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AEC RESEARCH AND
DEVELOPMENT REPORT

GA-9975

RESEARCH ON GRAPHITE

MASTER

THREE-YEAR SUMMARY REPORT

MAY 15, 1967, THROUGH MAY 14, 1970

by

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

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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1. INTRODUCTION

This report summarizes the research work completed during the 3 years from May 15, 1967, through May 14, 1970. The major objective of the program was 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 fabrication and the service behavior of these materials. The materials studied during the course of the work were composed of carbon in a wide variety of structures, ranging from nearly amorphous forms to highly crystalline states. The experimental work consisted of studies on carbonization, catalytic graphitization, characterization of microstructures, and irradiation of the various materials.

The research efforts were directed toward defining the structure of the various materials, learning the relations between structure and properties relevant to reactor applications, and evaluating methods for the preparation of new or modified structures with improved properties.

The results during the 3-year period are summarized in this report in four topical sections. Topical reports have been completed to cover the work reported in all sections except those on highly oriented graphites (Section 6.3) and on thermal conductivity and irradiation creep of artificial graphites (Sections 6.4.4 and 6.4.5, respectively). The titles of these reports are listed in the Appendix. The reader is referred to the topical reports for full details.

Two types of materials were studied: (1) graphitic bodies prepared from conventional binder and filler materials, and (2) model materials. The artificial graphites were 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 model materials provided closely

controlled structures through adjustment of the deposition or annealing conditions. These materials are representative of various components of artificial graphites, as well as coatings for fuel particles.

The various conventionally processed artificial graphites and model materials were characterized by their crystallinity (X-ray diffraction parameters), preferred orientation, density, and microstructure. Work on cokes, graphites, and model materials also included studies of the structural transitions produced by heat treatment, both with and without catalytic additives. The investigations of artificial graphites included measurements of density and structural distributions by micrographic and X-ray examination of density fractions which were obtained by separating powdered specimens in a densimeter.

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

The irradiation experiments were conducted in fully instrumented capsules operated in conjunction with other programs, e.g., at Gulf General Atomic 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]. Cooperative irradiations were also done with the help of Battelle Pacific Northwest Laboratory and the Dragon Project. Close liaison was maintained with the above projects or laboratories and Oak Ridge National Laboratory.

2. CONCLUSIONS AND SUMMARY

2.1. CONCLUSIONS

The results of the studies of model carbons have provided several new viewpoints that are useful guides in the development of "ideally stable" nuclear graphites. It was found that mechanical interactions between distorting crystallites in addition to crystallite stability can be an important factor that enhances dimensional changes and contributes to instability at high fluences. For isotropic carbons or graphites with small to moderate crystallite sizes, there should exist a temperature ($T_{\text{max. int.}}$) where the effects of mechanical interactions are a maximum. High density in the unirradiated materials enhances the degree of mechanical interactions (and associated effects), and thus high bulk densities are not necessary for stability at high fluences and extremely high densities may be detrimental. Large crystallite sizes are no longer considered to be an unqualified requisite for stability at high fluences, because a high degree of crystalline perfection leads to low strength (few cross-links and low internal strength). Isotropic bodies with high "internal strength" are expected to be more stable at high fluence than weaker bodies (especially near $T_{\text{max. int.}}$).

These results, therefore, lead to the conclusion that the ideally stable nuclear graphite will likely be isotropic, have a moderate density, and have high internal strength, i.e., an intermediate crystallite size. Presently among the artificial graphites, certain Poco graphites have structures that most nearly approach the ideal structure.

The data from the characterization and irradiation of binder-filler graphites are consistent with those of the model carbons and show that the solid portion of the various artificial graphites, i.e., the crystallites, do in fact closely follow the irradiation behavior of the model materials.

The complicating factor of porosity has been further characterized in binder-filler graphites and its relationship to dimensional and property changes has been further revealed. The following criteria were developed for stable graphites from the graphite studies and tend to strongly reinforce the guides formulated from data on the model carbons.

Maximization of the crystallite size combined with isotropy and strength are desirable for better irradiation stability. However, there appears to be a maximum size of about 400 to 600 Å for binder-filler graphites, above which a further increase in crystallite size tends to reduce the strength and increase the anisotropy. Binder-filler graphites that have a wide range of crystallite sizes but contain structures that are predominantly graphitic and aligned will show the least stability. These materials are usually weak. Graphites composed of semigraphitic and isotropic structure coexisting with approximately equal amounts of highly aligned graphitic structure will have intermediate stability. These materials will have a wide range of crystallite sizes. Graphites that are composed predominantly of fine-grained, semigraphitic, isotropic structure will be the most stable. Poco and Gilsonite graphites, as mentioned previously, are current examples of materials that approach the ideally stable graphite.

2.2. SUMMARY

2.2.1. The Morphology of the Carbonaceous Mesophase Formed in the Pyrolysis of Coal-Tar Pitch

Observations by polarized light of the microstructures formed during the pyrolysis of coal-tar pitches used in the fabrication of graphitic artifacts have directed attention to the narrow range of temperature during which the carbonizing liquid exists as a liquid crystal called the carbonaceous mesophase. Three mechanisms - the mesophase transformation itself, the coalescence of the initial spherules to bulk mesophase, and the plastic flow before hardening - act to establish the lamelliform morphology of the carbonaceous mesophase. Prominent features in observations by crossed

polarizers are the nodal points and centers of crosses, which do not move when the plane of polarization is rotated. These features are identified as four types of linear defects in the stacking of the aromatic layer molecules. Fine insoluble particles are segregated by the mesophase transformation, and the effect of graphitic substrate particles is to align the mesophase layers parallel to the layer planes of the substrate. Upon heat treatment of the hardened mesophase to graphitizing temperatures, shrinkage-cracking and fine-scale mechanisms of fold-sharpening and polygonization take place to yield the final microstructure of the graphitic product.

2.2.2. Catalytic Graphitization of Pyrolytic Carbons, Petroleum Cokes, and Graphites

An isotropic pyrolytic carbon co-deposited at 2200°C with 9.7 wt % titanium started to recrystallize heterogeneously to well-ordered graphite at 2300°C during isochronal annealing, and recrystallization was complete at 2500°C. A laminar pyrolytic carbon that was deposited at 1225°C and contained 6.7 wt% titanium did not show catalytic graphitization. Both the titanium-doped laminar carbon deposited at 1225°C and an undoped companion carbon showed a steady increase in L_c and density and a steady reduction in layer spacing and microhardness over a wide temperature range (1400° to 2800°C). Significant reduction in electrical resistivity did not start until ~1800°C. Catalytically graphitized pyrolytic carbon changed dimensions at 0.3 to 0.10 of an ungraphitized pyrolytic carbon with the same preferred orientation when irradiated between 600° and 1250°C.

Graphite compacts prepared with aluminum-doped cokes graphitized completely at 2300°C. The transformation of the carbon structure to graphitic structure exceeded the amount expected from a simple decomposition of Al_4C_3 by a factor of 3 to 13 when the aluminum content was about 17 wt % in the baked article. The transformation from carbon to graphite is believed to take place by the solution of carbon in the Al_4C_3 and the rejection of graphite. The driving force for the reaction is the difference in free energy between the disordered carbon and the graphite.

The aluminum-doped graphite compacts had low bulk densities due to the loss of Al_4C_3 during heat treatment. The apparent density increased when the material was completely converted to graphite due to the higher density of the graphite crystals.

Zirconium carbide enhanced the graphitization of needle-coke carbons at 2400° to 2500°C after short heat treatments, but the samples were no better than the control samples after longer heating periods.

2.2.3. Characterization of Graphites

An apparatus was constructed and a procedure was developed to determine quantitatively the density and structural distributions within a solid graphite sample. The procedure provided for the recovery of the density fractions in sufficient quantity so that further structural examinations could be performed on each.

Anisotropic needle-coke materials were shown to contain regions of semigraphitic carbon structure (L_c values of $350 \text{ \AA}$) that were isotropic coexisting with regions of highly crystalline carbon structure (L_c values of $1600 \text{ \AA}$) that were highly aligned. The structural features correlated with the apparent density of the volumetric fractions and showed increasing crystallinity and orientation as the density increased. In near-isotropic materials the value and range of apparent crystallite sizes were considerably smaller than for anisotropic graphites and the dependence on density was less pronounced. Poco graphites, which are extremely isotropic, showed a minimum spread in L_c values.

Porosity was identified in three domains of the graphite microstructures: intercrystallite pores or defects (V_{p_1}), pores that are external to the sink-float particles but closed to measuring liquids in the bulk sample (V_{p_2}), and large open pores due to filler particle mismatches and frozen-in pores in the binder formed during carbonization (V_{p_3}). The characterization measurements led to a microstructural model for binder-filler graphites that was used in the irradiation studies to show the internal rearrangements that take place in graphites during irradiation at high temperatures.

No strong correlations were found between the thermal expansivity of the graphites and porosity, but a precise relationship was found between the mean $\bar{L}_c$ (determined from densimetric data) of the various materials and their volume thermal expansivities. The thermal expansivity decreased systematically with increasing volumes of crystalline material in the microstructures.

2.2.4. Model Materials

A considerable effort has been devoted to studies of model materials that are relatively simple and homogeneous in their crystal structure, easy to characterize, and free of complications imposed by the presence of complex networks of pores that are common in artificial graphites. Model materials studied were: (1) natural graphite crystals, (2) annealed massive pyrolytic graphite, (3) high-density, anisotropic turbostratic pyrolytic carbons, (4) catalytically graphitized high-density anisotropic carbons, and (5) isotropic turbostratic carbons deposited at high temperatures (HTI) and at low temperatures (LTI).

The data from irradiations of HTI and LTI carbons were useful in revealing the irradiation behavior of artificial graphites and in the design of carbon coated fuel particles for HTGRs.

These studies have shown that the effect of crystalline perfection on the rate at which crystallites change shape during irradiation varies markedly with irradiation temperature. If other factors are held constant, increasing the degree of crystalline perfection increases the dimensional stability. The effect was most pronounced for low fluences and at irradiation temperatures above 800°C. This conclusion is valid for all carbonaceous conglomerates irradiated to low fluences. At high fluences, especially at high temperatures, new effects were found that were caused by crystallite interactions and the above conclusion no longer applies.

As the degree of preferred orientation is increased the materials behave more anisotropically, and the behavior of the bulk dimensions approaches that of the individual crystallites that make up the aggregate. Other factors being constant, maximum stability should be obtained for isotropic bodies.

In the model carbons the density defect is made up of a uniform spectrum of submicroscopic pores that, for a given density, does not vary markedly from carbon to carbon. At low fluences the density increases. Eventually, however, the rate at which new pores are generated due to interactions between crystallites becomes important and the formation of new pores overwhelms the closure of pre-existing pores and eventually net volume expansion results. The volumetric data obtained for high-strength LTI model carbons suggest that high internal strength is important in retarding pore generation at high fluences.

During irradiation at low fluences isotropic carbons with $\rho_0 < 2.22 \text{ g/cm}^3$ shrink isotropically. At higher fluences and especially at high irradiation temperatures, these materials start to behave anisotropically, shrinking in the direction parallel to the deposition plane and expanding in the perpendicular direction. The effect is most pronounced for high-density deposits. High density enhances stability at low fluences but at high fluences the effect is reversed and high density leads to instability.

The complex behavior at high fluences is interpreted as follows. As the crystallites in an aggregate change shape, the interactions between crystallites are at first accommodated by internal porosity and inter-crystallite irradiation creep. Under these circumstances, the behavior of the bulk is closely approximated by the averaged value of the behavior of the crystallites. At high fluences, however, when the internal porosity is nearly gone, the interactions between crystallites become intense. Stresses between crystallites rise and new voids are formed either by stress-directed diffusion of vacancies or by fracture at boundaries. As a result of these interactions, the crystal structure is degraded, causing an acceleration in the rate at which the crystallites change dimension. Since the inter-

actions are most severe in dense, isotropic materials, the accelerations are most pronounced for these carbons.

The volume expansion and the accelerations at high fluences are more pronounced in HTI carbons than in the stronger LTI carbons. This is in spite of the fact that LTI carbons are less crystalline than HTI carbons. The apparently anomalous behavior has been attributed to the fact that cross-links present in the LTI carbons increase the internal binding and retard void generation. The fact that local displacements at boundaries are small when the crystallites are small may also be a factor.

Plastic strains at least as high as 10% in tension can be accumulated and creep rates of 2.5, 5, and 6% per 10^{21} n/cm² can be sustained at 600°, 900°, and 1250°C, respectively, in the model carbons without exceeding the fracture stress. No dependences of creep rate on structure have been found. Estimates of the creep constant for the model carbons are in the same range as those reported for artificial graphites.

Irradiations of model materials in experiments in which the temperature was changed during the exposure have shown that a prior irradiation at a high temperature accelerates the dimensional changes in a subsequent irradiation at a lower temperature. The effect appears to be general, occurring over the full range of experimental temperatures. The results from multiple irradiations at different temperatures have shown definitely that the irradiation-induced changes in dimensions that occur are not simply the cumulative sum of results obtained in isothermal irradiations.

The data for the model carbons indicate that at some intermediate irradiation temperatures, effects such as exaggerated volume expansion, rapid degradation of crystal structure, and accelerations in the dimensional change rate will be a maximum and the interactions will be most pronounced for the isotropic carbons of highest density.

The degradation in crystalline perfection for HTI carbons is more severe at 900°C than at 1200°C. Thermal conductivity changes caused by irradiation at 900° and 1200°C are also in accord with the concept of a temperature where mechanical interactions are at a maximum ($T_{\text{max. int.}}$).

The data indicate that at high temperature and especially near $T_{\text{max. int.}}$, high density will contribute to dimensional instability. Accordingly, the studies of model materials suggest that the near-isotropic nuclear graphites such as Poco or Gilsonite-coke graphites, which are of intermediate density, should be the most stable among graphites.

At high fluences the stronger LTI carbons neither expand as much nor exhibit the large accelerating effects observed for HTI carbons. From these observations an inference may be made that the effects of mechanical interactions between crystallites are less effective in causing accelerations in dimensional change rates for materials with high internal strength and that void generation is retarded in high-strength material. In general, increasing strengths are obtained by decreasing crystallite size. This means that increasing crystallite sizes to enhance the stability of the crystallites might actually cause a net decrease in stability at high fluences because of a loss of internal strength (or cross-links).

2.2.5. Annealing of Irradiated Pyrolytic Carbons

Isochronal annealing studies of pyrolytic carbons irradiated at 540° to 1060°C to 1.5 to 2.4×10^{21} n/cm² ($E > 0.18$ MeV) show that recovery of the dimensions, layer spacing, (002) peak width, electrical resistivity, and microhardness starts at ~1200° to 1600°C and occurs most rapidly at 2200° to 2400°C. For irradiation temperatures of 540° and 620°C the crystallite dimensions revert fully to their preirradiation value by 3000°C, but for higher irradiation temperatures 60 to 80% of the crystallite dimensional change is unannealable.

