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Ceramics, and Materials

RESEARCH ON GRAPHITE

QUARTERLY PROGRESS REPORT
FOR THE PERIOD ENDING AUGUST 14, 1969

by

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

MASTER

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

August 27, 1969

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Gulf General Atomic Incorporated

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GA-5033 - Annual Report, April 1, 1963, through March 31, 1964 (Task II)
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-9433 - Annual Report, May 15, 1968, through May 14, 1969

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FIGURE

1. Transverse sections of irradiated specimens of an originally dense (2.0 g/cc), nearly isotropic (BAF = 1.1), granular carbon. The upper edge of the specimens in the micrographs is an intersection of the prepared section with the outer face of the specimen: (a) irradiated at 1000 C to 2×10^{21} n/sq cm ($E > 0.18$ MeV), polarized light, (b) irradiated at 1250 C to 10^{22} n/sq cm ($E > 0.18$ MeV), polarized light, and (c) same as (b) but taken with bright field illumination. 22

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1. INTRODUCTION

This program is being conducted to develop an understanding of the relationships between the properties, microstructure, and irradiation behavior of the various carbonaceous and graphitic materials required for use in high-temperature reactors of advanced design. The carbons and graphites of current interest in nuclear technology are composed of carbon in a wide variety of structures, ranging from nearly amorphous forms to highly crystalline states. The research efforts are directed toward defining the structure of the various materials, learning the relation between structure and the properties relevant to reactor applications, and evaluating methods for the preparation of new or modified structures with improved properties.

The research program for the period covered by this report (May 15, 1969, through August 14, 1969) consisted of two principal tasks: (1) investigations of the structures and properties of carbon and graphites, and (2) studies of the effects of irradiation on these structures and properties. The two types of materials under study are (1) graphitic bodies prepared from conventional binder and filler materials, and (2) pyrolytic carbons prepared by the decomposition of hydrocarbons in fluidized beds.

2. SUMMARY

CHARACTERIZATION OF THE DEGREE OF GRAPHITIZATION OF CARBONS AND GRAPHITES

Studies to determine the degree of graphitization in a number of moderator graphites were completed. Anisotropic graphites consist of small (up to 10 vol-%) semigraphitic regions coexisting with highly graphitic regions, whereas near-isotropic graphites are predominantly semigraphitic with smaller amounts of crystalline material that is highly aligned. Calcined petroleum cokes are under study to determine the effect of calcined density on crystalline growth.

CATALYTIC GRAPHITIZATION

Metallic additives are being studied as an aid to low-temperature graphitization of compacts fabricated with aluminum-doped petroleum coke. A series of compacts was fabricated and baked to 900 C to evaluate the effect of aluminum content on the ratio of graphite conversion at 2100 to 2300 C.

Microhardness measurements were completed on titanium-doped and titanium-free pyrocarbons annealed for 1 hr at 100 C temperature increments between their deposition temperature and 3000 C. The hardness decreased during annealing paralleling the crystal growth, as is shown by X-ray diffraction. This behavior is explained by the relation between the effective elastic modulus and the crystallite size in carbons.

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

The influence of the pitch-binder content on the microstructure and physical properties and irradiation behavior of needle-coke graphites is

under investigation. Additional density measurements on loose needle-coke particles and compacts show that crystallite clusters expand more rapidly during irradiation in the loose particles than in compacts where they are restrained by binder coke.

VOLUMETRIC CHANGES IN ANISOTROPIC AND NEAR-ISOTROPIC GRAPHITES

A series of anisotropic and near-isotropic graphites is being irradiated to 15×10^{21} n/sq cm at 1000 to 1250 C. Specimens are currently under irradiation at Battelle Northwest Laboratory (BNWL). A series of experiments was initiated to measure the thermal conductivity of selected samples from this series.

IRRADIATION EFFECTS IN HIGHLY ORIENTED CARBONS AND GRAPHITES

A series of samples of hot-worked graphite, as-deposited massive pyrocarbon, and annealed massive pyrocarbon is under irradiation at approximately 1250 C and approximately 800 C in capsule GE-H-13-16 at the Engineering Test Reactor (ETR). The samples are expected to be available for measurement in September 1969.

GRAPHITE IRRADIATION CREEP EXPERIMENT IN COOPERATION WITH THE DRAGON PROJECT

A joint experiment between the Dragon Project and Gulf General Atomic Incorporated to investigate graphite creep is in progress. The specimens are being examined at Dragon after receiving a dose of 2×10^{21} n/sq cm. No data are currently available.

