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AEC RESEARCH AND
DEVELOPMENT REPORT

GA-9239

RESEARCH ON GRAPHITE

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QUARTERLY PROGRESS REPORT
FOR THE PERIOD ENDING FEBRUARY 14, 1969

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 19, 1969

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Gulf General Atomic Incorporated

P O Box 608, San Diego, California 92112

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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
GA-8852 - Quarterly Report, for period ending August 14, 1968
GA-9099 - Quarterly Report, for period ending November 14, 1968

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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 reactors of advanced design. The experimental approach emphasizes the definition of the structures of the various carbons and graphites, the development of the relationships between structure and relevant properties, and the evaluation of methods for the preparation of improved structure.

The program for the period November 15, 1968, to February 14, 1969, consisted of work in two areas: (1) investigations of the 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 investigations on structural characterization are being carried out to develop correlations between the properties and the structures of the various carbons and graphites. In the investigations of conventional graphites, techniques are developed 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 fast-neutron-flux and high-temperature conditions similar to the operating conditions of advanced reactors. In this work, the determination of structures of greatest stability and the definition of the dimensional changes and other properties as a function of structure are sought.

Work during this report period was concentrated on the postirradiation examination of specimens from capsule GE-H-13-15 and the preparation of new specimens for GE-H-13-16. Thus, the tasks in Sections 3 and 4 were curtailed to permit the irradiation to proceed on schedule.

Section 6 has been expanded to include work on a series of highly oriented graphites. These materials are under irradiation at Battelle Northwest Laboratory (BNWL) to study crystallite orientation effects at high temperatures and high doses. These experiments were previously reported under the HTGR Base Program.*

*Contract number AT(04-3)-167, Project Agreement No. 17.

2. SUMMARY

CHARACTERIZATION OF DEGREE OF GRAPHITIZATION OF CARBONS AND GRAPHITES

Additional grinding experiments were conducted on various graphites to determine the extent of pore removal. Grinding of up to 3 hr in a Pica mill produced only minimal reduction in closed porosity. The vigorous grinding produced unusually broad X-ray patterns that were not representative of the materials.

CATALYTIC GRAPHITIZATION

Compacts prepared from a petroleum-asphalt coke containing aluminum, titanium, or a combination of the two were heated for longer periods at 2100 or 2300 C. The specimens containing aluminum continued to convert to graphite, whereas the titanium-doped materials showed only traces of graphitic structure.

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

Graphite compacts prepared with needle-coke particles and various amounts of binder coke have been irradiated to 9.7×10^{21} n/sq cm at 1225 to 1250 C. For specimens deficient in binder coke, expansion in the c-axis direction has reached 20% while contraction ceased and expansion started in the a-axis direction. Samples high in binder coke also showed high expansions in the c-axis but continued to contract in the a-axis direction. Thermal expansivities have increased by as much as 2.5 in the c-axis direction. These results indicate that morphology and density are important along with crystallite size in predicting dimensional and volumetric changes in porous, polycrystalline graphites.

DIMENSIONAL AND VOLUMETRIC CHANGES OF ANISOTROPIC AND NEAR-ISOTROPIC GRAPHITES

A series of anisotropic and near-isotropic graphites has been irradiated to 7 and 11×10^{21} n/sq cm at 1000 and 1250 C, respectively. Expansion of the needle-coke materials in the c-axis direction ranged from 6% to 19%, whereas the near-isotropic materials showed only 2 to 4% after irradiation to 11×10^{21} n/sq cm at 1250 C. Thermal expansivity increased for needle coke and decreased for near-isotropic materials. Crystallite expansion consumes microporosity during the densification phase, but, when expansion begins, new porosity is generated in the microstructure. In a needle-coke specimen that had increased in volume by 18%, the porosity appeared to be between coke particles, where the binder coke resides. The volume contraction of specimens cut from large diameter needle-coke logs (13 in.) is about twice that of a Gilsonite-coke graphite (18 in. diameter) after irradiation to 3.5×10^{21} n/sq cm at 1000 to 1100 C. The Gilsonite material is nearly isotropic.

