aw

RECEIVED BY DTIC NOV 30 1971

GULF GENERAL ATOMIC

Gulf-GA-A10694

RESEARCH ON GRAPHITE

ANNUAL REPORT

MAY 15, 1970, THROUGH JUNE 30, 1971

by

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

THIS DOCUMENT CONFIRMED AS
UNCLASSIFIED
DIVISION OF CLASSIFICATION
BY QH Kahn / amh
DATE 12/7/71

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

Date Published - November 15, 1971

GULF GENERAL ATOMIC COMPANY
P.O. BOX 608, SAN DIEGO, CALIFORNIA 92112

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

R2343

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

GULF GENERAL ATOMIC

Gulf-GA-A10694

RESEARCH ON GRAPHITE
ANNUAL REPORT
MAY 15, 1970, THROUGH JUNE 30, 1971

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

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

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

Gulf General Atomic Project 271

Date Published - November 15, 1971

GULF GENERAL ATOMIC COMPANY
P.O. BOX 608, SAN DIEGO, CALIFORNIA 92112

UNCLASSIFIED DOCUMENT IS UNLIMITED

34

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

ABSTRACT

Nuclear graphites having a wide range of microstructures and properties and model carbon materials were irradiated in the range 1 to 20×10^{21} n/cm² at 500° to 1430°C. The materials were characterized prior to irradiation by measurement of physical and mechanical properties and densities, and examination of microstructure by X-ray diffraction and microscopy. Dimensional, density, structural, and property changes were measured after irradiation.

Anisotropic needle-coke graphites and isotropic graphites were shown to have structural and property variations that lead to variations in their high-temperature irradiation behavior. A high original strength leads to less initial contraction and a delay in the final expansion at high fluences. Isotropic graphites in general have higher strength values than the anisotropic materials. However, high preirradiation strength was found to be more important than isotropy in inhibiting breakaway growth in highly oriented graphites at high fluences. Graphites with intermediate apparent densities, as measured by immersion in liquid, tend to show smaller density changes than those of low or high densities. However, bulk density changes do not always follow the changes of these apparent densities.

When graphites are irradiated initially at a high temperature, i.e., 1000° to 1200°C, to an intermediate fluence and then taken to higher fluences at a temperature ~200°C lower, the dimensional change at the lower temperature appears to be influenced by the previous higher temperature irradiation in such a way that the data fall within the same band of data from similar samples irradiated to higher fluences at the higher temperatures. However, additional data are required at all fluences up to 10^{22} n/cm² to evaluate the magnitude of this effect. At 1000° to 1200°C thermal expansivity changes depend upon the graphite structure; certain needle-coke materials show an

increase coinciding with volume increase at high fluences, whereas isotropic materials show a decrease. The thermal expansivity of one graphite composed of both anisotropic and isotropic structure did not change up to 2×10^{22} n/cm². Thermal conductivity is reduced to about 0.02 cal/cm-sec-°C after irradiation to 2×10^{22} n/cm². This reduction coincides with the formation of large volumes of porosity in the graphites. Degradation of thermal conductivity is dependent on temperature in the range 800° to 1430°C at low fluences, the specimens irradiated at 1430°C showing the smallest fractional changes.

Cokes, which are the filler component in commercial graphites, were characterized and irradiated.

Irradiation of model carbons to high fluences at high temperatures shows that for maximum stability, carbonaceous materials should be perfectly isotropic and have high strength and intermediate densities. The thermal conductivity of carbons with L_c values greater than $100 \text{ \AA}$ showed a reduction in thermal conductivity that saturated with increasing fluence. The reduction was less for higher irradiation temperatures. The thermal conductivity of carbons with smaller L_c values increased or decreased depending on irradiation conditions.

CONTENTS

ABSTRACT	iii
1. INTRODUCTION	1
2. SUMMARY.	3
2.1. Graphites.	3
2.1.1. Description and Properties of Graphites.	3
2.1.2. Density and Structural Distributions in Graphites.	3
2.1.3. Dimensional and Structural Changes of Graphites at High Temperatures and High Fluences	3
2.1.4. Effect of Crystallite Size, Crystallite Orientation, Strength, and Original Density on Dimensional and Volumetric Changes in Graphites	4
2.1.5. Effect of Temperature History on Dimensional Changes of Graphites	4
2.1.6. Thermal Expansivity Changes in Graphites	4
2.1.7. Thermal Conductivity Changes in Graphite	5
2.1.8. Creep in Graphites	5
2.1.9. Irradiation Effects in Highly Oriented Carbons and Graphites.	5
2.2. Coke Studies	6
2.3. Characterization and Irradiation of Model Carbons.	6
2.4. Thermal Conductivity of Neutron-Irradiated Pyrolytic Carbons.	6
3. CHARACTERIZATION AND IRRADIATION OF COKES AND GRAPHITES.	8
3.1. Graphites.	8
3.1.1. Description and Properties of Graphites.	8
3.1.2. Density and Structural Distributions in Graphites.	8
3.1.3. Dimensional and Structural Changes of Graphites at High Temperatures and High Fluences	17
3.1.4. Effect of Crystallite Size, Crystallite Orientation, Strength, and Original Density on Dimensional and Volumetric Changes in Graphites.	24
3.1.5. Effect of Temperature History on Dimensional Changes of Graphites	36

3.1.6.	Thermal Expansivity Changes in Graphites	43
3.1.7.	Thermal Conductivity Changes in Graphites.	47
3.1.8.	Creep in Graphites	52
3.1.9.	Irradiation Effects in Highly Oriented Carbons and Graphites.	52
3.2	Coke Studies	58
4.	CHARACTERIZATION AND IRRADIATION OF MODEL CARBONS.	63
4.1.	Dimensional and Volumetric Changes of Model Carbons.	63
4.1.1.	Introduction	63
4.1.2.	Dependence of Irradiation-Induced Dimensional Changes on the Degree of Preferred Orientation . . .	63
4.1.3.	Dependence of Irradiation-Induced Volume Changes on Preirradiation Density.	64
4.1.4.	Dependence of Irradiation-Induced Dimensional Changes of Isotropic Carbons on Their Preirradiation Density	69
4.1.5.	Implications of the Behavior of the Model Carbons to Desired Properties in Artificial Graphites. . . .	69
4.2.	Thermal Conductivity of Neutron-Irradiated Pyrolytic Carbons.	73
4.2.1.	Experimental	73
4.2.2.	Irradiation-Induced Changes in Room-Temperature Conductivity	76
4.2.3.	Temperature Dependence of Thermal Conductivity . . .	80
5.	TOPICAL REPORTS AND PUBLICATIONS	89
	ACKNOWLEDGMENTS.	91
	REFERENCES	92

FIGURES

1.	Density distributions in a needle-coke graphite (CHN) and a Gilsonite-coke graphite (H-328)	12
2.	Apparent crystallite size (L_c) versus apparent density for a needle-coke graphite (CHN) and a Gilsonite-coke graphite (H-328). .	13
3.	SEM photomicrographs of CHN needle-coke graphite density fractions	15
4.	SEM photomicrographs of H-328 Gilsonite-coke graphite density fractions	16

5. Dimensional changes versus fluence for anisotropic needle-coke graphites and near-isotropic graphites.	18
6. Density changes of anisotropic needle-coke and near-isotropic graphites	20
7. Volume expansion rates of anisotropic needle-coke and near-isotropic graphites versus original modulus of rupture at 1175° to 1290°C	23
8. Photomicrographs of graphites after irradiation to 2×10^{22} n/cm ² at 1175° to 1290°C.	25
9. Dimensional changes of graphites irradiated at 1000° to 1330°C to 8.3×10^{21} n/cm ²	26
10. Original density measured by immersion in a liquid versus irradiated density for graphites at 1175° to 1330°C	33
11. Modulus of rupture (unirradiated) versus initial contraction of isotropic graphites irradiated to 3.85×10^{21} n/cm ² at 1000°C.	35
12. Dimensional changes of graphites irradiated initially at 1000°C or 1200°C and subsequently at reduced temperatures.	37
13. Thermal expansivity changes in the c-axis direction of graphites as a function of fluence.	44
14. Fractional change in thermal conductivity of needle-coke and Gilsonite-coke graphites as a function of fluence	48
15. Thermal conductivity of graphites versus fluence at 500° to 1430°C.	50
16. Dimensional changes in massive pyrolytic carbon and hot-worked graphite irradiated at 750° to 800°C.	55
17. Dimensional changes in annealed massive pyrolytic carbon irradiated at 1225° to 1300°C	56
18. Dimensional changes in hot-worked graphite irradiated at 1225° to 1300°C	57
19. Shape change data for anisotropic specimens at constant high density	65
20. Density changes of HTI carbons versus fluence	67
21. Dependence of the dimensional changes of HTI carbons on preirradiation density.	70
22. Dimensional changes of HTI carbons as a function of fast neutron fluence at 1250°C	72
23. Irradiation-induced change in room-temperature thermal conductivity of HTI pyrolytic carbons as a function of fast neutron fluence	77

24.	Irradiation-induced change in room-temperature thermal conductivity of HTI pyrolytic carbons irradiated to 3.1 to 5.7×10^{21} n/cm ² ($E > 0.18$ MeV) as a function of irradiation temperature	78
25.	Irradiation-induced change in room-temperature thermal conductivity of HTI pyrolytic carbons as a function of apparent crystallite height, L_c	79
26.	Irradiation-induced change in L_c of HTI pyrolytic carbons as a function of fast neutron fluence	81
27.	Irradiation-induced change in L_c of HTI pyrolytic carbons irradiated to 3.1 to 5.7×10^{21} n/cm ² ($E > 0.18$ MeV) as a function of irradiation temperature	82
28.	Irradiation-induced change in apparent crystallite height, L_c , of HTI pyrolytic carbons as a function of original apparent crystallite height.	83
29.	Thermal conductivity of HTI pyrolytic carbon 3353-147 as a function of measuring temperature	84
30.	Porosity-tortuosity factor, γ , for pyrolytic carbons as a function of their Bacon anisotropy factor, and mean phonon-scattering boundary spacing, L_a , for pyrolytic carbons as a function of apparent crystallite height, L_c , derived from X-ray line broadening.	86
31.	Structure of isotropic pyrolytic carbons.	88

TABLES

1.	Description of Graphites.	9
2.	Properties of Graphites Prior to Irradiation.	10
3.	Dimensional Changes of Graphites Irradiated at 500° to 1430°C and 0.9 to 5.2×10^{21} n/cm ² ($E > 0.18$ MeV).	31
4.	Thermal Conductivity of H-327 and H-328 Graphites Prior to Irradiation	49
5.	Structural Parameters for Highly Oriented Carbons and Graphites .	53
6.	Cokes for Irradiation Studies	59
7.	Density and X-ray Parameters of Cokes	60
8.	Densimetric Data on Petroleum Cokes A and B	61
9.	Structural Properties and Thermal Conductivities of Irradiated Pyrolytic Carbons	74

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 and thus to provide a basis for substantial improvements in the service behavior of these materials. The carbons and graphites of current interest in nuclear technology are composed of carbon in a variety of structural states, ranging from nearly amorphous forms to highly crystalline.

