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AEC RESEARCH AND
DEVELOPMENT REPORT

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RESEARCH ON GRAPHITE

QUARTERLY PROGRESS REPORT
FOR THE PERIOD ENDING FEBRUARY 14, 1968

by

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

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

February 21, 1968

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Gulf General Atomic Incorporated

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GA-6233—Annual Report, April 1, 1964, through March 31, 1965
GA-7100—Annual Report, May 15, 1965, through May 14, 1966
GA-7906—Annual Report, May 15, 1966, through May 14, 1967
GA-8202—Quarterly Report, for the period ending August 14, 1967
GA-8376—Quarterly Report, for the period ending November 14, 1967

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1. INTRODUCTION

This program is being conducted to develop an understanding of the properties and structure of the various types of carbons and graphites required for use in high-temperature nuclear reactors of advanced design. In the experimental approach emphasis is placed on defining the structures of the various carbons and graphites, defining the relationships between structure and relevant properties, and evaluating methods for the preparation of improved structure.

In the period of November 15, 1967, to February 14, 1968, investigations of the structures and properties of carbons and graphites and studies of the effects of irradiation on these structures and properties were performed. The work is described in Sections 3 through 8 of this report.

Structural characterization is being investigated to develop correlations between properties and structures of the various carbons and graphites. The various structures of conventionally processed graphites, as well as laboratory-prepared carbons or graphites, are characterized by their crystallinity, preferred orientation, density, and microstructure. Micro-graphite studies of the structural reactions that occur during carbonization and graphitization are being pursued. The investigations of conventional graphites include the development of techniques for characterizing the degree of graphitization by the separation and identification of the various structural components that exist in the graphites.

The work on irradiation effects is concentrated primarily on the behavior of carbons and graphites under the fast-neutron-flux and high-temperature conditions representative of the operating conditions of advanced reactors. The objectives are to determine the structures of greatest stability and to define the dimensional changes and other properties as a function of structure. The irradiation experiments are conducted on materials of fully characterized structure, and the principal areas of interest are dimensional changes, thermal expansivity, elastic properties, and irradiation creep.

A meeting was held with personnel at Oak Ridge National Laboratory (ORNL) to explore the possibility of performing high-dose irradiations at about 1000°C in the High Flux Isotope Reactor (HFIR) at ORNL. A letter has been sent to ORNL (John Coobs) requesting reactor space for experiments planned under their High-Temperature Gas-Cooled Reactor (HTGR) program.

2. SUMMARY

STRUCTURE OF CARBONIZED COAL-TAR PITCH

The literature relating to the mesophase transformation in the organic precursors of artificial graphites has been reviewed, and several potentially profitable areas of research have been identified. Work is tentatively planned in one of these areas: the mechanical properties of mesophase material, both in the plastic region and after carbonization.

CHARACTERIZATION OF DEGREE OF GRAPHITIZATION

An experimental effort is underway to develop methods to separate and identify the various structural states of carbon that comprise conventional artificial graphites. Two additional densitometric separations of CHN graphite confirmed earlier results that the crystallite size is dependent on the apparent density. A study was initiated to determine the structural characteristics of the densitometric fractions by a liquid oxidation technique. A preliminary experiment using sugar char and natural flake graphite was carried out to determine the feasibility of applying the modified technique to sink-float fractions. The results indicated a large difference in the oxidation rates of sugar char and natural flake graphite.

An artificial graphite is being fabricated to aid in testing the densitometric technique. A filler coke was prepared by coating needle-coke particles with a low density pyrolytic carbon. This coke will be ground and used to fabricate a graphite consisting of filler particles with two distinct densities and degrees of structural development.

CATALYTIC GRAPHITIZATION OF BINDER-FILLER ARTIFACTS

The use of ZrC powder as a catalyst in needle-coke graphite enhanced graphitization at 2400°C after heating for 2 hr, but the effect could not be observed after further heating to 30 hr. Catalytic graphitization of a petroleum asphalt coke with titanium or zirconium metals was not as pronounced as the reaction observed in titanium-doped pyrolytic carbons. Large primary graphite crystals were observed metallographically in the

petroleum asphalt coke graphitized at 2800°C when aluminum and titanium metal powders were added prior to carbonization. The presence of the large graphite crystals was confirmed by X-ray diffraction patterns.

IRRADIATION BEHAVIOR OF GRAPHITES

A series of molded bodies prepared with calcined coke in which the pitch-binder coke was varied is being reirradiated in the Engineering Test Reactor (ETR) for a second increment of dose to about 6×10^{21} n/cm² ($E > 0.18$ MeV) at about 1225°C. Bulk densities of unirradiated specimens showed an increase with increasing binder-coke content, whereas the apparent density measured by immersion in a liquid showed no dependence on the binder-coke content. Additional thermal expansivity measurements were made on unirradiated specimens in preparation for comparison with values of measurements after specimen irradiation.

