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GENERAL ATOMIC

DIVISION OF **GENERAL DYNAMICS**

AEC RESEARCH AND
DEVELOPMENT REPORT

GA-7827

ADVANCED GRAPHITE FUEL SYSTEMS

QUARTERLY PROGRESS REPORT
FOR THE PERIOD ENDING FEBRUARY 14, 1967

by

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

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

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

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GENERAL ATOMIC
DIVISION OF
GENERAL DYNAMICS

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I. INTRODUCTION

The objective of this program is to develop an understanding of the properties of the various types of carbons and graphites required for use in high-temperature reactors of advanced design and thus to provide a basis for substantial improvements in their service behavior. The experimental approach places emphasis on defining the structures of the various carbons and graphites, learning the relationships between structure and relevant properties, and evaluating methods for the preparation of improved structures.

The research program for the period covered by this report, November 15, 1966, to February 14, 1967, consists of work in two principal areas: (1) investigation of the structures and properties of carbons and graphites, and (2) studies of the effects of irradiation on these structures and properties. The progress during this period is described in this report in six topical sections.

The objective of the work on structural characterization is to develop a systematic correlation between properties and structure, without need for reference to the fabrication history of the carbons and graphites. 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 work on pyrolytic carbons includes studies of the structural transitions produced by heat treatment, both with and without catalytic additives. The investigations of conventional graphites include micrographic studies of the structural reactions which occur during carbonization and graphitization. Experimental techniques for characterizing the degree of graphitization of carbonaceous and graphitic materials by densitometric separation are also being evaluated.

The work on irradiation effects is focused primarily on the behavior of carbons and graphites under the fast-neutron-flux and high-temperature conditions representative of the operating conditions of advanced reactor systems. The objectives are to determine which structures possess greatest stability under irradiation and to define the changes in dimensions and other relevant properties as a function of structure. The irradiation experiments are conducted on materials of controlled and fully characterized structure, and the principal areas of interest are the dimensional effects; the mechanical properties of strength, elastic modulus, and irradiation creep; and the thermal conductivity.

II. SUMMARY

THE STRUCTURE OF PITCH BINDER AT VARIOUS STAGES OF CARBONIZATION

Further micrographic investigations have been made of the mesophase structures formed in an extracted coal-tar pitch during carbonization. Four basic configurations of extinction contours have been found from observation of the coalesced mesophase by polarized light with crossed polarizers. These configurations comprise both co-rotating and counter-rotating nodes and crosses, the rotation occurring when the plane of polarization of the incident light is rotated. These regions have been mapped out in terms of the intersections of the mesophase layer planes with the micrographic plane of section, and the nodal regions and the counter-rotating cross have been found to correspond to three types of defect in the stacking of the mesophase layer planes. A topical report⁽¹⁾ has been prepared on the initial phase of this work.

These investigations have been extended to include the effects of filler coke particles and pitch insolubles on the mesophase structures. On carbonizing an extracted pitch containing particles of calcined petroleum coke, the mesophase layer planes have been found to align themselves with the layer planes of coke particles. The insoluble particles of a typical impregnating pitch appear to offer nucleation sites for the mesophase transformation. The insoluble particles are not incorporated in the mesophase, but are swept along in the boundaries with the isotropic pitch. This leads to the segregation of the insolubles in clumps in the fully transformed pitch. The mesophase has the same characteristics of nodes and crosses in the polarized-light extinction contours as are found in extracted pitch.

CHARACTERIZATION OF DEGREE OF GRAPHITIZATION

An experimental effort is being made to separate and identify the various structural states of the carbon which comprise conventional binder-filler bodies. A relationship between crystallinity, as measured by layer plane spacing, C_0 , and apparent liquid density has been shown for sugar-char particles which were heated to 2800°C. The separation of powdered samples of nuclear graphites by the densitometric method indicates a variation in the structure of various components of the materials and the existence of low-density fractions. When the particle size used in the

densitometric separation column was reduced, the liberation of the non-graphitic carbon structure was improved, and the relationship between the crystallinity, as measured by apparent crystallite height, L_c , and the apparent liquid density was more apparent.

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

High-temperature irradiations have been completed on a series of molded bodies prepared with either uncalcined coke filler or calcined coke. Micrographic examination of samples irradiated at 1450°C and $3.25 \times 10^{21} \text{ n/cm}^2$ ($E > 0.18 \text{ MeV}$) showed a dramatic reduction of the crack structure which lies parallel to basal planes in the filler particles. The changes were accompanied by a significant reduction in the closed porosity and the bulk thermal expansivities of the samples prepared with a pitch binder.

THERMAL EXPANSIVITY OF NONGRAPHITIC CARBONS

The final measurements needed to bring to a conclusion the work on the relationship of thermal expansivity to the preferred orientation of nongraphitic carbons require low-density, highly oriented pyrolytic carbons. One such sample has been prepared, and the thermal expansivity has been measured; other structures of this general type are being prepared in a fluidized-bed coater.

