

HIGH TEMPERATURE ANNEALING OF IRRADIATED NUCLEAR GRADE GRAPHITE

W. David Swank, David T. Rohrbaugh,
David L. Cottle, William E Windes

October 2018



The INL is a U.S. Department of Energy National Laboratory
operated by Battelle Energy Alliance

HIGH TEMPERATURE ANNEALING OF IRRADIATED NUCLEAR GRADE GRAPHITE

W. David Swank, David T. Rohrbaugh, David L. Cottle, William E Windes

October 2018

**Idaho National Laboratory
Idaho Falls, Idaho 83415**

<http://www.inl.gov>

**Prepared for the
U.S. Department of Energy
Under DOE Idaho Operations Office
Contract Unknown**

HIGH TEMPERATURE ANNEALING OF IRRADIATED NUCLEAR GRADE GRAPHITE

*W. David Swank, David T. Rohrbaugh, David L. Cottle and William E. Windes
Idaho National Engineering Laboratory
PO Box 1625, Idaho Falls, ID 83415, USA
phone: 208-526-1698, W.Swank@INL.GOV*

Abstract – Previous work has shown that the properties of nuclear grade graphite are substantially affected by neutron irradiation. Understanding the details of how these changes occur and exactly what the damage consists of will enable prediction of the property changes as a function variables like dose, temperature, composition, micro and macrostructure. Other work has shown these atomic level changes or damage can be healed or annealed out by raising the irradiated graphite above its irradiation temperature. Experiments were carried out at the Idaho National Laboratory to investigate how the properties of irradiated graphite recover. By showing property recovery as a function of annealing temperature or energy, insight is provided into the type of damage that occurred during neutron irradiation. The data presented here shows recovery of thermal diffusivity, coefficient of thermal expansion, Young's modulus and electrical resistivity between annealing temperatures of 500°C and 2380°C. Graphite grades NBG-18, IG-110 and PCEA are considered in both stressed and unstressed irradiation conditions.

I. INTRODUCTION

When graphite is irradiated with fast neutrons various lattice defects are produced. These defects range from simple single vacancies and interstitials to more complex vacancy groups which can collapse causing disturbance in the graphite basal planes. As the damage accumulates, even three dimensional interstitial clusters can form. Proposed models of this damage vary from relatively simple Frenkel pair vacancy-interstitial explanations to more complex sp² – sp³ bonding transitions [1,2]. To date a definitive model does not exist and it is likely that only a combination of theory's will explain the changes in physical properties observed in graphite following irradiation[3]. In order to examine these and future theories, detailed experimental data describing the change in physical properties of the graphite is a necessity. Understanding the physics behind different material properties and the changes that occur to those properties during irradiation allows theories and models to be tested. Models that

can describe and support the measurable physical changes that result from neutron irradiation must also work for the reverse process of annealing those changes by raising the material temperature above the irradiation temperature.

This paper seeks to provide both the change in properties due to neutron irradiation and the recovery of those properties during thermal annealing. The properties investigated here for both irradiation damage and isothermal - isochronal annealing are: dimensional change, electrical resistivity, Young's modulus of elasticity, coefficient of thermal expansion and thermal diffusivity. The graphite specimens used for this study are from the US Department of Energy (DOE) Advanced Reactor Technologies (ART) Materials Research and Development program's second irradiation capsule, AGC-2.

II. EXPERIMENTAL PROGRAM

The ART Program is conducting an extensive graphite irradiation experiment to provide data for licensing of a high temperature reactor (HTR) design. New nuclear graphite grades have been developed and are considered suitable candidates for new HTR reactor designs. To support the design and licensing of HTR core components within a commercial reactor, a complete properties database must be developed for these current grades of graphite. Quantitative data on in-service material performance are required for the physical, mechanical, and thermal properties of each graphite grade, with a specific emphasis on data accounting for the life-limiting effects of irradiation creep on key physical properties of the HTR candidate graphite grades.

The Advanced Graphite Creep (AGC) experiment is currently underway to determine the in-service behavior of these new graphite grades for HTR. Irradiation data are provided through the AGC test series that is comprised of six planned capsules irradiated in the Advanced Test Reactor (ATR) at Idaho National Laboratory (INL). The AGC irradiation conditions are similar to the anticipated environment within a high temperature core design. Each irradiation capsule is composed of more than 400 graphite specimens that are characterized before and after irradiation to determine the irradiation-induced changes in material properties and the rate of life-limiting irradiation creep for each graphite grade.

In addition to determining the irradiation-induced changes to the material properties of selected nuclear graphite grades, the AGC experiment dedicates a significant amount of scope to determining rates of irradiation-induced creep for different nuclear graphite grades. The traditional method for measuring irradiation-induced creep is to apply a significant mechanical load (inducing a mechanical stress within the graphite) to half the specimens during irradiation while leaving the remaining half of the specimens unloaded (unstressed). Mechanically loaded (stressed) specimens are designated as the creep specimens, and the unloaded (unstressed) specimens are designated as the control specimens. The resulting difference in dimensional change between the loaded and unloaded specimens (assuming the temperature and dose levels are the same) provides the amount of irradiation-induced strain for each “matched pair” of graphite specimens.