ANNEALING STUDIES OF IRRADIATED PYROLYTIC CARBON STRUCTURES

Microhardness measurements were completed on samples of irradiated pyrocarbon annealed to temperatures at 100 C intervals between 400 and 3000 C. Annealing took place over the range of approximately 1400 to 2600 C.

The isochronal annealing curves were similar in shape to those observed previously for the dimensions and crystallographic parameters.

IRRADIATION EFFECTS IN CARBONS AND GRAPHITES

Irradiation-induced dimensional changes in a variety of pyrolytic carbons at 900 to 1000 C and at 1200 to 1300 C show that during the irradiation the rate at which the specimens change dimensions accelerates. The accelerations are most pronounced in dense, isotropic carbon and are accompanied by the generation of pores in the structure, which cause a volume expansion.

At 900 C, the accelerations are primarily caused by a degradation in crystal structure that enhances the instability of the crystallites. At the higher irradiation temperatures, increases in anisotropy contribute significantly to the accelerations. The volume expansions, the degradation of the crystal structure, and the changes in thermal conductivity are all less for irradiations above 1200 C than for irradiation at 1000 C. Micrographic evidence was obtained to show highly oriented regions in granular pyrocarbons coexisting with isotropic regions. These regions behaved quite differently during high-temperature irradiation to high doses, but this behavior did not cause disintegration of the pyrocarbon.

3. CHARACTERIZATION OF THE DEGREE OF GRAPHITIZATION OF CARBON AND GRAPHITE

G. B. Engle and L. Bailey

Studies to determine the degree of graphitization in carbons and graphites have been underway for the past 2 years. A densitometric technique (i.e., a sink-float method) is being used to separate the various carbon structures for subsequent identification by X-ray or microscopy techniques. A description of the apparatus and procedure has been reported elsewhere (Ref. 1).

A series of experiments extending over the past year in which a number of commercial moderator graphites were examined for density and structural distribution has been completed, and a report is being written to present the data. Many of the materials are under irradiation in capsule GE-H-13-16 at the ETR (see Section 6).

These studies showed that anisotropic porous artificial graphites consist of semigraphitic regions coexisting with highly graphitic regions. The transition of the structure from semigraphitic to highly graphitic was smooth and the apparent crystallite size was correlated with the apparent density of sink-float fractions from the various graphites. The near-isotropic graphites have semigraphitic structures that are more uniform in apparent crystallite size L_c than the anisotropic graphites. The mean apparent crystallite size $\bar{L}_c$ of the graphites showed a systematic correlation with the volume thermal expansivity of the samples. Materials that were nearly isotropic, such as Poco or Gilsonite graphites, had the highest thermal expansivities and the smallest apparent crystallite sizes and range of crystallite sizes.

The effort on this task has been shifted to a study of the ability of calcined petroleum cokes to graphitize. The recent studies described above indicated that artificial, anisotropic graphites, such as those made with needle-coke and coal-tar pitch, contain a wide range of carbon structure (L_c from 350 to 1600 Å). The current study with calcined cokes is being conducted to determine what structural inhomogeneity in manufactured graphite filler is caused by structural inhomogeneity in calcined coke.

Two dissimilar calcined cokes (both currently used for graphite production) are being separated into approximately 6 to 8 density fractions. Each density fraction will be heat treated through 3000 C, and structural changes will be determined as a function of the calcined density. Preliminary separations of the two cokes showed a median density of 2.09 g/cc vs 2.01 g/cc, with one of the cokes having a large volume of low-density structure.

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 are currently under irradiation in capsule GE-H-13-16 at 1250 C to about 4.0×10^{21} n/sq cm.

4. CATALYTIC GRAPHITIZATION

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.

LOW-TEMPERATURE GRAPHITIZATION OF COKES AND BINDER-FILLER COMPACTS

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

Recent work has been concentrated on the use of aluminum in combination with petroleum asphalt to produce cokes that graphitize at low temperatures. Aluminum is of particular interest because it not only promotes graphitization at low temperatures but also evolves from the coke during the reaction to leave a product that is low in metal content.

Compacts were prepared with the aluminum-doped coke in combination with a coal-tar pitch binder and were subjected to heat treatments at 1900, 2100, and 2300 C. The addition of metallic particles produced material with a considerable portion of graphitic structure.

