NOV 22 1965

MASTER

GENERAL ATOMIC

DIVISION OF **GENERAL DYNAMICS**

AEC RESEARCH AND
DEVELOPMENT REPORT

GA-6181

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

ADVANCED, GRAPHITE-MATRIX, DISPERSION-TYPE
FUEL SYSTEMS
AND
RESEARCH ON GRAPHITE

QUARTERLY PROGRESS REPORT
FOR THE PERIOD ENDING FEBRUARY 14, 1965

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

February 15, 1965

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.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

GENERAL ATOMIC

DIVISION OF

GENERAL DYNAMICS

JOHN JAY HOPKINS LABORATORY FOR PURE AND APPLIED SCIENCE

P.O. BOX 608, SAN DIEGO, CALIFORNIA 92112

AEC RESEARCH AND
DEVELOPMENT REPORT

GA-6181

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

ADVANCED, GRAPHITE-MATRIX, DISPERSION-TYPE FUEL SYSTEMS

AND

RESEARCH ON GRAPHITE

QUARTERLY PROGRESS REPORT
FOR THE PERIOD ENDING FEBRUARY 14, 1965

by

J. C. Bokros, W. V. Goedel, H. K. Lonsdale,
R. J. Price, J. L. White, and L. R. Zumwalt

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

February 15, 1965

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

CONTENTS

I. INTRODUCTION	1
II. SUMMARY	3
III. STUDIES OF PYROLYTIC-CARBON COATINGS DEPOSITED IN FLUIDIZED BEDS	5
Effect of Coating Variables on the Structure of Pyrolytic Carbons Deposited Above 1900°C	5
Effect of Structure on the Thermal Conductivity of Pyrolytic Carbons	10
Effect of Coating Variables on the Structure of Pyrolytic Carbons Deposited Below 1900°C	12
Mechanical Properties of Pyrolytic Carbons Deposited Above 1900°C	17
Annealing Behavior of Low-temperature Carbon Deposits	24
Effect of Structure on the Radiation Stability of Pyrolytic Carbon	29
IV. DIFFUSION OF URANIUM AND THORIUM IN PYROLYTIC CARBON	30
Effect of Structure on Diffusion of Thorium in Pyrolytic Carbon	30
V. FISSION-PRODUCT RELEASE FROM CARBIDE FUEL SYSTEMS	32
Effect of Coating Structure on Release of Metallic Fission Products Through Pyrolytic Carbon	32
VI. CHARACTERIZATION OF MICROSTRUCTURE OF GRAPHITIC MATERIALS	34
Electron Micrography	34
Kinetics of Oxidation of Graphitic Bodies in Liquid Media	38
VII. RELATION OF PHYSICAL PROPERTIES OF GRAPHITIC MATERIALS TO MICROSTRUCTURE	43
Radiation-induced Dimensional Changes	43
Influence of Filler and Binder Composition on Structure and Properties	43

VIII. CHEMICAL AND METALLURGICAL PROCESSES FOR MODIFYING THE MICROSTRUCTURE OF GRAPHITE	44
Pitch Content as a Hot-working Variable	44
Graphite-Carbide Materials Prepared by Hot-working . . .	47
REFERENCES	59
Appendix: GENERAL ATOMIC TOPICAL REPORTS	61

I. INTRODUCTION

The purpose of this program is to obtain substantial improvements in the materials required for use in high-temperature, gas-cooled reactors of advanced design. The approach is based on gaining a more complete understanding of their properties and behavior in order to provide effective guidance for the development of improved materials. Two principal lines of effort have been pursued: Task I, "Advanced Graphite-Matrix Fuel Systems," is concerned with the various materials directly involved in the fuel systems; Task II, "Research on Graphite," is concerned with the graphitic materials employed either in the fuel systems or in other structural components of the high-temperature reactor. Because of the close relationship between the items of work on Task I and Task II of this program, the reports of progress are combined into a single report.

In the period covered by the present report, November 15, 1964, through February 14, 1965, investigations have been conducted in the following areas:

1. Investigations of Pyrolytic-carbon Coatings Deposited in Fluidized Beds. The structures of pyrolytic carbons deposited in a fluidized bed are being characterized in order to establish the relationships existing between bed deposition conditions, coating structure, and the physical and mechanical properties relevant to reactor performance. The earlier studies are being extended to consider deposition temperatures greater than 1900°C. The property studies include measurements of the effects of annealing and irradiation on pyrolytic carbons.
2. Diffusion of Uranium and Thorium in Pyrolytic Carbon. The rates of diffusion of uranium and thorium in pyrolytic carbons typical of those employed in graphite-matrix fuel systems are being determined. Particular emphasis is being given to determining the effect of coating structure on diffusion.
3. Fission-product Release from Carbide Fuel Systems. The release of fission products through pyrolytic-carbon coatings typical of those employed in graphite-matrix fuel systems is being determined in an effort to relate release rates to coating structure.
4. Characterization of Microstructure of Graphitic Materials. Methods of characterizing the degree of graphitization of carbons and graphitic materials are being investigated.

5. Relation of Physical Properties of Graphitic Materials to Microstructure. The relationship of certain physical properties, including Young's modulus and the dimensional changes under irradiation, to the preferred orientation of various graphitic materials is being studied.
6. Chemical and Metallurgical Processes for Modifying the Microstructure of Graphite. The process of hot-working graphitic materials is being investigated, with current emphasis on evaluating the variables of pitch content and additives in the graphite bodies.

II. SUMMARY

Pyrolytic-carbon coating studies have been extended from 1900° to 2400°C. The densities of the structures deposited increased uniformly with deposition temperature. Both isotropic and granular structures were deposited; low methane concentrations, high temperatures, and small surface areas favored deposition of granular structures. Thermal diffusivity measurements performed on the above deposits showed that carbons deposited from 15% methane have higher thermal diffusivities than granular deposits formed from 3% methane.

Mechanical property measurements performed on the above high-temperature deposits showed that the modulus, fracture stress, and fracture strain increase with increasing deposition temperature for granular structures. Isotropic and transition structures showed a slight decrease in modulus and fracture stress with increasing deposition temperature.

X-ray scattering techniques were developed for measuring the amount of amorphous carbon and the fraction of single unassociated and associated layers present in pyrolytic carbon deposits. These techniques have been applied to carbons deposited at 1400°C from 5% and 40% methane.

Measurement of the physical and mechanical properties of annealed laminar structures, which were deposited at 1400°C under various conditions, has shown that while various properties respond differently to annealing, the order of "annealability" between structures remains the same. In general, the "annealability" increases with a decrease in the amount of single layers in a structure.

Seven representative structures of pyrolytic carbon, together with samples cut from the wall of an extruded graphite tube, are presently being exposed to a fast-neutron flux in the GETR.* After completion of irradiation (in April 1965), the dimensional, structural, and mechanical property changes will be measured and compared with predicted values.

Tracer-level diffusion studies conducted on granular pyrolytic carbon structures using Th^{228} as the diffusive species have shown that the diffusion coefficients for this type structure are about a factor of 10 greater than for laminar pyrolytic carbon. These results confirm that the diffusion coefficient is strongly dependent on the structure of the pyrolytic carbon.

*Irradiation of these samples is being conducted under Project Agreement No. 17 of Contract AT(04-3)-167.

Experimental work is continuing on diffusion studies that should make it possible to determine concentration profiles and diffusion coefficients of metallic fission products in pyrolytic carbon.

Techniques are being developed for characterization of the micro-structure of graphitic materials. A cathodic etching device has been assembled and is being used for the preparation of electron micrography samples. Methods for measuring the degree of graphitization are under study for the purpose of following structural changes taking place in carbonaceous materials during heat-treatment and in graphitic materials during irradiation. A chemical method, in which the kinetics of oxidation by a hot dichromate solution are measured manometrically, is currently being tested.

