects in graphite has switched to its use as plasma facing components for fusion reactors.[9-12] Because the stress levels anticipated in these applications can be quite high, a growing interest in the radiation effects of C/C composites has occurred. The thermal conductivity of C/C composites has been published for materials of about the same conductivity as nuclear graphites, and shows degradation similar to that expected from the graphite literature. For example, Burchell[11] has shown a saturation thermal conductivity for a good 3-dimensional composite (FMI-222, $K_{unirr.}$ = 200 W/m-K) is reduced to ~40% original room temperature conductivity following fast neutron irradiation at 600°C. However, to this point there has been no published work on the very high (>300W/m-K) thermal conductivity composites.

The purpose of this paper is to present the radiation induced thermal conductivity degradation in several graphites ranging in room temperature conductivity from 114 W/m-K for H-451 graphite, to 670 W/m-K for the unidirectional FMI-1D C/C composite. These materials represent both conventional graphites for reference, as well as the state of the art in high thermal conductivity composites. All materials were irradiated in a range of damage levels from 0.01 dpa to 0.24 dpa at a single irradiation temperature of ~150°C. Such a temperature would represent the lowest service temperature for graphite tile in an ITER-like fusion machine. The effect of postirradiation annealing on the recovery in conductivity is also presented.

Experimental

Six materials were selected for this irradiation study and are listed in Table 1 in order of increasing thermal conductivity. It is important to note that for the high thermal conductivity graphites there is a significant variation in the published values of conductivity even for nominally the same material. This variation can be attributed not only to the method of measurement but also on the manipulation of the measured signal. In general, the values quoted in this paper are lower than the manufacturer's data. Room temperature thermal diffusivity was measured using a xenon thermal flash method. Cylindrical samples of 6 mm diameter were used with thickness ranging from 4 to 10 mm depending on the unirradiated thermal conductivity. As the thermal conductivity degrades substantially following irradiation, sample thickness was chosen to be the thinnest which would yield accurate data in the unirradiated condition. By doing so, measurement complications arising from radial heat loss were minimized. A series of samples of varying thickness were measured and compared to arrive at this minimum value. The thermal conductivity of the material was calculated from the measured thermal diffusivity using the following relation:

$$(1) \quad K = \alpha \rho C_p$$

where α is the measured diffusivity (m^2/s), ρ the density (kg/m^3), and C_p is the specific heat (J/kg-K). The specific heat has not been measured for these materials but was assumed to be the standard value for graphite (684 J/kg-K.) Moreover, it is further assumed that the specific heat of the material is not significantly affected by irradiation. This assumption has been verified in previous studies.[13] For the case of the RGTi material, the specific heat was assumed to be a mass average of graphite and titanium including 7 weight percent titanium.

Table 1. Selected Graphite Information

Material	Manufacturer	Structure	Fiber	Room Temp. Conductivity (W/m-K)
H451	Segri-Great Lakes	Extruded Graphite	–	115
FMI-222	Fiber Materials	3-D Composite	Amoco P-120	200
Hercules 3D	Hercules	3-D Composite	Amoco P-120	345
RGTi	Efremov Institute	Ti Doped Graphite	–	450
MKC-1PH	Mitsubishi Kasei	1D Composite	MKC K-139	555
FMI-1D	Fiber Materials	1D Composite	Amoco K1100	650

The cylindrical graphite samples were stacked axially, wrapped in aluminum foil, and loaded into aluminum capsules for irradiation. The aluminum foil served to contact the inside of the irradiation capsule, which was nominally at reactor coolant temperature, and to conduct the heat generated in the samples to the capsule wall. The temperature of the samples was calculated to be 150°C, though could have been as high as 200°C in the worst case. Capsules were irradiated in the core region of the High Flux Isotope Reactor at the Oak Ridge National Laboratory at a flux of 7.8×10^{18} n/m^2-s (E >0.1 MeV). Total fluences were for 1.26×10^{23} n/m^2, 1.26×10^{24} n/m^2 and 3.22×10^{24} n/m^2. The calculated value of displacements per atom (dpa) for these fluences was 0.01, 0.1, and 0.24 dpa, respectively.