RADIATION-INDUCED DIMENSIONAL CHANGES IN SINGLE-PHASE PYROLYTIC CARBONS AND GRAPHITES

Data from several irradiation experiments carried to high neutron exposures show that the irradiation induced densification that is familiar at low exposures is replaced by an expansion process at high exposures. It is suggested that the expansion is a consequence of porosity generated by intercrystallite irradiation creep. When the expansion process becomes apparent at high exposures, the shape changes of all the carbons taken as a group depart from the changes predicted in crystallite averaging methods. The nearly isotropic carbons behave as if either the shape-change rate of the crystallites is enhanced by the irradiation itself or the new porosity generated at high exposures is directed perpendicularly to the original deposition plane. The data also show that, for turbostratic carbons with L_c values of 120 to 200 Å, a preirradiation at ~600°C to $\sim 1 \times 10^{21}$ n/cm² does not influence the neutron-induced dimensional changes that occur in a subsequent irradiation at ~900°C.

ANNEALING STUDIES OF PYROLYTIC CARBON STRUCTURES

Isochronal annealing at temperatures up to 2500°C has been completed for the series of irradiated pyrocarbons and the carbons containing codeposited titanium. The trends in the changes in electrical resistivity, dimensions, density, and apparent crystallite size previously reported for lower annealing temperatures continued at an increasing rate. The changes in the

laminar carbons irradiated in the as-deposited condition were not sensitive to irradiation conditions and are probably attributable to thermal annealing of the as-deposited structure. However, changes in a laminar carbon annealed at 2800°C before irradiation, and in an isotropic carbon unresponsive to thermal annealing, were strongly dependent on irradiation conditions. These latter changes may be attributed to the rearrangement of irradiation induced defects.

An isotropic pyrolytic carbon deposited at 2200°C and containing 9.7 wt-% titanium was transformed to crystalline graphite by a heterogeneous catalytic recrystallization process which started at 2300°C and was almost complete at 2400°C . In contrast, a laminar carbon deposited at 1225°C and containing 6.7 wt-% titanium showed no evidence of catalytic graphitization under the same conditions.

3. THE STRUCTURE OF CARBONIZED COAL-TAR PITCH

R. J. Price

During the pyrolysis of the organic precursors of artificial graphites, the principal step that determines the structure of the final product is the mesophase transformation which takes place at $\sim 425^{\circ}\text{C}$. The mesophase consists of droplets that separate from the parent liquid and that have the properties of a liquid crystal. The aromatic molecules in the mesophase are parallel to each other, and this makes the resulting carbon easily graphitizable.

During the present program, the microstructure of hardened mesophase has been studied micrographically.^(1,2) In addition, the structure of mesophase material heat treated to temperatures between 1000° and 3000°C has been studied micrographically by X-ray diffraction and by the densitometric technique.^(2,3)

After a survey of the literature, several potentially fruitful areas of research were discussed in correspondence with J. L. White.* These areas included the mechanical properties of the mesophase material (both in the plastic region and after carbonization), the electron microscope studies of the mesophase structure, the kinetics of the mesophase transformation, and the wetting of substrate materials by liquid mesophase. It is tentatively planned to start work in the first of these areas.

* J. L. White is currently on leave of absence from Gulf General Atomic Incorporated with Euratom at Petten, The Netherlands.

4. CHARACTERIZATION OF DEGREE OF GRAPHITIZATION OF CARBON AND GRAPHITE

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

The objective of this portion 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., sink-float techniques) has been adapted and is being developed for this purpose. A description of the apparatus, the operating procedure, and the sample preparation has been given previously.⁽¹⁾

Work was continued to determine the relationship between apparent crystallite size L_c and apparent density. Two graphites, CHN and H-315-A, have been chosen for this purpose. CHN, an anisotropic graphite, was prepared with needle coke and a pitch binder and was heavily impregnated with a nongraphitizing carbon, whereas H-315-A, a near-isotropic graphite, was prepared with spherical coke (Gilso-carbon) and a pitch binder. These graphites have different microstructures and show different degrees of graphitization.