For isotropic carbons irradiated below 900°C a slight increase in electrical resistivity occurs on annealing past the irradiation temperature. For samples irradiated at 890° to 1060°C, postirradiation annealing reduced the layer spacing, (002) peak width, and thermal resistivity to below their preirradiation levels.

An activation energy of 5 to 5.5 eV was calculated for the earliest annealing steps, with a peak in the distribution function at ~8.5 eV. The annealing processes may be explained by the presence of irradiation-induced vacancy loops within the layer planes, which are removed during annealing, and larger sheets of interstitials located at crystallite twist boundaries that resist annealing.

2.2.6. Highly Oriented Graphites

In this work, the specimens consisted of highly oriented ATJ hot-worked graphite, massive pyrolytic carbon deposited at about 2200°C, and massive pyrolytic carbon annealed at 2900° to 3300°C. The apparent crystallite sizes (220 to 1600 Å) spanned the range encountered in the components of artificial nuclear graphites. The materials were irradiated to a maximum fluence of 14×10^{21} n/cm² at 1225° to 1300°C.

The parallel and perpendicular dimensional changes increased linearly with neutron exposure except for the hot-worked graphite irradiated at ~1250°C. For this material the dimensional change rates were significantly lower for fluences beyond 6×10^{21} n/cm² than for fluences up to 6×10^{21} n/cm².

Crystallite change rates increase with decreasing crystallite size and increasing irradiation temperature over the temperature range from ~800° to 1250°C.

A "turn-down" in the thermal expansion coefficient in the preferred c-direction of hot-worked graphite at high exposures at 1250°C was found, which resembles that reported in isotropic graphites. Both the turn-down of the thermal expansion coefficient and the decrease in dimensional change rate at high exposures in the hot-worked graphite may be due to an increase in intercrystallite restraints at high damage levels.

Metallographic examination of as-deposited massive pyrolytic carbon irradiated at ~1250°C showed that macroscopic delamination cracks started to form at about 4×10^{21} n/cm². No visible change in the microstructure of hot-worked graphite was observed.

The fractional change in L_c was greatest for the most crystalline material.

2.2.7. Artificial Commercial Graphites

A number of anisotropic and near-isotropic commercial graphites were irradiated at 300° to 1500°C to 1.5×10^{22} n/cm² ($E > 0.18$ MeV). At 1175° to 1280°C, where fluences were taken to 1.5×10^{22} n/cm², the graphites changed dimensions in both the preferred a-axis and c-axis directions by initial contraction followed by turnaround and rapid expansion. The dimensional changes were quite sensitive to the microstructures of the individual graphites. The maximum volume contraction of each material was shown to correlate with the mean apparent crystallite size $\bar{L}_c$ and crystallite size distribution of the graphites provided they had similar crystallite orientation parameters (BAFs), i.e., anisotropic or near-isotropic structures. Pores, shown to be located between crystallite clusters (V_{p2}), were eliminated during densification by accommodating c-axis expansion. The rate of elimination of these pores increased with increasing irradiation temperature. Intercrystallite pores were also formed during densification and expansion. Larger pores were observed to form between filler particles during the expansion phase at high fluences and accounted for the large volume expansions of the graphites. The ease of formation of these pores and cracks and the expansion rate after turnaround were dependent on the volume

percent of highly graphitic material in the structure. The near-isotropic materials had lower expansion rates and contained the lowest volumes of graphitic structure. These results were consistent with those obtained on model carbons and substantiate that isotropic structures are more stable than anisotropic structures during high-temperature irradiation. The above results on binder-filler graphites provide additional data on the interaction of the crystallites and porosity that exists only in materials processed by the binder-filler manufacturing technique.

The thermal expansivity of near-isotropic materials decreased with fluence at the onset of bulk volume expansion, while the anisotropic needle-coke materials showed either no change or a rapid increase. Materials that had a predominance of highly oriented graphitic structure increased in thermal expansivity, but a systematic shift toward a predominance of isotropic and semigraphitic structure shifted the thermal expansivity changes to a decrease. The thermal expansivity did not change in a material that had evenly balanced volumes of the two types of structure.

Considerable scatter was found in the dimensional data of specimens cut from production-grade needle-coke graphites irradiated above 900°C. The scatter was particularly high among the specimens after maximum densification had been achieved at about $3 \text{ to } 5 \times 10^{21} \text{ n/cm}^2$ and expansion had begun. In this range of fluence and temperature, needle-coke graphites are highly unpredictable and the rate of expansion depended critically on the microstructure of the particular specimen under test. The data for a near-isotropic Gilsonite material contrasted with the needle-coke data and showed considerably less scatter.

No differences in the dimensional or volumetric changes were observed between samples located at the center or edge of a particular production log. However, this result may not hold for other needle-coke materials that show property gradients across the logs.

The thermal conductivity of the production-grade graphites was found to range from 0.04 to 0.08 cal/cm-sec-°C when irradiated and measured at 500° to 1000°C after 1.70 to 6.0×10^{21} n/cm² and was not dependent on material, temperature, or fluence in the above range.

Needle-coke graphites prepared in the laboratory under controlled conditions where the fraction of the pitch-binder coke was varied systematically over the range 5.5 to 14.2 wt % were irradiated to $\sim 10^{22}$ n/cm² at 1225°C. Dimensional changes were strongly affected by the binder-coke fraction. Changes along the longitudinal axis (parallel) were sensitive to the binder-coke fraction, showing decreasing expansion with increasing binder-coke fraction, up to an optimum value of about 11 wt %, and an increase again at higher values. The perpendicular changes were also dependent on binder-coke fraction, showing larger contractions by a factor of 2 when the coke fraction was increased to 14 wt %. Thermal expansivity changes followed the dimensional changes.

The solid material underwent little change in density during the bulk densification phase, but started to expand when the bulk expanded. In the materials with a deficiency of binder coke, the breakaway expansion was observed at low fluences and proceeded at a more rapid rate than in materials of optimum binder content. The data suggest an optimum binder content for this series of materials of about 11 wt %, but the optimum value may be different when other filler particles and binders are used and fabrication processes differ.

The volume change of loose needle-coke particles, which were irradiated along with the above compacts, showed a significant increase in volume expansion even at low fluences over the formed compact, which had not expanded to the same extent at 9.7×10^{21} n/cm². The needle-coke particles expanded rapidly when they were not restrained by the binder coke. The binder coke is believed to provide a condition of restraint on the filler particles in addition to the restraints resulting from crystallite interactions within the filler particles. By increasing the binder-coke content, the contraction of the filler particles was enhanced but their expansion was restricted.

When anisotropic needle-coke graphites and near-isotropic graphites were irradiated initially to $\sim 3 \times 10^{21}$ n/cm² at $\sim 1000^\circ\text{C}$ and then to higher fluences at 760° to 800°C , the rate of dimensional change did not adjust to the slower rate expected for the lower temperature. When the initial irradiation was done at 1450°C to $\sim 3 \times 10^{21}$ n/cm² and was followed by irradiation at 1225° to 1250°C to 9×10^{21} n/cm², the dimensional change rate was higher than that for specimens irradiated to 9×10^{21} n/cm² entirely at 1225° to 1250°C . These data are consistent with the more extensive data on model carbons and indicate that temperature history effects are important in utilizing the graphite data for design purposes.

Thermal conductivity has been measured at room temperature on Gilsonite and needle-coke materials after irradiation to about 6×10^{21} n/cm² at 1000° and 1200°C . The fractional change in thermal conductivity was large, ranging from 70 to 80% after irradiation at $\sim 1000^\circ$ to 1100°C to only about 50% after irradiation at 1200°C . Annealing for 5 or 10 min at or above 1250°C produced a rapid rate of recovery of the thermal conductivity, followed by a much slower rate up to 500 to 1800 min. A graphite irradiated at 1190°C , which had smaller initial fractional changes, recovered to about the same fractional change as those irradiated at 1000° to 1100°C . The specimens that had progressed furthest in dimensional changes, those irradiated at $\sim 1200^\circ\text{C}$, had the smallest fractional changes in thermal conductivity. The specimens irradiated at $\sim 1200^\circ\text{C}$ do not contain as many annealable defects as those irradiated at 1000°C , implying that considerable thermal annealing is accomplished during irradiation at 1200°C over that at 1000°C . The damage was considerably more difficult to remove as the fluence was increased, even though the total fractional change did not increase considerably with fluence. This indicates that the defects that cause changes in thermal conductivity at high temperatures are more numerous at 1000°C than at $\sim 1200^\circ\text{C}$. A spectrum of vacancy cluster sizes is indicated above 1000°C , with the 1200°C samples having the fewest and largest. This condition may result because thermal annealing is more rapid at 1200°C , causing rapid removal of the small defects by diffusion to produce larger clusters.

An activation energy of ~ 5.8 eV was estimated from the annealing of fractional changes of thermal conductivity in a specimen of H-327 graphite irradiated at $\sim 1000^\circ\text{C}$ to $\sim 6.7 \times 10^{21}$ n/cm².

The Dragon creep work has been extended to the examination of U.S. graphites currently under consideration for HTGRs. The experimental arrangement provided for dumbbell specimens, restrained by pad materials that changed dimensions at a different rate than the dumbbells, to be irradiated in the Dragon Reactor to 2×10^{21} n/cm² at 875° to 1235°C . The restrained specimens were strained at three different rates by the selection of pad materials that varied in dimensional changes.

The dimensional changes for the pad materials were about -0.7 +1.25, and +5% at 2×10^{21} n/cm² at 1090° to 1295° and confirmed pre-irradiation estimates that three widely different strain rates would result in the creep assemblies. All creep specimens, except one, fractured under the high strain rate after irradiation at 1090° to 1235°C to 2.4×10^{21} n/cm², while all those under the low strain rate survived. About one-half of the specimens under the intermediate strain rate survived and one-half fractured; thus, it was possible to determine a preliminary critical strain rate ($\sim 10^{-3}/10^{20}$ n/cm²) from the slope of a line separating the failed and survived specimens on a plot of estimated strain versus fluence. Assuming a common fracture stress for all graphites of ~ 1500 psi, a preliminary creep constant was estimated to be about $K = 6.7 \times 10^{-7} (\text{psi})^{-1} (10^{-20} \text{ n/cm}^2)$ for all materials, which is in excellent agreement with data for Dragon graphites. The estimated creep constant at 880° to 1060°C agreed with the data at 1090° to 1235°C .

3. THE MORPHOLOGY OF THE CARBONACEOUS MESOPHASE FORMED IN THE PYROLYSIS OF COAL-TAR PITCH*

J. L. White

3.1. INTRODUCTION

Recent investigations by several groups (Refs. 1-7) on the structural conditions for graphitizability have demonstrated the significance of the mesophase transformation that takes place in graphitizable organic materials during pyrolysis at temperatures in the neighborhood of 450°C. This transformation is a two-phase, liquid-state, structural transition in which the polymerizing, aromatic, layer molecules are aligned in a parallel array to form a viscous liquid crystal.

In the initial stages of nucleation and growth, the carbonaceous mesophase appears as spherules with the simple structure originally defined by Brooks and Taylor (Ref. 1) (see Fig. 1). The aromatic layer molecules lie perpendicular to a polar diameter and curve to meet the pitch-mesophase interface normally. However, as carbonization progresses, the growing spherules coalesce and deform to form relatively complex structures that are the precursors to the structures observed in fully graphitized materials. The purpose of the work summarized here was to characterize the structural features of the coalesced mesophase, to investigate the effects of heat treatment on these structures, and to learn the relationships between mesophase morphology and certain graphitic substrate materials that may be used as fillers in the fabrication of graphites for reactor fuel systems.

*The results summarized in this section are contained in EUR-4094. See report number 5 in the Appendix for full reference. A portion of this work was also reported in Refs. 4, 5, and 7.

CROSSED POLARIZERS

STRUCTURAL SKETCH OF
MESOPHASE SPHERULES

K77932

Fig. 1. Structure of mesophase spherules formed by the pyrolysis of an extracted coal-tar pitch to 464°C

Various types of coal-tar pitch were studied, including typical binder and impregnating pitches. A process of solvent extraction with tetrahydrofuran was used to remove the insoluble particles in order to simplify the micrographic studies in the initial work.

Although no quantitative studies of the kinetics of the mesophase transition have been made, it is clear that the transition is quite sensitive to temperature (Refs. 1,2,6,7). Accordingly, a temperature-gradient heat-treatment technique was used to obtain a series of specimens representative of slightly varying degrees of heat treatment (Ref. 7).

3.2. MESOPHASE MORPHOLOGIES ESTABLISHED BY COALESCENCE AND DEFORMATION

The mesophase is readily distinguishable from the isotropic parent liquid phase from which it is formed by its optical anisotropy. When a micrographic section of the mesophase is examined under polarized light with crossed polarizers, extinction contours are observed depending on the orientation of the layer planes relative to the plane of section and to the plane of polarization of the incident light. By using an overlay-sketching technique with polarized-light and sensitive-tint photomicrographs, the mesophase microstructure can be sketched in terms of the intersections of the layer planes with the plane of section (Ref. 4).

As indicated by the schematic diagram in Fig. 2, four basic configurations of extinction contours are found in the coalesced mesophase. These configurations comprise both co-rotating and counter-rotating nodes and crosses, the rotation occurring when the plane of polarization of the incident light is rotated, and correspond to four types of defects in the stacking of the mesophase layer planes.

Specimens illustrating the process of coalescence between spherules to form the bulk mesophase were examined to learn how the defect structures are initially formed. The cross structures were found to predominate in the freshly coalesced mesophase.

K82513

Fig. 2. Schematic diagram of the four types of layer-stacking defects found in the carbonaceous mesophase

When pyrolysis is continued beyond the temperature of the mesophase transformation, gas bubbles nucleate and grow in the mesophase. As the bubbles percolate through the viscous mesophase, various regions are subjected to large plastic strains, leading to an increasingly fine texture of extinction contours. Two types of fine texture can be distinguished: a fibrous texture and a more equiaxed, mosaic texture. The fibrous texture is usually found in the vicinity of a bubble and is comprised of tightly folded mesophase layers. Although these textures become too fine in scale to be readily sketched by the overlay technique, examination at the highest optical magnifications reveals that the nodes and crosses in the extinction contours possess essentially the same character as found in the mesophase immediately after the initial coalescence (Ref. 5).

3.3. EFFECTS OF HEAT TREATMENT

The carbonaceous mesophase loses its plasticity on being pyrolyzed to temperatures in excess of about 500°C, the precise hardening temperature depending on the heating rate. The principal effects of further heat treatments to calcining or graphitizing temperatures are: (1) anisotropic shrinkage which produces delamination cracks, (2) sharpening of the folded regions, and (3) formation of mosaic blocks and kinks. By relieving boundary restraints and providing void space for small displacements of bulk material, the process of shrinkage-cracking appears to be an essential precursor to fold-sharpening and graphitization. Diffraction studies showed that the layer spacing decreases and the apparent crystallite size increases with increasing heat-treatment temperature, reaching values characteristic of fully graphitized material in the specimen annealed at 3000°C.