Postirradiation annealing was carried out on each specimen followed by ambient temperature thermal diffusivity measurements. Annealing temperatures were 300, 600, 900, 1200 and 1374°C. Samples were annealed in an argon environment and held at temperature for a period of one hour. The 3-D C/C composite manufactured by Hercules underwent delamination from repeated handling and heating and is not included in the annealing results. This problem stemmed from the need for the small diameter specimen and the large unit cell of the Hercules composite, rather than any radiation-induced degradation.

Results

Shown in Figure 2a and 2b are plots of the absolute and normalized thermal conductivities of the irradiated samples. The normalized data is given as the fraction of original thermal conductivity, K_{irr}/K_{unirr}. Figure 2a also gives the value for dispersion strengthened Glidcop™ copper as reference. All samples in Figure 2 are seen to sharply decrease to less than 40% of their original thermal conductivity by 0.01 dpa. The conductivity is seen to further decrease above this displacement level and approaches an apparent saturation above 0.1 dpa. It is seen from Figure 2b that the conductivity seems to be asymptotically approaching ~10% of original conductivity for all materials studied, irregardless of their initial thermal conductivity. At the highest dose studied (0.24 dpa), the conductivity underwent a very small decrease from the 0.1 dpa values, though there was a small amount of scatter attributable to measurement error.

The effect of isochronal annealing of the irradiated material is demonstrated in Figures 3a and 3b for absolute and normalized thermal conductivity. This figure is for the 0.01 dpa irradiated graphites. In this case, significant recovery in thermal conductivity is seen to occur following the 300°C anneal and increases steadily through the final annealing at 1370°C. It is seen that at this highest annealing temperature, the

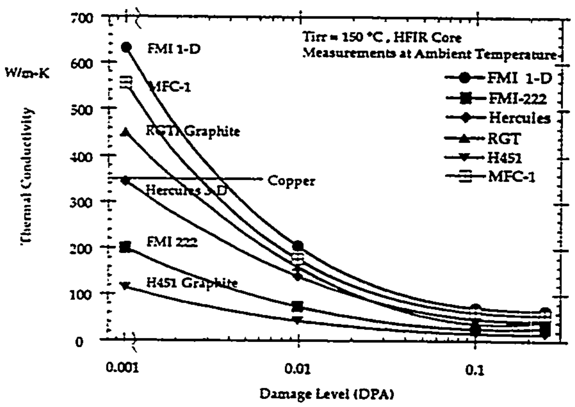

Fig. 2a. Irradiation induced degradation of thermal conductivity.

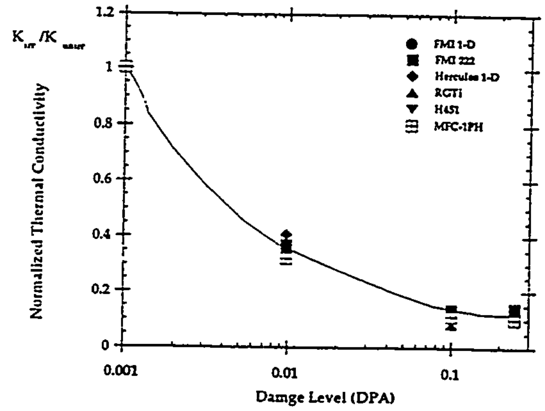

Fig. 2b. Normalized irradiation induced degradation of thermal conductivity.

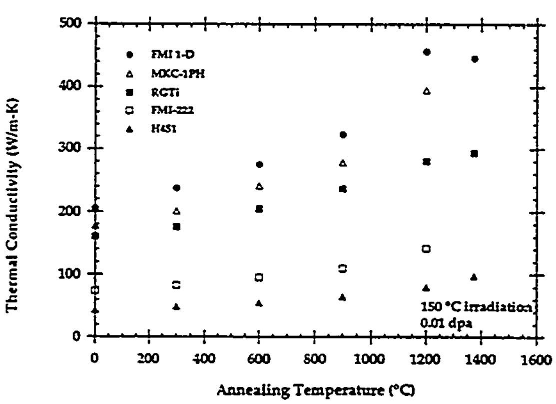

Fig. 3a. Thermal conductivity recovery following isochronal annealing.