Previously it was determined that specimens ground to pass a 400-mesh standard screen ($<38\text{-}\mu$ particle size) were consistent in showing a dependence of crystallite size on the apparent density of the particles. Two additional duplicate specimens of CHN graphite have now been separated in two different sink-float columns. The densitometric curves for the new specimens are shown in Fig. 1. These curves are consistent with earlier experiments; thus, reproducibility has been achieved. The various fractions were examined by X-ray diffraction techniques. The data in Fig. 2 show the relationship between L_c and the apparent density of the particles of four separations performed on replicate specimens of CHN graphite and one specimen of NC-8 graphite (fabricated with needle coke but impregnated only once with coal-tar pitch). The light fractions below 2.10 g/cm^3 represent about 4% to 6% of the total samples and consist of carbon that is less graphitic than that in the range of 2.10 to 2.26 g/cm^3 . This fraction may represent the nongraphitic impregnant carbon present in this material. The data points for the NC-8 graphite fall in the same band as those for the CHN graphite but do not contain a substantial portion of the low density

Fig. 1. Densitometric separation curves for CHN graphite

Fig. 2. Apparent crystallite size L_c as a function of apparent density ρ for CHN and NC-8 graphites (composed of $<38\text{-}\mu$ particles)

particles. The particles for the CHN graphite extend over a density range of 1.70 to 2.26 g/cm³ and an L_C range of 400 to 1300 Å. A similar relation could not be found for the near-isotropic graphite H-315-A (see Fig. 3). Although the microporosity varies throughout the body, the crystalline size is uniform, ranging from about 450 to 550 Å. These data suggest that the volume of microporosity surrounding the crystallites is independent of the crystallite sizes in the materials prepared with Gilso-carbons. A similar result was observed previously for graphite H-207-85, also fabricated with Gilso-carbon coke.⁽²⁾

The densitometric experiments will be continued on CHN and H-315-A graphites. Attempts will be made to determine the structural spectrum after the particle size of the specimens has been reduced to the 1 to 10-μ range.

A new material is under preparation in the laboratory which will be used for characterization studies. A filler coke has been prepared by coating calcined needle-coke particles with a low density pyrolytic carbon (about 1.70 g/cm³ and L_C of 40 Å). This coke will be crushed to form a flour and the flour subsequently bonded with pitch to form a porous binder-filler artifact. The resulting binder-filler artifact will consist of two component fillers, each having a wide difference in density and crystallite size. It is intended to characterize this material in the densitometric column and to correlate the results with the known history of the raw material and processing.

Oberlin and Mering⁽⁴⁾ have shown that all carbons are oxidized to CO₂ in a hot mixture of H₂SO₄ and Ag₂Cr₂O₇. The kinetics of the reaction vary by a factor of 1000, depending on the state of graphitization of the carbons. The lowest reaction rate constant was observed with nongraphitic carbons, and the highest rate was observed with natural flake graphite or with artificial graphite.

Liquid oxidation may afford another method of determining the degree of graphitization in the various densitometric fractions. It may be especially attractive for examining the lighter fractions which are difficult to analyze with the standard X-ray techniques because of the limitations imposed by small sample sizes.

In the method used by Oberlin and Mering, the fraction of carbon remaining after oxidation was determined by calculation from pressure and volume relations derived from collection of the CO₂ evolved during the experiment. For our purposes the procedure of Oberlin and Mering has been altered. The fraction of carbon remaining after oxidation was detected by a gravimetric technique rather than by collecting the CO₂. This technique, if feasible, will allow for oxidation of the fractions without the necessity of

Fig. 3. Apparent crystallite size L_c as a function of apparent density ρ for H-315-A graphite (composed of $<38\text{-}\mu$ particles)

removing the powders from the frits. Potassium dichromate was chosen in place of silver dichromate because of its better solubility and therefore its ease of removal by filtration.

A preliminary experiment was performed using a mixture of H_2SO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ to oxidize sugar-char carbon (heated to 2800°C) and natural flake graphite. A sample of natural flake graphite and one of sugar char, each of which had been screened thru a 325-mesh screen, were outgassed at 1800°C under vacuum and then at 3000°C for 1/2 hr in helium. The samples were again passed through a 325-mesh screen to break up any agglomerates. The oxidizing reagent consisted of a saturated solution of 95% H_2SO_4 and 5% $\text{K}_2\text{Cr}_2\text{O}_7$ (5 g of $\text{K}_2\text{Cr}_2\text{O}_7$ to 50 cm^3 H_2SO_4). Fritted crucibles containing the sugar-char and natural flake samples were placed in triplicate in pyrex crucibles and the liquid oxident poured into and around the fritted crucibles. After 1 hr in a constant temperature bath, the crucibles were removed and the samples quickly washed with distilled water. After filtration the samples were dried in a vacuum to constant weight. Subsequent oxidation runs were performed in a manner identical to the first run except that the oxidation period was increased.

The fraction of carbon remaining after 9 hr of oxidation was 0.72 and 0.16 for sugar-char and natural flake graphites, respectively. The difference in the reaction rates of nongraphitic sugar-char and natural flake graphite are large enough to warrent continuation of the experiments with the sink-float fractions.