In the process of fold-sharpening, small displacements take place to form sharp and nearly linear boundaries, suggesting twinned regions in the ideal case. The mosaic blocks and kinks are formed on a fine scale as the final step in graphitization. The photomicrographs in Fig. 3 illustrate fold-sharpening and the formation of mosaic blocks and kinks in specimens heat treated to 1400° and 3000°C, respectively.

20 μm

HEAT TREATED TO 1400°C

OIL IMMERSION
PARALLEL POLARIZERS

20 μm

HEAT TREATED TO 3000°C

OIL IMMERSION
PARALLEL POLARIZERS

K78558

Fig. 3. Fold-sharpening and polygonization of the carbonaceous mesophase formed from extracted coal-tar pitch after heat treatment to calcining and graphitizing temperatures

3.4. EFFECTS OF SUBSTRATE AND INSOLUBLE PARTICLES

On carbonizing extracted pitch containing particles of calcined petroleum coke or natural graphite flakes, the mesophase layer planes have been found to align themselves with the layer planes of the substrate particles. The plastic mesophase wets the graphitic substrate materials, and the particles are agglomerated by the mesophase. The tendency toward mesophase alignment is illustrated in the structural sketches of Fig. 4. When a coal-tar pitch containing insoluble particles is carbonized, these particles are not incorporated in the mesophase, and, by accumulating at the mesophase interface, act to retard the coalescence process. These effects lead to the segregation of the insolubles in clumps in the fully transformed pitch. However, the bulk mesophase has the same characteristics of nodes and crosses in the polarized-light extinction contours as are found in extracted pitch pyrolyzed through the mesophase transformation.

3.5. FURTHER STUDIES

The foregoing studies of mesophase morphology were extended to a broader range of precursor materials in work undertaken in 1967 at the Petten (Netherlands) Establishment of EURATOM, the European Atomic Energy Community, and the results have been described in two topical reports (Refs. 5,7). In summary, the results corroborate the foregoing work and have shown further that:

1. The mesophase morphologies for a variety of coal-tar pitches are quite similar, aside from the matter of insoluble content.
2. The petroleum-base starting materials, as compared with the coal-base materials, develop a wider range of mesophase morphologies, including specifically a fine-structured isotropic morphology, which was not observed in the work with coal-tar pitches.
3. The same four basic types of layer-stacking defects occur in all the specimens of carbonaceous mesophase that have been examined, but the densities can vary greatly depending on the starting material and the extent of mesophase deformation before hardening.

K77938

Fig. 4. The alignment of mesophase layers with graphitic substrates: top - natural graphite flakes in pitch-base mesophase pyrolyzed to 436°C; bottom - calcined needle coke in pitch-base mesophase pyrolyzed to 600°C

4. The fine-structured isotropic mesophase is formed at lower temperatures than the coarse-structured mesophase and is less easily deformed to fibrous structures by bubble percolation.

4. CATALYTIC GRAPHITIZATION OF PYROLYTIC CARBONS, PETROLEUM COKES, AND GRAPHITES

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

Catalytic recrystallization is a potential method for increasing the irradiation stability and thermal conductivity of pyrolytic carbons or graphites for nuclear applications. Several investigators (Refs. 8-10) have shown that carbonaceous materials such as petroleum cokes or carbon blacks can be graphitized at 1400° to 2500°C. Another investigation (Ref. 11) showed that samples made by the co-deposition of pyrolytic carbon and 75 wt % titanium can undergo partial or complete graphitization during heat treatment at 2200°C for 4 hr.

In the present work the kinetics of titanium-doped pyrolytic carbons were studied by isochronal annealing. Metal-doped petroleum cokes were prepared and utilized for the preparation of graphite compacts. A quantitative study was made of the transformation of these carbon compacts to graphitic materials.

4.1. PYROLYTIC CARBONS*

A series of isochronal 1-hr anneals was conducted on a laminar pyrolytic carbon that was deposited at 1225°C and contained 6.7 wt % titanium, an isotropic pyrolytic carbon that was deposited at 2200°C and contained 9.7 wt % titanium, and titanium-free companion carbons. The annealing temperature was increased from 1300° to 3000°C in 100°C increments. Changes in layer spacing, apparent crystallite size (L_c), density, electrical resistivity, and microhardness were followed.

*The results summarized in this section are contained in GA-9974. See report number 15 in the Appendix for full reference.

Heterogeneous recrystallization to graphite started in the titanium-doped isotropic carbon at 2300°C and was completed at 2500°C. This is illustrated by the appearance of the (002) diffraction peak following annealing at 2200° to 2500°C, shown in Fig. 5. The graphite peak (at $\theta = 13.3^\circ$) grew at the expense of the carbon peak upon continued annealing, but the layer spacing and apparent crystallite size of the graphitic phase did not change. An undoped companion isotropic pyrolytic carbon was unresponsive to annealing.

The titanium-doped laminar carbon did not show catalytic recrystallization. Both the titanium-doped and titanium-free laminar carbons showed a steady increase in L_c and density and a steady reduction in layer spacing and microhardness over a temperature range from 1400° to 2800°C, but significant reduction in electrical resistivity did not start until ~1800°C.

The anticipated improvement in irradiation stability and thermal conductivity in recrystallized pyrolytic carbons was verified by experiments. During neutron irradiation at ~900°C, a catalytically recrystallized pyrolytic carbon changed dimensions about 10 times slower than a comparable ungraphitized carbon (Ref. 12). In addition, it was found that a catalytically graphitized isotropic pyrolytic carbon had a room-temperature thermal conductivity that was higher by an order of magnitude than that of as-deposited material (Ref. 13).

4.2. PETROLEUM COKES AND GRAPHITES*

The high-temperature irradiation behavior of carbons and graphites depends sensitively on their apparent crystallite size, L_c (Ref. 14); the stability of the materials increased with increasing crystalline perfection when irradiated above 500°C. The average apparent crystallite size of artificial moderator graphites falls in the range 400 to 1200 Å; however, if the crystallinity of these materials could be significantly improved,

*The results summarized in this section are contained in GA-9970. See report number 17 in the Appendix for full reference.

LC82219

Fig. 5. (002) X-ray diffraction peaks for isotropic pyrolytic carbon containing 9.7 wt % titanium annealed for 1 hr at (a) 2200°C, (b) 2300°C, (c) 2400°C, and (d) 2500°C

then considerable improvement in their irradiation behavior can be expected. The use of metallic additives to enhance graphitization below $\sim 2800^{\circ}\text{C}$ is attractive for this purpose, provided the additive can be removed or does not constitute a nuclear poison. Aluminum was of particular interest because of its low capture cross section for neutrons.

Coke specimens were prepared with aluminum or a combination of aluminum and titanium in the range zero to 20 wt %. Compacts were prepared from the various metal-doped cokes by mixing with a coal-tar pitch binder and molding at 4500 psi.

The metal-doped specimens were more easily graphitized than the control specimens when heated at 2300°C . Metallographic examination of the metal-doped specimens revealed small areas of well-developed graphite crystals, which appeared to be growing around the remnants of metallic particles. The (002) X-ray curves for specimens containing aluminum and titanium had a distinct graphite peak superimposed on the broad carbon curve at 1700° to 2100°C . The graphite peak became more prominent with increasing temperature, until at 2300°C the structure was transformed to graphite. This was in contrast to samples containing only aluminum, which showed only a carbon peak at 1700° to 2100°C and then an abrupt shift to graphite at 2300°C .

The effect of aluminum content on the graphitization process was studied (Table 1). Specimens with aluminum contents of 5 or 10 wt % showed only a slight improvement over the control, whereas the specimens containing 20 wt % graphitized. The compacts were comminuted to small particles (0.1 to 30 μ , average $\sim 10 \mu$) and separated in a densimetric column, as described in Ref. 16, and L_c and C_o values were measured on the density fractions. The data on the density fractions showed the structural distribution within each specimen, and when the data from the density fractions were arbitrarily divided according to L_c values of >500 , 500 to 1000, and $>1000 \text{ \AA}$ and C_o values of greater than and less than 6.750, a semiquantitative analysis of the conversion of the carbon structure to graphite emerged

TABLE 1
METALLIC CONTENT, DENSITIES, AND X-RAY DATA OF
ALUMINUM-DOPED COMPACTS HEATED AT 2300°C FOR 6 HOURS

Specimen Number	Aluminum Content (wt %)			Density (g/cm ³)			X-Ray Data (Å)		
	In Petroleum Asphalt	Compacts		Bulk	Immersion in Liquid		L _c (a)	$\bar{L}_c$ (b)	C _o
		900°C	2300°C		Bulk	Particles			
3726-24-B	0	0	0	1.83	2.16	2.14	270	245	6.769
3726-27-A	5	4.2	0.0045	1.63	2.08	2.10	238	295	6.747
3726-27-B		4.1							
3726-27-C		4.2							
3726-27-D		4.2							
3726-27-10A	10	10.2	0.0038	1.33	2.02	1.975	290	310	6.755
3726-27-10B		10.0							
3726-27-10C		10.3							
3726-27-10D		10.3							
3726-27-20A ^(c)	20	16.7	0.0038	1.18	2.17	2.165	1160	1370	6.718
3726-27-20B		16.8							
3726-27-20C		16.9							
3726-27-20D		16.8							
3726-26-1	20	~17.0	~0.0040	0.895	--	2.19	2000	3100	6.714

(a) L_c obtained from aggregate specimen.

(b) Specimens were comminuted to ~10 μ average particle size and separated in a density column.
 $\bar{L}_c = \sum_i L_{c_i} f_i$, where f_i is the volume fraction of material of given density ρ , and L_{c_i} is the apparent crystallite size of each fraction of a given density ρ (Ref. 15).

(c) Thermal expansivity: parallel, 3.10×10^6 °C⁻¹; perpendicular, 2.2×10^6 °C⁻¹.

(see Table 2). The specimens of highest aluminum content converted almost completely to a graphitic structure. In contrast, the control specimen was only semigraphitic.

In the case of aluminum, the transformation to a graphitic structure may result from carbon deposited due to dissociation of Al_4C_3 . However, if the transformation to graphitic structure resulted from the simple decomposition of Al_4C_3 with all of the aluminum subsequently evolving, then it would be expected that the yield would be low (see Table 2). However, yields considerably higher, by a factor of about 3 to 13, were obtained. Thus, there appears to be a mechanism for graphite formation either by reuse of the available aluminum to form additional Al_4C_3 as it passes out of the compacts or by some other mechanism. A more probable explanation, advanced by Fitzner and Kegel (Ref. 17), is that Al_4C_3 can encounter fresh carbon structure as it evolves and convert it to graphite. The driving force would be the difference in free energy between the disordered carbon and graphite in the carbide.

Where titanium was present the reaction of the carbon structure with titanium carbide proceeded by solid-state diffusion and greatly reduced the rate of conversion at 2300°C or below. Higher temperatures are necessary to convert a sizable portion of the coke structure to graphite with titanium. In the case of titanium the graphitization appeared to be heterogeneous.

The addition of zirconium carbide enhanced the graphitization of needle coke after short heating periods at 2400° to 2500°C, but the metal-doped specimens were no better than the control specimens after longer periods.

The use of metal-doped cokes to produce highly graphitic materials below 2300°C is feasible with aluminum. However, low compact densities resulted due to the evolution of the aluminum during heat treatment. The use of titanium requires temperatures above 2300°C for conversion of large volumes of the carbon structure to graphite.

TABLE 2
SEMIQUANTITATIVE ANALYSIS OF ALUMINUM-DOPED COMPACTS

Specimen Number	Aluminum Content in Sample (wt %)	Wt % of Sample with L _c Values of				Wt % of Sample with C _o Values of	
		Measured			Calculated ^(a) >1000		
		<500	500-1000	>1000		>6.750	<6.750
24-B	0	100	0	0	0	100	0
A-5	4.2	100	0	0	1.60	99.20	0.8
A-10	10.2	89.95	0	10.05	4.10	79.50	20.5
A-20	16.8	11.63	14.79	73.58	7.30	0	100
26-1	~17.0	12.50	13.86	73.64	7.30	0	100

(a) Assuming all Al_4C_3 decomposed in situ. to form near-perfect graphite crystals.

5. CHARACTERIZATION OF GRAPHITES*

G. B. Engle

Artificial graphites can be manufactured with a wide variety of carbon fillers that are bonded with the residual coke from a carbonized coal-tar pitch binder. Additional carbon can be added to the basic structure by impregnating the open pores with various carbonaceous materials. Forming is usually accomplished by extrusion or molding, but processing methods can vary considerably depending on the practice of a particular manufacturer. Thus, there is available a variety of artificial graphites that are useful as potential moderator graphites, but they vary in physical and mechanical properties, crystallite orientation, porosity, and irradiation behavior. The high-temperature irradiation behavior, particularly the dimensional changes of model materials, has been shown to depend sensitively on the apparent crystallite size of the materials (Ref. 14). This was thought to be especially significant in obtaining an understanding of the irradiation behavior of conventional artificial graphites that have improved densities and properties through the use of various isotropic cokes and nongraphitizing impregnant carbons.

The present investigation was undertaken to characterize the microstructure of a wide variety of anisotropic and near-isotropic artificial graphites (see Table 3) by determining the range and distribution of density and carbon structures in the various materials. A densimetric separation technique was developed for this purpose. In this method the graphites were comminuted to fine particles (called sink-float particles), which were separated into density fractions and then recovered and examined for structural features (Ref. 16). The densimetric measurements were combined with density measurements of

*The results summarized in this section are contained in GA-9421 and GA-9617. See reports number 7 and number 8, respectively, in the Appendix for full reference.

TABLE 3
MANUFACTURING METHODS, RAW MATERIALS, AND FORMING METHODS OF GRAPHITES
USED IN CHARACTERIZATION AND IRRADIATION STUDIES

Material	Forming Method	Type	Raw Materials		
			Filler	Binder	Impregnant
NC-8	Extrusion	Anisotropic	Needle coke	Coal-tar pitch	Coal-tar pitch
H-283	(a)	Anisotropic	Needle coke	Coal-tar pitch	Coal-tar pitch
711-TS-N	Extrusion	Anisotropic	Needle coke	Coal-tar pitch	Coal-tar pitch
CHN	Extrusion	Anisotropic	Needle coke	Coal-tar pitch	N.C. ^(b)
H-327	Extrusion	Anisotropic	Needle coke	Coal-tar pitch	Coal-tar pitch
18-2-9	Molding	Anisotropic	Natural flake	Coal-tar pitch	None
TS-688	Extrusion	Anisotropic	Needle coke	Coal-tar pitch	Coal-tar pitch
9567	Extrusion	Anisotropic	Needle coke	Coal-tar pitch	Coal-tar pitch
H-315-A	(a)	Near-isotropic	Gilsonite coke	Coal-tar pitch	Coal-tar pitch
H-207-85	Extrusion	Near-isotropic	Gilsonite coke	Coal-tar pitch	Coal-tar pitch
H-378	Molding	Near-isotropic	Gilsonite coke	Coal-tar pitch	Coal-tar pitch
H-328	Molding	Near-isotropic	Gilsonite coke	Coal-tar pitch	Coal-tar pitch
ATJ-SG	Molding	Near-isotropic	Gilsonite coke	(c)	(c)
AXF-5QB	(c)	Near-isotropic	(c)	(c)	(c)
AXF-5QGB	(c)	Near-isotropic	(c)	(c)	(c)
H-319	(a)	Near-isotropic	Raw petroleum coke	Coal-tar pitch	Coal-tar pitch

(a) Baked under pneumatic pressure by a continuous forming method (Ref. 18).

