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RESEARCH ON GRAPHITE

ANNUAL REPORT

May 15, 1968, through May 14, 1969

by

G. B. Engle, J. C. Bokros, 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

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June 17, 1969

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Gulf General Atomic Incorporated

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I. INTRODUCTION

The objective of this program is 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 and thus to provide a basis for substantial improvements in the service behavior of these materials. 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, 1968, to May 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 progress during this period is described in this report in eight topical sections. In cases where topical reports have been prepared on completed work, only brief abstracts are given, and the reader is referred to the topical report for full details. A list of topical reports and publications resulting from work on this program during the reporting period is given in Section XI.

Two types of materials are under study: (1) graphitic bodies prepared from conventional binder and filler materials, and (2) pyrolytic carbons prepared by the decomposition of hydrocarbons in fluidized beds. The conventional graphites are either prepared in the laboratory in order to have full knowledge and control of the processing history or obtained from the major carbon and graphite companies. The pyrolytic carbons provide

model materials whose structures can be closely controlled through adjustment of the deposition and annealing conditions. The pyrolytic carbons are representative of various components of conventional graphites, as well as coatings for fuel particles.

The various structures of conventionally processed graphites as well as pyrolytic carbons are characterized by their crystallinity (X-ray diffraction parameters), preferred orientation, density, and microstructure. Work on pyrolytic carbons includes studies of the structural transitions produced by heat treatment, both with and without catalytic additives. The investigations of conventional graphites include micrographic studies of the structure and characterization of the degree of graphitization of carbonaceous and graphitic materials by densitometric separation.

The irradiation studies are focused on the behavior of carbons and graphites under the fast-neutron-flux and high-temperature conditions that are representative of the operating conditions of advanced reactor systems. The objectives are to define the changes in dimensions and other relevant properties as a function of structure and thus reveal the structures of greatest stability under irradiation. The irradiation experiments are conducted on materials of controlled and fully characterized structure; the principal properties of interest are dimensional changes, mechanical properties, irradiation creep, and thermal properties.

For reasons of economy, the irradiation experiments have been conducted in irradiation capsules operated in conjunction with other programs, e.g., the HTGR Base Program [Contract AT(04-3)-167, Project Agreement No. 17] and the Public Service Company of Colorado program [Contract AT(04-3)-633]. Close liaison has been maintained with other organizations, and cooperative irradiations have also been arranged with the Battelle Pacific Northwest Laboratories, the Dragon Project, and the Oak Ridge National Laboratory. The engineering capsules used for the majority of the work are fully instrumented, and adequate space has

been available without disturbing the engineering experiments. These irradiations have been conducted with the cooperation of a number of individuals; special acknowledgment is made to A. L. Pitner and R. E. Nightingale of the Pacific Northwest Laboratories, E. Voice, M. Everett, and L. W. Graham of the Dragon Project, and R. J. Grenda of Gulf General Atomic Incorporated.

II. SUMMARY

DENSITY AND STRUCTURAL DISTRIBUTIONS IN POROUS ARTIFICIAL GRAPHITES

A densitometric (sink-float) technique, which differentiates the particles of a powdered sample in terms of their apparent densities, has been adapted and developed for the purpose of characterizing artificial graphites. This apparatus has been used during this report period primarily to determine the structural and density distributions of various commercial graphites that were irradiated to high temperatures and high doses. These measurements combined with apparent density measurements on bulk samples provide quantitative information on the various domains of microporosity that exist in the various materials. The median densities of the graphites vary depending on the coke source and manufacturing procedures, and the density distribution of the particles varies depending on the material.

The needle-coke graphites and a raw-coke material consist of crystallites that vary in size; the crystallite size increases with increasing apparent density. The near-isotropic Gilsonite graphites are composed of a rather narrow range of crystallites of intermediate size.

The particles for the anisotropic needle-coke graphites extend over a density range of 1.50 to 2.26 g/cc and an L_c range of 350 to 1600 Å. Although the microporosity varied throughout the specimens of Gilsonite materials, the crystallite size fell in a narrow range from about 450 to 550 Å.

Metallographic examinations of sink-float particles collected from the various graphites revealed that the low-density (~ 1.70 g/cc) particles of the anisotropic needle-coke materials were predominantly equiaxed, while those of highest density (~ 2.24 g/cc) were predominantly needle-shaped. The low-density sink-float particles had L_c values of about 400 Å, whereas the high-density particles were in the range 1300 to 1600 Å.

An experimental material was prepared in the laboratory for use in the characterization studies. The final artifact consisted of a two-component filler, each component having a different density and crystallite size, plus a third component from the binder and impregnant. A quantitative record of each carbon component was obtained during the fabrication. This material has been characterized in the densitometric column and by other techniques, and its irradiation behavior is under study at 1250 C. Correlations will be made between fabrication history and physical properties.

CATALYTIC GRAPHITIZATION

A series of isochronal anneals at temperatures increasing by 100 C increments up to 3000 C was completed for a low-temperature laminar pyrolytic carbon containing 6.7 wt-% titanium, a high-temperature isotropic pyrolytic carbon containing 9.7 wt-% titanium, and their metal-free controls. The metal-doped laminar carbon behaved similarly to its metal-free companion, except for a density decrease due to titanium evaporation, which took place between 2400 and 2800 C. In contrast, at 2300 C the metal-doped isotropic carbon started to recrystallize heterogeneously to graphite. During subsequent anneals the amount of graphitic phase increased at the expense of the carbon phase, but the layer spacing and crystallite size of the graphite remained unchanged.

The effect of metal additives on the low-temperature graphitization of petroleum cokes has been under investigation. Aluminum- or titanium-doped asphalts showed evidence of graphitic structure when heated to 1700 to 2300 C. These cokes would not graphitize in the absence of the metals.

Compacts were prepared with these cokes and coal tar pitch and were examined by X-ray and microscopic techniques after heat treatment. The titanium-doped compacts showed a sharp peak superimposed on the broad carbon curves, but with aluminum the transformation from carbon to

graphite was accompanied by a gradual shift in the position and shape of the curves. The titanium reaction was interpreted as a heterogeneous process, whereas that with the aluminum was homogeneous.

Microstructural and physical property measurements made on a compact containing 20 wt-% aluminum in the asphalt showed conversion to graphite. Densitometric separation followed by X-ray examination of the fractions revealed 70% of the structure equivalent to natural-flake graphite and 30% equivalent to needle-coke graphite.

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

A series of molded specimens was prepared with calcined coke and various levels of pitch-binder coke in the range 5.5 to 14.2 wt-%. The specimens were irradiated to 9.7×10^{21} n/sq cm ($E > 0.18$ MeV) at 1225 to 1250 C.

The dimensional changes of the specimens were sensitive to the microstructural differences due to differences in the binder-coke content. Material that was low in binder content (5.5 wt-%) expanded considerably more at all doses, while that of intermediate content (7 to 9 wt-%) showed better stability. Thermal expansivity changes followed the same pattern as the volume changes, showing large increases by a factor of two or more for the lowest binder-coke content.

Crystallite clusters (sink-float particles) in loose particles of needle coke, from the same raw material batch that was used for the compacts, irradiated to 3.9×10^{21} n/sq cm at 1250 C, expanded at a higher rate than those in the compacts when irradiated to 3.9×10^{21} n/sq cm at 1250 C.

The results indicate that the presence of unyielding binder-coke bridges inhibits the expansion of the particles. Stresses are induced at the junction of the particles and binder-coke that can be relieved to some extent by creep. However, when the stresses exceed the strength

of the bonds, they separate and growth within the grist particles proceeds unrestrained causing a gross expansion of the bulk material.

VOLUMETRIC CHANGES IN ANISOTROPIC AND NEAR-ISOTROPIC GRAPHITES

Commercial graphites that differ widely in microstructure, crystallite orientation and size, porosity, and properties have now been irradiated at 950 to 1250 C to doses of 7 to 11×10^{21} n/sq cm ($E > 0.18$ MeV). The additional data obtained this year have been added to the previous data to obtain complete curves as a function of dose. The graphites, obtained from the major United States carbon companies, were of three types: (1) anisotropic materials prepared with needle-coke particles and upgraded in strength and density by multiple impregnations, (2) a near-isotropic material prepared with Gilsonite coke, and (3) a near-isotropic material prepared with raw petroleum coke. Changes in dimensions, thermal expansivity, apparent density, distribution of apparent density, and microstructure were investigated.

The curves of volumetric change were similar in shape for all graphites, i.e., initial contraction at low doses followed by expansion with increasing dose. The high alignment of the crystallites in the needle-coke materials was reflected in a high degree of anisotropy in their dimensional changes. The near-isotropic materials also exhibited a significant degree of anisotropy, but less than that of the needle-coke materials. In the direction of preferred c-axis alignment, the needle-coke graphites showed maximum contraction strains of about 1 to 1.5% at 5 to 6×10^{21} n/sq cm followed by expansions of 6 to 19% at 10^{22} n/sq cm. In the a-axis direction, maximum contraction strains of about 8% were observed. In the a-axis direction the irradiation-induced strains were beginning to saturate at 10^{22} n/sq cm. A needle-coke graphite, formed under pneumatic pressure during baking, was an exception. It had a contraction in the a-axis direction of only 4% at 5 to 6×10^{21} n/sq cm followed by a rapid expansion of 4%, making a net volume change of zero at 11×10^{21} n/sq cm. The maximum contraction of the near-isotropic graphites ranged from 1.5 to

3.5% for both directions followed by expansion to give net changes of -1 to +3%. The anisotropy of their dimensional change increased with increasing dose. The dimensional changes were similar at 950 to 1015 C.

The thermal expansivity of the needle-coke graphites did not change significantly with dose. An exception was the material prepared under pneumatic pressure during baking. It showed a significant increase, by a factor of 2, when irradiated at 1175 to 1250 C, which coincided with its large expansion in the c-axis direction above 5×10^{21} n/sq cm. Conversely, the expansivity of the near-isotropic materials remained unchanged at low doses followed by a sharp decline, by a factor of about 2, above 5×10^{21} n/sq cm.

Apparent density changes, measured by immersion of solid samples in a liquid, increased at low doses coinciding with volumetric densification of the bulk and then decreased during the expansion phase. The densities ranged from 2.04 g/cc, unirradiated, to 2.10 to 2.13 g/cc at 5×10^{21} n/sq cm and about 2.04 g/cc at 11×10^{21} n/sq cm.

The density distribution of unirradiated and irradiated graphites was measured. Upon irradiation* it appeared that a portion of the particles (believed to be the lighter fractions) first densified at low doses and then expanded, while those in intermediate and highest density fractions showed only expansion. The distribution of the apparent density changed as a function of dose.

The sink-float particles were considered as small volumetric increments within the solid sample. Each particle consisted of crystallites plus intercrystalline microporosity. The volumetric expansion of these particles represented the volume expansion of the crystallites reduced by any restraints due to crystallite misalignment and microporosity within the particles. Expansion of the sink-float particles in the

*The graphites were irradiated as solid samples and comminuted for density measurements.

c-axis direction is accommodated by microporosity which is present in the sample but is external to the sink-float particles. The volumetric changes of the sink-float particles combined with other changes in microporosity of the bulk sample represent an upper limit for the contribution of the crystallite changes to the bulk volume changes. An equation is presented that relates the bulk volume changes to the crystallite and porosity changes.

All materials show significant crack formation after expansion at 1175 to 1250 C to 10^{22} n/sq cm, but in graphites CHN and H-283 (the anisotropic needle-coke materials), and especially in H-283, it appears to be more severe than in the near-isotropic materials.

Two graphites, H-327, a needle-coke graphite, and H-328, a near-isotropic graphite manufactured with Gilsonite coke, were irradiated in Capsules GE-H-13-14 and -15 at Battelle Northwest Laboratories at 1000 to 1100 C to about 7 to 8×10^{21} n/sq cm. The H-328 was manufactured by molding as an 18-in.-diameter log, and the H-327 was extruded as a 13-in.-diameter log. The H-328 graphite contracted 0.80% in the longitudinal direction and 0.96% radially, whereas the H-327 contracted 2.40% longitudinally and 1.20% radially after irradiation to 3.5×10^{21} n/sq cm.

IRRADIATION EFFECTS ON HIGHLY ORIENTED CARBONS AND GRAPHITES

Samples of hot-worked graphite, as-deposited massive pyrolytic carbon, and massive pyrolytic carbon annealed at 3300 C have been irradiated at 750 to 800 C to a total exposure of 1.5×10^{21} n/sq cm ($E > 0.18$ MeV) and at 1225 to 1290 C to 9.7×10^{21} n/sq cm ($E > 0.18$ MeV). Plots of crystallite dimensional change as a function of exposure were obtained for each material and temperature. All materials showed c-axis expansion and a-axis contraction whose magnitude increased approximately linearly with exposure, with the dimensional change rates increasing with decreasing crystallinity. For irradiation at 1225 to 1290 C the thermal expansivity of the samples was changed. In the principal c-direction, the expansivity of the hot-worked graphite first increased

then passed through a maximum, and finally decreased to about half its initial value. In the corresponding direction, as-deposited massive pyrolytic carbon showed a rise but no subsequent decrease. At 1225 to 1290 C the massive pyrolytic carbon developed macroscopic delamination cracks when irradiated beyond $\sim 4 \times 10^{21}$ n/sq cm. The annealed pyrolytic carbon developed fine microcracks ~ 10 μ m long. The microstructure of the hot-worked graphite was not visibly changed.

GRAPHITE IRRADIATION CREEP EXPERIMENT IN COOPERATION WITH THE DRAGON PROJECT

An experiment to measure irradiation-induced creep in a number of nuclear graphites is in progress. The experiment was designed to restrain the specimens in tension by the use of graphites that shrink at a lower rate or expand. Comparison of the dimensional changes with unrestrained samples irradiated concurrently provides a basis for determining the induced creep. The specimens were irradiated in the Dragon Reactor during the past 3 years and were recently discharged after a dose of 1.5 to 2.0×10^{21} n/sq cm ($E > 0.18$ MeV) in the range 850 to 1100 C. Postirradiation examination of the specimens for changes in dimension, thermal expansivity, Young's modulus, and creep constants is in progress.

ANNEALING STUDIES OF IRRADIATED PYROLYTIC CARBON STRUCTURES

Isochronal anneals were carried out at 100 C increments of temperature between 400 and 3000 C on a variety of neutron-irradiated pyrolytic carbons. Recovery of most irradiation-induced property changes started at ~ 1400 C. The rate of change of most properties increased with increasing temperature, passed through a maximum at ~ 2300 C, and decreased thereafter. Annealing-induced changes in a laminar carbon were largely independent of irradiation conditions and could be attributed to annealing of the as-deposited structure. In the remainder of the carbons, the recovery depended on the irradiation conditions. For samples irradiated at 900 to 1050 C, only $\sim 1/4$ to $1/2$ of the irradiation-induced dimensional change was recovered. For property changes attributable to the rearrangement of irradiation-induced vacancy clusters, the spectra

of apparent activation energies were calculated. The lowest activation energy was 5 to 5.5 eV, and the peaks of the distributions occurred at about 8.5 eV. It is suggested that the first value corresponds to the annealing of loops in the presence of a supersaturation of vacancies, and the second value to the annealing of loops by self diffusion. The thermal diffusivity of several irradiated pyrolytic carbons was measured between room temperature and 800 C, both with and without postirradiation annealing to 3000 C. Postirradiation annealing increased the conductivity by a factor of 1.5 to 3 over the irradiated levels. The diffusivities showed a strong negative temperature dependence similar to that of crystalline graphite, but the absolute values were lower by a factor of ~ 10 than for crystalline graphite.

