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AEC RESEARCH AND
DEVELOPMENT REPORT

GA-8852

RESEARCH ON GRAPHITE

QUARTERLY PROGRESS REPORT
FOR THE PERIOD ENDING AUGUST 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

September 1, 1968

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GA-5016 - Annual Report, April 1, 1963, through March 31, 1964
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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-8681 - Annual Report, May 15, 1967, through May 14, 1968

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1. INTRODUCTION

The objective of the research on graphite program is to develop an understanding of properties and structure of various types of carbons and graphites required for use in high-temperature reactors of advanced design. The experimental approach emphasizes defining the structures of various carbons and graphites, developing the relationships between structure and relevant properties, and evaluating methods for preparing material with improved properties.

The program for the period May 15, 1968, to August 14, 1968, consisted of work in two areas: (1) investigations of structures and properties of carbons and graphites, and (2) studies of the effects of irradiation on these structures and properties. The work is described in Sections 3 through 9 of this report.

The objective of the investigations on structural characterization is to develop correlations between properties and structure 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, their preferred orientation, their density, and their microstructure. The investigations of conventional graphites include the development of techniques for characterizing the degree of graphitization by separation and identification of the various structural components that exist in the various 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 that are fully characterized, and the principal areas of interest are dimensional changes, thermal expansivity, elastic properties, and irradiation creep.

A single graphite crucible is being prepared for irradiation in the High Flux Isotope Reactor (HFIR) by Oak Ridge National Laboratory (ORNL). Specimens of binder-filler artifacts and model carbons and graphites were selected for this experiment.

2. SUMMARY

STRUCTURE OF CARBONIZED COAL-TAR PITCH

No work in progress during this report period.

CHARACTERIZATION OF THE DEGREE OF GRAPHITIZATION OF CARBON AND GRAPHITE

An experimental effort is in progress to separate and identify the various structural states of carbon that comprise conventional artificial graphites. Additional densitometric separations were made on a near-isotropic graphite that had been comminuted to a particle size of less than 10 microns. The finer grinding shifted the densities of the particles to higher values and removed additional porosity. The rate of decrease in porosity as a function of particle size leveled off at small particle sizes.

An experimental graphite has been fabricated that consists of a two-component filler; i.e., low-density PyC and high-density needle-coke. Densitometric separations of the loose coke and the formed artifact are in progress. The formed artifact is being characterized by X-ray and physical property measurements for future irradiation experiments.

CATALYTIC GRAPHITIZATION

A series of 1-hour anneals on two titanium-doped pyrolytic carbons and titanium-free control carbons was concluded after anneals up to 3000 C. The metal-doped carbons decreased in density as the metal evaporated over the interval 2400 to 2800 C. There was no evidence for catalytic recrystallization in a laminar carbon deposited at 1225 C. An isotropic titanium-doped carbon deposited at 2200 C started to recrystallize at 2300 C. The amount of residual ungraphitized carbon decreased as the annealing temperature increased, but the crystallinity of the graphitic phase remained unchanged.

Petroleum coke containing aluminum and aluminum-titanium are under examination to determine their worth as catalytic agents in the graphitization process. Coke specimens that had aluminum and titanium admixed prior to carbonization contained graphite crystals that were optically visible after heating in the range 1700 to 2300 C. X-ray curves from these

specimens showed strong graphite peaks superimposed on the broad carbon curves. The graphite crystals appeared to be growing around the remnants of metallic particles.

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

Molded graphite specimens are currently under irradiation at Battelle Northwest Laboratories (BNWL) for the third increment of exposure; therefore, no specimens were available for examination during this report period.

VOLUMETRIC CHANGES IN ANISOTROPIC AND NEAR-ISOTROPIC GRAPHITES

The changes in microporosity associated with mosaic clusters of crystallites and macroporosity are being measured after irradiation on an anisotropic and near-isotropic graphite. Specimens of CHN and H-315-A graphites irradiated at 955 and 1000 C were measured and the results confirmed those of duplicate specimens irradiated previously. Specimens irradiated at 320 C showed large expansions of the crystallite clusters. The extent of the expansion depended upon the density of the crystallite clusters.

