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

by

G. B. Engle, J. C. Bokros, 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

February 26, 1970

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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

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1. INTRODUCTION

The objective of this program is to develop an understanding of the relationships between the properties, microstructure, and irradiation behavior of the various carbonaceous and graphitic materials required for use in high-temperature reactors of advanced design. The research efforts are directed toward defining the structure of model carbons and porous graphites, learning the relation between structure and the properties relevant to reactor applications, and evaluating methods for the preparation of new or modified structures with improved properties.

The research program for the period covered by this report (November 15, 1969, through February 14, 1970) consisted of two principal tasks: (1) investigations of the structures and properties of carbon and graphites, and (2) studies of the effects of irradiation on these structures and properties.

The majority of the experimental data reported this period was obtained from capsule GE-H-13-17,* which was discharged in November 1969. The experimental work on this program has been essentially completed except for a few postirradiation measurements. The remainder of the contract period will be devoted to preparing topical reports on the various tasks plus a three-year summary report.

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

2. SUMMARY

Summaries are included only for sections in which data are reported. The data for the other tasks can be found in the references listed in the sections on these tasks.

DIMENSIONAL AND VOLUMETRIC CHANGES OF ANISOTROPIC AND NEAR-ISOTROPIC GRAPHITES

Needle-coke graphites expanded up to 50 vol-% when irradiated to 1.5×10^{22} n/sq cm at 1175 to 1280°C, whereas expansion of near-isotropic materials ranged up to 20%. Irradiation of a number of graphite specimens at 1000°C to 3×10^{21} n/sq cm followed by irradiation at 760 to 800°C to 5×10^{21} n/sq cm showed no reduction in the rate of dimensional change over other specimens irradiated to 5×10^{21} n/sq cm at 1000°C. Thermal expansivities of near-isotropic graphites were reduced, whereas those of needle cokes either remained unchanged or increased during irradiation. The changes were correlated with structural features of the materials. Large pores were observed micrographically in the graphites that expanded at high fluences.

IRRADIATION EFFECTS ON HIGHLY ORIENTED CARBONS AND GRAPHITES

Samples of hot-worked graphite and massive pyrolytic carbon (as-deposited and annealed) were measured after an additional irradiation period in capsule GE-H-13-17. Maximum exposures were 1.4×10^{22} n/sq cm at 1225 to 1300°C and 2×10^{21} n/sq cm at 750 to 800°C. Changes in dimensions, thermal expansivity, and X-ray diffraction parameters were measured.

GRAPHITE IRRADIATION CREEP EXPERIMENT IN COOPERATION WITH THE DRAGON PROJECT

Dimensional changes of graphite specimens irradiated in Dragon at 975 to 1240°C to 0.9 to 2.4×10^{21} n/sq cm compared favorably with data from the ETR experiments.

3. CHARACTERIZATION OF THE DEGREE OF GRAPHITIZATION OF CARBON AND GRAPHITE

G. B. Engle and L. Bailey

Studies of the structural and density distributions in a wide variety of nuclear graphites have been completed. The results were reported in two topical reports (Refs. 1,2).

An experimental graphite containing a two-phase filler, low-density carbon and needle coke, was prepared to study the behavior of a multiphase graphite under high-temperature irradiation. Fabrication details, properties, and characterization work have been reported (Ref. 3). Irradiation at 1250°C to 4×10^{21} n/sq cm has been completed, and post-irradiation examinations are underway. A topical report, "Irradiation-Induced Changes in a Multiphase Graphite," is being written (GA-9975).

4. CATALYTIC GRAPHITIZATION

G. B. Engle and J. M. Pontelandolfo

This task was undertaken to determine the effects of metal additives on the kinetics of annealing and on the properties of annealed pyrolytic carbon, and to explore the use of metal catalysts to promote enhanced crystal growth in filler cokes or binder-filler artifacts.

The experimental work on this task has been completed. A topical report is being written to cover the work on the annealing studies of pyrolytic carbons. The final phase of the experimental work concerning metal additive to cokes was reported previously (Ref. 4). This work will be reported in a topical report, "Low-Temperature Graphitization of Cokes and Binder-Filler Compacts" (GA-9970).

5. INFLUENCE OF PITCH-BINDER CONTENT ON THE PROPERTIES AND IRRADIATION
BEHAVIOR OF MOLDED GRAPHITE BODIES

G. B. Engle and L. Bailey

The influence of pitch-binder content on the microstructure, physical properties, and irradiation behavior of graphite bodies prepared by a standardized molding process has been under investigation. The objective of the work was to provide an understanding of the influence of the binder coke on the microstructure and irradiation behavior of conventional graphitic materials in terms of measurable physical and structural parameters.

The experimental work on this task has been completed and a topical report will be written (GA-9971).

