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Radiation Effects on Materials
(TID-4500, 10th Ed.)

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DISTRIBUTION OF RADIATION DAMAGE IN GRAPHITE

By

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DISTRIBUTION OF RADIATION DAMAGE IN GRAPHITE

I. INTRODUCTION

The radiation damage effects occurring in graphite have been thoroughly studied.^(1, 2) As a result of interstitials, vacancies and other defects created by fast energetic neutrons and carbon atoms, the distance between layer planes increases. Electrical and thermal conductivity are greatly reduced, the crystallites are strained and disordered and large dimensional changes result. Graphite is gradually changed from a soft, lubricating, to a hard abrasive material.

Some of these effects are of practical importance in the design and operation of graphite moderated reactors. Dimensional changes resulting from radiation damage are of particular interest. The total dimensional change as a function of neutron exposure is known for a number of different types of graphite. Much less well known is the manner in which the damage effects are distributed, say, as measured by the ease with which they may be annealed. This suggests another method of studying the mechanism by which property changes occur. Damage distribution may be specified in several ways. Through thermal annealing experiments the amount of property annealed at a given temperature may be determined. It is also possible to estimate the activation energy for a given temperature-time annealing history and this may be used to characterize the damage annealed.

In this report the distribution of damage of several properties is presented. Annealing experiments of the type to be described are not suited for a detailed study of any part of the damage release curve. Instead, the purpose of these experiments was to determine, over a wide range of

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- (1) W. K. Woods, L. P. Bupp, and J. F. Fletcher, Proceedings of the International Conference on Peaceful Uses of the Atom, Paper 746 (1955).
(2) G. R. Hennig and J. E. Hove, *ibid*, Paper 751 (1955).

activation energy (or annealing temperature), the gross annealing characteristics of several properties. An effort has been made to relate changes in length of graphite samples with changes in C_o , the distance between alternate layer planes, and L_c , the crystallite size along the C_o axis. These and other studies are part of an effort to answer the question: How does reactor radiation cause dimensional changes in graphite?

II. SUMMARY AND CONCLUSIONS

A series of graphite samples with 30 C reactor irradiation exposure ranging from 400 - 5700 MD/T was thermally annealed. Changes in length, l , interlayer spacing, C_o , and crystallite size, L_c , were observed. Annealing was performed with temperature increases in 50 C - 150 C intervals and an approximate activation energy, E , was calculated for each time-temperature annealing schedule. Changes in properties with activation energy were compared through the exposure range.

C_o changed almost linearly with E up to about 100 kcal. All but the highest exposure sample (5700 MD/T) were almost back to their virgin values at $E = 140$ kcal/g-atom. A larger fraction of the C_o damage accumulated in the higher activation energies as the sample exposure was increased. This probably resulted from an accumulation of larger polyatomic carbon species between the layer planes.

L_c annealing began first in the less damaged samples. It was essentially complete at $E = 130$ for the 400 MD/T sample but had only begun in the 5700 MD/T sample. Like C_o damage, a greater fraction of L_c damage was found in the higher activation energies in the more highly damaged samples.

Length and C_o annealing were somewhat similar. Both were approximately linear in the low activation energy region. In all but the 5700 MD/T sample, length annealing was completed at about 145 kcal/g-atom. Thermal annealing of C_o damage allowed the crystallite to contract about 6 times faster than the length. It is likely that the crystallites contracted into void volumes so that only a fraction of the C_o contraction resulted in length contraction.

III. EXPERIMENTAL

A series of seven CSF* graphite samples having a wide range of exposures (400 - 5700 MD/T**) was chosen for the annealing experiments. Each sample was approximately four inches long by 0.426 inches in diameter. They were cut perpendicular to the long axis of a 4 inch x 4 inch x 4 foot bar. The cooled test-hole facilities in the Hanford reactors were used to irradiate the samples. Temperature during irradiation of these samples was $20\text{ C} \pm 10\text{ C}$. The uncertainty in the neutron exposures was approximately ± 15 per cent.