The graphitic structure may result from carbon deposited because of dissociation of Al_4C_3 . If this is the case, aluminum may not be acting as a true catalytic agent, and large amounts of aluminum may be required to convert the carbon structure. Thus, it is necessary to determine the effect of metal content on the conversion ratio of the carbon structure in molded compacts. The experiment was initiated with the fabrication of several compacts of varying aluminum content. The specimens, along with a control compact, were baked to 900 C, and the

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metallic content is being determined. The specimens will be heat treated systematically in the range of 2100 to 2300 C, and the conversion to graphitic structure will be measured in the densitometer.

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

A series of isochronal anneals was performed on a laminar pyrolytic carbon containing 6.7 wt-% titanium and its undoped control carbon, both deposited at 1225 C, and on an isotropic pyrolytic carbon containing 9.7 wt-% titanium and its control carbon that were deposited at 2200 C. The response to annealing of the density, electrical resistivity, apparent crystallite size, and layer spacing was described in the last annual report (Ref. 2). During the current reporting period, microhardness measurements were made on samples set aside after each anneal. These measurements complete the experimental work in this area.

When graphite or carbon is indented in a conventional hardness test, the unusual elastic properties of the material cause the indentation to "spring back" when the load is removed. However, if the surface of the sample is covered by a thin film of a polymer or evaporated metal, an impression is left which shows the deepest penetration during the test. Thus, a measurement of this type gives an indication of the elastic modulus of the sample rather than a flow stress, which is determined in hardness measurements on metals. In the present work, samples of pyrocarbon suitable for microhardness measurements were set aside after each successive 1-hr anneal of 100 C temperature increments between the deposition temperature and 3000 C. The samples were mounted in metallographic mounts and shadowed with a thin layer of evaporated aluminum. Microhardness measurements were then performed, using a diamond indenter and a 15 g load, on all except the metal-free laminar carbon whose samples were too thin for a reliable hardness measurement.

The hardness of all the carbons showed a decrease during annealing that closely paralleled the change in apparent crystallite height and layer spacing reported previously (Ref. 2). The titanium-doped laminar carbon showed a steady decrease in hardness from DPH 200 at approximately 1500 C to DPH 50 at 2600 C, with no further decrease at higher temperatures. The undoped isotropic carbon deposited at 2200 C showed very little change in hardness, while the titanium-doped isotropic carbon showed a sharp drop from approximately DPH 70 at 2300 C to approximately DPH 35 at 2500 C. This is the temperature range where X-ray diffraction measurements show that catalytic graphitization takes place (Ref. 2). Full data will be included in a forthcoming topical report.

The X-ray diffraction results reported previously (Ref. 2). showed that the titanium-doped laminar carbon undergoes steady, uncatalyzed crystal growth at annealing temperatures between 1400 and 2800 C, whereas the titanium-doped isotropic carbon experiences catalytic recrystallization to graphite between 2300 C and 2500 C. The microhardness measurements followed the changes in crystallographic parameters. This relationship may be explained by the dependence of the apparent elastic modulus of carbons on the reversible anelastic strain contributed by the bowing of basal dislocations during stressing. Crystallite growth allows longer free lengths of dislocations between pinning points, which cause a lower effective elastic modulus. The lower modulus is reflected in the lower microhardness values.

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 pitch-binder content on the microstructure, physical properties, and irradiation behavior of graphite bodies prepared by a standardized molding process is under investigation. The objective of this work is to provide an understanding of the influence of the binder coke on the microstructure and irradiation behavior of conventional graphitic materials in terms of measureable 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 of 5.5 to 14.2 wt-%. 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 ETR at Idaho Falls, Idaho. Battelle Northwest Laboratory (BNWL) conducted the irradiation capsule experiments, and the space was shared jointly by Gulf General Atomic and BNWL. The specimens were irradiated at 1225 C to 1.9×10^{21} n/sq cm ($E > 0.18$ 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 and 3.95×10^{21} n/sq cm in capsule GE-H-13-15, giving a total exposure of 9.70×10^{21} n/sq cm at 1225 to 1250 C. The dimensional and property data were reported previously (Ref. 2).