IRRADIATION EFFECTS ON HIGHLY ORIENTED CARBONS AND GRAPHITES

Samples of highly oriented, single phase -carbons and graphites are being irradiated in cooperation with BNWL. Samples of hot-worked graphite, as-deposited massive pyrocarbon, and annealed massive pyrocarbon irradiated at 750 to 800 C to 0.5 to 1.5×10^{21} n/sq cm (E greater than 0.18 MeV) and at 1250 to 1290 C to 3.8 to 9.7×10^{21} n/sq cm have been examined. The massive pyrocarbon irradiated at the higher temperature and exposure showed extensive delamination with c-axis true strains exceeding 120% and a-axis contractions of 50%. The other materials showed smaller changes and retained their integrity. The thermal expansivity of the hot-worked graphite parallel to the hot-working axis first increased with increasing exposure, passed through a maximum, and finally leveled off at about one half its initial value. Perpendicular to the hot-working axis, the thermal expansivity increased with neutron exposure.

ANNEALING STUDIES OF IRRADIATED PYROLYTIC CARBON STRUCTURES

The annealing studies of irradiated pyrolytic carbon structures have been completed except for hardness measurements, which are currently underway.

IRRADIATION-INDUCED CHANGES IN SINGLE-PHASE CARBONS AND GRAPHITES

Irradiation-induced dimensional changes in a variety of carbonaceous materials have been measured to exposures of 10^{22} n/sq cm at approximately 1250 C. The c-direction growth for natural crystals is about 3%/ 10^{22} n/sq cm. The dimensional changes for nearly isotropic turbostatic carbon are extremely sensitive to the original density. The degradation of the crystal structure of carbon appears to be more pronounced at 900 than at 1250 C. This is apparent from thermal conductivity changes as well as changes in apparent crystallite size L_c and layer spacing caused by fast-neutron irradiation.

3. CHARACTERIZATION OF DEGREE OF GRAPHITIZATION OF CARBON AND GRAPHITE

G. B. Engle and L. Bailey

In this portion of the program, methods for determining the amounts of various carbon structures present in carbonaceous and graphitic materials are evaluated and the degree of graphitization of these structures is defined. A densitometric method (i.e., a sink-float technique) is being used for this purpose. A description of the apparatus, the operating procedure, and sample preparation has been given previously (Ref. 1). Work was limited on this task because of the heavy work loads on the tasks given in Sections 5, 6, 7, and 9.

Previous densitometric separations were carried out on specimens of CHN and H-315-A graphites that were ground with a mortar and pestle to pass a 400 mesh screen (less than 38 μm . Specimens of H-315-A and CHN graphites have been ground in the Pica mill for 1-1/2 and 3 hr to particles with diameters in the range of 0.1 to 10 μm . The mean density of the particles milled in the Pica mill were 2.200 to 2.210 g/cc compared to 2.195 g/cc for material ground in a mortar. There was no significant difference in the density distribution or mean density of the specimens ground for 1-1/2 or 3 hr. The reduction in closed porosity was not significant with the more vigorous grinding attained in the Pica. Furthermore, the severe beating that the particles received in the Pica affected the X-ray parameters; the (002) lines were unusually broad and not representative of the material. Thus, the sample preparation will not be changed and will continue as in past experiments.

An experimental material containing a two-phase filler, low-density carbon and needle coke, has been prepared for characterization studies. Fabricational details and properties were reported previously (Ref. 2). This material has been characterized by densitometric separation, thermal expansivity, and Bacon Anisotropy Factor (BAF) (Ref. 2). Specimens of the material with two-phase filler were included in capsule GE-H-13-16 for irradiation at 1250 C to about 4.0×10^{21} n/sq cm.

4. CATALYTIC GRAPHITIZATION IN COKE AND BINDER-FILLER ARTIFACTS

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

This task is being conducted 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. The studies on titanium-doped pyrolytic carbons have been completed except for hardness measurements (see Section 8). Work on this task was curtailed due to the increased work load on the tasks outlined in Sections 5, 6, 7, and 9.

The first phase of this work consisted of a series of exploratory experiments where 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 in that large primary crystals were present when it was heated to 2800 C (Ref. 3). Additional experiments showed enhanced crystal growth in petroleum asphalt cokes that were doped with 2.5 and 5 wt-% aluminum and titanium, respectively (Ref. 3).

Large batches of the cokes were prepared and binder-filler artifacts were fabricated. The compacts were subjected to heat treatments at 1900, 2100, and 2300 C, and the development of the graphitic structure is being observed as a function of time. The initial data were reported previously (Ref. 4). Additional data are shown in Table 1 along with the previous data.