The research program for the period covered by this report, May 15, 1970, through June 30, 1971, consisted of two principal tasks: (1) characterization and irradiation of graphites and (2) characterization and irradiation of model carbons. A list of topical reports and publications resulting from work on this program during the reporting period is given in Section 5.

Two types of materials are under study: (1) graphitic bodies prepared from conventional binder and filler materials, and (2) pyrolytic carbons prepared by the decomposition of hydrocarbons in fluidized beds. The conventional graphites are either prepared in the laboratory or obtained from the major carbon and graphite companies. The pyrolytic carbons provide model materials whose structures can be closely controlled through adjustment of the deposition and annealing conditions.

The various structures of conventionally processed graphites as well as pyrolytic carbons are characterized by their crystallinity (X-ray diffraction parameters), preferred orientation, density, and microstructure. The investigations of conventional graphites include micrographic studies

of the structure and characterization of the degree of graphitization of carbonaceous and graphitic materials by densimetric separation.

The irradiation studies were carried out under the fast-neutron-flux and high-temperature conditions that are representative of the operating conditions of advanced reactor systems. The objectives are to define the changes in dimensions and other relevant properties as a function of structure and thus reveal the structures of greatest stability under irradiation. The principal properties of interest are dimensional changes, mechanical properties, irradiation creep, and thermal properties.

The irradiation experiments have been conducted in irradiation capsules operated in conjunction with other programs, e.g., the HTGR Base Program (Contract AT(04-3)-167, Project Agreement No. 17) at Gulf General Atomic, and in cooperative irradiations with the Battelle Pacific Northwest Laboratory. The capsules were fully instrumented.

2. SUMMARY

2.1. GRAPHITES

2.1.1. Description and Properties of Graphites

The graphites under study in this program are summarized in this report. The graphites range from highly anisotropic materials made with natural flakes to monolithic graphites that have no apparent second binder phase. These materials represent a wide range of microstructures and properties.

2.1.2. Density and Structural Distributions in Graphites

Anisotropic and isotropic graphites were comminuted and separated more completely than previously. Examination of the density fractions of an impregnated needle-coke material revealed two types of carbon in the light fractions, small platelets and glassy carbon, and needle-like particles in the heavy fractions. The density fractions of the isotropic graphites were composed of small uniform platelets throughout. The small platelets in the isotropic graphites and the light fractions of the needle-coke graphites were similar in size to the distance between extinction contours observed in calcined isotropic cokes.

2.1.3. Dimensional and Structural Changes of Graphites at High Temperatures and High Fluences

A number of anisotropic and isotropic graphites were irradiated to 2×10^{22} n/cm² at 1175° to 1290°C. The rate of expansion of the bulk volume at high fluences after the initial densification was dependent upon the strength of the graphites before irradiation; the strongest materials expanded at the lowest rates. Expansion of the fine structure was more

dependent upon the crystallite orientation; the isotropic structures expanded at the lowest rates. Needle-coke materials start net expansion at 4 to 6 $\times 10^{21}$ n/cm², whereas net expansion in isotropic material is delayed until about 8 to 11 $\times 10^{21}$ n/cm² at about 1200°C.

2.1.4. Effect of Crystallite Size, Crystallite Orientation, Strength, and Original Density on Dimensional and Volumetric Changes In Graphites

Graphites of low apparent density (as measured on a bulk sample by immersion in liquid) contract at 1200° to 1330°C and low fluences (3×10^{21} n/cm²), while those of intermediate or high densities show little change. At higher fluences (8×10^{21} n/cm²) all graphites originally between 1.95 to 2.21 g/cm³ reach the same density, or about 2.14 g/cm³. Isotropic graphites (isotropy factors of 1.01 to 1.09 and apparent crystallite sizes of 200 to 600 Å) have an initial contraction rate that appears to be dependent on the preirradiation strength, the strongest contracting at the lowest rate.

2.1.5. Effect of Temperature History on Dimensional Changes of Graphites

Graphites were irradiated initially to 3 to 5 $\times 10^{21}$ n/cm² at 1000°C or 1200°C and then to higher fluences of 5 to 12 $\times 10^{21}$ n/cm² at 800° or 1000°C, respectively. The dimensional change of the specimens irradiated at the reduced temperatures appears to be influenced by the previous higher temperature irradiation in such a way that the data fall within the same data population of samples irradiated to higher fluences at the higher temperatures. Some of the graphite specimens showed net expansions.

2.1.6. Thermal Expansivity Changes in Graphites

Thermal expansivity changes were measured on graphites irradiated to 2×10^{22} n/cm² at 1175° to 1290°C. The thermal expansivity values show little change up to fluences of about 4 to 6 $\times 10^{21}$ n/cm². In the range 6 to 15 $\times 10^{21}$ n/cm², certain needle-coke structures show an increase, while isotropic structures show a decrease. In the range 15 to 20 $\times 10^{21}$ n/cm², there was no further change. One material, which is a combination of

anisotropic and isotropic structures, showed no change over the entire range from 0 to 2×10^{22} n/cm².

2.1.7. Thermal Conductivity Changes in Graphite

The thermal conductivity changes of a needle-coke graphite and a Gilsonite-coke graphite have been measured after irradiation to 2×10^{22} n/cm² at 1175° to 1290°C. The fractional change in the thermal conductivity was less (50%) after irradiation to about 3 to 7×10^{21} n/cm² at about 1200°C than at 1000°C (70%). The thermal conductivity of all materials measured was reduced to about 0.02 cal/cm-sec-°C after irradiation to 2×10^{22} n/cm² at about 1200°C. This degradation coincides with the large pore generation due to volume expansion.

2.1.8. Creep in Graphites

No new data were obtained from the cooperative Gulf General Atomic and Dragon creep experiment. A decision is pending by Dragon on whether to continue with further measurements or to terminate the experiment.

2.1.9. Irradiation Effects in Highly Oriented Carbons and Graphites

Samples of hot-worked graphite and massive pyrolytic carbon annealed at various temperatures before irradiation are being irradiated at 750° to 800°C and 1225° to 1300°C. At 750° to 800°C the dimensional change rates increase with increasing fluence. At 1225° to 1300°C the dimensional change rates of the annealed pyrolytic carbons remain constant with increasing fluence, with the carbons annealed at the highest temperature showing the lowest change rates. At the same irradiation temperature, the dimensional change rates of the hot-worked graphite decrease with increasing fluence. This indicates that high strength, and not isotropy, is the important factor in inhibiting breakaway growth in polycrystalline graphites at high fluences.

2.2. COKE STUDIES

Cokes prepared from various feedstocks were characterized and irradiated at 800° to 1330°C to 5×10^{21} n/cm² to determine changes in density. Cokes from air-blown asphalt, vacuum-reduced crudes, de-ashed coal, Gilsonite, and other petroleum crudes were included in this study. Postirradiation examinations have not been completed on these materials.

2.3. CHARACTERIZATION AND IRRADIATION OF MODEL CARBONS

Irradiation of model materials was continued to fluences of 1.8×10^{22} n/cm² at 1000° to 1250°C. These studies show maximum irradiation stability in carbonaceous materials to result from perfectly isotropic structures. The rate of crystallite dimensional changes is higher at 1250°C than at 1000°C. At high fluences the dimensional changes accelerate continuously with increasing density. At 1000° and 1250°C, the initial densification in carbon structures is followed by expansion until all carbons reach the same density. If mechanical strength of the carbon is high, it will not enter the expansion phase as quickly as a weaker material. The information developed on the model carbons indicates that artificial graphites should be isotropic and have intermediate densities and high mechanical strength, which implies an intermediate crystallite size.

2.4. THERMAL CONDUCTIVITY OF NEUTRON-IRRADIATED PYROLYTIC CARBONS

Measurements of the thermal conductivity of high-temperature isotropic (HTI) pyrolytic carbons obtained in earlier years were assembled and analyzed. For carbons with L_c greater than ~ 100 Å, the conductivity was always reduced by irradiation. The reduction tended to saturate with increasing fluence and was less for higher irradiation temperatures. Carbons with smaller L_c values experienced either an increase or decrease in conductivity, depending on the irradiation conditions. The temperature dependence of the thermal conductivity was analyzed by Kelly's model for thermal conduction in defected graphite crystals. The analysis indicated high values (80 to 180) for the

porosity-tortuosity factor and values of ~ 0.5 to $1 \mu\text{m}$ for the phonon mean-free path between scattering boundaries. These values are reasonable if conduction takes place through the oriented "skins" of the spherules from which isotropic pyrolytic carbons are built up.

3. CHARACTERIZATION AND IRRADIATION OF COKES AND GRAPHITES

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

3.1. GRAPHITES

3.1.1. Description and Properties of Graphites

A description of the graphites being studied is given in Table 1. Some of the graphites described in Table 1 have been under irradiation during previous years (Refs. 1-4), others have been under irradiation only during the current contract year, and others were added to the program during the current year and, thus, have not been irradiated. The properties of the graphites prior to irradiation are given in Table 2.