ANNEALING STUDIES OF IRRADIATED PYROLYTIC CARBON STRUCTURES

Isochronal annealing of the series of irradiated pyrolytic carbon samples was completed up to 3000 C. The property changes in the laminar carbons were almost independent of annealing conditions and followed a sigmoidal annealing curve with saturation of the property changes at the highest temperatures. The laminar carbons annealed before irradiation, and the isotropic carbons, responded to annealing according to the amount of irradiation damage received; the property changes were spread over a wide range of annealing temperatures. The crystallite dimensions of the samples irradiated at approx 900 to 1050 C recovered one-third to one-half their irradiation-induced change.

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

At 600 or 900 C, the low-temperature isotropic (LTI) carbons densify at a much higher rate than high-temperature isotropic (HTI) carbons that have larger crystallites. The rate at which the linear dimensions change under irradiation and the exposure at which the isotropic material (Bacon Anisotropy Factor (BAF) less than 1.1) exhibits pronounced anisotropic behavior are lower for LTI carbons than for HTI carbons.

Turbostratic carbons ($L_c = 170$ Ang) expanded 60% in the perpendicular direction and contracted 30% parallel while graphitized carbons ($L_c = 800$ Ang) expanded 6% perpendicular and contracted 3% parallel at 900 C and 7×10^{21} n/sq cm.

No seeding effects were observed on carbons irradiated first at 530 C and then again at 900 C to a total exposure of 6.5×10^{21} n/sq cm.

Carbon specimens with an initial density of 2 g/cc that were taken to 8×10^{21} n/sq cm at 800 to 1000 C showed an initial densification followed by expansion to a final density of 1.88 g/cc. At 600 C and to over 6×10^{21} n/sq cm the density of these same specimens steadily rose to a final density of 2.1 g/cc.

3. STRUCTURE OF CARBONIZED COAL-TAR PITCH

No work in progress during this report period.

4. CHARACTERIZATION OF DEGREE OF GRAPHITIZATION OF CARBON AND GRAPHITE

G. B. Engle and L. Bailey

The objective of this characterization 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., a sink-float technique) is being used for this purpose. A description of the apparatus, the operating procedure, and the sample preparation have been given previously (Ref. 1).

The experiments to characterize graphites by the densitometric method were continued by: (1) further separation of specimens as a function of particle size, and (2) separation of a two-component material. The particle size studies were concentrated on the CHN and H-315-A graphites.

Specimens of CHN and H-315-A were ground to pass a 400-mesh screen (less than 38 microns), and the powders were separated in the sink-float apparatus. The densitometric curves, along with those for specimens ground to 75 to 150 microns were given previously (Ref. 2). Specimens of CHN graphite and H-315-A have now been ball-milled for 300 hr. The particles of these samples were estimated by microscopic observation to be less than 10 microns. The CHN curve was given previously (Ref. 2). The finer grinding has shifted the average density of the particles to higher values and removed more of the closed microporosity (Table 1). The shift in the densitometric curves was more pronounced for the H-315-A graphite, which is less crystalline than the CHN material. Both materials still contain a measurable volume of microporosity that is not penetrated by the liquids.

While the average density of the graphite fractions increased upon further comminution, the rate of increase leveled off, with only a small decrease in microporosity being achieved by prolonged milling. Therefore, the more simple and less time consuming method of grinding in a mortar has been adopted for the study of irradiated specimens (Section 7).

TABLE 1
CLOSED MICROPOROSITY IN CHN AND H-315-A GRAPHITES

Particle Size (μ)	Closed Microporosity (%)	
	CHN	H-315-A
75-150	3.40	7.10
< 38	2.20	2.60
< 10	1.80	2.10

An experimental material has been prepared in the laboratory for use in the characterization studies. A filler coke was prepared by coating calcined needle-coke particles with a low-density pyrolytic carbon (about 1.70 g/cc and L_c of 40 Ang). The coke was crushed to pass a 200-mesh screen, and the flour was subsequently mixed with a 25 wt-% Barrett No. 30 pitch binder to form a porous binder-filled artifact by warm-pressing at 800 C and 5400 psi. The resulting binder-filler artifacts had a density of 1.48 g/cc. They were then impregnated with pitch at 200 C and 140 psi for 3 hr and heated to 900 C to increase the strength and density, and finally heated to 2800 C. The final artifacts consisted of a two-component filler, each having a different density and crystallite size, plus the residue coke from the binder and impregnant. A quantitative record of each carbon component was obtained from the fabrication steps (Table 2). This material has been characterized in the densitometric column (Fig. 1), by thermal expansivity, and by BAF (Table 3). Additional densitometric curves will be obtained on each of the individual components to determine the analytical worth of the densitometric curve of the composite. These data will be correlated with the irradiation behavior of the artifact if it can be irradiated in one of the HFIR experiments at ORNL.