RADIATION-INDUCED DIMENSIONAL CHANGES IN MODEL CARBONS AND GRAPHITES

Investigations of radiation-induced dimensional effects are currently being conducted on three types of materials: turbostratic carbons of poor crystallinity, annealed pyrolytic carbons of good crystallinity, and carbons which have been catalytically graphitized by means of a titanium additive. A topical report⁽²⁾ on irradiation-induced dimensional changes in pyrolytic carbons has been prepared. Postirradiation examinations of irradiated specimens of annealed pyrolytic carbon are in progress. The irradiation results for the specimens of catalytically graphitized carbon are being compiled for a forthcoming topical report.⁽³⁾

ANNEALING STUDIES OF PYROLYTIC-CARBON STRUCTURES

Specimens of pyrolytic carbon irradiated at temperatures between 540° and 1060° C to 1.5 to 2.4×10^{21} n/cm² ($E > 0.18$ MeV) show the first small increases in density and apparent crystallite size on annealing at 1500° and 1600° C. A pyrolytic carbon containing 6.7% titanium and a titanium-free "control" carbon show parallel annealing behavior between their deposition temperature (1225° C) and 1600° C, with no catalyzed crystal growth occurring in the metal-doped carbon.

III. THE STRUCTURE OF CARBONIZED COAL-TAR PITCH J. L. White, G. L. Guthrie, and J. M. Pontelandolfo

Recent investigations by several groups⁽⁴⁻⁶⁾ on the structural conditions for the graphitizability of organic materials have demonstrated the important role of the mesophase transformation during carbonization, i. e., the transformation of the isotropic liquid to a liquid crystal. It is through the mechanism of this transformation taking place near 425°C that the planar aromatic molecules of the carbonizing liquid are aligned parallel to facilitate the high-temperature graphitization process. The purpose of the present work is to investigate the structures formed in the mesophase as it coalesces, deforms, and hardens during the carbonization heat treatment and to learn the effects of insolubles, filler materials, and other material variables on these structures.

A topical report⁽¹⁾ entitled "Mesophase Microstructures in Carbonized Coal-Tar Pitch" was prepared, and it is planned to present this material at the Eighth Biennial Carbon Conference in June 1967. The following is an abstract of this report:

Polarized-light micrography has been employed to investigate the microstructure of the coalesced mesophase formed in the carbonization of coal-tar pitch. Prominent features in the polarized-light extinction contours are the nodal points which do not move when the plane of polarization is rotated. These nodal points are found to correspond to two types of linear defects in the stacking of the aromatic layer planes. When the mesophase is further carbonized, the nucleation, growth, and percolation of gas bubbles cause extensive plastic deformation of the mesophase. This deformation leads to an increasingly fine texture of extinction contours and nodal points.

Other work during the quarter has been concerned with further studies of the microstructures formed in coalesced mesophase, with the effect of calcined coke particles on the mesophase structures, and with the mesophase structures found in a typical impregnating pitch. In these studies the specimens were carbonized by the temperature-gradient heat-treatment technique described previously⁽⁷⁾ in order to obtain a series of specimens representative of various stages of heat treatment. It should be noted that a program-control unit has been applied to the temperature-gradient apparatus to obtain more satisfactory control over heating rate and to facilitate lengthy runs made at the slow heating rates typical of the baking schedules used in the manufacture of binder-filler artifacts.

The studies of mesophase structure have been made primarily by optical micrography using polarized light with crossed polarizers. Previous work had established the structures in the neighborhood of the nodal points in the extinction contours, which are the most conspicuous features of the polarized-light micrographs of the coalesced mesophase. However, as is apparent from Fig. 1, crosses in the extinction contours are also quite prevalent, and an effort has been made to define the structures in their neighborhood.

The micrograph in Fig. 1 is of a specimen of coal-tar pitch (Barrett No. 30) from which the insolubles were removed by extraction with tetrahydrofuran. This specimen was heat-treated to 470°C at a heating rate averaging less than $0.3^{\circ}\text{C}/\text{min}$.

As previously observed for the nodal points in the extinction contours, the centers of the crosses are fixed on the specimen surface when the plane of polarization of the incident light is rotated. Both co-rotating and counter-rotating crosses are found as marked by C and D, respectively, in Fig. 1. The rate of rotation is just half that of the extinction contours around the nodal points; thus, the co-rotating crosses rotate in the same direction and at the same rate as the plane of polarization of the incident light.

The structure shown in Fig. 1 has been sketched by the overlay technique, (7) and the results are shown in Fig. 2.

The co-rotating crosses are seen to correspond to the circular structures marked C. These structures, which resemble the laminar coatings of fuel particles, may be due to cross sections through dome-like layer formations.