IRRADIATION EFFECTS IN CARBONS AND GRAPHITES

A variety of model materials has been irradiated at temperatures in the range 600 to 1300 C to fluences in excess of 10^{22} n/sq cm ($E > 0.18$ MeV). The materials irradiated included natural graphite crystals ($L_c > 2000 \text{ \AA}$), annealed pyrolytic carbon ($L_c = 1600 \text{ \AA}$), catalytically graphitized carbon ($L_c = 800 \text{ \AA}$), and turbostratic carbons ($L_c = 25$ to $200 \text{ \AA}$). The data show that the irradiation-induced changes in crystallite dimensions for dense materials are slightly dependent on crystallite size at irradiation temperatures near 600 C, but are strongly dependent on crystallite size at temperatures above 1000 C. For example, at 1250 C and 1×10^{22} n/sq cm the c-direction growth was +3% for the natural crystals, +50% for the annealed pyrolytic graphite, +120% for the catalytically graphitized material, and +800% for turbostratic carbon.

The data that describe the dimensional behavior of dense, anisotropic, turbostratic carbons at irradiation temperatures of 900 and 1250 C show that the changes are linear functions of the preferred orientation parameter, R , at low exposures, but at high fluences the departures from linearity are substantial. At 1250 C, it has been established that the sigmoidal shape is due, at least in part, to irradiation-induced increases in anisotropy. At 900 C, however, changes in anisotropy have not been detected to fluences of about 5×10^{21} n/sq cm.

Since it is not likely that the crystallite averaging methods are invalid at high exposures, other explanations of the behavior at high exposures are being sought. If the crystallite changes in each sample are derived from Bacon extrapolations and plotted as a function of exposure, one finds that the crystallite c-axis growth rate for crystallites in anisotropic carbons is nearly linear. There is a slight acceleration in the rate at high exposures. In contrast, the c-axis growth rate for crystallites in dense, nearly isotropic samples (R_1 near 2/3) accelerates rapidly with exposure without changes in preferred orientation. These observations may be rationalized by noting that the crystal structure is degraded by the irradiation, i.e., L_c is decreased, so that the autocatalytic acceleration is to be expected. Since a great part of the structural degradation must be due to the interaction between adjacent, distorting crystallites, the degradation, and hence the acceleration, is expected to be most pronounced for the more isotropic, dense carbons. This is because the crystallite interactions are most severe for the dense, random materials.

Analysis of the data for irradiation at 1250 C using the same procedure described above leads to similar conclusions but with two specific differences. First, at 1250 C, the rate at which the crystalline structure is degraded by the irradiation is less than the corresponding rate at 900 C. This is likely due to the fact that irradiation creep at boundaries between adjacent crystallites is higher at 1250 C than at 900 C and is effective in reducing internal stresses. The second difference is that the acceleration of the crystallite c-axis growth rate in nearly isotropic, dense carbons is more pronounced at 1250 C than at 900 C. The rate obtained from the extrapolation, in fact, exceeds the value for the case in which all the interstitials generated end up at interlayer sites that cause c-axis growth. Since this is impossible, the explanation must be that the anisotropy is increased by the irradiations at temperatures above about 1000 C.

Observations of increases in anisotropy and less degradation of the crystal structure at 1250 C than at 900 C are likely both related to the more effective irradiation creep at crystallite boundaries at the higher irradiation temperature. The suggestion is that intercrystalline creep is pronounced at 1250 C and that it is this process which causes the observed increases in anisotropy. Furthermore, this same process is likely to relax internal stresses between crystallites and prevent the same degree of structural degradation at 1250 C that is observed to occur during irradiation at 900 C.

The results that are available for isotropic carbon ($\text{BAF} < 1.1$) with L_c values greater than $50 \text{ \AA}$ indicate that the dimensional changes and the anisotropy of the changes increase 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. The rationalization of these data follows the same lines as given above; i.e., the crystallite interactions are most severe for the carbons with the highest density.

III. DENSITY AND STRUCTURAL DISTRIBUTIONS IN POROUS ARTIFICIAL GRAPHITES

G. B. Engle and L. Bailey

The simultaneous coexistence of various structural states of carbon in conventional binder-filler artifacts has been established. However, a quantitative characterization of such materials in terms of the relative amounts of the various structural components has proven difficult.

The existence of different structural states of carbon in artificial graphite has been demonstrated by the micrographic studies of Hales and Woodruff (Ref. 1). The work of Loch et al. (Ref. 2) has also shown that even highly graphitic materials are inhomogeneous and contain on the order of 10% low-density components, which were found to have the structure of disorganized carbon. These facts may be critically important to an understanding of the behavior of conventional graphite artifacts in reactor applications because irradiation studies of various types of carbon structures indicate that the dimensional effects can be markedly different from those in the fully graphitic structure (Refs. 3-5). Yoshikawa (Ref. 6) has shown that carbon bodies consisting of disorganized carbon structure will contract more than crystalline graphites when irradiated at 600 C, and more recent data (Ref. 7) indicate that contraction of these types of carbon structures is also high during irradiation at 900 to 1500 C.

Chemical techniques, based on differences in reaction rates (Refs. 8 and 9), have been used to quantitatively differentiate the various structural states of carbon in conventional graphite materials. However, the most highly graphitic structures are generally the most chemically reactive, and, therefore, the chemical methods have been less attractive for determining the various amounts of carbon structures.

The aim of the present work is to characterize the degree of graphitization of conventional graphitic artifacts, primarily in terms of the various structural states of the carbon components, and the microporosity associated with the crystallites, and to use this information to better understand the irradiation behavior of these materials.

A densitometric (sink-float) technique, which differentiates the particles of a powdered sample in terms of their apparent densities, has been adapted and developed for the purpose of characterizing artificial graphites. The apparatus and procedure for separating the graphite and carbon powders has been described elsewhere (Ref. 10). This apparatus has been used during this report period primarily to determine the structural and density distribution of various commercial graphites that are reported in the irradiation studies in Section VI. During the past year the various graphites that are under irradiation have been carefully remeasured in the unirradiated conditions, and numerous specimens have been measured subsequent to irradiation at 950 to 1250 C. These measurements provide a detailed account of the volume changes of small crystallite clusters plus their associated microporosity, believed to result from mismatches in crystallite stacking during coking and graphitization. The crystallite structure and orientation determine the volume of microporosity that surrounds the crystallite and allow for a quantitative determination of the structural gradient by densitometric separation. These measurements combined with apparent density measurements on bulk samples provide quantitative information on the various domains of microporosity that exist in the various materials (see Section VI).

The data obtained to characterize the graphites by the densitometric technique are summarized in this section; these data provide the basis for the analytical treatment of the microstructures that is given in Section VI.

DENSITOMETRIC STUDIES

Specimens of CHN, NC-8, H-283, 711-TS-N (needle-coke graphites), H-315-A and H-207-85 (Gilsonite graphites), and H-319, a material fabricated with raw petroleum coke, were ground to pass a 400-mesh screen ($< 38 \mu$). The powders were separated in the sink-float apparatus (Ref. 10). The densitometric curves are shown in Fig. 1.

The average density of the sink-float particles was plotted as a function of their distribution throughout the total volume of the specimen. There are two significant features of these curves: (1) the median density of the graphites varies depending on the coke source and manufacturing procedures, and (2) the distribution of the particles varies from material to material. Certain of the graphites consist of particles that lie in a narrow density range, whereas others are distributed over a wide range.

X-RAY STUDIES

The powdered density fractions collected from the densitometric column were examined by standard X-ray diffraction techniques to determine their crystallite sizes. The results are shown in Fig. 2. The needle-coke graphites and the raw-coke material consist of crystallites that vary in size; the crystallite size increases with increasing apparent density. The near-isotropic Gilsonite graphites are composed of a rather narrow range of crystallites of intermediate size.

The particles for the anisotropic needle-coke graphites extend over a density range of 1.50 to 2.26 g/cc and an L_c range of 350 to 1600 Å. Although the microporosity varied throughout the specimens of Gilsonite materials, the crystallite size fell in a narrow range from about 450 to 550 Å. These data suggest that the volume of microporosity associated with the crystallites is independent of the crystallite sizes in materials prepared with Gilsonite coke.

Fig. 1. Densitometric separations of graphites

Fig. 2. Apparent crystallite size (L_c) as a function of apparent density

Fig. 2 (continued). Apparent crystallite size (L_c) as a function of apparent density

Fig. 2 (continued). Apparent crystallite size (L_c) as a function of apparent density

Metallographic examinations on sink-float particles collected from the various graphites revealed that the low density (~ 1.70 g/cc) particles of the anisotropic needle-coke materials are predominantly equiaxed, while those of highest density (~ 2.24 g/cc) were predominantly needle-shaped. The low-density sink-float particles had L_c values of about $400 \text{ \AA}$, whereas the high-density particles were in the range 1300 to $1600 \text{ \AA}$. The intermediate particles showed a continuous gradation in particle shape from low-density to high-density, as well as a continuous gradation to higher L_c values (see Fig. 3).

Combining the various density measurements gives a quantitative description of the microstructure of the various graphites with respect to structure and microporosity. The description of the microstructure is given in Section VI, along with the irradiation discussion on these graphites. Other measurements of structural characterization such as pore volumes, thermal expansivity, apparent crystallite size and orientation, and lattice parameters C_o and L_c are also tabulated in Section VI.

MULTICOMPONENT MATERIAL

An experimental material was prepared in the laboratory for use in the characterization studies. The final artifact consisted of a two-component filler, each component having a different density and crystallite size, plus the residue coke from the binder and impregnant. This material has been characterized in the densitometric column and by other techniques, and its irradiation behavior is under study in Capsule GE-H-13-16 at 1250 C.

FABRICATION

A filler coke was prepared by coating calcined needle-coke particles with a low-density pyrolytic carbon at 1375 to 1400 C with CH_4 (about 1.70 g/cc and L_c of $40 \text{ \AA}$). 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-filler artifact by warm-pressing at 800 C and 5400 psi. The resulting binder-filler artifacts had a density of

M29796-1

500X

$$(a) \quad \begin{aligned} \rho &= 1.70 \text{ g/cc} \\ L_c &= 435 \text{ \AA} \end{aligned}$$

M30350-1

500X

$$(b) \quad \begin{aligned} \rho &= 2.05 \text{ g/cc} \\ L_c &= 640 \text{ \AA} \end{aligned}$$

Fig. 3. Photomicrographs of sink-float particles separated in graphite 711-TS-N

M30351-1

500X

$$(c) \quad \rho = 2.17 \text{ g/cc}$$

$$L_c = 1000 \text{ \AA}$$

M29797-1

500X

$$(d) \quad \rho = 2.24 \text{ g/cc}$$

$$L_c = 1350 \text{ \AA}$$

Fig. 3 (continued). Photomicrographs of sink-float particles separated in graphite 711-TS-N

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 1).

CHARACTERIZATION

This material has been characterized in the densitometric column, by thermal expansivity, and by BAF. Additional densitometric curves were obtained on each of the component carbon species (see Table 1). Correlations will be sought between the characterization parameters and properties, fabrication history, and the irradiation behavior.

TABLE 1

RAW MATERIALS AND PROPERTIES FOR SPECIMEN 2317-108-6

Components (wt-%)		
Filler Coke		Binder and Impregnant Coke
Pyrolytic Carbon	Needle Coke	
34.5	53	12.5

Density (g/cc)					Thermal Expansivity $\alpha \times 10^6, \text{C}^{-1}$ at 400 C		BAF
Compact (2317-108-6)		Powder (Sink-Float Median)					
Bulk	Sink-Float Median	Pyrolytic Carbon - Needle Coke	Needle Coke	Pyrolytic Carbon	Parallel	Perpendicular	
1.59	1.91	1.84	2.22	1.70	5.62 5.21	3.37 3.20	1.35

IV. CATALYTIC GRAPHITIZATION

Metallic catalysts have been reported in the literature to enhance crystallization in pyrolytic carbons and in porous graphites prepared with petroleum coke and pitch (Refs. 11-14). Small amounts of titanium enhanced the graphitization of pyrolytic carbon at temperatures below 2500 C and produced materials with relatively large crystallite sizes (L_c of about 800 Å). This material showed more dimensional stability than pyrolytic carbons prepared without titanium when irradiated above 600 C (Ref. 11).

The above work has been extended to the preparation of petroleum cokes with metal catalysts to explore the possibility of obtaining enhanced graphitization in binder-filler artifacts and thus improve their high-temperature irradiation stability. Previous work (Ref. 15) has shown that titanium, zirconium, or aluminum and titanium in combination promote crystal growth at temperatures of 2300 C or above. Zirconium carbide also promoted graphitization when admixed with calcined coke and a pitch binder during fabrication. Foster *et al.* (Ref. 16) have produced large graphite crystals by the decomposition of Al_4C_3 . Davidson *et al.* (Ref. 17) found a highly isotropic material had formed when boron was added to the graphite and heat treatment was taken to 2500 C, where the boron reacted with the carbon to recrystallize the microstructures.

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 can be achieved is by the co-deposition of titanium, followed by annealing. Therefore, a study of annealing effects in titanium-doped pyrolytic carbon was 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). Results obtained in the last contract year were reported in the previous annual report (Ref. 15).

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, were studied. 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 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 VIII). 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. 15). Plots of the changes up to 3000 C will be published later.

The behavior of the low-temperature laminar carbon containing 6.7 wt-% titanium contrasted with that of the high-temperature isotropic carbon containing 9.7 wt-% titanium. The low-temperature laminar titanium-doped carbon annealed in a manner almost identical to that of its titanium-free control. Both materials showed a steady increase in apparent crystallite size and a steady decrease in interlayer spacing as the temperature was increased. The changes started at about 1400 C and leveled off at about 2800 C. The densities of both carbons showed a steady increase

TABLE 2
 PROPERTIES OF TITANIUM-DOPED PYROLYTIC CARBONS AND TITANIUM-FREE
 CONTROLS UNDERGOING ANNEALING

Specimen Number	Deposition Temperature (C)	Titanium Concentration (wt-%)	Structural Properties				Starting Temperature of Annealing (C)
			Density (g/cc)	L_c (Å)	Layer Spacing (Å)	Bacon Anisotropy Factor	
2814-77	1225	6.7	2.169	33	3.45	ND*	1300
2814-79	1225	0	2.078	34	3.44	5.3	1300
2814-81	2200	9.7	2.300	158	3.40	1.2	2000
2814-83	2200	0	2.150	183	3.40	ND*	2000

*Not determined.

over the same range, except that evaporative loss of titanium from the doped samples caused a density loss, which started at 2400 C and was complete by 2800 C. Thus, the titanium additive did not catalyze the graphitization of the low-temperature laminar pyrolytic carbon during isochronal annealing.

On the other hand, the behavior of the titanium-doped high-temperature isotropic carbon was markedly different from that of its metal-free companion. The metal-free carbon showed almost no increase in crystallite size over the temperature range 2200 to 3000 C, but there was a slow, steady decrease in layer spacing and resistivity, and a steady increase in density, over this range. The titanium-doped carbon in the as-deposited condition showed a broadened (002) peak corresponding to turbostratic carbon, but after the 2300 C anneal a small sharp side peak appeared at the position corresponding to crystallite graphite. During subsequent anneals the graphite peak grew at the expense of the carbon peak, which was not visible after treatment to temperatures of 2500 C and above. The width and position of the graphite peak remained unchanged during the remainder of the annealing treatments. The electrical resistivity of the doped carbon showed a sharp drop between 2300 and 2400 C, and remained almost level afterwards. The density of the doped carbon decreased sharply over the temperature range 2400 to 2800 C due to titanium evaporation.

The results show that the titanium-doped isotropic carbon graphitizes by a heterogeneous recrystallization process, which starts at 2300 C and is complete by 2500 C. On the other hand, the titanium-doped low-temperature laminar carbon does not recrystallize, but shows the same steady improvement in crystal parameters as an undoped laminar carbon. This result is in contrast to the observation that a very similar doped laminar carbon containing 6.4 wt-% titanium does undergo catalytic graphitization when heated at 2200 C for 4 hr in a fluidized bed (Ref. 14). The probable reason for the difference in behavior is that the isochronally annealed metal-doped laminar carbons experience considerable crystallite growth before reaching the potential recrystallization temperature of 2200 to 2300 C (apparent crystallite size $\sim 150 \text{ \AA}$). Thus, the driving force

for graphitization is reduced below what it would be if the temperature were rapidly raised to 2200 to 2300 C. The effect is similar to that recently reported by Fitzer (Ref. 18), who found that molten vanadium causes rapid recrystallization in glassy carbons of low crystallinity but has little or no effect on more perfect graphites.