TABLE 2
RAW MATERIALS IN SPECIMEN 2317-108-6

Components (wt-%)		
Filler-Coke		Binder-Impregnant Coke
PyC	Needle-coke	
34.5	53	12.5

Fig. 1. Densitometric curve of Specimen 2317-108-6

TABLE 3
 PROPERTIES OF SPECIMEN 2317-108-6

Bulk Density (g/cm ³)	Thermal Expansivity $\alpha \times 10^6, \text{ }^\circ\text{C}^{-1} @ 400 \text{ C}$		BAF
	Parallel	Perpendicular	
1.59	5.62	3.37	1.35
	5.21	3.20	

5. CATALYTIC GRAPHITIZATION

The aim of the catalytic graphitization work in this portion of the program is to determine the effects of metal additives on the kinetics of annealing and on the properties of annealed pyrolytic carbons, and to explore the use of metal catalysts to promote enhanced crystal growth and isotropy in filler cokes or binder-filler artifacts. Since the recrystallized materials are for nuclear reactor applications, the nuclear properties and/or the ease of removal of the last traces of the catalyst from the materials are important. Therefore, the choice of catalysts is limited to metals of reasonably small capture cross sections or those that can be easily removed after the catalytic reaction.

ANNEALING EFFECTS IN TITANIUM-DOPED PYROLYTIC CARBON

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

To increase the thermal conductivity and dimensional stability of pyrolytic carbons under irradiation, it is desirable to increase their crystallinity. One way in which this may be achieved is by the co-deposition of titanium, followed by annealing. Therefore, a study of annealing effects in titanium-doped pyrolytic carbon is being conducted. In addition, this study is relevant to the exploratory work on the use of metallic additives in forming fully-graphitic coke (reported later in this section).

A pyrolytic carbon containing 6.7 wt-% titanium and a titanium-free control carbon, deposited at 1225 C, together with samples of a second titanium-doped carbon containing 9.7 wt-% titanium and its titanium-free control, deposited at 2200 C, are undergoing annealing. The microstructure of the carbon deposited at 1225 C was laminar and that of the carbon deposited at 2200 C was isotropic. The structural properties of these carbons are given in Table 3 of Ref. 2.

The carbons were given a series of successive 1-hr anneals at temperature increments of 100 C. The samples were annealed together with a series of neutron-irradiated pyrolytic carbons (Section 8). Annealing of the carbons deposited at 1225 C was started at 1300 C, and annealing of the carbons deposited at 2200 C was started at 2000 C. Anneals were conducted at temperatures up to 3000 C. Changes in density, electrical

resistivity, apparent crystallite size, and layer spacing of the titanium-doped carbons and their titanium-free controls were measured.

Property changes up to 2600 C were reported in the last annual report (Ref. 2). Plots of the changes at higher temperatures are being held over until the final measurements and analysis are complete.

During the final annealing steps both titanium-doped carbons showed a decrease in density due to the evaporation of titanium. The evaporation started at 2400 C and was completed by 2800 C. The 1225 C carbon did not undergo catalytic graphitization. Both the titanium-doped carbon and its titanium-free control showed a steady increase in crystallinity as the temperature was increased.

The titanium-doped carbon deposited at 2200 C underwent catalytic graphitization starting at 2300 C. The amount of ungraphitized carbon remaining, decreased as the temperature increased, but the apparent crystallite size and layer spacing of the graphitic phase remained constant.

CATALYTIC EFFECTS IN COKES AND BINDER-FILLER ARTIFACTS

G. B. Engle, J. M. Pontelandolfo, and J. M. Dixon

Two approaches were considered in this study: (1) admixtures of fine metal powders to coal-tar pitch or a petroleum asphalt prior to carbonization, and (2) admixtures of fine metal or metallic carbide powders to a mixture of calcined coke and pitch binder prior to molding. The metals used are titanium, zirconium, and aluminum; zirconium carbide was also used.

For the first phase of this work, a series of exploratory experiments were made in which the metals were mixed with the various carbonaceous materials, the specimens were heat-treated to promote graphitization, and the results were followed by measurements of the lattice parameter C_0 and the apparent crystallite size L_C .