3.1.2. Density and Structural Distributions in Graphites

The wide variety of coke sources and processing methods utilized to manufacture graphites leads to a wide range of microstructures and properties. Thus, the response of these graphites to high-temperature neutron irradiation has been observed to differ considerably depending upon their microstructural features and morphology (Ref. 1). Studies conducted with model carbons (Ref. 6) have shown the irradiation behavior of carbonaceous materials at high temperatures to be sensitive to the crystallite size. The materials that were strong, of intermediate crystallite size, and isotropic were found to be most stable (Ref. 1). In earlier work (Ref. 7), a number of artificial graphites were studied by means of a densimetric technique (Ref. 8) where the specimens were comminuted to powder and the particles were separated according to their densities. The density fractions of the anisotropic graphites were shown to vary in apparent crystallite size, whereas the density fractions of the isotropic materials were

TABLE 1
DESCRIPTION OF GRAPHITES

Material	Source ^(a)	Type	Forming Method	Filler Coke	Binder	Impregnant	Remarks	Ref.
AXF-5QB	PoCo	Isotropic	(b)	(b)	(b)	(b)	(c)	1
AXF-5QGB	PoCo	Isotropic	(b)	(b)	(b)	(b)	(c)	1
AXF-8QGB	PoCo	Isotropic	(b)	(b)	(b)	(b)	(d)	--
H-419	GLCC	Isotropic	(b)	(b)	(b)	(b)	(d)	-
HL-18	ACS	Isotropic	(b)	(b)	(b)	(b)	(c,d)	--
H-315-A	CLCC	Isotropic	BKR	Gilsonite	Coal-tar pitch	Coal-tar pitch	(e)	1,2,3
H-328	GLCC	Isotropic	Molded	Gilsonite	Coal-tar pitch	Coal-tar pitch	--	1,4
H-378	GLCC	Isotropic	Molded	Gilsonite	Coal-tar pitch	Coal-tar pitch	--	1
ATJ-SG	UCC-ORNL	Isotropic	(b)	Gilsonite	(b)	(b)	(c)	1
A-681	SCC	Isotropic	(b)	Carbon black	(b)	(b)	(d)	--
H-421	GLCC	Isotropic	BKR	(b)	(b)	(b)	(d,e)	--
H-319	GLCC	Isotropic	BKR	Uncalcined petroleum coke	Coal-tar pitch	Coal-tar pitch	(e)	1,2,3
H-337	GLCC	Isotropic	(b)	Uncalcined petroleum coke	(b)	(b)	(c,d)	--
H-429	GLCC	Isotropic	Extruded	Petroleum coke	Coal-tar pitch	(b)	(d)	--
H-430	GLCC	Isotropic	Molded	Petroleum coke	Coal-tar pitch	(b)	(d)	--
H-431	GLCC	Isotropic	(b)	Needle coke	Coal-tar pitch	(b)	(d)	--
CHN	UCC	Anisotropic	Extruded	Needle coke	Coal-tar pitch	Nongraphitizing carbon	--	1,2,3
711-TS	ACS	Anisotropic	Extruded	Needle coke	Coal-tar pitch	Coal-tar pitch	--	1,2,3
H-327-Pro	GLCC	Anisotropic	Extruded	Needle coke	Coal-tar pitch	Coal-tar pitch	Prototype, 13-in.-diam	1,4
H-327-P	GLCC	Anisotropic	Extruded	Needle coke	Coal-tar pitch	Coal-tar pitch	Production, 18-in.-diam ^(d)	--
H-283	GLCC	Anisotropic	BKR	Needle coke	Coal-tar pitch	Coal-tar pitch	(e)	1,2,3
NF-15	GGA	Anisotropic	Molded	Natural flake graphite	Coal-tar pitch	None	(d)	--
NF-25	GGA	Anisotropic	Molded	Natural flake graphite	Coal-tar pitch	None	--	1

(a) PoCo Graphite Co. (PoCo), Great Lakes Carbon Co. (GLCC), AirCo Speer, Division of Air Reduction Corp. (ACS), Union Carbide Co. (LCC), Stackpole Carbon Co. (SCC), Gulf General Atomic Co. (GGA).

(b) Unknown to author.

(c) Supplied by ORNL from Molten Salt Reactor Materials Program.

(d) Added to the program during current contract year.

(e) Fabricated under pressure (Ref. 5).

TABLE 2
PROPERTIES OF GRAPHITES PRIOR TO IRRADIATION

Material	Density (g/cm ³)			Anisotropy Ratio (α_c/α_a)	BAF	Thermal Expansivity x 10 ⁶ (°C ⁻¹) (RT-1000°C)			Modulus of Rupture (psi)						Mean Apparent Crystallite Size, $\bar{L}_c$ (Å°)
	Bulk	Immersion in Liquid					⊥ ₁	⊥ ₂		σ	⊥ ₁	σ ₁	⊥ ₂	σ ₂	
		Bulk	Powder												
AFX-5QB	1.88	2.114	2.190	1.05	1.06	8.35	7.95	--	--	--	--	--	--	--	400
AFX-5QGB	1.90	2.161	2.190	1.06	1.03	8.00	8.45	--	--	--	--	--	--	--	400
AFX-8QGB	1.90	2.066	2.155	1.06	--	7.60	7.20	--	14,180	840	13,200	755	--	--	~400
H-419	1.79	2.143	2.195	1.01	--	8.15	7.95	--	9,885	655	10,160	425	--	--	328
HL-18	1.86	2.100	2.115	1.02	--	5.60	5.50	--	8,810	374	8,685	325	--	--	273
H-315-A	1.85	2.040	2.190	1.09	1.11	5.30	4.85	--	5,535	170	6,195	185	--	--	520
H-328	1.73	2.035	2.165	1.04	1.10	6.25	6.00	--	4,955	490	5,050	400	--	--	430
H-378	1.81	2.032	2.175	1.07	1.00	6.70	6.25	--	--	--	--	--	--	--	435
ATJ-SG	1.79	1.955	2.100	1.18	1.09	4.95	4.20	--	--	--	--	--	--	--	530
A-681	1.63	2.095	2.110	1.01	--	6.45	6.40	--	5,740	320	5,540	40	--	--	186
H-421	1.77	2.045	2.155	1.01	--	6.65	6.70	--	4,050	405	3,950	325	--	--	280
H-319	1.80	1.980	2.140	1.02	0.90	4.05	4.15	--	3,955	805	4,750	630	--	--	620
H-337	2.02	2.140	2.190	1.05	--	5.90	5.60	--	5,545	270	5,640	345	--	--	730
H-429	1.73	2.075	2.225	1.19	--	4.65	5.55	--	4,925	220	4,555	290	--	--	618
H-430	1.73	2.080	2.227	1.11	--	5.55	5.00	--	4,390	305	4,285	425	--	--	486
H-431	1.74	2.141	2.235	1.05	--	3.25	3.10	3.10	2,495	110	3,245	200	2775	400	832
CHN	1.85	2.040	2.215	1.67	0.74	2.10	3.50	--	6,560	265	3,970	295	--	--	880
711-TS	1.78	1.900	2.150	1.33	0.80	2.15	2.85	--	7,220	135	4,815	730	--	--	850
H-327-Pro	1.75	2.080	2.230	1.77	0.70	1.75	3.10	--	2,860	225	2,555	295	--	--	1240
H-327-PC	1.73	2.060	2.225	1.94	--	1.60	3.10	--	4,210	295	2,965	330	--	--	1065
H-327-PE	1.79	2.080	2.225	2.10	--	1.50	3.15	--	--	--	--	--	--	--	1122
H-283	1.78	2.100	2.175	2.55	1.22	2.55	1.00	--	--	--	--	--	--	--	975
NF-15	1.76	2.130	2.200	5.87	--	11.15	1.90	--	--	--	--	--	--	--	--
NF-25	1.62	2.130	2.200	4.37	2.05	8.95	2.05	--	--	--	--	--	--	--	1740

more uniform. Thus, from the data in Refs. 6 and 7 it was concluded that in certain artificial graphites which contain a range of crystallite sizes, each structure will respond differently to fast neutrons at high temperatures. The response of each fraction will depend upon its apparent crystallite size, crystallite orientation, and internal strength in a manner analogous to the model carbons of Ref. 6, and the bulk dimensional changes of the aggregate will depend in a complex way on the behavior of its components. An additional complication is introduced by interactions among the structural components and by the network of pores within the aggregate.

The work during this contract year was an extension and refinement of experiments reported in Ref. 7. Several of the graphites studied in Ref. 7 were separated more completely, and the scanning electron microscope (SEM) was used to examine the particles. Several anisotropic graphites and isotropic graphites were remeasured. These materials were comminuted to particles in the range 0.1 to 38 μm and separated into six density fractions. Several of the heavier fractions from each material were re-separated. This procedure promoted more complete physical separation within the density column and provided up to 18 separate density fractions for examination by X-ray diffraction or SEM.

The density-distribution curves for a needle-coke graphite (CHN) and a Gilsonite-coke graphite (H-328) are shown in Fig. 1. The horizontal portion of the needle-coke curve extending from about 2.15 to 2.21 g/cm^3 shows that the particles have separated into two distinct density regions. This graphite may be divided into two general components by structure, one that is dense (2.21 to 2.26 g/cm^3) and another of lower density ($\sim$ 1.50 to 2.15 g/cm^3) with the high-density region representing approximately 76 vol % of the solid aggregate and the low-density region 24 vol %. The needle-coke curve of apparent crystallite size versus density in Fig. 2 shows a distinct break in the slope at about 2.10 to 2.15 g/cm^3 , in agreement with the density-distribution curve of Fig. 1. In contrast, the microstructure of the near-isotropic Gilsonite-coke graphite was considerably more uniform

Fig. 1. Density distributions in a needle-coke graphite (CHN) and a Gilsonite-coke graphite (H-328)

Fig. 2. Apparent crystallite size (L_c) versus apparent density for a needle-coke graphite (CHN) and a Gilsonite-coke graphite (H-328)

than that of the needle-coke graphite; the particles did not separate into two distinct bands, but had a crystallite size range of 300 to 600 Å.

Examination of the density fractions with SEM revealed differences in size and shape among the particles within a single graphite aggregate and also among the various graphites. The particles of the low-density fractions from the needle-coke aggregate (CHN) were of two types: very small thin platelets approximately 0.5 to 2 μm in diameter and larger equiaxed particles of about 10 μm (Figs. 3a and 3b). The heavy fractions had a wider range of particle sizes and were plate- or needle-like in shape (Figs. 3c and 3d). The particles of the Gilsonite-coke fractions were primarily platelets throughout the density range (Fig. 4). A highly isotropic Poco graphite consisted of small uniform-sized platelets throughout.

In many cases the small platelets resulting from comminution of the aggregates were similar in size to the distance between extinction contours observed by polarized light microscopy of calcined isotropic cokes (Ref. 9). The correlation was especially good for the SEM photographs of a Gilsonite-coke graphite, where the low-density particles were similar in size (~2 μm) to the fine-structured optical domains and the high-density particles resembled the coarser-structured optical domains (Ref. 9). The size of the density fraction particles of the Poco graphite aggregate was similar to the optical domain size in fine-grained isotropic cokes (Ref. 9). The needle-coke graphite (CHN) contained particles that resembled the fine-structured isotropic microstructural components and the needle-structured acicular components, and a third type that resembled the microstructure of a glassy carbon (Fig. 3b). The glassy carbon structure probably originated from the impregnants used in manufacture to close the pores and reduce the permeability to gases.

