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RESEARCH ON GRAPHITE
QUARTERLY PROGRESS REPORT
FOR THE PERIOD ENDING FEBRUARY 14, 1971

by
G. B. Engle, R. J. Price, and J. C. Bokros

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

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ABSTRACT

The work concerning research on graphite completed during the period November 15, 1970, to February 14, 1971, is reported. Irradiations of nuclear graphites and model carbons were continued to a maximum fluence of 2×10^{22} n/cm² ($E > 0.18$ MeV) at a maximum temperature of about 1280°C. Physical properties and structural characterizations for the unirradiated graphites are reported. The microstructure of a needle-coke type nuclear graphite was determined in some detail. It was shown to consist of a range of carbon structures with varying crystallite sizes and particle shapes.

1. INTRODUCTION

The objective of this program is to advance the understanding of relationships between microstructure, properties, and irradiation behavior of carbonaceous materials for advanced high-temperature reactors. The research efforts are directed toward defining the structure of model carbons and porous graphites and evaluating methods for the preparation of new or modified carbon structures with improved irradiation behavior.

The research effort covered by this report (November 15, 1970, through February 14, 1971) consisted of two principal tasks: (1) characterization and irradiation of graphites, and (2) characterization and irradiation of model carbons.

The characterization of graphite and carbon specimens currently being irradiated in capsule GE-H-13-18* was continued during this report period. Capsule GE-H-13-18 is operating in the range 550° to 1400°C, and irradiation will be completed when fluences of 0.5 to 4.0×10^{21} n/cm² ($E > 0.18$ MeV) are reached. Capsule GE-H-13-18 will be discharged on March 25, 1971. About 50 graphite specimens are being irradiated concurrently in two other capsules at BNWL, which are operating at 550° and 800°C. These irradiations will continue until a fluence of about 3×10^{21} n/cm² is reached; the capsule will be discharged February 25, 1971. Data from these specimens will complement the low-temperature data from the GE-H-13-18 specimens by providing additional data points at higher fluences.

*Being irradiated in the Engineering Test Reactor (ETR) by Battelle Northwest Laboratory (BNWL).

2. SUMMARY

CHARACTERIZATION AND IRRADIATION OF GRAPHITES

A series of specimens of graphites with a wide range of structures is currently being irradiated at 1000° to 1280°C to determine the effect of crystallite size, crystallite orientation, and density on dimensional and property changes. Three new pilot-scale isotropic graphites (Great Lakes Carbon Company Grades H-429, H-430, and H-431) are being added to the above series. Density and thermal expansivity data have been obtained on these materials.

Density fractions of a needle-coke graphite (CHN) and an isotropic Poco graphite were examined with a scanning electron microscope following improvements in the sensitivity of the densitometric separation technique. The shape, size, and surface texture of the samples were observed. The apparent crystallite size of each fraction was also determined.

The bulk density and density distribution were measured on a series of Poco graphites irradiated at BNWL to 0.9 to 7.2×10^{21} n/cm² at 1000° to 1300°C.

Samples are currently under irradiation in the GE-H-13-18 capsule to obtain data in the following areas: effect of changes in irradiation temperature on graphite dimensional changes; irradiation effects in highly oriented carbons and graphites; effect of coke structure on irradiation behavior; and irradiation-induced changes in thermal conductivity.

Measurements of irradiation-induced creep in specimens irradiated in the Dragon reactor are still in progress at RCN, Petten, Holland.

CHARACTERIZATION AND IRRADIATION OF MODEL CARBONS

Model carbons are being irradiated in the GE-H-13-18 capsule in both the restrained and unrestrained condition. A new series of restrained specimens, employing special graphite substrates to enforce different creep strain rates, is being prepared.

3. CHARACTERIZATION AND IRRADIATION OF GRAPHITES

G. B. Engle, R. J. Price, L. Bailey, and
K. Koyama

EFFECT OF CRYSTALLITE SIZE, CRYSTALLITE ORIENTATION, AND DENSITY ON DIMENSIONAL AND PROPERTY CHANGES OF GRAPHITES

A series of graphites is being irradiated at 1000° to 1280°C to determine the effect of crystallite size, crystallite orientation, and original density on irradiation behavior. This series includes graphites that range from highly oriented materials with large crystallite sizes to isotropic graphites such as Poco materials. The materials are described elsewhere (Ref. 1) and preliminary irradiation results were reported previously (Ref. 2). Structural characterization measurements have been completed on these materials and were reported last quarter (Ref. 3). Specimens are currently being irradiated in capsule GE-H-13-18 to a total fluence of about 3 to 8 $\times 10^{21}$ n/cm².