Graphite Annealing

Physical properties were measured prior to and following irradiation. Annealing of all samples in the series was carried out simultaneously and was begun at 90 C . Property measurements were repeated and the samples annealed at a higher temperature. Up to 250 C annealing was done in a conventional laboratory oven for periods of approximately one day. Above 250 C , 6 - 7 hour anneals were carried out in a graphite tube furnace. This consisted of a graphite resistance tube 4 feet long by 2-3/4 inches O. D. by 2 inches I. D. The furnace was heated electrically by passing current through the tube between large graphite electrodes 27 inches apart. It was insulated with thermax, fire brick and asbestos. The samples were placed inside graphite carriers containing four samples each and positioned at the center of the furnace. Temperatures were controlled and measured with chromel-alumel thermocouples in the range 300 C to 900 C , with Pt, Pt-Rh thermocouples in the range 1000 C - 1300 C , and with an optical pyrometer above 1300 C . Temperature variation in these ranges was $\pm 3\text{ C}$, $\pm 4\text{ C}$, and $\pm 20\text{ C}$ respectively. A slow stream of argon or nitrogen was passed through the furnace to prevent oxidation.

* CSF graphite is manufactured from Cleves coke and standard pitch and is purified by the F process.

** The unit of exposure, megawatt-days per ton, MD/T, is the amount of neutron irradiation received by the sample during the time required to generate one megawatt-day of fission energy in a ton of uranium nearest the sample.

The annealing schedule was determined from the amount of property change expected for a given time and temperature. A convenient time of approximately 7 hours was used in the tube furnace. This allowed a sufficiently long isothermal anneal to make very small, when compared with the total annealing done, that amount of annealing occurring while the temperature was increasing to the desired value and decreasing back to room temperature. With the annealing time thus established, the annealing temperature was chosen to give an amount of property change that could be accurately measured. At the same time the amount of annealing accomplished during a single run was kept to a minimum in order to better define the distribution of damage in the sample.

IV. RESULTS AND DISCUSSION

Figure 1 shows the annealing results on C_0 . X-ray measurements were made with a Norelco 180 degree x-ray diffractometer using Cu $K\alpha$ x-rays and Ni-Co monochromatizing Ross filters. C_0 values were calculated from the 002 reflection taken from the end of the samples. In order to improve the precision of these measurements, the samples were removed from the holder, remounted, and the 002 peak position re-determined. This was repeated several times and average values and the standard deviation from the average were calculated. These are represented on the annealing curve (Figure 1) by vertical lines of appropriate length. The uncertainty in C_0 is greater for the highly damaged samples where considerable line broadening has occurred.

The per cent property change has been plotted as a function of approximate activation energy. The activation energy used was calculated by $E = RT \ln Ct$

where

R	=	gas constant
T	=	annealing temperature in degrees Kelvin
t	=	annealing time
C	=	collisional constant

Vand⁽³⁾ introduced the concept of a large number of kinetic processes distributed in activation energy and found that for certain simplifications, the activation energy was given by the above equation. Primak⁽⁴⁾ has discussed the kinetics of processes distributed in activation energy and generalized the Vand treatment. These ideas have been applied to the thermal annealing kinetics of irradiated graphite⁽⁵⁾ for which a value for the collisional constant, $C = 7.5 \times 10^{13} \text{ sec}^{-1}$, was found to be satisfactory.

Physical property change vs activation energy was preferable in this work to make more comparable annealing runs in which annealing times were different. Accurate activation energies are not claimed since reaction order, the relation between number of defects annealed and resulting property change, true collisional constants, and other factors have not been thoroughly evaluated.

In Figure 1 it is seen that the per cent decrease in C_O is almost linear with exposure at the lower activation energies. A more detailed study of the kinetics of C_O annealing⁽⁵⁾ shows that for samples with 550 MD/T exposure, a rather large decrease in C_O occurs at about 33 kcal/g-atom*. The sensitivity of this method is insufficient to show that here. Significant

(3) V. Vand, Proc. Roy Soc (London), 55, 222 (1943).

(4) W. Primak, Phy Rev, 100, 1677 (1955).

(5) R. E. Nightingale, Thermal Annealing Kinetics of Interlayer Spacing Damage in Irradiated Graphite, HW-37406, June 21, 1955.

* Several properties show a pronounced peak in the damage release curves at ~ 33 kcal and this has often been referred to in the graphite literature as the "200 ° C peak" because, for convenient annealing periods, it anneals at about this temperature. This region has been studied in most detail and it is found that the peak becomes broader and much less pronounced in samples above 600 MD/T exposure.

departures from a linear curve occur, but it is not yet possible to associate these with specific annealing processes. It should also be noted that not only is C_0 damage greater for samples with greater neutron exposure, but also the damage accumulates at higher activation energies. For the highest exposure (5700 MD/T) an activation energy of 100 kcal/g-atom is necessary to anneal one-half of the C_0 damage, while, for the 400 MD/T exposure only 65 kcal/g-atom is required.

