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J. M. Davidson
E. M. Woodruff and
H. H. Yoshikawa

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HIGH TEMPERATURE RADIATION INDUCED

GRAPHITE CONTRACTION

J. M. Davidson
E. M. Woodruff
H. H. Yoshikawa

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HIGH TEMPERATURE RADIATION INDUCED GRAPHITE CONTRACTION

By

J. M. Davidson, E. M. Woodruff and H. H. Yoshikawa

Dimensional changes in graphite have been summarized in a recent Geneva Conference paper.⁽¹⁾ Subsequently, other data have been obtained which extend and clarify the contraction data. The purpose of this report is to present information concerning graphite contraction applicable to high temperature, graphite moderated reactors. The scope includes relevant data from all available sources, interpretation and extrapolations as can reasonably be made, and a discussion of the effects observed in terms of current radiation damage theory. Limits of accuracy and a discussion of experimental techniques are presented.

SUMMARY

High temperature radiation induced contraction of physical dimensions has been observed in graphite samples irradiated above 300° C. At 400 to 500° C four types of graphite, KC, SGBF, CSGBF and CSF, in order of decreasing structure development and anisotropy, display contractions at 5000 MWD/AT ranging from .00 per cent for KC to .06 per cent for CSF. However, the rate of contraction as a function of exposure is positive for all four types at 5000 MWD/AT. High temperature graphite irradiations at 600 to 1150° C are in progress at the Materials Testing Reactor and preliminary results indicate contractions ranging from .13 to 1.0 per cent for integrated fast fluxes (> 1 mev) of 1.9×10^{20} and 2.6×10^{20} respectively. An attempt has been made to relate these irradiations to Hanford equivalent damaging exposures.

Since this contraction, which is believed to result from a more efficient packing of the crystallites, is radiation induced, a model involving the production of vacancies and mobile interstitials by high energy knock-on carbon atoms is suggested in explanation for this contraction. From this model, possible criteria for a more dimensionally stable product are: increased graphitization, higher density, uniformly smaller pore size and larger grain size. High density, low porosity graphites have been procured and are being tested.

DISCUSSION

Hanford Test Hole Data. Figure 1 presents a complete account of graphite distortion at 300° C for reactor graphites to exposures in excess of 6000 MWD/AT.* These data are shown in this

*Exposures are given in terms of megawatt days per adjacent ton, abbreviated MWD/AT or sometimes, MD/AT. This unit is defined as the amount of reactor radiation received by the sample during the time required for the ton of uranium adjacent to the sample to generate one megawatt-day of fission energy. One MWD/AT is equivalent to approximately 3.9×10^{17} nvt thermal or 6.5×10^{17} nvt total. Neutron exposure has also been reported as "megawatt days per central ton" (MWD/CT) and "megawatt days per ton" (MWD/T). In early work it was customary to estimate exposure from the average central reactor power level and the results were expressed in units of MWD/CT. More recently exposures have been determined from the power generation of adjacent fuel channels and the results expressed in MWD/AT. Because MWD/T does not indicate the method of exposure determination, the use of this unit has been discontinued.

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Discussion of high temperature contraction to illustrate the effect of temperature. In KC graphite, which has the most highly developed structure and the highest degree of preferred orientation, differences resulting from orientation are magnified. CSF, like KC, is graphitized at 2800° C but the structure is not as fully developed—crystallites are smaller, less perfect and probably more poorly oriented by extrusion. TSCBF, graphitized at about 2450° C, has the least developed structure and the smallest degree of preferred orientation; hence, damage effects which are dependent upon crystal orientation are less distinct.

