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RADIATION EFFECTS IN CARBONS AND GRAPHITES⁺

H.H. Yoshikawa, E.M. Woodruff, J.M. Davidson, J.W. Helm, and R.E. Nightingale

INTRODUCTION

The results of both low and high temperature irradiations on graphite were presented in previous papers at the 1955 and 1958 Geneva Conferences^[1,2] and at the Biennial Carbon Conferences in the United States^[3,4,5]. In this paper, radiation effects up to a maximum exposure of 8.6×10^{21} nvt ($E > 0.18$ Mev), and up to a maximum temperature of 1200 C are presented. The data include high temperature radiation effects on a variety of carbons and graphites. Based on these data, a phenomenological theory for high temperature radiation effects in graphite has been developed.

The high temperature radiation-induced contraction in graphite is of concern in the design and operation of high temperature graphite-moderated reactors. This dimensional instability can affect the alignment of reactor components and cause operational problems. Another potential hazard is the cracking of graphite in regions with appreciable flux gradients because of the differential contraction in portions of a graphite bar.

SUMMARY AND CONCLUSIONS

Two simultaneous effects occur during the irradiation of polycrystalline graphite which account for the observed dimensional instability. The first is a disordering of the crystallites which results in an expansion parallel to the c axis and a contraction parallel to the a axis. This process is highly

⁺ For presentation at the Symposium on Radiation Damage in Solids and Reactor Materials, Venice, May 7-11, 1962. The work was sponsored by the U.S. Atomic Energy Commission under Contract AT-(4501)-1350.

temperature dependent and at room temperature is the principal effect. The second effect is a non-annealable contraction, which acts primarily in the transverse direction in anisotropic nuclear graphite, and seems to occur primarily in the non-graphitic part of the polycrystalline structure.

DIMENSIONAL CHANGES IN NUCLEAR GRAPHITES

Irradiations at 30 C produced the dimensional changes shown in Fig. 1. These results are an extension to higher exposures of previously published work.^[3] The transverse expansion of KC graphite[‡] appears to approach saturation near 6 per cent, but no apparent trend toward saturation of parallel contraction is observed. Transverse expansion is caused by the accumulation of interstitials within the lattice, which forces the graphite layers apart. It has been suggested that parallel contraction is caused by buckling of the planes around the interstitials and by relaxation of the lattice around vacancies.

When graphite is irradiated above 300 C, the relation between length change and exposure is complex. In the transverse direction, an initial expansion is generally observed to an exposure* of at least 2000 Mwd/At. At higher exposures a contraction is observed as seen in Fig. 2. In the parallel direction, a small initial expansion is observed below 2000 Mwd/At. Contraction is observed at higher exposures. The contraction in both directions is linear to an exposure of at least 12,000 Mwd/At, the maximum exposure for these samples.

Maximum exposures of approximately 8.7×10^{21} nvt equivalent to approximately 58,000 Mwd/At, have been achieved during high-temperature irradiations

[‡] Transverse and parallel orientation refer to directions transverse and parallel to the predominant layer-plane orientation. The properties of KC graphite and other graphite grades are given in Ref. 3.

* One Mwd/At for these irradiations is equal to 1.3×10^{17} nvt. Neutron exposures given in this paper are for neutrons with energy greater than 0.18 Mev.

in the General Electric Test Reactor. CSF and EGCR (Experimental Gas Cooled Reactor) graphites were included in these tests. During these irradiations at 475 to 800 C, the graphites contracted at approximately a linear rate as shown in Fig. 3 through 6.

The above results, in conjunction with data^[4] obtained to a maximum exposure of 3.2×10^{21} nvt at 800 to 1200 C indicate a minimum in contraction rate near 800 C. At 800 C the contraction after the maximum exposure of 8.7×10^{21} nvt was 0.55 per cent transverse to the extrusion axis of the graphite bar and 1.2 per cent parallel to the extrusion axis for CSF, and 0.30 per cent transverse and 1.2 per cent parallel for EGCR graphite.

