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GULF GENERAL ATOMIC

Gulf-GA-A12138

RESEARCH ON GRAPHITE
ANNUAL REPORT
JULY 1, 1971, THROUGH JUNE 30, 1972,
AND
SUMMARY OF PROGRAM SINCE INCEPTION
by
G. B. Engle

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GULF GENERAL ATOMIC COMPANY
P.O. BOX 608, SAN DIEGO, CALIFORNIA 92112

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Gulf General Atomic Project 271

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PREVIOUS REPORTS IN THIS SERIES

GA-4022 - Annual Report, April 1, 1962, through March 31, 1963
GA-5016 - Annual Report, April 1, 1963, through March 31, 1964
GA-5033 - Annual Report, April 1, 1963, through March 31, 1964 (Task II)
GA-6233 - Annual Report, April 1, 1964, through March 31, 1965
GA-7100 - Annual Report, May 15, 1965, through May 14, 1966
GA-7906 - Annual Report, May 15, 1966, through May 14, 1967
GA-8681 - Annual Report, May 15, 1967, through May 14, 1968
GA-9433 - Annual Report, May 15, 1968, through May 14, 1969
GA-9975 - Three Year Summary Report, May 15, 1967, through May 14, 1970
Gulf-GA-A10694 - Annual Report, May 15, 1970, through June 30, 1971

TOPICAL REPORTS AND PUBLICATIONS
APRIL 1, 1962, THROUGH JUNE 30, 1972

- GA-3985 "Pitch Binders for Graphite: A Survey of the Literature," J. R. Hooker, March 7, 1963.
- GA-4267 "Fission Product Release from Monogranular UC_2 Particles," L. R. Zumwalt, P. E. Gethard, and E. E. Anderson, June 5, 1963 [Nucl. Sci. Eng. 21, 1 (1965)].
- GA-4318 "Chemical Studies of Binders for Graphite," J. R. Hooker and R. E. Norman, January 28, 1964.
- GA-4778 "Random Pyrolytic Carbon," J. C. Bokros, November 22, 1963 [Nature 202, 1004 (1964)].
- GA-5084 "Influence of Structure on Mechanical Properties of Pyrolytic Carbon," J. C. Bokros, R. J. Price, and T. A. Trozera, April 13, 1964 [Nature 204, 371 (1964)].
- GA-5102 "The Anisotropy of Extruded Graphite Tubes," J. C. Bokros, R. J. Price, and G. R. Tully, April 24, 1964 [J. Nucl. Mater. 15, 33 (1965)].
- GA-5163 "The Structure of Pyrolytic Carbon Deposited in a Fluidized Bed," J. C. Bokros, June 10, 1964 [Carbon 3, 17 (1965)].
- GA-5348 "Hot-Working of Graphite for Graphite-Matrix Nuclear Fuels," J. L. White and R. J. Price, July 17, 1964 [Carbon 2, 327 (1965)].
- GA-5571 "Relationship Between Preferred Orientation, Thermal Expansion, and Radiation-Induced Length Changes in Graphite," R. J. Price and J. C. Bokros, October 6, 1964 [J. Appl. Phys. 36, 1897 (1965)].
- GA-5793 (C/RD) "Uranium Migration Through Pyrolytic Carbons Deposited in a Fluidized Bed," (U), J. C. Bokros and N. L. Sandefur, November 1964.
- GA-5882 (C/RD) "Hot-Worked Graphite-Matrix Fuel Bodies," (U), J. L. White and J. M. Pontelandolfo, January 1965.
- GA-6031 "Absorption Factors for a Modified Bacon Preferred-Orientation Technique," J. C. Bokros, February 4, 1965 [Carbon 3, 167 (1965)].