To provide all necessary material property tests in the AGC experiments, each test series capsule contains “creep” specimens that are stressed at three different levels during the irradiation, 13.8, 17.2 and 20.7 MPa. Control specimens are not stressed and the dimensional change of the creep and control specimens is used to determine the creep coefficient as a function of stress, dose and irradiation

temperature. “Piggyback” specimens provide thermal material property behavior for the graphite. The piggyback specimens are not mechanically loaded and are subjected only to neutron irradiation.

All specimens are 12.7 mm (0.5 in.) in diameter, with the larger creep and control specimens being 25.4 mm (1.0 in.) long and the button-sized piggyback specimens being 6 mm (0.25 in.) long. The large creep and control specimens provide accurate dimensional change, elastic modulus, thermal expansion, electrical resistivity, and mechanical strength measurements. However, the longer creep specimens make them unsuitable for thermal diffusivity measurements. The small piggyback specimens permitted only dimensional measurements, density, and thermal diffusivity testing to be performed. Together, both types of specimens provide the changes in material properties for stressed and unstressed graphite grades.

Unless otherwise specified, the specimen dose and irradiation temperature range for the data contained here is 2.5 to 4.7 dpa and 540 to 680°C respectively. These ranges are a result of the flux profile and cooling design of the experiment capsule. This is not to say that the temperature and flux varied during the irradiation experiment but rather that the individual specimens were irradiated at various constant temperatures and fluxes within this range. The three graphite grades chosen for the annealing experiments cover a wide range of manufacturing and forming processes, coke source, and grain size, Table 1.

Table 1: Graphite types used.

Grade	Coke source	Grain size	Forming Process	Vendor
PCEA	Petroleum	Med.	Extrusion	Grahtech, USA
NBG-18	Pitch	Med.	Vibration Molding	SGL, Germany
IG-110	Petroleum	Fine	Isostatic Pressed	ToyoTanso, Japan

III. MATERIAL PROPERTY DATA

All measurements were made according to the applicable American Society of Testing and Materials (ASTM) standards. The specific standard for each measurement is called out in the corresponding section below. Further details of how these measurement standards are applied to the graphite specimens can be found in INL PLN-4657 [4]. This plan describes the measurement techniques, equipment, and standards used to gather the data that is analyzed here.

The annealing experiments were carried out consistently for all data reported. A minimum of one specimen of each particular geometry, graphite type,

and stressed condition was annealed at the specified constant temperatures between 500°C and 2380°C for 24 hours in a stepwise manner. Following each annealing step, the specimen's material properties were measured and compared to the un-irradiated value, typically by normalizing the annealed value with the un-irradiated value.

III.A. Irradiation Induced Dimensional Changes and Creep

The phenomenon of irradiation-induced creep within graphite has been shown to be critical in determining the total useful lifetime of graphite components. Irradiation-induced creep occurs under the simultaneous application of neutron irradiation and applied stresses within the graphite components. This creep or relaxation of the graphite can help to accommodate the significant internal stresses within graphite components that arise from irradiation induced dimensional changes, differential thermal expansion and externally applied loads. Irradiation induced creep relaxes these large internal stresses, thus reducing the risk of crack formation and component failure. Higher levels of irradiation creep will relieve more internal stress that allows the components longer useful lifetimes within a reactor core.

Figure 1 shows the percent dimensional change for graphite grades NBG-18, IG-110 and PCEA as a function of the applied stress for specimens irradiated between 600°C and 675°C and a dose range of 3.7 to 4.5 dpa. The change in specimen length for those which were not stressed falls in a narrow band between 0.75 to 1.0 percent. This small change drastically increases when the specimens are compressively stressed. The level of radiation induced creep is different for the three grades of graphite with PCEA graphite exhibiting a maximum deformation of over 3%. This data is consistent with historical findings and in agreement with the mechanism of creep described by Kelly and Foreman [5]. The described mechanism is in addition to graphite dimensional change due to irradiation only. It consists of basal plane slip as dislocations pin and unpin in a ratcheting fashion inside the stressed graphite crystals as the defect clusters are created and destroyed with subsequent irradiation.

Two specimens of each graphite type were annealed at the temperatures shown in Figure 2. Both unstressed and stressed specimens were evaluated. The unstressed specimens showed no dimensional recovery up to a temperature of 2380°C and the stressed specimens of IG-110 and PCEA only showed a small amount of recovery starting at an annealing temperature of 1500°C. Again, this behavior is consistent with theorized closure of cracks and porosity in the graphite microstructure

due to c-axis expansion, resulting in densification. As the neutron damaged graphite is annealed at higher temperatures, only the atomic level defects are repaired, thus significant dimensional recovery is not expected.