In the absence of catalytic effects, the graphitization of the carbons under isochronal annealing conditions takes place gradually over a very broad range of temperatures. Such behavior is typical of complex annealing processes that take place with a wide range of either frequency factors or activation energies, or both (Ref. 19). Isothermal annealing data obtained on massive pyrolytic carbon and petroleum cokes by Fischbach (Ref. 20) have been interpreted in terms of a range of frequency factors and a single activation energy of 11.3 eV. The annealing behavior of irradiated pyrolytic carbons (described in Section IX) has been analyzed in terms of a single frequency factor and a spectrum of activation energies. In the absence of a well-established mechanistic model for the graphitization of carbons, the value of performing a similar treatment is dubious. However, it is of interest to note that the graphitization kinetics of unirradiated carbons are generally similar to the annealing kinetics of irradiated carbons, which involve the rearrangement of irradiation-induced point defects and defect clusters.

LOW-TEMPERATURE GRAPHITIZATION OF COKES AND BINDER-FILLER COMPACTS

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

Coke Studies

Recent work has concentrated on the use of titanium and aluminum, particularly aluminum. The end products are for use in nuclear reactor cores; therefore, the nuclear properties and/or the ease of removal of the last traces of the metallic constituents from the graphite are important. Thus, the choice of catalysts is limited to materials of small capture cross sections that can be easily removed during or after graphitization. Aluminum is of particular interest because it has been shown

that 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.

The first phase of the work during the current year consisted of a continuation of the previous year's work, during which metals were added to petroleum coke and the cokes were examined after systematic heat treatment for the presence of graphitic structure. In the second phase, compacts were molded and the examinations were continued. During this phase an effort was made to obtain a quantitative measure of the graphitic structure present in a converted compact.

Petroleum asphalt carbonized with aluminum and titanium showed evidence of recrystallization by the presence of large primary crystals when heated to 2800 C (Ref. 15). 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. 15). These positive results led to the preparation of specimens of higher metal content (5 and 10 wt-% Al, 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_o (Table 3).

The coke containing 5 wt-% aluminum showed no signs of recrystallization by 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 (see Fig. 4a). The coke sample that contained 10 wt-% aluminum showed evidence of recrystallization from both X-ray and metallographic examinations when heated to 2300 C (Fig. 4b), 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 C to 2300 C. This specimen had large areas of primary graphite crystals that responded to sensitive tint lighting (Fig. 4c).

TABLE 3
HEAT TREATMENT AND X-RAY PARAMETERS OF PETROLEUM ASPHALT -
ALUMINUM-TITANIUM ADMIXTURES

Specimen Number	Composition (wt-%)			Heat Treatment					Metal Content (wt-%)		X-ray Parameter (002) (Å)	
				Bake		Specimen Number	Temp (C)	Time (hr)				
	Petro- leum Asphalt	Al*	Ti*	Temp (C)	Carbon Yield (wt-%)							
	Al	Ti	C _o	L _c								
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
						115-3	2300	2	-	-	6.745	290
						115-3	2300	8	-	-	6.734	330
114-3	85	5	10	900	67.8	115-3	2300	32	-	-	6.734	350
						120-4	1700	2	-	-	6.886†	-
											6.726†	
114-4	70	10	20	900	75.2	121-4	1900	2	-	-	6.821†	-
											6.721†	
											6.810†	
											6.726†	
						122-4	2100	2	-	-	6.726†	
						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

* Added to petroleum asphalt after distillation but prior to carbonization.

[†] The X-ray diffraction curves had two distinct peaks.

M26424-3

250X

(a) 5 wt-% Al

M26425-1

250X

(b) 10 wt-% Al

M26426-1

250X

(c) 10 wt-% Al, 20 wt-% Ti

Fig. 4. Photomicrographs showing crystal growth in petroleum coke heated for 32 hr at 2300 C

The X-ray curves (002) of the specimen containing 10 wt-% Al and 20 wt-% Ti 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 (see Fig. 5). A spot check of the metal content of two of the samples (Table 3) showed 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.

Compact Studies

Larger batches of the cokes in combination with aluminum and titanium were prepared for fabricating binder-filler artifacts. The metal was added to the petroleum asphalt prior to carbonization; the petroleum asphalt was then carbonized to form a coke that contained finely divided metallic particles, and the coke was used to produce compacts in combination with a coal-tar pitch binder. These compacts were then subjected to heat treatments at 1900, 2100, and 2300 C, and the development of the graphitic structure was observed as a function of time. The data are shown in Table 4.

In the material where metallic constituents were absent, there was no pronounced crystal growth when heat treatment was carried out for 3 hr at 2300 C. The addition of metallic particles produced material with a considerable portion of graphitic structure. This was particularly in evidence in cokes prepared with aluminum and to some extent in those prepared with titanium and aluminum in combination. The X-ray traces of the materials prepared with titanium showed a broad carbon peak with graphite peaks superimposed. The materials prepared with aluminum showed sharp graphite peaks and in some cases the graphite peaks were assymmetric, indicating some residual carbon structure. Metallographic examination of these cokes revealed relatively large graphite crystals that were responsive to sensitive tint

Fig. 5. (002) X-ray diffraction curves of petroleum-asphalt cokes heated for 2 hr at 2100 C

TABLE 4
HEAT TREATMENT OF METAL-DOPED COMPACTS

Specimen Number	Component wt-%*			Heat Treatment		Lattice Parameter (Å)				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.

lighting. The graphite crystals appeared to grow from a metallic nucleus. No graphite crystals were present in the nonmetallized coke.

Another significant feature of the experiment was the large weight losses observed when aluminum was used. The weight loss of aluminum is dependent on temperature and was rapid in the range 1900 to 2300 C. After 3 hr at 2300 C, it appears that the aluminum may be near depletion.

An additional graphite compact was molded with petroleum coke that had been carbonized with 20 wt-% of finely dispersed aluminum metal. The compact was heated slowly to 900 C to carbonize the pitch binder. A control compact was also prepared without aluminum. The compacts were then heated for 6 hr at 2300 C.

The compact containing aluminum showed no signs of hydrolysis when placed in the atmosphere for 1 week or when immersed in water at room temperature, indicating that Al_4C_3 was not present. X-ray diffraction examination showed the values given in Table 5.

TABLE 5
X-RAY PARAMETERS OF Al-DOPED COKE

Specimen No.	Aluminum Content in Petroleum Asphalt (wt-%)	X-ray Parameters (Å)	
		L_c	C_o
3726-24B	0	270	6.769
3726-26-1	20	2000	6.714

Thermal expansivity values were 2.20×10^{-6} in./in.-C⁻¹ in the radial direction and 3.10×10^{-6} in./in.-C⁻¹ in the longitudinal direction for the compact that contained aluminum.

Both compacts were comminuted and separated in the sink-float column (see Section III). The median density of the control material was 2.14 g/cc, and that of the aluminum-doped sample was 2.19 g/cc. Density fractions were collected; their X-ray parameters are given in Table 6.

TABLE 6

X-RAY PARAMETERS OF ALUMINUM-COKE AND CONTROL COMPACTS

Specimen Number	Aluminum Content in Petroleum Asphalt (wt-%)	Vol-% of Sample	Average Density (g/cc)	X-ray Parameter (Å)	
				L _c	C _o
3726-24-B	0	1.43	1.48	-	-
		1.32	1.52	-	-
		1.22	1.58	240	6.861
		0.63	1.63	220	6.771
		1.38	1.69	-	-
		1.32	1.73	-	-
		1.16	1.81	270	6.769
		1.59	1.87	-	-
		2.01	1.94	-	-
		0.79	1.99	290	6.769
		3.70	2.05	-	-
		7.09	2.10	400	6.776
		22.91	2.14	-	-
		29.31	2.17	-	-
		17.99	2.19	-	-
		6.14	2.21	242	6.766
3726-26-1	20	0.87	1.73	-	-
		1.14	1.80	-	-
		3.16	1.95	900	6.719
		11.16	2.09	435	6.719
		10.89	2.17	900	6.716
		27.38	2.19	2000	6.714
		16.49	2.20	2700	6.714
		14.15	2.22	4000	6.719
		14.75	2.25	8000	6.711

Metallographic examination of the compacts revealed that large graphite crystals had formed in the aluminum-doped specimen, while the control specimen showed a typical carbon or nongraphitic structure (see Fig. 6). The specimen that contained aluminum apparently converted completely to a graphitic structure. This is evident from the densitometric separation where about 70 vol-% of the specimen was above 2.17 g/cc with X-ray parameters equivalent to or better than natural flake graphite. The lighter 30 vol-% is equivalent to needle-coke graphite. In contrast, the control specimen has a large network of microporosity and is only semi-graphitic.

The weight loss during graphitization of the aluminum-doped sample was 41%, which is about equivalent to removal of all the aluminum. However, the bulk density of this material was quite low (0.895 g/cc), indicating that large pores were formed during the crystallization process while the aluminum was escaping.

Discussion

The results indicate that carbon structure can be converted to an extremely graphitic structure by a number of metallic constituents below 2300 C. Complete conversion was effected in a petroleum-asphalt coke by the addition of 20 wt-% aluminum metal as a finely divided powder. The graphitic transformation in the aluminum-doped cokes was gradual in contrast to that observed with titanium. In the titanium-doped specimens, a graphite peak appears superimposed on the broad carbon curves. This indicates that graphitization is occurring in a heterogeneous recrystallization process, whereas with aluminum it appears to be a homogeneous process that gradually transforms the carbon to a graphitic structure. In the case of aluminum, the graphitic structure may result from the carbon deposited due to dissociation of Al_4C_3 . If this is the case, then the aluminum is not acting as a true catalytic agent, and large amounts of aluminum may be required to convert the carbon structure. This may present problems in fabrication,

M29658-2

200X

(a) Control specimen, no Al

M29622-2

200X

(b) 20 wt-% Al in petroleum asphalt
prior to carbonization

M29622-4

200X

(c) 20 wt-% Al in petroleum asphalt
prior to carbonization

Fig. 6. Photomicrographs of molded compacts heated for 6 hr at 2300 C

such as handling large amounts of aluminum, or low bulk densities and low strength due to the evolution of the dissociation products of the Al_4C_3 .

The orientation factor of the molded specimen that was converted to graphite with aluminum was 1.40 (ratio of longitudinal coefficient of thermal expansion to radial coefficient of thermal expansion). While this is not very isotropic in comparison with naturally isotropic cokes such as Gilsonite, it is quite good in comparison with materials such as compacted natural flake graphite, which is its equivalent with respect to crystallite size and perfection. In this respect, the structure may be expected to show better irradiation stability, since it has excellent crystallinity coupled with a small degree of anisotropy.

V. 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 prepared by a standardized molding process is under investigation. The objectives of this work are to provide an understanding of the influence of the binder coke on the microstructure and 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-%. The preparation of the specimens has been described previously (Ref. 15). The specimens were 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 (BNWL) conducted the irradiation capsule experiments, and the space was shared jointly between 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.

At this exposure all specimens had passed through maximum contraction strains in the c-axis direction (parallel to molding ram direction) and had entered the expansion phase. During the third increment of dose from 5.75 to 9.70×10^{21} n/sq cm ($E > 0.18$ MeV), many of the specimens had started to distort or warp, which is characteristic of highly anisotropic graphites after large expansions. Therefore, the experiment was terminated. The additional data obtained from Capsule GE-H-13-15 have been

added to the data obtained last year to give a complete set of dimensional and property data.

Dimensional changes are presented in Fig. 7 as a function of binder-coke content and neutron dose ($E > 0.18$ MeV) and are presented as curves drawn through the data points at the respective increments of dose. Volumetric changes are plotted in the same manner in Fig. 8.

The effect of the binder-coke content is not clearly shown after low exposures, but becomes more apparent after irradiation to higher exposures, where contraction has ceased and expansion has commenced in the preferred c-axis direction (parallel). There is an optimum binder-coke content of about 7 to 9% where expansion is minimized, whereas the compacts of lower or higher binder-coke content expand more. In the a-axis direction (perpendicular), the highest contraction occurred in specimens with a binder-coke content above 9%.

Thermal expansivity data are given in Table 7 and apparent density changes measured by immersion in a liquid are shown in Table 8. The thermal expansivity increased by a factor of about 2 to 2.5 in the c-axis direction for compacts that were deficient in binder-coke, while those of higher content increased by a lower factor of about 1.5. The results in the a-axis direction were similar.

The apparent density by immersion in a liquid, which is a measure of the crystallite volume plus the closed porosity, changed very little until structural expansion had become large. After a significant expansion had occurred, there was an increase in the closed porosity and in the open porosity. The increase in closed porosity was not dependent on binder-coke content.

Fig. 7. Dimensional changes of molded needle-coke graphites as a function of binder-coke content and fast-neutron dose irradiated at 1225 to 1250 C

Fig. 8. Volumetric changes of molded needle-coke graphites as a function of binder-coke content and fast-neutron dose irradiated at 1225 to 1250 C

TABLE 7

THERMAL EXPANSIVITY CHANGES OF MOLDED GRAPHITES IRRADIATED AT 1225 TO 1250 C

Specimen Number	Binder Coke Content (wt-%)	Coefficient of Thermal Expansion, $\alpha \times 10^6$ (C ⁻¹)							
		Parallel				Perpendicular			
		Unirradiated	Exposure ($\times 10^{21}$ n/sq cm)			Unirradiated	Exposure ($\times 10^{21}$ n/sq cm)		
			1.9	5.75	9.70		1.9	5.75	9.70
10-5	5.5	3.70	---	9.05	10.15	2.80	---	3.85	5.20
10-5		4.35	---	---	---	2.20	---	---	---
15-1	6.6	3.20	---	7.05	6.90	2.75	---	3.45	4.45
15-3		3.65	6.60	7.75	---	2.00	2.75	3.05	--
20-1	7.6	4.15	---	5.80	8.45	3.20	---	3.50	4.55
20-3		3.75	---	5.90	---	2.30	---	3.90	---
20-5		4.15	4.85	5.80	---	2.00	2.30	2.35	---
25-3	8.4	3.45	---	4.05	4.65	2.60	---	3.65	4.10
25-7		2.55	4.30	4.95	---	2.40	2.35	3.00	---
30-2	9.0	3.20	---	5.10	5.55	2.60	---	4.25	---
30-7		3.80	---	6.10	---	2.90	---	4.25	3.45
30-8		3.75	4.85	4.90	---	1.80	2.60	2.60	---
40-3	11.7	3.35	---	4.70	---	2.15	---	2.20	---
40-8		4.20	---	4.60	4.90	2.15	---	2.65	---
40-5		3.75	5.10	4.45	---	2.50	2.60	2.60	---
50-2	14.2	4.10	---	---	---	2.00	---	2.35	---
50-6		4.00	---	5.75	6.35	2.10	---	2.45	2.50
50-7		4.45	5.15	5.15	---	2.10	3.00	2.75	---

TABLE 8

DENSITY CHANGES OF MOLDED GRAPHITES IRRADIATED AT 1225 TO 1250 C

Specimen Number	Coke Content (wt-%)	Bulk Density Unirradiated (g/cc)	Apparent Density (Immersion in Liquid) (g/cc)			
			Unirradiated	Exposure ($\times 10^{21}$ n/sq cm)		
				3.70	5.75	9.70
10-5	5.5	1.59	2.212	2.209	2.212	2.167
15-1	6.6	1.65	2.206	--	--	2.152
15-3		1.62	2.206	--	2.207	--
20-1	7.6	1.68	2.200	--	--	2.147
20-3		1.69	2.204	2.210	2.205	--
20-5		1.65	2.205	--	2.201	--
25-3	8.4	1.68	2.201	2.210	--	2.138
25-7		1.65	2.202	--	2.206	--
30-2	9.0	1.69	2.196	2.205	2.194	2.150
30-7		1.68	2.203	2.210	--	--
20-8		1.64	2.199	--	2.201	--
40-3	11.7	1.70	2.190	--	--	--
40-8		1.67	2.187	2.196	2.190	2.138
40-5		1.70	2.190	--	--	--
50-2	14.2	1.71	2.184	2.191	2.195	--
50-6		1.68	2.18	--	--	2.145
50-7		1.72	2.187	--	2.204	--

DISCUSSION

The dimensional changes in any porous artificial graphite will ultimately depend upon the dimensional changes of the individual units of its structure or its crystallites. However, the exact dimensional changes in the bulk dimensions will depend to a large extent on the collective contribution of the crystallites.