- GA-6050 "Variations in the Crystallinity of Carbons Deposited in Fluidized Beds," J. C. Bokros, April 1, 1965 [Carbon 3, 201 (1965)].
- GA-6052 "Graphite-Carbide Materials Prepared by Hot-Working," J. L. White and J. M. Pontelandolfo, February 3, 1965 [Nature 209, 1018 (1966)].
- GA-6053 "Young's Modulus of Pyrolytic Carbon in Relation to Preferred Orientation," R. J. Price, March 30, 1965 [Phil. Mag. 12, 561 (1965)].
- GA-6332 "Deformation and Fracture of Pyrolytic Carbons Deposited in Fluidized Beds," J. C. Bokros and R. J. Price, May 21, 1965 [Carbon 3, 503 (1966)].
- GA-6506 "Structure and Properties of Pyrolytic Carbons Prepared in a Fluidized Bed Between 1900° and 2400°C," R. J. Price, J. C. Bokros, K. Koyama, and J. Chin, September 13, 1965 [Carbon 4, 263 (1966)].
- GA-6670 "Irradiation of Graphite Impregnated with Furfuryl Alcohol," G. B. Engle, B. F. Disselhorst, G. R. Tully, and W. P. Wallace, October 5, 1965 [Carbon 3, 543 (1966)].
- GA-6736 "Radiation-Induced Dimensional Changes in Pyrolytic Carbons Deposited in a Fluidized Bed," J. C. Bokros and R. J. Price, November 25, 1965 [Carbon 4, 441 (1966)].
- GA-6854 "Dimensional Changes in Graphite Irradiated Between 500° and 1100°C," R. J. Price and J. C. Bokros, January 25, 1966 [Carbon 5, 73 (1967)].
- GA-6926 "Mechanical Properties of Neutron-Irradiated Pyrolytic Carbons," R. J. Price and J. C. Bokros, May 24, 1966 [J. Nucl. Mater. 21, 158 (1967)].
- GA-6927 "Neutron-Induced Changes in Crystallinity and Thermal Conductivity of Pyrolytic Carbons," J. C. Bokros, R. J. Price, and K. Koyama, February 8, 1966 [Carbon 4, 293 (1966)].
- GA-6975 "The HTGR Coated Particle Fuel," W. V. Goeddel and J. C. Bokros, March 15, 1966 (paper presented at the 1966 AIME Nuclear Metallurgy Symposium).
- GA-7046 "Graphite-Carbide Materials Prepared by Hot-Working with a Dispersed Liquid-Carbide Phase," J. L. White and J. M. Pontelandolfo, April 14, 1966 [Carbon 4, 305 (1966)].

- GA-7075 "A Unifying Coating Parameter," J. C. Bokros and A. S. Schwartz, May 4, 1966 [Carbon 5, 90 (1967)].
- GA-7146 "Irradiation-Induced Densification of Pyrolytic Carbon Coatings," J. C. Bokros and A. S. Schwartz, May 27, 1966 [Trans. Met. Soc. AIME 239, 7 (1967)].
- GA-7078 "Dimensional Changes in Isotropic Graphites Irradiated at Elevated Temperatures," G. B. Engle, May 23, 1966.
- GA-7326 "Dimensional and Property Changes of Impregnated and Isotropic Graphites Irradiated at 300° to 1500°C," G. B. Engle, April 14, 1967 [Carbon 6, 455 (1968)].
- GA-7339 "Dimensional Changes Induced in Pyrolytic Carbon by High-Temperature Fast-Neutron Irradiation," J. C. Bokros and R. J. Price, December 15, 1966 [Carbon 5, 301 (1967)].
- GA-7437 "Graphitic Materials Hot-Worked with a Dispersed Liquid Carbide: Thermal and Electrical Conductivity," J. L. White and K. Koyama, June 5, 1967 [J. Am. Ceram. Soc. 51, 394 (1968)].
- GA-7457 "The Influence of the Pitch Binder Content on the Structure and Properties of Molded Graphites," G. B. Engle, April 12, 1967 [Carbon 6, 447 (1968)].
- GA-7458 "The Influence of Pitch Binder Content on the High-Temperature Irradiation Behavior of Molded Graphites," G. B. Engle, May 8, 1967 [Carbon 6, 447 (1968)].
- GA-7515 "Structural Dependence of the Tracer-Level Diffusion of Thorium in Pyrolytic Carbons," H. K. Lonsdale and J. N. Graves, December 15, 1966 [J. Appl. Phys. 38, 3620 (1967)].
- GA-7694 "Mesophase Microstructures in Carbonized Coal-Tar Pitch," J. L. White, G. L. Guthrie, and J. O. Gardner, February 7, 1967 [Carbon 5, 517 (1967)].
- GA-7700 "A Model to Describe Neutron-Induced Dimensional Changes in Pyrolytic Carbon," J. C. Bokros and A. S. Schwartz, March 3, 1967 [Carbon 5, 481 (1967)].
- GA-7812 "Effect of Irradiation at 300°-1500°C on the Thermal Conductivity and Electrical Resistivity of Impregnated Graphites," G. B. Engle and K. Koyama, July 19, 1967 [Carbon 6, 455 (1968)].