The counter-rotating crosses are due to a more complicated structure, marked D, which possesses four-fold symmetry in the idealized case and in which the curvature of the layer planes is convex relative to the center of the cross. The counter-rotating cross structure is thus a four-fold version of the three-fold delta structure found at the counter-rotating nodes. This relationship between the two types of counter-rotating structures may extend to the mechanism of formation, since the four-fold structure can be formed, in principle, by the juncture of two three-fold delta structures.

In another phase of the current work, a series of experiments has been undertaken to learn how the presence of various filler materials affects the mesophase structure. The first temperature-gradient carbonization run was made with 10 wt-% calcined petroleum coke added to the extracted pitch. The petroleum coke particles were from a batch of needle-coke particles sized to approximately 125 ± 25 microns.

Problems were encountered in polishing the carbonized specimens owing to the wide difference between the hardness of the mesophase and that of the calcined coke particles. Thus far, satisfactory micrographs (see Fig. 3) have been obtained only for the highest temperature of heat treatment, 600°C. However, it was ascertained from examination of the lower-temperature specimens that all the coke particles were surrounded by the mesophase in the partially transformed specimens; this is consistent with the observations by Brooks and Taylor,⁽⁴⁾ who found a tendency for the mesophase to surround graphite flakes in a similar experiment with the graphite flakes used as an additive.

The calcined petroleum coke is seen to possess a texture of extinction contours which is similar to but of a finer scale than that of the mesophase matrix. In many cases the extinction contours of the petroleum coke run across the boundary and into the mesophase matrix, thus indicating a strong tendency toward an epitaxial alignment of the layer planes of the mesophase with the layer planes of the calcined coke.

Figure 4 is a structural sketch of the coarse-textured region of Fig. 3a. This sketch illustrates the alignment of the mesophase layer planes with the layer planes of a highly oriented needle-coke particle, and the curvature of the mesophase layers to accommodate the orientations of other coke particles is also evident.

These observations of an epitaxial relationship between the layer planes of the mesophase and the calcined petroleum coke would appear to afford an explanation of the difficulty in locating the pitch coke in binder-filler artifacts heat-treated above the baking temperature. Such effects have been observed in earlier work under the present program⁽⁸⁾ as well as by other workers.⁽⁹⁾

Another phase of the current work is concerned with the mesophase transformation in conventional coal-tar pitches (i. e. , nonextracted pitches) and specifically with learning the effects of the insoluble particles on the mesophase structures. The first pitch chosen for study was an impregnating pitch which is low in insoluble content and which should have easily recognizable mesophase structures (as compared with a previously investigated⁽⁸⁾ binder pitch with a high insoluble content). This pitch is Reilly Impregnating Pitch Type I, which has a softening point of 70° to 80°C and a quinoline insoluble content of less than 3 wt-%.

The carbonizing heat treatment involved 13 hr to reach the maximum temperature and a 2-hr hold before cooling. The atmosphere was argon. Specimens were obtained for heat-treatment temperatures from 410° to 540°C.

M-18711-6

-15°

M-18711-7

0°

M-18711-8

+15°

- A: co-rotating node
- B: counter-rotating node
- C: co-rotating cross
- D: counter-rotating cross

Fig. 1--The rotation of polarized-light extinction contours at nodal points and crosses in coalesced mesophase formed by carbonization of an extracted coal-tar pitch. 600x. Polarized light, with crossed polarizers

Fig. 2--Structural sketch of coalesced mesophase illustrated by polarized-light micrographs of Fig. 1. 600×

M-18373-3

(a)

(450x)

M-18373-21

(b)

(1000x, oil)

Fig. 3--Polarized-light micrographs of coal-tar pitch carbonized to approximately 600°C in the presence of sized particles of calcined petroleum coke. Crossed polarizers

Fig. 4--Structural sketch of a portion of Fig. 3a. 1000x

M-19264-1

(200x)

(a)

M-19265-1

(100x)

(b)

Fig. 5--Mesophase spherules formed in an impregnating pitch by heat treating to 411°C (upper micrograph) and to 423°C (lower micrograph).
Polarized light with crossed polarizers

M-19265-2

(600x)

(a)

M-19265-3

(600x)

(b)

Fig. 6--Mesophase spherules formed in an impregnating pitch heat-treated to 423°C; a region of Fig. 5b. Upper micrograph: polarized light with crossed polarizers. Oblique lighting used for lower micrograph brings out insoluble particles in boundary between mesophase and isotropic matrix

Figure 5 illustrates the structures found at the two lowest temperatures. The pitch appears to possess a heterogeneous structure even as the mesophase transformation begins. One region is relatively clear, with only very infrequent and small mesophase spherules, and thus resembles the mesophase structure as it develops in an extracted pitch. The regions with fine structure and in which larger spheres of mesophase are found are difficult to polish and appear to consist of clumps of the insoluble particles. Thus, in agreement with the observations of Brooks and Taylor, ⁽⁴⁾ the insolubles appear to offer preferential nucleation sites for the mesophase.