A batch of needle-coke particles (300- to 350-micrometer particle size), samples from the same batch used for the compact preparation, was irradiated in capsule GE-H-13-15 to 3.9×10^{21} n/sq cm at 1250 C along with the graphite specimens. The density changes in these particles were measured by immersion in liquid before and after irradiation as whole particles and after comminution to less than 38 micrometers in an effort to determine the changes that occurred during the densification phase of the irradiation. The data were reported previously (Ref. 2).

Additional irradiated compacts have been comminuted and the density changes measured. The complete data are shown in Table 1. The solid structure (sink-float particles) of the graphite compacts containing 5.5 wt-% binder coke does not start to expand until the breakaway expansion of the bulk dimensions begins at a dose of about 6×10^{21} n/sq cm. However, the structural expansion of the loose needle-coke particles (the filler particles) begins immediately when there is no binder-coke present, i.e., when there is no restraint. It should be noted that the unrestrained coke particles actually densify if they are measured prior to comminution to a fine powder. By combining the data in Table 1 on coarse and fine particles it is evident that the crystallite clusters (sink-float particles) are expanding and the expansion is being absorbed by pores or cracks that are present in the coarse particles but eliminated during comminution. These data are consistent with the observations in the moderator graphites reported on previously (Ref. 2) where V_{p2} (closed porosity in a bulk sample) was eliminated during irradiation by absorbing c-axis expansions.

TABLE 1

DENSITY CHANGES IN NEEDLE-COKE GRAPHITES

Specimen Form	Particle Size		Exposure $\times 10^{-21}$ (n/sq cm)	Apparent Density (Immersion in liquid) (g/cc)
	Irradiated	Measured		
Particles	--	300-350	--	1.84
Particles	300-350	300-350	3.90	2.05
Particles	300-350	<38	--	2.22
Particles	300-350	<38	3.90	2.14
Compact 10-5	--	Compact	--	2.21
	Compact	Compact	3.70	2.21
	Compact	Compact	5.75	2.21
	Compact	Compact	9.70	2.17
	--	<38	--	2.22
	--	<38	3.70	2.21
	--	<38	9.70	2.16
Compact 50-7	--	Compact	--	2.19
	Compact	Compact	3.70	2.19
	Compact	Compact	5.75	2.20
	Compact	Compact	9.70	2.15
	--	<38	--	2.21

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

G. B. Engle, L. Bailey, J. Dixon, K. Koyama, and H. Evans

In this work the changes in dimensions, properties, microporosity, macroporosity, and structural features are being measured on a series of anisotropic and near-isotropic graphites. The graphites are described elsewhere (Ref. 2).

The specimens in this series have now been irradiated to 11×10^{21} n/sq cm at 1250 C and 7×10^{21} n/sq cm at 1000 C. The data were reported previously (Ref. 2). A few of the specimens of each graphite type are being reirradiated in capsule GE-H-13-16 in ETR at 1250 C to about 15×10^{21} n/sq cm.

A new series of graphites has been placed in capsule GE-H-13-16 to determine the effect of crystallite orientation, crystallite size, and original density on densification. This series included graphites that range from highly oriented materials made with natural flakes to extremely isotropic graphites such as Poco materials. The next discharge date for capsule GE-H-13-16 is scheduled for September 1969, after three cycles and a maximum exposure of about 3 to 4×10^{21} n/sq cm.

A series of experiments has been initiated to measure the thermal conductivity of a number of irradiated graphites. Specimens that were irradiated at high temperatures (625 to 1230 C) to high doses (2.9 to 7.8×10^{21} n/sq cm) were measured at room temperature. A number of the specimens are being annealed as a function of time in the range 1250 to 1700 C in an effort to gain information on the nature of the irradiation defects that cause degradation of the thermal conductivity. The initial data are shown in Table 2. The annealing experiments will be continued as a function of time.