Studies of the influence of additives dispersed within a graphite matrix on the hot-working process and on the properties of the hot-worked bodies have resulted in the development of unique carbide-graphite cermets. These new materials have been prepared by hot-working carbide-bearing graphite bodies at temperatures such that the dispersed carbide phase is in the liquid state. Under these conditions, the bodies are readily hot-worked, and the structure of the graphite matrix after hot-working is very dense, with a uniform dispersion of fine carbide particles. Hot-working of graphite bodies containing MoC or ZrC in the liquid state has resulted in large increases in compressive strengths parallel to the direction of hot-working, and modest increases in the perpendicular direction. The helium permeability of these carbide-graphite cermets is near the limit of detection with existing apparatus ($<10^{-6}$ cm²/sec).

III. STUDIES OF PYROLYTIC-CARBON COATINGS DEPOSITED IN FLUIDIZED BEDS

J. C. Bokros, R. J. Price, J. Chin,
K. Koyama, J. O. Gardner, W. E. Ellis

EFFECT OF COATING VARIABLES ON THE STRUCTURE OF PYROLYTIC CARBONS DEPOSITED ABOVE 1900°C

Studies of the structure of carbons deposited from 1900° to 2400°C in a 3.5-cm-diameter coater have continued. Details of the coating conditions for deposits made from 3%, 7%, and 15% methane, as well as the corresponding coating rates and efficiencies, have been reported in the previous quarterly progress report.⁽¹⁾

The densities of these carbons are reported in Table 1 and plotted in Fig. 1 as a function of the bed temperature and methane concentration used in their preparation. Comparison of these data with the density data reported previously for deposits prepared in a 2.5-cm-diameter coater⁽²⁾ shows good agreement at 1900°C. This good agreement is probably fortuitous, since it is known that structural data for carbons deposited in different coatiers are, in general, not directly comparable. The intermediate "shoulder" on Fig. 1 is undoubtedly a consequence of the transition from a high-density granular structure to a lower-density isotropic structure during the coating run in this region of temperature, methane concentration, and bed surface areas.

Table 1

DENSITIES OF CARBONS DEPOSITED AT 1900° TO 2400°C
FROM METHANE IN A 3.5-CM-DIAMETER COATER

Temperature of Bed (°C)	Density (g/cm ³) of Carbon Deposited		
	From 3% CH ₄	From 7% CH ₄	From 15% CH ₄
1900	1.97, 1.97 ^a	1.68	1.61
2000	2.02, 2.02 ^a	1.78	1.67
2100	2.02, 2.03 ^a	1.91	1.79
2200	2.06	1.93	----
2300	2.08	1.90	1.77
2400	2.09	2.12	1.89

^aDuplicate runs.

Fig. 1--Density of carbons deposited in a 3.5-cm-diameter coater plotted as a function of the bed temperature and methane concentration used in their preparation. Total flow was 18,000 cm³/min (at 23°C and 1 atm) and the initial bed surface area was 1140 cm².

The apparent crystallite sizes, L_c , of these carbons are given in Table 2 and are plotted in Fig. 2 as a function of the bed temperature and methane concentration used in their preparation. These data also show good agreement with those reported previously for carbons deposited in a 2.5-cm-diameter coater.⁽²⁾

Table 2
APPARENT CRYSTALLITE SIZE, L_c , FOR PYROLYTIC CARBONS
DEPOSITED FROM 3%, 7%, AND 15% METHANE AT 1900° TO
2400°C IN A 3.5-CM-DIAMETER COATER

Temperature of Bed (°C)	L_c (Å) of Carbon Deposited		
	From 3% CH ₄	From 7% CH ₄	From 15% CH ₄
1900	102, 115, 103 ^a	64	54
2000	124	76	54
2100	134, 128 ^a	102	80
2200	154	107	--
2300	135	118	100
2400	168	161	115

^aDuplicate runs

Because of the large particle size of the charge used in these studies (70 g of 300- to 420- μ UC₂ particles), the bed surface area changes rather slowly with coating thickness and, as a result, the influence of the bed surface area on the formation of the granular deposits is clearly defined. Table 3 of the previous quarterly progress report⁽¹⁾ shows the bed surface areas at which the transition from a granular to an isotropic structure occurs for various combinations of bed temperature and methane concentration. These data, together with metallographic results, were used to construct the schematic diagram shown in Fig. 3. This diagram shows that low methane concentrations and high temperatures favor the granular deposits and that, for a given methane concentration and bed temperature, the granular deposits are most likely to form when small surface areas are used. These results are consistent with results previously reported for a 2.5-cm-diameter coater and lower deposition temperatures.

Metallographic examination of the carbons deposited from 3% methane shows a decrease in grain size* with increasing temperature and a gradual

*These grains are those visible metallographically using polarized light and should not be confused with the apparent crystallite size measured by X-ray diffraction.

Fig. 2--Apparent crystallite sizes, L_c , of carbons deposited in a 3.5-cm-diameter coater plotted as a function of the bed temperature and methane concentration used in their preparation. The total flow was $18,000 \text{ cm}^3/\text{min}$ (at 23°C and 1 atm) and the initial bed surface area was 1140 cm^2 .

Fig. 3--Schematic representation of the metallographic appearance of carbons deposited in a 3.5-cm-diameter coater using a total flow of 18,000 cm³/min (at 23°C and 1 atm) and an initial bed surface area of 1140 cm². The numbers on the figure correspond to the bed surface area at which the transition from a granular to an isotropic structure occurs.

increase in anisotropy (Fig. 4). As the anisotropy increases (with deposition temperature), the granular structure becomes obscure and the deposits take on a laminar appearance. Distinctly laminar structures deposited at 2000°C from 2.7% methane in a 6.3-cm-diameter coater were observed in earlier work.⁽²⁾

The measurement of the degree of preferred orientation of these deposits is in progress.

EFFECT OF STRUCTURE ON THE THERMAL CONDUCTIVITY OF PYROLYTIC CARBONS

The thermal diffusivities of the carbons described in the preceding section have been measured in a direction perpendicular to the deposition plane using the flash technique described in the previous quarterly progress report.⁽¹⁾ From these data, the thermal conductivities were calculated using measured densities and a specific heat of 0.25 cal/g°C. These results are presented in Table 3 and show that the carbons deposited from 15% methane have higher thermal conductivities than the granular deposits formed from 3% methane. The gradual decrease in thermal conductivity with increasing deposition temperature for the carbons deposited from 3% methane is most likely due to the increase in anisotropy in this series.

Table 3

ROOM TEMPERATURE THERMAL CONDUCTIVITY^a (CAL/CM-SEC-°C)
OF CARBONS DEPOSITED AT 1900° TO 2400°C FROM METHANE
IN A 3.5-CM-DIAMETER COATER

Temperature of Bed (°C)	Thermal Conductivities for Carbon Deposited		
	From 3% CH ₄	From 7% CH ₄	From 15% CH ₄
1900	1.7×10 ⁻²	2.1×10 ⁻²	3.0×10 ⁻²
2000	1.6×10 ⁻²	2.6×10 ⁻²	2.4×10 ⁻²
2100	1.6×10 ⁻²	2.4×10 ⁻²	4.1×10 ⁻²
2200	1.2×10 ⁻²	3.3×10 ⁻²	-----
2300	1.4×10 ⁻²	2.2×10 ⁻²	3.0×10 ⁻²
2400	1.4×10 ⁻²	1.6×10 ⁻²	3.4×10 ⁻²

^a Calculated from the thermal diffusivity using a specific heat of 0.25 cal/g °C.

