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AEC RESEARCH AND
DEVELOPMENT REPORT

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RESEARCH ON GRAPHITE
QUARTERLY PROGRESS REPORT
FOR THE PERIOD ENDING AUGUST 14, 1970

MASTER

by

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

Prepared under
Contract AT(04-3)-167
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- 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
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- GA-9975 - Three Year Summary Report, May 15, 1967, through May 14, 1970

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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 (May 15, 1970, through August 14, 1970) consisted of two principal tasks: (1) characterization and irradiation of graphites, and (2) characterization and irradiation of model carbons.

The majority of the experimental efforts during this report period were concerned with the preparation and characterization of graphite and carbon specimens for capsule GE-H-13-18.* New specimens along with previously irradiated specimens were loaded into the capsule in August 1970. Capsule GE-H-13-18 will operate in the range 550° to 1400°C to fluences of 0.5 to 4.0×10^{21} n/cm² ($E > 0.18$ MeV). About 50 new or previously irradiated specimens were also included in two other capsules at BNWL, which will operate at 550° and 800°C to about 3×10^{21} n/cm². 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.

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

2. SUMMARY

2.1. CHARACTERIZATION AND IRRADIATION OF GRAPHITES

A series of previously irradiated graphites and a number of new isotropic materials were organized to study the effect of crystallite size, crystallite orientation, and density on dimensional and property changes. Dimensional changes from a portion of the specimens irradiated in capsule GE-H-13-17 are reported.

Experiments to study the temperature-history effects on dimensional changes, the behavior of highly oriented graphites, and the changes in thermal conductivity are outlined. In these experiments both previously irradiated materials and new materials have been included.

A series of experiments was initiated to study the effect of coke structure on irradiation behavior. Fine-structured isotropic cokes, heated to 2600° to 2800°C, are being emphasized in these studies.

During the past 3 years, specimens have been irradiated in the Dragon reactor to measure irradiation-induced creep in a number of graphites. These specimens are awaiting measurement at RCN, Petten, Holland.

2.2. CHARACTERIZATION AND IRRADIATION OF MODEL CARBONS

A number of natural graphite flakes, low-temperature isotropic (LTI) carbons, and high-temperature isotropic (HTI) carbons were prepared for further irradiations. Irradiations will be performed on both unrestrained and restrained specimens at temperatures up to 1400°C.

3. CHARACTERIZATION AND IRRADIATION OF GRAPHITES

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

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

A series of graphites is being irradiated 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. These specimens were irradiated in capsule GE-H-13-17 to 1.80 to 3.75×10^{21} n/cm² at about 1000° to 1280°C. The materials have been described elsewhere (Ref. 1). Dimensional and volume changes resulting from the first irradiation are shown in Table 1. These specimens are being reirradiated in capsule GE-H-13-18 to a total fluence of about 3 to 8×10^{21} n/cm².

Additional specimens of the graphites from GE-H-13-17 and a number of new materials were added to this series and will be irradiated in capsule GE-H-13-18. A description of the new materials is given in Table 2.

3.2. 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.

In previous work a number of graphites were irradiated to intermediate fluences at ~1000° and 1450°C, and the irradiation was continued to higher fluences at lower temperatures (Ref. 3). These experiments showed an

TABLE 1

IRRADIATION DATA FOR GRAPHITES

Specimen No.	Material	Neutron Exposure $\times 10^{-21}$ (n/cm ²) (E > 0.18 MeV)	Irradiation Temperature (°C)	Dimensional Changes (%)		Bulk Volume Change (%) (2 $\perp$ + 1 $\parallel$)
				$\perp$	$\parallel$	
7	AXF-5QB	3.10	1220	-0.51	(-0.51)	-1.53
11	AXF-5QGB			-0.43	(-0.43)	-1.29
15	ATJ-5G			-3.04	-2.58	-8.66
2	H-319			-2.93	-2.27	-8.13
29	H-327 (edge) (a)			-1.69	-3.71	-7.09
38	H-378			-2.07	-1.79	-5.93
34	H-327 (center) (a)			-1.97	-2.95	-6.89
5	AXF-5QB	3.75	1280	-0.59	(-0.59)	-1.77
10	AFX-5QGB			-0.40	-0.41	-1.21
14	ATJ-5G			-3.07	-5.68	-11.82
1	H-319			-3.10	-	-
36	H-378			-2.40	-1.95	-6.75
37	H-378			-2.37	-1.60	-6.34
1A	H-328			-0.68	-0.73	-2.09
20	NF-15	2.35	1100	-0.90	+3.94	+2.14
28	NF-25			-2.52	+11.08	+6.04
40	H-378			-1.21	-0.96	-3.38
41	H-378			-1.09	-0.83	-3.01
42	H-378			-1.08	-0.84	-3.00
43	H-378			-1.15	-0.72	-3.02
2A	H-328	1.80	1010	-0.68	-0.65	-2.01
31	H-327 (edge) (a)			-0.47	-1.18	-2.12
22	NF-15			-0.17	-0.17	-0.42
25	NF-25			-0.10	-1.18	-1.38

(a) Specimens cut from production log of H-327.