5. CATALYTIC GRAPHITIZATION OF BINDER-FILLER ARTIFACTS

G. B. Engle, J. C. Bokros, J. Pontelandolfo, W. H. Morris,
and R. F. Stetson

The use of metallic catalysts to enhance the graphitization process in pyrolytic carbons and binder-filler artifacts has been well established.⁽⁵⁻⁷⁾ The codeposition of small amounts of metallic catalyst, such as titanium, with pyrolytic carbon resulted in enhanced graphitization at temperatures below 2500°C and materials with relatively large crystallites (L_c of ~ 800 Å). When irradiated in a fast-neutron environment at temperatures above 600°C,⁽⁵⁾ these materials were considerably more stable than pyrolytic carbons prepared without a catalyst. This improvement in stability has been attributed to a reduction in the distortion rate of the crystallites.

The objective of the work in this portion of the program is to explore the use of metal catalysts, to promote enhanced crystal growth and isotropy in filler cokes, and to study the catalytic process.

A series of exploratory experiments in which finely ground zirconium metal (0, 2.5, 5.0, and 10.0 wt-%) was incorporated into coal-tar pitch and petroleum asphalt (precursors of binder and filler components) prior to carbonization was reported previously.⁽³⁾ These mixtures were heated slowly in air to 550° to 600°C and then in helium to 900°C. The resultant cokes were heated to 2200°, 2500°, or 2800°C.

Heating the specimens in air during the carbonization process produced an isotropic structure on a fine scale in the petroleum-asphalt coke, whereas the effect was less pronounced in the coal-tar pitch. Although the petroleum coke remained isotropic, heating the cokes to 2800°C in helium did not promote the growth of large crystals in any of the specimens. Analyses by X-ray diffraction showed L_c values in the range of 150 to 300 Å and layer spacing C_o values of about 6.8 Å for all specimens. The introduction of oxygen during carbonization also retarded the crystal growth in the pitch, and the metallic catalysts could not overcome the effect of the oxygen.

A second series of coke specimens was prepared from petroleum asphalt, and 10 wt-% of finely ground zirconium or titanium metal was

added prior to carbonization. This series of specimens, along with a reference sample which contained no additive, was carbonized in helium or in a mixture of helium and air (90:10) at 400°C. Further heat treatment was carried out to 900°C in helium. The specimens were then heated to 2800° and 3000°C and examined by X-ray diffraction techniques for L_c and C_o values.

The X-ray diffraction results are shown in Figs. 4 and 5. The results after carbonization in either helium or a helium-air mixture were similar and the conclusions were the same in both cases. Therefore, for brevity, only the results from the helium experiments are reported here. Heating the cokes at 2800°C for 1 hr resulted in no apparent catalytic effect of the titanium or zirconium over the control sample. Further heating at 2800°C for a total of 4 hr failed to produce any further significant crystal growth or layer plane closure. Heat treatment to 3000°C for 1 hr improved the crystallinity somewhat in all specimens, but the material was still considerably inferior to well-graphitized petroleum cokes. One exception was noted. One of the coke clinkers, prepared with titanium and heated to 3000°C, had L_c and C_o values of 950 Å and 6.699 Å, respectively. When a second clinker from the same batch was examined, it was found to be less crystalline. The entire batch was then ground up and the resulting powder thoroughly mixed before examination. When the X-ray specimen was prepared in this manner, four duplicate specimens had L_c values of 300 to 350 Å and C_o values of 6.708 to 6.714 Å (see Figs. 4 and 5). Closer examination of the (002) X-ray peaks for the coke prepared with titanium metal and heated to 3000°C showed an asymmetric shape, whereas the shape of the coke prepared without an additive was symmetric (see Fig. 6). The shift of the peak to a higher angle and the asymmetry of the peak of the coke specimen containing titanium show that graphitization may have started in this specimen. Although micrographic examination of this specimen failed to show any significant changes, the highly crystalline nature of the one sample indicates that recrystallization may have occurred by catalytic action at isolated regions, probably around the metallic particles, but the bulk of the material remained ungraphitized.

Another set of specimens prepared previously with calcined needle coke (an anisotropic and graphitizing coke) and 5 wt-% ZrC powder was heat treated at 2400° and 2500°C. These specimens differed from the above specimens in that they were prepared with a graphitizing coke and the catalyst was added after carbonization of the coke in the form of a carbide. X-ray parameters of these specimens after heat treatment at 2400° and 2500°C are shown in Figs. 7 and 8. At both temperatures there was an apparent effect of the catalyst after very short heat treatments, but the advantage decreases with time. Examination of the (002) X-ray peaks of specimens heat treated for 32 hr at 2400°C were symmetrical for both specimens, indicating a uniform graphitization of all particles.