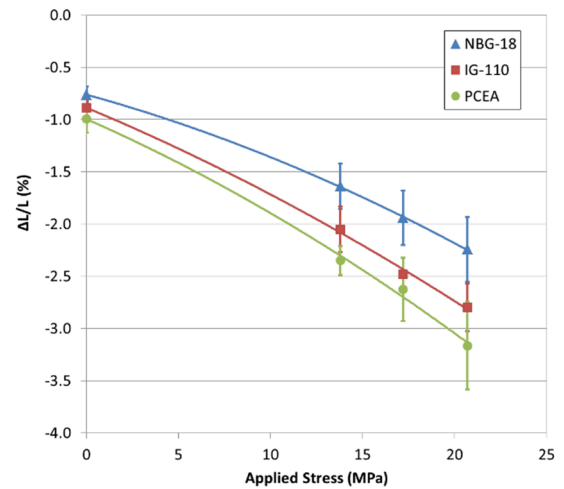


Figure 1: Irradiation dimensional change and creep as a function of applied stress for 3 different grades of graphite.

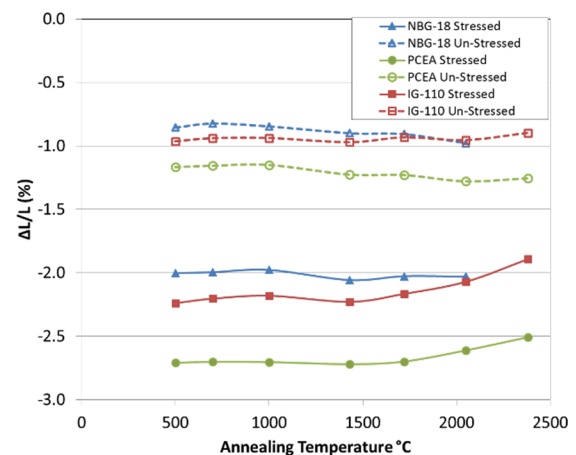


Figure 2: The effect of thermal annealing on the irradiation induced dimensional changes for the three different graphite grades. Solid symbols indicate specimens that were stressed at 20.7 MPa during the irradiation. Hollow symbols represent unstressed specimens.

III.B. Young's Modulus

A material's elastic moduli are a measure of how compliant (or stiff) the material behaves and is useful for ascertaining a graphite grade's mechanical properties, irradiation creep response, and the structural strength and integrity of graphite components. Measured fundamental resonant frequency, specimen dimensions, and mass are used

to calculate Young's modulus in accordance with ASTM C747-16. This test method measures the fundamental resonant frequency of test specimens of suitable geometry by exciting them mechanically with a singular elastic strike. Specimen supports, impulse locations, and signal pick-up points are selected to induce and measure specific modes of the transient specimen vibration. The transient signals are analyzed and the fundamental resonant frequency is isolated by a signal analyzer.

In Figure 3 the average change in Young's modulus due to irradiation is shown for the three different graphite types as a function of stress applied to the specimens. Variation in the data is represented by ± 1 standard deviation error bars and is a result of the different variables within the experiment that include irradiation temperature, dose and grain orientation. The overall increase in modulus is significant with that of IG-110 being almost double the un-irradiated condition. Modulus change for all graphite grades gradually decreases as the applied stress (and the resulting sustained creep strain) is increased. Stressed specimens exhibiting larger plastic strain are shown to experience less change in modulus than the unstressed control specimens exhibiting smaller plastic strain.

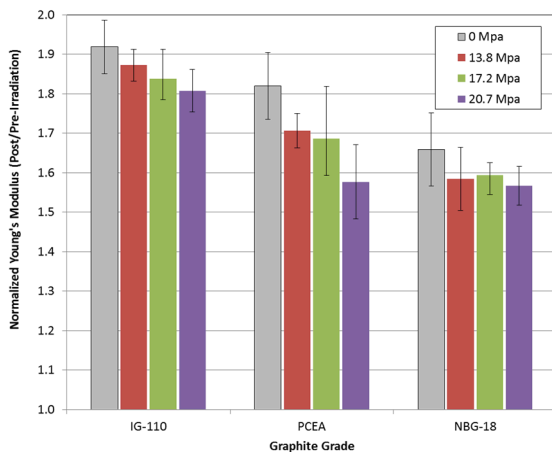


Figure 3: A comparison between different graphite grades of the increase in Young's modulus as a function of applied stress during irradiation.

During annealing, reduction in the irradiation induced high modulus begins to occur at temperatures above $\sim 700^\circ\text{C}$, Figure 4, and is nearly fully recovered to the original un-irradiated modulus by 2380°C . Due to the lack of dimensional recovery with annealing it is thought that few if any cracks or pores are recreated. This is consistent with the incomplete recovery of the modulus. Based on the full recovery of the thermal diffusivity (shown below) it is surmised that the atomic level defects are completely annealed out at a temperature of 2380°C , therefore consistent with the near full recovery of the elastic modulus. Only the

contribution of the original cracks and pores is missing from fully reestablishing the compliance of the graphite to the un-irradiated condition.

III.C. Electrical Resistivity

Electrical resistivity is used as a rapid, simple means for determining the isotropy or grain orientation of manufactured graphite. Changes in electrical resistivity due to irradiation can be used to ascertain the level of defects as well as the type of defects that develop at various irradiation temperatures [6].

Resistivity is measured following ASTM C 611-98. The measurement technique is commonly referred to as four-point probe. It consists of passing a known current through the sample and measuring voltage across the sample at known locations.