Though little has been done between 50 to 400° C, a limited amount of data at 100 to 200° C, shown in Figures 2 and 3, indicate that dimensional changes are highly temperature dependent in this range. Only one experiment at 335° C has been performed in the range 200 to 400° C and it indicates that CSF is dimensionally stable to 1500 MWD/AT.⁽²⁾

High temperature contraction was first observed in samples irradiated above 300° C. Figure 4 shows dimensional changes in CSF graphite in the temperature range 400 to 500° C, to the highest available exposures and represents a composite of Hanford experience in this temperature range. It should be understood that the temperature was not controlled during these irradiations and is believed to have varied between 400° C and 500° C. For convenience in assessing the precision, limits of error which represent plus and minus one standard deviation of the mean have been added to the originally published⁽¹⁾ curves. Each point has been rechecked and new points added as they became available. A further check into the history of the samples revealed that the lower curve was obtained from parallel samples of Bar 73. This bar does not seem to be typical of CSF graphite and for this reason too much significance should not be placed upon the fact that these samples seem to contract at a higher rate. The parallel contraction rate of other more typical CSF samples does not appear to differ significantly from the transverse rate.

The effect of different cokes and manufacturing treatments on high temperature contraction is shown in Figure 5. KC graphite shows the least transverse distortion and also the greatest anisotropy. This is consistent with the hypothesis of graphite contraction which will be developed later.

Recent experience during thermal expansion measurements has indicated that the preparation of standard graphite samples (.426" diameter, 4" length cylinders) introduced a compression set which, upon annealing at 600° C, gave rise to a small positive length change. Although experiments to confirm that the annealing of a compression set is responsible for the initial expansion shown in Figures 4 and 5 have not been completed, there is a strong presumption that this may be the case and, hence, the details of the initial portion of these curves should be considered with some reservations.

From the data shown in Figures 4 and 5, it is apparent that, with the possible exception of CSF material, contraction is less in the transverse orientation. Differences in rates appear to be a function of graphite coke and manufacturing process, the latter concerned principally with the graphitizing temperature. Figure 6, which is self explanatory, shows the effect on contraction caused by large variations in graphitization temperature.

MTR High Temperature Irradiations. Irradiation of graphite has been performed in the temperature range 600 to 1050° C in the MTR L-42 position. These irradiation temperatures were carefully controlled and accurate flux measurements were made. Table I shows the results obtained in the limited number of GEH-9 irradiations conducted to date. The GEH-9-5 flux was calculated from flux traverses of L-42 while GEH-9-6 contained individual monitors at each sample position for cobalt-cadmium ratio, fast and thermal flux. It is recognized that flux spectrum differences, particularly in the resonance and fast region, cause differences in radiation damage to graphite and, as a result, the data are difficult to correlate to conditions existing in graphite moderated reactors.

Two equivalent HAPD exposure estimates, a minimum and a maximum, are given for the samples where possible. The first column represents a neutron count and may be considered the lowest applicable exposure. The correspondence to MWD/AT is based on 6.46×10^{17} nvt (total) being equivalent to one MWD/AT.⁽¹⁾ The second column is the preliminary best estimate of the damage equivalence due to spectral differences between Hanford test hole and MTR L-42. This equivalence is based on a number of graphite samples exposed in the MTR and compared, through the use of electrical resistivity, x-ray and thermal conductivity changes, to Hanford experience. An empirical relationship

$$\text{MTR MWD} = \frac{(K) \text{ MWD/AT}}{\rho_{\text{fast}}}$$

was developed and the value, K, (variable, depending on the location in the reactor) was determined. For the MTR VH-2 position the constant was determined to be 8×10^{12} and because of this position's spectral similarity with L-42, it is the value used here.

Some justification for doing this is based upon the following reasoning. It is known that graphite contraction is radiation induced. The effect requires that high energy particles transmit to the graphite lattice sufficient energy for times long enough for diffusion and re-arrangement of atoms or groups of atoms to occur. At low temperatures, motion is more restricted and the end result of these same damaging neutrons is the accumulation of atoms between layer planes which expand as much as 15 per cent. Although expansion into voids or non-crystalline areas reduces the expansion of gross dimensions of a sample that would otherwise result, some gross expansion is observed (see Figure 1). In the second method of correlating Hanford and MTR high temperature data, it is assumed that the contraction results from high energy transfer processes and is proportional to the damage produced by high energy transfer processes at low temperature. This second method probably results in a high estimate of the equivalent Hanford exposure. Both methods should be used with the understanding that there is lack of knowledge regarding damage effects of spectral differences and/or intensities.