M-10904-1

(a)

(500x)

M-10900-1

(b)

(500x)

M-10903-1

(c)

(500x)

Fig. 4--Photomicrographs of carbons deposited from 3% methane in a 3.5-cm-diameter coater at (a) 1900°C, (b) 2200°C, and (c) 2400°C. The total flow rate was 18,000 cm³/min (at 23°C and 1 atm) and the initial charge area was 1140 cm².

EFFECT OF COATING VARIABLES ON THE STRUCTURE OF PYROLYTIC CARBONS DEPOSITED BELOW 1900°C

It has been found that fractographs of pyrolytic carbon can reveal structural features not revealed by microscopy of polished surfaces or by X-ray scattering. Figure 5 shows a fractograph of a high-density laminar carbon deposited at 1400°C in a 2.5-cm-diameter coater using 40% methane in helium. The initial charge area was 400 cm² and the total flow was 2750 cm³/min. The fractograph shows that the dispersion in the pole figure of this structure is caused by undulations in what appears to be a continuous layer structure, rather than being caused by a dispersion of the C-axes of distinct "grains" or "growth cones" (see Fig. 6). This is consistent with the suggestion⁽²⁾ that laminar structures such as that shown in Fig. 5 are built up from planar complexes that form in the gas phase, condense directly on the bed surface, and become aligned with it. It is thought that for large bed surface areas, only occasional gas-phase condensation to droplets occurs. The incorporation of these droplets into the deposits interferes with the alignment of the planar complexes with the original deposition surface. Decreasing the surface area or increasing the contact time (decreasing the total flow rate) is thought to increase the frequency of gas-phase condensation to droplets. The incorporation of a high concentration of these droplets into the deposit decreases the degree of preferred orientation. Figure 7 shows the fractograph of a deposit made using the same conditions as those used to prepared the deposit shown in Fig. 5, except that the total flow rate was reduced by 45% (i.e., the contact time was increased) and the initial bed surface area was reduced by 47%. These changes in deposition conditions enhanced gas-phase nucleation of droplets, and the incorporation of the droplets into the deposit reduced the Bacon anisotropy factor from 3.5 to near 1.0. The fractograph reflects the more isotropic texture of this deposit and reveals a higher concentration of features that are thought to be gas-phase-nucleated particles incorporated into the deposit.

Decreasing the methane concentration at 1400°C from 40% to 5%, while keeping all the other coating parameters the same as those used to deposit the carbon shown in Fig. 5, reduced the degree of preferred orientation, the apparent crystallite size, and the density of the carbon deposited in spite of the concomitant decrease in deposition rate. A fractograph of the carbon deposited from 5% methane is shown in Fig. 8 and reveals a finer structure than those shown in Fig. 5 or 7 and a more poorly defined layered structure. Decreasing the methane concentration at 1400°C is thought to decrease the size of the planar complexes at the instant of deposition because of the reduced growth rate of these complexes in the gas phase at lower methane partial pressures. The smaller complexes cannot align themselves with the deposition surface or with one another as well as the larger ones formed at higher methane concentrations;

P-5321

(17,000 $\times$)

Fig. 5--Fractograph of a high-density, oriented, laminar carbon deposited from 40% methane at 1400°C in a 2.5-cm-diameter coater. The initial bed surface area was 400 cm² and the total flow (at 23°C and 1 atm) was 2750 cm³/min.

(a)

(b)

Fig. 6--Schematic diagrams contrasting an undulating layer structure with a structure made up of distinct grains or growth cones: (a) an undulating layer structure with gas-phase-nucleated particles incorporated in the deposits:
 (b) a structure made of "grains" or "growth cones."

P-5664

(17,000x)

Fig. 7--Fractograph of a carbon deposited from 40% methane at 1400°C in a 2.5 cm-diameter coater. The initial bed surface area was 210 cm^2 and the total flow (at 23°C and 1 atm) was $1500\text{ cm}^3/\text{min}$.

P-5452

(17,000x)

Fig. 8--Fractograph of a carbon deposited from 5% methane at 1400°C in a 2.5-cm-diameter coater. The initial bed surface area was 400 cm^2 and the total flow (at 23°C and 1 atm) was $2400\text{ cm}^3/\text{min}$.

as a result, the deposits are less dense, less anisotropic, have smaller apparent crystallite sizes, and are more difficult to graphitize.

X-ray scattering data for carbon deposits made at 1400°C support the ideas expressed above. Using an approach similar to that described by Short and Walker,⁽³⁾ the weight fraction of these deposits which is amorphous, single unassociated layers, and associated layers has been measured. The results show that the carbons deposited from 5% methane (i. e., involving small planar complexes) contain 23% single unassociated layers. The carbon deposited from 40% methane (i. e., involving larger planar complexes), on the other hand, contains only 1.7% single unassociated layers. The apparent crystallite size of the deposit from 40% methane was $42\text{ \AA}$ compared with $27\text{ \AA}$ for the carbon deposited from 5% methane. All the X-ray scattering data available to date are reported in Table 4.

A topical report entitled "Absorption Factors for a Modified Bacon Preferred Orientation Technique" by J. C. Bokros is in preparation.

MECHANICAL PROPERTIES OF PYROLYTIC CARBONS DEPOSITED ABOVE 1900°C

Measurements of the mechanical properties of pyrolytic carbons deposited below 1900°C were reported in the two previous quarterly reports.^(1,4) The samples all had laminar or isotropic microstructures with the exception of a single set of coarse-grained granular samples deposited at 1730°C from 3% methane. The same techniques have been used to measure the mechanical properties of pyrolytic carbon deposited in a 3.5-cm-diameter coater between 1900° and 2400°C from helium containing 3%, 7%, and 15% methane, using a charge of 70 g of 300- to $420\text{-}\mu$ -diameter UC_2 particles (initial surface area 1140 cm^2) and a total flow rate of $18,000\text{ cm}^3/\text{min}$. Coating rates and efficiencies are reported in Ref. 1. The samples had microstructures that cover the transition from isotropic to granular and included a range of granular structures of different densities and anisotropies. In several samples, the microstructure was granular at the start of the coating run but turned to isotropic before the end of the run. In cases like this, extra sets of mechanical property samples were made and a series of bend tests were made with either the granular or the isotropic face of the sample in tension.

The samples deposited from 3% methane all had fully granular structures. The densities and anisotropies increased steadily with deposition temperature (see section on the structure of pyrolytic carbons deposited above 1900°C). The mechanical properties (mean and maximum flexural elastic modulus, fracture stress, and fracture strain) are plotted in Fig. 9.

Table 4

STRUCTURAL DATA FOR CARBON DEPOSITS MADE FROM METHANE AT
1400°C IN A 2.5-CM-DIAMETER COATER

Methane Concentration (%)	Total Flow Rate (cm ³ /min)	Initial Bed Surface Area (cm ²)	Density (g/cm ³)	Bacon Anisotropy Factor	L _{oc} (Å)	Single Layers (%)	Amorphous (%)
5	2400	400	1.51	1.9	27	23	0
28	2780	400	1.94	1.7	35	10	0-1
40	2750	400	2.11	3.5	42	1.7	3-4
40	1500	210	1.94	1.0 ^a	32	7.3	4

^a Estimated; will be measured.

Fig. 9--Dependence of mechanical properties on deposition temperature for deposits produced in a 3.5-cm-diameter coater, using 3% methane in-helium and a 1140-cm² (70-g) charge of UC₂ particles: (a) room-temperature flexural modulus; (b) maximum fiber stress at fracture; (c) maximum fiber strain at fracture.

The error bands on the figure refer to the standard deviation of the determinations. There were no significant differences between the properties of samples tested with the inside of the deposit in tension and those tested with the outside in tension. There is a systematic increase in elastic modulus, fracture stress, and fracture strain as the deposition temperature increases. This is probably caused by the parallel increase in density and anisotropy over the same deposition temperature range.