(b) Nongraphitizing carbon.

(c) Unknown to author; manufactured by Poco.

the solid samples prior to comminution and X-ray diffraction measurements to further characterize the microstructure of the graphites.

The graphites selected for the characterization studies were obtained as experimental or production-grade graphites and had a wide range of density, strength, thermal expansivity, crystallinity, and crystallite orientation. These materials were also chosen for irradiation to high fluences at high temperatures, and many of the characterization measurements were repeated after irradiation (see Section 6.3).

The graphite particles in the density fractions were composed of crystallites plus intercrystallite pores that could not be removed during the comminution of the bulk sample. The anisotropic needle-coke graphites contained a wide range of crystallite sizes L_c that varied systematically with the density of the sink-float particles, whereas in the near-isotropic materials the L_c values fell in a narrower band. The crystallite sizes of the anisotropic needle cokes ranged from 350 to 1600 Å, whereas the materials fabricated with Gilsonite coke ranged from 350 to 550 Å, and showed only a slight dependence on density. The Poco graphites and the material fabricated from raw petroleum coke were unique. The former had a range of 350 to 450 Å and no observable dependence on density. The material fabricated from raw petroleum coke was similar to that made with needle cokes, but had bulk properties that were similar to those of the near-isotropic materials. The needle-coke graphites consisted predominantly of crystalline material coexisting with smaller regions of semigraphitic structure. The reverse was the case for the near-isotropic materials, where the structures were predominantly semigraphitic with smaller volumes of more perfect crystalline structure. Microscopic examinations reinforced the results obtained by X-ray examinations and also indicated that the semigraphitic regions were isotropic and the highly graphitic regions were highly oriented.

To further define the microstructure, the distribution of porosity in the graphites was determined by measuring the density of solid samples by immersion in a liquid. The closed and open pore volumes of the bulk material were determined from this measurement. From measurements of density, orientation parameters, and structural parameters and from a knowledge of the raw materials and manufacturing methods, it was possible to determine in a qualitative manner the location of porosity in the various materials. A sketch of a needle-coke graphite is shown in Fig. 6 to illustrate the porosity and structural distributions. In the sketch the subdivisions represent the sink-float particles, which may consist of fragments of filler particles, binder carbon, impregnant carbon, or combinations of these residual coke structures. Each sink-float particle that was less than theoretical density contained porosity (V_{p_1}) that was due to either structural defects or microporosity among the crystallites resulting from mismatches in crystallite stacking during graphitization or from cracks that open during cooldown from graphitization temperatures due to differential thermal shrinkage (Ref. 19). In addition to this porosity, there was found a domain of porosity or cracks (V_{p_2}) external to the sink-float particles that was not penetrated by the measuring liquids during density measurements of the bulk sample, but was removed during comminution along with the larger open pores. The larger open pores (V_{p_3}) were penetrated by the liquid during measurement of the bulk sample. The pores in V_{p_2} were formed either by differential thermal shrinkage during cooling or by clogging of pores by either binder or impregnant carbon during manufacture.

The characterization of porosity and structure is essential to the discussion of dimensional changes in Section 6.4, where the interactions between the crystallites and porosity are described and related to the bulk dimensional changes during high-temperature irradiation.

The thermal expansivities of the graphite could not be correlated with any of the measured porosities. This was not unexpected since there was no reason to believe that the porosities measured were wholly

LC76084

Fig. 6. Proposed microstructure of anisotropic graphite (CHN - needle coke)

those that accommodated thermal expansion. It was noted, however, that progression from the anisotropic needle-coke material to the more isotropic materials was accompanied by a shift in the distribution and magnitude of the apparent crystallite sizes within the materials. In comparison with the needle-coke graphites, Poco graphites were semi-graphitic, near-isotropic, quite uniform in crystallite structure, and had thermal expansivities approaching the theoretical value. However, when small anisotropic regions of crystalline material were found in the microstructure coexisting with the major phase that is semigraphitic and isotropic, as, for example, in the Gilsonite-coke graphites, then the L_c values were larger and the range of sizes was greater. This suggested that the thermal expansivity of the graphites was related to the apparent crystallite sizes and their distributions as well as to crystallite orientation. Mean $\bar{L}_c$ values were calculated from the densimetric curves by the following summation

$$\bar{L}_c = \sum_i L_{c_i} f_i,$$

where f_i is the volume fraction of the material of a given density and L_{c_i} is the crystallite size of each density fraction. The dependence of f_i volume expansivity on $\bar{L}_c$ was excellent and contrasted with poor correlations with microporosity.

6. IRRADIATION EFFECTS

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6.1. MODEL MATERIALS*

6.1.1. Structure of Model Materials

It is well known that the irradiation damage that causes dimensional changes in artificial graphites is sensitive to both the irradiation temperature and the structural details of the conglomerate. The structural details of such graphites, as mentioned previously, are complex and vary widely with processing variables and the materials used in the initial formulation. Recognizing the complexity of the structure of such an aggregate, a considerable effort has been devoted to studies of model materials that are relatively simple and homogeneous in their crystal structure, easy to characterize, and free of complications imposed by the presence of complex networks of pores and cracks that are common in artificial graphites.

The individual model carbons that were studied are:

1. Natural Graphite Crystals. These crystals provide the upper limit of crystalline perfection and anisotropy that is practically attainable ($L_c = \infty$).
2. Annealed Massive Pyrolytic Graphite. The structure of this material is representative of a pseudo-single crystal that is an order of magnitude less crystalline than natural crystals ($L_c \sim 1600 \text{ \AA}$). The crystalline perfection as measured by the L_c parameter is in the upper range of those characteristic in needle-coke graphites.

*The results summarized in this section are contained in GA-8001, GA-8555, GA-8700, GA-8888, GA-9600, GA-9900, and GA-9919. See numbers 1 (GA-8001), 2 (GA-8555), 3 (GA-8700), 4 (GA-8888), 6 (GA-9600), 9 (GA-9900), and 11 (GA-9919) in the Appendix for full references.

3. High-Density, Anisotropic Turbostratic Pyrolytic Carbons. These materials are idealized models of poorly crystalline ($L_c \sim 170 \text{ \AA}$), anisotropic phases that may exist in commercial graphites. They allow definitive experimentation, the results of which reveal the dependence of irradiation-induced dimensional changes on anisotropy at constant preirradiation density and crystallite size. Because of their small crystallite sizes, these materials are more sensitive to irradiation than moderator graphites. Hence, irradiation effects tend to be more easily identified at lower fluences than in artificial graphites.
4. Catalytically Graphitized High-Density, Anisotropic Carbons. Catalytic graphitization of an anisotropic turbostratic carbon provided a moderately crystalline ($L_c \sim 800 \text{ \AA}$) material with which poorly crystalline, anisotropic turbostratic carbons can be compared. The comparison demonstrates the influence of crystalline perfection on the dimensional behavior at constant preirradiation density and anisotropy.
5. Isotropic Turbostratic Carbons Deposited at High Temperatures (HTI Carbons). These materials are isotropic with Bacon anisotropy factors (BAF) less than 1.1. They can be deposited with different densities and provide quantitative volumetric and dimensional data for isotropic materials at constant preirradiation crystallite size ($L_c \sim 150 \text{ \AA}$).
6. Isotropic Turbostratic Carbons Deposited at Low Temperatures (LTI Carbons). This family of carbons is analogous to the HTI carbons except that they have smaller crystallite sizes ($L_c \sim 30 \text{ \AA}$) and are about twice as strong as HTI carbons. Hence, the dimensional behavior of poorly crystalline, isotropic phases can be compared at a level of crystalline perfection which is less than that represented by the HTI carbons.

The data from irradiations of HTI and LTI carbons are not only useful in revealing the irradiation behavior of artificial graphites, but are also relevant to the design of carbon coated fuel particles for HTGRs.

In the following sections, the dependence of irradiation-induced dimensional changes on crystallite size, anisotropy, and initial density of the model materials is summarized. In addition, complicated, structurally dependent effects that occur at high fluences are illustrated using data obtained from irradiations of the model materials. Finally, the relevance of the data obtained from the idealized structures to the interpretation of polycrystalline artificial graphites is discussed.

6.1.2. Dependence of Irradiation-Induced Dimensional Changes on Crystalline Perfection

A direct comparison between the bulk dimensional behavior during irradiation at 900°C of two high-density materials with the same anisotropy factor but different L_c values is shown in Fig. 7 (Ref. 12). Data comparing the crystallite dimensional changes caused by irradiation for materials over a wider range of L_c values (Fig. 8) (Ref. 20) reveal the strong dependence on crystallite size at 1200°C.

These studies have shown that the effect of crystalline perfection on the rate at which crystallites change shape during irradiation varies markedly with irradiation temperature. Since the crystallites change shape at constant volume, a comparison of the temperature dependence of the shape change for crystallites with different degrees of crystalline perfection (L_c values) has been made by plotting for each the crystallite c-direction growth rate as a function of irradiation temperature. Such a plot is shown in Fig. 9 (Refs. 13,14). An explanation of the temperature and crystallite size dependences in terms of atomic processes has been published (Ref. 14).

If other factors are held constant, increasing the degree of crystalline perfection increases the dimensional stability. The effect is most pronounced for low fluences and at irradiation temperatures above 800°C. This conclusion is valid for all carbonaceous conglomerates irradiated to low fluences. At high fluences, especially at high temperature,

LC65002

Fig. 7. Dimensional change versus neutron exposure at 900°C for high-density ($\rho > 2.1 \text{ g/cm}^3$) anisotropic carbons with different crystallite sizes. The material with $L_c = 800 \text{ \AA}$ was catalytically graphitized with titanium. Both deposits have R_1 values of about 0.45 (Ref. 12)

LC65003

Fig. 8. Crystallite dimensional changes versus neutron exposure for dense carbons having various L_c parameters; irradiated at about 1200°C (Ref. 20)

LC65010

Fig. 9. Average crystallite growth rates, $\ln [1 + (\Delta X_c/X_c)]$, per 10^{21} nvt for model carbons with various crystallite sizes and densities greater than 2.1 g/cm^3 (from Refs. 13 and 14)

new effects caused by crystallite interactions become important and the above conclusion no longer applies. These effects will be described in Section 6.1.6.

6.1.3. Dependence of Irradiation-Induced Dimensional Changes on the Degree of Preferred Orientation of Crystallites

The data obtained from irradiations of the high-density, anisotropic pyrolytic carbons provide a quantitative illustration of dependence of the changes that occur in the bulk on those that occur in the individual crystallites. Results obtained from irradiations at 900°C (Fig. 10) show that as the degree of preferred orientation is increased (R varies from $R = 2/3$) (Ref. 21), the deposits behave more anisotropically, and as R approaches 0 or 1, the behavior of the bulk dimensions approaches that of the individual crystallites that make up the aggregate. Other factors constant, maximum stability should be obtained for isotropic bodies. It is worth noting that at high fluences, the relationship between the R parameter and the dimensional change is nonlinear. The departure from linearity indicates either a basic change in crystallite behavior at high fluence or an irradiation-induced increase in the degree of preferred orientation. An interpretation in terms of crystallite behavior has been given in Refs. 22 and 23.

When graphites or carbon coatings are chosen for high stability especially to high fluences at high irradiation temperatures, isotropy is obviously a prime requisite.

6.1.4. Dependence of Irradiation-Induced Volume Changes on Preirradiation Density

In artificial graphites, the density defect is made up of a complex spectrum of pores and cracks, the morphology of which varies widely with the graphite type. In the model carbons, however, the density defect is made up of a relatively uniform spectrum of submicroscopic pores that,

LC74820

Fig. 10. Plots of $\ln [1 + (\Delta L_i/L_i)]$ versus the preferred orientation parameter R_i for model HTI carbons with $\rho_o > 2.1 \text{ g/cm}^3$; irradiated at 900°C (Ref. 21)

for a given density, does not vary markedly from carbon to carbon. Accordingly, the volume changes caused by the elimination of pores are more predictable. The data in Fig. 11 (from Ref. 24) show the nature of the volumetric changes. Low-fluence irradiations cause the pores responsible for the preirradiation density defect to close and the density to increase. Eventually, however, the rate at which new pores are generated in the structure due to interactions between adjacent, misaligned crystallites becomes important; the contribution of the new pores overwhelms that due to the closure of pre-existing pores and eventually net volume expansion results.

Analogous volumetric changes occur in polycrystalline artificial graphites, but the changes vary from graphite to graphite depending on the morphology of the original voids and the rate at which new voids are generated. It is worth noting that volumetric data obtained for high-strength LTI model carbons suggest that high internal strength is important in retarding pore generation at high fluences (Ref. 25).

6.1.5. Dependence of Irradiation-Induced Dimensional Changes of Isotropic Carbons on Their Preirradiation Density

During irradiation at low fluences, isotropic carbons with $\rho_0 < 2.22 \text{ g/cm}^3$ shrink isotropically. At higher fluences and especially at high irradiation temperatures, these materials start to behave anisotropically, shrinking in the direction parallel to the deposition plane and expanding in the perpendicular direction. The effect is most pronounced for high-density deposits (Fig. 12) (Refs. 12,23). This observation is technically important in applications of both carbon coatings and graphite components in nuclear reactors. The magnitude of the effect and its dependence on the preirradiation density are shown more clearly by the data in Fig. 13. It was concluded from the examples in Fig. 13 that whereas high density enhances stability at low fluences, at high fluences the effect is reversed; high density leads to instability. Similar accelerating effects at high fluences have been observed for some artificial graphites and it is expected that as additional data are obtained at higher fluences, these effects will be observed more frequently.

LC79622

Fig. 11. Density versus fluence for model HTI carbons irradiated at 900° to 1000°C (Ref. 24)

LC80414

Fig. 12. Length change versus fluence for a low-density and high-density isotropic (BAF < 1.1) model carbon irradiated at 1250°C (data from Refs. 12 and 23)

LC79623

Fig. 13. Dimensional changes plotted as a function of preirradiation density for model HTI carbons irradiated at 1000°C (Ref. 24)

6.1.6. Interpretation of High-Fluence Effects

At low fluences, the dimensional behavior of the model materials has been found to be simple and well-defined functions of the original structure. The densification was found to be first order with respect to the density defect (Ref. 26), and the dimensional changes were found to be represented quite well by relationships derived using crystallite averaging methods (Ref. 27). At high fluences and especially at high irradiation temperatures, however, the dimensional behavior is more complex. Plots of the linear changes versus the preferred orientation parameter R depart from linearity (Fig. 10), the densification rate decreases more rapidly than predicted by first-order kinetics, densification finally ceases, and the materials expand (Fig. 11). The dimensional behavior of isotropic model carbons ceases to be isotropic (Fig. 12); the effect is dramatically dependent on density (Fig. 13).