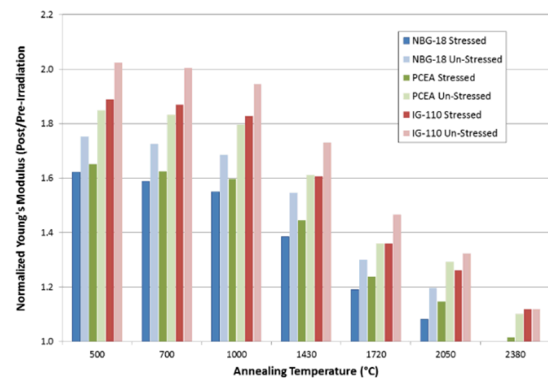


Figure 4: Recovery of elastic modulus in irradiated graphite as a function of the annealing temperature.

While there are significant similarities between all tested specimens, there are some differences between the different graphite grades. **Error! Reference source not found.** illustrates the effects on electrical resistivity from irradiation as a function of stress in the specimen during irradiation. The change in resistivity is normalized by the un-irradiated value and the error bars represent ± 1 standard deviation in the group of approximately 20 specimens. On average, resistivity changes for all graphite grades remained relatively constant across the increasing applied stress. It appears resistivity changes for unstressed specimens may be slightly higher than stressed specimens for all graphite grades, but the difference is small and within the one standard deviation error bars.

Still, the overall change in electrical resistivity for the three grades of graphite tested is significant. The extruded PCEA specimens demonstrated nearly a 300% increase in resistivity, while the IG-110 specimens exhibits the least change. As mentioned above, when graphite is exposed to fast neutron radiation, carbon atoms are knocked out of their equilibrium positions in the lattice structure to form a vacancy and interstitial pair (Frenkel pair). At

higher irradiation temperatures these simple defects grow into more complex formations of interstitial atoms and basal plane vacancies. Also, as the dose of neutrons builds, the complexity and number of defects formed increases. These defects decrease mobility of the electrons by acting as scattering sites and, the more complex defects, can even trap electrons. Together a significant increase in electrical resistivity is seen.

Thermal annealing of the irradiated graphite at high enough temperatures should increase the electrical conductivity by rearranging carbon atoms back to their lower energy states and when the annealing temperature is near the graphitization temperature, the basal plane hexagonal formation will be reformed that is efficient in electron transfer. Figure 6 shows the effect of annealing on the change in irradiation up to a temperature of 2380°C for both the stressed and unstressed specimens. Starting at 1000°C there is an obvious decline for all graphite grades and conditions. Both stressed and unstressed specimens decline at nearly the same rate. Although typically seen when annealing graphite that has been irradiated at lower temperatures than was done here, there is a slight increase in resistivity up to ~1000°C. This has been attributed to the changes in defect structure when vacancies become increasingly mobile and coalesce to produce effective electron traps that reduce the charge carrier density. [6,7,8]

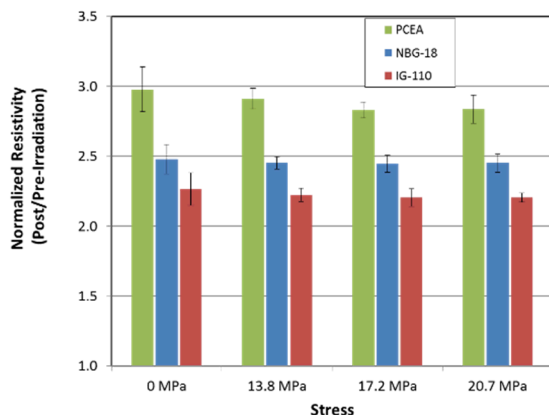


Figure 5: The change in electrical resistivity due to irradiation relative to the un-irradiated condition. 3 Three graphite types are shown as a function of stress during irradiation.

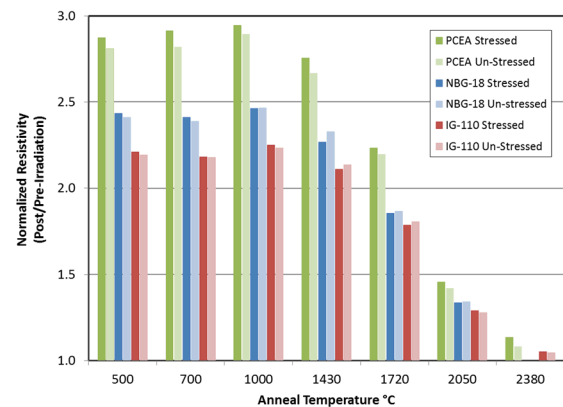


Figure 6: The effect of annealing temperature on electrical resistivity for three graphite grades, stressed at 20.7MPa and un-stressed.

III.D. Coefficient of Thermal Expansion

The coefficient of thermal expansion (CTE) defines how the physical size of an object changes with a change in temperature. Specifically, it measures the fractional change in size per degree change in temperature at a constant pressure. CTE is a key parameter for determining thermally induced stress states, volumetric changes, and irradiation creep rates within graphite reactor core components.