TABLE 2
THERMAL CONDUCTIVITY OF GRAPHITES

Material	Specimen Number	Exposure $\times 10^{-21}$ n/sq cm	Temp (C)	Annealing		K [cal/(cm)(sec)(C)]	$1 - \frac{K}{K_0}$
				Time (min)	Temp (C)		
H-315-A ↓	--	--	--	--	--	0.355	0.00
	15-3	6.85	1015	--	--	0.096	0.73
	15-1	6.85	1015	--	--	0.105	0.70
	15-1	6.85	1015	5	1250	0.139	0.61
	15-2	6.85	1015	--	--	0.130	0.63
	15-2	6.85	1015	5	1400	0.160	0.55
	15-4	6.85	1015	--	--	0.120	0.66
	15-4	6.85	1015	5	1700	0.211	0.41
GHV ↓	--	--	--	--	--	0.300	0.00
	174-0	2.9	1000	--	--	0.063	0.79
	17-3	6.85	1005	--	--	0.121	0.60
	17-2	6.85	1005	--	--	0.092	0.69
	17-2	6.85	1005	5	1250	0.138	0.54
	17-1	6.85	1005	--	--	0.080	0.73
	17-1	6.85	1005	5	1400	0.155	0.52
	17-4	6.85	1005	--	--	0.075	0.75
	17-4	6.85	1005	5	1700	0.220	0.27
	166-3	4.7	1175	--	--	0.264	0.12
	166-2	4.7	1175	--	--	0.235	0.22
	166-1	4.7	1175	--	--	0.251	0.16
	169-5	7.7	1190	--	--	0.159	0.47
	169-5	7.7	1190	5	1250	0.179	0.40
	168-5	7.7	1190	--	--	0.111	0.63
	168-4	7.7	1190	--	--	0.158	0.47
	168-4	7.7	1190	5	1250	0.171	0.43
	169-4	7.7	1190	--	--	0.141	0.53
	169-1	7.7	1190	--	--	0.155	0.48
	169-1	7.7	1190	5	1400	0.179	0.40
	168-3	7.7	1190	--	--	0.165	0.45
	168-3	7.7	1190	5	1400	0.171	0.43
	168-1	7.7	1190	--	--	0.110	0.63
	168-2	7.7	1190	--	--	0.156	0.48
	168-2	7.7	1190	5	1700	0.175	0.42
	169-2	7.7	1190	--	--	0.131	0.67
	169-3	7.7	1190	--	--	0.145	0.52
	169-3	7.7	1190	5	1700	0.182	0.40
	55-3	7.8	1175-1230	--	--	0.173	0.42
	55-1	7.8	1175-1230	--	--	0.140	0.53
H-327 ↓	--	--	--	--	--	0.279	0.00
	195-2	2.30	625	--	--	0.068	0.76
	195-1	2.30	625	--	--	0.041	0.85
	195-0	2.30	625	--	--	0.065	0.77
	184-2	2.30	625	--	--	0.072	0.74
	184-1	2.30	625	--	--	0.074	0.73
	184-0	2.30	625	--	--	0.057	0.80
	197-2	5.20	910	--	--	0.126	0.55
	197-1	5.20	910	--	--	0.058	0.79
	197-0	5.20	910	--	--	0.075	0.73
	196-2	5.20	910	--	--	0.072	0.74
	196-1	5.20	910	--	--	0.078	0.72
	196-0	5.20	910	--	--	0.050	0.80
	171-3	5.25	1000	--	--	0.062	0.78
	171-2	5.25	1000	--	--	0.068	0.76
	171-0	5.25	1000	--	--	0.033	0.81
	171-0	5.25	1000	5	1250	0.075	0.73
	171-0	5.25	1000	10	1250	0.075	0.73
	171-0	5.25	1000	25	1250	0.088	0.69
	171-0	5.25	1000	90	1250	0.088	0.69
	171-0	5.25	1000	510	1250	0.093	0.67
	171-0	5.25	1000	900	1250	0.092	0.66
	171-1	5.25	1000	--	--	0.069	0.75
	171-1	5.25	1000	5	1400	0.135	0.52
	171-1	5.25	1000	10	1400	0.158	0.43
	171-1	5.25	1000	15	1400	0.185	0.34
	174-3	5.60	1000	--	--	0.063	0.77
	174-2	5.60	1000	--	--	0.157	0.44
	174-1	5.60	1000	--	--	0.151	0.46
	168-4	7.8	1090	--	--	0.091	0.67
	168-3	7.8	1090	--	--	0.073	0.74
	168-3	7.8	1090	5	1250	0.081	0.71
	168-2	7.8	1090	--	--	0.070	0.75
	168-2	7.8	1090	5	1400	0.102	0.63
	168-1	7.8	1090	--	--	0.065	0.77
	168-1	7.8	1090	5	1700	0.119	0.59

7. IRRADIATION EFFECTS ON HIGHLY ORIENTED CARBONS AND GRAPHITES

Data useful for interpreting and predicting irradiation effects in polycrystalline graphites may be obtained from experiments on highly oriented, single-phase carbons and graphites of various crystallite sizes that are free from gross porosity. Samples of such materials are being irradiated in the GE-H-13 series of capsules in cooperation with BNWL. The samples consist of hot-worked graphite, as-deposited massive pyrocarbons, and massive pyrocarbon annealed at various temperatures between 2900 and 3300 C. The apparent crystallite sizes of these materials cover the range encountered in polycrystalline nuclear graphites.