The weight loss of aluminum is temperature dependent and rapid in the range of 1900 to 2300 C. After heating for 3 hr at 2300 C, it appears that the metal may be near depletion; (metal content of the samples will be checked later). Sharp X-ray patterns were observed in the aluminum-bearing cokes, whereas those containing titanium showed less conversion to graphite.

TABLE 1
HEAT TREATMENT OF METAL-DOPED COMPACTS

Specimen No.	Component* (wt-%)			Heat Treatment		Lattice Parameter				Weight Loss (%)
						Graphite		Carbon		
	Coke	Al	Ti	Temp (C)	Time (hr)	L _c	C _O	L _c	C _O	
2317-133	100	--	--	1900	0.5	--	--	110	6.871	4.2
				2100	0.5	--	--	162	6.813	5.3
				2100	1.0	--	--	180	6.847	5.8
				2100	2.0	--	--	280	6.845	--
				2100	3.0	--	--	230	6.834	6.59†
				2300	0.5	--	--	270	6.755	6.0
				2300	1.5	--	--	260	6.794	--
				2300	3.0	--	--	280	6.784	6.83†
2317-134	80	20	--	1900	0.5	460	6.742	tr**	tr	7.6
				2100	0.5	535	6.720	--	--	25.9
				2100	1.0	460	6.742	134	6.816	30.3†
				2100	2.0	900	6.721	--	--	--
				2100	3.0	545	6.724	197	6.826	37.68†
				2300	0.5	770	6.716	--	--	34.5
				2300	1.5	1250	6.721	--	--	--
				2300	3.0	--	6.739	--	--	42.58†
2317-135	80	--	20	1900	0.5	tr	tr	96	6.858	9.5
				2100	0.5	††	tr	125	6.844	11.0
				2100	1.0	tr	tr	170	6.856	12.0
				2100	2.0	††	6.752	--	6.840	--
				2100	3.0	tr	tr	130	6.808	13.74†
				2300	0.5	tr	tr	180	6.770	12.0
				2300	1.5	††	6.720	150	6.805	--
				2300	3.0	tr	tr	193	6.747	13.8†
2317-136	70	10	20	1900	0.5	tr	tr	78	6.844	2.0
				2100	0.5	††	6.738	125	6.830	8.8
				2100	1.0	††	6.736	132	6.820	6.0
				2100	2.0	tr	tr	--	6.840	--
				2100	3.0	††	6.742	tr	6.858	16.99†
				2300	0.5	850	6.718	--	--	17.6
				2300	1.5	405	6.720	tr	6.810	--
				2300	3.0	††	6.740	tr	tr	22.39

*Wt-% in the asphalt.

†New specimens were used for these heat treatments.

**Indicates faint trace of graphite or carbon peak superimposed on major peak.

††Peak was visible and angle of 2θ could be established, but line breadth was not resolvable.

Heat treatment of the present series of samples will be continued with emphasis on the aluminum-containing specimens. Quantitative measurements of the conversion to graphitic structure will be attempted in the densitometric apparatus.

5. 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, physical properties, and irradiation behavior of graphite bodies that are prepared by a standardized molding process is under investigation. In this work, these materials are characterized in terms of selected physical properties and structural parameters, and this information is correlated with the results obtained after subjecting the specimens to high-temperature irradiation.

The specimens for the current studies were prepared with calcined needle coke and various amounts of pitch-binder coke in the range of 5.5 to 14.2 wt-%. A description of the specimens was given previously (Ref. 3). The specimens were irradiated in a series of capsules designated GE-H-13-13, GE-H-13-14, and GE-H-13-15 in the Engineering Test Reactor (ETR) at Idaho Falls, Idaho. Battelle Northwest Laboratory is conducting the irradiation capsule experiments, and the space is shared by Gulf General Atomic Incorporated 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, at 1250 C for an additional 3.85×10^{21} n/sq cm in capsule GE-H-13-14, and finally for another increment of 3.95×10^{21} n/sq cm, giving a total exposure of 9.70×10^{21} n/sq cm at 1225 to 1250 C.

The specimens continued to expand in the parallel direction (c-axis), reaching 20% for specimens of lowest binder-coke content. The expansion was lowest for a binder content of about 9 to 12 wt-%. In the perpendicular direction (a-axis) the specimens high in binder coke continued to contract while those of lowest binder coke ceased contraction and began expanding. The volume changes were highest for specimens deficient in binder coke.