Petroleum asphalt carbonized with aluminum and titanium showed evidence of recrystallization by the presence of large primary crystals when heated to 2800 C (Ref. 2). Additional experiments showed enhanced crystal growth in petroleum asphalt cokes that were doped with 2.5 and 5 wt-% of aluminum and titanium, respectively (Ref. 2). These positive results have led to the preparation of specimens of higher metal content (5 and 10 wt-% aluminum, 5 wt-% Al and 10 wt-% Ti, and 10 wt-% Al and 20 wt-% Ti). Heat treatment of these specimens was done in the range 1700 to 2300 C, and the resulting cokes were examined by X-ray diffraction for apparent crystallite size L_C and lattice parameter C_0 (Table 4).

TABLE 4

HEAT-TREATMENT AND X-RAY PARAMETERS OF PETROLEUM ASPHALT -
ALUMINUM-TITANIUM ADMIXTURES

Sp. No.	Composition (wt-%)			Heat Treatment					Metal Content (wt-%)		X-ray Data (002)	
				Bake		Sp. No.	Temp (C)	Time (hr)				
	Petro- leum Asphalt	Al ^(a)	Ti ^(a)	Temp (C)	Carbon Yield (wt-%)				Al	Ti	C _O (Å)	L _C (Å)
114-1	95	5	-	900	65.2	115-1	2300	2	-	-	6.837	200
						115-1	2300	8	-	-	6.813	250
						115-1	2300	32	-	-	6.805	225
114-2	90	10	-	900	66.4	120-2	1700	2	-	-	6.874	-
						121-2	1900	2	-	-	6.850	-
						122-2	2100	2	-	-	6.824	-
						115-2-2	2300	2	0.17	-	6.758	200
						115-2	2300	8	-	-	6.739	280
						115-2	2300	32	-	-	6.739	285
						114-3	85	5	10	900	67.8	115-3
115-3	2300	8	-	-	6.734	330						
115-3	2300	32	-	-	6.734	350						
114-4	70	10	20	900	75.2	120-4	1700	2	-	-	6.886(b) 6.726(b)	-
						121-4	1900	2	-	-	6.821(b) 6.721(b) 6.810(b) 6.726(b)	-
						122-4	2100	2	-	-	6.726(b)	
						115-4-2	2300	2	0.24	31.8	6.734	540
						115-4	2300	8	-	-	6.715	600
115-4	2300	32	-	-	6.715	770						

(a) Added to petroleum asphalt after distillation, but prior to carbonization.

(b) The X-ray diffraction curves had two distinct peaks.

The coke containing 5 wt-% aluminum showed no signs of recrystallization from X-ray examination when heated at 2300 C. However, metallographic examination revealed small areas that contained large, well developed graphite crystals. These crystals appeared to be growing around the remnants of a metallic particle. The coke sample that contained 10 wt-% aluminum showed evidence of recrystallization from both X-ray and metallographic examinations when heated to 2300 C, but below 2300 C there was no evidence of growth. The sample containing 10 wt-% aluminum and 20 wt-% titanium showed evidence of graphite crystal growth at 1700 to 2300 C. This specimen had large areas of primary graphite crystals that responded to sensitive tint lighting.

The X-ray curves (002) show a distinct graphite peak superimposed on a broad carbon curve. The graphite peak becomes more prominent with increasing temperature until at 2300 C the carbon peak is quite weak. This is in contrast to the sample containing only aluminum which shows a gradual shift from a carbon structure toward a graphite structure. The formation of graphite crystals is not the same for aluminum and aluminum in combination with titanium. A spot check on the metal content of two of the samples (Table 4) shows that aluminum was reduced to less than 0.25 wt-% after 2 hr. at 2300 C while the titanium was still present in about the same ratio as it was in the coke after heat treatment to 900 C.

Larger batches of the cokes in combination with aluminum and titanium are being prepared for fabricating binder-filler artifacts. These compacts will be subjected to heat treatments at 2100 and 2300 C, and the development of the graphitic structure will be observed as a function of time. Some of the compacts will be characterized and purified for future irradiation experiments.

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

G. B. Engle and L. Bailey

The influence of the pitch-binder content on the microstructure, the physical properties, and the irradiation behavior of graphite bodies that are prepared by a standardized molding process is under investigation. The immediate objectives of this work are: (1) to prepare a systematic set of specimens of known ingredients and known processing history, (2) to characterize these materials in terms of selected physical properties and structural parameters, and (3) to correlate this information with the results obtained after subjecting the specimens to high-temperature irradiation. The ultimate goal is the understanding of the influence of the binder-coke on the irradiation behavior of conventional graphitic materials in terms of measurable physical and structural parameters.