The mechanical properties of carbons deposited from 7% methane are shown as a function of deposition temperature in Fig. 10. Of this group of samples, the microstructure of those deposited at 1900°C was fully isotropic, while that deposited at 2400°C was fully granular. The remainder had a mixed microstructure, with a granular microstructure on the inside changing to an isotropic structure at the outside of the deposit. Nevertheless, there was no systematic difference in properties according to whether the inside or the outside of the deposit was stressed in tension. The elastic moduli of the samples with isotropic or mixed microstructures showed a gradual decrease with increasing temperature, whereas the fracture stress remained approximately constant. Both the modulus and the fracture stress of the fully granular structure were much lower than the isotropic or mixed structures.

Of the samples prepared from 15% methane, those made at 1900°C and 2000°C were fully isotropic and the rest contained a transition from granular to isotropic microstructure. The mechanical properties (Fig. 11) showed a steady decrease in elastic modulus and fracture stress with increasing deposition temperature, while the fracture strain remained approximately constant.

The dependence of the mean modulus, fracture stress, and fracture strain on the deposition temperature and methane partial pressure is shown in the form of three-dimensional plots in Fig. 12, together with an indication of the microstructure of each of the sample groups tested. Several conclusions may be drawn. Among samples with a purely granular microstructure, the modulus, fracture stress, and fracture strain increase with increasing deposition temperature, the increase corresponding to increases in density and anisotropy and a decrease in grain size. The occurrence of very low moduli (1 to 1.3×10^6 psi) and fracture stresses (15 to 20×10^3 psi) seems to be limited to a narrow band of coarse-grained, low-anisotropy, granular structures. The fine-grained granular material that forms immediately after the transition from the isotropic microstructure has the same strength (30×10^3 psi) as the isotropic structures, as shown by tests where samples with a transition microstructure were tested with either the inside or the outside of the deposit in tension. Among the isotropic and transition structures, there is a slight decrease in modulus and fracture stress with increasing deposition

Fig. 10--Dependence of mechanical properties on deposition temperature for deposits produced in a 3.5-cm-diameter coater, using 7% methane in helium and a 1140-cm² (70-g) charge of UC₂ particles: (a) room-temperature flexural modulus; (b) maximum fiber stress at fracture; (c) maximum fiber strain at fracture.

Fig. 11--Dependence of mechanical properties on deposition temperature for deposits produced in a 3.5-cm-diameter coater, using 15% methane in helium and a 1140-cm² (70-g) charge of UC₂ particles; (a) room-temperature flexural modulus; (b) maximum fiber stress at fracture; (c) maximum fiber strain at fracture.

Fig. 12--Diagrams relating the mechanical properties of pyrolytic carbon deposits to deposition conditions; deposits were prepared in a 3.5-cm-diameter coater using 1140-cm² initial charge surface area: (a) mean flexural modulus; (b) fracture stress; (c) fracture strain; (d) microstructural type of the deposits tested.

temperature. It is interesting to note that the surfaces representing mechanical properties versus deposition temperature and methane pressure (Fig. 12) form almost continuous extensions of the surfaces based on samples made at lower temperatures in a different (2.5-cm-diameter) coater.

ANNEALING BEHAVIOR OF LOW-TEMPERATURE CARBON DEPOSITS

Annealing studies are being carried out on four different laminar pyrolytic carbons to investigate the relationship between the structure of the carbon and its "annealability" (see Ref. 1). Three of the structures (designated Nos. 1 through 3) were deposited at 1400°C from helium containing 40%, 28%, and 5% methane, respectively, in a 2.5-cm coater with an initial charge area of 400 cm^2 ; the other structure (designated No. 8) was prepared at 1375°C in a 2.5-cm coater from 40% methane, using a low initial charge surface area of 210 cm^2 . Other coating and structural parameters are reported in Refs. 1 and 4.

The first series of anneals has been completed. The annealing temperature was 1500°C and the annealing times were progressively increased from 30 min to 96 hr. Eight samples of each structure were used to measure the flexural modulus and electrical resistivity at each annealing stage, and pairs of samples from each structure were used to follow changes in density and apparent crystallite size, L_c . In addition, the thermal diffusivity of pairs of samples of each structure was measured before and after the series of anneals, and finally the fracture stresses and strains after annealing were determined by bend tests on the elastic modulus samples.

The fractional changes in the flexural modulus, electrical resistivity, and L_c during the course of the anneal are shown in Figs. 13 through 15. The error bands delineate the standard deviations of the measurements. The changes in the mean values of thermal diffusivity and fracture stress and strain are given in Tables 5 and 6. The densities of structures 2, 3, and 8 did not change significantly during the anneal, but structure 1 increased in density from 2.126 to 2.164 g/cm^3 .

Annealing produced the largest changes in elastic modulus, electrical resistivity, L_c , and thermal diffusivity in structure 1. There were also substantial increases in the thermal diffusivity and L_c for structure 2 and in L_c for structure 8 (diffusivity measurements were not made for structure 8). The electrical resistivity was significantly reduced in all the carbons, but L_c for structure 3 and the elastic modulus in structures 2, 3, and 8 were not changed significantly. The apparent increase in the modulus of structure 3 (Fig. 13) is probably not significant and may have

Table 5

EFFECT OF ANNEALING FOR 96 HR AT 1500°C ON THE ROOM-TEMPERATURE THERMAL CONDUCTIVITY OF THREE LAMINAR CARBONS DEPOSITED AT 1400°C IN A 2.5-CM-DIAMETER COATER

Deposit	Thermal Conductivity (cal/cm-sec-°C)		Change (%)
	Before Annealing	After Annealing	
Laminar I ^a	1.1×10^{-2}	2.2×10^{-2}	+100
Laminar II ^b	2.4×10^{-2}	4.7×10^{-2}	+96
Laminar III ^a	1.9×10^{-2}	2.1×10^{-2}	+11

^a Average of two specimens.

^b Average of three specimens.

Table 6

MEAN FRACTURE STRESSES AND STRAINS OF LAMINAR PYROLYTIC CARBONS DEPOSITED AT 1400°C AS-DEPOSITED AND AFTER ANNEALING AT 1500°C FOR 96 HR

Structure Number	Fracture Stress			Fracture Strain		
	As-deposited (10 ³ psi)	Annealed (10 ³ psi)	Change (%)	As-deposited (%)	Annealed (%)	Change (%)
1	58.9 ±13.9	59.1 ±10.6 ^a	0	0.94 ±0.20	1.22 ±0.17	+30
2	62.3 ±10.4	61.8 ±17.6	-1	1.27 ±0.23	1.27 ±0.32	0
3	45.2 ±8.0	29.1 ±5.0	-36	0.98 ±0.21	0.66 ±0.12	-33
8	42.7 ±5.9	39.3 ±5.5	-8	1.11 ±0.14	1.07 ±0.17	-4

^a The ± limits refer to the standard deviations of the determinations.

Fig. 13--Fractional changes in flexural modulus as a function of annealing time at 1500°C for laminar pyrolytic carbons deposited at 1400°C. Details of each of the four structures are given in the text.

Fig. 14--Fractional changes in electrical resistivity as a function of annealing time at 1500°C for laminar pyrolytic carbons deposited at 1400°C . Details of each of the four structures are given in the text.

Fig. 15--Fractional changes in apparent crystallite size, L_c , as a function of annealing time at 1500°C for laminar pyrolytic carbons deposited at 1400°C . Details of each of the four structures are given in the text.

been due to errors in measuring the modulus of the as-deposited samples. The only changes in mechanical properties (Table 6) were the increase in fracture strain of structure 1 associated with the decrease in elastic modulus, and decreases in the fracture stress and strain of structure 3, which were apparently caused by an unexplained surface cracking that developed during the final stages of the anneal.