Fig. 4. Apparent crystallite size L_c of petroleum-asphalt cokes as a function of heat treatment time

Fig. 5. Layer spacing C_0 of petroleum-asphalt cokes as a function of heat treatment time

Fig. 6. (002) X-ray diffraction peak of (a) 10 wt-% Ti, and (b) no additive, heat treated to 3000^oC for 1 hr in helium

Fig. 7. Apparent crystallite size L_c of ZrC-graphite bodies as a function of heat treatment time

Fig. 8. Layer spacing C_0 of ZrC-graphite bodies as a function of heat treatment temperature

While these preliminary experiments on isotropic cokes show some degree of catalytic action when the titanium is used, the effect is not as dramatic as that shown in the pyrolytic carbons. One of the major differences in the two materials (petroleum asphalt and pyrolytic carbons) is the presence of oxygen in the petroleum asphalt. This impurity may be of particular importance in the formation of the coke substructure during the transformations that take place in the carbonization process.

Although the titanium metal apparently promoted crystal growth in isolated regions of the petroleum asphalt coke described above, the effects were not significant. Thus, an additional experiment was performed in which aluminum metal was added to the petroleum asphalt along with the titanium. The decomposition of Al_4C_3 has been reported to deposit large graphite crystals above 2400°C .⁽⁸⁾ Duplicate batches of about 50 g of the asphalt containing the metals were prepared along with a control sample. The samples were carbonized slowly in helium to 900°C , and smaller samples were subsequently heated to 2800°C for 2 hr.

The X-ray results are shown in Table 1. Photomicrographs are shown in Fig. 9. The control specimen behaved similar to previous samples and did not graphitize well; L_c was $540 \text{ \AA}$ and C_o was $6.71 \text{ \AA}$. However, large primary crystals of graphite were observed in the cokes that contained the metal additives. A metallic appearing matrix surrounded the crystals and appeared to be that of a eutectic composition. The graphite crystals showed a pronounced optical response under examination with sensitive tint lighting. The X-ray patterns also contained strong TiC lines.

These specimens appear to have been high in metal content, and the graphite crystals apparently formed during cooling from a melt. It should be noted, however, that graphite crystals were not formed in the same coke after heating to 3000°C when only titanium was present. In the case of the titanium or zirconium specimens the metal contents were 44 and 50 wt-%, respectively. The total metal content in the premix was the same for these specimens; thus, the reaction of the aluminum appears to be important, as was reported by Foster, et al.,⁽⁸⁾ in forming the graphite crystals.

Further experiments will be carried out with aluminum and titanium at lower metal contents.

TABLE 1
X-RAY PARAMETERS OF PETROLEUM ASPHALT COKE WITH
METAL ADDITIVES HEATED TO 2800°C FOR 2 HR

Specimen Number	Metal Additive (wt-%)		X-Ray Parameters (Å)	
	Al	Ti	L _c	C _o
2317-91	0	0	540	6.71
2317-90	10	10	∞	6.69
2317-89A	10	10	∞	6.69

M-23918-2

(350x)

(a)

M-23920-2

(350x)

(b)

Fig. 9. Photomicrographs of petroleum asphalt cokes heated to 2800°C for 2 hr: (a) 10 wt-% Al and 10 wt-% Ti added to the petroleum asphalt prior to carbonization and (b) no additives

6. IRRADIATION BEHAVIOR OF GRAPHITES

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

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

A series of investigations is in progress to study the influence of pitch-binder content on the microstructure, physical properties, and irradiation behavior of graphite bodies that were prepared by a standardized molding process. The objectives of this work are to characterize the materials in terms of selected physical properties and structural parameters and to correlate this information with the results obtained after subjecting the specimens to irradiation at elevated temperatures.

The specimens were prepared with calcined coke and various levels of pitch-binder content. A full description of the specimens has been given previously. (2) The specimens have been irradiated for two cycles at 1225°C in Capsule GE-H-13-14 in the Engineering Test Reactor (ETR) to a dose of 1.8×10^{24} n/cm² ($E > 0.18$ MeV). The results of this first irradiation period have also been reported. (2) The specimens were reirradiated at about 1250°C for an additional 3 cycles in Capsule GE-H-13-15 in the ETR to a total dose of about 6×10^{24} n/cm². The capsule was discharged on January 28, 1968, and postirradiation examinations are in progress. Both irradiation capsule experiments were conducted by Battelle Pacific Northwest Laboratory.

Additional thermal expansivity measurements were made on unirradiated specimens. The data are plotted in Fig. 10 as a function of linear dimensional changes. These are the same correlations given previously except the data for the unirradiated specimens now represent the average of three specimens instead of single points. The data show that the thermal expansivity has increased after irradiation when measured in the direction normal to the layer planes, whereas those in the direction parallel to the layer planes have increased only a small amount. A linear relationship still exists; however, the slope of the line has decreased. The thermal expansivity increases may be interpreted as the closure of microcracks that lie parallel to the basal planes. These correlations will be observed

Fig. 10. Dimensional change of molded graphite bodies as a function of thermal expansivity

again after irradiation to higher doses. There appeared to be a dependence of thermal expansivity increase on binder-coke content, with the smallest increase occurring at 6.7 wt-%. However, this correlation may become clearer after higher doses have been achieved.