The contribution of each crystallite can be modified by certain aspects of the microstructure such as crystallite orientations that deviate from perfect alignment and internal microporosity, which results from the misalignment of crystallites, grist particles, or cracks that are formed by differential shrinkage during the manufacturing process.

It is expected that the addition of a binder carbon during the fabrication of binder-filler artifacts will provide a microstructure that is different from that of the grist particles alone. This difference is difficult to detect microscopically when materials such as needle-coke and pitch are used. However, the data presented here show that dimensional changes of this type material are quite sensitive to the variation in microstructure that is imparted as the binder-coke content is increased. The only significant physical characteristic that correlated with the increase in binder-coke content, aside from the dimensional changes, was the bulk density, which increased with increasing binder-coke content. Crystallite orientation (BAF), crystallite lattice parameters, and thermal expansivity values, which are generally used for characterization purposes, were not significantly variable with binder-coke content.

If it is assumed that the crystallites within the grist particles behave alike in each compact since they are from a common source, then the observed differences in the dimensional changes and corresponding volume changes have to be attributed to the differences in the binder-coke volumes. This is unrealistic since only a small variance in binder-coke volume can cause rather large differences in bulk volume changes. This is especially noted after high doses. Thus, it must be recognized

that the grist particles behave differently in each microstructure and the difference must be attributed to modifications wrought in the microstructure by the various binder-coke grist-particle combinations.

A batch of needle-coke particles (300 to 350 microns, particle size), sampled 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 <38 microns in an effort to determine the changes that occurred during the densification phase of the irradiation. The measurements were made in the densitometric apparatus (Ref. 10) and the median density was used for comparative purposes with those of compacts.

Prior to irradiation the median density of the large needle-coke particles was 1.84 g/cc, compared with 2.22 g/cc after comminution. This signifies that the coke particles before comminution contain a considerable volume of closed porosity that was destroyed during the grinding operation. After irradiation the large particles densified to a value of 2.05 g/cc, while the crystallite clusters represented by the sink-float particles expanded from 2.22 g/cc to 2.14 g/cc. (It should be noted that the apparent density of the material of lowest binder-coke content is comparable to the <38 -micron grist needle-coke particles, while that of the compacts of highest binder-coke content was slightly less.) Closed porosity was not generated in the compacts until after bulk expansion had begun at a dose of about 6×10^{21} n/sq cm, whereas in the loose particles a considerable amount was generated even during bulk contraction to a dose of 4×10^{21} n/sq cm.

It is assumed that the loose particles that are highly aligned change volume anisotropically in a manner similar to the hot-worked or massive annealed graphites described in Section VII. Their crystallites are free to expand in the c-axis direction, with the only restraint being the interference

among crystallites due to a small degree of anisotropy. The shape change of the crystallites is accompanied by volume changes that produce internal porosity. When the particles are fastened together by a network of unyielding binder coke, the free expansion of the coke particles in the c-axis direction is restrained to a degree preventing internal porosity generation. The restraint produces internal stresses at the binder-filler interfaces which build up with dose. These stresses are relieved somewhat by creep and finally by crack formation similar to that observed in the loose particles when the strength of the bonds is exceeded. Bulk expansion of the compacts accompanies this breakaway. The largest expansion occurs in the materials that exhibit the weakest binder-filler bonds, i.e., the lowest binder-coke content.

It will be necessary to grind up a selected number of irradiated specimens and to determine the volumetric changes in their crystallite clusters (sink-float particles). These measurements can then be compared directly to those made on the loose particles (binder-free) to determine the effect of the binder-coke additions on the expansion of the crystallites within the needle-coke grist particles. These experiments are in progress.

From the data presented, it appears that small changes in binder-coke components of needle-coke based graphites can effect subtle changes in the microstructure of the resultant binder-filler artifacts that can then cause significant variations in irradiation behavior at elevated temperatures. Many of these changes are not measurable by common characterization techniques such as X-ray measurements and microscopy because these techniques measure predominantly the characteristics of the grist particles, which constitute the major portion of the specimens. However, the determination of volumetric changes of small crystallite clusters and internal microporosity of both loose particles and bonded grist particles helps to explain these differences.

VI. VOLUMETRIC CHANGES OF ANISOTROPIC AND NEAR-ISOTROPIC GRAPHITES

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

A number of models have been published to describe the neutron-induced dimensional and volumetric changes of graphites. These models treat graphite as a single-phase (Refs. 21-23) or as a two-phase (Ref. 24) material. The single-phase models worked reasonably well at low doses for highly graphitic materials. Simmons (Ref. 23) used a thermodynamic approach to derive an expression for the rate of dimensional change as a function of neutron exposure, in terms of the dimensional changes in individual crystallites and a parameter obtained from thermal expansion measurements. Price and Bokros (Ref. 22) suggested a model following analyses of the thermal expansion of polycrystalline graphite by Bacon (Ref. 25) and Sutton and Howard (Ref. 26), wherein the bulk dimensional change is obtained by integrating the contributions of individual crystallites allowing for accommodation of part of the c-direction crystal expansion by basal-plane microcracks. The work of deHalas and Yoshikawa (Ref. 24) indicated that radiation-induced length changes at temperatures above ~ 500 C are effected by changes in the less graphitic regions and that theories based on single-phase crystalline models do not apply. However, no quantitative relationships were derived.

More recent data by Bokros et al. (Ref. 11) have shown that in single-phase carbons the dimensional changes are sensitive to their crystallinity (L_c) above about 500 C; graphites with large L_c values showed less dimensional change. Data in Section III for densitometric separations of nuclear graphites indicate that crystallite sizes in needle-coke graphites range from 350 to 1600 Å. Thus, it is expected that the volumetric changes in the individual crystallites in the porous artificial graphites will also be sensitive to their sizes at high temperatures in a manner analogous

to the changes in the single-phase carbons, with allowance for restraints imposed by misalignment of crystallites and porosity.

Simmons (Ref. 27) has modified the original growth equations to account for changes in the macrostructure. Recently, Thrower (Ref. 28) has examined a variety of graphites using electron microscopy and has identified at least four types of crystalline regions that he indicates are affected differently by high-temperature fast-neutron irradiation. These crystals can coexist in the various graphites. Thrower's findings are similar to the data obtained in Section III and reinforce the idea that the microstructure of porous, artificial graphites is quite complex and can be nonuniform with respect to crystallinity and porosity. Thus, it is quite possible that small, rather subtle differences in microstructure may cause reasonably large differences in bulk behavior.

Early in the program, a general relationship was presented (Ref. 15) that attempted to relate the crystallite changes in porous graphites to porosity changes in the graphites as a function of neutron dose. It was proposed that crystallite changes would be obtained from measurements on pyrolytic carbons or highly aligned graphites of equivalent crystallite size by various averaging techniques (see Section VII). This relationship was based on the assumption that c-axis expansion would be absorbed by intercrystalline microporosity, which could be determined from sink-float measurements. However, as more data have become available at higher doses, it has become evident that c-axis expansion is being absorbed by micropores or cracks other than intercrystalline cracks. The observed expansion of the sink-float particles leads to the conclusion that either new porosity is being generated within the sink-float particles by crystallite shape changes, or that c-axis expansion is being absorbed by the intercrystalline cracks within the particles, leaving the crystallites full of vacancy defects that cause a reduction in the particle density. In either case, it appears that individual crystallite changes cannot be separated from the intercrystalline microporosity changes. Therefore, the volume expansion of the sink-float particles gives an upper limit

to the volume expansion of the crystallites that they contain. This upper limit is an experimental value and includes all restraints due to misalignment of crystallites and intercrystalline microporosity. The volume changes of the bulk material are then related to the volume expansion of the crystallites (viz., sink-float particles) and the changes effected in microporosity that resides in domains outside the sink-float particles. This presents a much more complicated picture of structural changes for porous artificial graphites than had been previously assumed, and it may not be valid to calculate crystallite changes for artificial graphites based on data from materials of dissimilar crystallite orientation or microporosity.

EXPERIMENTAL RESULTS*

Commercial graphites that differ widely in microstructure, crystallite orientation and size, porosity, and properties have now been irradiated at 950 to 1250 C to doses of 7 to 11×10^{21} n/sq cm ($E > 0.18$ MeV). The additional data obtained this year have been added to the previous data to obtain complete curves as a function of dose. The graphites, obtained from the major United States carbon companies, were of three types: (1) anisotropic materials prepared with needle-coke particles and upgraded in strength and density by multiple impregnations, (2) a near-isotropic material prepared with Gilsonite coke, and (3) a near-isotropic material prepared with raw petroleum coke. A complete description of the materials and properties is given in Ref. 29. A summary of the properties and structural parameters of the graphites is given in Table 9. Changes in dimensions, thermal expansivity, apparent density, distribution of apparent density, and microstructure were investigated.

Dimensional changes for the anisotropic needle-coke materials are given in Fig. 9. Data for the near-isotropic graphites are shown in Fig. 10. Volumetric changes are shown in Fig. 11.

* This work was sponsored by the USAEC under Contract AT(04-3)-167, Project Agreements 12 and 17. The irradiation capsules were designed and constructed at Battelle Northwest Laboratories and were irradiated at the Engineering Test Reactor, Idaho Falls.

TABLE 9

PHYSICAL PROPERTIES AND STRUCTURAL PARAMETERS OF GRAPHITES

Material Designation	Apparent Density (g/cc)		Coefficient of Linear Thermal Expansion, $\alpha \times 10^6$ (C ⁻¹ at 400 C)		Apparent Crystallite Size (Å)		Bacon Anisotropy Factor	Lattice Parameters (Å)	
			Preferred Orientation					C _o	A _o
	Bulk	Powder	c-axis Direction	a-axis Direction	L _c	L _a			
NC-8*	1.72	2.20	3.40	1.75	900	870	0.64	6.725	2.461
H-283*	1.78	2.18	3.50	1.50	800	530	1.36	6.722	2.460
CHN*	1.85	2.21	3.50	2.10	700	530	0.78	6.724	2.459
711-TS-N*	1.88	2.15	3.15	2.15	735	710	0.80	6.724	2.462
H-319†	1.80	2.15	4.40	3.70	480	430	0.90	6.731	2.460
H-315-A**	1.85	2.18	5.70	4.70	400	400	1.13	6.725	2.459

* Needle-coke filler

† Raw petroleum coke filler

** Gilsonite coke filler

Fig. 9. Dimensional changes of anisotropic, needle-coke graphites as a function of fast-neutron dose

Fig. 9 (continued). Dimensional changes of anisotropic, needle-coke graphites as a function of fast-neutron dose

Fig. 9 (continued). Dimensional changes of anisotropic, needle-coke graphites as a function of fast-neutron dose

Fig. 9 (continued). Dimensional changes of anisotropic, needle-coke graphites as a function of fast-neutron dose

Fig. 9 (continued). Dimensional changes of anisotropic, needle-coke graphites as a function of fast-neutron dose

Fig. 10. Dimensional changes of near-isotropic graphites as a function of fast-neutron dose

Fig. 11. Volumetric changes of graphites as a function of fast-neutron dose. (a) 950 to 1015 C, and (b) 1175 to 1250 C

The curves of volumetric change (Fig. 11) were similar in shape for all graphites, i.e., initial contraction at low doses followed by expansion with increasing dose. The high alignment of the crystallites in the needle-coke materials was reflected in a high degree of anisotropy in their dimensional changes. The near-isotropic materials also exhibited a significant degree of anisotropy, but less than that of the needle-coke materials. In the direction of preferred c-axis alignment, the needle-coke graphites showed maximum contraction strains of about 1 to 1.5% at 5 to 6×10^{21} n/sq cm, followed by expansions of 6 to 19% at 10^{22} n/sq cm at 1175 to 1250 C. In the a-axis direction, maximum contraction strains of about 8% were observed, and the irradiation-induced strains were beginning to saturate at 10^{22} n/sq cm. A needle-coke graphite, formed under pneumatic pressure during baking, was an exception. It had an a-axis direction contraction of only 4% at 5 to 6×10^{21} n/sq cm followed by a rapid expansion of 4%, making a net volume change of zero at 11×10^{21} n/sq cm. The maximum contraction of the near-isotropic graphites ranged from 1.5 to 3.5% for both directions followed by expansion to give net changes of -1 to +3%. The anisotropy of their dimensional change increased with increasing dose. The dimensional changes were similar at 950 to 1015 C.

The thermal expansivity data are shown in Fig. 12. The expansivity of the needle-coke graphites did not change significantly with dose. An exception was the material prepared under pneumatic pressure during baking. It showed a significant increase, by a factor of 2, when irradiated at 1175 to 1250 C, which coincided with its large expansion in the c-axis direction above 5×10^{21} n/sq cm. Conversely, the expansivity of the near-isotropic materials remained unchanged at low doses, followed by a sharp decline, by a factor of about 2, above 5×10^{21} n/sq cm.

The increase in thermal expansivity of the needle-coke graphite was not unexpected, since in this particular material, micropores that apparently provided for c-axis accommodation in thermal expansion were eliminated just prior to the onset of the observed increase. However, the decrease

Fig. 12. Thermal expansivity changes of the graphites as a function of fast-neutron dose

in the near-isotropic graphites presents a different situation, where new cracks for the accommodation of thermal expansivity are apparently being formed during the expansion phase. However, no evidence of a significant increase in microporosity was observed. This behavior is not consistent with current ideas relating microporosity to thermal expansivity.

Apparent density changes, measured by immersion of solid samples in a liquid, increased at low doses coinciding with volumetric densification of the bulk and then decreased during the expansion phase (Fig. 13). The densities ranged from 2.04 g/cc, unirradiated, to 2.10 to 2.13 g/cc at 5×10^{21} n/sq cm and about 2.04 g/cc at 11×10^{21} n/sq cm.

The density distribution of unirradiated and irradiated graphites was measured (Fig. 14). Several features of these measurements are of interest:

1. The unirradiated specimens were subdivided by crushing the solid samples into small increments of volume (called sink-float particles) where only a small percentage of the original porosity remained.* These particles consisted of crystallite clusters that varied in density as a function of their distribution over the total volume of the sample. Furthermore, the crystallite sizes of the anisotropic materials varied over the range 300 to 1500 Å as a function of the particle density. An exception to this was the material manufactured with Gilsonite coke, which contained crystallites of a narrow size range (450 to 550 Å). In this case the apparent crystallite size was not dependent on the particle density.
2. Upon irradiation[†] it appeared that a portion of the particles (believed to be the lighter fractions) first densified at low doses and then expanded, while those in intermediate and highest density fractions showed only expansion.

* Described in Section III and Ref. 5.

[†] The graphites were irradiated as solid samples and comminuted for density measurements.

Fig. 13. Changes in apparent density of H-315-A and CHN graphite as a function of fast-neutron dose

Fig. 14. Density distribution of graphites as a function of fast-neutron dose

Fig. 14 (continued). Density distribution of graphites as a function of fast-neutron dose

Fig. 14 (continued). Density distribution of graphites as a function of fast-neutron dose

3. The distribution of the apparent density changed as a function of dose.
4. The rate of expansion of the sink-float particles slowed with increasing dose.