Detailed structural examination of a number of moderator graphites shows these materials to vary from extremely fine-grained isotropic structure to highly heterogeneous aggregates consisting of a wide range of crystallite sizes. The present work has shown this result in considerably more detail

(a)

(b)

(c)

(d)

Fig. 3. SEM photomicrographs of CHN needle-coke graphite density fractions. (a) $< 1.60 \text{ g/cm}^3$, (b) $< 1.65 \text{ g/cm}^3$, (c) $2.20 \text{ to } 2.26 \text{ g/cm}^3$, (d) $2.23 \text{ to } 2.26 \text{ g/cm}^3$

(a)

(b)

(c)

(d)

Fig. 4. SEM photomicrographs of H-328 Gilsonite-coke graphite density fractions. (a) $< 1.75 \text{ g/cm}^3$, (b) 2.00 g/cm^3 , (c) 2.10 g/cm^3 , (d) 2.26 g/cm^3

than the previous work in Ref. 7. The various structural components within the aggregates have been identified by SEM and related to the microstructures of their coke precursors.

3.1.3. Dimensional and Structural Changes of Graphites at High Temperatures and High Fluences

A number of the anisotropic and isotropic graphites shown in Tables 1 and 2 have been under irradiation for several years. Irradiation in capsule GE-H-13-18 has raised the total fluence on these graphites to 2×10^{22} n/cm² ($E > 0.18$ MeV) at 1175° to 1290°C. The dimensional data are shown in Fig. 5.

The density changes (volume changes) of the graphites are shown in Fig. 6. These data were obtained by mensuration of dimensions (bulk density) and by immersion in liquid (apparent density of bulk and apparent density of powder, 0.1 to 38 μ m). An interpretation of the relationships between dimensional and structural changes in these graphites has been given previously (Refs. 1, 2). The maximum volume contraction of each material was shown to correlate with the mean apparent crystallite size $\bar{L}_c$ and the crystallite size distribution of the graphites provided they had similar crystallite orientations (Refs. 1,2). Pores, located between crystallite clusters, were eliminated during densification by the crystallite c-axis expansion. The rate of elimination of these pores increased with increasing irradiation temperature. Larger pores were observed to form between filler particles during the expansion phase at high fluences, accounting for the large volume expansions of the graphites. The ease of formation of these pores and cracks and the expansion rate after turnaround were found to be dependent on the volume percent of highly graphitic (low-strength) material in the structure.

The effect of original strength has been studied further by measuring the modulus of rupture of virgin specimens. The bulk volume expansion rates of the graphites after maximum densification were dependent on their original strengths (see Fig. 7). Those of highest strength expanded at the

Fig. 5. Dimensional changes versus fluence for anisotropic needle-coke graphites and near-isotropic graphites. (a) H-283, CHN, and 711-TS

Fig. 5. Dimensional changes versus fluence for anisotropic needle-coke graphites and near-isotropic graphites. (b) H-315-A, H-319, and H-328

Fig. 6. Density changes of anisotropic needle-coke and near-isotropic graphites. (a) Bulk

Fig. 6. Density changes of anisotropic needle-coke and near-isotropic graphites. (b) Bulk by immersion in liquid

Fig. 6. Density changes of anisotropic needle-coke and near-isotropic graphites. (c) Powder by immersion in liquid

Fig. 7. Volume expansion rates of anisotropic needle-coke and near-isotropic graphites versus original modulus of rupture at 1175° to 1290°C

slowest rate. In contrast, the crystallite clusters (mean of the sink-float particles) did not densify but expanded, and their expansion was more dependent on crystallite orientation than on the original strengths of the various materials. Photomicrographs of the graphites after irradiation to 2×10^{22} n/cm² were similar to those shown previously of graphites after irradiation to about 1.6×10^{22} n/cm² (Refs. 1, 2) and showed large pores continuing to develop between the filler-coke particles by disintegration of the binder-carbon bridges. This effect is considerably more pronounced in the anisotropic needle-coke materials than in the near-isotropic Gilsonite graphite (see Fig. 8). The volume expansions of the needle-coke materials range from about 25 to 70%, whereas that of the Gilsonite-coke material was about 15%. The needle-coke specimens were weak and distorted and had passed the point of being useful as structural members of a reactor core, whereas the Gilsonite-coke material was considerably better. The data in Fig. 6 show the needle-coke materials entering the net expansion regime at about 4 to 6×10^{21} n/cm² in the c-axis direction of preferred orientation at 1175° to 1290°C, while the Gilsonite-coke graphites do not show net expansion until a fluence of 8 to 11×10^{21} n/cm².

Irradiation of this series of specimens has been terminated.

3.1.4 Effect of Crystallite Size, Crystallite Orientation, Strength, and Original Density on Dimensional and Volumetric Changes in Graphites

A number of the graphites shown in Table 1 are being irradiated in the temperature range 500° to 1430°C to explore the effect of crystallite size and orientation, original strength, and density on their irradiation behavior. The graphites are being irradiated in two series. The first series has been irradiated at 1220° to 1330°C to 8.3×10^{21} n/cm² and the second series at 500° to 1430°C to 0.9 to 5.2×10^{21} n/cm². The dimensional changes for the first series are shown in Fig. 9, and those for the second series are given in Table 3.

K89375

(a)

K89376

(b)

Fig. 8. Photomicrographs of graphites after irradiation to 2×10^{22} n/cm² at 1175° to 1290°C. (a) H-315-A (Gilsonite coke) and (b) 711-TS (needle-coke)

Fig. 9. Dimensional changes of graphites irradiated at 1000° to 1330°C to $8.3 \times 10^{21} \text{ n/cm}^2$. (a) Natural flake

Fig. 9. Dimensional changes of graphites irradiated at 1000° to 1330°C to 8.3×10^{21} n/cm². (b) H-327

Fig. 9. Dimensional changes of graphites irradiated at 1000° to 1330°C to $8.3 \times 10^{21} \text{ n/cm}^2$. (c) H-378

Fig. 9. Dimensional changes of graphites irradiated at 1000° to 1330°C to $8.3 \times 10^{21} \text{ n/cm}^2$. (d) H-319 and AXF-5QB

Fig. 9. Dimensional changes of graphites irradiated at 1000° to 1330°C to $8.3 \times 10^{21} \text{ n/cm}^2$. (e) ATJ-SG and AXF-5QGB

TABLE 3
DIMENSIONAL CHANGES OF GRAPHITES IRRADIATED AT 500° TO 1430°C AND 0.9 TO 5.2×10^{21} N/CM² (E > 0.18 MeV)

Fluence $\times 10^{-21}$ (n/cm ²)	Temp (°C)	H-327 ^(a)		CHN		H-319		H-315-A		H-328		H-419		H-337		H-421		A-681		AXP-8QGB		HL-18		H-283		711-TS	
		I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II
0.90	500	(C)+0.01 (E)+0.02	0.00 -0.03	--	--	--	--	--	--	+0.02	+0.02	+0.06	+0.04	0.00	-0.02	-0.03	-0.06	-0.16	-0.10	+0.01	+0.05	-0.17	-0.12	--	--	--	--
2.10	750	--	--	--	--	--	--	--	--	--	--	--	--	--	--	-0.13	-0.04	--	--	--	--	--	--	--	--	--	--
1.55	830	(C)-0.09 (E)-0.09	-0.22 -0.15	--	--	-0.39	--	--	--	--	--	+0.20	+0.17	0.00	+0.04	-0.05	-0.02	-0.23	-0.28	+0.16	+0.13	-0.21	-0.23	--	--	--	--
2.80	840	(C)-0.76 (E)-0.60	-0.99 -0.90	--	--	--	--	--	--	--	--	+0.39	+0.29	--	--	--	--	--	--	--	--	--	--	--	--	--	--
3.40	1000	--	--	--	--	--	--	--	--	--	--	-0.14 +0.06	-0.32 -0.11	--	--	--	--	--	--	--	--	--	--	--	--	--	--
3.85	1090	(C)-1.39 (E)-1.11	-2.84 -2.77	(-1.50)	(-2.35)	(-2.40)	(-3.00)	(-1.85)	(-1.00)	-1.94	-1.79	-0.20	-0.37	-0.59	-0.42	--	--	-1.01	-1.38	-0.17	-0.33	-0.77	-0.64	(-2.80)	(-0.90)	(-1.00)	(-3.00)
4.30	1000	(C)-1.11 (E)-0.98	-2.71 -2.63	--	--	--	--	--	--	--	--	+0.33	+0.13	--	--	--	--	--	--	--	--	--	--	--	--	--	--
5.15	1290	--	--	--	--	--	--	--	--	--	--	-0.55	-0.98	--	--	--	--	--	--	--	--	--	--	--	--	--	--
4.55	1330	(C)-1.49 (E)-1.11	-4.24 -4.24	--	--	--	--	--	--	--	--	-0.56	-0.74	--	--	--	--	--	--	--	--	--	--	--	--	--	--
5.20	1430	--	--	-0.02	-5.90	-1.97	-3.55	-3.15	-0.54	-2.46	-2.26	-0.73	-1.19	--	--	--	--	--	--	--	--	--	--	--	--	--	--
		(E)-1.07	-5.24	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--

NOTE: Values in parentheses were taken from Ref. 2 and included for comparison with current materials.

(a) C indicates specimen was taken from center of 18-in.-diameter production log. E indicates edge.

Data for the first series of graphites have been combined with the data of a series of high-density needle-coke graphites reported previously in Ref. 10. The graphites in Ref. 10 and the graphites in the first series were irradiated in the same capsule series at comparable temperatures and fluences. The two series combined represent graphites that have a wide range of densities.

The density data are shown in Fig. 10. The graphites of low density (measured by immersion in liquid) contract at low fluences, while those of intermediate or high density show little change. At the highest fluence the graphites have all reached about the same density; that is, those of lowest density have not begun to expand after their initial densification, those of intermediate density have remained the same, and those of highest density have started to expand. These changes are exclusive of the large open pores and include only the solid graphite plus the closed pores.

The solid graphite structure appears to behave in a systematic pattern, but this is not the case for the bulk volume changes, which are shown in Fig. 9. Unfortunately, the bulk changes are the important property with respect to reactor operation. However, it is not unexpected that the solid volume and the bulk volume do not correlate since there is no systematic correlation between bulk density and the liquid density. Thus, some other structural feature is apparently more important than the original bulk density.