The specimens for the current studies were prepared with calcined needle coke and various levels of pitch-binder coke content in the range 5.5 to 14.2 wt-%. A description of the specimens was given previously (Ref. 2). The specimens are being irradiated in a series of capsules designated GE-H-13-13, -14 and -15 in the Engineering Test Reactor (ETR) at Idaho Falls, Idaho. Battelle Northwest Laboratories is conducting the irradiation capsule experiments, and the space is shared jointly between Gulf General Atomic and BNWL. The specimens were irradiated at 1225 C to 1.9×10^{21} n/sq cm (E greater than 0.18 Mev) in Capsule GE-H-13-13 and at 1250 C for an additional 3.85×10^{21} n/sq cm in Capsule GE-H-13-14, giving a total exposure of 5.75×10^{21} n/sq cm at 1225 to 1250 C. The irradiation data were reported previously in Ref. 2.

The specimens were returned to BNWL for reencapsulation. They are currently being reirradiated in ETR in Capsule GE-H-13-15. Further data will be available in October or December, 1968.

7. VOLUMETRIC CHANGES IN ANISOTROPIC AND NEAR-ISOTROPIC GRAPHITES

G. B. Engle and L. Bailey

A general relationship, which has been described and discussed previously in Ref. 2, that attempts to relate the neutron-induced changes in porous graphites to their crystallite changes and changes in porosity is under study. In this work the changes in microporosity associated with the mosaic clusters of crystallites (obtained by the sink-float technique) and the changes in the macroporosity are being measured on two graphites, an anisotropic graphite CHN and on near-isotropic graphite H-315-A. These materials and their irradiation history have been reported in Ref. 3.

Previous data (Ref. 2) obtained on specimens irradiated in the range 950 to 1490 C at 2.85×10^{21} to 7.8×10^{21} n/sq cm showed the low-density fractions of the graphites to first densify at low exposures and then expand at higher exposures, while the heavy fractions showed only expansion. This behavior was similar to that observed in the single-phase pyrocarbons (Ref. 4).

Additional samples of CHN and H-315-A graphites were measured after irradiation at 320, 955, and 1000 C to 1.70 and 2.9×10^{21} n/sq cm (Table 5).

The results on the CHN and H-315-A specimens irradiated at 955 and 1000 C were essentially the same as those reported previously (Ref. 2) on duplicate specimens. The specimens irradiated at 320 C showed large expansions of the mosaic clusters of crystallites at much lower exposures than those irradiated at 955 to 1000 C. The lighter fractions show more expansion than the heavier fractions in a manner similar to the specimens irradiated at higher temperatures.

These studies will be continued by obtaining densitometric curves on the remaining CHN and H-315-A specimens from Capsule GE-H-13-14 and on specimens taken to higher exposures from GE-H-13-15 when they are available.

TABLE 5
DENSITY CHANGES OF CHN AND H-315-A GRAPHITE

(a)	Vol-% of Sample Within Interval	Volume Change (%)			
		CHN		H-315-A	
		320 C (1.7×10^{21})	1000 C (2.9×10^{21})	320 C (1.7×10^{21})	955 C (2.85×10^{21})
Least dense fraction	1	+12.6	-1.6	- 0.6	+3.6
	1	+13.4	-2.1	+ 9.7	+4.3
	3	+14.9	0.0	+18.0	+6.8
	5	+12.0	+0.9	+11.0	+4.6
	10	+ 9.0	+1.9	+ 6.4	+2.6
	30	+ 5.3	+1.9	+ 2.1	+6.9
	30	+ 4.2	+1.8	+ 0.9	+0.9
Most dense fraction	10	+ 3.5	+1.6	+ 0.5	+0.4
	10	+ 0.4	+0.4	+ 0.4	+0.5

(a) Volume fractions of sample tabulated in order of increasing density.

