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RADIATION-EFFECTS IN GRAPHITE
AT HIGH TEMPERATURES

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1. INTRODUCTION

Graphite continues to be of interest as a moderator material for nuclear reactors.⁽¹⁾ In some reactors, such as the High Temperature Gas - Cooled Reactor and the Hallam Nuclear Power Facility, graphite serves as a structural component and in others, such as Enrico Fermi and EBR-II, it serves as part of the reactor shielding. Graphite is an attractive moderator material because of its low atomic mass, low absorption cross section, and relatively low cost.

One of the problems in the use of graphite as a moderator is the radiation-induced dimensional changes which occur in the reactor. There are considerable data available on the dimensional stability of graphite in the irradiation temperature range of 450 to 800 C.⁽²⁻⁴⁾ Considerably more data have been obtained in this temperature range since data were presented previously⁽⁵⁾ and neutron exposures have been extended 80 percent to a maximum of 16×10^{21} nvt.* Data in the temperature range of 800 - 1200 C are limited⁽⁶⁻⁹⁾ even though this range is of particular interest to operators and designers of graphite-moderated reactors. Irradiations are being conducted in this temperature range and data are available to a maximum exposure of 4.5×10^{21} nvt. Data are also available for several types of raw-coke and isotropic graphites over the temperature range of 500 - 1150 C. These materials are of special interest since they appear to

*All neutron exposures refer to the number of neutrons with energies greater than 0.18 MeV.

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be potentially more stable than nuclear-grade graphites.

2. EXPERIMENTAL

Materials tested included transverse and longitudinal samples of CSF, TSGBF, KC, EGCR, TSX, and several types of raw-coke or isotropic graphites. All the graphites are described in Table I. The 400 - 800 C data are obtained from the long-term irradiations of EGCR graphite in the GETR,⁽²⁾ while the 800 to 1200 C data are obtained from a high-temperature test in the ETR⁽¹⁰⁾. The basic instrumented capsule is the same in both cases and has been described previously.^(2,3,6) Data on comparative dimensional behavior of the raw-coke and isotropic graphites were obtained from simple non-instrumented "hot" capsules.^(8,11) Neutron exposures are based on the foils of nickel and iron contained in each capsule. The foil activations are used in conjunction with the activation cross sections and neutron spectra calculations to determine the exposure.^(2,3,10) The neutron exposures for the long-term 400 - 800 C data are now based on foils rather than the physics calculation used previously.⁽⁶⁾ The previous exposures⁽⁵⁾ were reduced by about 35 percent because of this change.

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TABLE I
GRAPHITE DESCRIPTION

BNW Designation	BNW Block Numbers	Coke Source and Type	Block Size in.	Remarks (1)
CSF ⁽²⁾	142	Cleves (conventional type)	4 x 4 x 50	Reactor grade; F-purified at 2700 density: 1.66 g/cm ³
TSGBF ⁽²⁾	125	Texas - Lockport (conventional type)	3-3/4 x 3-3/4 x 48	Reactor grade; graphitized and F-purified in one step at 2450 C; density: 1.65 g/cm ³
KC ⁽²⁾	187	Kendal (needle type)	3-3/4 x 3-3/4 x 48	Reactor grade: AGOT; thermally purified, very well graphitized; density: 1.7 g/cm ³
EGCR ⁽²⁾	NC8	Continental-Lake Charles (needle type)	17-1/2 x 17-1/2	Reactor grade: AGOT, EGCR graphite density: 1.72 g/cm ³
EGCR Proto-type ⁽²⁾	NC7-33	Continental-Lake Charles (needle type)	16-3/8 x 16-3/8	Electrode stock; similar to graphite used for EGCR; density 1.70 g/cm ³ .
TSX ⁽²⁾	185	Continental-Lake Charles (needle type)	6 x 6 x 48	Reactor grade; graphitized at 3000C; very anisotropic (CTE _⊥ /CTE = 4.7); density: 1.71 g/cm ³
Raw-coke ⁽³⁾ Base Stock	63-16	Texas - Lockport (raw coke)	6.5 dia. x 6	Experimental grade; volatile content of raw coke: 12%; coal tar derivative binder; amount of binder carbon in baked product: negligible; graphitized at 2500 C; very isotropic (CTE _⊥ /CTE = 1.02); density: 1.72 g/cm ³
Raw-coke ⁽³⁾ 1-impreg.	63-17	Texas- Lockport (raw coke)	4.1 dia. x 6	Experimental grade; same base stock as 63-16 with one coal tar pitch impregnation; amount of carbon from impregnant in final product: 5.7%; graphitized at 2500 C; very isotropic; (CTE _⊥ /CTE = 1.02); density: 1.78 g/cm ³
Raw-coke ⁽³⁾ No binder	63-38	Texas-Lockport (raw coke)	4 x 4 x 6	Experimental grade; volatile content of raw coke: 12%; binder: none; graphitized at 2500 C; isotropic (CTE _⊥ /CTE = 1.27); density: 1.35 g/cm ³
Raw-coke ⁽⁴⁾ Pechiney	63-42	Shell H 200 coke (raw coke)	2 dia. x 6	Experimental grade; coke uncalcined (raw); graphitized at 2700 C; density: 1.24 g/cm ³ .
Acheson ⁽⁵⁾ isotropic	63-48		4-1/2 x 13 x 4-1/2	High thermal expansion; isotropic
AGL ⁽⁶⁾ isotropic	63-49		2-3/4 x 4-3/4 x 8	High thermal expansion; isotropic