The standard deviation from the average of repetitive measurements on the samples is $\pm .02$ per cent. Although the precision of these measurements is good, it is important to consider the possibility that in the remote handling of samples, the edges could have been damaged resulting in a misleadingly large contraction. GEH-9 samples measure an inch across the face and it may readily be calculated, for example, that the loss of only one thousandth of an inch on the edge would result in an apparent one-tenth per cent contraction. Every effort has been made to prevent scuffing on the samples and it seems unlikely that this could be the source of the dimensional changes. Future GEH-9 samples will incorporate scribed platinum reference pins and the pin spacing measurements will provide an intercheck for the edge to edge measurements.

A Possible Interpretation of Graphite Contraction. A model, which yields consistent explanations for a number of phenomena at 300°C , can be constructed on the basis of the production of interstitials and vacancies by the high energy knock-on carbon atoms. From the nature of the inter-atomic forces in the graphite structure, the interstitials will predominately cause an expansion in the direction of the c axis. Vacancies have less effect on the spacing in the a direction, but may cause a puckering and contraction of the planes due to the relaxation of the lattice around a vacancy. As the particles are more highly oriented in the extrusion process one notes a more rapid expansion in the direction transverse to the extrusion direction. This more rapid expansion in one direction is accompanied by a more rapid contraction in the longitudinal direction. Such behavior is expected in this model since increasing orientation would increase the number of grains expanding in the transverse direction while simultaneously decreasing the number contracting in that direction; similarly the parallel direction would include a larger number of contracting grains accompanied by a smaller number of expanding grains.

The reduction in radiation damage at higher temperatures can be understood. An increase in temperature increases the mobility of the interstitials and facilitates recombination with

vacancies or diffusion to free grain surfaces. Because of this enhanced recombination probability, the rates of parallel contraction and transverse expansion are reduced.

Contraction of perpendicular samples above 300° C might, at first, be thought due to a further development of the graphite structure. However, changes in the C_0 spacing and apparent crystallite size, parameters often used to measure the degree of development of graphitic carbon, are in disagreement with this idea. Figure 7 shows that the C_0 distance increases and the apparent crystallite size decreases in both the C_0 and A_0 directions. The contraction apparently results from a more efficient packing of the crystallites. Thermal cycling experiments in the laboratory have not accomplished any dimensional changes in CSF material, and it appears that contraction occurs only in the presence of reactor irradiation.

The collision of fast displaced carbon atoms with lattice atoms dissipates a large amount of energy over a small volume and may supply the activation energy for the diffusion of many atoms in localized volumes of the crystallite. Crystallites which are snagged at edges and corners during the development of their structure may be freed by this radiation induced diffusion. In this way the stresses frozen-in during fabrication can be relieved by irradiation at high temperature and result in an increase in density.

Criteria for Dimensional Stability in Graphite. A series of experiments most relevant to this problem were reported in Reference (3). Pertinent data are shown in Figure 6. For 400 to 500° C irradiation up to 1000 MWD/AT, it appeared that greater graphitization would yield a more dimensionally stable product if all other factors were kept constant. However, it was also clearly shown that greater graphitization in itself was not a sufficient condition for dimensional stability.

On volumetric grounds, it would be expected that more densely packed material would ultimately display less contraction than less dense material. Commercial graphites are now available with densities of 1.90 to 2.0 gm/cm³. This is to be compared with the graphites currently in use which have a density of 1.65 gm/cm³. Since the theoretical density of graphite is 2.26 gm/cm³, this implies a 50 per cent reduction in the void volume.