Strength (modulus of rupture) of the unirradiated isotropic graphites is plotted in Fig. 11 as a function of their initial dimensional contraction after irradiation at 1000°C and 3.85×10^{21} n/cm². All materials fall in a narrow band of crystallite sizes (200 to 600 Å), and their isotropy ratios are all near one. No correlation between density and strength of the graphites was observed. The graphites of highest strength contract initially at the slowest rate. The only anomaly is H-337 graphite, which contracts only about one-half as much as it should. However, H-337, while meeting the criteria for isotropy, has an $\bar{L}_c$ value of 730 Å; thus, there is

Fig. 10. Original density measured by immersion in a liquid versus irradiated density for graphites at 1175° to 1330°C. (a) 3.0 to 3.75 $\times 10^{21}$ n/cm²

Fig. 10. Original density measured by immersion in a liquid versus irradiated density for graphites at 1175° to 1330°C. (b) 7.65 to 9.70 x 10²¹ n/cm²

Fig. 11. Modulus of rupture (unirradiated) versus initial contraction of isotropic graphites irradiated to 3.85×10^{21} n/cm² at 1000°C

the possibility that its dimensional changes may be influenced by a crystallite size effect. The anisotropic graphites cannot be correlated in this manner due to crystallite orientation effects. The preferred a-axis direction is always the strongest, but due to the high contraction rate of the crystallite in the a-axis direction, it also exhibits the highest contraction rate.

The effect of the original strength of the graphites on their rate of expansion after maximum densification was described in Section 3.1.3.

The important conclusion from these data is the strong dependence of the initial contraction on strength provided the graphites have about the same crystallite orientation and size.

The effect of crystallite size and crystallite size distribution on dimensional changes will be examined using the current data. Correlations with strength will be examined again with data from the second series of graphites after the specimens have been irradiated to higher fluences and expansions have begun.

3.1.5. Effect of Temperature History on Dimensional Changes of Graphites

The effect of irradiating graphite initially at a high temperature followed by irradiation to higher fluences at a lower temperature has been under study for several years. The preliminary data were reported previously (Ref. 11). Additional data have been accumulated on the samples from Ref. 11, plus some new data on H-327 graphite specimens. The graphites have been irradiated first to $3 \text{ to } 5 \times 10^{21} \text{ n/cm}^2$ at $\sim 1000^\circ$ or 1200°C and then to about $5 \text{ to } 12 \times 10^{21} \text{ n/cm}^2$ at 800° or 1000°C , respectively.

The solid curves in the graphs of Fig. 12 are isothermal data taken from Refs. 2 and 11. The set of points at the lowest fluence was obtained at the same temperature as the isothermal curves. All subsequent points at

Fig. 12. Dimensional changes of graphites irradiated initially at 1000°C or 1200°C and subsequently at reduced temperatures. (a) CHN

Fig. 12. Dimensional changes of graphites irradiated initially at 1000°C or 1200°C and subsequently at reduced temperatures. (b) CHN

Fig. 12. Dimensional changes of graphites irradiated initially at 1000°C or 1200°C and subsequently at reduced temperatures. (c) H-315-A and 711-TS

Fig. 12. Dimensional changes of graphites irradiated initially at 1000°C or 1200°C and subsequently at reduced temperatures. (d) H-319

Fig. 12. Dimensional changes of graphites irradiated initially at 1000°C or 1200°C and subsequently at reduced temperatures. (e) H-327

Fig. 12. Dimensional changes of graphites irradiated initially at 1000°C or 1200°C and subsequently at reduced temperatures. (f) H-327

higher fluences were obtained about 200°C below the initial points. With one exception the dimensional changes of the series of specimens irradiated at the reduced temperature fell within a band or close to the average dimensional change curve of data from similar samples irradiated to higher fluences at the higher temperatures. The perpendicular specimens have all gone through turnaround and are now expanding, several showing a net expansion. These specimens, plus additional specimens, have been returned to capsule GE-H-13-19 for further irradiation to evaluate the magnitude of this effect at all fluences up to 10^{22} n/cm².

3.1.6. Thermal Expansivity Changes in Graphites

Thermal expansivity changes were measured on a variety of graphites after irradiation to 1.5×10^{22} n/cm² and reported previously in Ref. 2. The data in Ref. 2 showed the changes in thermal expansivity to be sensitive to the graphite structure; certain anisotropic needle-coke structures (H-283) increased with fluence, isotropic structures (H-315-A) decreased, and another needle coke (711-TS) that had been heavily impregnated showed no change. These specimens (described in Section 3.1.1) have been taken to 2×10^{22} n/cm² and their thermal expansivity has been remeasured.

The previous data for these graphites are reproduced in Fig. 13 along with the additional curves at the highest fluence. Only one orientation (c-axis direction) of each material is shown in Fig. 13. The thermal expansivities have leveled off in those materials where the changes were large. The leveling off of the thermal expansivity changes coincides with the leveling off of the dimensional changes as shown in Fig. 5. The graphites have apparently expanded to the point where they are no longer behaving as integral solid materials, but more as a loose bed of granules.

Measurements are being made of thermal expansivity changes in graphites irradiated at 1000° to 1430°C and 4 to 5×10^{21} n/cm².

Fig. 13. Thermal expansivity changes in the c-axis direction of graphites as a function of fluence
(a) H-283

Fig. 13. Thermal expansivity changes in the c-axis direction of graphites as a function of fluence
(b) 711-TS

Fig. 13. Thermal expansivity changes in the c-axis direction of graphites as a function of fluence
(c) H-315-A

3.1.7. Thermal Conductivity Changes in Graphites

Irradiation-induced thermal conductivity changes are important in the design of high-temperature reactors where the graphite is utilized to transfer heat from the fuel to the coolant. Unfortunately, thermal conductivity is reduced rapidly and saturates at relatively low fluences when graphites are irradiated at high temperatures. The fractional change in thermal conductivity is large when measurements are made at room temperature, but becomes less significant as the measuring temperature is raised due to phonon-phonon interactions that mask the scattering effects of lattice defects. The fractional change in thermal conductivity decreased with increasing irradiation temperature in the range 300° to 1200°C at fluences up to 3×10^{21} n/cm² when measured at room temperature (Ref. 3). However, when the measuring temperature was raised to the irradiation temperature, there was little or no dependency on irradiation temperature.

In the series of graphites described in Section 3.1.3, thermal conductivity has now been measured on Gilsonite-coke and needle-coke graphites after irradiation at about 1000° and 1200°C to fluences of 6 to 7×10^{21} n/cm² and 2×10^{22} n/cm², respectively (see Fig. 14).

The new data at 2×10^{22} n/cm² show the rapid degradation of thermal conductivity that accompanies the large volume expansions which occur over the fluence range of 1 to 2×10^{22} n/cm².

In a new series of the same type of graphites (H-327 and H-328), thermal conductivity changes were measured prior to irradiation (see Table 4) and after irradiation to 0.9 to 5.2×10^{21} n/cm² at 500° to 1430°C (see Fig. 15). The data in Fig. 15 show the strong effect of irradiation annealing above 800°C. The specimens in this series are being reirradiated to higher fluences.

Fig. 14. Fractional change in thermal conductivity of needle-coke and Gilsonite-coke graphites as a function of fluence

TABLE 4
THERMAL CONDUCTIVITY OF H-327 AND H-328 GRAPHITES
PRIOR TO IRRADIATION

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
	91		0.525
	92		0.505
H-328	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

Fig. 15. Thermal conductivity of graphites versus fluence at 500° to 1430°C. (a) Needle-coke graphite (H-327), parallel

Fig. 15. Thermal conductivity of graphites versus fluence at 500° to 1430°C. (b) Needle-coke graphite (H-327) and Gilsonite-coke graphite (H-328), perpendicular

3.1.8. Creep in Graphites

The Dragon Project has made space available for 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 were done by the Dragon Project at Dragon or RCN, Petten, Holland. The details of the materials, the dimensional change data for unrestrained specimens, a critical strain rate, and an estimated creep constant were reported previously (Ref. 1).

Further measurements of the restrained specimens had been planned by the Dragon Project during this report period, but due to their work in the Petten Laboratory that had priority, no new results were obtained. Correspondence has been sent to Dragon requesting a decision on whether any further measurements will be made on these specimens.

3.1.9. Irradiation Effects in Highly Oriented Carbons and Graphites

Samples of highly oriented carbons and graphites of various crystallite sizes are being irradiated because such materials give direct information on the dimensional change rates of crystallites without the complications of gross porosity and crystallite interactions inherent in data from polycrystalline graphites. In the present work the samples consist of hot-worked ATJ graphite and massive pyrolytic carbon annealed at various temperatures before irradiation. The properties of the materials are listed in Table 5. The samples are being irradiated in the GE-H-13 series of capsules at 750° to 800°C and at 1225° to 1300°C. Results obtained before May 1970 were reported in Ref. 1.

During the present reporting period, the samples from capsule GE-H-13-18 were measured. Maximum exposures are now 4.1×10^{21} n/cm² for the 750°C samples and 1.95×10^{22} n/cm² for the 1290°C series.

TABLE 5
STRUCTURAL PARAMETERS FOR HIGHLY ORIENTED CARBONS AND GRAPHITES

Material	Density (g/cm ³)	BAF ^(a)	Apparent Crystallite Size (Å)		Interlayer Spacing ^(b) (Å)
			L _a	L _c ^(b)	
Massive pyrolytic carbon	2.18	8.9	250 ^(c)	220	3.420
Hot-worked ATJ graphite	2.04	4.1	630 ^(d)	570	3.360
3300°C-annealed pyrolytic carbon	2.25	13	1300 ^(d)	1600	3.353
3100°C-annealed pyrolytic carbon	2.25	(e)	(e)	1400	3.358
3000°C-annealed pyrolytic carbon	2.25	(e)	710	750	3.366
2900°C-annealed pyrolytic carbon	2.20	(e)	(e)	675	3.365

- (a) Bacon anisotropy factor.
(b) Evaluated from the (002) reflection.
(c) Evaluated from the (11) band.
(d) Evaluated from the (110) reflection.
(e) Not measured.

The dimensional changes of the pyrolytic carbon and hot-worked graphite at 750°C are shown as a function of fluence in Fig. 16. Both materials show an increase in the rates of c-axis expansion and a-axis contraction as a function of neutron exposure. In contrast, at 1290°C the dimensions of the annealed massive pyrolytic carbon specimens change linearly with neutron exposure (Fig. 17). The different behavior at the two temperatures indicates that at 750° to 800°C, additional nucleation sites for irradiation-induced defect clusters are introduced as irradiation progresses. At 1225° to 1300°C, where the mobility of point defects is much higher, the density of nucleating sites remains essentially the same as at the start of irradiation, resulting in a linear dependence of accumulated damage on the neutron fluence.

At 1225° to 1300°C, the rates of dimensional change of the annealed pyrolytic carbons decrease with increasing preirradiation annealing temperature (Fig. 17). The material annealed at higher temperatures has a higher degree of crystalline perfection and consequently a lower concentration of nucleating sites for irradiation-induced defect clusters. One apparent exception to this pattern is the anomalously high c-axis expansion rate in the material annealed at 3300°C before irradiation (Fig. 17). This is probably explained by the tendency of this material to form delamination cracks during annealing, resulting in a faster c-axis expansion rate than the other samples that are more resistant to delamination.