Thermal expansivity in the c-axis direction continued to increase, correlating with the volume expansions. A value of $10 \times 10^{-6} \text{C}^{-1}$ was observed for a specimen with a low binder-coke level. This is an increase of a factor of 2.5 over the unirradiated value.

Density and porosity changes were measured as a function of neutron dose. The closed porosity (closed to a penetrating liquid during density measurement) varied with binder-coke content, increasing as binder coke increased. A portion of this porosity is believed to be associated with the binder coke since all filler particles were of a common origin. The filler-coke particles also contain some closed porosity. The closed porosity is reduced during the densification phase from 2 to 5×10^{21} n/sq cm and then increases again during the expansion phase above 5×10^{21} n/sq cm. This porosity may be accommodating the c-axis growth during irradiation at low doses. New porosity appears above 5×10^{21} n/sq cm after the original porosity has been saturated. Concurrently, the open porosity undergoes similar changes, again dependent on binder-coke content.

Another aspect of this work deals with the effect of crystallite size versus changes in the bulk dimensions of the graphites. In the current series, the filler coke for all specimens is from a common source and contains crystallites in a narrow range from 1000 to 1300 Å. Thus, the changes in the crystallites should be essentially constant for the filler portion of each specimen in the series. However, the volume changes are quite different, depending on binder-coke content. While the dimensional changes in model carbons and graphites have been shown to depend sensitively on crystallite size over a wide range of sizes (Ref. 5) under high-temperature irradiation, the changes in porous polycrystalline graphite do not appear to depend entirely on crystallite size but rather on crystallite size and morphology and density of the structure. Where the crystallite sizes vary over a relatively narrow range, which is the case for artificial graphites (300 to 1300 Å), other features of the microstructure such as orientation and porosity appear to be more important, and the changes cannot be predicted from crystallite data alone.

Filler particles, from which the pitch-coke series was prepared, have been irradiated concurrently with the molded specimens. Attempts are underway to measure the density changes of these particles to obtain data on an unrestrained filler particle. In this case changes will be due only to the restrictive forces of porosity and orientation within the particle.

6. DIMENSIONAL AND VOLUMETRIC CHANGES OF ANISOTROPIC AND NEAR-ISOTROPIC GRAPHITES

G. B. Engle and L. Bailey

A general relationship, which has been described and discussed previously (Ref. 3), 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 clusters of crystallites (obtained by the sink-float technique) and the changes in macroporosity and structural features are being measured on a series of anisotropic and near-isotropic graphites. Efforts have been concentrated on anisotropic graphite (CHN) and on a near-isotropic graphite (H-315-A).

Detailed descriptions of all graphites now included in this study, their physical and mechanical properties, and their structural parameters have been given elsewhere (Refs. 6, 7). Data have been reported previously (Ref. 3) for specimens irradiated in the range of 320 to 1490 C at 2.85×10^{21} n/sq cm.

The specimens in this series have now been taken to 11×10^{21} n/sq cm at 1250 C and 7×10^{21} n/sq cm at 1000 C. A few of the specimens of each graphite type are being reirradiated in capsule GE-H-13-16 at 1250 C to about 15×10^{21} n/sq cm.

The dimensional changes of the needle-coke graphites ranged from expansions of 6% to 19% in the c-axis direction and contractions of from 1% to 8% in the a-axis direction, whereas the near-isotropic graphites showed expansions of 2% to 4% and contractions of 1%, respectively. The data were similar at 1000 C, but the rate of change was slower. The a-axis direction of one of the needle-coke graphites (H-283) ceased to contract at 5 to 7×10^{21} n/sq cm at 1250 C and expansion progressed rapidly up to a dose of 11×10^{21} n/sq cm. The other needle-coke graphites showed turnaround in the a-axis direction, but at higher doses. The near isotropic graphites show expansion in both directions between 5 and 11×10^{21} n/sq cm. Thermal expansivity increased for the needle-coke graphites, whereas in the near-isotropic materials it decreased.

Density changes (measured by immersion in liquid, all open porosity penetrated) have been obtained on bulk samples and subsequently on ground particles of about 10 μm . The density of the bulk samples increased during the densification phase at low exposures and increased during the expansion phase. The mean density of the particles (which contain only about 1% to 1.5% porosity) decreased with dose. These data show that the expansion of the crystallites opens the microporosity among the crystallites and consumes the larger pores during the densification phase. When expansion begins, new cracks and pores appear in both the macro and micro domains. In one graphite (H-283), which has proceeded to an expansion of 19% in the c-axis direction, a contraction of 1% in the a-axis direction, and an expansion of 18% in volume, the microstructure had large cracks. The cracks appear to be located between the needle-coke particles where the binder coke would be expected to reside.