6. DIMENSIONAL AND VOLUMETRIC CHANGES OF ANISOTROPIC AND NEAR-ISOTROPIC GRAPHITES

G. B. Engle, L. Bailey, J. Dixon, K. Koyama, and H. Evans

In this work the changes in dimensions, properties, microporosity, macroporosity, and structural features are being measured on a series of anisotropic and near-isotropic graphites. The graphites were described in Ref. 2.

The specimens in this series were previously irradiated to 11×10^{21} n/sq cm at 1250°C and 7×10^{21} n/sq cm at 1000°C. The data were reported previously (Ref. 3). A few of the specimens of each graphite type were reirradiated in capsule GE-H-13-17 in the ETR at 1250°C to about 15×10^{21} n/sq cm.

DIMENSIONAL CHANGES

Needle-coke graphites expanded 10 to 34% in the c-axis direction and -8 to +7.5% in the a-axis direction at 1175 to 1280°C. All needle-coke samples had gone through turnaround in the a-axis direction and were expanding. Volume expansions ranged from 20 to 50%. Gilsonite and raw-coke materials, which are near-isotropic, showed expansions of 7 to 9% in the c-axis direction and 2 to 5% in the a-axis direction under the same conditions. Again both directions were in the expansion phase after turnaround. Volume expansions ranged from 11 to 20%.

A number of needle-coke and near-isotropic graphite specimens were irradiated to 3×10^{21} n/sq cm at 1000°C and subsequently reirradiated an additional 2×10^{21} n/sq cm at 760 to 800°C to 5×10^{21} n/sq cm. All of these specimens continued to change dimensions

after the reduction in temperature at about the same rate as those specimens irradiated to the full 5×10^{21} n/sq cm at 1000°C. The total strain was the same in both sets of specimens. This behavior, which has been reported previously for pyrolytic carbons (Ref. 5), has now shown up in porous polycrystalline graphites.

Additional dimensional-change data on H-327 graphite irradiated at 600 to 1250°C to 10×10^{21} n/sq cm do not revise the present curves, but add further statistical evidence to confirm the present curves.

A near-isotropic Gilsonite graphite (grade H-378) contracted -2.30% perpendicular and -1.60% parallel at 1280°C and 3.75×10^{21} n/sq cm. Another Gilsonite material, H-328, showed contraction of -0.72% perpendicular and -0.73% parallel under identical conditions. The data on the H-378 graphite compare favorably with recent data from Dragon on No. 95 graphite (Ref. 6), which is a molded, triply pitch-impregnated Gilsonite graphite with a high modulus and a high coefficient of thermal expansion (CTE). The Dragon data were obtained under irradiation conditions similar to those for the H-378 graphite. The difference in the H-378 and H-328 graphites is quite interesting, since a number of other properties and parameters are nearly the same.

Natural flakes bonded with pitch (15 and 25 wt-%) and formed by hot molding showed large differences in dimensional changes at 1280°C and 3.75×10^{21} n/sq cm. With 15 wt-% pitch, the changes were -0.90% in the a-axis direction and +3.95% in the c-axis direction; with 25 wt-% pitch, the changes were -2.50% in the a-axis direction and +11.00% in the c-axis direction.

THERMAL EXPANSIVITY

Thermal expansivity measurements were made on a number of near-isotropic and anisotropic graphites taken to 1.5×10^{22} n/sq cm at

1175 to 1280°C and on H-327 graphite taken to 9.7×10^{21} n/sq cm at 1000°C. In the former series the changes in CTE are quite sensitive to structure and behave in a systematic manner. By including similar data, obtained on Poco graphite at BNWL (Ref. 7), with our data, a pattern emerges that shows the CTE of the near-isotropic materials (with initially high CTEs) to be drastically reduced (by a factor of 6 in the extreme case), whereas the CTE of needle cokes either does not change or increases considerably (by a factor of 2.8 in the extreme case). The other materials fall between these extremes. These changes can be correlated with structural differences through their mean apparent crystallite sizes $\bar{L}_c$, which are determined by combining sink-float separations with X-ray measurements (Ref. 2).

The H-327 data show the following changes with a dose at 1000°C to 9.7×10^{21} n/sq cm. The measurements were made on specimens from 13-in. diameter logs.

Dose x 10^{-21} (n/sq cm)	$\alpha \times 10^6 \text{ } ^\circ\text{C}^{-1}$ (22 to 500°C)		$\Delta\alpha/\alpha_0$ (%)	
		⊥		⊥
0	1.10	3.25	0	0
5.75	1.05	3.40	-4.5	+4.6
9.70	1.80	5.10	+63.0	+57.0

The increase appears to be significant and coincides with the volume expansion.