C_0 expansion results largely from interstitial carbon atoms trapped between the layer planes. Because the planes are bound by weak van der Waal forces, they may be forced apart quite easily to accommodate the interstitial atoms. Single interstitial carbon atoms would be quite mobile since no strong chemical bonds would likely be formed with the layer plane carbon atoms. As a result, in lightly damaged samples, C_0 damage is quite easily annealed. As damage accumulates, the probability increases that two carbon atoms will combine to form larger, less mobile C_2 molecules requiring greater activation energy for annealing. This mechanism by which less mobile groups of carbon atoms are formed, combined with a large number of different environments presented by vacancies or multi-vacancies in the carbon layer planes probably accounts for the distribution of activation energies which complicates the annealing process.

The effect of annealing on the average crystallite size along the C_0 axis, L_c , was estimated from the integral breadths of the 002 reflection using the method of Jones.⁽⁶⁾ The results are shown in Figure 2. In the early annealing runs, L_c was calculated from the 002 peaks of the sample ends. Because of the x-ray penetration effect and the ability to get better precision, it was decided to change to thin powders for this measurement. After the 600 C (E = 75 kcal) anneal this was done with much more reproducible L_c values. The average deviation of the data points from the curves was about 30 Å.

(6) F. W. Jones, Proc Roy Soc., 166A, 16 (1938).

Very little annealing to L_c was accomplished at activation energies less than 50 kcal. For the samples with up to 1200 MD/T exposure a considerable amount of annealing was done in the region $E = 50 - 100$, while little annealing occurred until $E > 100$ for the more highly damaged samples. L_c did not start to anneal in the 5700 MD/T sample until $E > 130$ were reached (~ 1300 C). Again, a greater fraction of the radiation damage is distributed in the higher activation energies in the more highly damaged samples.

For samples exposed at 30 C to less than about 800 MD/T (C_o less than $7.1 \text{ \AA}$) the lattice strains resulting from vacancies, interstitial atoms and other more complex defects probably account for most of the 002 peak broadening. However, as crystal damage accumulates broadening resulting from a decrease in crystallite size becomes more important and after about 1000 MD/T the broadening becomes much more rapid. Because of the similarity between peak shapes and positions of the 002 reflections from highly irradiated graphite and carbon or lamp blacks, the line broadening for samples exposed to 1700 MD/T and greater (C_o greater than $7.4 \text{ \AA}$) has been ascribed principally to the decrease in crystallite size. (7) In very highly damaged samples only a skeleton of the crystallite may finally be left and very high activation energies will be required to repair the damage.

Length changes vs activation energy are shown in Figure 3. Measurements were made with a micrometer at room temperature and are accurate to $\pm .0002$ inch. In general annealing begins immediately at the lowest activation energy. An exception to this is the 5700 MD/T sample where a small but significant amount of expansion occurs before contraction begins. Length annealing does not closely follow the L_c annealing, particularly in the highly damaged samples. For example, a considerable amount of length annealing was accomplished at 130 kcal/g-atom in the 5700 MD/T

(7) J. R. Townsend and C. A. Lund, X-ray Diffraction Peak Shapes from Irradiated Graphites, HW-25019, May 12, 1952.

sample, while practically no L_c annealing was done. C_o and length annealing are somewhat more similar in their annealing behavior, the per cent change in C_o being some 6 times as great as the per cent length change.

Length changes in graphite from radiation damage are not easy to understand. Perhaps the most satisfactory explanation for samples exposed around room temperature relates C_o and length changes. Thermal annealing of C_o expansion allows the crystallite to contract about 6 times faster than the length contraction. Many of the crystallites contract leaving voids or amorphous carbon volumes so that only a fraction of the C_o contraction results in length contraction. While this mechanism of length changes has probably been vastly oversimplified, it does account for the gross features. When graphite is exposed at higher temperatures a different mechanism must exist since no such simple relationship between C_o and length changes is found.

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FIGURE 1

Thermal Annealing of C_0 Changes for Graphite Irradiated at 30 C
Based on Initial $C_0 = 6.71 \text{ \AA}$

FIGURE 2

Thermal Annealing of L_c for Graphite Irradiated at 30 C

FIGURE 3

Thermal Annealing of Physical Length Changes for Graphite Irradiated at 30 C