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RESEARCH ON GRAPHITE

QUARTERLY PROGRESS REPORT

FOR THE PERIOD ENDING SEPTEMBER 30, 1971

by

G. B. Engle and R. J. Price

Prepared under
Contract AT(04-3)-167
Project Agreement No. 12
for the
San Francisco Operations Office
U. S. Atomic Energy Commission

Date Submitted to AEC - October 29, 1971

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GULF GENERAL ATOMIC COMPANY
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PREVIOUS REPORTS IN THIS SERIES

GA-4022 - Annual Report, April 1, 1962, through March 31, 1963
GA-5016 - Annual Report, April 1, 1963, through March 31, 1964
GA-5033 - Annual Report, April 1, 1963, through March 31, 1964 (Task II)
GA-6233 - Annual Report, April 1, 1964, through March 31, 1965
GA-7100 - Annual Report, May 15, 1965, through May 14, 1966
GA-7906 - Annual Report, May 15, 1966, through May 14, 1967
GA-8681 - Annual Report, May 15, 1967, through May 14, 1968
GA-9433 - Annual Report, May 15, 1968, through May 14, 1969
GA-9675 - Quarterly Report for period ending August 14, 1969
GA-9828 - Quarterly Report for period ending November 14, 1969
GA-9968 - Quarterly Report for period ending February 14, 1970
GA-9975 - Three Year Summary Report, May 15, 1967, through May 14, 1970
GA-10268 - Quarterly Report for period ending August 14, 1970
GA-10433 - Quarterly Report for period ending November 14, 1970
GA-10533 - Quarterly Report for period ending February 14, 1971
GA-10694 - Annual Report, May 15, 1970, through June 30, 1971

ABSTRACT

The results of research on graphite for the period July 1 through September 30, 1971, are reported. Postirradiation measurements were continued on specimens irradiated previously in capsule GE-H-13-18 in the range 500° to 1430°C up to fluences of 10^{22} n/cm². Correlations between apparent crystallite size, crystallite size distribution, isotropy, strength, thermal expansivity, and irradiation behavior are discussed along with exceptions. The results of X-ray measurements on highly oriented graphites are presented. Irradiation-induced dimensional changes are given for petroleum- and coal-derived cokes.

1. INTRODUCTION

The primary objective of this program is to develop an understanding of the relationships between the properties, microstructure, and irradiation behavior of graphites required for high-temperature reactors of advanced design. A number of anisotropic and isotropic graphites and petroleum cokes, which constitute the filler particles in a manufactured graphite, are under investigation. This report provides current accounts of research on graphite for the period July 1 through September 30, 1971.

The postirradiation examination of specimens irradiated in capsule GE-H-13-18* was continued by measurement of dimensional and density changes on coke specimens and thermal expansivity changes on graphite specimens after irradiation in the range 3.80 to 7.20×10^{21} n/cm² at 1000° to 1430°C . Postirradiation density measurements were made on density fractions from an isotropic and an anisotropic graphite which had been separated prior to irradiation.

Capsule GE-H-13-19,* containing a number of specimens irradiated previously in GE-H-13-18 to fluences of up to 10^{22} n/cm² at 500° to 1400°C plus additional virgin specimens, is currently under irradiation in the Engineering Test Reactor. Capsule GE-H-13-19 is in the first of a scheduled 3-cycle irradiation and is operating at design temperatures.

A review of the current and recent literature concerning high-temperature irradiation behavior of graphites is being done to guide future work in this field. The results of the review will be issued as a topical report and submitted to a scientific journal for publication. W. P. Eatherly of Oak Ridge National Laboratory and G. B. Engle of Gulf General Atomic are collaborating on this review.

*These capsules are operated by Battelle Northwest Laboratory (BNWL) and the space is shared between BNWL and Gulf General Atomic on a cooperative basis.