The rates of dimensional change in the hot-worked graphite irradiated at 1225° to 1300°C (Fig. 18) decrease with increasing neutron exposure. This decrease is accompanied by a decrease in thermal expansivity (Ref. 1). The probable reason for this effect is an increasing restraining effect on the c-axis expansion as irradiation progresses, resulting in a progressively "tighter" structure. Such an effect is only possible in a material of high mechanical strength, such as the hot-worked graphite, and does not occur in the annealed massive pyrolytic carbons, which have a low c-axis cleavage strength. An analogous effect is observed in polycrystalline graphites, where "breakaway growth" at high neutron exposures occurs in

Fig. 16. Dimensional changes in massive pyrolytic carbon and hot-worked graphite irradiated at 750° to 800°C

Fig. 17. Dimensional changes in annealed massive pyrolytic carbon irradiated at 1225° to 1300°C

Fig. 18. Dimensional changes in hot-worked graphite irradiated at 1225° to 1300°C

needle-coke graphites but is restrained in high-strength, isotropic graphites (Section 3.1.3). The present observations on hot-worked graphite show that high strength, rather than isotropy, is the principal factor in retarding breakaway growth at high damage levels.

3.2. 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 are given in Table 6. The cokes have a fine-structured isotropic texture as observed micrographically. The air-blown asphalts are the finest in texture and generally consist of very fine-structured regions in a fine-structured matrix. Sample 223A3 is the most uniform of the air-blown asphalts. The Huntington Beach vacuum-reduced crude produced a coke with a similar texture, although less uniform and with greater contrast between the two levels of fineness. The de-ashed coal is the coarsest of the fine-structured isotropic textures in the 223A group.

Three of the fine-grained isotropic petroleum cokes were comminuted and separated into density fractions. The density and X-ray data are given in Table 7.

The cokes from the Great Lakes Carbon Company were separated in the densimetric column and the fractions were heated to 2300° or 2600°C. X-ray diffraction parameters were obtained on the heat-treated fractions. The data are shown in Table 8. Coke A did not graphitize as well as coke B and showed a slight inhomogeneity, whereas coke B was uniform and graphitized

TABLE 6
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 ^(b)	223A1	2675	-	2.038	Flake
Air-blown asphalt ^(b)	223A2	2675	-	1.967	Flake
Air-blown asphalt ^(b)	223A3	2675	-	1.986	Flake
Vacuum-reduced petroleum crude ^(c)	223A4	2800	-	2.033	Flake
De-ashed coal ^(d)	223A5	2810	1.04	2.115	Flake
Vacuum-reduced petroleum crude ^(c)	223B1	2680	3.19	-	<38-μm powder
Vacuum-reduced petroleum crude ^(c)	223B2	2805	6.2	-	<38-μm powder
Gilsonite coke ^(e)	223B3	2815	-	-	<38-μm powder
Petroleum crude ^(f)	A	2800	-	2.24	<38-μm powder
Petroleum crude ^(f)	B	2800	-	2.21	<38-μm powder

(a) Density measured by immersion in liquid.

(b) Edgington Asphalt Company.

(c) Gulf Oil Corporation.

(d) Pittsburgh and Midway Coal Company.

(e) American Gilsonite Company.

(f) Great Lakes Carbon Company.

TABLE 7
DENSITY AND X-RAY PARAMETERS OF COKES

Source Material	Specimen No.	Estimated Heat-Treatment Temperature (°C)	Graphitized Density (g/cm ³) (a)	X-Ray Parameters, Å	
				$\bar{L}_c$ (b)	C_o
Vacuum-reduced petroleum crude	223B1	2680	2.140	382	6.740
Vacuum-reduced petroleum crude	223B2	2805	2.150	300	6.745
Gilsonite coke	223B3	2815	2.165	395	6.745

(a) Measured by immersion in liquid.

(b) Method for calculating $\bar{L}_c$ given in Ref 2.

TABLE 8
DENSIMETRIC DATA ON PETROLEUM COKES A AND B

Calcined Density (g/cm ³)	Approximate Volume % of Total Sample As Calcined for Coke A (a)	Apparent Crystallite Size (Å)					
		Coke A			Coke B		
		2300°C	2600°C	2800°C	2300°C	2600°C	2800°C
<1.90	1	580	700	--	460	700	--
1.90-1.95	1	540	700	--	505	1000	--
1.95-2.00	3	540	675	--	505	900	--
2.00-2.05	15	675	735	--	460	900	--
2.05-2.10	70	580	900	--	475	900	--
2.10-2.26	10	675	810	--	--	--	--
2.10-2.15	--	--	--	--	505	900	--
2.15-2.26	--	--	--	--	505	900	--
Composite	--	--	--	1160	--	--	1160

(a) The density fractions of Coke B were collected at the same densities as those of Coke A, but were not weighed. The crystallite size distributions of Coke B should be similar, but not necessarily the same, as those in Coke A.

well. However, measurement of L_c on the composite cokes after heat treatment to 2800°C showed no difference between the cokes even though their densities were different. X-ray measurements will be made on the density fractions after heat treatment to 2800°C and $\bar{L}_c$ will be calculated.

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 μm); one-half of the coke particles was irradiated in capsule GE-H-13-18 and one-half was retained for preirradiation measurements. Irregularly shaped flakes, approximately 0.200 in. by 0.200 in. in cross section, were also included. The coke particles were irradiated at 800° to 1330°C to 3.0 to 4.5×10^{21} n/cm². The flakes were irradiated at 1290°C to 5.2×10^{21} n/cm².

Dimensional changes of the flakes and density changes of the powders will be determined from the irradiated specimens.

4. CHARACTERIZATION AND IRRADIATION OF MODEL CARBONS

J. C. Bokros, J. L. Kaae, and R. J. Price

4.1. DIMENSIONAL AND VOLUMETRIC CHANGES OF MODEL CARBONS

4.1.1. Introduction

Model carbons that are relatively simple and homogeneous in crystal structure are being studied (Ref. 1). These materials are easier to characterize than graphites because they are free of the complex network of pores that are common in artificial graphites.

Model carbons that have been studied are: (1) natural graphite crystals, (2) annealed massive pyrolytic graphite, (3) high-density anisotropic turbostratic pyrolytic carbons, (4) catalytically graphitized high-density anisotropic carbons, and (5) isotropic turbostratic carbons deposited at high temperatures (HTI) and low temperatures (LTI). Irradiations of these materials have yielded information on the effect of crystalline perfection, preferred orientation, initial density, and mechanical strength on the irradiation-induced dimensional changes. The results that were summarized in the last annual report (Ref. 1) have aided in the interpretation of the behavior of polycrystalline artificial graphites.

During the current contract year, the model carbons were irradiated to 1×10^{22} n/cm² at 1000°C and 1.8×10^{22} n/cm² at 1250°C. Data from these irradiations complete the work on model carbons under this program.

4.1.2. Dependence of Irradiation-Induced Dimensional Changes on the Degree of Preferred Orientation

As the degree of preferred orientation of high-density turbostratic carbons is increased, the bulk dimensional changes increasingly reflect the anisotropic dimensional changes of the individual crystallites. This is

shown quantitatively in Figs. 19a and 19b for irradiation temperatures of 1000° and 1250°C for fast-neutron fluences up to 1.04×10^{22} and 1.80×10^{22} n/cm², respectively. The maximum irradiation stability is obtained for perfectly isotropic carbons with $R_1 = 0.667$; thus, the isotropy for maximum stability in a graphite body is the same. The effect of temperature on the rate of crystallite dimensional change is reflected in the higher dimensional changes at 1250°C in comparison with those at 1000°C. The nonlinear behavior of the dimensional changes with R_1 at high fluences has been noted and discussed previously (Ref. 12).

4.1.3. Dependence of Irradiation-Induced Volume Changes on Preirradiation Density

The effect of the initial density on the irradiation-induced density changes of turbostratic carbons with $50 \text{ \AA} < L_c < 150 \text{ \AA}$ at temperatures of 1000° and 1250°C is shown in Figs. 20a and 20b. The degree of preferred orientation does not affect these density changes. At both temperatures, an initial period of densification is followed by expansion, until all of the carbons reach the same density. Subsequently, there do not appear to be any changes in density. The strong expansion of the high-density carbons has been attributed to crystallite interactions, since the interactions are likely to be strongest when pores are not available to accommodate the crystallite dimensional changes (Ref. 12). The high-fluence equilibrium density can be attributed to this effect also, since it may represent the density where the expansion caused by the crystallite interaction is balanced by the densification caused by the crystallite dimensional changes. Since interactions are thought to be strongest at about 1000°C (Ref. 1), this may account for the early achievement of the constant density at 1000°C relative to 1250°C.

The mechanical strength of the carbon has an effect on the expansion phase. The LTI carbons, which are considerably stronger than the HTI carbons discussed above, do not enter an expansion phase until at least fluences greater than 7×10^{21} n/cm² at an irradiation temperature of

Fig. 19. Shape change data for anisotropic specimens at constant high density.
(a) 1000°C

Fig. 19. Shape change data for anisotropic specimens at constant high density.
 (b) 1250°C

Fig. 20. Density changes of HTI carbons versus fluence. (a)1000°C

Fig. 20. Density changes of HTI carbons versus fluence. (b) 1250°C

1000°C (Ref. 13). This is also consistent with the concept of crystallite interactions since the stronger carbons would be more resistant to the opening of pores by interaction stresses.

4.1.4. Dependence of Irradiation-Induced Dimensional Changes of Isotropic Carbons on Their Preirradiation Density

The dimensional changes of isotropic carbons with $50 \text{ \AA} < L_c < 150 \text{ \AA}$ irradiated at 1000° and 1250°C are shown in Figs. 21a and 21b, respectively. At high fluences the dimensional changes accelerate continuously with increasing preirradiation density. This is also shown in Fig. 22 where the data are cross-plotted to show the behavior of a high-density and a low-density isotropic carbon as a function of fast neutron fluence. At high fluences the rate of dimensional change is linear with fluence, with the rate of change of the high-density carbon being much greater than that of the low-density carbon. It is probable that the increased rate of change of the high-density carbon is related to the volume expansions discussed previously, since both appear at about the same fluence.

4.1.5. Implications of the Behavior of the Model Carbons to Desired Properties in Artificial Graphites

The results of the studies of the model carbons imply certain structures and properties that are desirable for irradiation stability in artificial graphites. These have been discussed in detail previously (Ref. 1), but in order to reemphasize them, the desired structures and properties are repeated here.

