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HIGH-TEMPERATURE IRRADIATION BEHAVIOR OF PRODUCTION-GRADE NUCLEAR GRAPHITES

by

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ABSTRACT

A number of production-grade needle-coke and Gilsonite graphites were irradiated at 600° to 1280°C to maximum fluences of about 13×10^{21} n/cm² ($E > 0.18$ MeV). The needle-coke graphites behaved similarly and showed marked anisotropy in dimensional changes. At temperatures from 900° to 1280°C, they contracted in the perpendicular direction to a maximum shrinkage of about 1.5% at an exposure of 3 to 5×10^{21} n/cm², and then expanded upon further irradiation. In the parallel direction, they contracted rapidly with irradiation to ~10% shrinkage after fluences of 8 to 10×10^{21} n/cm², and then the contraction rate slowed. In contrast, the Gilsonite material showed near-isotropic behavior in dimensional changes when irradiated at 1000° to 1250°C to a fluence of 11×10^{21} n/cm². No differences in dimensional changes were observed between edge-cut and center-cut specimens from an 18-in.-diameter production log of needle-coke graphite.

Thermal expansivity of a needle-coke graphite irradiated at 900° to 1000°C increased by a factor of 1.7 after the exposure exceeded the point where volumetric expansion becomes evident ($\sim 5 \times 10^{21}$ n/cm²). Thermal conductivity (measured at the temperature of irradiation) decreased rapidly at low fluences and ranged from 0.04 to 0.08 cal/cm-sec-°C (initial value ranged from 0.09 to 0.15) after irradiation to 1.7 to 6.0×10^{21} n/cm² at 500° to 1000°C.

INTRODUCTION

The present work concerns experiments* to determine the changes induced by irradiation in dimensions and properties of four production-grade graphites. Of particular interest is the comparison of graphites derived from needle coke having preferred orientation with those derived from Gilsonite coke having near-isotropic orientation.

Commercial graphites are used as moderator and structural components for High-Temperature Gas-Cooled Reactors (HTGRs). These graphites are usually manufactured as cylindrical logs approximately 18 in. in diameter and 30 to 34 in. long. These materials are manufactured with either calcined needle coke or Gilsonite coke, bonded with coal-tar pitch, and formed by extrusion or molding. The green stock is baked slowly to $\sim 900^{\circ}\text{C}$ and then impregnated with coal-tar pitch to increase the density and strength. The baked logs are heated to $\sim 2800^{\circ}\text{C}$ to graphitize the structure. Additional impregnations may be carried out on the graphitized articles and the baking and graphitization steps may be repeated if necessary to further improve the properties. The variations in raw materials and processing lead to variations in microstructure and, thus, to variations in high-temperature irradiation behavior.

*Structural and property measurements were made by Gulf General Atomic (GGA). Irradiation experiments were done independently at GGA and Battelle Northwest Laboratory (BNWL) on materials supplied by GGA. The irradiation data from GGA and BNWL were combined to produce smooth dimensional-change curves.

MATERIALS

The graphites under investigation were:

H-327, Great Lakes Carbon Company (GLCC)	Currently under production for the GGA Fort St. Vrain high-temperature reactor. (A 13-in.-diameter production prototype material was used for the experiments described in this report.)
9567, AirCo Speer	An 18-in.-diameter production-grade needle-coke graphite
TS-688, Union Carbide Corporation (UCC)	A needle-coke graphite (20 in. by 20 in. cross section) produced for the Experimental Gas-Cooled Reactor (EGCR).
H-328, GLCC	A 17-in.-diameter Gilsonite-coke graphite similar to material produced by Anglo Great Lakes for the UKAEA Advanced Gas-Cooled Reactors (AGRs).

The manufacturing methods and raw materials are summarized in Table 1. Structural and property data are given in Table 2.

TABLE 1
MANUFACTURING METHODS AND RAW MATERIALS

Vendor	Material	Forming Method	Type	Raw Materials			Diameter as Manufactured (in.)
				Filler	Binder	Impregnant	
GLCC	H-327*	Extrusion	Anisotropic	Needle coke	Coal-tar pitch	Coal-tar pitch	13
AirCo Speer	9567	Extrusion	Anisotropic	Needle coke	Coal-tar pitch	Coal-tar pitch	18
UCC	TS-688	Extrusion	Anisotropic	Needle coke	Coal-tar pitch	Coal-tar pitch	20 x 20
GLCC	H-328	Molding	Near-isotropic	Gilsonite coke	Coal-tar pitch	Coal-tar pitch	17

*Prototype of 18-in.-diameter production material.