- GA-7905 "Thermal Expansivities and Preferred Orientation of Pyrolytic Carbons," R. J. Price, J. C. Bokros, and K. Koyama, May 25, 1967 [Carbon 5, 423 (1967)].
- GA-7996 "HWLC Graphites Prepared by Hot-Working Extruded Stock," J. L. White and J. M. Pontelandolfo, September 12, 1967 [Carbon 6, 1 (1968)].
- GA-8001 "The Influence of Crystallite Size on the Dimensional Changes Induced in Carbonaceous Materials by High-Temperature Irradiations," J. C. Bokros, G. L. Guthrie, and A. S. Schwartz, July 28, 1967 [Carbon 6, 55 (1968)].
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- 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)).
- GA-8888 "The Structure and Properties of Pyrolytic Carbon," J. C. Bokros, September 6, 1968 (paper presented at First International Conference on Materials Science - Ceramic Science and Technology, Trezzano (Como), Italy, September 1968).
- GA-9054 "Fission-Recoil Damage to Pyrolytic Carbon," J. C. Bokros, December 10, 1968 [Carbon 7, 703 (1969)].
- 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 [Carbon 8, 393 (1970)].
- 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)].
- GA-9617 "Density and Structural Distributions in Artificial Graphites," G. B. Engle, July 29, 1969 [Carbon 8, 485 (1970)].
- GA-9900 "Irradiation Behavior of Isotropic Carbons," J. C. Bokros and D. W. Stevens, February 24, 1970 [Carbon 9, 19 (1971)].
- GA-9919 "Irradiation-Induced Dimensional Changes and Creep of Isotropic Carbon," J. L. Kaae and J. C. Bokros, March 11, 1970 [Carbon 9, 111 (1971)].

- GA-9970 "Low-Temperature Graphitization of Cokes and Binder-Filler Artifacts," G. B. Engle, July 17, 1970 (accepted for publication in Carbon).
- GA-9971 "The Influence of Pitch-Binder Coke Content on the Properties and Irradiation Behavior of Molded Graphites," G. B. Engle, March 12, 1970 [Carbon 9, 383 (1971)].
- GA-9972 "Irradiation Behavior of Nuclear Graphites at Elevated Temperatures," G. B. Engle, March 4, 1970 [Carbon 9, 539 (1971)].
- GA-9973 "High-Temperature Irradiation Behavior of Production-Grade Nuclear Graphites," G. B. Engle and A. L. Pitner, July 10, 1970.
- GA-9974 "Isochronal Annealing Kinetics and Neutron-Induced Dimensional Changes of Titanium-Doped Pyrolytic Carbons," R. J. Price and J. C. Bokros, May 11, 1970 [Carbon 9, 205 (1971)].
- GA-10001 "Effect of Temperature History on the Dimensional Changes of Nuclear Graphites," G. B. Engle, March 23, 1970.
- GA-10101 "Irradiation-Induced Dimensional Changes in Imperfect Graphite Crystals," J. C. Bokros, G. L. Guthrie, and D. W. Stevens, June 29, 1970 [Carbon 9, 349 (1971)].
- GA-10162 "Annealing of Neutron-Irradiated Pyrocarbons," R. J. Price and J. C. Bokros, June 8, 1970 [Carbon 9, 555 (1971)].
- GA-10507 "Irradiation-Induced Microstructural Changes in a Two-Phase Binder-Filler Graphite," G. B. Engle, September 17, 1971 (paper presented at 24th Annual Pacific Coast Regional Meeting of the American Ceramic Society, 1971, Anaheim, California).
- GA-A10988 "A Review of High-Temperature Graphite Irradiation Behavior," G. B. Engle and W. P. Eatherly, April 1972 (to be published in High Temperatures - High Pressures).
- GA-A12080 "Effect of Temperature History on the Dimensional Changes of Nuclear Graphites," G. B. Engle (to be published).
- GA-A12099 "High-Temperature Neutron Irradiation of Highly Oriented Carbons and Graphites," R. J. Price, June 2, 1972.
- GA-A12124 "Relationship Between Crystal Structure, Properties, and Irradiation Behavior of Reactor Graphites," G. B. Engle (to be published).
- GA-A12137 "Effect of High-Temperature High-Fluence Irradiation on Thermal Conductivity of Reactor Graphites," G. B. Engle and K. Koyama (to be published).

ABSTRACT

The research project "Research on Graphite," is reviewed from its inception date April 1962 through the completion date June 30, 1972. Studies to modify and characterize the graphite microstructure, carbonization mechanisms of carbonaceous materials, fission-product release in fuel compacts, fabrication and irradiation of pyrolytic carbons, and the irradiation behavior of artificial reactor graphites are summarized. A qualitative interpretation of the high-fluence, high-temperature irradiation behavior of pyrolytic carbons and reactor graphites is given.