8. ANNEALING STUDIES OF IRRADIATED PYROLYTIC CARBON STRUCTURES

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

The annealing kinetics of irradiated carbonaceous materials give useful information about the nature of the irradiation-induced defects. For example, when graphite irradiated between 150 and 350 C is annealed, the property changes attributable to small groups of interstitials (such as changes in elastic modulus) start to anneal out as soon as the irradiation temperature is exceeded. On the other hand, property changes caused by larger groups of interstitials or by vacancies (such as changes in thermal conductivity and dimensions) do not start to anneal until at approx 1200 C. The large dimensional changes observed in pyrolytic carbons irradiated at approx 1000 C suggest that a large amount of damage is retained, probably in the form of large clusters. The annealing processes in these irradiated carbons, therefore, may be expected to differ from those observed in the crystalline graphites irradiated at lower temperatures.

In the present work annealing studies were used to clarify the nature of irradiation damage in a variety of pyrolytic carbons irradiated between 540 and 1060 C in Capsule G-9*. A series of successive isochronal 1-hr anneals were carried out on the irradiated pyrolytic carbons, together with a series of titanium-doped and titanium-free pyrolytic carbons whose annealing behavior is described in Section 5. The irradiated carbons include a laminar carbon irradiated in each of five cells in Capsule G-9, 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 9 of Ref. 2.

*The irradiation of this capsule was conducted under USAEC Contract AT(04-3)-167, Project Agreement Number 17.

The properties being measured are density, linear dimensions, layer spacing, apparent crystallite size, and electrical resistivity. The layer spacing and apparent crystallite size were evaluated from the angular position and width of the (002) peak as determined from an X-ray diffractometer. In addition, samples for hardness measurements were set aside after each anneal. The thermal diffusivity of a disk sample of each carbon was measured prior to annealing, and the same disks will be remeasured after the final anneal. The samples were annealed in a helium atmosphere for 1-hr periods at a series of increasing temperatures. The starting temperature was 400 C. The 1-hr anneals were continued at temperatures increasing by 100 C increments to 3000 C. Property measurements were completed, except for X-ray diffraction measurements following the 3000 C anneal.

To avoid repetition, the plots showing the property changes will not be presented until they are prepared in their final form after all measurements are complete. The curves show several trends which are summarized:

- (1) The property changes in the laminar pyrocarbon are almost independent of irradiation conditions and result from the annealing of the as-deposited structure. The isochronal annealing curves are typical sigmoidal annealing curves with a sharp "knee" whose maximum slope occurs at about 2300 C. The shape of the curve is consistent with a thermally activated annealing process with a single activation energy.
- (2) The laminar pyrocarbon annealing at 2800 C before irradiation and the unannealable isotropic pyrocarbons show a response to postirradiation annealing that is approximately proportional to the amount of damage retained after irradiation. In the isochronal curves the property changes are spread out over a wider range of annealing temperatures than in the case of the as-deposited laminar pyrocarbons. This indicates that the annealing process in this case takes place with a range of activation energies. This annealing process is attributed to the rearrangement of irradiation-induced defects.
- (3) The dimensional changes that occur during annealing are related to the preferred orientation of the carbons. This enables the dimensional changes of the constituent crystallites to be calculated. Such calculations show that in all cases the crystallites contract in the c-direction and expand in the a-direction during annealing. In the laminar carbons annealed before irradiation the ratio of a-axis expansion to c-axis contraction is low (approx 0.3). In the isotropic carbons this ratio rises from approx 0.35 to approx 0.45 to 0.5 as the annealing temperature is increased. The ratio for the unannealed laminar carbons remains constant at approx 0.45. These results show that the annealing of irradiation-induced defects takes place accompanied by a crystallite volume decrease, whereas

the annealing of the as-deposited structure takes place at nearly constant volume. Among the samples irradiated at approx 900 to 1000 C, the crystallite dimensions recovered one-third to one-half their irradiation-induced change.

(4) After showing an increase in bulk density over most of the annealing steps, many samples underwent a slight decrease in density at temperatures above approx 2700 C.

9. RADIATION-INDUCED DIMENSIONAL CHANGES IN SINGLE-PHASE CARBONS AND GRAPHITES

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

The analysis of the results from the P13J* capsule has been completed. Irradiations were done at approx 600 and 900 C, and the neutron exposure accumulated for virgin samples was approx 3×10^{21} n/sq cm (E greater than 0.18 Mev). The exposures of samples that had been previously irradiated were extended to approx 8×10^{21} n/sq cm.