DENSITY CHANGES

Density measurements showed the graphites were becoming porous during the expansion phase at high fluences. Metallographic examination confirmed the density measurements and indicated that the pores form between grit particles at particle/binder-coke interfaces.

The results of the experimental work described above will be reported in two topical reports: "Irradiation Behavior of Nuclear Graphites at Elevated Temperature" (GA-9972) and "High-Temperature Irradiation Behavior of H-327 and H-328 Graphite" (GA-9973).

MISCELLANEOUS

A second series of graphites was irradiated in capsule GE-H-13-17 to determine the effect of crystallite orientation, crystallite size, and original density on neutron-induced densification. This series includes graphites that range from highly oriented materials made with natural flakes to extremely isotropic graphites such as Poco materials. Postirradiation examination of these materials is underway.

A series of experiments initiated earlier this year to measure the thermal conductivity of a number of irradiated graphites was completed. The thermal conductivity of specimens that were irradiated at high temperatures (625 to 1230°C) to high doses (2.9×10^{21} to 7.8×10^{21} n/sq cm) was measured at room temperature. A number of the specimens were annealed as a function of time in the range 1250 to 1700°C for 565 to 1700 min in an effort to gain information on the nature of the irradiation defects that cause degradation of the thermal conductivity.

Preliminary results of the annealing experiments showed an immediate recovery of a portion of the thermal conductivity degradation, followed by small changes up to the longest annealing times at 1250 to 1700°C.

The results of the thermal conductivity experiments will be reported in a topical report, "Effect of High-Temperature Irradiation on Thermal Conductivity of Graphites at High Neutron Fluences" (GA-9974).

7, IRRADIATION EFFECTS ON HIGHLY ORIENTED CARBONS AND GRAPHITES

R. J. Price

Highly oriented, single-phase carbons and graphites of various crystallite sizes that are free from gross porosity were irradiated in capsule GE-H-13-17. The samples consisted of hot-worked graphite, as-deposited massive pyrolytic carbons, and massive pyrolytic carbon annealed at various temperatures between 2900 and 3300°C. The apparent crystallite sizes of these materials cover the range encountered in polycrystalline nuclear graphites.

Previous results were described in Ref. 3. During the present reporting period, the samples were measured after receiving an increment of fluence of 3.8×10^{21} n/sq cm at 1300°C and 0.55×10^{21} n/sq cm at 780°C. The changes in dimensions were measured on all samples, and the postirradiation thermal expansivities, X-ray diffraction parameters, and metallographic microstructures were measured on selected samples. Full results will be presented in a topical report, and only a summary is given here.

At ~800°C the rate of c-axis expansion and a-axis contraction of both hot-worked graphite and massive pyrolytic carbon as a function of exposure slowly increases with exposure. At ~1250°C, the dimensional changes of massive pyrolytic carbon (both as-deposited and annealed) in both directions are a linear function of neutron exposure, whereas the dimensional change rates in hot-worked graphite decrease with increasing exposure. For $\sim 1.4 \times 10^{22}$ n/sq cm at ~1250°C, expansions parallel to the hot-working axis are about 50% true strain, and the perpendicular contractions are about 18% true strain.

Samples of massive pyrolytic carbon annealed at 2900, 3000, and 3100°C before irradiation showed decreasing dimensional changes with increasing annealing temperature. Since the macroscopic dimensional changes in these materials are very close to the a-axis and c-axis crystallite strains, these measurements provide direct data on the variation of crystallite strain rate with the degree of crystallinity for material in the intermediate crystallite size range.

The thermal expansivity of massive pyrolytic carbon measured parallel to the deposition plane is not affected by irradiation. Perpendicular to the deposition plane, the thermal expansivity measured at 400°C rises from $25 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ at zero fluence to $27 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ at $\sim 2 \times 10^{21} \text{ n/sq cm}$ at $\sim 1250^{\circ}\text{C}$ and then remains constant. For irradiation at $\sim 800^{\circ}\text{C}$, the expansivity remains unchanged up to $2 \times 10^{21} \text{ n/sq cm}$.

The thermal expansivity of hot-worked graphite changes considerably upon irradiation. As reported previously (Ref. 3), during irradiation at $\sim 1250^{\circ}\text{C}$ the thermal expansivity parallel to the hot-working axis first increases, then passes through a maximum, and then progressively decreases with increasing fluence. The present results show that this trend continues to $1.4 \times 10^{22} \text{ n/sq cm}$, where the thermal expansivity has been reduced to $6 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ from its peak value of $19 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$. The trends in volume expansivity of hot-worked graphite as a function of neutron exposure are, therefore, very similar to those observed in isotropic graphites, in spite of the high degree of orientation in the former material. Metallographic examination shows that hot-worked graphite is also resistant to the irradiation-induced opening of cleavage cracks.