These data emphasize the heterogeneous nature of the graphite microstructure and show that various regions within the graphites undergo neutron-induced changes depending on their apparent crystallite size or their original density, or both.

DISCUSSION

The dimensional changes of graphites during fast-neutron irradiation depend ultimately on the changes that take place within the crystallites. However, the changes of the bulk dimensions depend not only upon the crystallite changes but also on the microstructure or the interaction of the crystallites with each other (orientation effects) and modification of the transmittal of their changes to the bulk by porosity that is present. The data in Figs. 9 and 10 illustrate the importance of microporosity. While it has been shown that dimensional changes of nonporous materials depend quite sensitively on the crystallite parameter L_c (Ref. 11) when it varies over a wide range from 30 Å to ∞ or single crystals, it is quite clear that factors such as crystallite orientation and porosity are also important in the analysis of dimensional changes in porous artificial graphites of the type used for moderator or reflector blocks.

The various regions in graphites are defined as follows:

Bulk volume of solid sample = $V_c + V_{p(t)}$, where V_c is the volume of crystallites and $V_{p(t)}$ is the total pore volume

Apparent volume of solid sample = $V_c + V_{cp(s)}$, where $V_{cp(s)}$ is the volume of closed pores measured on solid samples

Apparent volume of sink-float particles ($\sim 10 \mu$ average diameter) = $V_c + V_{cp(p)}$, where $V_{cp(p)}$ is the volume of closed porosity measured on particles.

Curves were constructed (Fig. 15) that show the changes of these regions as a function of neutron dose. The ordinates between the curves define the pore volumes (V_p) and pore volume changes (ΔV_p) of the various domains of porosity as defined below:

V_{p1} = volume of closed pores in sink-float particles

V_{p2} = volume of closed pores in solid sample minus V_{p1} (closed porosity external to particles)

V_{p3} = volume of open pores

The sink-float particles were considered as small volumetric increments within the solid sample. Each particle consisted of crystallites plus intercrystalline microporosity. The volumetric expansion of these particles represented the volume expansion of the crystallites reduced by any restraints due to crystallite misalignment and microporosity within the particles. Expansion of the sink-float particles in the c-axis direction is accommodated by microporosity within V_{p2} and V_{p3} , which are present in the sample but are external to the sink-float particles. The volumetric changes of the sink-float particles combined with the changes in V_{p2} and V_{p3} represent an upper limit for the contribution of the crystallite changes to the bulk volume changes. The bulk volume changes are then related to the crystallite and porosity changes by:

$$\frac{1}{V_o} \int_0^\gamma \Delta(V_c + V_{p(t)}) (\gamma) d\gamma = \frac{1}{V_o} \int_0^\gamma \left[\overline{\Delta(V_c + V_{cp(p)})} (\gamma) d\gamma + \Delta V_{p2} (\gamma) d\gamma + \Delta V_{p3} (\gamma) d\gamma \right] \quad (1)$$

where γ is the dose, $\Delta(V_c + V_{p(t)})$ is the bulk volume change, $\overline{\Delta(V_c + V_{cp(p)})}$ is the median volume change of the sink-float particles, and ΔV_{p2} and ΔV_{p3} are as defined previously.

The volume change of the sink-float particles $\overline{\Delta(V_c + V_{cp(p)})}$ can be

Fig. 15. Volume changes of graphites as a function of fast-neutron dose

Fig. 15 (continued). Volume changes of graphites as a function of fast-neutron dose

Fig. 15 (continued). Volume changes of graphites as a function of fast-neutron dose

Fig. 15 (continued). Volume changes of graphites as a function of fast-neutron dose

obtained by using the median density change or by integrating from ρ_1 to ρ_2 to get $\Delta(V_c + V_{cp(p)})'$.

$$\overline{\Delta(V_c + V_{cp(p)})}' = \frac{\int_{\rho_1}^{\rho_2} \Delta(V_c + V_{cp(p)})'(\rho) d\rho}{\rho_2 - \rho_1}, \quad (2)$$

where ρ_2 is the density of the heaviest fraction, and ρ_1 is the density of the lightest fraction.

At low doses a portion of the c-axis expansion may be consumed by micropores in V_{p_1} while, concurrently, the expansion of the sink-float particles is accommodated in V_{p_2} and V_{p_3} . During the expansion phase, when V_{p_2} has been consumed and the effectiveness of V_{p_3} has been exhausted, the c-axis expansions are transmitted directly to the bulk and cause crack generation in V_{p_3} . These are the significant factors accounting for volumetric expansion. During this period, $\Delta(V_c + V_{cp(p)})'$ and V_{p_3} are both positive in Eq. 1 and account for the positive slope of $\Delta(V + V_{p(t)})'$ as observed experimentally. Volume changes calculated from Eq. 1 using $\overline{\Delta(V_c + V_{cp(p)})}'$ from Eq. 2 were in good agreement with measured values of the bulk volume changes (Table 10).

During the bulk contraction phase, various regions within the graphites will densify or expand depending on the size of the crystallites and the original density. The curves in Fig. 14 show the densification and expansion of the sink-float particles after irradiation, but unfortunately they give only the distribution of density in the irradiated sample and it is not possible to determine the volume changes for the individual density fractions of the original unirradiated specimen. However, based on work in pyrolytic carbons (see Section X), one expects the dense particles to expand while the light particles first densify and then expand. Since these regions coexist in the microstructures, it is not unreasonable to expect simultaneous closure of porosity and the formation of new porosity due to differential volume changes during densification and to observe porosity generation and gross distortion during expansion.

TABLE 10

COMPARISON OF VOLUME CHANGES BY MENSURATION AND CALCULATION FROM POROSITY
CHANGES OF AN ANISOTROPIC AND A NEAR-ISOTROPIC GRAPHITE IRRADIATED AT 1175 to 1250 C

Material Type	Dose x 10^{-21} (E > 0.18 MeV) (n/sq cm)	Volume Change (%)	
		Measured	Calculated
Anisotropic (CHN)	4	-6.00	-5.12
	8	-3.30	-3.87
	11	+0.60	+1.98
Near-isotropic (H-315-A)	3	-6.00	-5.19
	8	-2.90	-1.67
	10.5	+2.00	+1.86

These data indicate that materials which contain large volumes of structure of an intermediate density coupled with isotropy should show more stability than those which contain predominantly low-density or high-density structures. Examination of the densitometric curves show graphites CHN and H-315-A to have particles in a narrow range of intermediate density. These materials also showed the better stability within their orientation types; that is, CHN was the most stable of the anisotropic needle-coke materials and H-315-A was the better of the near-isotropic materials. It should be noted that this observation applies only to materials that have crystallite sizes within the range of artificial graphites and does not include natural-flake or single-crystal materials, which are also dense and quite stable.

The photomicrographs in Fig. 16 show the degree of crack and pore formation in the graphites after irradiation at 1175 to 1250 C to about 10^{22} n/sq cm. All materials show significant crack formation, but in graphites CHN and H-283 (the anisotropic needle-coke materials), and especially in H-283, it appears to be more severe than in the near-isotropic materials.

CONTINUATION OF HIGH-TEMPERATURE IRRADIATIONS

A number of the graphite specimens from the series described above are undergoing irradiation to about 14×10^{21} n/sq cm ($E > 0.18$ MeV) at 1200 C in Capsule GE-H-13-16 at Battelle Northwest Laboratories. These specimens will extend the data well into the expansion phase and may provide information concerning the useful life of anisotropic or near-isotropic graphites for advanced reactor use at high temperatures.

A new series of graphites were initiated 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.

K53228

Fig. 16. Photomicrographs of unirradiated and irradiated graphites

K69824

Fig. 16 (continued). Photomicrographs of unirradiated and irradiated graphites

K70794

Fig. 16 (continued). Photomicrographs of unirradiated and irradiated graphites

H-283 IRRADIATED AT 1175-1230 C,
 10.7×10^{21} N/SQ CM

K69826

Fig. 16 (continued). Photomicrographs of unirradiated and irradiated graphites

K53226

Fig. 16 (continued). Photomicrographs of unirradiated and irradiated graphites

K69822

Fig. 16 (continued). Photomicrographs of unirradiated and irradiated graphites

K69825

Fig. 16 (continued). Photomicrographs of unirradiated and irradiated graphites

H-319 IRRADIATED AT 1175-1230 C,
 10.80×10^{21} N/SQ CM

K69823

Fig. 16 (continued). Photomicrographs of unirradiated and irradiated graphites

Capsule GE-H-13-16 will be discharged from the ETR in September 1969, after three cycles and a maximum exposure of about $3 \text{ to } 4 \times 10^{21}$ n/sq cm.

Two graphites, H-327 (a needle-coke graphite) and H-328 (a near-isotropic graphite manufactured with Gilsonite coke), were irradiated in Capsules GE-H-13-14 and -15 at Battelle Northwest Laboratories at 1000 to 1100 C in Capsule GE-H-13-16. The H-328 was manufactured by molding as an 18-in.-diameter log, and the H-327 was extruded as a 13-in.-diameter log. The H-328 graphite contracted 0.80% in the longitudinal direction and 0.96% radially, whereas the H-327 contracted 2.40% longitudinally and 1.20% radially after irradiation to 3.5×10^{21} n/sq cm. These experiments are being continued in Capsule GE-H-13-16 to about 6×10^{21} n/sq cm.

VII. 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 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. 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 Battelle Northwest Laboratories.* 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 750 to 800 C and 1225 to 1290 C to successively higher doses. Samples were cut from these graphites at 0°, 30°, 60°, and 90° to the symmetry axis. Samples cut parallel to the substrate plane of massive pyrolytic carbon annealed at 3300 C are also included. The structural parameters are listed in Table 11. The apparent crystallite sizes (250 to 1600 Å) 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 dimensional change data are being used to calculate 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

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

TABLE 11
STRUCTURAL PARAMETERS FOR HIGHLY ORIENTED CARBONS AND GRAPHITES

Material	Density (g/cc)	Bacon Anisotropy Factor	Apparent Crystallite Size (Å)		Interlayer Spacing* (Å)
			L _a	L _c	
Massive pyrolytic carbon	2.18	8.9	250 [†]	220	3.420
Hot-worked ATJ graphite	2.04	4.1	630**	570	3.360
Annealed pyrolytic carbon	2.25	13	1300**	1600	3.353

* Evaluated from the (002) reflection.

[†] Evaluated from the (11) band.

** Evaluated from the (110) reflection.

in commercial polycrystalline graphites based on analysis of their constituent phases. The irradiation-induced changes in thermal expansivity, microstructure, apparent crystallite size, layer spacing, and mechanical integrity of the samples are also being followed.

The samples were irradiated* in three increments to total exposures of 1.5×10^{21} n/sq cm ($E > 0.18$ MeV) at 750 to 800 C and 9.7×10^{21} n/sq cm ($E > 0.18$ MeV) at 1225 to 1290 C. The dimensional changes, changes in thermal expansion coefficient, the X-ray diffraction parameters of layer spacing and apparent crystallite height (L_c), and the optical microstructure were examined.

DIMENSIONAL CHANGE MEASUREMENTS

Dimensional measurements were made to an accuracy of 0.05% on all samples. Because of the fragility of samples of annealed pyrolytic carbon cut perpendicular to the deposition plane, measurements of the changes in this direction were obtained from the changes in density of samples cut parallel to the deposition plane. Delamination cracks developed in the as-deposited pyrolytic carbon samples irradiated beyond $\sim 4 \times 10^{21}$ n/sq cm at 1250 C. However, most samples remained in one piece, enabling approximate measurements to be made. The measurements are summarized in Figs. 17 and 18. For the highest exposures at ~ 1250 C, the true strains in the principal c-direction were $\sim 115\%$ for as-deposited pyrolytic carbon, 44% for hot-worked graphite, and 21% for annealed pyrolytic carbon. The parallel and perpendicular dimensional changes, calculated as true strains, increased linearly with neutron exposure except for the hot-worked graphite that was irradiated at ~ 1250 C. For this material, the dimensional change rates were significantly lower over the increment 5.9 to 9.7×10^{21} n/sq cm than for virgin samples irradiated over the same interval.

*The irradiation capsules were designed and constructed at Battelle Northwest Laboratories and were irradiated in the Engineering Test Reactor, Idaho Falls.

Fig. 17. Dimensional changes of massive pyrocarbon and hot-worked graphite irradiated at 750 to 800 C

Fig. 18. Dimensional changes in massive pyrocarbon, hot-worked graphite, and massive pyrocarbon annealed at 3300 C; irradiated at 1225 to 1290 C

CRYSTALLITE DIMENSIONAL CHANGES

When the crystallite dimensional changes are small (c-axis expansion <5%), the bulk dimensional changes bear the same relationship to the crystallite dimensional changes as the respective thermal expansion coefficients bear to each other (Ref. 30). For larger dimensional changes, these relationships are no longer valid, and it is better to relate the dimensional changes to preferred orientation factors (Ref. 21). For highly oriented materials, the correction factors that take into account inter-crystalline restraints are minimized. Crystallite dimensional changes were calculated from the present data according to the thermal expansivity relations for the dimensional changes occurring at 750 to 800 C and according to the preferred orientation relations for samples irradiated at ~1250 C. Details of the calculation methods have been described previously (Ref. 31). Because of the high degree of preferred orientation in the materials employed, the values obtained are not particularly sensitive to the method of extrapolation.

The calculated crystallite changes are shown in Figs. 19 and 20. The results illustrate the fact that the crystallite change rates increase with decreasing crystallite size and increasing irradiation temperature over the temperature range ~800 to 1250 C.

THERMAL EXPANSION COEFFICIENTS

The thermal expansion coefficients of the hot-worked graphite and massive pyrolytic carbon samples in the two principal directions were measured as a function of fast-neutron exposure. The results are shown in Figs. 21 and 22. At 750 to 800 C the expansion coefficient of the hot-worked graphite parallel to the hot-working axis showed a gradual increase with neutron exposure, rising from $15 \times 10^{-6} \text{ C}^{-1}$ (unirradiated) to $17 \times 10^{-6} \text{ C}^{-1}$ at $1.5 \times 10^{21} \text{ n/sq cm}$. The coefficient remained unchanged perpendicular to the axis. However, at 1250 C the expansion coefficient parallel to the axis showed an initial rise, passed through a maximum of $19 \times 10^{-6} \text{ C}^{-1}$ at $2 \times 10^{21} \text{ n/sq cm}$ ($E > 0.18 \text{ MeV}$), and

Fig. 19. Crystallite dimensional changes in massive pyrocarbon, hot-worked graphite, and massive pyrocarbon annealed at 3300 C; irradiated at 750 to 800 C

Fig. 20. Crystallite dimensional changes in massive pyrocarbon, hot-worked graphite, and massive pyrocarbon annealed at 3300 C; irradiated at 1225 to 1290 C

Fig. 21. Thermal expansivity of massive pyrocarbon and hot-worked graphite irradiated at 750 to 800 C

Fig. 22. Thermal expansivity of massive pyrocarbon and hot-worked graphite irradiated at 1225 to 1290 C

then fell to about half its original value by 9.7×10^{21} n/sq cm ($E > 0.18$ MeV). In the perpendicular direction it increased from $1 \times 10^{-6} \text{ C}^{-1}$ to $2 \times 10^{-6} \text{ C}^{-1}$ over the same neutron exposure. The massive pyrolytic carbon behaved somewhat differently. At 750 to 800 C the thermal expansion coefficient was unchanged by the irradiation. At 1250 C perpendicular to the deposit, it increased rapidly from 25 to $27 \times 10^{-6} \text{ C}^{-1}$ and showed no sign of a subsequent decrease, despite the formation of delamination cracks. Parallel to the deposit there was no significant change.