CTE is measured here in accordance with ASTM E228-06. This test method uses a push-rod dilatometer to determine the change in length of a graphite specimen relative to that of the holder as a function of increasing/decreasing temperature. The temperature is varied over the desired range at a slow constant heating or cooling rate. Using calibration to subtract the growth of instrument fixtures, the change in specimen length is recorded as a function of temperature. The mean CTE is calculated from the slope of a line drawn from the reference temperature, typically 20°C, and a specified temperature. This is performed for specific temperatures covered by the growth curve to produce mean CTE values. Mean CTE was calculated at successive 100°C increments over the temperature range of 100 to 500°C. The upper temperature limit of 500°C is set by the nominal irradiation temperature of 600°C to prevent the influence of annealing in the CTE data.

Error! Reference source not found. illustrates the irradiation induced CTE changes of the three graphite grades. The small-grained, iso-molded grade of IG-110 demonstrates the largest CTE increase while the larger grained NBG-18 and PCEA have less of an increase. It is important to note that each data point at the discrete material temperature is the average of approximately 20 specimens that cover the full temperature and dose range of the AGC-2 experiment capsule. Stress in the specimens makes a significant difference in increasing the

average CTE at all material temperatures up to 500°C. Also note that each of the stressed data points is an average of all 3 stress levels applied in the AGC experiment. Error bars represent ± 1 standard deviation from the mean.

The effect of stress on the percent change in CTE was investigated further in Figure 8. This data represents the increase in CTE as a function of the 3 distinct stress levels at a material temperature of 500°C. Error bars represent ± 1 standard deviation from the mean. The large CTE difference between stressed and unstressed specimens is immediately observed. As an example, an un-stressed specimen of PCEA had a $\sim 6\%$ increase in CTE, while the specimen compressively stressed at 20.7 MPa had an increase of $\sim 32\%$.

The increase in CTE in graphite irradiated up to turnaround was described by Sutton and Howard in 1962 and commonly seen in later publications [9,10]. In a polycrystalline graphite as much as 37% of the thermal expansion can be attributed to the expansion of the crystallites along the c-axis. In addition, when graphite is irradiated, some of the porosity and cracks that accommodate the crystallite expansion are closed up. With the addition of stress during irradiation the creep strain experienced in the graphite continues to densify the graphite and decrease the accommodation cracks and porosity which in turn results in the bulk thermal expansion being significantly higher.

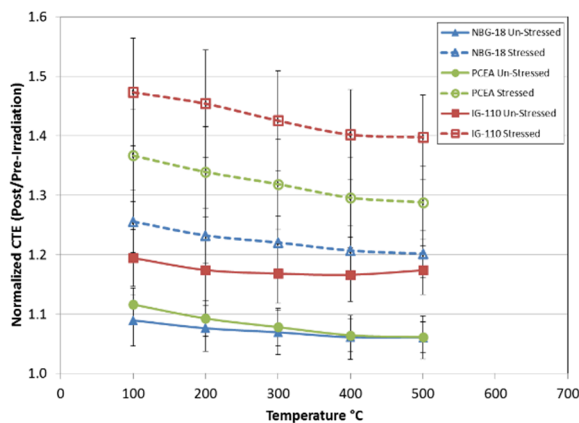


Figure 7: Normalized coefficient of thermal expansion for NBG-18, IG-110 and PCEA as a function of material temperature for both the irradiated and un-irradiated conditions.

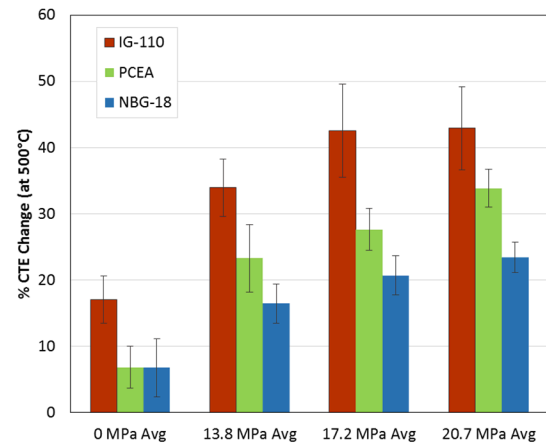


Figure 8: Percent change in CTE for the three graphite grades, comparing the effects of stress in the graphite during irradiation at a material temperature of 500°C.

What is unclear is the response of bulk CTE to thermal annealing. Figure 9 shows significant, but not full, recovery up to an annealing temperature of 2380°C. If the increase in CTE due to irradiation is predominately a function of densification during irradiation, the annealing process would need to form cracks and pores that would accommodate the expansion as in the un-irradiated material. If cracks and pores are forming, one would surmise that the graphite would also recover dimensionally. This is contradictory to Figure 2 (that shows little to no dimensional recovery) unless the cracks and pores are of a size and distribution that would accommodate thermal growth of the crystallites but not result in recovery of bulk dimensions. As the graphite is cycled thermally during the annealing experiment it is possible that differential thermal expansion due to varying crystallite orientation would cause micro cracking and at temperatures near the graphitization temperature, Mrozowski cracks will most certainly form.