Two graphites (H-327*, a needle-coke graphite, and H-328, a near-isotropic material manufactured with Gilso-coke) are being irradiated at 1000 to 1100 C. The H-328 was manufactured as an 18-in.-diameter log and the H-327 as a 13-in.-diameter log. The H-328 graphite contracted 0.80% in the parallel direction and 0.96% in the perpendicular, whereas the H-327 contracted 2.40% in the parallel and 1.20% in the perpendicular after 3.5×10^{21} n/sq cm.

These materials are being reirradiated in capsule GE-H-13-16 to about 7 to 8 $\times 10^{21}$ n/sq cm.

*Previous irradiations were carried out under Contract AT(04-3)-633. Current irradiations are being conducted in capsules GE-H-13-15 and GE-H-13-16 at BNWL.

7. IRRADIATION EFFECTS ON HIGHLY ORIENTED CARBONS AND GRAPHITES

R. J. Price

The irradiation-induced dimensional and physical property changes in polycrystalline graphite are complex and difficult to interpret because the changes in the constituent crystallites are modified by intercrystalline interactions and the effects of porosity. Data necessary for interpreting and predicting irradiation effects in polycrystalline graphites may be obtained from experiments on highly oriented, single-phase carbons and graphites that are of various crystallite sizes and that are free from gross porosity. In particular, accurate estimates of the dimensional changes in constituent crystallites may be obtained from such materials without large extrapolations.

Samples of highly oriented carbons and graphites are being irradiated in the GE-H-13 series of capsules in cooperation with BNWL.* Two graphites, ATJ graphite hot-worked to 50% to 60% compressive strain at about 2700 C and massive pyrolytic carbon deposited at about 2200 C, are being irradiated at 800 and 1250 C. Samples were cut from these graphites at 0, 30, 60, and 90 deg to the symmetry axis. Samples cut parallel to the substrate plane of massive pyrolytic carbon annealed at 3300 C are also included. The apparent crystallite sizes (250 to 1600 A) span the range encountered in the components of polycrystalline nuclear graphites. The capsule currently under irradiation also includes similar samples of annealed massive pyrolytic carbon (with intermediate crystallite sizes) in the intervals not covered by the initial series. The data are being used to check theoretical predictions of the effect of orientation on bulk dimensional change and to provide reliable values for the crystallite dimensional changes. The crystallite dimensional changes are needed because an eventual aim of this work is the prediction of irradiation-induced dimensional changes in commercial polycrystalline graphites based on analysis of their constituent phases. The irradiation-induced changes in thermal expansivity, microstructure, and

*Work was formerly reported under Contract No. AT(04-3)-167, Project Agreement No. 17.

mechanical integrity of the samples are also being followed to provide basic data on the dependence of these changes on the structure of the material.

The data from capsules GE-H-13-13 and GE-H-13-14 were reported previously (Ref. 6). During the present reporting period, the "orientation" series of samples of hot-worked graphite, as-deposited massive pyrocarbon, and annealed massive pyrocarbon irradiated in capsule GE-H-13-15 were examined. The samples had been exposed to approximately 0.5 and 1.5×10^{21} n/sq cm (E greater than 0.18 MeV) at 750 to 800 C, and approximately 3.8 and 9.7×10^{22} n/sq cm (E greater than 0.18 MeV) at 1250 to 1290 C. The massive pyrocarbons were severely delaminated after the highest exposures at 1250 to 1290 C, but some were measurable and approximate dimensional changes could be obtained.

All samples showed continued expansion in the c-direction and contraction in the a-direction, with the rates of dimensional change increasing with decreasing crystallite size. The maximum c-direction expansions exceeded 120% true strain for the as-deposited massive pyrocarbon, and the maximum a-direction contractions were about 50% true strain in the same material. The true strains increased approximately linearly with neutron exposure with the exception of the previously irradiated hot-worked graphite, whose dimensional change over the last increment of exposure was significantly smaller than that of virgin material irradiated over the same increment.