The complex behavior at high fluences is interpreted as follows (Ref. 23). As the crystallites in an aggregate change shape, the interactions between crystallites are at first accommodated by internal porosity and intercrystallite irradiation creep. Under these circumstances, the behavior of the bulk is closely approximated by the averaged value of the behavior of the crystallites. At high fluences, however, when the internal porosity is nearly gone, the interactions between crystallites become intense. Stresses between crystallites rise and new voids are formed either by stress-directed diffusion of vacancies or by fracture at boundaries. As a result of these interactions, the crystal structure is degraded causing an acceleration in the rate at which the crystallites change dimension. Since the interactions are most severe in dense isotropic materials, the accelerations are most pronounced for these carbons. Accordingly, the plots in Fig. 10 become sigmoidal in shape and the strong dependence on density shown in Fig. 13 results. A more detailed discussion has been published (Ref. 23).

Recent results (Refs. 24,25) that compare the behavior of LTI and HTI carbons show that the volume expansion and the accelerations at high fluences are more pronounced in HTI carbons than in the stronger LTI carbons. This is in spite of the fact that LTI carbons are less crystalline than HTI carbons. The apparently anomalous behavior has been attributed to the fact that cross-links present in the LTI carbons increase the internal binding and retard void generation. The fact that local displacements at boundaries are small when the crystallites are small may also be a factor (Ref. 24).

6.1.7. Irradiation Creep

A large amount of creep data has been accumulated for the model carbons. The bulk of the creep data has been summarized in Ref. 26. The results show that plastic strains at least as high as 10% in tension can be accumulated and that creep rates of 2.5, 5, and 6% per 10^{21} n/cm^2 can be sustained at 600°, 900°, and 1250°C, respectively, without exceeding the fracture stress. As yet, no dependences of creep rate on structure have been found. Estimates of the creep constant k_c for the model carbons indicate that creep constants for these materials are in the same range as those reported for artificial graphites (Ref. 28).

6.1.8. Temperature-History Effects on Irradiation-Induced Dimensional Changes

Irradiations of model materials in experiments in which the temperature was changed during the exposure have shown that a prior irradiation at a high temperature accelerates the dimensional changes in a subsequent irradiation at a lower temperature (Refs. 20,24). This effect is illustrated by the example from Ref. 24 shown in Fig. 14. In Fig. 14, the density of an HTI carbon is plotted as a function of fluence for two types of irradiation. In one case, the specimens were irradiated at a constant temperature of 630°C to a total fluence of $7.4 \times 10^{21} \text{ n/cm}^2$ in two steps. In the other case, identical specimens were irradiated first at 950°C to $4.2 \times 10^{21} \text{ n/cm}^2$

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Fig. 14. Density versus fluence for a model HTI carbon irradiated: (1) at 630°C to 7.4×10^{21} n/cm², and (2) at 950°C to 4.2×10^{21} n/cm² and then to an additional 3.6×10^{21} n/cm² at 630°C. The dashed curve represents the density data for 950°C to 7×10^{21} n/cm² (Ref. 24)

and then continued to a total of 7.8×10^{21} n/cm² at 630°C. The prior irradiation at 950°C had a significant influence on the subsequent behavior at 630°C. The effect appears to be general, occurring over the full range of temperatures expected in the various HTGR designs now under construction. More recent data suggest that similar effects may occur for artificial moderator graphites (Section 6.4.3.).

The results from multiple irradiations at different temperatures have shown that the irradiation-induced changes in dimensions that occur are not simply the cumulative sum of results obtained in isothermal irradiations. The identification of the effect is, of course, important because it signals a warning to those who design carbonaceous components that available isothermal data may not always be directly applicable to carbonaceous components that experience varied and complex thermal histories during their lifetime in the reactor. Until more extensive and complete studies are carried out, the designer is put at a disadvantage and must be careful to include margins of safety that will be sufficient to allow for the noncumulative character of the irradiation-induced dimensional changes when the irradiations are not isothermal.

6.1.9. Relevance of Irradiation Behavior of Model Materials to that of Artificial Graphites

Early results from the irradiation of model materials showed that for low fluences, the most stable graphites would be those that were as isotropic (Fig. 10) and crystalline (Figs. 7 through 9) as possible and that the most stable aggregates should be dense (Fig. 11). At that time the magnitude of the effects of crystallite interactions at high fluences and high irradiation temperatures was not appreciated. The data for the poorly crystalline turbostratic pyrolytic model materials have clarified the effects of crystallite interaction at high fluences and analogous but less well-defined effects may be expected for artificial graphites at even higher fluences.

It is clear from the data in Fig. 10 that for any carbon body dimensional stability as measured by a shape change, $\sum_{i=1}^3 \left| \ln[1+(\Delta L_i/L_i)] \right|$ (L_i represents the three orthogonal principal directions in the body), the body should be isotropic. With this established, one must next determine what the other characteristics of isotropic bodies must be in order to minimize the shape change. In the following paragraphs, a rationalization based on the behavior observed for model materials will be presented, which will lead to conclusions that are at variance with the old idea that the isotropic graphites should be dense and crystalline if one requires dimensional stability to high fluences at high irradiation temperatures.

As mentioned previously interaction effects at high fluences, for a given value of irradiation-induced crystallite strain, are maximum for isotropic carbons (or graphites) because for isotropic bodies the mismatch between crystallites is maximum. Furthermore, for isotropic bodies interaction effects must be maximum for the most dense aggregates, because in these materials there are fewer voids to accommodate opposing crystallite strains. Recalling that the irradiation creep rate increases monotonically in the range 600° to 1300°C and that in the same range the irradiation-induced crystallite strain also increases rapidly with increasing irradiation temperature but then saturates, we are led to the conclusions that there must exist a temperature ($T_{\text{max. int.}}$) at which the effects of crystallite interactions are a maximum. The effect is illustrated by Fig. 15, in which the creep constants and crystallite strain rate are plotted as a function of irradiation temperature for an HTI carbon. The "interaction stress" obtained by dividing the crystallite strain rate by the creep constant shows a pronounced maximum at an intermediate irradiation temperature. Hence, data obtained from irradiation of model carbons predict that at some intermediate irradiation temperatures, effects such as exaggerated volume expansion, rapid degradation of crystal structure, and accelerations in the dimensional change rate will be a maximum and the interactions will be most pronounced for the most dense of the isotropic graphites. Note that the curve representing the crystallite strain rate in Fig. 15 shifts to high temperatures for more crystalline materials, making

Fig. 15. Plots of irradiation-induced crystallite strain rate, $d\epsilon/d\gamma$; creep constant, k_c ; and internal stress factor, $(d\epsilon/d\gamma)/k_c$, for HTI carbons. The data illustrate the factors that lead to a $T_{(max. int.)}$. All units are arbitrary

the "interaction stress" lower at the maximum. It is also worth noting that the isotropic Poco and Gilsonite graphites have relatively small crystallite sizes and we may expect that a $T_{\text{max. int.}}$ will be found near about 1000°C for these materials.

The data in Fig. 16 comparing the change in L_c for irradiations at 900° and 1200°C show that for HTI carbons the degradation in crystalline perfection is more severe at 900°C than at 1200°C, which is consistent with the data in Fig. 15. Thermal conductivity changes caused by irradiation at 900° and 1200°C are in accord with the data in both Figs. 15 and 16 (Ref. 23).

The data in Fig. 13 are at variance with an earlier concept that for stability nuclear graphites should be dense. The data for the model carbons predict that at high temperature and especially near $T_{\text{max. int.}}$, high density will contribute to dimensional instability. Accordingly, our studies of model materials suggest that the near-isotropic nuclear graphites such as Poco or Gilsonite-coke graphites, which are of intermediate density, should be the most stable among graphites. This observation is in accord with data in Section 6.4.1. and Refs. 28 and 29 and should hold especially for irradiations near $T_{\text{max. int.}}$.

Pore generation due to mechanical interactions between crystallites, especially in dense isotropic materials, suggests that increasing the internal strength (e.g., cross-linking) might retard the volume expansion at high fluences. Corresponding dimensional data for LTI and HTI carbons add credence to this speculation, since LTI carbons are strongly cross-linked and, as a result, are about twice as strong as HTI carbons. Data in Figs. 17 and 18 compare the density changes and dimensional behavior of LTI and HTI carbons. The data show that at high fluences the stronger LTI carbons neither expand as much nor exhibit the large accelerating effects that are observed for HTI carbons. From these observations for model materials, an inference may be made that the effects of mechanical interactions between crystallites are less effective in causing accelerations in dimensional change rates for materials with high internal strength

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Fig. 16. Change in L_c due to irradiation at 900° and 1200°C versus the original L_c parameter for model HTI carbons (Ref. 23)

Fig. 17. Density versus fluence for isotropic model carbons (BAF < 1.1)

Fig. 18. Dimensional changes versus density for isotropic model carbons

and that void generation is retarded in high-strength material. In general, increasing strengths are obtained by decreasing crystallite size. This means that increasing crystallite sizes to enhance the stability of the crystallites might actually cause a net decrease in stability at high fluences because of a loss of internal strength (or cross-links). The crystalline needle-coke graphites are examples (see Section 6.4.1). The high strength of the Poco graphites is undoubtedly an important factor that contributes to their outstanding stability during irradiation.

In summary, results from the study of model materials have provided several new viewpoints that are useful guides in the development of "ideally stable" nuclear graphites that may be useful at high irradiation temperatures and irradiations to high fluences. These are:

1. Mechanical interactions between distorting crystallites can be an important factor that enhances dimensional changes and contributes to instability at high fluences.
2. For isotropic carbons or graphites with small to moderate crystallite sizes, there should exist a temperature ($T_{\text{max. int.}}$) at which the effects of mechanical interactions are a maximum.
3. Isotropic bodies with high "internal strength" are expected to be more stable at high fluences than weaker bodies (especially near $T_{\text{max. int.}}$).
4. Because high density enhances the degree of mechanical interactions (and associated effects), high bulk density is not necessary for stability at high fluences and extremely high densities may be detrimental.
5. Large crystallite sizes are no longer considered to be an unqualified requisite for stability at high fluences, because a high degree of crystalline perfection leads to low strength (few cross-links and low internal strength).

Therefore, the ideally stable nuclear graphite will likely be isotropic, have a moderate density, and have high internal strength, i.e., an intermediate crystallite size. Presently among the artificial graphites, certain Poco graphites have structures that most nearly approach the ideal structure.

Additional evidence of temperature-history effects for nuclear graphites that are analogous to those revealed by irradiating model HTI carbons (Refs. 24,27) is expected.

6.2. ANNEALING OF IRRADIATED PYROLYTIC CARBONS*

R. J. Price and J. C. Bokros

The annealing behavior of neutron-irradiated carbons and graphites provides an important technique for studying the nature of the irradiation damage. By following the changes in several physical properties during postirradiation annealing, conclusions can be drawn about the fundamental annealing processes. Transmission electron microscope observations of the defect clusters, which provide more direct information, can only be used for single crystals and highly crystalline annealed pyrolytic carbons.

A variety of pyrolytic carbons irradiated with fast neutrons to 1.5 to 2.4×10^{21} n/cm² ($E > 0.18$ MeV) at 540° to 1060°C were annealed at 100°C temperature increments between 400° and 3000°C . Changes in density, linear dimensions, layer spacing, (002) peak width, electrical resistivity, and microhardness were followed. The thermal diffusivity of some samples was measured following irradiation and again after the final 3000°C anneal.

In the case of laminar carbon deposited at 1400°C , most of the annealing effects resulted from annealing of the as-deposited structure and were independent of irradiation conditions. The annealing behavior of these samples represents a progressive increase in crystallinity, which takes

*The results summarized in this section are contained in GA-10162. See report number 16 in the Appendix for full reference.

place over a wide range of annealing temperatures and is essentially the same as that observed for unirradiated laminar carbons deposited at low temperatures. On the other hand, the postirradiation annealing behavior of laminar samples annealed at 2800°C before irradiation depends only on the rearrangement of irradiation-induced defects. In the latter samples, recovery of all properties started at 1200° to 1600°C and occurred most rapidly at 2200° to 2400°C. For irradiation temperatures of 540° and 620°C, the crystallite dimensions reverted to their preirradiation values, but for higher irradiation temperatures 60 to 80% of the crystallite dimensional change was unannealable. For samples irradiated at 890° to 1060°C, postirradiation annealing reduced the layer spacing, (002) peak width, and thermal resistivity to below their preirradiation levels.

The annealing processes may be explained by the presence of irradiation-induced vacancy loops within the layer planes that are removed during annealing, and larger sheets of interstitials located at crystallite twist boundaries that resist annealing. The distributions of activation energies for the loop annealing process were calculated by the Vand-Primak method (Ref. 30) assuming a single-value pre-exponential factor. The distribution functions for the apparent activation energies derived from measurements of electrical resistivity, dimensions, layer spacing, density, and (002) peak width are shown for several carbons in Fig. 19. The calculations indicate an activation energy of 5 to 5.5 eV for the earliest annealing steps, and a peak in the distribution function at ~8.5 eV. These two values are in good agreement with the activation energies determined from electron microscope observations on irradiated graphite for loop annealing in the presence of excess vacancies and loop annealing by self diffusion, respectively.

6.3. HIGHLY ORIENTED CARBONS AND GRAPHITES

R. J. Price

The work in Section 6.1 dealt with the characterization and irradiation behavior of model materials with a wide range of crystallite sizes and crystallite orientation. As mentioned previously the irradiation-induced dimensional and physical property changes in polycrystalline artificial

Fig. 19. Distribution of apparent activation energies for annealing processes in pyrolytic carbons irradiated at 1060°C to 2.2×10^{21} n/cm² ($E > 0.18$ MeV)

graphites are complex and difficult to interpret because the changes in the constituent crystallites are modified by crystallite interactions and the effects of porosity. Additional data that are useful for interpreting irradiation effects in polycrystalline graphites can be obtained from experiments on highly oriented, single-phase carbons and graphites of various crystallite sizes, free from gross porosity. In particular, accurate estimates of the dimensional changes in the constituent crystallites can be obtained from such materials without large extrapolations.

In the present work, the specimens consisted of two series of samples cut at 0°, 30°, 60°, and 90° to the symmetry axis of (1) ATJ graphite hot-worked to 50 to 60% compressive strain at about 2700°C, (2) massive pyrolytic carbon deposited at about 2200°C, (3) samples cut parallel to the substrate plane of massive pyrolytic carbon annealed at 3300°C, and (4) parallel and perpendicular cut samples of massive pyrolytic carbon annealed at 2900°, 3000°, and 3100°C before irradiation. The densities, orientation factors, and apparent crystallite sizes of these materials are listed in Table 4. It can be seen that the apparent crystallite sizes (220 to 1600 Å) span the range encountered in the components of artificial nuclear graphites.

Samples of the first three materials were irradiated in four increments to total fluences of 2×10^{21} n/cm² at 750° to 800°C and 14×10^{21} n/cm² at 1225° to 1300°C. Samples of the fourth material (3100°C-annealed pyrolytic carbon) were only included in the last irradiation and the fluence was 4.6×10^{21} n/cm² at 1300°C. The dimensional changes, the 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.