Three pilot-scale isotropic graphites were received in January from Great Lakes Carbon Company. Two of the materials, H-429 and H-430, were made by extrusion and molding, respectively, from a proprietary isotropic coke. The third, H-431, was produced from needle coke but with near-isotropic properties. Density and thermal expansivity data are shown in Table 1. The thermal expansivity measurements show values similar to Gilsonite-coke materials for the isotropic petroleum-coke graphites and intermediate values for the isotropic needle-coke samples. These materials will be added to the above series.

Density fractions of a needle-coke graphite (CHN) on which a considerable amount of high-temperature irradiation data are available were prepared and examined with a scanning electron microscope (SEM). The characteristics of the particle shape, size, and surface texture were described previously (Ref. 3). The density fractions were re-separated, and the sensitivity of

TABLE 1
CHARACTERIZATION DATA FOR ISOTROPIC GRAPHITES

Material	Forming Method	Coke Source	Anisotropy Ratio ($\alpha_{\parallel}/\alpha_{\perp}$)	Density (g/cm ³)		Thermal Expansivity x 10 ⁶ °C ⁻¹ (RT to 1000°C)		
				Bulk	Immersion in Liquid	$\parallel$	$\perp_1$	$\perp_2$
H-429	Extrusion	Pet. coke (isotropic)	0.85	1.73	2.075	4.63	5.55	--
H-430	Molded	Pet. coke (isotropic)	1.10	1.73	2.080	5.54	4.99	--
H-431	Not revealed	Pet. coke (needle)	1.05	1.74	2.141	3.23	3.10	3.07

separation has been improved. Isotropic graphites have also been separated and the density fractions examined. Representative SEM photographs of the CHN and Poco graphite fractions are shown in Figs. 1 and 2, respectively. The shape of the particles in the $<1.65\text{-g/cm}^3$ fraction in Fig. 1a (L_c estimated from Fig. 3 to be ~ 100 to $200\text{ \AA}$) is different than that of the 2.24-g/cm^3 fraction in Fig. 1b (L_c of $1000\text{ \AA}$); the former are equiaxed and boxy, whereas the latter are needle or plate-like in shape. However, a small volume of very fine particles, which appear as flakes (Fig. 1c), was also found in the light fractions. These particles are comparable in size, shape, and crystallinity to fractions found throughout an isotropic Poco graphite (see Fig. 2).

The apparent crystallite size of each fraction was determined and the results are shown in Fig. 3. These data are similar to a curve published in Ref. 1; however, the present curve has more data points due to the further refinement in separation.

Another needle-coke graphite, H-327, and a Gilsonite-coke graphite, H-378, will be examined to complete the study.

DENSITY CHANGES OF ISOTROPIC POCO GRAPHITE

A series of irradiated Poco graphites, obtained from BNWL, was measured for density and density distribution changes. These specimens were irradiated in the GE-H-13-X series at 520° to 1100°C up to $7.4 \times 10^{21}\text{ n/cm}^2$. The density changes of the Poco graphites are shown in Table 2. Expansion was less for the Poco graphites than for Gilsonite or needle-coke materials at 1000° to 1100°C , showing their increased resistance to internal pore formation. At 1300°C the powder volume contracted in correspondence with the bulk volume. Additional specimens irradiated to $\sim 1.5 \times 10^{22}\text{ n/cm}^2$ at 1000° to 1300°C are being shipped to GGA for continuation of this study.