(1) Further details may be found in Nuclear Graphite (1)

(2) Manufactured by Carbon Products Division, Union Carbide Corporation

(3) Manufactured by Great Lakes Carbon Corporation

(4) Manufactured by Pechiney Company

(5) Manufactured by Acheson Company

(6) Manufactured by Anglo-Great Lakes Company

3. RESULTS

The length change data for CSF graphite are presented in Figures 1 and 2. The solid lines are from the long-term tests in the GETR and the circles are from the high-temperature test in the ETR. The X's are the data from the raw-coke graphites.

Data for the samples taken transverse to the extrusion axis are shown in Figure 1. The 800 C samples have gone through a maximum contraction or "turnaround" and are expanding rapidly. Curves at the lower temperatures suggest that the same behavior will be observed but at higher exposures and with a larger maximum contraction. The higher temperature data show a rapid increase in the contraction at 1000 C and indicate that the contraction does not increase between 1000 C and 1200 C.

Both the parallel and transverse data points for the raw-coke graphites are shown on Figure 1 since these materials are quite isotropic (See Table I). At 950 C the base stock (63-16) shows some anisotropy with the transverse sample expanding over three times as much as the parallel sample. At 1150 C the same material contracts 0.2 percent while the raw coke with no binder (63-38) expands nearly 0.6 percent and a parallel sample of the impregnated material (63-17) contracts over 0.9 percent.

Data from the CSF parallel samples are presented in Figure 2. For the long-term tests at 450 - 800 C the contraction is continuing. At 800 C the contraction has reached 6.3 percent and the rate of contraction appears to be constant. The contraction at 1000 C is about 5 times as much as that at 800 C and nearly 3 times that at 450 C. The contraction rate at 1200 C appears to be about the same as that at 1000 C.

Data for the transverse samples of EGCR graphite are presented in Figure 3. The 800 C sample shows very dramatic behavior, having expanded over 10 times

as much as the maximum contraction it reached. The expansion is proceeding extremely rapidly. At 700 C the turnaround has also been passed but the expansion to date is much slower than at 800 C.

The dimensional behavior of the raw-coke and isotropic graphites are presented in Figure 4. The raw-coke data presented in Figure 1 is repeated here so that all available data can be readily compared. At irradiation temperatures up to 800 C all materials exhibit quite isotropic behavior under irradiation and all show less contraction than the CSF transverse samples. The raw-coke graphites show much less contraction than the Pechiney, AGL, and Acheson graphites. As discussed above the raw-coke graphites show anisotropic behavior at irradiation temperatures of 950 C and above, although at lower temperatures they are quite isotropic. Thus at these higher temperatures it appears the slight amount of binder carbon in 63-16 causes a significant increase in density and results in a contraction rather than the expansion shown by the graphite having no binder (63-38). Since the impregnated sample was of parallel orientation and the base stock(63-16) does show the anisotropic behavior at 950 C, the large difference in contraction of 63-16 and 63-17 at 1150 C probably is due to a combination of the effects of orientation and impregnation.