The properties that were measured during the anneal are all sensitive to some type of structural imperfection in the carbon. It is evident from the results reported above that different properties respond to annealing to different extents, but the order of "annealability" between the four carbons remains the same. Structure 1 is readily annealable, but structure 3 is completely unaffected by treatment at 1500°C. Structures 2 and 8 are intermediate in behavior. The "annealabilities" are in reverse order to the percentage of single layers in the structure as revealed by X-ray scattering measurements (see section on the structure of carbons deposited below 1900°C).

The annealing of the same physical properties in the same carbon structures will be followed at higher temperatures so that a complete picture will be built up of the annealing kinetics of several different properties as a function of the structure of the pyrolytic carbon.

EFFECT OF STRUCTURE ON THE RADIATION STABILITY OF PYROLYTIC CARBON

Samples of seven different types of pyrolytic carbon are being irradiated in a fast-neutron flux in the GETR.* Details of the preparation of the samples, pre-irradiation measurements, and construction of the capsule were reported in Ref. 4. The capsule is now in the fifth cycle of a scheduled six-cycle irradiation. The samples are being irradiated in five different cells whose temperatures range from 670° to 1075°C. The total estimated dose in the highest exposure position will be 1.8×10^{21} nvt ($E > 0.18$ Mev). The irradiation is scheduled to be completed in April.

* This irradiation is being performed under Project Agreement No. 17 of Contract AT(04-3)-167.

IV. DIFFUSION OF URANIUM AND THORIUM IN PYROLYTIC CARBON

H. K. Lonsdale, J. Graves

EFFECT OF STRUCTURE ON DIFFUSION OF THORIUM IN PYROLYTIC CARBON

The diffusion of Th^{228} through pyrolytic carbon is being investigated in a series of tracer-level diffusion studies. In an attempt to relate diffusion to structure, experiments have been performed using laminar, isotropic (random), and granular pyrolytic carbon. ^(1,4)

During the present quarter, several diffusion experiments have been completed in the system Th^{228} -granular pyrolytic carbon. The experimental method and techniques and coating conditions are as described in previous reports. ^(1,4) The results are summarized in Table 7.

These diffusion coefficients are about a factor of three greater than the values reported by Wolfe, *et al.*, ⁽⁵⁾ of UCRL for "perpendicular" diffusion in commercial columnar pyrolytic carbon, and they are about a factor of ten greater than the values determined at General Atomic ⁽¹⁾ for laminar pyrolytic carbon. Figure 16 shows comparison of these sets of results, along with the data of Evans, *et al.*, ⁽⁶⁾ of ORNL, also with columnar pyrolytic carbon. (The size of the circles used to indicate the General Atomic data is not significant.)

A program has been written for the IBM-7044, with which diffusion coefficients can be calculated from the raw concentration and distance data.

Table 7

TRACER-LEVEL DIFFUSION COEFFICIENTS OF THORIUM IN GRANULAR PYROLYTIC CARBON--PERPENDICULAR TO THE PLANE OF DEPOSITION

Experiment Number	Temperature (°C)	D (cm ² /sec)
22-1	1734	2.0×10^{-12}
23-1	1804	1.2×10^{-11}
23-2	1804	7.8×10^{-12}
24-1	1875	3.2×10^{-11}
24-2	1875	2.2×10^{-11}

Fig. 16--Comparison of several investigations of the diffusion of thorium in pyrolytic carbon--perpendicular to the plane of deposition.

V. FISSION-PRODUCT RELEASE FROM CARBIDE FUEL SYSTEMS

L. R. Zumwalt, P. Gethard, C. Adams, R. Precourt

EFFECT OF COATING STRUCTURE ON RELEASE OF METALLIC FISSION PRODUCTS THROUGH PYROLYTIC CARBON

In order to obtain information which will help to elucidate the mechanism by which metallic fission products penetrate pyrolytic carbon, disks of U^{235} -impregnated ATJ graphite were coated with several types of pyrolytic carbon for use in fission-product release studies. The procedure is to irradiate the disks to produce fission products within them. The concentration gradient of metallic fission products through the coatings is then determined as a function of annealing time and temperature.

Since earlier experiments indicated the need for assuring parallel surfaces, ⁽¹⁾ the ATJ graphite disks were machined parallel ($\pm 1.25 \mu$) prior to impregnation with U^{235} . After coating the impregnated disks, the flat surfaces were again machined parallel ($\pm 1.25 \mu$), since the pyrolytic carbon tends to build up on edges even though they are beveled as they were in this case.

The disks (5/16 in. in diameter, 1/16 in. thick) were impregnated by placing them in a concentrated solution of uranyl nitrate plus nitric acid and then placing the system under vacuum. About 7% volume impregnation is accomplished this way, and thus the amount of U^{235} ending up in the graphite is determined by its concentration in the solution. The impregnated disks, each containing 0.1 mg of U^{235} , were dried at 110°C and finally baked in vacuo at 1000°C for 1 hr to eliminate all traces of nitrate.

Three types of pyrolytic coatings were deposited on the impregnated disks (see Table 8). Using the TRIGA reactor King furnace, the steady-state release of fission gases was measured from one disk at 1200°C . The data obtained are shown in Table 9. As in the preliminary experiments, the release is relatively high in comparison with release measured for coated fuel particles. This is indicative of a significant level of fuel in the coating itself. It is believed, however, that this will not interfere with studies of the diffusion of metallic fission products such as Ba^{140} through the pyrolytic carbon. Accordingly, a series of experiments involving annealing of the coated disks and the determination of concentration profiles of Ba^{140} in the pyrolytic carbon layer have been started.

Table 8

PYROLYTIC-CARBON COATINGS DEPOSITED
ON U²³⁵-IMPREGNATED GRAPHITE DISKS

Type	Deposition Temperature (°C)	CH ₄ Concentration (%)	Coating Thickness (μ)
1. Isotropic ^a	1650	15	150
2. Grainy-isotropic ^b	2000	15	110
3. Granular ^c	1900	3	150

^a Coatings were deposited in a 2.5-cm-diameter coater using an initial charge of 400 cm² (15 g of 150- to 250-μ (Th, U)C₂ particles together with graphite disks). Total gas flow was 4,500 cm³/min and average deposition rate was 75 μ/hr.

^b Coatings were deposited in a 3.5-cm-diameter coater using an initial charge of 800 cm² (48 g of 295- to 350-μ UC₂ particles together with graphite disks). Total gas flow was 7,325 cm³/min and average deposition rate was 85 μ/hr.

^c Coatings were deposited in a 3.5-cm-diameter coater using an initial charge of 970 cm² (70 g of 350- to 420-μ (Th, U)C₂ particles together with graphite disks). Total gas flow was 18,300 cm³/min and average deposition rate was 25 μ/hr.

Table 9

STEADY-STATE RELEASE AT 1200°C OF FISSION GASES
FROM A U²³⁵-IMPREGNATED GRAPHITE DISK COATED
WITH PYROLYTIC CARBON^a

Isotope	Half-life (hr)	Fractional Release
Kr ^{85m}	4.4	2.1×10 ⁻³
Kr ⁸⁸	2.8	1.9×10 ⁻³
Kr ⁸⁷	1.3	1.9×10 ⁻³
Kr ⁸⁹	0.053	9.8×10 ⁻⁴
Xe ¹³⁸	0.28	4.4×10 ⁻⁴
Xe ¹³⁹	0.011	1.6×10 ⁻³

^a Type 2 in Table 8.