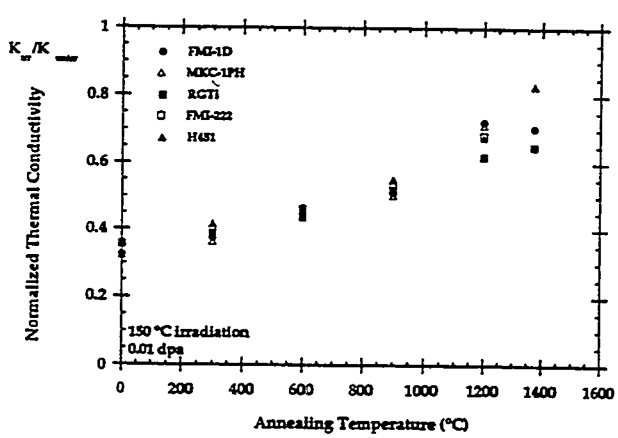

Figure 3b. Normalized thermal conductivity recovery following isochronal annealing.

thermal conductivity has recovered (Figure 3b) to 65-85% of its original value in the various specimens. Two samples (MFC-1PH and FMI 222) from this data set were damaged during a furnace excursion and were not tested at the highest annealing temperature. Shown in Fig. 4 is a compilation of the annealing data for the three fluences. In this case the actual data has been replaced with data-bands for clarity. Two features are of interest from this plot. Firstly, significant recovery has occurred in all the materials for all three fluences. The graphite materials with the lowest fluence (0.01 dpa) recovered to ~75% of their original thermal conductivity, while the highest fluence irradiated materials only recovered to ~45% original conductivity. Secondly, the graphites with the highest dose began thermal annealing at a higher temperature than those with a lighter irradiation.

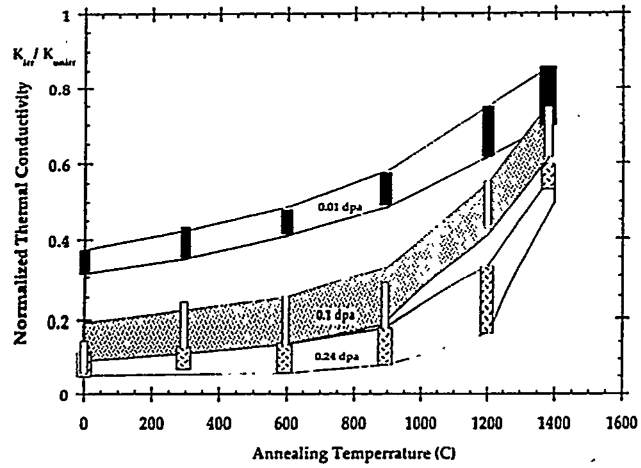

Fig. 4. Normalized thermal conductivity recovery at 0.01, 0.1 and 0.25 dpa.

Discussion

The physical processes governing the thermal conductivity of graphites, as well as the mechanisms responsible for the radiation induced degradation in conductivity, have been well established.[14] For all but the poorest grades of carbon, the thermal conductivity is dominated by phonon transport along the graphite basal planes and is reduced by scattering "obstacles" such as grain boundaries and lattice defects. For graphites with the largest crystallites, i.e. pyrolitic graphite or natural flake, the in-plane room temperature thermal conductivity is approximately 2000 W/m-K.[15]

The thermal conductivity of graphite based material can be written as a summation of the thermal resistance due to scattering obstacles:

$$(2)\quad K(x) = \beta(x)\left(\frac{1}{K_u} + \frac{1}{K_{GB}} + \frac{1}{K_i}\right)^{-1}$$

where the term b(x) is a coefficient which includes terms due to orientation (with respect to the basal plane), porosity and some other minor contributors. This coefficient is in most cases assumed to be constant with temperature, with a value of around 0.6. The first two terms inside the parentheses are the contributions to the thermal conductivity due to the umklapp scattering (K_u) and the grain boundary scattering (K_{gb}). The grain boundary phonon scattering dominates the thermal resistance ($1/K_{gb}$) at low temperatures and is insignificant above a few hundred Celsius, depending on the perfection of the graphite. The umklapp scattering, which defines the phonon-phonon scattering effect on the thermal conductivity, dominates at higher temperatures and scales nearly as T^2. The umklapp scattering therefore defines the upper limit to the thermal conductivity for a "perfect" graphite. Following Taylor's analysis,[16] the umklapp limited thermal conductivity of the graphite crystal would be ~2200 W/m-K at room temperature, which is not far removed from the best pyrolitic graphites or the vapor grown carbon fibers mentioned in the introduction.