Results obtained up to June 1969 were described in the last annual report (Ref. 2). The current irradiation in capsule GE-H-13-16 is expected to provide an increment of fluence of $3 \text{ to } 4 \times 10^{21} \text{ n/sq cm}$ for a group of samples at 1250 C and approximately $0.5 \times 10^{21} \text{ n/sq cm}$ for a group of samples at 800 C.

8. GRAPHITE IRRADIATION CREEP EXPERIMENT IN COOPERATION WITH THE DRAGON
PROJECT

G. B. Engle and R. J. Price

A joint experiment between Gulf General Atomic and Dragon to measure the irradiation-induced creep in a number of nuclear graphites is in progress at Dragon. The irradiation phase of this experiment has been completed and the specimens are undergoing postirradiation measurements at Dragon and Reactor Centrum Nederland (RCN), Petten. No results have been received. See Ref. 2 for details of the experiment.

9. 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

Annealing studies are being carried out on a series of pyrolytic carbons irradiated between 540 and 1060 C to 1.5 to 2.4 n/sq cm. Details of the samples and the annealing-induced changes in density, dimensions, layer spacing, apparent crystallite size, and electrical resistivity were reported previously (Ref. 2). In the present reporting period, microhardness measurements were made on samples set aside after each successive anneal. These measurements complete the experimental work on the annealing studies.

The technique and interpretation of indentation hardness measurements on carbon specimens are outlined in Section 4 of this report. Hardness measurements on carbons are related to the apparent elastic modulus, which in turn is related to the mobility of basal dislocations during stressing. Therefore, the annealing behavior of the microhardness is interesting for both practical and theoretical reasons.

Hardness measurements were made on the irradiated samples after successive 1-hr anneals at 100 C intervals between 400 and 3000 C. The hardness decreased with increasing annealing temperature. The annealing curves were similar in shape to those obtained for other properties, such as dimensions, apparent crystallite height, and layer spacing (Ref. 2). There was no significant downward trend in hardness until a temperature of approximately 1400 C was reached. Above this temperature there was a steady downward trend in hardness, which finally leveled off above approximately 2600 C. There was very little difference in the shape of the curves for different carbon structures and irradiation conditions, although the actual hardness numbers were different. The full data will be given in a forthcoming topical report.

The similarity in the shape of the annealing curves for hardness and the other properties suggests that annealing of the same defects is responsible for all property changes. For reasons given previously (Ref. 2), the defects that anneal between approximately 1400 and 2700 C are believed to be mainly vacancy loops, which grow and collapse by the absorption of vacancies, first from the radiation-induced vacancy population and at higher temperature by self-annealing. It is reasonable that the vacancy loops would have an effect on the apparent elastic modulus, and hence the hardness, because they could act as pinning points for basal dislocations.

In previous work on the annealing of the irradiation-induced changes in Young's modulus in polycrystalline nuclear graphite irradiated at lower temperature (less than 350 C) (Ref. 3), it was found that the bulk of the irradiation-induced changes annealed out below approximately 1000 C. This was attributed to the annealing out of small interstitial loops that act as dislocation pins. No change in hardness at such low temperatures was observed in the present work. The probable factors responsible for the different behavior are the smaller crystallite sizes and higher irradiation temperatures in the present work. Even for the lowest temperatures (540 and 620 C), the size and spacing of interstitial clusters would approach the crystallite size of the pyrocarbons (Ref. 4), indicating that interstitial clusters would probably not be distributed homogeneously but would be associated with crystallite boundaries. Thus, the mobility of basal dislocations would be controlled by the crystallite boundary spacing rather than by interstitial loops, as in the case for highly crystalline graphite irradiated at lower temperatures.

10. IRRADIATION EFFECTS IN CARBONS AND GRAPHITES

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

DIMENSIONAL CHANGES IN PYROLYTIC CARBONS

A series of experiments to measure dimensional changes in pyrolytic carbons at high temperature and high doses was completed and the data reported in Ref. 5. A brief summary of the data is presented here.