TABLE 2

DESCRIPTION OF NEW MATERIALS FOR IRRADIATION IN CAPSULE GE-H-13-18

Material	Source ^(a)	Type	Filler Coke	Remarks
H-327	GLCC	Anisotropic	Needle coke	Previously irradiated
H-328	GLCC	Isotropic	Gilsonite coke	Previously irradiated
AXF-8QGB	Poco	Isotropic	(b)	-
H-419	GLCC	Isotropic	-	Binderless graphite
H-421	GLCC	Isotropic	(b)	(c)
H-337	GLCC	Isotropic	(b)	(d)
HL-18	AirCo Speer	Isotropic	(b)	(d)
L-31	SCC	Isotropic	(b)	(d)

(a) Great Lakes Carbon Company (GLCC), Stackpole Carbon Company (SCC).

(b) Unknown to author.

(c) Baked under pressure (Ref. 2).

(d) Samples supplied by ORNL from Molten Salt Reactor Project: H-337, raw-coke-based graphite, heavily impregnated; HL-18, stable at 700°C and extremely isotropic; L-31, same as HL-18.

apparent temperature-history effect similar to that observed in model carbons (Ref. 4) but were not conclusive because of the small number of experimental data points. These studies are being continued to higher fluences, and additional specimens have been included to provide data at other temperatures.

Specimens of H-319, H-328, H-315-A, and CHN irradiated previously to about 2.8 to 3.7×10^{21} n/cm² at about 950° to 1015°C will be extended to about 6 to 8×10^{21} n/cm² at 760° to 800°C. Specimens of CHN, H-315-A, and H-319 irradiated previously to about 3×10^{21} n/cm² at about 1250°C will be extended to about 5×10^{21} n/cm² at about 1000°C, and specimens of H-327 irradiated previously to 5 to 6×10^{21} n/cm² at about 1250°C will be extended to 7 to 8×10^{21} n/cm² at about 1000°C. Additional specimens of these materials and specimens from materials in Table 2 will be added to this series.

3.3. IRRADIATION EFFECTS IN HIGHLY ORIENTED CARBONS AND GRAPHITES

Data obtained from irradiation experiments on highly oriented carbons and graphites with various crystallite sizes are useful for developing an understanding of irradiation effects in polycrystalline graphites. In the present series of experiments, samples of hot-worked graphite, as-deposited massive pyrolytic carbon, and massive pyrolytic carbon annealed at 2900°, 3000°, 3100°, and 3300°C before irradiation are being irradiated at 750° to 800°C and at 1225° to 1300°C. Results obtained in the previous contract period were summarized in Ref. 4. During the present contract period the samples were re-encapsulated for further irradiation 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.

3.4. 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 have been selected from various sources for characterization and irradiation to determine their behavior. While fine-structured isotropic cokes are emphasized, a needle coke has also been included. The cokes are described in Table 3.

The raw cokes were heated to 2800°C in helium prior to preparation for irradiation. A portion of each coke was crushed to pass a 400-mesh screen ($<38 \mu$); one-half of the coke particles is being included in capsule GE-H-13-18 and one-half is being retained for preirradiation measurements. The cokes will be irradiated to $3.0 \times 4.0 \times 10^{21} \text{ n/cm}^2$ at 1000° and 1275°C. Irregularly shaped flakes, approximately 0.200 in. x 0.200 in. in cross section, were also included.

3.5. 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.

Thermal conductivity has been measured previously (Ref. 4) on Gilsonite and needle-coke materials after irradiation to about 6 to $7 \times 10^{21} \text{ n/cm}^2$ at 1000° and 1200°C. These experiments showed the fractional change in thermal conductivity to be large, ranging up to 80% after irradiation at ~1000° to 1100°C. Annealing at 1250° to 1700°C for 5 or 10 min produced a rapid rate of recovery of the thermal conductivity, followed by a much slower rate. An activation energy of ~5.8 eV was estimated from the annealing data on materials irradiated at ~1000°C to ~ $6.7 \times 10^{21} \text{ n/cm}^2$.

TABLE 3
COKES FOR IRRADIATION STUDIES

Source Material	Specimen No.	Estimated Maximum Heat-Treatment Temperature (°C)	Sulfur Content (wt %)	Graphitized Density ^(a) (g/cm ³)	Type of Specimen Irradiated
Air-blown asphalt	223A1	2675	-	2.038	Flake
Air-blown asphalt	223A2	2675	-	1.967	Flake
Air-blown asphalt	223A3	2675	-	1.986	Flake
Vacuum-reduced petroleum crude	223A4	2800	-	2.033	Flake
De-ashed coal	223A5	2810	1.04	2.115	Flake
Vacuum-reduced petroleum crude	223B1	2680	3.19	-	<38-μ powder
Vacuum-reduced petroleum crude	223B2	2805	6.2	-	<38-μ powder
Gilsonite coke	223B3	2815	-	-	<38-μ powder
Petroleum crude	A	2800	-	2.00	<38-μ powder
Petroleum crude	B	2800	-	2.09	<38-μ powder

(a) Density measured by immersion in liquid.