VI. CHARACTERIZATION OF MICROSTRUCTURE OF GRAPHITIC MATERIALS

J. L. White, G. R. Tully, Jr., A. S. Schwartz,
J. O. Gardner, E. A. Taylor, D. E. Davis

ELECTRON MICROGRAPHY

Previous work on this program by optical micrography, including the recent work illustrated in the section on carbide-graphite materials prepared by hot-working, has indicated the existence of important structural detail at magnifications at or beyond the resolution of optical microscopy. Attempts to apply replication electron micrography to polished graphite surfaces have been of limited value owing to smearing, microcracking, and deposition of debris in pores even in the most careful polishing procedures. (7) Accordingly, an apparatus for etching by argon-ion bombardment has been set up, and some preliminary results on materials of interest to the present program are described here.

The cathodic etcher is similar in principle to that employed by other workers. (8-10) The initial work illustrated in Figs. 17 and 18 employed etching conditions of 3 kv with approximately 10 μ of argon pressure. This produced a discharge current of approximately 1 ma. It was found that specimens prepared by different polishing procedures, which produce somewhat different structures as observed optically, were brought to essentially equivalent structures after sufficient cathodic etching.

Figures 17 through 19 are representative structures found in replicas of a hot-pressed fuel-matrix graphite prepared with 25 wt-% Barrett No. 30 pitch binder and 75 wt-% GP-38 graphitized petroleum coke. This specimen had been annealed at 2800°C. The micrographic sections are longitudinal; i. e., the plane of section is parallel to the hot-pressing direction and therefore perpendicular to the preferred orientation of the graphite layer planes.

The effective action of cathodic etching in removing debris and in revealing the accommodation microcrack systems is apparent by comparing the etched structures of Figs. 17 and 18 with the as-polished structure of Fig. 19. The microcrack systems, occurring in both linear and curved regions, are similar to those observed in conventional graphites by other workers. However, it is not clear at this point that the etching conditions

P-5608

(5,000x)

Fig. 17--Electron micrograph of an annealed fuel-matrix graphite; cathodically etched; carbon replica, negatively shadowed with palladium; longitudinal section.

P-5611

(~14,000x)

Fig. 18--Electron micrograph of an annealed fuel-matrix graphite; cathodically etched; carbon replica, negatively shadowed with palladium; longitudinal section.

P-5620

(~14,000x)

Fig. 19--Electron micrograph of an annealed fuel-matrix graphite; no cathodic etching; carbon replica, negatively shadowed with palladium; longitudinal section.

have been optimized with respect to removal of all effects of polishing, and further work will be directed to this point.

The cathodic etching technique is currently being applied to study the fine structure of the carbide-graphite materials prepared by hot-working at temperatures such that the dispersed carbide phase is in the liquid state. Figures 20 through 22 are electron micrographs prepared from cathodically etched surfaces of graphite-molybdenum carbide bodies hot-worked at 2720°C to a true strain of 56%. Optical photomicrographs of this specimen are given in Fig. 30 of Section VIII of this report.

The micrograph of Fig. 20 is taken from a lightly etched region where the etching is inadequate to remove the graphite debris but is appropriate to reveal structure in the molybdenum carbide particles. The micrographs of Figs. 21 and 22 are taken from somewhat more heavily etched regions; the fine structure of the carbide particles has disappeared, but the microcrack systems of the graphite matrix are more clearly evident.

Several tentative observations may be drawn from these initial studies. The hot-worked carbide-graphite material does not show curved microcrack systems to the degree observed with the annealed matrix graphite, although the general appearance and spacing of the microcracks is approximately the same. Rather well-defined grain boundaries are also evident in the carbide-graphite material, and there appears to be good contact between the carbide particles and the graphite matrix. The carbide particles are rough in shape, but no strong tendency to elongated and oriented particles is noted.

KINETICS OF OXIDATION OF GRAPHITIC BODIES IN LIQUID MEDIA

An apparatus for measuring the rates of oxidation of graphitic materials in hot dichromic acid solution was described in the last quarterly report.⁽¹⁾ The object of this work is to develop methods to characterize the degree of graphitization of "graphite" bodies. A secondary object is to find out if such a property can be related to the behavior of graphite bodies under irradiation.

It is well known that bodies containing a high percentage of a non-graphitizing carbon, such as lampblack, contract more on high-temperature irradiation than do bodies made from predominantly graphitizing carbon sources and heat-treated to graphitizing temperatures. Commercial graphites, and, indeed, graphites especially designed for nuclear reactor use, often contain small amounts of non-graphitizing carbons as binders, fillers, or impregnants. Often the formulation is not available, but more

P-5636

(5,000 $\times$)

Fig. 20--Electron micrograph of a hot-worked graphite matrix containing molybdenum carbide particles; lightly cathodically etched; carbon replica, negatively shadowed with palladium; longitudinal section.

P-5629

(5,000x)

Fig. 21--Electron micrograph of a hot-worked graphite matrix containing molybdenum carbide particles; moderately cathodically etched; carbon replica, negatively shadowed with palladium; longitudinal section.

P-5630

(~14,000x)

Fig. 22--Electron micrograph of a hot-worked graphite matrix containing molybdenum carbide particles; moderately cathodically etched; carbon replica, negatively shadowed with palladium; longitudinal section.

importantly, it simply is not known exactly where and in what structure these materials finally locate in a finished graphite body. It is also not known if the "graphitizing" binder or filler does indeed graphitize fully in heat treatments. Furthermore, the effect of small amounts of carbon on irradiation contraction is not clear. As the designs of graphite-moderated reactors become more advanced, it becomes necessary to minimize the graphite contraction so that longer reflector and fuel element life may be obtained.

In light of the above, it is thought that a method of determining small amounts of ungraphitized carbon in graphite bodies could be used to give a characterization factor that, together with an anisotropy relationship, would correlate with irradiation behavior and serve to point the way to improved formulations and fabrication methods.

The method of Oberlin, *et al.*,⁽¹¹⁾ in which carbonaceous material is oxidized with $\text{H}_2\text{SO}_4\text{-Ag}_2\text{Cr}_2\text{O}_7$, is being used as a base for these studies. This previous work has demonstrated the existence of three reaction rates, which are presumed to define three constituents: F_1 , F_2 , and F_3 . The F_1 fraction corresponds to amorphous carbon and oxidizes at the lowest rate. The published work of Oberlin, *et al.*, does not indicate that they have attempted to detect small amounts of the F_1 fraction.

The apparatus used in these studies has been constructed and calibration runs with natural graphite are in progress (see Ref. 1 for a diagram of this apparatus). The initial runs with this material indicate that an incubation time is required before a logarithmic oxidation rate begins. Calibration of the effective system volume is now being checked by the usual $P_1V_1 = P_2V_2$ method.

After the system has been calibrated, the method will be verified by running samples of calcined coke that have been heat-treated to 1500° , 2000° , 2500° , and 3000°C . Highly graphitic material will then be mixed with small amounts of lampblack, and the limits of detection of the F_1 fraction will be determined. If possible, the equipment or method will be modified to optimize the determination of small amounts of the F_1 fraction. If the results of the above studies warrant, graphites that have been, or will be, irradiated will be analyzed. A relationship between contraction during irradiation and the $F_1/F_2/F_3$ factors will be sought.

VII. RELATION OF PHYSICAL PROPERTIES OF GRAPHITIC MATERIALS TO MICROSTRUCTURE

R. J. Price, G. B. Engle

RADIATION-INDUCED DIMENSIONAL CHANGES

The relationship between preferred orientation and radiation-induced dimensional changes in fully graphitic material is being investigated by irradiating samples cut from an extruded graphite tube. Details of the experiment are given in Ref. 4. The samples are being irradiated in the GETR in the same capsule as that containing pyrolytic carbon deposits. The temperatures and expected neutron exposure are given in Section III of this report. The capsule is in the fifth cycle of a scheduled six-cycle run and is due for discharge in April. *

INFLUENCE OF FILLER AND BINDER COMPOSITION ON STRUCTURE AND PROPERTIES

An experiment has been initiated to determine the role of pitch binder and binder content (binder film thickness) on the preferred orientation, microstructure, physical properties, and subsequently the neutron-induced-dimensional changes in graphitic bodies. Various techniques being developed in other phases of the current graphite research will be used to characterize the samples.