(a) 1000x

(b) 1000x

(c) 10,000x

Fig. 1. Scanning electron microscope photomicrographs of CHN graphite density fractions. (a) $<1.65 \text{ g/cm}^3$, (b) 2.24 g/cm^3 , and (c) $<1.60 \text{ g/cm}^3$

(a)

10,000x

(b)

10,000x

Fig. 2. Scanning electron microscope photomicrographs of AXF-8QGB Poco graphite.
 (a) $<1.60 \text{ g/cm}^3$, and (b) 2.24 g/cm^3

Fig. 3. Apparent crystallite size L_c versus apparent density of CHN graphite

TABLE 2
IRRADIATION-INDUCED DENSITY CHANGES IN POCO GRAPHITES

Material	Temperature (°C)	Fluence x 10 ⁻²¹ (n/cm ²)	Density (g/cm ³)
AXF-8QGB	--	--	2.155
AXF-8QGB	1000	0.9	2.155
AXF-8QGB	1090	7.2	2.145
AXF-5QGB	--	--	2.160
AXF-5QGB	1090	7.2	2.135
AXF-5QGB	1300	1.0	2.185

EFFECT OF TEMPERATURE HISTORY ON DIMENSIONAL CHANGES

There are regions in HTGR cores where the graphite temperatures are initially high but during the lifetime of the graphite drop to lower temperatures. Therefore, the effect of the temperature history on the dimensional changes of the graphite is of interest.

Preliminary data from previous irradiations in this study were reported in Ref. 4. Specimens in this series are currently being irradiated to higher fluences in capsule GE-H-13-18; therefore, no additional data are available at this time.

IRRADIATION EFFECTS IN HIGHLY ORIENTED CARBONS AND GRAPHITES

Irradiation data on highly oriented carbons and graphites with various crystallite sizes are being collected to aid in the interpretation of irradiation effects in polycrystalline graphites. Previous results were summarized in Ref. 5. The samples are being reirradiated in capsule GE-H-13-18. The additional neutron fluences anticipated are 0.6×10^{21} n/cm² at 800°C and 4×10^{21} n/cm² at 1275°C. No additional data are available at this time.

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.

Cokes were selected from various sources for characterization and irradiation and were described previously (Ref. 2). The cokes are being irradiated to 3.0 to 4.0×10^{21} n/cm² at 1000° and 1275°C in GE-H-13-18.

THERMAL CONDUCTIVITY CHANGES

Irradiation-induced thermal conductivity changes are important in the design of high-temperature reactors when the graphite is utilized to transfer heat from the fuel to the coolant.

A series of specimens is being irradiated in capsule GE-H-13-18. The preirradiation thermal conductivity data were given in Ref. 4. The specimens are being irradiated initially to about 0.3 to 4×10^{21} n/cm² at 550°, 800°, 1000°, and 1275°C. No new data are available at this time.

CREEP STUDIES

The Dragon Project has made space available to Gulf General Atomic in the Dragon reactor, on a cooperative basis, for the purpose of irradiating restrained shrinkage specimens.

Measurements of the restrained specimens have been delayed due to the heavy work load in the Petten Laboratory. Results were expected during this period, but have not been received due to difficulties encountered in the measurements.

4. CHARACTERIZATION AND IRRADIATION OF MODEL CARBONS

J. L. Kaae, W. Ellis, F. Gagnon, and J. C. Bokros

Model carbons, including new and previously irradiated specimens, are currently being irradiated in capsule GE-H-13-18. These include natural graphite crystals, as-deposited LTI and HTI pyrolytic carbons, and annealed pyrolytic carbons. The pyrolytic carbons are being irradiated in restrained and unrestrained conditions. Two restraining substrates are being employed, graphite discs and sapphire spheres.

A new series of restrained specimens is being prepared for irradiation in the next capsule. These specimens will employ different graphite substrates, which change dimensions at different rates, in order to force different strain rates on the model carbons. These specimens will also be accompanied by identical unrestrained specimens.

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, February 24, 1970 (accepted for publication in Carbon).
- 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, March 11, 1970 (accepted for publication in Carbon).
- GA-9971 "The Influence of Pitch-Binder Coke Content on the Properties and Irradiation Behavior of Molded Graphite," G. B. Engle, March 12, 1970 (accepted for publication in Carbon).
- GA-9974 "Isochronal Annealing Kinetics and Neutron-Induced Dimensional Changes of Titanium-Doped Pyrolytic Carbon," R. J. Price and J. C. Bokros, May 11, 1970 (accepted for publication in Carbon).

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2. Engle, G. B., R. J. Price, and J. C. Bokros, "Research on Graphite, Quarterly Progress Report for the Period Ending August 14, 1970," USAEC Report GA-10268, Gulf General Atomic, August 13, 1970.
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