A new and more extensive series of specimens has been prepared from the same materials and will be irradiated in capsule GE-H-13-18. The pre-irradiation thermal conductivity data for a portion of the specimens are given in Table 4. About 130 specimens will be irradiated initially to about 0.3 to 4×10^{21} n/cm² at 550°, 800°, 1000°, and 1275°C.

3.6. 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. The specimens were prepared at Gulf General Atomic, and the irradiation and postirradiation measurements are being done at Dragon or RCN, Petten, Holland. The graphites varied widely in apparent crystallite sizes (L_c 500 to 1600 Å), and the effect of L_c on creep constants is being sought. The details of the materials and initial results of the unrestrained specimens were reported previously (Ref. 4).

Measurements of the restrained specimens have not been completed during the past year due to the heavy work load in the Petten Laboratory. At this time it is not certain when these measurements will be forthcoming. It is planned to return the survived specimens and perhaps a few virgin creep assemblies to the Dragon reactor for additional fluence after the current samples have been evaluated.

TABLE 4
THERMAL CONDUCTIVITY OF H-327 AND H-328 GRAPHITES

Material	Specimen No.	Orientation	Thermal Conductivity (cal/cm-sec-°C)
H-327	1	⊥	0.364
	2		0.365
	3		0.369
	4		0.351
	5		0.371
	6		0.372
	7		0.363
	8		0.365
	9		0.374
	10		0.361
	11		0.360
	12		0.374
H-327	81		0.525
	82		0.563
	83		0.524
	84		0.554
	85		0.550
	86		0.541
	87		0.549
	88		0.525
	89		0.531
	90		0.502
H-328	91	⊥	0.525
	92		0.505
	150		0.285
	151		0.280
	152		0.283
	153		0.276
	154		0.293
	155		0.277
	156		0.284
	157		0.285
	158		0.280
	159		0.283
	160		0.281
	161		0.273

4. CHARACTERIZATION AND IRRADIATION OF MODEL CARBONS

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

A number of new and previously irradiated model carbon specimens were prepared for irradiation in capsule GE-H-13-18. The experiment will include natural graphite crystals, LTI pyrolytic carbons, and HTI pyrolytic carbons. The pyrolytic carbons will be irradiated unrestrained in the form of discs and under restraint by depositing the carbon over small sapphire balls, which are known to be dimensionally stable under irradiation. The specimens will be irradiated at 900°, 1275°, and ~1400°C to 3 to 4 x 10²¹ n/cm².

A topical report, "Irradiation-Induced Dimensional Changes in Imperfect Graphite Crystals," has been written (Ref. 5).

5. TOPICAL REPORTS AND PUBLICATIONS

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

- GA-9421 "Apparatus and Procedure to Determine Density and Structural Distributions in Carbons and Graphites," G. B. Engle, W. H. Morris, and L. Bailey, June 8, 1969 (accepted for publication in Carbon).
- GA-9617 "Density and Structural Distributions in Artificial Graphites," G. B. Engle, June 29, 1969 (accepted for publication in Carbon).
- 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 (submitted 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 (submitted for publication in J. Am. Ceram. Soc.)
- 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).

- GA-10162 "Annealing of Neutron-Irradiated Pyrocarbons," R. J. Price and J. C. Bokros, June 8, 1970 (submitted for publication in Carbon).
- GA-9970 "Low-Temperature Graphitization of Cokes and Binder-Filler Artifacts," G. B. Engle, July 17, 1970 (to be submitted for publication in Carbon).
- GA-10101 "Irradiation-Induced Dimensional Changes in Imperfect Graphite Crystals," J. C. Bokros, G. L. Guthrie, and D. W. Stevens, June 29, 1970 (submitted for publication in Carbon).

REFERENCES

1. Engle, G. B., "Density and Structural Distributions in Artificial Graphites," accepted for publication in Carbon (GA-9617).
2. Bailey, B. L., U.S. Patent No. 3,284,372, "Apparatus and Process for Continuously Making Baked and Graphitized Carbon Bodies," Great Lakes Carbon Company, September 1965.
3. Engle, G. B., "Effect of Temperature History on the Dimensional Changes of Nuclear Graphites," USAEC Report GA-10001, Gulf General Atomic, March 23, 1970.
4. Engle, G. B., R. J. Price, J. C. Bokros, and J. L. White, "Research on Graphite, Three Year Summary Report, May 15, 1967, through May 14, 1970," USAEC Report GA-9975, Gulf General Atomic, June 1, 1970.
5. Bokros, J. C., G. L. Guthrie, and D. W. Stevens, "Irradiation-Induced Dimensional Changes in Imperfect Graphite Crystals," Gulf General Atomic Report GA-10101, June 29, 1970.