TABLE 2
PROPERTIES OF GRAPHITES

Material	Apparent Bulk Density (g/cm ³)	Tensile Strength (psi)		Coefficient of Thermal Expansion $\alpha \times 10^6, ^\circ\text{C}^{-1}(22^\circ-500^\circ\text{C})$		Thermal Conductivity, c-axis Direction (cal/sec-cm- $^\circ\text{C}$)		Young's Modulus $\times 10^{-6}$ (psi)		Bacon Anisotropy Factor	Apparent Crystallite Size ($\text{\AA}$)	
											L_c	L_a
		c-axis Direction	a-axis Direction	c-axis Direction	a-axis Direction	100 $^\circ\text{C}$	1200 $^\circ\text{C}$	c-axis Direction	a-axis Direction			
H-327	1.79	1005 $\pm$ 180	2550 $\pm$ 250	3.35	1.10	0.26	0.09	0.80	--	0.70	1150	640
9567	1.72	1220 $\pm$ 80	2200 $\pm$ 80	3.45	1.35	0.26	0.09	0.90	1.90	--	1600	700
IS-688	1.72	1030 $\pm$ 125	1800 $\pm$ 80	2.75	1.30	0.23	0.09	0.70	1.55	0.64	1000	890
H-328	1.73	2560 $\pm$ 500	2780 $\pm$ 250	5.70	5.50	0.25	0.10	1.30	1.40	1.10	385	430

EXPERIMENTAL METHODS

The techniques for measuring thermal expansivity, thermal conductivity, and dimensional changes have been reported elsewhere (Refs. 1,2). The irradiation experiments were carried out in a capsule designed at GGA (G-12) and later in a series of capsules designed at BNWL (GE-H-13-14, -15, and -17). A description of the GGA capsule was given previously (Ref. 2), and the Battelle capsules were described in Ref. 1. Capsule G-12 was irradiated for four cycles in the Engineering Test Reactor (ETR) to $2 \text{ to } 6 \times 10^{21} \text{ n/cm}^2$ ($E > 0.18 \text{ MeV}$) at 600° to 1130°C . The BNWL capsule series was also irradiated in the ETR; each capsule was irradiated for two to three cycles. By successively shifting samples from one capsule to the next and adding new samples it was possible not only to build up the fluence on the original samples but also to obtain additional data at intermediate fluences, and thus to produce continuous curves as a function of fluence.

EXPERIMENTAL RESULTS

DIMENSIONAL CHANGES

The dimensional changes are shown in Figs 1 through 4. All data points are plotted, and where possible the scatter in the data is shown by dashed lines. The BNWL data are represented by open and closed circles and the GGA data are shown by open and closed triangles or squares. The dimensional change curves for the needle-coke materials are all similar in shape, showing initial contraction in both directions at low fluences followed by turnaround in the perpendicular direction to expansion at higher fluences. The reversal of the contraction is temperature dependent and occurs at lower fluences above 800°C. In the parallel direction the contraction continues to higher fluences and then starts to saturate. From other studies of needle-coke graphites (Refs. 1,3), it has been shown that the contraction in the parallel direction also reverses and expansion occurs at high fluences. The fluence at which the reversal occurs is again temperature dependent.

The H-328 graphite is near-isotropic and shows only a small degree of anisotropy in dimensional changes. The H-328 data have been added to comparable curves for the needle-coke graphites in Figs. 1c, 1e, 2c, 2d, 3c, and 3e. In all cases the marked difference in the stability of the two types of graphite is obvious. At 1015°C and 6×10^{21} n/cm², the Gilsonite graphite is apparently just entering turnaround in both directions. At 1100° to 1250°C turnaround has occurred at 4 to 6×10^{21} n/cm² and the graphite has expanded to about zero dimensional change at $\sim 11 \times 10^{21}$ n/cm². Other data on Gilsonite graphites (Refs. 1,4) were similar to the H-328 data.

Fig. 1. Dimensional changes as a function of fluence for H-327 graphite.
(a) 610° to 625°C and 720° to 800°C

Fig. 1. Dimensional changes as a function of fluence for H-327 graphite.
(b) 875° to 915°C

Fig. 1. Dimensional changes as a function of fluence for H-327 graphite.
(c) 950° to 1005°C

Fig. 1. Dimensional changes as a function of fluence for H-327 graphite.
(d) 1050° to 1100°C

Fig. 1. Dimensional changes as a function of fluence for H-327 graphite.
(e) 1130° to 1250°C

Fig. 2. Dimensional changes as a function of fluence for 9567 graphite.
(a) 610° to 625°C and 695° to 800°C