Irradiation-induced dimensional changes in a variety of pyrolytic carbons at 900 to 1000 C and at 1200 to 1300 C show that during the irradiation the rate at which the specimens change dimensions accelerates. The accelerations are most pronounced in dense, isotropic carbon and are accompanied by the generation of pores in the structure, which causes a volume expansion.

The data obtained at the lower irradiation temperatures (approximately 900 C) suggest that the accelerations are primarily caused by a degradation in crystal structure that enhances the instability of the crystallites. At the higher irradiation temperatures, increases in anisotropy contribute significantly to the accelerations. The volume expansions, the degradation of the crystal structure, and changes in thermal conductivity are all less for irradiations above 1200 C than at 1000 C. These observations, together with the increases in anisotropy, are believed to be manifestations of the fact that the intercrystallite irradiation creep rate is substantially higher at irradiation temperatures above 1200 C than at 1000 C. High creep rates provide an effective mechanism that relaxes the stresses that are generated between adjacent, misaligned crystallites during irradiation.

MICROSCOPIC EXAMINATION OF IRRADIATED MODEL CARBONS

About a dozen specimens irradiated to 10^{22} n/sq cm ($E > 0.18$ MeV) at 1250 C have been examined by microscopy. The procedure is time consuming because the individual specimens are very radioactive (2 to 4 R at 1 in.).

The microstructural changes that were observed in specimens of a granular carbon that was irradiated provides pictorial evidence of the large neutron-induced changes in crystallite dimensions (Fig. 1). The microstructure of granular carbons is not homogeneous but is made up of localized regions of large growth cones in which the degree of preferred orientation is high. The coarse-grained, anisotropic regions are surrounded by more fine grained isotropic carbon (see Fig. 8b of Ref 7, and note that the growth features visible metallographically under polarized light in granular carbons are much larger than the crystallites of which they are comprised).

The micrographs shown in Fig. 1 are of transverse sections of irradiated, plate-shaped, granular specimens. Originally, the upper faces (seen as the upper edge of the specimens in Fig. 1) were flat. After an exposure of 2.4×10^{21} n/sq cm at 1000 C, the distortion of the anisotropic regions caused the ground face to become roughened (Fig. 1a). After an exposure of 10^{22} n/sq cm at 1250 C, the effect was marked (Fig. 1b). The localized, anisotropic regions literally grew out of the surface to form a high population of pinnacles protruding from the originally flat surface.

In spite of the large local strains that occurred, there is no visible evidence of cracking between growth features (Fig. 1c). The porosity responsible for the volume expansion is not resolved by optical microscopy and is likely to be associated with the individual crystallites.

M12325-4

(a)

(500x)

Fig. 1. Transverse sections of irradiated specimens of an originally dense (2.0 g/cc), nearly isotropic (BAF = 1.1), granular carbon. The upper edge of the specimens in the micrographs is an intersection of the prepared section with the outer face of the specimen: (a) irradiated at 1000 C to 2×10^{21} n/sq cm ($E > 0.18$ MeV), polarized light (sheet 1 of 2)

M31111-1

(b)

(500x)

M31111-3

(c)

(500x)

Fig. 1. Transverse sections of irradiated specimens of an originally dense (2.0 g/cc), nearly isotropic (BAF = 1.1), granular carbon. The upper edge of the specimens in the micrographs is an intersection of the prepared section with the outer face of the specimen: (b) irradiated at 1250 C to 10^{22} n/sq cm ($E > 0.18$ MeV), polarized light, and (c) same as (b) but taken with bright field illumination (sheet 2 of 2)

11. 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., "Fission Recoil Damage to Pyrolytic Carbon," accepted for publication in Carbon (GA-9054).

Bokros, J. C., and K. Koyama, "Interpretation of Dimensional Changes Caused in Pyrolytic Carbon by High Fluence Neutron Irradiation," submitted to Carbon (GA-9600).

Engle, G. B., W. H. Morris, and L. Bailey, "Apparatus and Procedure to Determine Density and Structural Distributions in Carbons and Graphites," submitted to Carbon as a Letter to the Editor (GA-9421).

Engle, G. B., Trip Report: "Libby/Cockcroft Graphite Physics Meeting, Euratom Graphite Meeting, and Visits to Other European Laboratories," July 2, 1969, unpublished data.

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