Thermal expansion measurements were made on selected samples of irradiated material. The massive pyrocarbon samples showed little change on irradiation, but the CTE of the hot-worked graphite irradiated at 1250 to 1290 C continued to change during irradiation. Parallel to the hot-working axis, the CTE passed through a maximum of $19 \times 10^{-6} \text{C}^{-1}$ at 2×10^{21} n/sq cm, then showed a steady decrease with increasing exposure, finally reaching $7 \times 10^{-6} \text{C}^{-1}$ at approximately 9.7×10^{21} n/sq cm (E greater than 0.18 MeV). Perpendicular to the hot-working direction, the CTE showed a slow increase with increasing exposure.

Complete data will be included in a later report.

8. ANNEALING STUDIES OF IRRADIATED PYROLYTIC CARBON STRUCTURES

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F. J. Gagnon, J. M. Pontelandolfo, H. H. Evans, and K. Koyama

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. A series of successive isochronal 1-hr anneals was carried out on the irradiated pyrolytic carbons. The irradiated carbons include a laminar carbon, a high-density isotropic carbon, a low-density isotropic carbon, and an annealed laminar carbon with a large crystallite size. Details of the preirradiation treatment, irradiation conditions, as-irradiated structural properties, and description of the results of the annealing studies have been reported previously (Refs. 3, 4).

The properties measured were density, linear dimensions, layer spacing, apparent crystallite size, and electrical resistivity. Hardness measurements are now being made on samples from each anneal. These measurements will conclude the work on this task.

9. IRRADIATION-INDUCED CHANGES IN SINGLE-PHASE CARBONS AND GRAPHITES

J. C. Bokros, W. H. Ellis, F. J. Gagnon, and W. Bamford

The analysis of the results from the GE-H-13-15 irradiation experiment has been completed. Data for annealed pyrolytic carbon ($L_c = 1600$ A), natural graphite crystals ($L_c = \infty$), catalytically graphitized carbon ($L_c = 800$ A), and turbostratic carbons ($L_c = 50$ to 200 A) now extend to 10^{22} n/sq cm (E greater than 0.18 MeV) for irradiation temperatures in the range 500 to 1300 C. The crystallite changes in the c - and a -direction, respectively, caused by an exposure of 1×10^{22} n/sq cm at 1200 to 1300 C were $+3\%$ and -1% for the single crystals, $+50\%$ and -20% for the annealed pyrolytic graphite, $+115\%$ and -60% for the catalytically graphitized carbon, and $+800\%$ and -400% for the turbostratic carbon. The data for the single crystals offer hope that the dimensional behavior of commercial aggregates can be significantly improved if their crystalline perfection is substantially increased and they can be made isotropic.

The data for the anisotropic turbostratic carbons irradiated at 900 to 1250 C are plotted in Figs. 1a and 1b, respectively. The data depart substantially from the linear relation predicted by Bacon, and the deviations are most pronounced at 1250 C. The departure at irradiation temperatures near 900 C are thought to be caused by an acceleration of the crystallite dimensional change rate that is caused by the decrease in crystalline perfection that occurs during the irradiation. The degradation of the crystal structure is most pronounced for isotropic deposits since, in these structures, the interactions between crystallites are a maximum.

At irradiation temperatures near 1250 C the departures from linearity are even more pronounced than at 900 C. At these higher temperatures, changes in preferred orientation have been measured that are thought to contribute to the accelerations caused by the irradiation-induced deterioration of the crystal structure. The latter is less pronounced at 1250 C, as evidenced by the changes in L_c and thermal conductivity that were reported earlier (Ref. 4). At 1250 C,

(a)

(b)

Fig. 1. Length change $\ln \left(1 + \frac{\Delta \ell}{\ell} \right) \times 100$ plotted as a function of the corresponding preferred orientation parameter R_i : (a) for irradiations at approximately 900 C and (b) for irradiations at approximately 1250 C. The exposures are for $E > 0.18$ MeV neutrons

irradiation creep is more effective in relaxing intercrystalline stresses caused by incompatible dimensional changes that are induced in adjacent misaligned crystallites by neutron irradiation. These same hypotheses are in accord with the fact that the bulk expansion is more pronounced at 900 C (Fig. 2a) than at 1250 C (Fig. 2b).