8. GRAPHITE IRRADIATION CREEP EXPERIMENT IN COOPERATION WITH THE DRAGON PROJECT

G. B. Engle and R. J. Price

A joint experiment between Gulf General Atomic (GGA) and Dragon to measure the irradiation-induced creep in a number of nuclear graphites is in progress at Dragon. The irradiation phase of this experiment has been completed, and the specimens are undergoing post-irradiation measurements at Dragon and Reactor Centrum Nederland (RCN), Petten, Netherlands.

The results for the free-standing specimens have been forwarded to GGA. However, measurement of the creep assemblies has been further delayed due to a heavy work load in the Petten Laboratory. These measurements are now expected in March or April 1970.

The dimensional changes of the free-standing graphite specimens were measured after irradiation to 0.9×10^{21} to 2.4×10^{21} n/sq cm at 975 to 1240°C. The specimens included needle-coke graphites H-327, 9567, and TS-688; a Gilsonite graphite H-328; and highly aligned materials that were hot-worked to various strains, ZTA and GGA-HW. These materials were used either as samples or as straining pads in the creep assemblies. The dimensional changes of the needle cokes and Gilsonite graphites compared favorably with changes in similar materials irradiated in the ETR (Section 6), while the behavior of the hot-worked materials was similar to that of the specimens discussed in Section 7.

A joint GGA-Dragon report will be issued when the measurements of the creep assemblies are completed.

9. ANNEALING STUDIES OF IRRADIATED PYROLYTIC CARBON STRUCTURES

R. J. Price, J. C. Bokros, W. H. Ellis, J. M. Dixon,
F. J. Gagnon, and J. M. Pontelandolfo

Annealing studies were carried out on a series of pyrolytic carbons irradiated between 540 and 1060°C to 1.5×10^{21} n/sq cm. Details of the samples and the annealing-induced changes in density, dimensions, layer spacing, apparent crystallite size, and electrical resistivity were reported previously (Ref. 3). A topical report on these studies is being written.

10. IRRADIATION EFFECTS IN CARBONS AND GRAPHITES

J. C. Bokros, W. H. Ellis, F. Gagnon, and R. Weed

The experimental work on this task has been completed, and the results will be reported in GA-9900.

11. TOPICAL REPORTS AND PUBLICATIONS

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

Bokros, J. C., "Fission Recoil Damage to Pyrolytic Carbon," accepted for publication in Carbon (GA-9054).

Bokros, J. C., and K. Koyama, "Interpretation of Dimensional Changes Caused in Pyrolytic Carbon by High Fluence Neutron Irradiation," submitted to Carbon (GA-9600).

Engle, G. B., W. H. Morris, and L. Bailey, "Apparatus and Procedure to Determine Density and Structural Distributions in Carbons and Graphites," accepted by Carbon as a Letter to the Editor (GA-9421).

Engle, G. B., "Density and Structural Distributions in Artificial Graphites," accepted for publication in Carbon (GA-9617).

Bokros, J. C., and D. W. Stevens, "Irradiation Behavior of Isotropic Carbons," in preparation (GA-9900).

REFERENCES

1. Engle, G. B., W. H. Morris, and L. Bailey, "Apparatus and Procedure to Determine Density and Structural Distributions in Carbons and Graphites," accepted for publication in Carbon (GA-9421).
2. Engle, G. B., "Density and Structural Distributions in Artificial Graphites," accepted for publication in Carbon (GA-9617).
3. Engle, G. B., J. C. Bokros, and R. J. Price, "Research on Graphite, Annual Report, May 15, 1968, through May 14, 1969," USAEC Report GA-9433, Gulf General Atomic, June 17, 1969.
4. Engle, G. B., J. C. Bokros, and R. J. Price, "Research on Graphite, Quarterly Progress Report for the Period Ending November 14, 1969," USAEC Report GA-9828, Gulf General Atomic, November 20, 1969.
5. Bokros, J. C., and D. W. Stevens, "Irradiation Behavior of Isotropic Carbons," Gulf General Atomic Report GA-9900, February 24, 1970.
6. Everett, M. R., et al., "Dimensional and Physical Property Changes of High-Temperature Reactor Graphites Irradiated at Temperatures in the Range 600-1200°C," Dragon Project, unpublished data.

7. Pitner, A. J., "The Irradiation Behavior of Poco Graphites," paper presented at the 9th Biennial Conference on Carbon, Boston College, Boston, Massachusetts, June 16-20, 1969.
8. Engle, G. B., J. C. Bokros, and R. J. Price, "Research on Graphite, Quarterly Progress Report for the Period Ending August 14, 1969," USAEC Report GA-9675, Gulf General Atomic, August 27, 1969.