III.E. Thermal Diffusivity

Thermal conductivity and diffusivity are the most important thermophysical material parameters for describing the heat transport properties of a graphite component. Thermal diffusivity is a measure of the rate of heat transfer in a material (i.e., how fast heat is transferred from the hot side to the cold side of a material). It is useful for ascertaining heat conduction through the graphite core for passive decay heat removal, calculations of thermal stresses, and modeling core physics in a graphite moderated design.

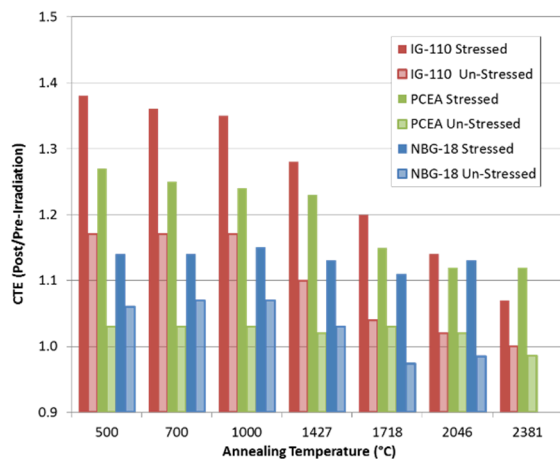


Figure 9: Normalized CTE for the three graphite grades as a function of annealing temperature and stress during irradiation.

The thermal diffusivity measurements were carried out in accordance with ASTM C714-17. This measurement is performed on small, thin, disk-shaped specimens. A pulsed laser is used to subject one surface of the specimen to a high-intensity, short-duration energy pulse. The energy of this pulse is absorbed on the front surface of the specimen and the resulting rise in rear-face temperature is recorded. Thermal diffusivity is calculated from the specimen thickness and the time required for the rear face temperature to reach 50% of its maximum value.

Thermal diffusivity is a strong function of the graphite temperature and is therefore measured as a function of material temperature, Figure 10. Because of the physical limitations necessary to conduct diffusivity measurements, i.e. a relatively thin specimen, the measurements were made on the piggyback specimens only and none of the piggyback specimens were subjected to an applied mechanical stress during irradiation. Therefore there are no data comparing the effects of different stress levels (and induced accelerated strains). With the exception of Figure 10, diffusivity was measured at successive 100°C increments over the temperature range of 100 to 500°C. The upper temperature limit of 500°C is set by the nominal irradiation temperature of 600°C to prevent the influence of annealing in the diffusivity data.

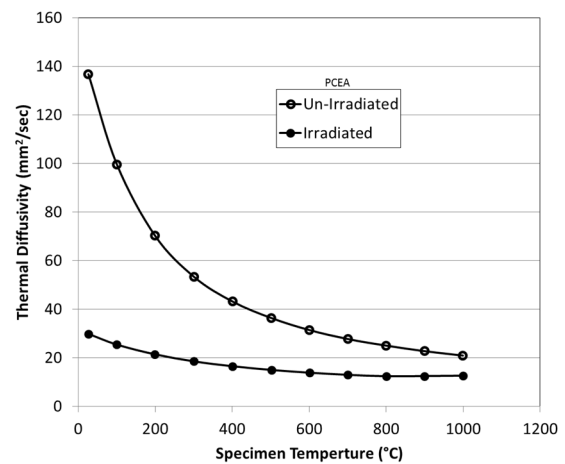


Figure 10: The behavior of thermal diffusivity as a function of the material temperature for irradiated and un-irradiated graphite.

Diffusivity in graphite is normally expected to gradually reduce as the material testing temperatures increase due to grain boundary and Umklapp scattering effects [11,12]. Grain boundary phonon scattering dominates thermal resistance at low temperatures but becomes insignificant above a few hundred degrees Celsius while the Umklapp scattering dominates at higher temperatures and defines the upper limit to the thermal conductivity for a “perfect crystalline” graphite. This gradual reduction due to phonon scattering effects is observed in both pre and post-irradiated data.

The reduction in diffusivity due to irradiation is commonly described as a result of phonon scattering from defects that form in the graphite lattice. Depending on the irradiation temperature these defects can range from single interstitial atoms and vacancies in the basal planes at low irradiation temperatures ($T_{irr} \leq 200^\circ\text{C}$) to more complex clusters of interstitials and vacancies that form due to their mobility at higher temperatures. In either case the phonon scattering is thought to be dominated by defects in the basal planes a-axis.

Error! Reference source not found. shows the ratio of average pre- and post-irradiation diffusivity for graphite grades IG-110, PCEA and NBG-18 as a function of measurement temperature. As with the other material property measurements, the change in thermal diffusivity was substantial. At a material temperature of 100°C the post irradiated diffusivity is approximately 25% of the un-irradiated value and at a material temperature of 500°C the post irradiation diffusivity is 40%. The error bars represent one standard deviation in the data, reflecting the different variables within the experiment, including irradiation temperature and dose.