The results that are available for isotropic carbon (BAF less than 1.1) with L_c values greater than 50 Å are presented in Fig. 3. In Fig. 3a, the bulk dimensional changes in the directions parallel and perpendicular to the deposition plane are plotted as a function of the original density. The curves are for constant neutron exposure and for irradiation temperatures near 900 C. The corresponding data for irradiation temperatures near 1000 C are plotted in Fig. 3b on a reduced scale. The curves for 4.6×10^{21} n/sq cm on Fig. 3a have been replotted on Fig. 3b for easy comparison. The magnitude of the dimensional changes and the anisotropy increases with increasing density. The dependence of the dimensional changes on the original density is strong, and catastrophic changes can occur for the high-density carbon deposits. It may be noted from Fig. 5 of Ref. 4 that the carbons with the highest density also have the largest L_c values and the degradation of the crystal structure is most pronounced for the carbons with the highest density. Again, the explanation may be that the crystallite interactions are most severe for the carbons with the highest density. In addition, however, it must be kept in mind that the residual anisotropy in these most isotropic carbons (BAF less than 1.1) has been found to correlate with the original density (see Figs. 11 and 12 of Ref. 8) and this may be an additional factor. Similar data for isotropic carbons irradiated at 1250 C are plotted in Fig. 4.

The data in Figs. 1 through 4 show that the simple phenomenological relationship that was established to describe the dimensional behavior of turbostratic carbon at low to moderate exposures (Eq. 10 of Ref. 9) is not valid at high exposures, especially at high irradiation temperatures. It is still useful to use a modified version of the simple phenomenological relation. The rate at which a bulk dimension of a carbon with an initial structure identified by L_c , R_i , and ρ_o changes in a neutron flux γ at a constant irradiation temperature T may still be thought of as a superposition of a shape change and a volume change:

$$\dot{\epsilon}_{\ell_i} = \dot{\epsilon}_c (\gamma, ST) \left[1 - \frac{3}{2} R_i (\gamma, ST) \right] - \frac{1}{3} \left[\frac{k_d (\rho_{th} - \rho_o) e^{-k_d \gamma}}{\rho_{th} - (\rho_{th} - \rho_o) e^{-k_d \gamma}} \right] + \dot{\epsilon}_v (\gamma, ST)$$

Fig. 2a. Plot of density vs neutron exposure ($E > 0.18$ MeV) at 900 to 1000 C

Fig. 2b. Plot of density vs neutron exposure ($E > 0.18$ MeV) at approximately 1250 C

Fig. 3. Length changes $\ln \left(1 + \frac{\Delta \rho}{\rho} \right) \times 100$ for nearly isotropic carbons (BAF less than 1.1) with L_c values between 50 and 200 Å plotted as a function of the original density: (a) for irradiations at approximately 900 C and (b) for irradiations at approximately 1000 C. The curve for 4.6×10^{21} n/sq cm from (a) has been replotted on (b) for easy comparison.

Fig. 4. Plots of $\ln\left(1 + \frac{\Delta\ell}{\ell}\right) \times 100$ versus the original density for nearly isotropic carbons (BAF < 1.1) with L_c values between 50 and 200 Å irradiated at ~1250 C. The exposures are for $E > 0.18$ MeV neutrons.

The first term, which represents the shape change, no longer depends only on the dose and two constants R_i and $\dot{\epsilon}_c$. Instead, $\dot{\epsilon}_o$, the crystallite c-direction growth rate, and the preferred orientation parameter R_i both become a function of γ and structure. In addition, an expansion term $\dot{\epsilon}_v$ become important at high exposures. The latter term must result from the accumulation of vacancies or vacancy clusters. These voids may be formed preferentially between crystallites and, hence, be an inherent manifestation of intercrystalline irradiation creep. The anisotropy of ϵ_v has not yet been established.

10. 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. S. Schwartz, "Effect of High Neutron Exposure on the Dimensions of Pyrolytic Carbon," to be published in Carbon (GA-8555).

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

Bokros, J. C., G. L. Guthrie, R. W. Dunlap, and A. S. Schwartz, "Radiation-Induced Dimensional Changes and Creep in Carbonaceous Materials," to be published in J. Nucl. Mater. (GA-8700).

Bokros, J. C., "The Structure and Properties of Pyrolytic Carbon," presented at the First International Conf. on Material Science-Ceramic Science and Technology, Tremezzo (Como) Italy, Sept. 1968, to be published in the Proceedings (GA-8888).

Bokros, J. C., "Fission Recoil Damage to Pyrolytic Carbon," submitted to J. Nucl. Mater. (GA-9054).

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