1. Isotropy
2. Intermediate density (when measured by immersion in liquid)
3. High mechanical strength, which implies an intermediate crystallite size

Fig. 21. Dependence of the dimensional changes of HTI carbons on preirradiation density. (a) 1000°C

Fig. 21. Dependence of the dimensional changes of HTI carbons on preirradiation density. (b) 1250°C

Fig. 22. Dimensional changes of HTI carbons as a function of fast neutron fluence at 1250°C

The artificial graphites that best approximate the above structural features are found to be the most stable graphites at high fluences and high temperatures (see Sections 3.1.3 and 3.1.4).

4.2. THERMAL CONDUCTIVITY OF NEUTRON-IRRADIATED PYROLYTIC CARBONS

A knowledge of the thermal conductivity of pyrolytic carbons is important for analyzing the performance of coated-particle nuclear fuel. In addition, from the temperature dependence of the thermal conductivity some conclusions can be drawn about the defect structure of the carbons.

Some miscellaneous measurements of the thermal conductivity of irradiated pyrolytic carbons have been reported on the present program in previous years (Ref. 14, 15). During the past year these earlier data, together with other results not previously reported, were assembled and analyzed. The temperature dependence of the thermal conductivity was analyzed using the theoretical treatments of thermal conduction in defected graphite crystals developed by Kelly, Taylor, and others (Refs. 16-19).

4.2.1. Experimental

The samples were fluidized-bed pyrolytic carbons deposited from methane. Details of the structural parameters are given in Table 9. The majority of these carbons fall into the category of "high-temperature isotropic" (HTI). The samples were obtained from earlier irradiation capsules designated G-9, G-10, and G-12, which were irradiated in the General Electric Test Reactor (GETR). Irradiation temperatures ranged from 550° to 1650°C and fluences ranged from 1.5 to 5.7×10^{21} n/cm² ($E > 0.18$ MeV). Temperatures were monitored by thermocouples in the specimen crucibles. Irradiation conditions are shown in Table 9.

Thermal diffusivity measurements were made on discs of pyrolytic carbon measuring approximately 8 mm in diameter by 0.1 mm thick. The pyrolytic carbon was deposited from methane-helium mixtures onto graphite discs

TABLE 9
STRUCTURAL PROPERTIES AND THERMAL CONDUCTIVITIES OF IRRADIATED PYROLYTIC CARBONS

Structure No.	Structural Parameters				Capsule No.	Irradiation Conditions			Thermal Conductivity (10 ⁻² cal/cm-sec-°K)	
	Density (g/cm ³)	Bacon Anisotropy Factor	L _c (Å)	Layer Spacing (Å)		Mean Temp (°C)	Fast Fluence x 10 ⁻²¹ (n/cm ²)	Post-Irradiation Annealing	At 300°K	At 800°K
2811-77	1.55	1.00	50	3.430	G-12	--	0	--	2.28	1.41
	1.92	--	26	3.404		950	4.6	None	1.85	1.26
	2.05	--	43	3.417		1160	5.7	None	3.75	2.05
3353-147	1.76	1.00	81	3.425	G-12	--	0	--	2.47	1.41
	1.98	--	49	3.423		950	4.6	None	1.15	0.57
	1.96	--	74	3.413		1160	5.7	None	3.73	1.69
3353-131	2.00	1.00	114	3.43	G-12	--	0	--	2.46	1.25
	2.03	--	61	3.421		950	4.6	None	1.04	0.40
	1.94	--	105	3.410		1160	5.7	None	1.91	0.98
3363-15	2.09	1.10	146	3.427	G-12	--	0	--	2.58	1.42
	2.04	--	74	3.402		950	4.6	None	0.86	0.46
	1.91	--	106	3.399		1160	5.7	None	2.48	1.16
3762-79	2.12	1.27	137	3.417	G-12	--	0	--	1.96	0.89
	2.04	--	77	3.420		950	4.6	None	0.51	0.25
	1.98	--	114	3.405		1160	5.7	None	1.10	0.48
1-G (2701-101)	2.19	2.54	226	3.35	G-9	--	0	--	--	--
	2.19	--	279	3.340		540	1.5	None	0.98	0.45
	2.19	--	261	3.334		540	1.5	3000°C	2.37	0.72
4 (2701-59)	2.01	1.05	139	3.42	G-9	--	0	--	2.10	--
	2.05	--	120	3.41		540	1.5	None	1.36	--
	2.05	--	110	3.41		620	1.6	None	1.14	--
	2.10	--	78	3.41		890	2.4	None	1.20	--
	2.08	--	76	3.41		1040	2.4	None	0.98	--
	2.09	--	77	3.41		1060	2.2	None	0.94	--

TABLE 9 (Continued)

Structure No.	Structural Parameters				Capsule No.	Irradiation Conditions			Thermal Conductivity (10 ⁻² cal/cm-sec-°K)	
	Density (g/cm ³)	Bacon Anisotropy Factor	L _c (Å)	Layer Spacing (Å)		Mean Temp (°C)	Fast Fluence x 10 ⁻²¹ (n/cm ²)	Post-Irradiation Annealing	At 300°K	At 800°K
5 (2701-43)	1.55	1.00	49	3.43	G-9	--	0	--	2.30	--
	1.69	--	53	3.42		540	1.5	None	2.60	--
	1.71	--	64	3.40		620	1.6	None	3.30	--
	1.95	--	53	3.41		890	2.4	None	4.50	--
	1.96	--	51	3.40		1040	2.4	None	3.70	--
	1.91	--	51	3.41		1060	2.2	None	3.95	--
6 (2576-98)	2.00	1.28	145	3.42	G-9	--	0	--	1.80	--
	2.04	--	154	3.400		540	1.5	None	1.33	0.69
	2.03	--	138	3.375		540	1.5	3000°C	2.71	1.15
	2.03	--	132	3.41		620	1.6	None	1.30	--
	2.08	--	95	3.405		890	2.4	None	0.65	0.38
	2.13	--	208	3.353		890	2.4	3000°C	2.73	1.01
	2.07	--	86	3.41		1040	2.4	None	1.00	--
	2.08	--	89	3.41		1060	2.2	None	1.20	--
7 (2576-102)	1.82	1.06	105	3.43	G-9	--	0	--	3.00	--
	1.87	--	106	3.42		540	1.5	None	2.10	--
	1.88	--	98	3.42		620	1.6	None	2.00	--
	2.04	--	76	3.41		890	2.4	None	1.70	--
	2.05	--	71	3.41		1040	2.4	None	2.70	--
	2.03	--	71	3.42		1060	2.2	None	2.30	--
6 (2576-106)	2.03	1.26	145	3.41	G-10	--	0	--	1.80	--
	2.07	1.35	105	3.42		600	1.9	None	0.97	--
	2.08	1.45	115	3.41		1180	2.6	None	1.09	--
	2.03	1.55	100	3.39		1330	3.1	None	0.77	--
9 (2813-3)	1.98	1.14	121	3.42	G-10	--	0	--	1.56	--
	2.02	1.25	105	3.41		600	1.9	None	1.13	--
	2.09	1.33	105	3.41		1180	2.6	None	1.34	--
	2.06	1.22	90	3.40		1330	3.1	None	1.06	--
	2.10	1.24	125	3.41		1650	3.3	None	1.74	--

levitated in fluidized beds of particles. Some samples were annealed after irradiation at 3000°C for 1 hr. The thermal diffusivity of the samples was measured perpendicular to the deposition plane by the heat-pulse method at temperatures between room temperature and 600° to 800°C.

4.2.2. Irradiation-Induced Changes in Room-Temperature Conductivity

Figure 23 shows the change in the room-temperature thermal conductivity of HTI pyrolytic carbons (density = 1.97 to 2.12 g/cm³, L_c = 114 to 146 Å, Bacon anisotropy factor = 1.0 to 1.3) as a function of fast-neutron fluence at three irradiation temperatures (540° to 620°C, 890° to 950°C, and 1160° to 1180°C). The conductivity was reduced by ~10 to 70% by irradiation, with the changes tending to saturate with increasing fluence. The changes were greatest for the lowest irradiation temperatures.

The irradiation-induced conductivity changes for the same group of carbons are shown as a function of irradiation temperatures in Fig. 24, where the data are restricted to fluences between 3.1 and 5.7×10^{21} n/cm² ($E > 0.18$ MeV). The conductivity is fairly insensitive to fluence over this range (Fig. 23). The reduction in conductivity was greatest for the lowest irradiation temperatures; for the highest irradiation temperatures the conductivity increased in comparison with its preirradiation value.

For a constant set of irradiation conditions, the change in conductivity depends on the structure of the carbon. Figure 25 shows the conductivity change of a set of isotropic carbons plotted as a function of initial L_c value for three sets of irradiation conditions. The initial densities of these carbons, which are lower for carbons of smaller L_c , are indicated at the top of the figure. Since there was significant irradiation-induced densification in the low-density carbons, conductivity changes were corrected for the changes in density as indicated in the figure. It can be seen that at all three irradiation temperatures the greatest decrease in conductivity occurred in the carbons of highest density and largest crystallite size. The carbons of low density and small crystallite size usually showed an increase in conductivity following irradiation.

Fig. 23. Irradiation-induced change in room-temperature thermal conductivity of HTI pyrolytic carbons as a function of fast neutron fluence

Fig. 24. Irradiation-induced change in room-temperature thermal conductivity of HTI pyrolytic carbons irradiated to 3.1 to $5.7 \times 10^{21} \text{ n/cm}^2$ ($E > 0.18 \text{ MeV}$) as a function of irradiation temperature

Fig. 25. Irradiation-induced change in room-temperature thermal conductivity of HTI pyrolytic carbons as a function of apparent crystallite height, L_c

The irradiation-induced changes in apparent crystallite size, L_c , closely parallel the changes in conductivity. Figures 26 through 28 show the changes in L_c plotted in a manner analogous to Figs. 23 through 25. The similarity in trends between the plots of thermal conductivity and L_c is evident. However, the correspondence is not exact. For example, the fractional reduction in conductivity following irradiation at 540° to 620°C is higher than the fractional reduction in L_c (Figs. 23 and 26).

4.2.3. Temperature Dependence of Thermal Conductivity

Typical curves of thermal conductivity versus temperature for an isotropic pyrolytic carbon irradiated at 950° and 1160°C are shown in Fig. 29. Additional thermal conductivity values are shown in Table 9. The conductivity decreased with increasing measurement temperature for all samples, with the rate of decrease being greatest for carbons annealed at 3000°C after irradiation and carbons irradiated at 1160°C.