Fig. 2. Dimensional changes as a function of fluence for 9567 graphite.
(b) 875° to 915°C

Fig. 2. Dimensional changes as a function of fluence for 9567 graphite.
(c) 975° to 1005°C

Fig. 2. Dimensional changes as a function of fluence for 9567 graphite.
(d) 1105° to 1285°C

Fig. 3. Dimensional changes as a function of fluence for TS-688 graphite.
(a) 610° to 625°C

Fig. 3. Dimensional changes as a function of fluence for TS-688 graphite.
(b) 695° to 800°C

Fig. 3. Dimensional changes as a function of fluence for TS-688 graphite.
(c) 875° to 1005°C

Fig. 3. Dimensional changes as a function of fluence for TS-688 graphite.
(d) 1050° to 1180°C

Fig. 3. Dimensional changes as a function of fluence for TS-688 graphite.
(e) 1200° to 1280°C

Fig. 4. Dimensional changes as a function of fluence for H-328 graphite at 760°C, 950° to 1015°C, and 1100° to 1250°C

There is considerable scatter in the needle-coke data obtained above 900°C. This scatter could result from variations in the irradiation temperature among the samples or from variations in the microstructure of the samples. The scatter is particularly high among the specimens irradiated above 900°C after maximum densification has been achieved at about $3 \text{ to } 5 \times 10^{21} \text{ n/cm}^2$. This is the region where the rapid expansion in the c-axis direction is no longer accommodated by microcracks, and the crystallite distortions are interacting to form large pores or cracks that provide additional bulk volume expansion (Ref. 1). In this range of fluence and temperature, needle-coke graphites are highly unpredictable and the rate of expansion depends critically on the microstructure of the particular specimen under test.

An experiment was included to study the effect of sample location (center to edge) within a large production log (18-in. diameter). Specimens were removed from a production log of 9567 graphite as shown in Fig. 5a. The specimens (wedge-shaped and about 1 in. long) were irradiated in capsule G-12 where they were arranged to form a cylinder (see Fig. 5b). The inner surface of the samples was curved so that a hole was provided at the center of the cylinder for a thermocouple. This arrangement allowed for a uniform temperature distribution both radially and axially. Center and edge specimens were alternated around the cylinder, thus assuming the same temperature and fluence. The data are shown in Table 3. There were no apparent large differences in the dimensional or volumetric changes of samples located at the center or the edge of this particular graphite.

THERMAL EXPANSIVITY

Changes in thermal expansivity as a function of fluence at 760° to 1015°C for 9567, H-327, and H-328 are shown in Fig. 6. The thermal expansivity of the H-327 and 9567 starts to increase rapidly with fluence at about $5 \times 10^{21} \text{ n/cm}^2$. This increase coincides with the onset of volumetric expansion. A discussion of the structural changes that cause thermal

TABLE 3
COMPARISON OF EDGE AND CENTER SAMPLES
FROM A PRODUCTION LOG OF 9567 GRAPHITE

Temp (°C)	Exposure $\times 10^{-21}$ (n/cm ²) (E > 0.18 MeV)	$\frac{\Delta L}{L_0}$ (%)								$\frac{\Delta V}{V_0}$ (%)	
		Parallel				Perpendicular				Center	Edge
		Center	Avg	Edge	Avg	Center	Avg	Edge	Avg		
610	2.00	-0.33		-0.40		-0.23		-0.20		-0.79	-0.80
625	2.30	-0.51		-0.51		-0.20		-0.21		-0.91	-0.93
695	4.90	-0.66		-0.65		-0.35		-0.28		-1.36	-1.21
720	3.75	-0.76		-0.71		-0.39		-0.40		-1.54	-1.51
880	4.85	-1.74 -1.75	-1.745	-1.66 -1.73	-1.695	-0.63 -0.50	-0.565	-0.66 -0.56	-0.61	-2.875	-2.715
950	4.00	-1.23 -1.72	-1.475	-1.22 -1.24	-1.23	-0.43 -0.63	-0.53	-0.51 -0.51	-0.51	-2.535	-2.25
950	4.35	-1.39 -1.49	-1.44	-1.39 -1.30	-1.345	-0.65 -0.57	-0.61	-0.48 -0.67	-0.575	-2.46	-2.495
965	5.00	-2.35 -2.23	-2.29	-2.12 -2.16	-2.14	-0.71 -0.59	-0.65	-0.54 -0.66	-0.60	-3.59	-3.34
1000	5.60	-3.91 -3.87	-3.89	-4.08 -3.69	-3.885	+0.10 +0.42	+0.26	-0.51 -0.27	-0.39	-3.37	-4.665
1005	5.75	-4.22 -3.28	-3.75	-4.13 -3.92	-3.525	-0.36 +0.09	-0.085	-0.10 -0.40	-0.25	-3.92	-4.025
1005	5.95	-4.66 -4.50	-4.58	-4.44 -4.14	-4.29	+0.19 +0.65	+0.42	+0.33 +0.13	+0.23	-3.74	-3.83
1005	6.00	-4.28 -4.32	-4.30	-4.55 -4.25	-4.40	-0.13 +0.30	+0.085	-0.40 -0.01	-0.205	-4.13	-4.81
1105	5.60	-4.10 -4.32	-4.21	-4.29 -4.24	-4.265	-0.70 -0.54	-0.62	-0.33 -0.54	-0.435	-5.45	-5.135