Figure 6 illustrates the point that the insolubles are not incorporated within the mesophase spherules and are swept along in the boundary between the mesophase and the isotropic pitch. This effect has also been noted by Brooks and Taylor. ⁽⁴⁾

Figure 7 illustrates the further growth that occurs when the structure is heat-treated to 437°C. The isotropic pitch is still the matrix phase, and the heterogeneity in texture appears in patches on the order of 300 microns wide.

At the next step in the heat treatment (to 452°C), the mesophase becomes the continuous matrix, and the insolubles are swept into small islands of isotropic pitch (see Fig. 8). Most of these islands also display mesophase spherules growing within them. Figure 9 shows more highly magnified views of a region of Fig. 8. It is clear that the polarized-light extinction contours display the same features of nodal points and crosses as are found in an extracted pitch. Although extensive bubbling has not yet occurred in the mesophase heat-treated to this point, the texture of the extinction contours is relatively fine.

At the next step in the heat treatment (469°C), the transformation of the isotropic pitch phase to the mesophase is virtually complete. Measurements of the carbon yield show that the yield declines steadily with increasing heat treatment until the transformation is complete; beyond that point the yield levels off at about 46.5 wt-%.

M-19266-2

(100x)

(a)

M-19266-1

(100x)

(b)

Fig. 7--Mesophase formed in an impregnating pitch heat-treated to 437°C .
Upper micrograph: polarized light with crossed polarizers. Lower micro-
graph: oblique lighting of same region

M-19267-1

(200x)

(a)

M-19267-2

(200x)

(b)

Fig. 8--Mesophase forming the continuous matrix in an impregnating pitch heat-treated to 452°C. Upper micrograph: polarized light with crossed polarizers. Lower micrograph: oblique lighting of same region

M-19267-3

(750x)

(a)

M-19267-4

(750x)

(b)

Fig. 9--Higher-magnification micrographs of a region of Fig. 8

IV. CHARACTERIZATION OF DEGREE OF GRAPHITIZATION OF CARBON AND GRAPHITE

G. B. Engle, W. H. Morris, and R. F. Stetson

The concept of the simultaneous existence of various structural components of carbon in conventional binder-filler artifacts is well known. The objective of this part of the program is to evaluate methods for determining the amounts of various carbon structures present in carbonaceous and graphitic materials and to define the degree of graphitization of these structures.

A densitometric method (i. e., a sink-float technique) has been adopted and is being developed for this purpose. Descriptions of the apparatus⁽¹⁰⁾ and the operating procedures⁽⁷⁾ have been given previously. Several preliminary experiments have been performed⁽⁷⁾ in which mixtures of sugar char and NC-8 graphite powders were used to demonstrate the feasibility of separating the nongraphitic and graphitic carbon structures according to their apparent liquid densities.

The density fractions which were collected during the separation of the sugar-char powder have been examined by X-ray diffraction methods to show the relationship between the apparent liquid density (i. e., the density of the liquid in which the particles just float) and the degree of graphitization of the particles in each fraction. In this case the layer plane spacing, C_0 (as shown in Fig. 10), was used as a measure of the crystallinity. In Fig. 10, the C_0 value is shown as a line which represents the density range over which the specimen for X-ray diffraction was taken. The fraction of the total sample which each line represents is given in weight percent above the line. In this sample about 0.65 wt-% was quite graphitic and floated in a density range of 1.70 to 2.25 g/cm³, while the remainder floated in the range 1.00 to 1.70 g/cm³. The full sink-float curve is included in Fig. 11. These data demonstrate that a small but measurable amount of material with a highly graphitic structure was developed in the sugar-char particles during heat treatment to 2800°C, and that this fraction can be separated by the densitometric method.

This technique should also be applicable to materials which are believed to contain large amounts of graphitic structure and lesser amounts of carbon structure. However, before a densitometric separation can be effected, the various structures must be liberated from each other by comminution. A set of preliminary experiments was made in an effort to

Fig. 10--The relationship between layer spacing, C_O , and apparent liquid density of sugar-char particles heated to 2800°C. Fractions separated by the densitometric method

Fig. 11--Densitometric separation curves of nuclear graphites. Particle size range: 75 to 150 microns

Fig. 12--Densitometric separation curves of nuclear graphites, showing the low-density sections of the curves in Fig. 11. Two curves for CHN graphite are shown to illustrate the liberation achieved by working with a finer particle size

determine the amount of separation that could be achieved with a relatively mild grinding action. For this purpose, a number of nuclear graphites were crushed with a mortar and pestle and a rather coarse (75 to 150 microns) particle fraction was screened from the resulting powder. These graphites represent a wide variety of nuclear graphites and include three materials which contained needle coke [NC-8, CHN, and 711-TS(N)] and three materials which contained isotropic cokes [H-315-A, H-319, and H-207-85]. All were bonded with coal-tar pitch, and some were heavily impregnated with pitch or a nongraphitizing carbon. Specimens of these materials have been irradiated at high temperatures, and the materials are described in more detail elsewhere.⁽¹¹⁾