A series of molded samples are being prepared with the following filler materials: (1) uncalcined needle coke, (2) calcined needle coke, (3) natural flake graphite, and (4) Gilsocarbon coke (isotropic). The binder (coal tar pitch) content will be varied to observe the effect of binder film thickness, if possible, on the various fillers and, in particular, the regions of binder-filler interface. Special attention will be directed toward observation of the uncalcined coke materials and how the microstructure and orientation are affected by carbonization and graphitization of the binder.

Irradiation experiments are planned later to determine the effect of fast neutron flux on properties and dimensional change and to correlate the effect of binder content.

* This irradiation is being performed under Project Agreement No. 17 of Contract AT(04-3)-167.

VIII. CHEMICAL AND METALLURGICAL PROCESSES
FOR MODIFYING THE MICROSTRUCTURE
OF GRAPHITE

J. L. White, J. M. Pontelandolfo, L. C. Foster

During the period covered by this report, emphasis has been placed on further determinations of the promising properties of graphite-carbide bodies hot-worked at temperatures such that the carbide-bearing phase is in the liquid state. The initial results of this work are given in a topical report. (12)

The reader is referred to previous topical and annual reports (7,13,14) for details concerning the device and methods applied to hot-work graphitic bodies in compression at temperatures from 2250° to 3000°C.

PITCH CONTENT AS A HOT-WORKING VARIABLE

Some further property measurements have been made on hot-pressed fuel-matrix graphite prepared with 20 wt-% binder (Barrett No. 30 pitch) and 80 wt-% filler (GP-38 graphitized petroleum coke). This is the same graphite matrix as used in the preparation of the carbide-graphite bodies, and the results are primarily of interest in showing the important changes obtained in the physical properties when the graphite matrix is hot-worked with a liquid carbide phase present in the pore structure.

The data on compressive strength are summarized in Fig. 23 for specimens that were hot-worked in the neighborhood of 2700°C. The compressive strengths were measured on cylindrical specimens, 0.25 in. in diameter by 0.375 in. high, cut with the cylinder axis either parallel or perpendicular to the direction of hot-working. Data for hot-pressed fuel-matrix graphite prepared with 10 wt-% pitch binder are included to demonstrate the favorable effect of using greater pitch contents in specimens to be hot-worked than are used in conventional graphite-matrix fuel bodies. It is clear that pitch contents of the order of 20 wt-% or greater are necessary in order to obtain beneficial effects by hot-working and that these beneficial effects cannot be obtained at high strain levels.

A favorable effect of hot-working fuel-matrix graphite is illustrated by the results on helium permeability given in Fig. 24. Although

Fig. 23--The compressive strength of fuel-matrix graphites hot-worked in compression at temperatures in the neighborhood of 2700°C.

Fig. 24--The helium permeability of fuel-matrix graphites, with and without carbide additives, as a function of compressive strain in hot-working.

measurements have been completed on only a limited number of the hot-worked specimens prepared with 20 wt-% pitch binder, the preliminary data on additional specimens are in agreement with the data shown in Fig. 24 in showing that the helium permeability can be reduced by an order of magnitude by hot-working.

Additional property measurements currently in progress include porosity, density, thermal diffusivity, and thermal expansion.

GRAPHITE-CARBIDE MATERIALS PREPARED BY HOT-WORKING

In the previous quarterly report, ⁽¹⁾ some preliminary results were reported for the properties of graphite bodies containing a dispersion of carbide particles and hot-worked at temperatures above the carbide-graphite eutectic temperature. Work during the period covered by the present report confirms that very substantial improvements in the properties of graphite can be obtained by means of this modified hot-working process, and present efforts are directed to a full characterization of these promising materials.

The results described here have been obtained with two carbides, molybdenum carbide and zirconium carbide, with carbide-graphite eutectic temperatures at 2400°C ⁽¹⁵⁾ and 2835°C , ⁽⁷⁾ respectively. The carbide-bearing bodies were prepared by hot-pressing a dispersion of fine carbide particles in a graphite matrix comprised of 20 wt-% binder (Barret No. 30 pitch) and 80 wt-% filler (GP-38 graphitized petroleum coke). The nominal carbide content before hot-working was 12 vol-%. The bodies were hot-worked in compression to strain levels as high as 60% true strain. Although no measurements have been made of the creep rate of the graphite bodies containing the liquid carbide phase, it is clear that high hot-working strains are accomplished more easily than with graphite bodies containing no carbide additive.

During the hot-working process, the carbon-saturated liquid carbide tends to be squeezed out of the graphite matrix, and carbide droplets are formed on the surface of the specimen after hot-working (see Fig. 25). The results of chemical analysis of the specimens containing molybdenum carbide (see Fig. 26) indicate that the molybdenum content is reduced from approximately 6 at.-% (34 wt-%) to 3.2 at.-% (21 wt-%) on hot-working to a strain level of 55% true strain. The carbide beads are readily removed from the hot-worked body if care is taken to keep the cutting edge of the lathe tool below the beads and in the graphite substrate.

Photomicrographs of the matrix graphite containing molybdenum carbide particles are shown in Figs. 27 through 30 for four levels of

M-10556-1

(1.85x)

Fig. 25--Photograph of carbide-containing specimen after hot-working to a compressive strain of approximately 25%. Original specimen was 2 in. in length and 1 in. in diameter.

Fig. 26--Results of chemical analysis of hot-worked matrix graphite containing molybdenum carbide.

M-10357-12

(400x)

(a)

M-10530-1

(400x)

(b)

Fig. 27--Photomicrographs of graphite matrix containing molybdenum carbide particles: (a) longitudinal section; (b) transverse section. Specimen annealed at 2700°C; no hot-work.

M-10358-10

(400x)

(a)

M-10531-1

(400x)

(b)

Fig. 28--Photomicrographs of graphite matrix containing molybdenum carbide particles: (a) longitudinal section; (b) transverse section. Specimen hot-worked at 2720°C to true strain of 24%.

M-9924-10

(400x)

(a)

M-10532-1

(400x)

Fig. 29--Photomicrographs of graphite matrix containing molybdenum carbide particles: (a) longitudinal section; (b) transverse section. Specimen hot-worked at 2720°C to true strain of 41%.

M-10359-10

(400x)

(a)

M-10533-1

(400x)

(b)

Fig. 30--Photomicrographs of graphite matrix containing molybdenum carbide particles: (a) longitudinal section; (b) transverse section. Specimen hot-worked at 2720°C to true strain of 56%.

hot-working strain and for both longitudinal and transverse sections. The progressive reduction in porosity and increasing uniformity of structure are illustrated by these photomicrographs. The carbide particles appear as a uniform dispersion, with a particle size generally less than $4\ \mu$. The particles show little tendency to depart from an equiaxed geometry even in the highly hot-worked specimens. The structure of the matrix graphite containing zirconium carbide particles is similar to that of the graphite containing molybdenum carbide; two photomicrographs are shown in Fig. 31.

Techniques of replication electron micrography are being developed to study the structures of the graphite bodies hot-worked with a dispersed liquid carbide phase. Some electron micrographs of the molybdenum-bearing specimen of Fig. 30 are given in Section VI of this report.