6.3.1. Dimensional Changes

Delamination cracks developed in the as-deposited pyrolytic carbon samples irradiated beyond $\sim 4 \times 10^{21}$ n/cm² at 1250°C. However, most

TABLE 4
STRUCTURAL PARAMETERS FOR HIGHLY ORIENTED CARBONS AND GRAPHITES

Material	Density (g/cm ³)	BAF ^(a)	Apparent Crystallite Size (Å)		Interlayer Spacing ^(b) (Å)
			L _a	L _c ^(b)	
Massive pyrolytic carbon	2.18	8.9	250 ^(c)	220	3.420
Hot-worked ATJ graphite	2.04	4.1	630 ^(d)	570	3.360
3300°C-annealed pyrolytic carbon	2.25	13	1300 ^(d)	1600	3.353
3100°C-annealed pyrolytic carbon	2.25	(e)	(e)	1400	3.358
3000°C-annealed pyrolytic carbon	2.25	(e)	710	750	3.366
2900°C-annealed pyrolytic carbon	2.20	(e)	(e)	675	3.365

(a) Bacon anisotropy factor.

(b) Evaluated from the (002) reflection.

(c) Evaluated from the (11) band.

(d) Evaluated from the (110) reflection.

(e) Not measured.

samples remained in one piece, enabling approximate measurements to be made. The measurements are summarized in Figs. 20 and 21 for the first three materials in Table 4. The parallel and perpendicular dimensional changes increased linearly with neutron exposure, except for the hot-worked graphite irradiated at $\sim 1250^{\circ}\text{C}$. For this material the dimensional change rates were significantly lower for fluences beyond $6 \times 10^{21} \text{ n/cm}^2$ than for fluences up to $6 \times 10^{21} \text{ n/cm}^2$.

6.3.2. 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. For larger dimensional changes, these relationships are no longer valid, and it is better to relate the dimensional changes to preferred orientation factors. For highly oriented materials the correction factors that take into account intercrystallite 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 $\sim 1250^{\circ}\text{C}$. 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 at $4.6 \times 10^{21} \text{ n/cm}^2$ and 1225° to 1300°C are shown as a function of L_c in Fig. 22. The results again illustrate that crystallite change rates increase with decreasing crystallite size and increasing irradiation temperature over the temperature range $\sim 800^{\circ}$ to 1250°C .

Fig. 20. Irradiation-induced dimensional changes in hot-worked graphite and massive pyrolytic carbon as a function of neutron exposure at 750° to 800°C

Fig. 21. Irradiation-induced dimensional changes in hot-worked graphite, massive pyrolytic carbon, and massive pyrolytic carbon annealed at 3300°C as a function of neutron exposure at 1225° to 1300°C

Fig. 22. Irradiation-induced crystallite strains in highly oriented carbons as a function of apparent crystallite size L_c . Irradiation temperature was 1225° to 1300°C, neutron fluence was 4.6×10^{21} n/cm²

6.3.3. Thermal Expansion Coefficients

At 750° to 800°C the expansion coefficient of the hot-worked graphite parallel to the hot-working axis showed a gradual increase with fluence, rising from $15 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ (unirradiated) to $17 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ at $2 \times 10^{21} \text{ n/cm}^2$. 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 $19 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ at $2 \times 10^{21} \text{ n/cm}^2$, and then fell to about $6 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ by $14 \times 10^{21} \text{ n/cm}^2$. In the perpendicular direction it increased from $1 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ to $2.5 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ 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 $27 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ 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 the 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 isotropic graphites irradiated at ~1000° to 1250°C or 170° to 200°C (Section 6.4.1 and Ref. 31), where the damage retention is also very large. Both the turn-down thermal expansion coefficient and the decrease in dimensional change rate at high exposures in the hot-worked graphite may be due to an increase in intercrystallite restraints at high damage levels.

6.3.4. Metallographic Examinations

Metallographic examination of as-deposited massive pyrolytic carbon irradiated at ~1250°C showed that macroscopic delamination cracks 2 to 3 mm long started to form at about $4 \times 10^{21} \text{ n/cm}^2$, 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 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.

6.3.5. X-ray Diffraction Examinations

Irradiation caused an increase in X-ray peak width for all materials. Changes in L_c are shown in Fig. 23. The fractional change 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 spacings decreased by 0.3 to 0.4%.

6.4. ARTIFICIAL COMMERCIAL GRAPHITES

G. B. Engle, R. J. Price, K. Koyama, and A. L. Pitner*

6.4.1. Dimensional and Property Changes**

The irradiation studies in this section are a continuation of the characterization work described in Section 5. The characterization work identified the differences among the various artificial graphites in terms of their properties, crystallite orientations and sizes, and their morphologies due to raw materials and processing. The densimetric work showed that certain graphites contain distributions of crystallite sizes and pores, i.e., a mixture of the model carbons described in Section 6.1. These variations lead to considerable differences in the irradiation behavior of the various graphites, and an understanding of the relationships between their microstructures, properties, and irradiation behavior is critical to the selection of graphites in the design of the reactors.

*The results summarized in this section are contained in GA-9972 and GA-9973. See reports number 10 and number 14, respectively, in the Appendix for full reference.

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Fig. 23. Irradiation-induced change in apparent crystallite size L_c of highly oriented carbons as a function of neutron exposure at 750° to 800°C and 1225° to 1300°C

The investigations in this portion of the program were concerned with the irradiation of a number of the commercial nuclear graphites described in Table 3 of Section 5. The graphites irradiated were of three general types: needle-coke base materials, some with multiple impregnations; near-isotropic graphites prepared with Gilsinite coke; and a near-isotropic graphite prepared with raw petroleum coke. Irradiations were done on specimens cut from 2- to 6-in.-diameter logs or tubes (Ref. 32) and from 13- to 20-in.-diameter production logs (Ref. 33). The materials were representative of those that are currently used or proposed for graphite-moderated reactors. Changes in dimensions, thermal expansivity, porosity, distribution of porosity, and microstructure were investigated.

The shape of the dimensional change curves at 1000° to 1250°C to $7 \text{ to } 15 \times 10^{21} \text{ n/cm}^2$ ($E > 0.18 \text{ MeV}$) was similar in all materials and similar to data of others (Refs. 34-36): an initial contraction in the c-axis and a-axis directions followed by expansion at higher fluences. The anisotropy of the dimensional changes was greatest for needle-coke materials. Examples of anisotropic and near-isotropic materials are shown in Figs. 24 and 25.

The thermal expansivity of the needle-coke graphites showed either no change or an increase with fluence, the behavior being dependent on the particular material. The thermal expansivity of several needle-coke graphites increased significantly after irradiation at 1000° to 1250°C to fluences of $1.5 \times 10^{22} \text{ n/cm}^2$. The expansivities of the near-isotropic materials decreased at intermediate fluences and finally leveled off at the highest fluences (see Fig. 26).

The densification of the solid portion of the samples was more rapid at 1175° to 1280°C than at 950° to 1051°C. Expansion began at about $7 \times 10^{21} \text{ n/cm}^2$ at 1175° to 1280°C. The median density of sink-float particles obtained from comminuting irradiated specimens decreased. The rate of expansion slowed with increasing fluence and was dependent on the type of graphite; the near-isotropic graphites showed the slowest expansion.

Fig. 24. Dimensional changes of two production-grade graphites as a function of fluence: H-327 (needle coke) and H-328 (Gilsonite coke) (Ref. 33)

Fig. 25. Dimensional changes of needle-coke graphite (CHN) impregnated with a nongraphitizing carbon as a function of neutron fluence (Ref. 32)

Fig. 26. Thermal expansivity changes as a function of neutron fluence (Ref. 32)

By combining the dimensional and density changes discussed above, it was possible to describe the internal changes that take place in the various graphites under high-temperature irradiation using the model for microstructure developed in Section 5. An example of the volume and porosity changes as a function of fluence, derived from the dimensional and density changes, is shown in Fig. 27. The curves represent the bulk volume changes (V_b), the volume change of crystallites plus total closed microporosity (V_x), and the volume changes of the sink-float particles (V_y) (crystallites plus closed microporosity in the sink-float particles). The ordinates between the curves represent pore volumes (as defined in Section 5); V_{p1} is the intercrystallite pores, V_{p2} is the closed porosity external to the sink-float particles and closed to liquids when a bulk sample is measured, and V_{p3} is the open porosity. The shape of the curves was consistent for all graphites during densification: (1) the closed micropore volume V_{p2} that was external to the sink-float particles was eliminated during the initial densification up to the maximum contraction strain, and (2) the median volume of the sink-float particles increased with fluence. Concurrently, the open porosity (V_{p3}) decreased up to volumetric turnaround, but thereafter new porosity was generated and appeared predominantly in V_{p3} .

The volume expansion of the sink-float particles represented the volume expansion of the crystallites in that fraction of the material, modified by interactions due to crystallite interferences and formation of microporosity. The expansion of the sink-float particles was accommodated by microcracks in V_{p2} and V_{p3} . The closure of microcracks in V_{p2} and V_{p3} resulted from two distinct but related processes: (1) a-axis contraction which is responsible for the change in V_b and V_x , and (2) the accommodation of c-axis expansion represented by the expansion of V_y (see Fig. 27). The volumetric changes of the sink-float particles combined with the changes in V_{p2} and V_{p3} represent the average contribution of the crystallite volume changes and pore volume changes to the bulk volume changes; the curves in Fig. 27 show the internal rearrangements that occurred within the microstructure.

Fig. 27. Volume changes in CHN graphite at 300°, 950° to 1015°, 1175° to 1280°, and 1500°C (Ref. 32)

During the expansion phase at high fluences when the effectiveness of V_{P_2} and V_{P_3} for accommodating c-axis expansion has been exhausted, the c-axis expansions were transmitted directly to the bulk and created pores in V_{P_3} which added to the volumetric expansion of the bulk.

The pore volumes V_{P_2} and V_{P_3} , consumed during the densification phase, are distributed throughout the graphite in domains other than inter-crystallite regions. This crack network lies between clusters of crystallites and adjacent to basal plane surfaces and accommodates c-axis expansion over greater distances than the intercrystallite pores. After expansion it appeared that pores and cracks formed in the micro-structure at the boundaries between filler particles, and the materials started to disintegrate by the breakage of interparticle bonds (pitch-binder coke) between the grist particles after expansion exceeded about 30 vol %.

In the needle-coke graphites the bulk volume strain was maximum for the materials that contained the largest volume of graphite structure (see Fig. 28), and V_{P_2} was almost entirely eliminated in these materials at maximum densification. The same correlation held for the near-isotropic materials, except they are composed of predominantly semigraphitic structure and have a relatively narrow distribution of crystallite sizes.

The rate of expansion after turnaround could also be correlated with the volume percent of graphitic structure of the graphites; the expansion rates were highest for those materials with the largest volumes of graphitic structure. This appeared to hold only when the materials had similar isotropy. During densification the volume changes of the sink-float particles were largest at 300°C, but the rate of a-axis contraction was slow resulting in a slow depletion of pore volumes V_{P_2} and V_{P_3} . As the irradiation temperature was raised, there was a decrease in the rate of expansion of the sink-float particles accompanied by an increase in the a-axis contraction due to the migration of vacancies and an increase in c-axis expansion which resulted in a higher depletion rate of V_{P_2} and V_{P_3} .

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Fig. 28. Volume distribution of apparent crystallite sizes L_c within each graphite

The higher depletion rate of V_{p_2} and V_{p_3} resulted because irradiation creep of the crystals improved as the temperature was raised allowing for large crystallite shape changes without disrupting the structure except to deplete the internal porosity. This effect is similar to that observed in the model materials (Section 6.1). New porosity formed more slowly in the sink-float particles at the highest temperature.

The volume expansion of the sink-float particles gave an upper limit for the volume change of the crystallites in the presence of intercrystallite porosity. However, a meaningful measure of the crystallite dimensional changes cannot be obtained from the sink-float measurements because the ratio of a-axis contraction to c-axis expansion cannot be measured. However, the sink-float measurements represent the crystallite volume changes of the artificial graphites and may be viewed as effective crystallite volume changes that include accommodation due to porosity.

Thermal expansivity did not change significantly during bulk densification of the graphites at low fluences; however, at the onset of volume expansion it started to change, being quite sensitive to the microstructures of the various materials. The thermal expansivity of the needle cokes either did not change or increased, whereas that of the near-isotropic graphites decreased. If the depletion of V_{p_2} and V_{p_3} were responsible for the reduction of thermal expansivity during densification, then it would be expected that upon closure the thermal expansivity values would increase and approach theoretical values. The experimental results showed this to be the case only when the structure was predominantly anisotropic and graphitic, but any dilution of this structure with isotropic and semigraphitic structure reversed this trend until at the other extreme, represented by the Poco graphites (Ref. 29), the thermal expansivity underwent a large decrease. The thermal expansivities correlated with the mean apparent crystallite size $\bar{L}_c$ of the various graphites (Section 5). The $\bar{L}_c$ parameter is a sensitive measure of the volume of anisotropic and graphitic structure in a material. The distribution of crystallite size was shifted to higher values in the needle-coke graphites that showed thermal expansivity

increases (Fig. 26), but in the material that showed no change in thermal expansivity the distribution was wide, showing an even distribution over a large range of crystallite sizes encompassing sizes of both anisotropic and isotropic materials. The materials that decreased in thermal expansivity had distribution curves that peaked at low values with a narrow range of crystallite sizes. The mean apparent crystallite size $\bar{L}_c$ and the distribution of L_c values correlated systematically with the thermal expansivity changes.

There was considerable scatter in the dimensional data of specimens cut from production-grade needle-coke graphites irradiated above 900°C. The scatter was particularly high among the specimens after maximum densification had been achieved at about $3 \text{ to } 5 \times 10^{21} \text{ n/cm}^2$ and expansion had begun. This is the region where rapid expansion in the c-axis direction was no longer accommodated by microcracks, and the crystallites were interacting to form large pores or cracks that provided additional bulk volume expansion. In this range of fluence and temperature, needle-coke graphites are highly unpredictable, and the rate of expansion depends critically on the microstructure of the particular specimen under test. The data for the near-isotropic Gilsonite material contrasts with data for the needle-coke materials and shows considerably less scatter (Fig. 24).

No differences in the dimensional or volumetric changes were observed between samples located at the center or edge or a production log of 9567 needle-coke graphite.

The thermal conductivity of the production-grade graphites decreased after irradiation in the range $1.70 \text{ to } 6.0 \times 10^{21} \text{ n/cm}^2$ at 500° to 1000°C. The conductivity, about 0.10 to 0.17 cal/cm-sec-°C before irradiation, decreased to a range of 0.04 to 0.08 cal/cm-sec-°C after irradiation when measured at the temperature of irradiation. The conductivity after irradiation was not dependent on material, temperature, or fluence in the above temperature and fluence range.