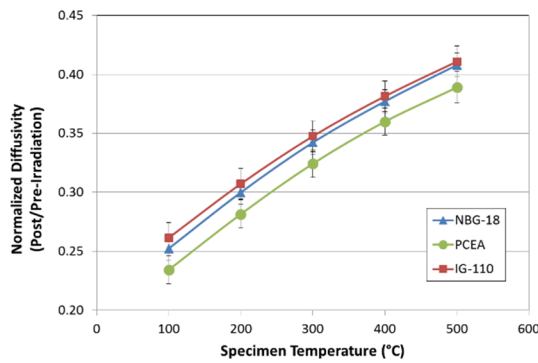


Figure 11: The effect of radiation damage on three different graphite grades as a function of the material test temperature.

In Figure 12, a small group of specimens from each of the three grades of graphite was selected with a narrow range of irradiation temperatures ($600 \pm 50^\circ\text{C}$) in order to examine the effect of irradiation dose. Their reduction in diffusivity is plotted as a function of irradiation dose at material test temperatures of 100°C and 500°C . Over the dose range of 2.0 to 4.5 all three grades trend to lower diffusivities as the dose is increased indicating the continued formation of phonon scattering defects. The rate of decrease is similar for both the low material temperature of 100°C that is dominated by grain boundary scattering and the higher Umklapp dominated material temperature of 500°C . This similar reduction in conductivity at the two temperatures would indicate that a similar mechanism is responsible for this reduction. The obvious being increased defect density in the basal planes.

The effects of annealing on the reduction of thermal diffusivity due to irradiation are seen in Figure 13. Two irradiation dose levels are represented. As seen previously, specimens at the higher dose have increased resistance to heat transfer. This trend continues consistently throughout the range of annealing temperatures. It is not until an annealing temperature of 1000°C that the energy threshold is met for the reduction of phonon scattering defects in the graphite. The rate of defect repair as a function of annealing temperature remains constant up to 2380°C at which point only the lower dose specimens have fully recovered their original values of thermal diffusivity.

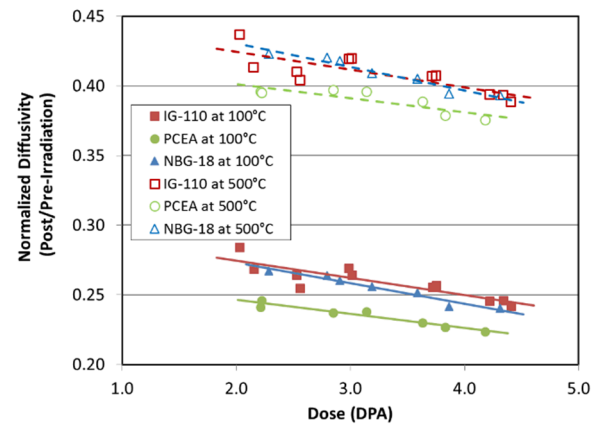


Figure 12: Reduction in thermal diffusivity at material test temperatures of 100°C and 500°C as a function of irradiation dose at an irradiation temperature of $600 \pm 50^\circ\text{C}$.

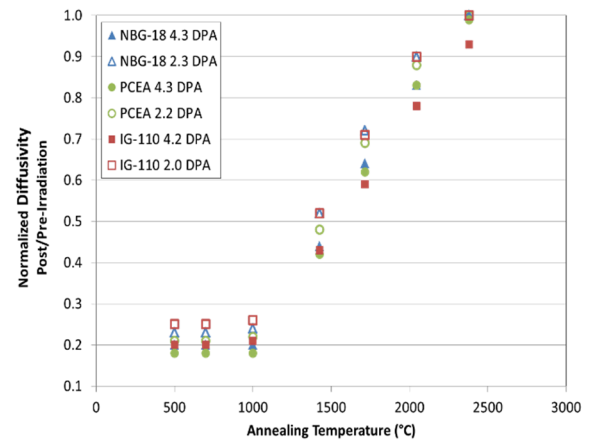


Figure 13: Thermal diffusivity recovery as a function of annealing temperature.

IV. Summary and Observations

This paper seeks to provide both the change in properties in nuclear grade graphite due to neutron irradiation and the recovery of those properties during thermal annealing. The properties investigated here for both irradiation damage and isothermal - isochronal annealing are: dimensional change, electrical resistivity, Young's modulus of elasticity, coefficient of thermal expansion and thermal diffusivity. These properties are investigated as a function of irradiation dose, temperature, stress and annealing temperature.

The change in specimen length for unstressed specimens falls in a narrow band between 0.75 and 1.0 percent. This small change drastically increases when the specimens are compressively stressed. The level of radiation induced creep is different for the three grades of graphite with PCEA graphite exhibiting a maximum deformation in length of over 3%. The annealed unstressed specimens showed no

dimensional recovery up to a temperature of 2380°C and the stressed specimens of IG-110 and PCEA showed only a very small amount of recovery starting at an annealing temperature of 1500°C. This lack of dimensional recovery has been attributed to only atomic level defects being repaired during the annealing process. It is possible that some level of Mrozowski and differential thermal expansion cracks formed at the upper annealing temperatures during the heating cycles that resulted in the slight dimensional recovery of IG-110 and PCEA. However, no micrographs were prepared to verify this.