The initial increase in thermal expansion coefficient parallel to the axis of the hot-worked graphite at 750 to 800 C and at 1250 C is probably caused by the closure of microcracks. The "turn-down" in expansion coefficient at high exposures at 1250 C resembles that reported in several polycrystalline graphites irradiated at 170 to 200 C, where the damage retention is also very large (Ref. 32). The effect may be due to the generation of fresh porosity at high damage levels.

METALLOGRAPHIC EXAMINATION

Metallographic examination of as-deposited massive pyrolytic carbon irradiated at ~ 1250 C (Fig. 23) showed that macroscopic delamination cracks 2 to 3 mm long started to form at about 4×10^{21} n/sq cm, and their number increased with increasing exposure. The cracks tended to follow bands of inhomogeneity in the growth cone structure. No microcracks were detected in this material. In contrast, annealed pyrolytic carbon (Fig. 24) showed no gross cracking, but irradiation produced many fine microcracks $\sim 10 \mu\text{m}$ long. The microcracks formed parallel to the basal planes and did not extend beyond one growth cone. There was no visible change in the microstructure of hot-worked graphite (Fig. 25).

The fact that the annealed pyrolytic carbon forms microcracks more readily than as-deposited material, despite its greater dimensional stability, probably results from the lower cleavage strength of the

M25239-1

(a)

M25239-2

(b)

M25240-2

(c)

M25240-1

(d)

Fig. 23. Photomicrographs of massive pyrocarbon: (a) and (b) unirradiated, and (c) and (d) irradiated to 5.9×10^{21} n/sq cm at 1225 to 1290 C; (a) and (c) bright field, and (b) and (d) polarized light; original X200, reduced 75% in reproduction

M24288-1

(a)

M24288-2

(b)

M25241-3

(c)

M25241-4

(d)

Fig. 24. Photomicrographs of massive pyrocarbon annealed at 3300 C: (a) and (b) unirradiated, and (c) and (d) irradiated to 5.9×10^{21} n/sq cm at 1225 to 1250 C; (a) and (c) bright field, (b) and (d) polarized light; original X200, reduced 75% in reproduction

M25237-1

(a)

M25237-2

(b)

M25238-1

(c)

M25238-2

(d)

Fig. 25. Photomicrographs of hot-worked graphite: (a) and (b) unirradiated, and (c) and (d) irradiated to 5.9×10^{21} n/sq cm at 1225 to 1290 C; (a) and (c) bright field, and (b) and (d) polarized light; original X500, reduced 75% in reproduction

annealed material. Thus the stresses generated at the low-angle boundaries between growth cones are sufficient to cause cleavage cracks within a single cone

X-RAY DIFFRACTION

Irradiation caused an increase in X-ray peak width for all materials. The changes are shown in Fig. 26. The fractional increase was greatest for the most crystalline material. The interlayer spacings showed a small increase (0.2 to 0.3%) on irradiation for all materials and conditions, except for as-deposited pyrolytic carbon irradiated at 1250 C, in which the layer spacing decreased by 0.3 to 0.4%. Limited data for material irradiated at the lower temperature (750 to 800 C) show that the peak width and layer spacing change more rapidly than at the higher temperature, reflecting the smaller defect clusters formed at the lower temperatures.

Fig. 26. Change in layer spacing and apparent crystallite size for as-deposited massive pyrocarbon, hot-worked graphite, and massive pyrocarbon annealed at 3300 C as a function of neutron exposure. Irradiation temperature was 1225 to 1290 C except where otherwise indicated.

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

G. B. Engle and R. J. Price

An experiment to measure the irradiation-induced creep in a number of nuclear graphites has been in progress since May 1966. This experiment was started on the HTGR Base Program at Gulf General Atomic.* The experiment was first described in a Base Program Quarterly Report (Ref. 33) and was later described in more detail in another Base Program Quarterly Report (Ref. 34). The experiment was patterned along the lines of previous work started by the Dragon Project (Ref. 35). The irradiation of the specimens has proceeded for about 3 yr, and the irradiation phase has been completed. The postirradiation examinations and formal report of the results will be done by Dragon personnel. Monitoring of the post-irradiation examination, correspondence of preirradiation data to the Dragon Project, interpretation of the data, and report writing for Gulf General Atomic have been transferred to this program.

A summary of the experimental method is given here, along with the results of visual inspection of the specimens at the Dragon Project on May 15 and 16, 1969.

In selecting graphites for advanced high-temperature gas-cooled reactors, it is essential to have a knowledge of the dimensional changes and creep constants at relatively high temperature, i.e., > 800 C. It is believed that the creep constant may be dependent on the microstructure and, therefore, the crystallite size of the graphite. The dimensional changes and creep constants are therefore being measured on four graphites, designated H-328, H-327, 9567, and TS-688. All of these graphites are produced in large diameters and represent materials with crystallite sizes

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

in the range 300 to 1500 Å. Other properties have ranges as follows: strength, 1000 to 3000 psi in tension; crystallite orientation by BAF, 1.00 to 1.75; and thermal expansivity, 0.9×10^{-6} to $5.7 \times 10^{-6} \text{ C}^{-1}$.

For the creep-strain samples (see Fig. 27), the pads or split sleeves were prepared from a variety of graphites for which dimensional changes were known up to 1200 C and $4 \times 10^{21} \text{ n/sq cm}$. The dumbbell sections were prepared in such a manner that the samples would be stressed by differential shrinkage between the pads and the dumbbells, and the differential strain could be obtained by comparison with the unrestrained specimens. The creep-strain assemblies were constructed for use in the range 800 to 1150 C. The creep assemblies were designed to cover three strain rates.

The irradiation period began in 1966, and the samples were discharged in April 1969. They have accumulated about 1.5 to $2.0 \times 10^{21} \text{ n/sq cm}$ ($E > 0.18 \text{ MeV}$) at 850 to 1100 C.

The specimens were visually inspected in May by representatives from Gulf General Atomic and Dragon. The specimens were in good condition and showed no signs of corrosion. Radioactivity was low, and all specimens could be handled on the bench for postirradiation examinations. All creep assemblies of high strain rate were broken in their gage lengths, whereas all those of low strain rate survived. Those of medium strain rate survived or broke in a systematic manner, depending on temperature or neutron flux.

Postirradiation measurements will be made at Dragon or Reactor Centrum Nederland, Petten, Holland, and will include:

1. Dimensions on all free-standing pads and creep specimens.
2. Measurements of thermal expansion on all creep assemblies that survived, both as-assembled and with pads removed. Selected free-standing specimens will also be measured. The measurements will be made from room temperature to the irradiation temperature.

LC75624

Fig. 27. Creep specimens and split pads for Dragon creep experiment

3. Room temperature measurements of Young's modulus will be made on creep and free-standing specimens.

After the data have been examined, a decision will be made by Dragon personnel with regard to continuing irradiation of the specimens that survived.

IX. ANNEALING STUDIES OF IRRADIATED PYROLYTIC CARBON STRUCTURES

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

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 approximately 1200 C. The large dimensional changes observed in pyrolytic carbons irradiated at approximately 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. 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 12.

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

TABLE 12
PROPERTIES OF IRRADIATED CARBONS USED IN ANNEALING STUDIES

Structure Number	Deposition Temp. (C)	Annealing Treatment	Irradiation Conditions		Structural Properties			
			Temp. (C)	Neutron Exposure $\times 10^{-21}$ (E > 0.18 MeV) (n/sq cm)	Density (g/cc)	L_c (Å)	Bacon Anisotropy Factor	Layer Spacing (Å)
2	1400	None	540	1.6	2.074	43	1.65	3.44
2	1400	None	620	1.5	2.078	42		3.43
2	1400	None	890	2.4	2.073	56		3.42
2	1400	None	1040	2.4	2.064	60		3.42
2	1400	None	1060	2.2	2.069	47		3.42
6	2000	None	540	1.6	2.036	154	1.30	3.40
6	2000	None	620	1.5	2.038	154		3.40
6	2000	None	890	2.4	2.082	95		3.41
6	2000	None	1040	2.4	2.076	94		3.40
6	2000	None	1060	2.2	2.084	87		3.41
1-G	1400	2 hr at 2800 C	540	1.6	2.193	279	2.6	3.34
1-G	1400	2 hr at 2800 C	890	2.4	2.104	127		3.36
1-G	1400	2 hr at 2800 C	1060	2.2	2.156	123		3.36
2-A	1400	4 hr at 1900 C	1040	2.4	2.027	75	1.66	3.41
5	1650	None	540	1.6	1.685	61	1.0	3.39
5	1650	None	1060	2.2	1.914	46		3.42

The properties measured were 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 selected disk samples of an isotropic and an annealed laminar carbon was measured prior to annealing, and the same disks were 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 increased by 100 C increments to 3000 C. Property measurements have been completed, except for the hardness measurements. Results obtained up to 2600 C were reported in the last annual report (Ref. 15).

To avoid repetition, the plots showing the property changes will be presented in a forthcoming topical report. The curves show trends in properties during annealing that are generally similar for all irradiated carbons. At about 1400 C, the electrical resistivity, layer spacing, and X-ray peak width start to decrease. At the same temperature, the samples start to contract perpendicular to the deposit and to expand parallel to the deposit. These changes are in the opposite direction to those occurring during irradiation. However, the density of the samples tended to increase during annealing, which is a continuation of the irradiation-induced change. The rate of property change increased with increasing annealing temperature up to 2300 to 2400 C, after which the rates of change decreased. Most property changes were almost saturated by 2800 C.

The property changes in the laminar pyrolytic carbon were almost independent of irradiation conditions and result from the annealing of the as-deposited structure. This point is illustrated by the fact that recovery of the properties of several samples went considerably beyond

the irradiation-induced changes. The isochronal annealing curves were typical sigmoidal annealing curves with a sharp "knee," whose maximum slope occurs at about 2300 C.

The laminar pyrolytic carbon annealed at 2800 C before irradiation and the unannealable isotropic pyrolytic carbons show a response to post-irradiation 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 pyrolytic carbons. This annealing process is attributed to the rearrangement of irradiation-induced defects. In the samples irradiated at 900 to 1000 C, only 1/4 to 1/2 of the irradiation-induced dimensional change was recovered; however, the reduction in layer spacing and X-ray peak width was more complete in these high-temperature irradiated samples than in the less severely damaged low-temperature irradiated samples.

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 that were annealed before irradiation, the ratio of a-axis expansion to c-axis contraction is low (approximately 0.3). In the isotropic carbons, this ratio rises from approximately 0.35 to approximately 0.45 to 0.5 as the annealing temperature is increased. The ratio for the unannealed laminar carbons remains constant at approximately 0.45. These results suggest that the annealing of irradiation-induced defects is accompanied by a crystallite volume decrease, whereas the annealing of the as-deposited structure takes place at nearly constant volume.

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

The interpretation of annealing effects in irradiated materials is a difficult problem. In the present experiments the problem is complicated by the fact that several of the carbons were taken above their deposition temperature during annealing and, in the case of the laminar carbons, the annealing effects resulted from annealing of the as-deposited structure and were independent of irradiation conditions. However, other experimental work on annealing irradiated graphite (Refs. 36-40), and in particular recent electron microscope observations by Thrower (Refs. 39 and 40) of irradiated and annealed massive pyrocarbon, provides grounds for hypothesis about the probable nature of the irradiation-induced defects and their annealing processes. Under the present conditions of irradiation, the defects in the pyrolytic carbon samples may be assumed to consist of relatively small vacancy loops within the basal planes and large sheets of interstitials between the basal planes at twist boundaries. During irradiation many vacancies would have been lost to the lattice in collapsed vacancy lines or at crystallite boundaries, but these defects would not be expected to contribute to subsequent annealing behavior.

The observed property changes that occur on annealing may be explained in terms of these defect arrangements. The decrease in electrical resistivity may be attributed to the reduction in the number of vacancy loops, which act as electron scattering centers (Ref. 41). No quantitative relationships between loop concentration and resistivity have been proposed.

The crystallite dimensional changes (c-axis contraction and a-axis expansion) may be explained partially by the growth and collapse of vacancy loops, which would cause c-axis shrinkage and a "Poisson's ratio" a-axis expansion. However, the magnitude of the dimensional change recovery, particularly in the a-direction, seems too large to be explained by this process alone, and it is probable that some of the smaller interstitial loops are also eliminated. To a first approximation the crystallite

c-axis expansion is proportional to the number of atoms present in interstitial clusters plus the number of vacancies in uncollapsed vacancy loops. The unannealable part of the dimensional change may be attributed to the large interstitial sheets between the layer planes and the vacancies lost at crystallite edges.

Both the crystallite density and the layer spacing would be affected principally by uncollapsed vacancy loops. The fact that the fractional change in density is close to the fractional change in layer spacing supports this explanation. The change in layer spacing and density would be roughly proportional to the number of atoms in uncollapsed loops.

The X-ray line-broadening in carbons is complex and difficult to interpret, but the presence of vacancy loops would certainly increase the line broadening. This effect has been analyzed for cubic materials (Ref. 42). The analysis indicated that the broadened line profiles would approximate to a Gaussian or a Lorentzian curve, depending on the amount of lattice distortion. In the present case the profiles were close to a Lorentzian curve; for this case, in cubic materials, the line width is proportional to the number of atoms present in loops and is independent of the loop radius (Ref. 42).

When annealing processes take place over a wide temperature range, the kinetics of the processes may be interpreted in terms of a range of frequency factors or a range of activation energies, or both (Ref. 19). Complete determination of the kinetic parameters in this case is difficult, and, in any case, a single series of isochronal anneals does not yield sufficient data for a complete analysis. However, it is possible to estimate the range of activation energies of the annealing process by making the simplifying assumption that the annealing out of the defect loops involves a single frequency factor of $\sim 10^{13} \text{ sec}^{-1}$. The estimates will be fairly insensitive to the value chosen.

In the present work the hour-long anneals were performed at a series of 100 C temperature increments. This may be approximated to an annealing temperature that steadily increases at the rate of 2.8×10^{-2} C/sec. The appropriate equations that lead to the distribution function for the activation energy are given by Primak (Ref. 19):

$$p_o(\bar{\epsilon}) = -\left(\frac{dP}{d(KT)}\right) \left(\frac{1}{1 + \frac{\bar{\epsilon}}{KT}}\right) \quad (1)$$

$$\bar{\epsilon} = \epsilon_o + 0.577KT \quad (2)$$

$$\frac{\epsilon_o}{KT} + \ln \left(\frac{\epsilon_o}{KT} + 2 \right) = \ln AcKT \quad (3)$$

In the above equations, $p_o(\bar{\epsilon})$ is the relative number of kinetic processes that can occur with a characteristic activation energy $\bar{\epsilon}$; P is a property that is proportional to the number of processes which can occur, for example, the number of atoms present in annealable loops; K is Boltzmann's constant; T is the absolute temperature, ϵ_o is another characteristic activation energy specific to a certain annealing temperature, which can be determined by solving Eq. 3; A is the frequency factor, here assumed to be 10^{13} sec^{-1} ; and c is the rate of heating, $2.8 \times 10^{-2} \text{ K/sec}$.

For the reasons given above, most of the property changes measured during annealing can be assumed to be proportional to the number of atoms remaining in annealable loops. The slopes of the smoothed curves for property versus annealing temperature can therefore be used in Eqs. 1 through 3 to determine the distribution functions for the activation energies of the kinetic processes involved. The results of such calculations for samples irradiated at 1060 C to $2.2 \times 10^{21} \text{ n/sq cm}$ are shown in Fig. 28. With the exception of the curves derived from the X-ray line

Fig. 28. Distribution function of the activation energies for annealing the irradiation effects in pyrolytic carbons

broadening, the distribution functions have similar shapes for all properties of the three carbons studied. This supports the assumption that the properties are roughly proportional to the same structural parameter, such as the number of atoms remaining in loops. Activation energies start at 5 to 5.5 eV, pass through a low peak or plateau at ~ 6 eV, and rise to a second and usually higher peak at 8.5 eV. The activation energies for annealing the line broadening cover the same range, but the distribution curves are different. This is probably because the assumptions leading to the conclusion that the line width is proportional to the concentration of atoms in loops are oversimplified.