6.4.2. Effect of Pitch-Binder Coke on Irradiation Behavior*

In Sections 6.3 and 6.4.1 the bulk dimensional changes of artificial or highly oriented graphites were shown to be related to crystallite changes and porosity changes. The filler and binder carbons are the two major components that determine the nature of the graphite structure, and the ratio of the binder coke to the filler coke is known to affect the microstructure and properties of artificial graphites (Refs. 37-40). Thus, variations in the microstructure due to a variation of the ratios of a particular combination of filler and binder cokes were expected to produce corresponding effects in neutron-induced dimensional and property changes.

This portion of the work was based on the results of irradiating needle-coke graphites to $\sim 10^{22}$ n/cm² at 1225°C utilizing specimens prepared in the laboratory under controlled conditions where the fraction of the pitch-binder coke was varied systematically over the range 5.5 to 14.2 wt %.

In fabricating the specimens it was found that the binder-coke yield decreased when the binder content was increased in the green mix and the binder-coke fraction was a linear function of binder content in the green mix. Physical properties and structural parameters of the graphites are given in Table 5. The bulk density increased with increasing binder-coke content, whereas the density of the solid samples, measured by immersion in a liquid, decreased indicating the closure of very small pores in the filler particles. The thermal expansivity was not affected by the binder-coke fraction, nor was the degree of crystallite orientation. The action of the molding process aligned the needle-coke particles, with their long axes normal to the molding direction. The apparent crystallite size L_c of the compacts decreased with increasing binder-coke fraction, giving an indication that either the binder coke is less graphitic than the needle-coke filler material or its amount affects the graphitization of the filler particles.

*The results summarized in this section are contained in GA-9971. See report number 12 in the Appendix for full reference.

TABLE 5
PHYSICAL PROPERTIES AND STRUCTURAL PARAMETERS
OF GRAPHITES WITH VARYING BINDER-COKE FRACTIONS ^(a)

Binder-coke fraction, β (wt-%)	Density (g/cm ³)		Coefficient of thermal expansion α $\times 10^6$, °C ⁻¹ at 400°C			BAF	L_c (Å)
	Bulk	Immersion in liquid		⊥	+ 2⊥		
5.5	1.59	2.212	4.00	2.50	9.00	1.70	1250
6.6	1.64	2.206	3.40	2.40	8.20	1.80	1150
7.6	1.67	2.203	4.00	2.50	9.00	1.60	1150
8.4	1.66	2.202	3.00	2.50	8.00	1.70	1080
9.0	1.67	2.199	3.60	2.45	8.50	1.65	900
11.7	1.68	2.198	3.75	2.25	8.25	1.70	740
14.2	1.70	2.185	4.20	2.10	8.40	1.55	780

^(a) Average values of three or more specimens.

Dimensional changes were strongly affected by the binder-coke fraction (β) (Fig. 29). The shape of the dimensional-change curves was similar to that observed in irradiation studies of needle-coke graphites (Section 6.4.1), but the parallel changes were sensitive to the binder-coke fraction, showing decreasing expansion with increasing β , up to an optimum value of about 11 wt %, and an increase again at higher values of β . The perpendicular changes were also dependent upon β , showing larger contractions by a factor of 2 when β was increased to 14 wt %. Volumetric expansion was largest when β was low and smallest at the optimum value of 11 wt %.

Thermal expansivity changes followed the dimensional changes. The pattern established in the thermal expansivity changes was that of large increases when the material expanded dimensionally in the c-axis direction (parallel) or did not contract rapidly in the a-axis direction (perpendicular).

Irradiation produced a bulk densification followed by expansion. However, the solid material underwent little change in density during the bulk densification phase, but started to expand when the bulk expanded.

The binder coke is believed to provide a condition of restraint on the filler particles in addition to the restraints resulting from crystallite interactions within the filler particles. By increasing the binder-coke content, the contraction of the filler particles was enhanced but their expansion was restricted. This point is illustrated by the data in Fig. 30, where the volume changes of loose needle-coke particles, which were irradiated along with the above compacts, showed a significant increase in volume expansion even at low fluences over the formed compact, which had not expanded to the same extent at $9.7 \times 10^{21} \text{ n/cm}^2$. The needle-coke particles expanded rapidly when they were not restrained by the binder coke.

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Fig. 29. Dimensional changes versus β , irradiated to 9.7×10^{21} n/cm² at 1225°C (Ref. 41)

LC80783

Fig. 30. Volumetric changes of molded compacts and needle-coke particles at 1225°C (Ref. 41)

During densification the dimensional changes were not strongly dependent on the binder-coke fraction, because most of the c-axis expansion in the filler particles was accommodated by porosity within the filler particles. At higher fluences, where c-axis expansion and a-axis contraction strains are large, the filler particles continue to change shape and expand in the c-axis direction, but are placed in a compressive stress at basal plane surfaces by the binder coke, which behaves more like an isotropic structure and does not undergo large volume changes (Section 6.4.1). This condition causes stresses to build up at the edges of the filler particles; cracks form at the filler-binder interfaces and add to volume expansion. This type of pore generation, and subsequently the rate of volume expansion, depends on the strength of the binder-filler bonds, which in turn appears to depend on the binder-coke fraction. In the materials with a deficiency of binder coke, the breakaway expansion was observed at low fluences and proceeded at a more rapid rate than in the materials of optimum binder content. The data suggest an optimum binder content for this series of materials of about 11 wt %, but the optimum value may be different when other filler particles and binders are used and fabrication processes differ.

6.4.3. Effect of Temperature History on Dimensional Changes*

There are regions in HTGR cores where the graphite temperatures are initially high ($\sim 1000^{\circ}\text{C}$) but during the lifetime of the graphite drop to lower temperatures ($\sim 700^{\circ}$ to 800°C). Therefore, the effect of the temperature history on the dimensional changes of the graphite was of interest.

In this work a number of graphites were irradiated to intermediate fluences at $\sim 1000^{\circ}$ and 1450°C , and the irradiation was continued to higher fluences at lower temperatures. The graphites utilized for this study were selected from the materials described in Section 5 (Table 3).

The dimensional changes for perpendicular specimens irradiated first to about $3 \times 10^{21} \text{ n/cm}^2$ at $\sim 1000^{\circ}\text{C}$ and then from 3 to $5 \times 10^{21} \text{ n/cm}^2$ at

*The results summarized in this section are contained in GA-10001. See report number 13 in the Appendix for full reference.

760° to 800°C resided in the same data population as those for specimens irradiated continuously at ~1000°C to 5×10^{21} n/cm². This is illustrated by the data in Fig. 31 for H-315-A graphite. Several other materials behaved in a similar manner. The perpendicular specimens that were irradiated to 3×10^{21} n/cm² at ~1000°C were just entering turnaround when the temperature was dropped to 760° to 800°C; therefore, it was expected that if the irradiation were continued at ~1000°C, their rate of dimensional change would be near zero for the next 2 to 3×10^{21} n/cm². The shift to 760° to 800°C did not alter this behavior.

The parallel data for one needle-coke material showed a somewhat slower rate of contraction after the temperature was dropped to 760° to 800°C. However, the volume changes for the specimens that were dropped in temperature showed turnaround to expansion, whereas those that were irradiated continuously at 1000°C did not.

A needle-coke graphite specimen expanded at a higher rate after an initial irradiation at 1450°C to 3×10^{21} n/cm² followed by irradiation to 9×10^{21} n/cm² at 1175° to 1280°C than a companion specimen irradiated only at 1175° to 1280°C to $\sim 9 \times 10^{21}$ n/cm². The initial irradiation at the higher temperature apparently initiated a more rapid turnaround and a higher expansion rate after turnaround.

These experiments showed an apparent temperature-history effect similar to that observed in model carbons (Section 6.1.8), but were not as conclusive because of the smaller number of experimental data points. In future work studies will be continued to higher fluences, and additional specimens will be included to provide data at other temperatures.

6.4.4. Thermal Conductivity Changes

Irradiation-induced thermal conductivity changes are important in the design of high-temperature reactors when the graphite is utilized to transfer heat from the fuel to the coolant. Unfortunately, thermal conductivity is reduced rapidly and saturates at relatively low fluences

Fig. 31. Dimensional changes of H-315-A graphite as a function of fluence at 1000°C followed by 760° to 800°C (Ref. 42)

when graphites are irradiated at high temperatures. The changes in thermal conductivity may be due to small interstitial clusters and small vacancy clusters and single vacancies in the graphite lattice rather than gross structural changes (Ref. 43). The fractional change in thermal conductivity is large when measurements are made at room temperature, but becomes less significant as the measuring temperature is raised due to phonon-phonon interactions that mask the scattering effects of lattice defects. The fractional change in thermal conductivity decreased with increasing irradiation temperature when measured at room temperature (Ref. 44); however, when the measuring temperature was raised to that of the irradiation temperature, there was little or no dependency on irradiation temperature (Section 6.4.1).

Thermal conductivity has been measured on Gilsonite and needle-coke materials after irradiation to about $6 \text{ to } 7 \times 10^{21} \text{ n/cm}^2$ at 1000° and 1200°C (see Table 6). These specimens have been taken to higher fluences than those described in Ref. 44.

The fractional change in thermal conductivity was large, ranging from 70 to 80% after irradiation at ~1000°C to 1100°C to only about 50% after irradiation at 1200°C. Annealing for 5 or 10 min produced a rapid rate of recovery of the thermal conductivity, followed by a much slower rate up to 500 to 1800 min. The graphite irradiated at 1190°C, which had smaller initial fractional changes, recovered to about the same fractional change as those irradiated at 1000° to 1100°C. The specimens utilized for these annealing studies had undergone considerable dimensional changes and were expanding in volume, but had not yet reached a positive volume strain, whereas those in Ref. 44 were still contracting. It is interesting to note that the specimens that had progressed furthest in dimensional changes, those irradiated at ~1200°C, had the smallest fractional changes in thermal conductivity. This is further indication that the degradation of thermal conductivity results from irradiation-induced lattice defects and that macrostructural changes or porosity changes do not become important until very high fluences. The specimens irradiated at ~1200°C do not contain as many annealable defects as those

TABLE 6

THERMAL CONDUCTIVITY OF IRRADIATED GRAPHITES

Material	Specimen Number	Exposure $\times 10^{-21}$ (n/cm ²)	Temp (°C)	Annealing		K (cal/cm-sec-°C)	$1 - \frac{K}{K_0}$
				Time (min)	Temp (°C)		
H-315-A	--	--	--	--	--	0.355	0
	15-1	6.85	1015	0	--	0.105	0.70
	15-1	6.85	1015	5	1250	0.139	0.61
	15-1	6.85	1015	455	1250	0.151	0.58
	15-1	6.85	1015	895	1250	0.172	0.52
	15-1	6.85	1015	1350	1250	0.179	0.50
	15-1	6.85	1015	1770	1250	0.162	0.54
	15-2	6.85	1015	0	--	0.130	0.63
	15-2	6.85	1015	5	1400	0.160	0.55
	15-2	6.85	1015	10	1400	0.158	0.56
	15-2	6.85	1015	70	1400	0.197	0.45
	15-2	6.85	1015	185	1400	0.185	0.48
	15-2	6.85	1015	585	1400	0.197	0.45
	15-4	6.85	1015	0	--	0.120	0.66
	15-4	6.85	1015	5	1700	0.211	0.41
	15-4	6.85	1015	10	1700	0.211	0.41
	15-4	6.85	1015	70	1700	0.228	0.36
	15-4	6.85	1015	130	1700	0.221	0.38
	15-4	6.85	1015	565	1700	0.250	0.30
CHN	--	--	--	--	--	0.300	0
	17-2	6.85	1005	0	--	0.092	0.69
	17-2	6.85	1005	5	1250	0.138	0.43
	17-2	6.85	1005	455	1250	0.172	0.43
	17-2	6.85	1005	895	1250	0.174	0.42
	17-2	6.85	1005	1350	1250	0.169	0.44
	17-2	6.85	1005	1770	1250	0.151	0.50
	17-1	6.85	1005	0	--	0.080	0.73
	17-1	6.85	1005	5	1400	0.145	0.52
	17-1	6.85	1005	10	1400	0.152	0.49
	17-1	6.85	1005	70	1400	0.171	0.43
	17-1	6.85	1005	130	1400	0.176	0.41
	17-1	6.85	1005	585	1400	0.189	0.37
	17-4	6.85	1005	0	--	0.075	0.75
	17-4	6.85	1005	5	1700	0.220	0.27
	17-4	6.85	1005	10	1700	0.204	0.32
	17-4	6.85	1005	70	1700	0.206	0.31
	17-4	6.85	1005	130	1700	0.214	0.29
	17-4	6.85	1005	565	1700	0.231	0.23
	169-5	7.7	1190	0	--	0.159	0.47
	169-5	7.7	1190	5	1250	0.179	0.40
	169-5	7.7	1190	455	1250	0.179	0.40
	169-5	7.7	1190	895	1250	0.171	0.43
	169-5	7.7	1190	1350	1250	0.176	0.43
	169-5	7.7	1190	1770	1250	0.182	0.39
	168-4	7.7	1190	0	--	0.158	0.47
	168-4	7.7	1190	5	1250	0.171	0.43
	168-4	7.7	1190	455	1250	0.171	0.43
	168-4	7.7	1190	895	1250	0.193	0.36
	168-4	7.7	1190	1350	1250	0.168	0.44
	168-4	7.7	1190	1770	1250	0.173	0.42
	169-1	7.7	1190	0	--	0.155	0.48
	169-1	7.7	1190	5	1400	0.179	0.40
	169-1	7.7	1190	10	1400	0.185	0.34
	169-1	7.7	1190	70	1400	0.187	0.34
	169-1	7.7	1190	130	1400	0.184	0.39
	169-1	7.7	1190	585	1400	0.188	0.37
	168-3	7.7	1190	0	--	0.165	0.45
	168-3	7.7	1190	5	1400	0.171	0.43
	168-3	7.7	1190	10	1400	0.165	0.45
	168-3	7.7	1190	70	1400	0.157	0.48
	168-3	7.7	1190	130	1400	0.173	0.42
	168-3	7.7	1190	585	1400	0.191	0.36

TABLE 6 (Continued)