The sink-float curves are shown in Figs. 11 and 12. These data show that a large portion of the particles from the isotropic graphites float at a lower density than those from the needle-coke graphites, the majority of which floated in the range 2.11 to 2.19 g/cm³. All the samples contained a significant amount of particles which floated at densities above or below that of the bulk, and the curves indicate that each material contained particles with a wide range of densities. A correlation between apparent crystallite height, L_c , and apparent liquid density was indicated; however, this relationship was not unambiguous. Two factors are believed to be hindering the establishment of a more precise correlation: (1) the very small fraction of particles which concentrate in the higher region of the density column, thus requiring a wide range of densities in order to obtain a sample of adequate size for X-ray diffraction, and (2) incomplete liberation of the nongraphitic phase during comminution.

An additional experiment was performed to determine whether further reduction in particle size would improve the liberation of the nongraphitic phase. The nuclear graphite designated CHN was chosen for this experiment because it was known to be composed of needle-coke filler particles and also to be heavily impregnated with a nongraphitizing carbon. A sample of approximately 0.6 g was crushed until about 95 wt-% passed a 325-mesh screen (the upper limit of particle size was 40 microns and the lower was estimated to be about 0.1 micron*). The results are shown in Fig. 13. The low-density regions of the curves, expanded for better resolution of the low-density fractions, are shown in Fig. 12.

A considerable improvement in the liberation of the various structures was attained by using finer particle sizes. The low-density fractions

*The samples which contained particles of less than 40 microns were held in the differential density column for approximately 72 hr to allow for settling. Those with particles of greater than 40 microns were held approximately 24 hr. Calculations performed using the Stokes-Einstein equation and the best available data on viscosity indicate that these times are adequate for near-complete settling to occur.

Fig. 13--Densitometric separation curves of CHN graphite for two different conditions of particle sizing

increased in quantity and the bulk of the material, which apparently contained less of the light fraction than before, shifted to a higher density range. The correlation between apparent crystallite height, L_c , and apparent liquid density also improved considerably, but X-ray diffraction measurements were still difficult to make owing to the small amount of sample in the low-density fractions.

A similar experiment was made on NC-8 graphite in which samples consisting of 75 to 150, 60 to 75, 40 to 60, and less than 40 microns were prepared and separated. In general, the results were the same as those for the CHN graphite. However, this material is highly graphitic and contains still smaller amounts of the low-density fractions. Thus, the amount of sample available for X-ray measurements was again quite small, and a rather wide density range was necessary in the lower range to obtain an adequate sample for measurement. The same correlation between carbon structure and apparent liquid density was observed in this series of samples, but again with poor resolution in the lighter fractions.

Further efforts will be made to improve the liberation of the various phases and to adjust the densitometric separation technique in order to obtain more complete and precise data in the low-density region of the curves. Micrographic examinations of the various fractions are also planned.

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

G. B. Engle, W. H. Morris, and R. F. Stetson

A series of investigations is in progress to determine the influence of pitch-binder content on the microstructure, physical properties, and irradiation behavior of graphite bodies prepared by a standardized molding process. The objectives of this work are: (1) to prepare a systematic set of specimens of known composition and of known processing history, (2) to characterize the materials in terms of selected properties and selected structural parameters, and (3) to correlate this information with the results of measurements obtained after subjecting the specimens to various irradiation conditions.

Three sets of specimens have been prepared with the following fillers: (1) uncalcined coke, (2) calcined coke, and (3) natural-flake graphite. Three levels of coal-tar pitch binder (Barrett No. 30) were used: 0, 15, and 25 wt-%.

Dimensional changes and physical-property measurements have been reported previously. (7, 8, 10)

A series of specimens prepared with uncalcined coke and irradiated at 1450°C and 3.25×10^{21} n/cm² ($E > 0.18$ MeV) has been examined micrographically, and the liquid densities of samples irradiated at 915°C and 2.65×10^{21} n/cm² and 1450°C and 3.25×10^{21} n/cm² have been remeasured. The liquid-density values which were reported previously⁽⁷⁾ were found to be too low due to insufficient degassing of the samples prior to immersion in the liquid mixture. The new measurements were made after degassing for 1 hr at 300°C and 10⁻⁵ mm Hg. The changes effected in the open and closed porosities* by irradiation are shown in Fig. 14 with the corresponding changes in the bulk thermal expansivities. The changes in the microstructure resulting from irradiation at 1450°C and 3.25×10^{21} n/cm² are shown by the photomicrographs in Figs. 15 through 18.