The apparent bulk densities are plotted in Fig. 11 as a function of binder-coke content. There is a gradual increase in the bulk density as the binder coke is increased. However, the apparent densities, when measured by immersion in liquid, show no such dependence. The increase in binder-coke content reduces the total porosity and the open porosity but not the closed porosity. There appears to be an increase in densification with an increase in the binder-coke content after irradiation at 1225°C to 1.8×10^{21} n/cm² (see Fig. 12). Again these trends will become clearer after high doses are reached.

VOLUMETRIC CHANGES OF ARTIFICIAL GRAPHITES

A number of models, which have been reported and describe the dimensional changes of graphite under neutron irradiation, were discussed previously.⁽³⁾ A new equation was introduced that relates the volumetric changes of porous graphites to changes in their crystallites and porosity.⁽³⁾ This new equation accounts for the inhomogeneity of crystallinity and porosity by determining the structural and pore spectra by a sink-float technique (see Section 4 of this report).

Two graphites, one anisotropic (CHN) and one near-isotropic (H-315-A), which are being irradiated at high temperatures under another program,⁽⁹⁾ are being used to test this equation. Graphite CHN was fabricated with needle coke and heavily impregnated with a nongraphitic carbon, whereas graphite H-315-A was fabricated with Gilso-carbon and pitch. A full description of these materials and their properties have been reported elsewhere.⁽¹⁰⁾

Apparent density measurements have been made on a number of unirradiated CHN specimens. The density measurements will be used in conjunction with irradiation data on specimens in Capsule GE-H-13-15 to calculate changes in the internal microporosity. The measuring technique has been described elsewhere.⁽¹⁰⁾ It was found that the density values increased with soaking time in the liquid but saturated after about 24 hr (see Fig. 13). In the future, specimens will be soaked for 24 hr prior to measurement.

A few specimens from Capsule G10⁽¹⁰⁾ measured after irradiation at 950°C, 1250°C, and 1500°C and 2.85 to 3.25×10^{21} n/cm² ($E > 0.18$ MeV)

Fig. 11. Density of molded graphite as a function of binder-coke content

Fig. 12. Volume change of molded graphite bodies irradiated at 1225°C to 1.8 to 1.9×10^{21} n/cm^2 as a function of binder-coke content

Fig. 13. Apparent densities of CHN graphite specimens irradiated at 950° to 1500°C and 2.85 to 3.25×10^{21} n/cm² (E > 0.18 MeV)

showed a significant amount of densification on a microscale, which indicates that the concept of micropore closure is correct. The densities of the irradiated specimens also show that considerable microporosity remains after exposure to 2.85 to 3.25×10^{21} n/cm² and 950° to 1500°C. This may be expected since volumetric expansion (turnaround) has not yet occurred at these doses and temperatures.

These studies will be continued by measuring the densities of unirradiated H-315-A and specimens from Capsule GE-H-13-15 after exposures of up to about 8×10^{21} n/cm² at 1200°C.

7. IRRADIATION INDUCED DIMENSIONAL CHANGES IN SINGLE-PHASE CARBONS AND GRAPHITE

J. C. Bokros, R. W. Dunlap, A. S. Schwartz,
W. H. Ellis, and F. J. Gagnon

A topical report on this subject has been prepared.⁽¹¹⁾ This report includes the data obtained under this section for several prior report periods, including the current period. Because the full report will be issued, only the abstract and conclusions are included here. The abstract is as follows:

"Data from several irradiation experiments carried to high neutron exposures show that the irradiation induced densification that is familiar at low exposures is replaced by an expansion process at high exposures. It is suggested that the expansion is a consequence of porosity generated by intercrystalline irradiation creep. When the expansion process becomes apparent at high exposures the shape changes of all the carbons taken as a group depart from the relations predicted by crystallite averaging methods. The nearly isotropic carbons behave as if either the shape-change rate of the crystallites is enhanced by the irradiation itself or that of the new porosity generated at high exposures is directed perpendicular to the original deposition plane. The data also show that, for turbostratic carbons with $L_c = 120$ to $200 \text{ \AA}$, a preirradiation at $\sim 600^\circ\text{C}$ to $\sim 1 \times 10^{21} \text{ n/cm}^2$ does not influence the neutron induced dimensional changes that occur in a subsequent irradiation at $\sim 900^\circ\text{C}$." The significance of the results in coating design are discussed.

The carbon samples in the G12* capsule have been examined and the data are being analyzed.

*Specimens for this experiment were deposited under Contract AT(04-3)-167, Project Agreement No. 17. The specimens were irradiated under Contract AT(04-3)-633.