The length change data for all the transverse samples from the high-temperature test are presented in Figure 5. The constant isotherm lines are drawn through the data points only ^{to indicate general trends. Since there is} one data point in most cases, the lines can not be assumed to show exact indications of dimensional behavior. For all graphites (excluding the raw-coke graphites) the KC contracts the least, the TSX next, the CSF next, and the EGCR the most. The most striking behavior is exhibited by the TSGBF graphite which expanded nearly 3.3 percent. This would appear to indicate the TSGBF has gone through a turnaround and is

expanding extremely rapidly. Based on other data at lower neutron exposures,⁽⁹⁾ which show much larger contractions than those indicated by the trend lines drawn on Figure 5, there is a possibility the EGCR, CSF, and TSX graphites may be rapidly approaching or even past turnaround at the exposures given.

The parallel sample data from the high-temperature test are presented in Figure 6. The needle-coke graphites, KC, TSX, and EGCR show less contraction than the conventional-coke graphites, CSF and TSGBF. Again the lines indicate trends only. It appears the contraction is greatest at 1000 C.

Contraction rates based on the trend lines shown in Figures 5 and 6 at an exposure of 4×10^{21} nvt are presented in Figure 7. For the CSF transverse samples the rate decreases from 450 to 800 C, increases fairly rapidly to 1000 C and finally decreases and levels out at 1200 C. The parallel CSF data show a slight decrease in contraction rate from 450 to 800 C, a very rapid increase to 1000 C and a leveling off to 1200 C. The raw-coke graphites generally have a smaller contraction rate than transverse CSF samples.

The coefficient of thermal expansion as a function of temperature is presented in Figures 8 and 9. As shown in Figure 8, the CTE (25 C to the final temperature) for the more graphitic materials, CSF, KC, TSX, and EGCR, changes only slightly with irradiation. The CTE of the less graphitic materials shows a much larger change with irradiation (Figure 9). The CTE of the TSGBF transverse material increases about 25 percent while that of the raw-coke graphite (63-38) decreases about 21 per cent and that of the base material (63-16) decreases about 62 per cent. These CTE results indicate that the less-graphitic areas in a graphite piece play an important role in the physical-property changes occurring during neutron irradiation.

The samples of the less-graphitic materials were annealed for 1 hour at 1700 C at a pressure of 3×10^{-4} torr. The changes in CTE resulting from the annealing are^{also} shown in Figure 9. The CTE for the TSGBF sample shows a large increase of approximately 86 per cent compared to the unirradiated value, or about 61 per cent in addition to the increase resulting from the irradiation. The CTE of the raw-coke graphite (63-38) also increases from the irradiated result, thus showing a partial recovery back to the unirradiated value. The CTE of the base material (63-16) also shows a slight recovery back toward the unirradiated value. The raw-coke graphites did not change in length during the annealing, but the TSGBF sample expanded 0.30 per cent, or about one-tenth of the expansion during irradiation.

The surface appearance of several of the materials were examined after the irradiation and compared with unirradiated specimens. The changes in the TSGBF graphite are striking while the other materials show no major changes. The appearance of the TSGBF sample is shown in Figure 10. This material has a very porous structure as is seen in the unirradiated specimen. After irradiation, a network of cracks is readily observable, particularly in the transverse surface. These cracks extend completely across the surfaces.

The microstructures of the samples were also examined and the appearances of the surfaces are shown in Figures 11 and 12. The surface of the irradiated graphite shows a somewhat "crumbled" appearance. The crack structure has become noticeably more pronounced and a continuous but tortuous path of open cracks can be followed through the structure. This may partially account for the large growth seen in the TSGBF sample. The appearance of the TSGBF sample after the annealing study is also shown in Figure 11 and 12. The amount of "crumbling" appears to have stayed about the same or perhaps increased slightly and the crack structure continues to be evident.

The microstructure of the long-term NC7 800 C sample is shown in Figure 13 before irradiation and in Figure 14 after irradiation. It appears the crack structure may be opening up although there is not drastic change.

The tensile and compressive strengths of the TSGBF sample which showed the large crack structure were measured and compared to results on unirradiated materials. The results are tabulated in Table II. As expected the strength decreases markedly.