The third term in equation (2), K_i, is the contribution to the thermal resistance in the basal plane due to defect scattering. Following neutron irradiation, various types of defects will be produced depending on the irradiation temperature. These defects can be very effective in scattering phonons at flux levels which would be considered modest for most nuclear applications, and would quickly dominate the other terms in equation (2). Several types of defects have been identified in graphite, though at irradiation temperatures less than ~650°C, only simple defects are found in significant quantities. For the 150°C irradiation temperature of this study, simple point defects in the form of vacancies or interstitials along with small interstitial clusters are the predominant defects. It has been further shown[8] that at an irradiation temperature near 150°C, the defect which dominates the thermal resistance is the lattice vacancy.

The temperature at which graphite is irradiated has a profound influence on the thermal conductivity degradation. As an example, Fig. 5 shows one of the most complete sets of irradiation data on Pile Grade A nuclear graphite. This graphite is a medium grained, extruded, anisotropic material with a room temperature thermal conductivity of 172 W/m-K in the extrusion direction. Figure 5 presents the normalized room temperature thermal conductivity for this graphite for various irradiation temperatures. It is seen that as the irradiation temperature is decreased, the degradation in thermal conductivity becomes more pronounced. As an example, following irradiation at 150°C, this graphite appears to approach an asymptotic thermal conductivity of ~1% of original. As the irradiation temperature is increased, and the corresponding interstitial mobility becomes substantial, fewer defects remain in the structure and the thermal conductivity is not significantly reduced.

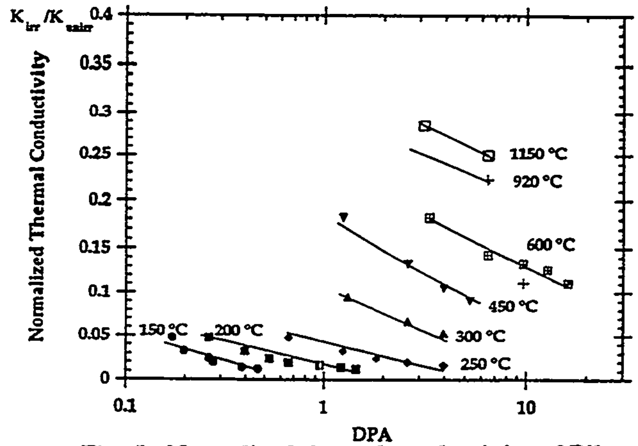

Fig. 5. Normalized thermal conductivity of Pile Grade A graphite.

As mentioned above, at the irradiation temperature of this study, the defect which contributes most to the thermal resistance is the basal plane vacancy.[8] Along with carbon interstitials, these defects can reside as single vacancies, as pairs, or small groups. Upon thermal annealing, interstitial atoms become more mobile and can recombine with the vacancies, restoring the thermal conductivity of the lattice. From Figure 4 it is seen that a significant recovery can occur in the graphites study for annealing temperatures above ~900°C as vacancy mobility becomes substantial. Of particular interest in Figure 4 is that the more heavily irradiated graphite samples exhibited recovery at higher annealing temperatures. One possible explanation for this is that as the fluence is increased, the relative fraction of agglomerated defects compared to single defects is increased leading to less efficient annihilation of basal plane vacancies.

CONCLUSIONS

The thermal conductivity of both standard H451 graphite, high conductivity recrystallized graphite (RGTi) as well as a few high thermal conductivity composites yielded a significant reduction in thermal conductivity near 150°C. Even though the conductivities of these materials varied substantially, the relative rate of degradation in thermal conductivity was very similar. An apparent saturation value of 10-14% original conductivity was achieved above 0.1 dpa for all materials in this study. Isochronal anneals have shown significant recovery in thermal conductivity, with the more heavily irradiated samples requiring a higher temperature before significant recovery began.

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