8. ANNEALING STUDIES OF PYROLYTIC CARBON STRUCTURES

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

The annealing kinetics of a variety of pyrolytic carbons irradiated between 540^o and 1060^oC are being studied to provide information about the nature of irradiation damage in poorly crystalline carbons irradiated at high temperatures. In addition, pyrolytic carbons containing codeposited titanium are being annealed to determine the effects of metal additives on the kinetics of annealing and on the properties of the annealed material. This part of the work is being performed because catalytically graphitized pyrocarbons have good dimensional stability under irradiation and because the use of metallic additives is being explored as a means of forming fully graphitic coke. A more complete description of the objectives of the experiment and details of the samples being studied are given in Refs. 1 and 2 and in Table 2.

The samples are being annealed for 1 hr at a series of temperatures, increasing by 100^oC increments. The properties under study are density, linear dimensions, layer spacing, apparent crystallite size, and electrical resistivity. Measurements of hardness and thermal diffusivity will be made after the final anneal. The samples have now been annealed at temperatures up to 2500^oC. The changes in linear dimensions, density, apparent crystallite size, and electrical resistivity are shown in Figs. 14 through 27.

The downward trend in electrical resistivity and the upward trend in density and apparent crystallite size continued at an accelerating rate as the annealing temperature was increased. The dimensional changes followed the anisotropy of the carbons (Figs. 22 through 24), with the laminar carbons showing an expansion parallel to the deposit and contraction perpendicular to the deposit. The more isotropic carbons (structures 5 and 6 from Table 2) showed less difference in the dimensional changes parallel to the deposit and perpendicular to the deposit.

The changes in dimensions and crystallite size in the laminar carbon structure No. 2 from Table 2, which was deposited at 1400^oC, did not depend markedly on the irradiation conditions. Because this structure is responsive to thermal annealing,⁽¹²⁾ it is probable that the property changes are largely the result of thermal annealing of the as-deposited structure, rather than the recovery of irradiation-induced changes. The carbon

TABLE 2
PROPERTIES OF CARBONS USED IN ANNEALING STUDIES

Structure Number	Deposition Temp (°C)	Annealing Treatment or Metal Additive	Irradiation Conditions		Structural Properties		
			Temp (°C)	Neutron Dose ($\times 10^{21}$ nvt) (E > 0.18 MeV)	Density (g/cm ³)	L _c (Å)	BAF
2	1400	None	540	1.6	2.074	43	1.65
2	1400	None	620	1.5	2.078	42	
2	1400	None	890	2.4	2.073	56	
2	1400	None	1040	2.4	2.064	60	
2	1400	None	1060	2.2	2.069	47	
6	2000	None	540	1.6	2.036	154	1.30
6	2000	None	620	1.5	2.038	154	
6	2000	None	890	2.4	2.082	95	
6	2000	None	1040	2.4	2.076	94	
6	2000	None	1060	2.2	2.084	87	
1-G	1400	2 hr at 2800°C	540	1.6	2.193	279	2.6
1-G	1400	2 hr at 2800°C	890	2.4	2.104	127	
1-G	1400	2 hr at 2800°C	1060	2.2	2.156	123	
2-A	1400	4 hr at 1900°C	1040	2.4	2.027	75	1.66
5	1650	None	540	1.6	1.685	61	1.0
5	1650	None	1060	2.2	1.914	46	
2814-77-1	1225	6.7 wt-% Ti	----	0	2.168	33	(a)
2814-77-2	1225	6.7 wt-% 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	
2814-81-1	2200	9.7 wt-% Ti	----	0	2.302	162	1.2
2814-81-2	2200	9.7 wt-% Ti	----	0	2.300	154	
2814-83-1	2200	None	----	0	2.150	188	(a)
2814-83-2	2200	None	----	0	2.150	178	

(a) Not determined

Fig. 14. Change in electrical resistivity of irradiated (a) isotropic and (b) laminar pyrolytic carbons as a function of annealing temperature

Fig. 15. Change in linear dimensions, parallel to the deposit, of irradiated (a) isotropic and (b) laminar pyrolytic carbons as a function of annealing temperature

Fig. 16. Change in linear dimensions, parallel to the deposit, 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 carbon as a function of annealing temperature

Fig. 17. Change in density of irradiated (a) isotropic and (b) laminar pyrolytic carbons as a function of annealing temperature

Fig. 18. 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. 19. Change in apparent crystallite size L_c of irradiated isotropic carbon as a function of annealing temperature

Fig. 20. Change in apparent crystallite size L_c of irradiated laminar pyrolytic carbon as a function of annealing temperature

Fig. 21. 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, and (c) low-density isotropic pyrolytic carbon as a function of annealing temperature