Material	Specimen Number	Exposure $\times 10^{-21}$ (n/cm ²)	Temp (°C)	Annealing		K (cal/cm-sec-°C)	$1 - \frac{K}{K_0}$
				Time (min)	Temp (°C)		
CHN (cont.)	168-2	7.7	1190	0	--	0.156	0.48
	168-2	7.7	1190	5	1700	0.175	0.42
	168-2	7.7	1190	10	1700	0.180	0.40
	168-2	7.7	1190	70	1700	0.180	0.40
	168-2	7.7	1190	130	1700	0.175	0.42
	168-2	7.7	1190	565	1700	0.190	0.37
	169-3	7.7	1190	0	--	0.145	0.52
	169-3	7.7	1190	5	1700	0.182	0.40
	169-3	7.7	1190	10	1700	0.171	0.43
	169-3	7.7	1190	70	1700	0.189	0.37
	169-3	7.7	1190	130	1700	0.183	0.39
	169-3	7.7	1190	565	1700	0.172	0.43
H-327	--	--	--	--	--	0.279	0
	171-0	5.25	1000	0	--	0.033	0.81
	171-0	5.25	1000	5	1250	0.075	0.73
	171-0	5.25	1000	10	1250	0.075	0.73
	171-0	5.25	1000	25	1250	0.088	0.69
	171-0	5.25	1000	90	1250	0.088	0.69
	171-0	5.25	1000	510	1250	0.093	0.67
	171-0	5.25	1000	900	1250	0.092	0.66
	171-1	5.25	1000	0	--	0.069	0.75
	171-1	5.25	1000	5	1400	0.135	0.52
	171-1	5.25	1000	10	1400	0.158	0.43
	171-1	5.25	1000	15	1400	0.185	0.34
	168-3	7.8	1090	0	--	0.073	0.74
	168-3	7.8	1090	5	1250	0.081	0.71
	168-3	7.8	1090	455	1250	0.089	0.68
	168-3	7.8	1090	895	1250	0.103	0.63
	168-3	7.8	1090	1350	1250	0.105	0.62
	168-3	7.8	1090	1770	1250	0.119	0.57
	168-2	7.8	1090	0	--	0.070	0.75
	168-2	7.8	1090	5	1400	0.102	0.63
	168-2	7.8	1090	10	1400	0.109	0.61
	168-2	7.8	1090	70	1400	0.116	0.58
	168-2	7.8	1090	130	1400	0.116	0.58
	168-2	7.8	1090	585	1400	0.119	0.57
	168-1	7.8	1090	0	--	0.065	0.77
	168-1	7.8	1090	5	1700	0.119	0.59
	168-1	7.8	1090	10	1700	0.139	0.50
	168-1	7.8	1090	70	1700	0.169	0.39
	168-1	7.8	1090	130	1700	0.208	0.25

irradiated at 1000°C, implying that considerable thermal annealing is accomplished during irradiation at 1200°C over that at 1000°C. The annealing data obtained on CHN graphite or H-315-A after a fluence of about $3 \times 10^{21} \text{ n/cm}^2$ (Ref. 44) showed nearly complete (97%) recovery of thermal conductivity after a few hours at 1500°C (Fig. 32). For H-315-A the fractional change was reduced to 15% and the original conductivity was completely restored only after heating to 2600°C. In contrast with the data of Ref. 44, the data here showed a fractional change of about 30 to 40% remaining in H-315-A or CHN. Thus, the damage was considerably more difficult to remove as the fluence was increased, even though the total fractional change did not increase considerably with fluence (see Fig. 33). This indicates that the defects that cause changes in thermal conductivity at high temperatures are more numerous at 1000°C than at ~1200°C. Kelly et al. (Ref. 43) indicate that thermal conductivity changes after irradiation at low temperatures are due to small interstitial clusters and small vacancy clusters and single vacancies. It is unlikely that single vacancies or small interstitial clusters survive during irradiation above 1000°C. Thus, one might expect a spectrum of vacancy cluster sizes above 1000°C with the 1200°C samples having the fewest and largest. This condition may result because thermal annealing is more rapid at 1200°C, causing rapid removal of the small defects by diffusion to produce larger clusters. The data at 1200°C show that as the fluence is increased, the defects that cause thermal degradation are more difficult to remove by thermal annealing. This is probably the case at 1000°C also, but unfortunately no annealing was done on the 1000°C specimens in Ref. 44 after irradiation at lower fluences. The rapidly changing slope of the annealing curves of specimens irradiated to high fluences indicates that the small vacancy clusters can be removed quickly until their population is small. Further heating at a given temperature accomplishes little in the way of restoring thermal conductivity due to the permanent nature of the remaining defects.

An activation energy of $\sim 5.8 \text{ eV}$ was estimated by a method described by Fischback (Ref. 45) from the annealing of fractional changes of thermal conductivity in a specimen of H-327 graphite irradiated at ~1000°C to $\sim 6.7 \times 10^{21} \text{ n/cm}^2$.

Fig. 32. Annealing of CHN graphite

Fig. 33. Fractional change in thermal conductivity of CHN and H-315-A graphites as a function of neutron fluence

6.4.5. Irradiation Creep*

Irradiation-induced plasticity occurs in graphite subject to stress (Refs. 28,46). The irradiation-induced deformation or creep affects stresses in graphite components that are exposed to temperature or flux gradients. Therefore, it is an important property to measure for the purpose of reactor design.

The Dragon Project has made space available to Gulf General Atomic in the Dragon reactor, on a cooperative basis, for the purpose of irradiating restrained shrinkage specimens. The specimens described in this section were prepared at Gulf General Atomic, and the irradiation and postirradiation measurements are being done at Dragon or RCN, Petten, Holland. The experiments described here were patterned after experiments that were already under way at Dragon (Refs. 28,47) and extend the Dragon creep work to the examination of U.S. graphites currently under consideration for HTGRs. The graphites selected for the creep assemblies were described in Section 5, Table 3, and unrestrained irradiation data for these materials were presented in Section 6.4.1. The graphites varied widely in apparent crystallite sizes (500 to 1600 Å), and the effect of L_c on creep constants will be sought. The experimental arrangement is shown in Fig. 34. In order to provide different strain rates, the straining pads were made from perpendicular specimens of TS-688 and parallel specimens of ZTA or hot-worked graphite prepared at Gulf General Atomic (GAHW). The latter two materials are hot-worked graphites that vary in thermal expansivity and irradiation expansion.

A series of restrained shrinkage specimens, of both parallel and perpendicular orientation, were machined along with the restraining pads described above. The restraining pad materials were selected to have shrinkage or expansion rates substantially different from the specimens so that the specimens are placed in a tensile stress as the fluence increases. From a knowledge of the stress, unrestrained and restrained

* Experiments were carried out at the Dragon Project, Winfrith, England. Postirradiation examination was done at Winfrith and RCN, Petten, Holland.

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Fig. 34. Sketch of restrained shrinkage samples irradiated in Dragon

dimensional changes, dimensions of the assembly, Young's modulus of the parts, thermal expansivities, and irradiation conditions, it should be possible to determine an irradiation creep constant of the restrained specimens (Ref. 28).

The specimens, both unrestrained and creep assemblies, were placed in the Dragon reactor in September 1966 and were irradiated for about 2-1/2 years to February 1969. The materials were irradiated at 880° to 1240°C to fluences of 0.85 to 2.4×10^{21} n/cm² ($E > 0.18$ MeV). The specimens were examined visually in May 1969 and found to be in excellent condition. Dimensional changes of the unrestrained specimens are given in Figs. 35 and 36. Data on dimensions of the restrained specimens have been delayed due to a heavy work load at the RCN Petten Laboratory during late 1969 and early 1970, and therefore cannot be included here. These data are now expected during the last half of 1970.

The data for the unrestrained graphites (Figs. 35 and 36) complement the data on specimens from the same materials irradiated in the Engineering Test Reactor at comparable temperatures (Refs. 32,33). One exception was noted in the Dragon data where the dimensional changes at one fluence point were considerably lower than the others and the data in Refs. 32 and 33. No explanation is available for these anomolous data. The dimensional changes for the pad materials, TS-688 ($\perp$), ZTA ($\parallel$), and GAHW ($\parallel$), showed strains of about -0.7, +1.25, and +5%, respectively, at 2×10^{21} n/cm² and confirmed preirradiation estimates that three widely different strain rates would result in the creep assemblies. The TS-688 pads provided only a very small strain rate due to the small differential in dimensional changes between it and the creep specimens, whereas the GAHW material provided a high strain rate and the ZTA an intermediate rate. The data in Table 7 are a record of the creep specimens that fractured or survived, and the differential strains between pad and creep specimen materials. At 1090° to 1235°C to 2.4×10^{21} n/cm² all creep specimens except one fractured at the high

Fig. 35. Dimensional changes as a function of fluence for GAHW, ZTA, and H-328 graphites at 1090° to 1240°C

Fig. 36. Dimensional changes as a function of fluence for H-327, TS-688, and 9567 graphites at 1090° to 1240°C

TABLE 7
RECORD OF SURVIVAL VERSUS FRACTURE AND DIFFERENTIAL STRAIN BETWEEN UNRESTRAINED CREEP SPECIMENS AND PAD MATERIALS

Reactor Position	Fluence $\times 10^{-21}$ (n/cm ²)	Irradiation Temperature (°C)	Orientation of Creep Specimens	Relative Strain Rate(a)	Condition and Differential Strain(%) ^(b)			
					H-328	H-327	9567	TS-688
1-2	0.95	1100	Parallel	H	F (1.75)	F (1.85)	F (1.85)	F (2.05)
1-3	1.15	1125	Parallel	M	S (0.85)	S (0.95)	S (0.95)	S (1.05)
2-2	1.30	1150	Parallel	L	S (0.05)	S (0.10)	S (0.15)	S (0.30)
2-3	1.50	1175	Parallel	H	F (3.70)	F (3.85)	F (4.00)	F (3.95)
3-3	1.75	1210	Parallel	M	F (1.60)	S (1.75)	F (1.95)	S (1.95)
4-3	2.00	1230	Parallel	L	S (0.05)	S (0.20)	S (0.40)	S (0.35)
5-2	2.15	1240	Perpendicular	H	--	F (5.85)	F (5.95)	F (6.05)
5-3	2.20	1235	Parallel	H	F (6.30)	F (6.45)	F (6.75)	F (6.70)
6-1	2.30	1215	Parallel	M	F (2.60)	F (2.75)	F (3.05)	F (2.95)
6-2	2.35	1195	Parallel	L	S (0.10)	S (0.20)	S (0.50)	S (0.40)
7-2	2.40	1130	Perpendicular	H	F (6.95)	F (6.85)	F (6.95)	F (7.00)
7-3	2.35	1110	Parallel	H	F (4.56)	F (4.30)	F (4.07)	S (5.42)
8-1	2.30	1060	Parallel	M	S (0.72)	S (1.04)	S (0.80)	S (1.07)
8-2	2.20	1040	Parallel	L	S (0.31)	S (0.60)	S (0.17)	S (0.60)
9-2	2.00	950	Parallel	H	--	F (2.60)	F (2.10)	F (2.53)
9-3	1.80	880	Parallel	M	S (0.72)	S (1.04)	S (0.80)	S (1.07)

(a) H = high, M = medium, L = low.

(b) Preliminary data assuming all strain is in the pads. F = fractured; S = survived.

strain rate, while all those of the low strain rate survived. The one specimen of high strain rate that survived is an anomaly. About one-half of the specimens of the intermediate strain rate survived and one-half fractured; thus, it was possible to determine a preliminary critical strain rate ($\sim 10^{-3}/10^{20}$ n/cm²) from the slope of a line separating the failed and survived specimens on a plot of estimated strain versus fluence. Assuming a common fracture stress for all graphites of ~ 1500 psi, a preliminary creep constant was estimated to be about $k = 6.7 \times 10^{-7}$ (psi)⁻¹ (10⁻²⁰ n/cm²) for all materials, which is in excellent agreement with data for Dragon graphites in Ref. 28. The estimated creep constant at 880° to 1060°C agreed with the data at 1090° to 1235°C.

The creep constant will be determined in a more precise manner after the restrained specimens are measured. It is planned to return the survived specimens and perhaps a few virgin creep assemblies to the Dragon reactor for additional fluence.

APPENDIX

TOPICAL REPORTS AND PUBLICATIONS FOR THE PERIOD MAY 15, 1967, THROUGH MAY 14, 1970

1. GA-8001 "The Influence of Crystallite Size on the Dimensional Changes Induced in Carbonaceous Materials by High-Temperature Irradiation," J. C. Bokros, G. L. Guthrie, and A. S. Schwartz, July 28, 1967 [Carbon 6, 55 (1968)].
2. GA-8555 "Effect of High-Neutron Exposure on the Dimensions of Pyrolytic Carbon," J. C. Bokros, R. W. Dunlap, and A. S. Schwartz, March 15, 1968 [Carbon 7, 143 (1969)].
3. GA-8700 "Radiation-Induced Dimensional Changes and Creep in Carbonaceous Materials," J. C. Bokros, G. L. Guthrie, R. W. Dunlap, and A. S. Schwartz, August 30, 1968 [J. Nucl. Mater. 31 25 (1969)].
4. GA-8888 "The Structure and Properties of Pyrolytic Carbon," J. C. Bokros, September 6, 1968 [Proceedings of the First International Conference on Materials Science - Ceramic Science and Technology, Tremezzo (Como), Italy, to be published].
5. EUR-4094* "Etude Micrographique de la Carbonisation et de la Graphitisation d'un Brai de Houille Extraite," J. L. White, J. Dubois, and C. Souillart, J. Chim. Phys. (special volume), 33 (April 1969).
6. GA-9600 "Interpretation of Dimensional Changes Caused in Pyrolytic Carbon by High-Fluence Neutron Irradiation," J. C. Bokros and K. Koyama, June 1, 1969 [J. Appl. Phys. 41 2146 (1970)].
7. GA-9421 "Apparatus and Procedure to Determine Density and Structural Distributions in Carbons and Graphites," G. B. Engle, W. H. Morris, and L. Bailey, June 8, 1969 (to be published in Carbon).
8. GA-9617 "Density and Structural Distributions in Artificial Graphites," G. B. Engle, July 29, 1969 (to be published in Carbon).

*The work reported in this article was done in part on this program during 1967. The remainder was done at the Petten (Netherlands) Establishment of EURATOM during 1967 and 1968.

9. GA-9900 "Irradiation Behavior of Isotropic Carbons," J. C. Bokros and D. W. Stevens, February 24, 1970 (to be published in Carbon).
10. GA-9972 "Irradiation Behavior of Nuclear Graphites at Elevated Temperatures," G. B. Engle, March 4, 1970.
11. GA-9919 "Irradiation-Induced Dimensional Changes and Creep of Isotropic Carbon," J. L. Kaae and J. C. Bokros, March 11, 1970 (submitted for publication in J. Am. Ceram. Soc.).
12. GA-9971 "The Influence of Pitch-Binder Coke Content on the Properties and Irradiation Behavior of Molded Graphite," G. B. Engle, March 12, 1970 (submitted for publication in Carbon).
13. GA-10001 "Effect of Temperature History on the Dimensional Changes of Nuclear Graphites, G. B. Engle, March 23, 1970.
14. GA-9973 "High-Temperature Irradiation Behavior of Production-Grade Nuclear Graphites," G. B. Engle and A. L. Pitner, March 30, 1970.
15. GA-9974 "Isochronal Annealing Kinetics and Neutron-Induced Dimensional Changes of Titanium-Doped Pyrolytic Carbon," R. J. Price and J. C. Bokros, May 11, 1970 (submitted for publication in Carbon).
16. GA-10162 "Annealing of Neutron-Irradiated Pyrocarbons," R. J. Price and J. C. Bokros, June 8, 1970 (submitted for publication in Carbon).
17. GA-9970 "Low-Temperature Graphitization of Cokes and Binder-Filler Artifacts," G. B. Engle, July 17, 1970 (submitted for publication in Carbon).

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