Activation energies for the annealing of vacancy and interstitial loops in irradiated graphite crystals have been determined from electron microscope observations (Refs. 38, 43). The present value of 5 to 5.5 eV for the activation energy at which annealing starts is in excellent agreement with the reported value of 5.4 eV for the removal of loops in the presence of a supersaturation of vacancies (Ref. 43), such as would be present after irradiation. The peak in the distribution function at ~ 8.5 eV agrees well with the value of 8.3 ± 0.3 eV for the removal of loops by self-annealing (Ref. 38). These values are the same regardless of the nature of the loop (Ref. 38). The good agreement may be partly coincidental because the values depend on the assumption of a single-valued frequency factor of 10^{13} sec^{-1} . However, because similar assumptions were made in the analysis of the electron microscope data, the suggested interpretation of the annealing effects in terms of the removal of vacancy and interstitial loops is supported.

The thermal diffusivity of several pyrolytic carbon disks was measured between room temperature and 800 C, using the flash method (Ref. 44). The samples included an isotropic pyrolytic carbon irradiated to $1.5 \times 10^{21} \text{ n/sq cm}$ ($E > 0.18 \text{ MeV}$) at 540 C; the same carbon structure irradiated to $2.4 \times 10^{21} \text{ n/sq cm}$ ($E > 0.18 \text{ MeV}$) at 890 C; and a laminar carbon annealed at 2800 C before irradiation to $1.5 \times 10^{21} \text{ n/sq cm}$ at 540 C. Comparison samples that had been annealed to 3000 C after irradiation

were also measured. The results are shown in Figs. 29 through 31, together with room temperature measurements made on as-deposited companion samples. The results show that the conductivity of the isotropic carbon was reduced more by irradiation at the high temperature than by irradiation at the low temperature. Postirradiation annealing at 3000 C increased the conductivity by a factor of 1.5 to 3 over the irradiated levels, and to higher values than for as-deposited material. The conductivities of the irradiated and annealed samples showed a strong negative temperature dependence. The temperature dependence was similar to that of well crystallized graphite, but the absolute values of the conductivity were less by a factor of 10 than for graphite.

Fig. 29. Thermal conductivity as a function of temperature for laminar pyrolytic carbon annealed at 2800 C before irradiation. Irradiation took place at 540 C to 1.5×10^{21} n/sq cm ($E > 0.18$ MeV). Postirradiation annealing temperature was 3000 C.

Fig. 30. Thermal conductivity as a function of temperature for isotropic pyrolytic carbon irradiated at 540 C to 1.5×10^{21} n/sq cm ($E > 0.18$ MeV). Postirradiation annealing temperature was 3000 C.

Fig. 31. Thermal conductivity as a function of temperature for isotropic pyrolytic carbon irradiated at 890 C to 2.4×10^{21} n/sq cm ($E > 0.18$ MeV). Postirradiation annealing temperature was 3000 C.

X. IRRADIATION EFFECTS IN CARBONS AND GRAPHITE^{*}

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IRRADIATION-INDUCED DIMENSIONAL CHANGES IN HTI CARBONS

Results from the third irradiation of carbon specimens in Capsule GE-H-13-15 and those from the P13J and P13K capsule specimens have significantly extended the data that relate the dimensional behavior of turbostratic carbons to their structure. The data are now sufficiently extensive to warrant an interim summary of all the data, together with a discussion of the implications of the results to our overall understanding of irradiation effects in carbons and graphite. Essential background material has been recently summarized in Ref. 45; accordingly, only a brief introduction is presented here.

When polycrystalline carbons and graphites are irradiated with fast neutrons, carbon atoms are displaced from their positions in the lattice to produce a homogeneous dispersion of interstitials and vacancies. Depending on the temperature, the defects interact and diffuse to various crystal defects, where they are annihilated. Many of the interstitials end up in new layer planes that are nucleated between the original layers. The net result is that the individual crystallite tends to grow in the c-direction and to contract in the a-direction (Fig. 32). Because the rates of rearrangement of the defects that are generated by the irradiation are determined by diffusion and because the annihilation sites are predominantly crystal defects, the temperature dependence of the shape change is complex and the changes are strongly structure sensitive (Ref. 46). The main obstacle to the development of a useful quantitative model based on simple atomistic processes to describe the dimensional behavior of practical carbonaceous materials, i.e., anything other than

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Fig. 32. Schematic diagram illustrating the dimensional changes induced in a carbon crystallite by fast-neutron irradiation. (a) before irradiation; (b) after irradiation

a single crystal, has been the inability to accurately characterize the crystal structure of quasicrystalline carbons and graphites. Hence, most attempts at developing a model have been based on phenomenology (Refs. 47, 48).

It has been shown that the dimensional changes of bulk samples of turbostratic carbon can be related to the individual crystallite changes if one uses the simple crystallite averaging procedures that were first applied by Bacon (Ref. 49) to describe the thermal expansion behavior of polycrystalline graphite and later used by others (Refs. 4, 22, 50) to interpret bulk dimensional changes induced in carbons and graphites by fast-neutron irradiation. In this approach, the strain in a bulk dimension, $\ln[1 + (\Delta\ell_i/\ell_i)]$, is related to the principal crystallite strains in the c- and a-directions, $\ln[1 + (\Delta X_c/X_c)]$ and $\ln[1 + (\Delta X_a/X_a)]$, by a preferred orientation parameter R that is determined by X-ray diffraction (Ref. 51):

$$\ln \left(1 + \frac{\Delta\ell_i}{\ell_i} \right) = R_i \ln \left(1 + \frac{\Delta X_a}{X_a} \right) + (1 - R_i) \ln \left(1 + \frac{\Delta X_c}{X_c} \right). \quad (1)$$

Since turbostratic pyrolytic carbons are crystallographically symmetrical about the normal to the deposition plane, each deposit is characterized by two R values, $R_{||}$ and $R_{\perp}$ (Ref. 22). The two R parameters are related by

$$R_{||} = 1 - (R_{\perp}/2). \quad (2)$$

$R_{\perp}$ is related to the Bacon Anisotropy Factor (BAF) by

$$R_{\perp} = \frac{2}{2 + \text{BAF}}. \quad (3)$$

All the values of $\ln [1 + (\Delta\ell_{||}/\ell_{||})]$ and $\ln[1 + (\Delta\ell_{\perp}/\ell_{\perp})]$ that are now available for turbostratic carbons irradiated at 900 C are plotted in Fig. 33 as a function of the original $R_{||}$ and $R_{\perp}$ values. The data are

Fig. 33. Plots of $\ln[1 + (\Delta l_i/l_i)]$ versus the preferred orientation parameter R_i for HTI carbons ($50 \text{ \AA} < L_c < 200 \text{ \AA}$) with $\rho_o > 2.1 \text{ g/cc}$ irradiated at 900°C

for dense ($\rho_o > 2.1$ g/cc) turbostratic carbons with $50 \text{ \AA} < L_c < 200 \text{ \AA}$ (HTI carbons). At low fluences ($< 3 \times 10^{21}$ n/sq cm, $E > 0.18$ MeV), the data for all the carbons fall on a single straight line, which means that the crystallites in all the carbons have changed shape by the same amount and that the crystallite strain is independent of the anisotropy of the deposits. There are no significant deviations due to crystallite interactions such as are observed for similar plots relating thermal expansivity to preferred orientation (Ref. 50). The principal crystallite changes can be obtained by extrapolating the linear plots to $R_{\perp} = 0$ and $R_{\parallel} = 1$.

For fluences $> 3.0 \times 10^{21}$ n/sq cm, the data for all the carbons at a given fluence do not fall on a single straight line, but rather describe a sigmoidal-shaped curve. Measurements of the degree of preferred orientation of specimens irradiated to 5.6×10^{21} n/sq cm at ~ 1000 C have shown that the sigmoidal shape is not due to changes in preferred orientation that are caused by the irradiation (Ref. 52). Since the sigmoidal shape is not due to changes in anisotropy, the explanation probably is that the rate at which the crystallites change shape accelerates due to the irradiation and the effect is most pronounced for the isotropic carbons, i.e., those with $R_{\perp}$ and $R_{\parallel}$ nearest $2/3$. Since it is well known that the rate at which the crystallites change dimensions during irradiation at 900 C is most rapid for the most poorly crystalline carbons, and since the degradation of the crystalline structure is expected to be most rapid for dense isotropic carbons in which crystallite interactions are a maximum, it is suggested that the sigmoidal-shaped curves in Fig. 33 develop as a result of an autocatalytic increase in the rate at which the crystallites in the dense, most isotropic deposits change shape. The increase is taken to be due to the structural degradation of these carbons during irradiation.

For an irradiation temperature of 900 C, the rate at which the crystallites in a dense, nearly isotropic (BAF = 1.2) carbon change dimension are compared in Fig. 34 with the corresponding rate for the

Fig. 34. Crystallite c-direction growth $\ln[1 + (\Delta X_c/X_c)]$ versus neutron exposure ($E > 0.18$ MeV) for dense ($\rho_o > 2.1$ g/cc) HTI carbons irradiated at 900 C.

crystallites in an anisotropic (BAF = 2.4) carbon. The data in Fig. 34 were derived from those in Fig. 33 by extrapolating the data for each exposure to $R_{\perp} = 0$ and $R_{\parallel} = 1$ for the cases BAF = 1.2 and 2.4. The curves in Fig. 34 show that the c-direction growth rate is nearly constant for the anisotropic carbon deposit, but accelerates rapidly with exposure for the nearly isotropic carbon. At an exposure between 4 and 5×10^{21} n/sq cm, the rate is about 0.8 per 10^{21} n/sq cm, which is nearly equal to the maximum rate possible for the case in which every displaced atom ends up in a position in a new layer plane that was formed during the irradiation (Refs. 53, 54).

Further insight into the damage to carbon caused by neutron irradiation at 900 C is obtained from the dimensional changes measured for nearly isotropic (BAF < 1.1) carbon. Of particular interest is the effect of the original density of the deposit on its dimensional behavior. Just as the acceleration effect noted for dense carbons approached a maximum as the BAF approached 1.0, one might expect that the acceleration effect for isotropic carbon would be maximum for the most dense deposits. This is because internal porosity can provide internal accommodation of crystallite strains (Ref. 50), which means that crystallite interactions must be most severe in dense deposits with a minimum of porosity.

The crystallite c-direction growth rate for dense anisotropic deposits during irradiation to low fluences at 900 C is about 0.2 per 10^{21} n/sq cm (Ref. 46). Hence, when the plot in Fig. 35 is used, the maximum rate of dimensional change for isotropic (BAF < 1.1) carbon can be estimated. Since the uncertainty in measured values of the BAF may be as much as 0.05, a value of 1.15 is used as the maximum possible BAF for carbons with measured values of BAF < 1.1. The plot shows that the perpendicular growth rate of a dense carbon with BAF = 1.15 is 0.01 per 10^{21} n/sq cm. Without acceleration, strains of about 0.1 are expected for an exposure of 10^{22} n/sq cm. If there is an acceleration effect and no change in anisotropy due to irradiation, the maximum theoretical limit for the perpendicular

Fig.35. Plot relating bulk dimensional changes, $\ln [1 + (\Delta \ell_i / \ell_i)]$, for bodies with various degrees of preferred orientation to the crystallite dimensional changes ($R = 0$ and 1) for dense HTI carbons irradiated at 900, 1000, and 1250 C

growth rate can be estimated from the maximum theoretical limit for the c-axis growth rate, i.e., 1 per 10^{21} n/sq cm (Refs. 53,54). The value for a dense, nearly isotropic carbon with BAF = 1.15 is 0.05 per 10^{21} n/sq cm, or 0.5 per 10^{22} n/sq cm.

The dimensional change data for isotropic (BAF < 1.1) carbons irradiated at 900 to 1000 C are plotted in Fig. 36 as a function of their preirradiation density. The upper curve for each exposure is for the perpendicular direction; the lower curve is for the parallel direction. The data show that all the carbons shrink isotropically at low exposures and the shrinkage rate is maximum for the carbons with the lowest density. At an exposure of about 3×10^{21} n/sq cm, all the carbons start to behave anisotropically; the effect is most pronounced for the densest carbons. At higher exposures, the anisotropy of the dimensional changes is more pronounced, and the dependence on density becomes strong for carbons with densities above about 1.9 g/cc. At an exposure of 5.6×10^{21} n/sq cm, the perpendicular growth for the most dense carbon is about 0.25. For no change in preferred orientation and no acceleration of the crystallite dimensional change rate, the curve for low fluences at 900 C in Fig. 35 predicts a bulk dimensional change of only 0.05 at an exposure of 5×10^{21} n/sq cm. Since postirradiation measurements have shown no significant change of preferred orientation for isotropic specimens irradiated to 5.6×10^{21} n/sq cm at 1000 C, the conclusion is the same as that reached for the anisotropic deposits discussed above; i.e., at 900 to 1000 C, there is an acceleration in the crystallite dimensional change rate and the effect is most pronounced for the most dense, isotropic carbons.

The dimensional changes for the specimens in Fig. 36 irradiated to 6.0×10^{21} n/sq cm and above are in excess of those predicted from the calculated maximum theoretical rate. This must mean that at exposures above about 6×10^{21} n/sq cm at 900 to 1000 C, changes in preferred orientation must be caused by the irradiation. Postirradiation preferred orientation measurements on specimens irradiated to in excess of 6×10^{21} n/sq cm at 900 to 1000 C have not been reported. In order to explain the measured changes plotted in Fig. 36 for the most dense carbons irradiated to 6.0×10^{21} to 6.6×10^{21} n/sq cm, the BAF would have had to increase to at least 1.3.

Fig. 36. Bulk dimensional changes $\ln[1 + (\Delta l/l)]$ plotted as a function of preirradiation density for isotropic (BAF < 1.1) carbons with L_c between 50 Å and 200 Å irradiated at 900 and 1000 C. The uppermost curve at each fluence is for the perpendicular direction; the lower curve is for the parallel direction. For easy comparison, the curve for 4.6×10^{21} n/sq cm (at 900 C) has been plotted on both graphs

In summary, it may be concluded that the crystal structure of turbostratic carbon ($50 \text{ \AA} < L_c < 200 \text{ \AA}$) irradiated at a temperature near 900 C is changed by the irradiation, and that for the most dense, isotropic carbons the changes cause an acceleration in the crystallite dimensional change rate. These changes are suggested to be due primarily to an irradiation-induced degradation of the crystal structure, which leads to increasing dimensional instability. At exposures above about 6×10^{21} n/sq cm, irradiation-induced increases in preferred orientation are suspected. These ideas are illustrated schematically in Fig. 37; the data relating the volume expansion associated with porosity generation during the irradiation to the neutron exposure are plotted in Fig. 38.

Although many features of the dimensional behavior of turbostratic carbon irradiated at 1250 C are similar to those observed for specimens irradiated at 900 C, there are several important differences. At 1250 C, the rate at which the crystallites change dimensions and the rate of initial densification are higher than they are at 900 C (Fig. 39). Comparison of the data in Figs. 38 and 39 shows that at 1250 C the maxima in the individual curves are greater than the corresponding maxima reached at 900 C, and, at high exposures, the magnitudes of the expansions at 900 C are greater than they are at 1250 C. The data in Fig. 40 emphasize the latter point.

Another difference between the effects of irradiation at 900 C and at 1200 C is brought out by data shown in Fig. 41, which compares the changes in the apparent crystallite height L_c for carbons with the same initial structure that were irradiated at 900 C and at 1200 C. The data show that the L_c parameter is reduced much more during irradiation at 900 C than it is at 1200 C. The fact that the crystal structure is degraded less rapidly at 1200 C than at 900 C, in spite of the fact that the rate at which the crystallite changes shape is much higher at 1200 C than it is at 900 C, has been attributed to more rapid and effective intercrystalline irradiation creep at the higher temperature (Ref. 45). The same rationalization is offered to explain the more rapid volume expansion at 900 C than at 1200 C (Fig. 40).