There is a significant closure of the crack structure in samples irradiated at 1450°C and 3.25×10^{21} n/cm². Closure of the large cracks

* Open porosity calculated from: $V_o = 1 - \rho_{\text{bulk}}/\rho_{\text{liquid}}$.

Closed porosity calculated from: $V_c = (\rho_{\text{bulk}}/\rho_{\text{liquid}} - \rho_{\text{bulk}}/\rho_{\text{solid}})$.

Fig. 14--Effect of irradiation on porosities and bulk thermal expansivities of molded graphites prepared with uncalcined coke as a function of pitch-binder level in the green mix

M-19037-1

(150x)

M-19037-5

(150x)

Fig. 15--Effects of irradiation on the microstructure of binder-filler artifacts prepared with uncalcined petroleum coke with no pitch binder. Upper micrograph: unirradiated condition. Lower micrograph: after 3.25×10^{21} n/cm² ($E > 0.18$ MeV) at 1450°C

M-19036-1

(150x)

M-19036-6

(150x)

Fig. 16--Effects of irradiation on the microstructure of binder-filler artifacts prepared with uncalcined petroleum coke and 15 wt-% pitch binder in the green mix. Upper micrograph: unirradiated condition. Lower micrograph: after $3.25 \times 10^{21} \text{ n/cm}^2$ ($E > 0.18 \text{ MeV}$) at 1450°C

which appear to lie parallel to the basal planes in the filler particles is readily observable in the micrographs of Figs. 15 through 18. Only large intergranular pores remain. These changes were accompanied by large changes in the bulk densities and in the thermal expansion coefficients (see Fig. 14). However, the reduction of closed porosity was only observed for samples which contained a pitch binder.

The large increase in the thermal expansion coefficients of compacts prepared without a pitch binder may result simply from the removal of basal-plane cracks which were available to accommodate c-axis thermal expansion of the unirradiated compacts. The reduction of thermal expansion coefficients for the samples prepared with a pitch binder is unusual and appears to depend upon irradiation temperature.

Additional micrographic studies are in progress on similar specimens which were irradiated at 915°C and $2.65 \times 10^{21} \text{ n/cm}^2$ ($E > 0.18 \text{ MeV}$).

Another irradiation experiment on molded binder-filler artifacts is presently under way. The specimens, which have been described in a previous report, (10) were prepared with calcined coke and various levels of pitch-binder content and are being irradiated in Capsule GE-H-13-12 in the ETR. Battelle Pacific Northwest Laboratories is conducting this capsule experiment. The capsule, which is currently in the second cycle of a scheduled four-cycle experiment, is operating at approximately 1200°C .

M-19035-6

(150x)

M-19035-5

(150x)

Fig. 17--Effects of irradiation on the microstructure of binder-filler artifacts prepared with uncalcined petroleum coke and 25 wt-% pitch binder in the green mix. Upper micrograph: unirradiated condition. Lower micrograph: after 3.25×10^{21} n/cm² ($E > 0.18$ MeV) at 1450°C

M-19035-4

(450x)

M-19035-8

(450x)

Fig. 18--Higher-magnification micrographs of Fig. 17, showing details of crack closure caused by irradiation to 3.25 n/cm^2 ($E > 0.18 \text{ MeV}$) at 1450°C . Upper micrograph: unirradiated condition. Lower micrograph: irradiated condition

VI. THERMAL EXPANSION AND PREFERRED ORIENTATION OF NONGRAPHITIC CARBONS

J. C. Bokros, R. J. Price, W. H. Ellis, K. Koyama,
H. H. Evans, and F. J. Gagnon

Previous work on the relationship between the preferred orientation and the thermal expansivity of polycrystalline graphite has established that some of the c-axis expansion of the graphite crystallites is accommodated by cleavage microcracks which lie parallel to the graphite layer planes. Similar studies are being conducted on pyrolytic carbons which are free from these cleavage microcracks. Experimental techniques and some data have been discussed in previous reports. (7, 8) Enough data have now been obtained to map out the general relationships between thermal expansion coefficient, preferred orientation, and density of the carbons. Current work is limited to filling in a few remaining gaps in the data for expansion perpendicular to the deposition plane of low-density, highly oriented carbons. This combination of structural characteristics in a carbon may be obtained, with some trial and error, in a fluidized-bed coater. One such carbon with a density of 1.73 g/cm^3 and a Bacon anisotropy factor of 4 was found to have an expansion coefficient perpendicular to the deposition plane of $13.3 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ at 400°C . Efforts are being made to adjust the coating conditions in order to prepare a lower-density carbon which retains a high degree of orientation.

With the foregoing exception, experimental work on this topic is virtually complete, and a topical report presenting the results will be prepared. In summary, the measurements show a relationship between preferred orientation and thermal expansion similar to that observed in polycrystalline graphite. (12) The accommodation of c-axis expansion is lower than in the case of crystalline graphite and shows a clear secondary dependence on density. The accommodation may be attributable to fine porosity present in the carbons.