Fig. 22. Anisotropy of the dimensional changes of irradiated isotropic pyrolytic carbon as a function of annealing temperature

Fig. 23. Anisotropy of the dimensional changes of irradiated laminar pyrolytic carbon as a function of annealing temperature

Fig. 24. Anisotropy of the dimensional changes 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 carbon as a function of annealing temperature

Fig. 25. Change in density and apparent crystallite size L_c of titanium-doped and titanium-free pyrolytic carbon deposited at 1255 °C as a function of annealing temperature

Fig. 26. Change in electrical resistivity of titanium-doped pyrolytic carbon deposited at 1225°C as a function of annealing temperature

Fig. 27. Change in density, apparent crystallite size, and electrical resistivity of titanium-doped and titanium-free pyrolytic carbon deposited at 2200°C as a function of annealing temperature

designated 2-A in Table 2 (annealed at 1900°C before irradiation) showed property changes between 1400°C and 1900°C which continued in the same direction but at a higher rate above 1900°C .

In contrast, the laminar carbon 1-G (annealed at 2800°C before irradiation), and the isotropic carbon number 6 (which is unresponsive to thermal annealing in the unirradiated state⁽¹²⁾) showed property changes that were strongly dependent on the irradiation conditions. The property changes occurred in the same direction as those taking place in the laminar carbons in response to thermal annealing. The magnitude of the changes was greatest for the carbons irradiated to the highest temperatures and doses and which had undergone the greatest changes during irradiation. These results show that the process of annealing of radiation damage in pyrolytic carbons is qualitatively similar to the annealing of those as-deposited carbons that respond to thermal annealing.

The laminar carbon codeposited with 6.7% wt-% titanium at 1225°C showed no evidence of catalytic graphitization after annealing at 2400°C for 1 hr (Fig. 25). This was unexpected because the same material has been shown⁽¹³⁾ to graphitize during a 4-hr treatment at 2200°C in a fluidized bed. It is possible that graphitization is enhanced by the thermal cycling experienced by samples circulating in a fluidized bed.

The isotropic carbon deposited at 2200°C and containing 9.7 wt-% titanium, on the other hand, showed clear evidence of catalytic graphitization (Fig. 27). The process is best illustrated by comparing the (002) X-ray diffraction peaks obtained from material annealed at 2200° , 2300° and 2400°C (Fig. 28). The 2200°C peak corresponds to a turbostratic carbon with an L_c of ~ 150 Å. After annealing for 1 hr at 2300°C , a small secondary peak appears at $\theta = 13.3$ deg, corresponding to fully crystalline graphite. After the 2400°C anneal the material is almost fully transformed to graphite, with an L_c value of 700 Å and with only a small asymmetric shoulder on the low- θ side of the profile to show that some turbostratic carbon remains. The appearance and subsequent growth of a separate graphite peak show that the catalytic graphitization occurs by a heterogeneous recrystallization process.

Fig. 28. (002) X-ray diffraction peak of titanium-doped pyrolytic carbon deposited at 2200°C after annealing at (a) 2200°C, (b) 2300°C, and (c) 2400°C for 1 hr

9. STATUS OF TOPICAL REPORTS AND PUBLICATIONS

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

- J. C. Bokros and A. S. Schwartz, "A Model to Describe Neutron-Induced Dimensional Changes in Pyrolytic Carbon," Carbon 5, 481 (1967) (GA-7700).
- R. J. Price, J. C. Bokros, and K. Koyama, "Thermal Expansivities and Preferred Orientation of Pyrolytic Carbons," Carbon 5, 423 (1967) (GA-7905).
- J. L. White, G. L. Guthrie, and J. O. Gardner, "Mesophase Microstructures in Carbonized Coal-Tar Pitch," Carbon 5, 517 (1967) (GA-7694).
- J. C. Bokros, G. L. Guthrie, and A. S. Schwartz, "The Influence of Crystallite Size on the Dimensional Changes Induced in Carbonaceous Materials by High-Temperature Irradiation," accepted for publication in Carbon (GA-8001).
- J. L. White and J. Pontelandolfo, "HWLC Graphites Prepared by Hot-Working Extruded Stock," accepted for publication in Carbon (GA-7996).
- G. B. Engle, "Properties and High Temperature Irradiation Behavior of Graphites Prepared with Uncalcined Coke," accepted for publication in Carbon, (GA-7457 and GA-7458, combined).
- J. L. White and K. Koyama, "Graphitic Materials Hot-Worked with a Dispersed Liquid Carbide: Thermal and Electrical Conductivity," accepted for publication in the Journal of the American Ceramic Society (GA-7437).
- J. C. Bokros, R. W. Dunlap, and A. S. Schwartz, "Effect of High Neutron Exposure on the Dimensions of Pyrolytic Carbon," in review (GA-8555).

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