Some results for the compressive strengths are given in Fig. 32. The test specimens were cylindrical in shape, 0.25 in. in diameter and 0.375 in. high, and were cut either parallel or perpendicular to the direction of hot-working. Hot-working of the carbide-bearing bodies results in large increases in strength parallel to the direction of hot-working and modest increases in the perpendicular direction. These effects are in sharp contrast to the results for a similar graphite matrix hot-worked without the carbide additives (see, for example, Fig. 23). As a further comparison, it may be noted that the compressive strength of ATJ graphite is reported to be 8,500 psi, essentially independent of direction.⁽¹⁶⁾

The effective strengthening of the graphite caused by the presence of the liquid carbide phase during hot-working is also shown by the measurements of moduli of rupture shown in Fig. 33. The flexure tests on the matrix graphite containing molybdenum carbide particles were made with a four-point loading jig using specimens of approximately square cross section, no larger than 0.1 in. on a side and approximately 0.6 in. long. Specimens were tested in the three orientations, relative to the preferred orientation imparted by hot-working, shown in Fig. 33. It should be pointed out that this strengthening is not found when the carbide-graphite body is hot-worked at temperatures such that the carbide phase is solid.^(1, 14)

In considering possible mechanisms whereby the sharp improvements in strength are obtained for the bodies hot-worked with a liquid carbide phase, it should be noted that the strength increases with increasing hot-working strain while the concentration of carbide is decreasing. Furthermore, the volume fraction of carbide is low, and the micrographic studies indicate that the graphite matrix is the continuous phase. Consequently, the effective strengthening would not appear to be attributable to the mere

M-10369-1

(200x)

(a)

M-9880-1

(200x)

(b)

Fig. 31--Photomicrographs of graphite matrix containing zirconium carbide particles: (a) longitudinal section, annealed at 2930°C ; (b) longitudinal section, hot-worked to 39% true strain at 2920°C .

Fig. 32--Compressive strengths of hot-worked matrix graphite with a dispersion of carbide particles.

Fig. 33--Moduli of rupture of hot-worked matrix graphite containing molybdenum carbide particles.

presence of a strong carbide phase, and the mechanism of strengthening would appear to be due to an interaction of the carbide phase with the graphite matrix.

Preliminary measurements of the helium permeability of the molybdenum carbide-bearing bodies hot-worked above the carbon-graphite eutectic temperature indicate that the liquid carbide is effective in blocking pores. These data have been included in Fig. 24. Difficulties have been encountered in making these measurements because the permeabilities are near the limit of detection with the existing apparatus; consequently, the measured values may be upper limits determined by problems of sealing or degassing rather than true measurements of permeability. The permeability of the starting material is of the order of 2×10^{-4} cm²/sec; on hot-working even to modest strain levels, the permeability is decreased to less than 10^{-6} cm²/sec.

Other property measurements are currently in progress, including measurements of porosity, density, thermal expansion, thermal diffusivity, and preferred orientation.

Attempts are currently being made to hot-work graphite-matrix bodies prepared by extrusion. Although previous attempts to hot-work extruded bodies encountered difficulties owing to the higher fracture risk of extruded bodies (as compared to hot-pressed bodies), the presence of the liquid carbide phase appears to reduce the seriousness of this problem. This work with extruded starting materials is aimed at gaining effective control over the preferred orientation in the hot-worked body.

REFERENCES

1. Bokros, J. C., et al., "Advanced, Graphite-Matrix, Dispersion-Type Fuel Systems and Research on Graphite, Quarterly Progress Report for the Period Ending November 14, 1964," General Atomic Report GA-5918 (Part 1), December 1, 1964.
2. Bokros, J. C., "The Structure of Pyrolytic Carbon Deposited in a Fluidized Bed," General Atomic Report GA-5163, June, 1964.
3. Short, M. A., and P. L. Walker, Carbon, 1, 3 (1963).
4. Bokros, J. C., et al., "Advanced, Graphite-Matrix, Dispersion-Type Fuel Systems and Research on Graphite, Quarterly Report for Period Ending August 14, 1964," USAEC Report GA-5606 (Part 1), General Atomic Division, General Dynamics Corporation, September 1, 1964.
5. Wolfe, J. R., D. R. McKenzie, and R. J. Borg, "The Diffusion of Nonvolatile Metallic Elements in Graphite," Lawrence Radiation Laboratory Report UCRL-7324, April 29, 1964.
6. Evans, R. B. III, J. O. Stiegler, and J. Truit, "Actinide Diffusion in Pyrocarbons and Graphite," Oak Ridge National Laboratory Report ORNL-3711, December, 1964.
7. Anderson, E. E., et al., "Advanced, Graphite-Matrix, Dispersion-Type Fuel Systems, Annual Report, April 1, 1962, through March 31, 1963," USAEC Report GA-4022 (Part 1), General Atomic Division, General Dynamics Corporation, April 1, 1962.
8. Newkirk, H. W., J. American Ceram. Soc., 41, 196 (1958).
9. Hales, R. L., and E. M. Woodruff, Proceedings Fifth Carbon Conference, 1, 456 (1962).
10. Thrower, P. A., and W. N. Reynolds, J. Nucl. Mater., 8, 221 (1963).
11. Oberlin, M., and J. Mering, "Kinetic Studies of the Oxidation of Graphitizable Carbons by Liquid Media," presented at the Sixth Conference on Carbon, Pittsburgh, Pa., June 17-21, 1963 (see General Atomic Report GA-tr-6049 for translation).
12. White, J. L., and J. M. Pontelandolfo, "Graphite-Carbide Materials Prepared for Hot-working," General Atomic Report GA-6052 (to be published).

13. Price, R. J., and J. L. White, "Research on Graphite, Annual Report, April 1, 1963 through March 31, 1964," USAEC Report GA-5033, General Atomic Division, General Dynamics Corporation.
14. White, J. L., and R. J. Price, "Hot-working of Graphite for Graphite-Matrix Nuclear Fuels," USAEC Report GA-5348, General Atomic Division, General Dynamics Corporation, July 17, 1964.
15. Hansen, M., and K. Anderko, Constitution of Binary Alloys, McGraw-Hill Book Company, New York, 1958, p. 371.
16. Nightingale, R. E., H. H. Yoshikawa, and H. H. W. Losty, "Physical Properties," Chapter 6 in Nuclear Graphite, R. E. Nightingale, ed., Academic Press, New York, 1962.

Appendix

GENERAL ATOMIC TOPICAL REPORTS

1. Bokros, J. C., R. J. Price, and G. R. Tully, Jr., "The Anisotropy of Extruded Graphite Tubes," GA-5102, March, 1964.
2. Bokros, J. C., R. J. Price, and T. A. Trozera, "Influence of Structure on Mechanical Properties of Pyrolytic Carbon," GA-5084, April, 1964.
3. Goeddel, W. V., and J. C. Bokros, "Coated Particle Fuels Research at General Atomic from December 1, 1963, through April 30, 1964," presented at the Seventh Meeting of the Coated Particle Fuels Working Group on May 20-21, 1964, GAMD-5216, April, 1964.
4. Bokros, J. C., "The Structure of Pyrolytic Carbon Deposited in a Fluidized Bed," GA-5163, June, 1964.
5. White, J. L., and R. J. Price, "The Hot-working of Graphite for Graphite-Matrix Nuclear Fuels," GA-5348, August, 1964.
6. Price, R. J., and J. C. Bokros, "Analysis of the Thermal Expansion and Radiation-induced Length Changes in Graphite in Terms of Preferred Orientation," GA-5571, August, 1964.
7. Bokros, J. C., "Absorption Factors for a Modified Bacon Preferred Orientation Technique," GA-6031 (to be published).
8. White, J. L., and J. M. Pontelandolfo, "Graphite-Carbide Materials Prepared for Hot-working," GA-6052 (to be published).