Thermal conduction in polycrystalline carbon or graphite takes place by phonon transport parallel to the layer planes. At a temperature T , the thermal conductivity, K_T , can be represented as follows (Ref. 18):

$$\frac{1}{K_T} = \gamma \left[\frac{1}{(K_U)_T} + \frac{C_d S^2}{(C_d S^2 K_D)_T} + \frac{1}{L_a} \left(\frac{L_a}{K_B} \right)_T \right] ,$$

where γ = the porosity-tortuosity factor and is always greater than 1 (γ approaches 1 for the a-direction of fully dense, highly oriented graphite)

$(K_U)_T$ = the thermal conductivity component due to Umklapp processes at temperature T

C_d = the concentration of point defects

PYROLYTIC CARBON
PROPERTIES:

$$\rho = 1.97-2.12 \text{ G/CM}^3$$

$$L_c = 114-146 \text{ \AA}$$

$$\text{BAF} = 1.0-1.3$$

○ SAMPLES FROM CAPSULE G-9

□ SAMPLES FROM CAPSULE G-10

△ SAMPLES FROM CAPSULE G-12

Fig. 26. Irradiation-induced change in L_c of HTI pyrolytic carbons as a function of fast neutron fluence

PYROLYTIC CARBON $\rho = 1.97-2.12 \text{ G/CM}^3$
 PROPERTIES: $L_c = 114-146 \text{ \AA}$

BAF = 1.0-1.3

FAST NEUTRON FLUENCE = $3.1-5.7 \times 10^{21} \text{ N/CM}^2$

□ - SAMPLES FROM CAPSULE G-10

△ - SAMPLES FROM CAPSULE G-12

Fig. 27. Irradiation-induced change in L_c of HTI pyrolytic carbons irradiated to 3.1 to $5.7 \times 10^{21} \text{ n/cm}^2$ ($E > 0.18 \text{ MeV}$) as a function of irradiation temperature

Fig. 29. Thermal conductivity of HTI pyrolytic carbon 3353-147 as a function of measuring temperature

S^2 = a point-defect scattering parameter

K_D = the thermal conductivity contribution from point defects

L_a = the phonon mean free path between extended defects that are large compared with phonon wavelengths, such as crystallite boundaries normal to the layer planes or (in irradiated samples) large vacancy loops

K_B = the thermal conductivity component from such extended defects

$(K_U)_T$ is known from measurements on well-annealed, highly oriented pyrolytic graphite and decreases with increasing temperature (Ref. 18). $(C_d S^2 K_D)_T$ and $(K_B/L_a)_T$ have been calculated (Refs. 16-18); the former is almost independent of temperature, while the latter increases with increasing temperature. The different temperature dependences of the three components make it possible to calculate "best-fit" values for the porosity-tortuosity factor, γ ; the point-defect concentration multiplied by a scattering parameter, $C_d S^2$; and the phonon mean free path between extended defects, L_a , from curves such as Fig. 29 (Ref. 18). While the derived values cannot be taken too literally, they do give some insight into the structure of the carbons.

For as-deposited carbons and the carbons annealed at 3000°C after irradiation, the calculated values of the porosity-tortuosity factor, γ , were between 80 and 180 and increased with increasing preferred orientation in the carbons (Fig. 30). These values compare with ~ 5 to 10 for polycrystalline graphites (Ref. 18). For carbon deposited above 2000°C or annealed at 3000°C after irradiation, the point-defect scattering term, $C_d S^2$, was near the lower limit of 0.76×10^{-4} imposed by the presence of 1.1% C-13 isotope (Refs. 16, 18). For the carbons deposited at lower temperatures there appeared to be a significant point-defect scattering contribution, whose magnitude suggests the presence of $\sim 0.05\%$ vacant

Fig. 30. Porosity-tortuosity factor, γ , for pyrolytic carbons as a function of their Bacon anisotropy factor, and mean phonon-scattering boundary spacing, L_a , for pyrolytic carbons as a function of apparent crystallite height, L_c , derived from X-ray line broadening. γ and L_a were calculated from thermal conductivity curves.

lattice sites. The calculated L_a values were 3,000 to 20,000 Å and tended to increase with the apparent crystallite height, L_c , obtained from X-ray line broadening measurements (Fig. 30).

Near-isotropic fluidized-bed pyrolytic carbons are built up from gas-phase-nucleated droplets in which the layer planes are aligned circumferentially. Figure 31 shows a scanning electron micrograph of an as-deposited surface and a transmission electron micrograph of a typical isotropic pyrolytic carbon, showing the buildup of the structure from droplets 0.5 to 1.0 μm in diameter. The present calculations of high porosity-tortuosity factors and high phonon L_a values suggest that thermal conduction in these carbons takes place through the "skins" of these spherules, and that the carbon in these skins is relatively free from defects that can scatter phonons. This explanation is supported by the similarity in calculated L_a values to the observed droplet size ($\sim 1 \mu\text{m}$).

Analysis of the data on the irradiated carbons showed no evidence for an increase in point-defect concentration following irradiation. The samples irradiated at or below 950°C generally showed a decrease in the phonon L_a value compared with the unirradiated carbon, while those irradiated at or above 1160°C generally showed an increase in L_a . These results indicate that above 540°C the irradiation-induced defect clusters are probably vacancy loops large enough to scatter phonons like extended barriers rather than point scattering centers. For irradiation at or above 1160°C the extensive re-arrangement of the pyrolytic carbon structure may eliminate more extended barriers (such as crystallite boundaries) than it creates. In addition to these changes in phonon scattering parameters, irradiation also appears to increase the porosity-tortuosity factor, γ , especially in the carbons of high density and large crystallite size. This is probably associated with an irradiation-induced increase in preferred orientation (Ref. 20).

(b)

(c)

Fig. 31. Structure of isotropic pyrolytic carbons. (a) Schematic illustration of formation of isotropic pyrolytic carbon, (b) scanning electron micrograph of as-deposited surface, and (c) transmission electron micrograph

5. 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 Graphites," 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, Carbon 9, 205 (1971).

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).

The following oral presentations were made at the Tenth Biennial Conference on Carbon held at Lehigh University, Bethlehem, Pennsylvania, June 28 - July 2, 1971.

"Structural Distributions in Anisotropic and Isotropic Graphites,"
G. B. Engle

"Interpretation of High-Temperature Irradiation Effects in Carbons and Graphites," G. B. Engle and J. C. Bokros

"Effect of High-Temperature Irradiation on Thermal Conductivity of Artificial Graphites," G. B. Engle and K. Koyama

"Annealing of Neutron-Irradiated Pyrocarbons," R. J. Price and J. C. Bokros (same as GA-10162)

ACKNOWLEDGMENTS

The authors of the various sections of this report gratefully acknowledge the HTGR Base Program [Contract AT(04-3)-167, Project Agreement No. 17], the Public Service Company of Colorado Program [Contract AT(04-3)-633], Battelle Northwest Laboratory, and the Dragon Project, Winfrith, England, for making irradiation space available for the specimens. The support of the hot cell, metallography laboratory, irradiation capsule group, X-ray diffraction laboratory, and thermal properties laboratory of Gulf General Atomic Company is also acknowledged. Individuals who have contributed to this work include W. J. Gray of Battelle Northwest Laboratory and F. Gagnon, H. Evans, J. Dixon, and J. Knipping of Gulf General Atomic Company. The work was performed under the technical and administrative supervision of J. P. Howe of Gulf General Atomic Company.

REFERENCES

1. 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.
2. Engle, G. B., "Irradiation Behavior of Nuclear Graphites at Elevated Temperatures," Gulf General Atomic Report GA-9972, March 4, 1970 (accepted for publication in Carbon).
3. Engle, G. B., and K. Koyama, "Dimensional and Property Changes of Graphites Irradiated at High Temperatures," Carbon 6, 455 (1968).
4. Engle, G. B. and A. L. Pitner, "High-Temperature Irradiation Behavior of Production-Grade Nuclear Graphites," USAEC Report GA-9973, Gulf General Atomic, July 10, 1970.
5. 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.
6. 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).
7. Engle, G. B., "Density and Structural Distributions in Artificial Graphites," Carbon 8, 485 (1970).
8. Engle, G. B., W. H. Morris, and L. Bailey, "Apparatus and Procedure to Determine Density and Structural Distributions in Carbons and Graphites," Carbon 8, 393 (1970).
9. Price, R. J., and J. L. White, "The Development of Mesophase Microstructures During Pyrolysis of Selected Coke Feedstocks," paper presented at the Tenth Biennial Conference on Carbon, Lehigh University, Bethlehem, Pennsylvania, June 28 - July 2, 1971.
10. Engle, G. B., "The Influence of Pitch-Binder Coke Content on the Properties and Irradiation Behavior of Molded Graphites," Gulf General Atomic Report GA-9971, March 12, 1970 (accepted for publication in Carbon).

11. Engle, G. B., "Effect of Temperature History on the Dimensional Changes of Nuclear Graphites," USAEC Report GA-10001, Gulf General Atomic, March 23, 1970.
12. Bokros, J. C., and K. Koyama, "Interpretation of Dimensional Changes Caused in Pyrolytic Carbon by High-Fluence Neutron Irradiation," J. Appl. Phys. 41, 2146 (1970).
13. Kaae, J. L., D. W. Stévens, and J. C. Bokros, "Dimensional Changes Induced in Poorly Crystalline Carbons By Irradiation," paper presented at the Tenth Biennial Conference on Carbon, Bethlehem, Pennsylvania, June 28 - July 2, 1971 (Gulf General Atomic Report GA-10518, March 1971).
14. Bokros, J. C., R. J. Price, and K. Koyama, "Neutron-Induced Changes in Crystallinity and Thermal Conductivity of Pyrolytic Carbons," Carbon 4, 293 (1966).
15. Bokros, J. C., G. B. Engle, and R. J. Price, "Research on Graphite, Quarterly Progress Report for Period Ending November 14, 1968," USAEC Report GA-9099, Gulf General Atomic, November 22, 1968.
16. Kelly, B. T., "The Effect of Defects on the Basal Plane Thermal Conductivity of a Graphite Crystal," Carbon 5, 247 (1967).
17. Kelly, B. T., "Theory of the Effect of Crystallite Boundaries on the Principal Thermal Conductivities of Highly Oriented Graphite," Carbon 6, 71 (1968).
18. Taylor, R., K. E. Gilchrist, and L. J. Poston, "Thermal Conductivity of Polycrystalline Graphite," Carbon 6, 537 (1968).
19. Taylor, R., B. T. Kelly, and K. E. Gilchrist, "The Thermal Conductivity of Fast Neutron Irradiated Graphite," J. Phys. Chem. Solids 30, 2251 (1969).
20. Bokros, J. C., and R. J. Price, "Dimensional Changes Induced in Pyrolytic Carbon by High-Temperature Fast-Neutron Irradiation," Carbon 5, 301 (1967).