Fig. 5. Sampling of production log of 9567 graphite (left) and specimen arrangement in capsule (right)

Fig. 6. Changes in thermal expansivity as a function of fluence for graphites 9567, H-327, and H-328 at 760° to 1015°C

expansivity to increase in needle-coke graphites has been given elsewhere (Ref. 1). Data for H-328 graphite were not obtained at high fluences, but Gilsonite graphites are known to show a decrease in thermal expansivity with fluence from unirradiated values of $\sim 5.50 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ to about $2 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ at 10^{22} n/cm^2 when irradiated at $\sim 1000^{\circ}\text{C}$ or above (Ref. 1).

THERMAL CONDUCTIVITY

Changes in thermal conductivity, measured in the perpendicular direction, as a function of irradiation and measurement temperature are shown in Fig. 7. All materials behave in a similar manner; the conductivity is reduced from the unirradiated value after irradiation in the range 1.70 to $6.0 \times 10^{21} \text{ n/cm}^2$ at 500° to 1000°C . The conductivity after irradiation, when measured at the temperature of irradiation, ranges from 0.04 to $0.08 \text{ cal/cm-sec-}^{\circ}\text{C}$ and is not dependent on material, temperature, or fluence. These data are in agreement with other work (Refs. 2,5) where the conductivity has been shown to degrade rapidly at low fluence and to saturate.

The initial degradation of thermal conductivity results from neutron-induced defects in the lattice rather than from gross changes in the microstructure. Thus, small amounts of damage at low fluences will bring about a large decrease in the conductivity. The degradation is greatest when measured at room temperature where lattice defects are responsible for a large portion of the scattering. When measurements are made at higher temperatures, the reduction from the unirradiated values is less due to the predominance of phonon-phonon over defect scattering. There should be no further significant degradation of the conductivity in these graphites until large volumetric expansions have occurred at about 6 to $8 \times 10^{21} \text{ n/cm}^2$ above 900°C .

Fig. 7. Changes in thermal conductivity of the graphites as a function of irradiation and measurement temperature

CONCLUSIONS

Production-grade needle-coke graphites contract in the perpendicular direction to as much as 1.5% at ~ 3 to 5×10^{21} n/cm² at temperatures above 900°C and then expand at higher fluences. In the parallel direction they contract up to about 8 to 10×10^{21} n/cm², where the contraction rate begins to slow. There is considerable scatter in the dimensional data resulting from variations in the microstructure of the test specimens.

In contrast, when irradiated to 6×10^{21} n/cm² or 11×10^{21} n/cm² at $\sim 1000^\circ\text{C}$ or 1100° to 1250°C molded Gilsonite material, in comparison with the needle-coke materials, showed only a small amount of anisotropic behavior, considerably more stability, less distortion, and less scatter among specimens. The Gilsonite material showed turnaround in both the parallel and perpendicular direction followed by a slow expansion, whereas the needle cokes showed the onset of expansion at 1000°C and 5×10^{21} n/cm² followed by a rapid expansion.

No differences in dimensional changes were observed between center-cut or edge-cut specimens from an 18-in.-diameter log of needle-coke graphite 9567.

Thermal expansivity of the needle-coke graphites increased with fluence by a factor of about 1.7 in both directions when irradiated at 900° to 1000°C . The increase in thermal expansivity corresponds with the large volumetric expansions, which begin at about 5×10^{21} n/cm². The thermal expansivity of Gilsonite materials have been shown to decrease by a factor of 2.5 under similar conditions of irradiation (Ref. 1).

Thermal conductivity decreased rapidly at low fluences and ranged from 0.04 to 0.08 cal/cm-sec-°C after irradiation to 1.70 to 6.00×10^{21} n/cm² at 500° to 1000°C when measured at the temperature of irradiation. The degradation of thermal conductivity was not dependent on fluence, irradiation temperature, or material.

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