2. SUMMARY

A number of graphites ranging from fine-grained isotropic to anisotropic needle-coke materials have been characterized by measuring their apparent crystallite size, crystallite size distribution, original density, isotropy, and strength. Correlations are shown among these properties. Isotropic graphites that have high strength, small crystallite sizes, and a narrow distribution of crystallite sizes show superior irradiation stability over anisotropic graphites that have lower strength and larger crystallites. An exception was observed in a graphite that contained two distinct carbon structures.

Density fractions, separated from an isotropic and an anisotropic graphite, were remeasured after irradiation. The high-density fractions expanded, whereas the low-density fractions densified.

Thermal expansivity measurements on graphites irradiated at 1000° to 1430°C up to fluences of 7×10^{21} n/cm² were consistent with previous data obtained at 1000° to 1280°C. A correlation between volume thermal expansion and mean apparent crystallite size $\bar{L}_c$ reported earlier has been reinforced by additional data.

X-ray measurements on highly oriented carbons and graphites showed that C_o values increased after irradiation at 750° to 800°C but remained unchanged or decreased at 1225° to 1300°C. Apparent crystallite size L_c decreased for all samples.

Coke specimens from air-blown asphalts contracted isotropically during irradiation at 4.5×10^{21} n/cm² and 1330°C, while cokes from vacuum-reduced crudes or de-ashed coal behaved anisotropically.

3. EFFECT OF CRYSTALLITE SIZE, CRYSTALLITE ORIENTATION, STRENGTH, AND ORIGINAL DENSITY ON DIMENSIONAL AND VOLUMETRIC CHANGES IN GRAPHITES

A number of graphites, described in Tables 1 and 2 of Ref. 1, are being studied to determine the effect of apparent crystallite size, crystallite orientation, strength, and original density on their irradiation behavior. Previous data indicated that graphites of intermediate density had the smallest changes when irradiated to about 8×10^{21} n/cm² at 1200° to 1300°C. Isotropic graphites having intermediate crystallite sizes in the range 200 to 600 Å showed a strong correlation between original strength and dimensional change after irradiation to 3.85×10^{21} n/cm² at 1000°C.

The distribution of apparent crystallite sizes L_c of the graphites in Tables 1 and 2 of Ref. 1 are shown in Fig. 1. This figure combined with the data in Table 2 of Ref. 1 shows the relationships between the apparent crystallite size, crystallite size distribution, crystallite orientation, and strength. As the apparent crystallite size increases the range of crystallite sizes increases, the isotropy factor increases (i.e., the materials become more anisotropic), and the original strength decreases. It was reported in Ref. 1 that initial dimensional or volumetric changes of the graphites do not depend upon the crystallite size. This does not necessarily indicate that increased crystallite size and perfection do not enhance stability as suggested in Ref. 2, but rather shows that some other structural feature dominates and perhaps masks any crystallite size effect. The dominant characteristic appears to be high original strength, which is associated with isotropy and small crystallite sizes.

It is apparent that fabrication processes which produce a fine-grained microstructure where the binder bridges blend with the coke structure also produce strong structurally homogeneous materials. These materials, which

Fig. 1. Apparent crystallite size and crystallite size distribution of graphites

are processed by methods and with raw materials that are held proprietary by the carbon manufacturers, do not have large ordered crystallites and are also isotropic. On the other end of the spectrum, graphites fabricated by the conventional method of mixing a coal-tar pitch binder with an anisotropic coke have distinct interfaces between the coke particles and the binder carbon. In these materials crystallites grow to intermediate or large size and are better ordered, but due to the nature of the raw materials and the processing methods strong bonding cannot be achieved between filler particles and binder carbon and the coke particles themselves are inherently weak. The two types of microstructures described above are represented by the graphites shown in Fig. 2. The microstructural features of the other graphites fall between the two extremes shown in Fig. 2.

The correlations described above will be followed to higher fluences where the materials are expanding.

The results in Fig. 1 and in Ref. 3 showed certain graphites to contain regions of different crystallite sizes, orientation, and density. It was postulated that these varying regions of carbon structure may respond differently to fast neutrons. To test this hypothesis density fractions were separated from a needle-coke graphite (H-327) and a Gilsonite-coke graphite (H-328).