The overall increase in Young's modulus is significant with that of IG-110 being almost double the un-irradiated condition. Modulus change for all graphite grades gradually decreases as the applied stress (and the resulting sustained creep strain) is increased. Stressed specimens exhibiting larger plastic strain are shown to experience less change in modulus than the unstressed control specimens exhibiting smaller plastic strain. During annealing, reduction in the irradiation induced higher modulus begins to occur at temperatures above ~700°C and nearly recovers to the original un-irradiated modulus by 2380°C. Due to the lack of dimensional recovery with annealing it is thought that few if any cracks or pores are recreated. This is consistent with the incomplete recovery of the modulus. Complete recovery would most likely require the regeneration of porosity or crack density that is on the order of that seen in the un-irradiated graphite.

The change in electrical resistivity for the three grades of graphite tested is significant. The extruded PCEA specimens demonstrated nearly a 300% increase in resistivity, while the IG-110 specimens changed the least at 225%. Resistivity changes for all graphite grades remained relatively constant with increasing applied stress. Reduction in resistivity during thermal annealing started at 1000°C for all graphite grades with both stressed and unstressed specimens declining at nearly the same rate.

All grades of graphite studied showed an increase in CTE between 5% and 20% due to irradiation with dose levels below that expected for turnaround. Stress during irradiation greatly increased the change in CTE to a range between ~20% (NBG-18) to 48% (IG-110). The increase for unstressed specimens is explained by the reduction in accommodation cracks and pores. This affect is only magnified by irradiation strain when the specimens are under a compressive stress. Thermal annealing begins to recover the un-irradiated CTE at temperatures above 500°C but it remained incomplete for stressed specimens even at 2380°C. There is little to no recovery of dimensional change during annealing, indicating that the annealing process is primarily at an atomic level and significant cracks and pores are not created. This is

in contrast to the near complete recovery of the CTE during annealing.

As with the other material properties of graphite, the change in thermal diffusivity was substantial. At a material temperature of 100°C the post irradiated diffusivity is approximately 25% of the un-irradiated value and at a material temperature of 500°C the post irradiation diffusivity is 40%. Over the dose range of 2.0 to 4.5 dpa at an irradiation temperature of $600 \pm 50^\circ\text{C}$, all three grades trend to lower diffusivities as the dose is increased indicating the continued formation of phonon scattering defects. The rate of decrease is similar for both the low material temperature of 100°C, which is dominated by grain boundary scattering, and the higher Umklapp scattering dominated material temperature of 500°C. This similar reduction in conductivity, as a function of irradiation dose, would indicate that a mechanism unrelated to Umklapp or grain boundary scattering is at play and is most likely an increase in irradiation induced defect densities in the basal planes. It is not until an annealing temperature of 1000°C that the energy threshold is met for the reduction of phonon scattering defects in the graphite. The rate of defect repair as a function of annealing temperature remains constant up to 2380°C at which point only the lower dose specimens have fully recovered their original values of thermal diffusivity.

REFERENCES

- [1] Kelly, B. T., "Physics of Graphite", Applied Science Publishers, London, 1981.
- [2] Tanabe, T., Radiation Damage of Graphite – Degradation of Material Parameters and Defect Structures, *Physica Scripta*, Vol. T64, 7-16, 1996.
- [3] Heggie, M.I., Suarez-Martinez, I., Davidson C., Haffenden G., Buckle, ruck and tuck: A proposed new model for the response of graphite in neutron irradiation, *Journal of Nuclear Materials*, 413 (2011) 150-155.
- [4] Swank, W. D., AGC-2 Graphite Specimen Postirradiation Characterization Plan," PLN-4657, Rev. 0, Idaho National Laboratory.
- [5] Kelly, B.T. and A.J.E. Foreman, The Theory of Irradiation Creep In Reactor Graphite – The Dislocation Pinning-Unpinning Model, *Carbon* 1974, Vol 12, 151-158.
- [6] Burchell, T.D., P.J. Pappano, J.P. Strizak, A study of the annealing behavior or neutron irradiated graphite, *Carbon* 49 (2011) 3-10.

- [7] Matsuo, H. Thermal Annealing effects on Electrical Resistivity of Reactor Grade Graphite Irradiated with Neutrons at 250°C and 350°C, *Journal of Nuclear Materials* 41 (1971) 235-237.
- [8] Kelly, B.T., D. Jones and A. James, Irradiation Damage to Pile Grade Graphite at 450°C, *Journal of Nuclear Materials* 7, No. 3 (1962) 279-291.
- [9] Sutton, A. L. and V. C. Howard, The Role of Porosity in the Accommodation of Thermal Expansion, *Journal of Nuclear Materials* 7, No. 1 (1962) 58-71.
- [10] Burtchell T.D. and W. P.I Eatherly, The Effects of Radiation Damage on the Properties of GraphNOL N3M, *Journal of Nuclear Materials* 179-181 (1991) 205-208.
- [11] B. Kelly, *Physics of Graphite*, Applied Science Publishers Ltd, London and New Jersey, 1981.
- [12] L. L. Snead and T. D. Burchell, "Thermal conductivity degradation of graphites due to neutron irradiation at low temperature," *Journal of Nuclear Materials* 224 (1995, 222-229.