If the hypothesis is correct that radiation induced processes result in diffusion of atoms which relieves frozen-in stresses and allows the crystallites to pack more efficiently, then a decrease in the average pore size should take place. Preliminary studies(4) indicate that this does occur. In order to reduce the amount of diffusion, it would be preferable to use material with larger grain size which would present a smaller surface to volume ratio. However, the coke mix should have such a distribution of particle sizes as to promote maximum packing which would reduce the average pore size. This decrease in pore volume should tend to reduce the amount of contraction if the mechanism of fracture and collapse of particles into pores is of importance in the contraction.

In summary, there appear to be several factors, interrelated and interdependent, which should tend to reduce the amount of contraction in graphite. These are increased graphitization, increased density, smaller pore size and larger particle size. Most of these criteria are fulfilled by the low permeability, high density graphites which have recently been developed by the National Carbon Company and the Graphite Specialties Corporation. Thus graphites of this type offer the best immediate hope for improvement in the dimensional stability of reactor graphite. Development work leading to improved graphites is being conducted by all major graphite manufacturers. The high temperature radiation behavior is now being determined on some of these materials in the Hanford reactors and others will be tested as they are developed. As irradiation facilities planned for the MTR and ETR come into use, they will be tested at 600 to 1100° C.

TABLE I

MTR GEH-9 HIGH TEMPERATURE GRAPHITE IRRADIATIONS

Sample Code a	Graphite Type & Density, gm/cm ²	Irradiation Temp., °C	Integrated Flux (nvt x 10 ⁻²⁰)					Exposure, MWD/AT		Pct Length Change	
			calculated b		measured c			minimum ^d	maximum ^e	optical	micro-meter
			0-115 ev	> 1mev	< .4ev	.4ev-1mev	> 1 mev				
5-3-3-4	TSGBF 1.6	750	14	1.4				(3125) ^f	7300	-.06	-.03
4-16-4-3	TSGBF 1.6	750est	12	1.8				(2320) ^f	8420	-.06	
6-5-2-4	TSGBF 1.6	750	11	1.0	5.6	9.6	.53	2410	5600	-.32	
5-4-4-4	TSGBF 1.6	975	18	2.6				(5600) ^f	15300	-1.11	-.87
6-6-3-4	TSGBF 1.6	975	12	1.9	9	16	1.0	4000	11300	-.13	
6-7-4-4	TSGBF 1.6	1050	14	2	9	16	1.0	4000	11700	-.49	
5-21-2-5	TSGBF 1.6	750		.4					2200	-.07	-.05
6-1-1-6	TSF 1.4	750		.3	2.3	1.7	.17	650	1630	+.02	

- a. Sample number for reference.
b. From MTR integrated MWD, and prior flux traverse of L-42.
c. From monitors at samples.
d. Based on 6.5×10^{17} nvt total/MWD/AT.
e. Based on damage correlating factor.
f. Estimated from cross reference with measured positions.

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- (4) Woodley, R. E., A Preliminary Study of the Effect of Neutron Irradiation and Oxidation at Moderate Temperature on the Structural Characteristics of CSF Graphite, HW-52375, (1957).

FIGURE 1

Physical Distortion of Reactor Grade Graphite Irradiated at 30°C

FIGURE 2
Temperature Dependence of Physical Distortion of CSF Graphite
(Perpendicular)

FIGURE 3

Length Change Isotherms of CSF Graphite (Perpendicular)

FIGURE 4
Physical Distortion of CSF Graphite Irradiated at 400-500°C

FIGURE 5

Physical Distortion of Reactor Grade Graphites Irradiated at 400-500°C

FIGURE 6

Effect of Graphitization Temperature on Contraction of Texas Coke Graphites Irradiated at 400-500°C

FIGURE 7

Crystallite Changes in CSF Graphite Irradiated at 400-500°C