The length changes in Fig. 1 through 6 were obtained on samples with a cross sectional area of 0.14 in.² or less and a length of 4 in. Measurements have also been made of radiation-induced dimensional changes of bars 4 x 4 x 24 in., which are the full cross section but half the length of Hanford moderator bars. The contraction of the bars at 18,600 Mwd/At is more than twice that predicted from small-sample results. Extrapolation of the transverse CSGBF data in Fig. 2 to 18,600 Mwd/At yields a contraction of 0.21 per cent, whereas the observed contraction is 0.57 per cent for the full bar. The reason for this difference is not known. The comparatively low value for the small samples could be caused by the absence of stresses which may accumulate in large bars during irradiation. More data are needed to test this possibility.

RADIATION EFFECTS IN EXPERIMENTAL GRAPHITES

The contraction rate of graphite in the transverse direction depends upon the graphitization temperature, the graphitizability of the coke, the extent of

grain orientation, and probably upon other factors which have not been investigated. Some of the factors responsible for the different contraction rates are shown in Fig. 2. For example, KC graphite, which has the lowest transverse contraction rate, was manufactured from a well-graphitizing coke and has a high degree of preferred orientation. The SGBF and CSGBF materials were not fully graphitized and are not as highly oriented as KC.

A number of experimental graphites are being tested at Hanford in an attempt to identify the factors responsible for radiation-induced contraction at high temperatures. The effect of graphitization temperature on the contraction rate is shown in Fig. 7. The results on this series of graphites have been published previously^[5] to an exposure of 4000 Mwd/At. It will be noted that at the high exposures the graphites that were processed at the lower temperatures have begun to contract at a significantly lower rate. This appears to be the first indication of saturation of contraction in carbons from high temperature radiation.

Additional evidence that carbons heat-treated below graphitization temperatures have high contraction rates comes from the irradiation of a lampblack - binder mixture heat treated to 1400 C. After an exposure of 1370 Mwd/At at 600 C, this material contracted 0.6 per cent. Similar samples heat-treated to 3000 C contracted only 0.2 per cent. In an effort to trace the cause of this difference, samples of unirradiated lampblack that had been heat-treated to 1400 C were heated to 3000 C. An average length change of -1.7 per cent was observed. It therefore appears that the higher contraction of the 1400 C lampblack may be partially due to radiation activation of processes which are normally thermally activated between 1400 and 3000 C.

Lampblack heat-treated to 1400 C have been irradiated to higher equivalent exposures in the Engineering Test Reactor at a temperature estimated to be between 600 and 800 C. After an exposure equivalent to approximately 6000 Mwd/At, the sample had contracted 2.2 per cent in the transverse orientation and 2.7 per cent in the parallel orientation. This is equivalent to a volume contraction of 7 per cent, roughly one-fourth the volume contraction necessary to attain theoretical density.

The radiation-induced contraction of several low-permeability graphites has been compared with CSF graphite. Table I gives the data from these tests. The irradiations were performed in non-instrumented capsules in the Materials Testing Reactor at a temperature estimated to be between 600 and 800 C.

B-10 and B-12 were both manufactured with lampblack added to the original mix. It is interesting to note that the ratio of contraction of these two graphites, 0.75, is nearly equal to the ratio of lampblack content, 0.7. The greater contraction noted in B-60 is attributed mainly to the low graphitization temperature of 2300 C compared to 2700 C for the other grades.

ANNEALING OF HIGH TEMPERATURE DAMAGE

During the annealing of irradiated nuclear graphites, it was noted^[5] that the transverse contraction did not anneal but that the parallel contraction annealed almost completely upon heating the samples to their original graphitization temperature of 2800 C. Therefore, it was surmised that there exists two separate components to high-temperature contraction. It has also been observed that lampblack samples which had been heat-treated to 3000 C and

irradiated at 600 C recovered approximately 20 per cent of the contraction when reheated to 3000 C, (see Table II). This observation tends to confirm the surmise that there exists an annealable and an unannealable component to high-temperature contraction.

DISCUSSION

In nuclear graphites an increase in c lattice spacing is generally noted even after high-temperature irradiation. This crystallite expansion implies that even during high-temperature irradiation there exists a vestige of low-temperature damage which is annealable. As in the case of low-temperature damage, this annealable component of damage causes a slight expansion in the transverse direction and a contraction in the parallel direction.

A clue as to the origin of the unannealable component of damage is obtained from the annealing results on the lampblack-based graphites. Lampblack does not graphitize fully even when heated to 3000 C. As previously noted, 80 per cent of the contraction does not anneal upon re-heating to 3000 C. Therefore, non-graphitic carbon could be the principal source of unannealable contraction. The effect of processing temperature can be explained since non-graphitic carbon would be more prevalent at lower processing temperature, and hence a higher contraction rate would be expected.