The results were similar in each material; the 2.15 to 2.26 g/cm³ fraction expanded slightly while the 2.05 to 2.15 g/cm³ fraction densified. The particles in the intermediate fractions, 1.95 to 2.05 and 1.85 to 1.95 g/cm³, showed both expansion and densification and were evenly distributed over the entire density range after irradiation. The lowest density fractions densified.

These results indicate that on a microscale expansion and densification occur simultaneously in some binder-filler graphites. Thus, pores or defects lying in different regions of the graphite are being both generated and closed at the same time. This situation could lead to the formation of an independent

M33549-4

(a)

800x

M36465-5

(b)

800x

Fig. 2. Photomicrographs of graphites. (a) Fine-grained isotropic and (b) needle coke

network of pores or cracks at a location within the microstructure at interfaces where the various carbon structures meet. This network of pores, which may be difficult to measure directly at low fluences, could be the nucleus for further rapid pore volume generation at higher fluences.

4. EFFECT OF TEMPERATURE HISTORY ON DIMENSIONAL CHANGES OF GRAPHITES

No work was performed on these specimens during this period. The specimens are currently undergoing irradiation to higher fluences of about 10^{22} n/cm² at 800° to 1200°C in capsule GE-H-13-19.

5. THERMAL EXPANSIVITY CHANGES IN GRAPHITES

Measurements of thermal expansivity were continued on specimens irradiated at 1000° to 1430°C to fluences of up to 7×10^{21} n/cm². The data are presented in Table 1. The results show a slight upward trend in the data for H-327 graphite, the needle-coke material, and a significant reduction in the isotropic H-419 material at 1290° to 1430°C. These results are consistent with those reported previously of specimens irradiated at 1000° to 1280°C (Ref. 1). Additional data points are being obtained at 1290° to 1430°C to fluences of 8 to 10×10^{21} n/cm².

Thermal expansivities of the graphites were shown previously to vary systematically with the mean apparent crystallite size $\bar{L}_c$ (Ref. 3). Considerably more data are now available on the graphites from Table 1 of Ref. 1, and these additional points have been added to the data in Ref. 3 (see Fig. 3). The dependency of thermal expansivity on crystallite size is still quite evident with the exception of graphite H-337 and those believed to be prepared with carbon blacks. The H-337, which has a relatively high CTE for its crystallite size, also contracts at a lower rate than the other graphites and does not show the same dependence of contraction with strength. Graphite H-337 has the largest crystallite size of the isotropic graphites and has only moderate strength. Examination of the microstructure of H-337 (see Fig. 4) reveals a continuous matrix of fine-grained isotropic structure with large regions of more graphitic structure. This material appears to be two-phased. The isotropic matrix may be intrinsically strong and therefore may control the irradiation behavior, whereas the presence of a second more graphitic and weaker phase may reduce the macrostrength on which the correlation in Ref. 1 is based. This material will be studied further to confirm its anomalous but encouraging behavior.