Data for a set of carbons deposited from propane at 1300 to 1400 C (LTI carbons) together with data from two earlier capsules are sufficiently complete to show the following: at both 600 and 900 C, the LTI carbons densify at a much higher rate than carbons that have larger crystallites and were deposited at higher temperatures (HTI carbon). Also, the rate at which the linear dimensions change under irradiation and the exposure at which the isotropic material (BAF less than 1.1) exhibits pronounced anisotropic behavior are lower for LTI carbons than for HTI carbons. These data provide the first quantitative comparison of the dimensional stability of LTI and HTI carbon. It is appropriate to mention at this point, that although LTI carbons are less stable under irradiation, they are of significantly higher strength than HTI carbon.

Data for turbostratic carbons and a catalytically graphitized carbon, both with the same degree of preferred orientation, have been extended to a dose of about 7×10^{21} n/sq cm at 900 C and to about 6×10^{21} n/sq cm at 600 C. As expected from previously established trends, the graphitized material ($L_c = 800$ Ang) is more stable than the turbostratic carbon ($L_c = 170$ Ang) and the effect is greatest at 900 C. For example, the turbostratic material expanded 60% in the perpendicular direction and contracted approx 30% in the parallel direction at 900 C. The graphitized material expanded about 6% in the perpendicular direction and contracted about 3% in the parallel direction. Hence, the more crystalline material was an order of magnitude more stable at 900 C. The difference in

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

dimensional stability for 600 C irradiations amounts to only a factor of two for the same two materials.

The irradiations of annealed pyrolytic carbon samples with nearly ideal single crystal orientation and $L_c = 1600$ Ang have been extended to about 6.5×10^{21} n/sq cm at 900 C in the P13J experiment. The near-single crystal changes in the c- and a-directions were about +7 and -3%, respectively, at about 900 C. Specimens irradiated first at 530 C and then again at 950 C had dimensional changes identical to specimens irradiated exclusively at 900 C to the same total dose. Hence, no seeding effects were observed.

Specimens with an initial density of 2.0 g/cc and BAF = 1.30 that were irradiated previously have been reirradiated in P13J. After an accumulation of about 8×10^{21} n/sq cm at 800 to 1000 C, the specimens showed perpendicular and parallel changes of +40 and -20%, respectively. The density data show the typical initial densification followed by an expansion so that at 8×10^{21} n/sq cm the final density was 1.88 g/cc. At 600 C, the perpendicular and parallel dimensional changes were only +1 and -3%, respectively, after over 6×10^{21} n/sq cm, and the density steadily rose during irradiation to a final value of 2.1 g/cc.

Data for anisotropic turbostratic carbons ($L_c = 160$ to 170 Ang) are consistent with past results by showing that at high exposures the shape changes are not consistent with the predictions of simple crystallite averaging methods. Possible explanations of this behavior have been presented previously in Ref. 2.

Results for titanium-doped (approx 10 wt-% Ti) HTI carbons with an initial BAF of 1.10 and $L_c = 160$ Ang (it was not graphitic) show that the titanium doping did not significantly improve the dimensional stability.

10. STATUS OF TOPICAL REPORTS AND PUBLICATIONS

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

Bokros, J. C., R. W. Dunlap, and A. Schwartz, "Effect of High Neutron Exposure on the Dimensions of Pyrolytic Carbons," accepted for publication in Carbon (GA-8555).

Bokros, J. C., G. L. Guthrie, and A. S. Schwartz, "The Influence of Crystallite Size on the Dimensional Changes Induced in Carbonaceous Materials by High-Temperature Irradiation," Carbon 6, 55 (1968) (GA-8001).

Engle, G. B., "Properties and High Temperature Irradiation Behavior of Graphites Prepared with Uncalcined Coke," accepted for publication in Carbon (GA-7457 and GA-7458, combined).

White, J. L., and K. Koyama, "Graphitic Materials Hot-Worked with a Dispersed Liquid Carbide: Thermal and Electrical Conductivity," accepted for publication in the J. Am. Ceram. Soc. (GA-7437).

White, J. L., and J. Pontelandolfo, "HWLC Graphites Prepared by Hot-Working Extruded Stock," Carbon 6, 1 (1968) (GA-7996).

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3. HTGR Base Program Quarterly Progress Report for the Period Ending May 31, 1968, USAEC Report GA-8662, Gulf General Atomic Incorporated, June 28, 1968.
4. Bokros, J. C., and A. S. Schwartz, "A Model to Describe Neutron-Induced Dimensional Changes in Pyrolytic Carbon," Carbon 5, 481-92 (1967).