The binder, coke filler, and impregnant all probably contribute to the total of non-graphitic material in artificial graphite. The binder and impregnant are prevented from more complete graphitization during high-temperature treatment by the presence of excessive nucleation sites on the

surface of the filler particles, or by the high degree of mismatch in the layer plane orientation between the filler and the binder. The filler particles also contribute to the amount of non-graphitic material, as indicated by the sensitivity of contraction to the type of coke. Since the coke particles are not single crystals of graphite, they contain many grain boundary regions where the carbon is poorly organized.

The unannealable contraction acts primarily in the transverse direction for two reasons. First, the filler particles are oriented so that a larger number of binder layers occur in the transverse direction. In addition, there is an internal orientation within the coke particles which causes a larger number of grain boundaries to occur in the c crystallite direction.

On the atomic level, there is little direct evidence of the mechanism by which radiation could cause poorly organized regions of carbon atoms to densify. However, it is known that graphitization will cause an increase in density of carbon, and it seems reasonable that radiation causes an atomic rearrangement in poorly organized regions with an increase in density analogous to that resulting from graphitization. Thermal and displacement spikes caused by radiation may supply the necessary activation energy for a graphitization-like process.^[2] If this is the case, the non-annealable contraction should be relatively independent of temperature. It is interesting that graphites produced from poorly graphitizing sugar coke have been observed^[6] to contract during irradiation at 30 C.

Other mechanisms may be of significance at the atomic level. Because of the anisotropy of the a axis and c axis coefficients of thermal expansion,

internal stresses accumulate in graphite during cooling from graphitization temperature. Microscopic stress fields would be more numerous in disordered regions. The stress could be relaxed during high temperature irradiation by the migration on interstitials and vacancies. Such processes will cause local migration of mass.

Stacking-fault loops, resulting from the collapse around vacancy agglomerates, have been detected in graphite by electron microscopy.^[7] There is evidence for preferential condensation of these 'vacancy loops' at dislocations.^[8] If such processes occur in disordered regions during irradiation, a non-annealable dimensional change would result.

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TABLE I - High Temperature Radiation-Induced Length Changes in Low-Permeability Graphites

<u>Graphite</u>	<u>Transverse change, %</u>		<u>Parallel change, %</u>	
	<u>0.79×10^{21} nvt</u>	<u>1.5×10^{21} nvt</u>	<u>1.5×10^{21} nvt</u>	<u>2.2×10^{21} nvt</u>
CSF	-0.064	-0.233	-0.233	-0.623
B-10	-0.127	-0.311	-0.327	-0.730
B-12	-0.171	-0.429	-0.436	-0.942
B-60	-0.397	-0.711	-0.645	-1.270

TABLE II - Annealing of Length Changes in Lampblack Graphite Irradiated at 600° C

<u>Sample</u>	<u>Exposure, nvt x 10⁻²⁰</u>	<u>Length change induced by radiation, in.</u>	<u>Length change on annealing to 3000 C, in.</u>	<u>Recovery, %</u>
2	0.64	-0.068	0.012	18
4	1.2	-0.094	0.021	21
6	1.6	-0.128	0.029	23

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FIGURE 1: RADIATION-INDUCED DIMENSIONAL CHANGES OF NUCLEAR GRAPHITE AT ~30 C

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FIGURE 2: RADIATION-INDUCED CHANGES IN NUCLEAR GRAPHITE AT ~500 C

FIGURE 3: RADIATION-INDUCED CONTRACTION OF CSF (L) GRAPHITE

FIGURE 4: RADIATION-INDUCED CONTRACTION OF CSF (II) GRAPHITE

FIGURE 5: RADIATION-INDUCED CONTRACTION OF EGCR (1) GRAPHITE

FIGURE 6: RADIATION-INDUCED CONTRACTION OF EGCR (II) GRAPHITE

FIGURE 7: RADIATION-INDUCED DIMENSIONAL CHANGES AT ABOUT 500 C AS A FUNCTION OF HEAT-TREATMENT TEMPERATURE. ALL MEASUREMENTS TRANSVERSE TO THE EXTRUSION AXIS