TABLE 1
THERMAL EXPANSIVITY CHANGES IN GRAPHITES IRRADIATED AT 1000° TO 1430°C

Fluence x10 ⁻²¹ (n/cm ²)	Temp (°C)	H-327				CHN		H-315-A		H-328		H-319		H-419	
		Center		Edge											
		a-axis ()	c-axis (⊥)	a-axis ()	c-axis (⊥)	a-axis ()	c-axis (⊥)	c-axis ()	a-axis (⊥)	c-axis ()	a-axis (⊥)	a-axis ()	c-axis (⊥)	()	(⊥)
--	--	1.45 1.55	2.95 2.70	1.45 1.35	3.05 3.05	1.85 2.05 1.75 2.15 1.50 1.55	2.95 3.15 3.50 3.50	4.30 4.95	4.80 5.30	5.60 5.80	5.75 5.30	2.85 3.55	3.15 3.60	7.75	7.45 7.85
3.85	1000	2.10 1.95 1.85 1.90	3.50 3.35 3.35 3.15 3.15	1.70 1.70 1.80 1.90	3.80 3.90 3.85 3.85 3.85					5.75	6.00				
7.15	1000									2.60 3.10 2.90	2.70 2.55 2.60 2.70 2.45				
5.15	1290													2.85 3.40 3.40 3.35	3.25 3.10 3.50 3.10
4.55	1330	1.80 1.90 2.15 1.75 1.85 2.15	3.40 3.30 3.30 3.45 3.70 3.25 3.65 3.30 3.45 3.60 3.70	2.15 2.05 1.90 1.60 1.80 1.55	3.60 3.90 3.55 3.72 3.70 4.00 3.50 3.85									4.70 3.70 3.50	4.85 4.65
5.20	1430			1.90	3.65	2.25	3.90	4.60	4.20	6.10	5.60	3.30	3.65	4.15	3.85

Fig. 3. Mean apparent crystallite size $\bar{L}_c$ vs volume thermal expansivity α_v

M33546-3

800x

Fig. 4. Photomicrograph of H-337 graphite

6. THERMAL CONDUCTIVITY CHANGES IN GRAPHITE

No work was performed on these specimens during this period. The specimens are currently undergoing irradiation to higher fluences of 2 to 10×10^{21} n/cm² at 500° to 1400°C in capsule GE-H-13-19.

7. IRRADIATION EFFECTS IN HIGHLY ORIENTED CARBONS AND GRAPHITES

Samples of hot-worked ATJ graphite and massive pyrolytic carbon annealed at various temperatures are being irradiated at 750° to 800°C and at 1225° to 1300°C in the GE-H-13 series of capsules. In the last annual report (Ref. 1) dimensional changes were reported for fluences up to 4×10^{21} n/cm² for the low irradiation temperature samples and 2×10^{22} n/cm² for the high irradiation temperature samples. During the current quarter X-ray diffraction measurements were made on the same batch of samples. Lattice parameter (C_o) and apparent crystallite size (L_c) were determined from the (002) peaks.

For irradiation temperatures of 750° to 800°C, C_o increased with irradiation by ~0.2% for both pyrolytic carbon and hot-worked graphite. The increase saturated after exposures of 1 to 2×10^{21} n/cm². At 1225° to 1300°C, C_o remained unchanged for the hot-worked graphite and highly annealed pyrolytic carbon but decreased by ~0.5% for as-deposited pyrolytic carbon. L_c was decreased by irradiation for all samples. For irradiation temperatures of 750° to 800°C, an exposure of 4×10^{21} n/cm² reduced L_c to ~100 Å for all samples, compared with preirradiation values ranging from 220 to 1600 Å. For irradiation at 1225° to 1300°C, L_c was again reduced but to a much smaller extent. After an exposure of 1.4×10^{22} n/cm², L_c for the pyrolytic carbon annealed at 3300°C was reduced from 1600 Å before irradiation to ~400 Å. For as-deposited pyrolytic carbon, the corresponding values were 220 and 150 Å.

8. COKE STUDIES

Calcined petroleum-coke particles constitute a major portion of binder-filler graphites. Therefore, the behavior of the filler particles is an important factor in the determination of the irradiation behavior of the binder-filler artifacts. An exploratory program has been started to determine the dimensional and density changes of cokes.

Cokes have been selected from various sources for characterization and irradiation to determine their behavior. Fine-structured isotropic cokes are emphasized. A description of the cokes and some preirradiation properties were given in Ref. 1.

Isotropic coke powders prepared from air-blown asphalts, vacuum-reduced crudes, and a de-ashed coal were irradiated in GE-H-13-18 at 840° and 1330°C to 2.8 and 4.5×10^{21} n/cm², respectively. These specimens were returned without measurement to GE-H-13-19 for further irradiation because there was not enough sample for measurement at more than one fluence.