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PORES

IRRADIATION-
INDUCED SUB-
BOUNDARIES

AFTER IRRADIATION

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Fig. 37. Schematic diagram illustrating irradiation-induced expansion and structural degradation of initially dense, isotropic turbostratic carbon irradiated at $\sim 900^\circ\text{C}$, where irradiation creep between crystallites is not very effective

Fig. 38. Density of turbostratic carbons ($50 \text{ \AA} < L_c < 200 \text{ \AA}$) versus neutron exposure for irradiation at 900 to 1000 C

Fig. 39. Density of turbostratic carbons ($50 \text{ \AA} < L_c < 200 \text{ \AA}$) versus neutron exposure for irradiations at 1250 C

Fig. 40. Density of a turbostratic carbon ($L_c = 145 \text{ \AA}$) versus neutron exposure for irradiations at 900 and 800 C followed by irradiations at either 1000 or 1280 C

Fig. 41. Change in L_c due to irradiation at 900 and 1200 C versus the original L_c parameter

The bulk dimensional changes $\ln[1 + (\Delta l_{\perp}/l_{\perp})]$ and $\ln[1 + (\Delta l_{\parallel}/l_{\parallel})]$ for turbostratic carbons irradiated at 1250 C are plotted in Fig. 42 as a function of the original $R_{\perp}$ and $R_{\parallel}$ values. The data are for dense ($\rho_0 > 2.1$ g/cc) turbostratic carbons ($50 \text{ \AA} < L_c < 200 \text{ \AA}$). The responses to irradiation are similar to those plotted in Fig. 33 for irradiations at 900 C. For exposures above about 2×10^{21} n/sq cm, the data points described a sigmoidal-shaped curve. Analysis of the data in Fig. 42 using the data for a highly oriented carbon (BAF = 2.4, $R_{\perp} = 0.45$, $R_{\parallel} = 0.775$) and a nearly isotropic carbon (BAF = 1.33, $R_{\perp} = 0.60$, $R_{\parallel} = 0.70$) yields the crystallite growth $\ln[1 + (\Delta X_c/X_c)]$ as a function of neutron exposure for the two structures (Fig. 43). These data are similar to those derived for carbons irradiated at 900 C (Fig. 34), except that crystallite growth rates for both carbons irradiated at 1250 C are greater. It should be noted specifically that the growth rate calculated for the carbon with an initial BAF of 2.4 is almost twice that calculated to be theoretically possible. An obvious explanation is that important changes in preferred orientation occur during irradiation at temperatures above 1000 C (Ref. 3).

The bulk dimensional changes for turbostratic HTI (BAF < 1.1) carbon irradiated at 1250 C are plotted in Fig. 44 as a function of their original density. The extrapolations in Fig. 35 show that if changes in anisotropy do not occur and the crystallite growth rate is constant and equal to 0.5 per 10^{21} n/sq cm, then the maximum bulk change $\ln[1 + (\Delta l/l)]$ in the perpendicular direction would be 0.5 for the samples irradiated to 9.3 to 10.3×10^{21} n/sq cm. The actual change was 1.0. These differences may be attributable to accelerations in the crystallite growth rate due to both degradation of the crystal structure caused by irradiation and irradiation-induced increases in preferred orientation. The two effects cannot be separated until the postirradiation anisotropy of the specimens has been measured. These measurements are in progress.

Fig. 42. Bulk dimensional change $\ln[1 + (\Delta l/l)]$ versus R_i for dense ($\rho_0 > 2.1 \text{ g/cc}$) HTI carbons ($50 \text{ \AA} < L_c < 200 \text{ \AA}$) irradiated at 1250 C

Fig. 43. Crystallite c-direction growth $\ln[1 + (\Delta X_c/X_c)]$ versus neutron exposure ($E > 0.18$ MeV) for dense ($\rho_o > 2.1$ g/cc) carbons irradiated at 1250 C

Fig. 44. Bulk dimensional changes $\ln[1 + (\Delta l/l)]$ versus the preirradiation density for isotropic (BAF < 1.1) HTI carbons irradiated at 1250 C. The open points are for the perpendicular direction and the solid points are for the parallel direction

The schematic diagram in Fig. 45 provides a summary of the rationalization of the dimensional changes that occur in HTI carbons at 1250 C. At 1250 C, effects similar to those that occur at 900 C are observed. The crystal structure is degraded by the irradiation at 1250 C, but to a lesser extent than that which occurs at 900 C. Changes in preferred orientation are more pronounced at 1250 C than at 900 C. Both effects are likely to be manifestations of the fact that irradiation creep is more effective in relieving internally generated stress between crystallites at 1250 C than at 900 C. Because crystallite interactions must be most intense for dense, isotropic deposits, the accelerations in bulk growth rates due both to increases in the rate at which the crystallites change shape and to increases in anisotropy are most pronounced for these carbons.

The changes in thermal conductivity of HTI carbon caused by irradiation at 900 C and at 1250 C that are shown in Fig. 46 are consistent with the above rationalization. After irradiation, the thermal conductivities of specimens irradiated at 900 C are all lower by at least a factor of two than those for specimens irradiated at 1200 C, and the lowest postirradiation conductivities are for those carbons with the highest preirradiation density. More extensive thermal conductivity data for irradiated HTI carbons can be found in Ref. 55.

For engineering purposes, it is most convenient to have data such as those in Figs. 36 and 44 plotted to show the dimensional changes as a function of exposure. Accordingly, the data in Figs. 36 and 44, together with data for irradiations at 600 and 1100 C given in Figs. 47a and 47b, have been plotted (Fig. 48) to illustrate the neutron-exposure dependence of the dimensional changes induced in isotropic ($\text{BAF} < 1.1$) HTI carbons for irradiation temperatures of 600, 900, 1100, and 1250 C. The data in Figs. 48a through 48c are for preirradiation densities of 1.55, 1.70, and 1.90 g/cc, respectively. Similar plots for slightly anisotropic ($\text{BAF} = 1.3$) carbon with a preirradiation density of 2.0 g/cc are presented in Fig. 49a and for a very anisotropic ($\text{BAF} = 2.2$) carbon with a preirradiation density of 2.1 g/cc in Fig. 49b.

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Fig. 45. Schematic diagram illustrating irradiation-induced expansion, structural degradation, and increases in preferred orientation for initially dense, nearly isotropic turbostratic carbons irradiated at 1250 C, where irradiation creep between crystallites is effective

Fig. 46. Thermal conductivity at 500 C for unirradiated HTI carbons and for carbons irradiated at 900 and 1200 C, plotted as a function of the preirradiation density

Fig. 47. Bulk dimensional change versus preirradiation density for isotropic (BAF < 1.1) HTI carbons. (a) Irradiated at 600 C. The open points are for perpendicular directions; the solid points are for parallel directions

Fig. 47. Bulk dimensional change versus preirradiation density for isotropic (BAF < 1.1) HTI carbons. (b) Irradiated at 1100 C

Fig. 48. Bulk dimensional change versus neutron exposure ($E > 0.18 \text{ MeV}$) for isotropic (BAF < 1.1) HTI carbons ($50 \text{ \AA} < L_c < 200 \text{ \AA}$) irradiated at 600, 900, 1100, and 1250 C. (a) Preirradiation density of 1.55 g/cc

Fig. 48. Bulk dimensional change versus neutron exposure ($E > 0.18 \text{ MeV}$) for isotropic (BAF < 1.1) HTI carbons ($50 \text{ \AA} < L_c < 200 \text{ \AA}$) irradiated at 600, 900, 1100, and 1250 C. (b) Preirradiation density of 1.7 g/cc

Fig. 48. Bulk dimensional change versus neutron exposure ($E > 0.18 \text{ MeV}$) for isotropic (BAF < 1.1) HTI carbons ($50 \text{ \AA} < L_c < 200 \text{ \AA}$) irradiated at 600, 900, 1100, and 1250 C. (c) Preirradiation density of 1.9 g/cc

Fig. 49. Bulk dimensional changes versus neutron exposure ($E > 0.18 \text{ MeV}$) for anisotropic carbon with $50 \text{ \AA} < L_c < 200 \text{ \AA}$ irradiated at 600, 900, 1100, and 1250 C (a) BAF = 1.3 and $\rho_0 = 2.0 \text{ g/cc}$

Fig. 49. Bulk dimensional changes versus neutron exposure ($E > 0.18 \text{ MeV}$) for anisotropic carbon with $50 \text{ \AA} < L_c < 200 \text{ \AA}$ irradiated at 600, 900, 1100, and 1250 C (b) BAF = 2.2 and $\rho_o = 2.1 \text{ g/cc}$

The data in Fig. 48 contrast the weak temperature dependence of the shrinkage due to densification at low exposures with the strong temperature dependence of the shape change at high exposures. Of particular interest is the fact that the lowest density ($\rho_0 = 1.55$ g/cc) isotropic carbons offer the best overall dimensional stability. To survive as a coating on a relatively unyielding support such as an overcoat on a SiC layer, however, a carbon with an initial density of 1.5 g/cc must endure high shrinkage rates early in life. The shrinkage rate for the carbon with $\rho_0 = 1.55$ g/cc is about 6% per 10^{21} n/sq cm at 1250 C. Irradiation creep data reported in Ref. 45 indicate that at 1250 C, a shrinkage rate of 6% per 10^{21} n/sq cm is just tolerable without fracture. In a recent test of coated nuclear fuel particles (Capsule P23), in which coatings on particles with and without underlying SiC layers were irradiated to $\sim 2 \times 10^{21}$ n/sq cm at 1200 to 1300 C, coatings with initial densities of 1.55 g/cc survived. Since a lower limit of 10% for the total creep strains has been established at 1250 C, these results suggest that low-density carbon coatings should survive to at least 6×10^{21} n/sq cm at 1250 C when irradiated as an overcoat on SiC substrates and to higher doses when irradiated as an overcoat on low-density buffer coatings such as on a BISO particle.

Only a meager amount of creep data has been accumulated since that in Ref. 45 was published. Additional data points at an exposure of 3.2×10^{21} n/sq cm have been added to the data for irradiation at 900 C (Fig. 50). The envelope of the data points in Fig. 50 approximates the creep curve at the fracture stress. These data, together with those in Ref. 45, show that creep strains of 2, 3, and 6% per 10^{21} n/sq cm are tolerable at 600, 900, and 1200 C, respectively, and that total creep strains of at least 10% are possible at 900 and 1200 C.

One of the questions that remains to be answered is the influence of prior irradiations at one temperature on subsequent irradiation at another temperature. Data in Ref. 52 show that for turbostratic carbons with $120 \text{ \AA} < L_c < 200 \text{ \AA}$, an irradiation to a low exposure at ~ 600 C has no

Fig. 50. Creep strain versus neutron exposure for irradiations at 900 C
(open points from Ref. 55)

influence on subsequent irradiation behavior at 900 C; i.e., there is no seeding effect. Other data in Ref. 45 indicate that irradiations to substantial exposures at high temperature have a pronounced effect on irradiations at lower temperatures. It was shown that a prior irradiation at 1650 C was much more damaging than an irradiation at 950 C to the same exposure. Difficulties arise, however, when one tries to establish an equivalent between the damage accumulated at high irradiation temperatures and that accumulated at low temperatures, because states of damage can be attained during irradiation at high temperature that are never achieved in the same carbon during irradiation at a lower temperature.

Data illustrating the effect of an irradiation at 800 to 900 C on subsequent dimensional behavior during irradiation at 1280 C are presented in Figs. 40 and 51. For this case (a temperature increase during irradiation), the data suggest that it may be possible to establish an equivalent-damage rule. If the data in Fig. 40 for the irradiation at 1280 C are translated horizontally to lower exposures and are fitted on the curve in Fig. 39 for $\rho_0 = 2.0$ g/cc, then the position of the segment of the curve in Fig. 40 for the 1280 C irradiation agrees reasonably well with the corresponding data in Fig. 39. Similarly, if the curves on Fig. 51 for the segment of the irradiation at 1280 C are translated horizontally to lower exposures until the points initially at 4.4×10^{21} n/sq cm fall on the corresponding curves in Fig. 49a for the carbon with the same initial structure, then the positions of the segments of the curve on Fig. 51 for the 1280 C irradiation agree reasonably well with corresponding data on Fig. 49a. Although the procedure works for this particular case, more data will be needed to determine if the correspondence is a mere fortuity. Work is in progress to obtain more data relating the effect of irradiation damage accumulated at one temperature on subsequent behavior during irradiation at another temperature.

Fig. 51. Bulk dimensional change for a carbon with $L_c = 145 \text{ \AA}$, BAF = 1.3, and $\rho_o = 2.0 \text{ g/cc}$ irradiated at 900 and 800 C and then at either 1000 or 1280 C

DEPENDENCE OF THE DIMENSIONAL STABILITY OF CARBON AND GRAPHITE ON THEIR CRYSTALLINE PERFECTION

The reactor cores of HTGRs are constructed of a variety of carbonaceous materials, the crystal structures and morphologies of which vary widely. Accordingly, studies have been carried out on the relationship between crystalline perfection and dimensional behavior.

Lineal bulk dimensional changes for dense materials with high degrees of preferred orientation are plotted in Fig. 52. The data are for natural graphite crystals, annealed pyrolytic graphite, catalytically graphitized carbon, and turbostratic carbon. Structural parameters characterizing each material are listed in Fig. 52a. For the natural crystals, the data give the crystallite changes directly. Since the other materials are not perfectly oriented, the crystallite changes must be obtained by a Bacon extrapolation. At low exposures, where changes in preferred orientation and the accelerating effects of accumulated irradiation damage are not pronounced, one can obtain an estimate of the crystallite changes by multiplying the lineal changes in Figs. 52a and 52b for the annealed pyrolytic, catalytically graphitized, and the turbostratic carbon by 1.2, 3.1, and 3.5, respectively. Note that because of the relations shown in Fig. 34, the crystallite changes obtained from the high-fluence data are peculiar only to these particular materials and cannot be used generally to determine the bulk changes of carbonaceous materials with different morphologies (i.e., different internal restraints) or different degrees of preferred orientation.

In any case, the data demonstrate the strong dependence at high irradiation temperature of neutron-induced dimensional changes on the initial crystalline perfection of carbonaceous materials. At 600 C (Fig. 52c), the data for all the materials fall together, and the dependence on crystalline perfection is minimal.

Fig. 52. Bulk lineal dimensional changes versus neutron exposure ($E > 0.18 \text{ MeV}$) for carbonaceous materials with structures that vary widely in crystalline perfection. (a) Irradiated at 1250 C

Fig. 52. Bulk lineal dimensional changes versus neutron exposure ($E > 0.18 \text{ MeV}$) for carbonaceous materials with structures that vary widely in crystalline perfection. (b) Irradiated at 900 to 1000 C (the data for the natural crystals irradiated at 900 C extend to $3 \times 10^{21} \text{ n/sq cm}$ and are coincident with those for annealed pyrolytic graphite)

Fig. 52. Bulk lineal dimensional changes versus neutron exposure ($E > 0.18$ MeV) for carbonaceous materials with structures that vary widely in crystalline perfection. (c) Irradiated at 600 C (at 600 C, the data for all materials fall in the indicated bands)

XI. TOPICAL REPORTS AND PUBLICATIONS

The following oral presentations were made at the Ninth Biennial Conference on Carbon, Boston, Massachusetts, June 16-20, 1969:

Price, R. J., "Effects of High-Temperature Neutron Irradiation on Highly Oriented Carbons and Graphites."

Engle, G. B., "Irradiation Behavior of Nuclear Graphites at 950 to 1250 C to 10^{22} n/sq cm."

Bokros, J. C., "The Control of the Structure and Properties of Pyrolytic Carbon."

The following reports have been issued:

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

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

Bokros, J. C., et al., "Radiation-Induced Dimensional Changes and Creep in Carbonaceous Materials," J. Nucl. Mater. 31, 25 (1969).

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