VII. RADIATION-INDUCED DIMENSIONAL CHANGES IN MODEL CARBONS AND GRAPHITES

J. C. Bokros, R. J. Price, A. S. Schwartz, G. L. Guthrie,
W. H. Ellis, and F. J. Gagnon

RADIATION-INDUCED DIMENSIONAL CHANGES IN TURBOSTRATIC CARBONS

A topical report⁽²⁾ entitled "A Model of Neutron-Induced Dimensional Changes in Pyrolytic Carbon" has been prepared. In this report a model is presented which describes the dimensional behavior of pyrolytic carbon during irradiation by fast neutrons at temperatures in the range 500° to 1100° C for exposures to $\sim 3 \times 10^{21}$ n/cm² ($E > 0.18$ MeV). The model uses crystallite averaging methods to describe the anisotropic distortion of the bulk in terms of its preferred orientation and the shape change of the individual crystallites. The densification, a simple first-order rate process, is assumed to be independent of the shape change and is superimposed isotropically on the shape change. The validity of the approach has been checked by comparing the predictions of the model with the dimensional changes observed in twelve carbons irradiated at 680°, 710°, 810°, and 980° C to neutron exposures of 1.7, 2.2, 2.0, and 1.4×10^{21} n/cm² ($E > 0.18$ MeV), respectively.

Strain rates calculated from the model are used to estimate the suitability of various carbon structures for use as coatings on an unyielding support. For example, using a creep constant of 1×10^{-27} (nvt psi)⁻¹ at 1200° C, the model predicts that a carbon with a Bacon anisotropy factor of 1.2 and crystallite size, L_c , in the range 120 to 155 Å would not fail due to neutron-induced dimensional changes if its original density were greater than 2.0 g/cm³. Similarly, carbons with the same crystallite size but a Bacon anisotropy factor of 1.0 would not fail under the same conditions if their original densities were greater than 1.7 g/cm³.

Results from the carbons irradiated in Capsule G11* in the temperature range 500° to 1000° C show that the densification constant, k_d , for carbons with L_c parameters in the range 25 to 45 Å is independent of temperature and equal to 3.3×10^{-22} (n/cm²)⁻¹. When L_c is relatively large (155 to 175 Å), k_d is independent of temperature and equal to 1.1×10^{-22} (nvt)⁻¹. For carbons with intermediate values of L_c , k_d increases with temperature.

*The irradiation of this capsule was conducted under Contract AT(04-3)-633.

The average crystallite growth rates, $\ln(1 + \Delta X_c/X_c)$ per 10^{21} n/cm² measured in the present work are consistent with those reported earlier for both lower and higher irradiation temperatures.

RADIATION-INDUCED DIMENSIONAL CHANGES IN SINGLE-PHASE CRYSTALLINE GRAPHITES

Specimens of annealed pyrolytic carbon that were irradiated to a fast-neutron dose of $\sim 6 \times 10^{21}$ n/cm² ($E > 0.18$ MeV) at $\sim 1000^\circ\text{C}$ in Capsule P14B* are currently being examined. The structure of this material and its irradiation behavior at lower neutron exposures have been reported previously (see Ref. 7, pp. 45-50).

IRRADIATION BEHAVIOR OF CATALYTICALLY GRAPHITIZED CARBON

Specimens of carbon catalytically graphitized by titanium at 2200°C have been irradiated to $\sim 6 \times 10^{21}$ n/cm² ($E > 0.18$ MeV) at $\sim 1000^\circ\text{C}$ in Capsule P14B* and are currently being examined. Details of the structure of this material and its preparation have been described in a previous report (see Ref. 7, pp. 50-56). The results of the postirradiation examination and data from Capsules P14* and P13F† are being compiled for a topical report entitled "Irradiation Stability of Catalytically Graphitized Carbon." (3)

*The irradiation of this capsule was conducted under Contract AT(04-3)-633.

†The irradiation of this capsule was conducted under Contract AT(04-3)-167, Project Agreement No. 17.

VIII. ANNEALING STUDIES OF PYROLYTIC-CARBON STRUCTURES

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

A series of successive isochronal 1-hr anneals is being carried out on a variety of irradiated pyrolytic carbons. Concurrently, a carbon deposited at 1225°C containing 6.7 wt-% titanium and a titanium-free "control" carbon are being annealed. The irradiated carbons include a laminar carbon irradiated in each of five cells in Capsule G9,* which operated at 540° to 1060°C; a high-density isotropic carbon similarly irradiated; a low-density isotropic carbon irradiated at 540° and 1060°C; and an annealed laminar carbon with a large crystallite size irradiated at 540°, 890°, and 1060°C. Details of the preirradiation treatment, irradiation conditions, and as-irradiated structural properties are given in Table 1.