Other isotropic coke specimens irradiated as flakes were measured for dimensional and density changes after irradiation at 4.5×10^{21} n/cm² and 1330°C. The data are shown in Table 2.

The cokes from the air-blown asphalts were relatively isotropic, while the cokes from the vacuum-reduced crude and the de-ashed coal were anisotropic.

The anisotropic needle-type cokes A and B expanded after irradiation at 4.5×10^{21} n/cm² and 1330°C.

TABLE 2

IRRADIATION OF COKE FLAKES AT 4.55×10^{21} N/CM² AND 1330°C

Source Material	Specimen No.	Estimated Heat-Treatment Temperature (°C)	Sulphur Content (wt %)	Density (g/cm ³) (a)		Dimensional Changes (%)	
				Unirradiated	Irradiated	Diameter	Thickness (b)
Air-blown asphalt (c)	223A1	2675	----	2.038	2.197	-3.60	-0.60
Air-blown asphalt (c)	223A2	2675	----	1.967	2.200	-3.91	-3.98
Air-blown asphalt (c)	223A3	2675	----	1.986	2.200	-4.12	-2.56
Vacuum-reduced (d) petroleum crude	223A4	2800	----	2.033	2.178	-5.20	+3.25
De-ashed coal (e)	223A5	2810	1.04	2.115	2.167	-10.44 (f)	+18.42 (f)
Petroleum crude (g)	A	2800	----	2.240	2.190	----	----
Petroleum crude (g)	B	2800	----	2.210	2.180	----	----

(a) Density measured by immersion in liquid.

(b) Thickness change calculated according to $2 \frac{\Delta d}{d_o} + \frac{\Delta t}{t_o} + \frac{\Delta \rho}{\rho_o} = 0$.

(c) Edginton Asphalt Company.

(d) Gulf Oil Corporation.

(e) Pittsburgh and Midway Coal Company.

(f) Corners on the specimen were rounded.

(g) Great Lakes Carbon Company.

9. TOPICAL REPORTS AND PUBLICATIONS

The current status of topical reports and publications resulting from investigations performed under this program is as follows:

- GA-9900 "Irradiation Behavior of Isotropic Carbons," J. C. Bokros and D. W. Stevens, Carbon 9, 19 (1971).
- GA-9972 "Irradiation Behavior of Nuclear Graphites at Elevated Temperatures," G. B. Engle, March 4, 1970 (accepted for publication in Carbon).
- GA-9919 "Irradiation-Induced Dimensional Changes and Creep of Isotropic Carbon," J. L. Kaae and J. C. Bokros, Carbon 9, 111 (1971).
- GA-9971 "The Influence of Pitch-Binder Coke Content on the Properties and Irradiation Behavior of Molded Graphites," G. B. Engle, March 12, 1970 (accepted for publication in Carbon).
- GA-10162 "Annealing of Neutron-Irradiated Pyrocarbons," R. J. Price and J. C. Bokros, June 8, 1970 (accepted for publication in Carbon).
- GA-9970 "Low Temperature Graphitization of Cokes and Binder-Filler Artifacts," G. B. Engle, July 17, 1970 (submitted for publication in Carbon).
- GA-10507 "Irradiation-Induced Microstructural Changes in a Two-Phase Binder-Filler Graphite," G. B. Engle. Presented at the 24th Annual Pacific Coast Regional Meeting of the American Ceramic Society, October 30 through November 3, 1971, Anaheim, California.

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1. Engle, G. B., J. C. Bokros, and R. J. Price, "Research on Graphite, Annual Report, May 15, 1970, through June 30, 1971," Gulf-GA-A10694, Gulf General Atomic, August 12, 1971.
2. Bokros, J. C., G. L. Guthrie, and A. S. Schwartz, "The Influence of Crystallite Size on the Dimensional Changes Induced in Carbonaceous Materials by High-Temperature Irradiation," Carbon 6, 55 (1968).
3. Engle, G. B., "Density and Structural Distributions in Artificial Graphites," Carbon 8, 485 (1970).