TABLE II
STRENGTH OF TSGBF GRAPHITE

<u>Sample Number</u>	<u>Strength, psi</u>	
	<u>Tensile</u>	<u>Compressive</u>
Unirradiated	1560	8540
Irradiated	180	3410
Per cent change	-88	-60

4. CONCLUSIONS

The length changes of the graphites tested over the temperature range of 450 - 1200 C show a dependence on the temperature of irradiation, particularly in the parallel direction. The transverse samples irradiated at 1200 C contract more than those irradiated at 800 C and about the same as samples irradiated at 450 C. Those irradiated at 1000 C contract at the highest rate. This may indicate that turnaround in the contraction curve has already been passed and that the samples are expanding at these exposures. The parallel samples of the extruded materials contract considerably more at 1200 C than at 800 C and the amount is significantly more than for samples irradiated at 450 C. The contraction rate appears to remain about constant for irradiation temperatures of 1000 - 1200 C. This may be an indication

of a lessening or even a saturation of contraction in the parallel direction which has not been observed previously for lower irradiation temperatures even at much higher exposures.⁽²⁾

The raw-coke graphites, which contract less than the other graphites, even expand in some cases. Some indication of anisotropic behavior is shown by the base material at 950 C, even though this material, as well as the impregnated material, is nearly isotropic ($CTE_{\perp}/CTE_{\parallel} = 1.02$) prior to irradiation and all these materials show isotropic behavior at irradiation temperatures below 800 C. It appears the binder phase has an effect on the amount of physical distortion induced by irradiation, since at 1150 C the material containing no binder expands while the base stock contracts and the parallel orientation of the impregnated material contracts significantly. Because the impregnated sample was of parallel orientation while the sample of the base stock was transverse, the large difference in contraction of 63-17 and 63-16 may be due to a combination of impregnation and orientation.

The CTE for the base material decreases significantly more than that of the no-binder material indicating that as the less-graphitic part of an isotropic material becomes oriented during irradiation it tends to increase the a alignment of the supporting structure and thus decrease the CTE.

The length changes observed on the transverse sample of TSGBF graphite provide several significant results: (1) The TSGBF graphite, which was heated to only 2450 C during manufacture, and is therefore less graphitic than any of the other conventional or needle-coke graphites, expands significantly upon irradiation. This suggests that the graphite may have gone through a very rapid contraction followed by a turnaround and even more rapid expansion. This, in turn may also indicate that transverse samples of some of the other materials may be near or even past turnaround and are

perhaps expanding at the exposures reported.

- (2) The irradiation expansion is not annealed out by heating above the irradiation temperature, but on the contrary, the sample continues to expand.
- (3) The CTE increases significantly during irradiation and increases even more upon annealing.
- (4) The graphite becomes full of cracks during irradiation and these do not close on annealing.
- (5) The strength decreases drastically upon irradiation under these conditions.

From these observations it appears that in an anisotropic graphite containing a large amount of less-graphitic material the expansion of the crystallites in the c direction becomes a controlling factor in physical property changes and causes a turnaround in the contraction behavior. The bulk expansion during annealing could be due to ordering of the more crystalline parts of the structure. A predominant expansion in the c direction would also explain the increases in CTE both during irradiation and subsequent annealing. A detailed discussion of the current concepts of the two-phase model for the explanation of the observed behavior of graphite is presented elsewhere.⁽¹²⁾

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PHYSICAL DISTORTION OF CSF GRAPHITE (TRANSVERSE)
AS A FUNCTION OF EXPOSURE

PHYSICAL DISTORTION OF CSF GRAPHITE (PARALLEL)
AS A FUNCTION OF EXPOSURE

PHYSICAL DISTORTION OF EGCR GRAPHITE
(TRANSVERSE) AS A FUNCTION OF EXPOSURE

RADIATION INDUCED DIMENSIONAL CHANGES OF RAW COKE AND ISOTROPIC GRAPHITES

Physical Distortion of Graphite (Transverse) as a Function of Exposure

Physical Distortion of Graphite (Parallel) as a Function of Exposure

RATE OF LENGTH CHANGE FOR GRAPHITE AS A FUNCTION OF IRRADIATION TEMPERATURE

Coefficient of Thermal Expansion of Graphite
(25 C to the Final Temperature)

Coefficient of Thermal Expansion of Graphite
(25 C to the Final Temperature)

Transverse

Parallel

Unirradiated (125-14)

Transverse

Parallel

Irradiated (125-23)

Structure of TSGBF Graphite (10X)

Unirradiated (125-14)

Irradiated (125-23)
Transverse

Annealed (125-23)

Microstructure of TSGBF Graphite (75X)

Unirradiated (125-14)

Irradiated (125-23)
Parallel

Annealed (125-23)

Microstructure of TSGBF Graphite (75X)