The properties being measured are density, linear dimensions, layer spacing, apparent crystallite size, and electrical resistivity. Annealing in helium was started at 400°C and has been continued in successive 100°C increments up to 1600°C. Thus far, no significant trends in linear dimensions or layer spacing have been observed. Changes in density, apparent crystallite size, and electrical resistivity are shown in Figs. 19 through 24. Except for the unirradiated titanium-doped carbon and its titanium-free "control," the property changes are all small. The isotropic (structure No. 6) carbons irradiated at 540°, 620°, and 890°C showed a general upward trend in resistivity beginning at roughly their irradiation temperature. The irradiated carbons showed a slight increase in density and apparent crystallite size after annealing at 1500° and 1600°C. The increases in apparent crystallite size were most marked in the laminar carbons (structures No. 1 and 2), both unannealed and annealed, prior to irradiation. Both the titanium-bearing carbon and its "control" showed a progressive increase in density and apparent crystallite size when annealed beyond their deposition temperature (Fig. 24). These properties increased at the same rate in both carbons; there was no evidence of catalyzed crystal growth in the titanium-bearing carbon up to 1600°C.

The lack of marked change in properties in the irradiated carbons and the upward trend in density is in contrast to the behavior of crystalline

*The irradiation of this capsule was conducted under Contract AT(04-3)-167, Project Agreement No. 17.

Table 1

PROPERTIES OF CARBONS USED IN ANNEALING STUDIES

Sample Number	Deposition Temp ($^{\circ}\text{C}$)	Annealing Treatment or Metal Additive	Irradiation Conditions		Structural Properties		
			Temp ($^{\circ}\text{C}$)	Neutron Exposure (n/cm^2 , $E > 0.18 \text{ MeV}$)	Density (g/cm^3)	L_c ($\text{\AA}$)	Bacon Anisotropy Factor
2-1-2	1400	None	540	1.6×10^{21}	2.074	43	1.65
2-2-4	1400	None	620	1.5×10^{21}	2.078	42	
2-3-2	1400	None	890	2.4×10^{21}	2.073	56	
2-4-2	1400	None	1040	2.4×10^{21}	2.064	60	
2-5-4	1400	None	1060	2.2×10^{21}	2.069	47	
6-1-4	2000	None	540	1.6×10^{21}	2.036	154	1.30
6-2-2	2000	None	620	1.5×10^{21}	2.038	154	
6-3-1	2000	None	890	2.4×10^{21}	2.082	95	
6-4-4	2000	None	1040	2.4×10^{21}	2.076	94	
6-5-1	2000	None	1060	2.2×10^{21}	2.084	87	
1-1-3-G	1400	2 hr at 2800°C	540	1.6×10^{21}	2.193	279	2.6
1-3-2-G	1400	2 hr at 2800°C	890	2.4×10^{21}	2.104	127	
1-5-3-G	1400	2 hr at 2800°C	1060	2.2×10^{21}	2.156	123	
2-4-3-A	1400	4 hr at 1900°C	1040	2.4×10^{21}	2.027	75	1.66
5-1-2	1650	None	540	1.6×10^{21}	1.685	61	1.0
5-5-3	1650	None	1060	2.2×10^{21}	1.914	46	
2814-77-1	1225	6.7% Ti	----	0	2.168	33	Not determined
2814-77-2	1225	6.7% Ti	----	0	2.170	33	
2814-79-1	1225	None	----	0	2.078	34	5.3
2814-79-2	1225	None	----	0	2.078	35	5.3

Fig. 19--Change in electrical resistivity of irradiated (a) isotropic and (b) laminar pyrolytic carbons as a function of annealing temperature

Fig. 20--Change in density of irradiated (a) isotropic and (b) laminar pyrolytic carbons as a function of annealing temperature

Fig. 21--Change in density of irradiated (a) laminar pyrolytic carbon annealed at 2800°C before irradiation; (b) laminar pyrolytic carbon annealed at 1900°C before irradiation; and (c) low-density isotropic pyrolytic carbon, as a function of annealing temperature

Fig. 22--Change in apparent crystallite size, L_c , of irradiated (a) isotropic and (b) laminar pyrolytic carbons as a function of annealing temperature

Fig. 23--Change in apparent crystallite size, L_c , of irradiated (a) laminar pyrolytic carbon annealed at 2800°C before irradiation; (b) laminar pyrolytic carbon annealed at 1900°C before irradiation; (c) low-density isotropic pyrolytic carbon, as a function of annealing temperature

Fig. 24--Change in density, apparent crystallite size (L_c), and electrical resistivity of titanium-doped and titanium-free pyrolytic carbon, as a function of annealing temperature

graphites irradiated at lower temperatures, which tend to revert to their unirradiated properties on annealing.⁽¹³⁾ These observations illustrate the fact that many nongraphitic carbons have a more ordered and stable structure after neutron irradiation than prior to irradiation.⁽¹⁴⁾

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