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INTRODUCTION

The current project has been titled "Research on Graphite" from May 15, 1967, through June 30, 1972. It was formerly titled "Advanced Graphite Fuel Systems" from May 15, 1965, through May 14, 1967, and "Advanced, Graphite-Matrix, Dispersion-Type Fuel Systems and Research on Graphite" from its inception April 1, 1962, through March 31, 1965. During the contract year from April 1, 1963, through March 31, 1964, the project was divided into two tasks and two annual reports were written: "Research on Graphite" and "Advanced, Graphite-Matrix, Dispersion-Type Fuel Systems."

The current project will be closed June 30, 1972. A summary of the research tasks, from the inception date April 1, 1962, through June 30, 1972, is given in this final report. During the course of the project, a number of research subjects have been studied. Each research task or study is reported in summary form separately, including work completed during the final year ending June 30, 1972. Topical reports are referenced where applicable; where no topical report was published, reference is made to the annual report that covers the work in more detail. All details and data generated during the final contract year are reported in a series of topical reports which have been published or are in preparation (Refs. 1-4) and therefore are not repeated in this report.

The research tasks undertaken during the course of the project have been divided into six broad categories as follows:

1. Studies to modify the graphite microstructure
 - 1.1. Hot-working
 - 1.2. Resin impregnation
 - 1.3. Chemical studies of pitch binders
 - 1.4. Catalytic graphitization

2. Characterization of microstructure and carbonization studies
 - 2.1. Mesophase studies
 - 2.2. Relation of physical properties of graphitic materials to microstructure
 - 2.3. Microstructural characterization of graphite
 - 2.4. Characterization of the degree of graphitization
3. Fuel particle and fuel compact studies
 - 3.1. Fission-product release studies
4. Pyrolytic carbons and model materials studies
 - 4.1. Fabrication and structure
 - 4.2. Deformation and fracture
 - 4.3. Diffusion of uranium
 - 4.4. Fission-recoil damage
 - 4.5. Thermal expansion
 - 4.6. Thermal conductivity
 - 4.7. Annealing
 - 4.8. Irradiation
5. Irradiation studies of artificial reactor graphites and carbons
 - 5.1. Highly oriented carbons and graphites
 - 5.2. Influence of pitch-binder coke content
 - 5.3. Reactor graphites
6. Conclusions and interpretation of model carbon and graphite irradiation studies

Throughout the program the major objective has been to develop an understanding of relationships between the properties, microstructure, fabrication processes, and irradiation behavior of carbonaceous materials and thus to provide a basis for substantial improvements in service behavior of these materials. The irradiation experiments were carried out over temperature and fluence ranges that were equal to or exceeded contemporary reactor design concepts.

1. STUDIES TO MODIFY THE GRAPHITE MICROSTRUCTURE

1.1. HOT WORKING

The feasibility of hot-working graphite-matrix fuel bodies for nuclear application was investigated as a means of obtaining improved properties such as decreased porosity and permeability in artificial graphite. Initial work (Ref. 5) consisted of compressing specimens of fuel-matrix graphite, both with and without a dispersion of ZrC particles, in the temperature range 2350° to 2950°C. Studies were made of the effects of changing the hot-working temperature, hot-working strain, pitch content, and method of fabrication of the starting material on the deformation during hot-working and on the properties of the hot-worked material. The hot-working produced a strong preferred orientation and an increase in density in all the samples. Except in the case of bodies containing ZrC particles deformed below the eutectic temperature, hot-working also sharply reduced the permeability of the samples, especially when the initial pitch content was high.

In further work (Ref. 6), graphitic bodies, originally prepared by molding and containing a fine dispersion of zirconium or molybdenum carbide particles, were hot-worked at temperatures above the carbide-graphite eutectic temperature where the carbide phase was in the liquid state. The resulting materials had relatively high density and strength and low permeability to helium. The excess carbide was squeezed from the surface of the body, resulting in a predominantly graphitic body with properties approaching those of the pyrolytic graphites. The initial carbide content of 10 vol % was reduced to about 6 vol % when hot-worked to true strain levels of the order of 60%. The initial stage of hot-working was rapid and corresponded to the effective elimination of open porosity and the reduction of permeability to gases. The second stage (beyond about 30% strain) was slower, but the preferred orientation, thermal expansivity, and strength continued to change appreciably with

increasing strain. The microstructure consisted of fine carbide particles, generally less than 5 μm , distributed uniformly in an oriented graphite matrix whose structure differed from that of conventional molded or hot-worked graphites. Molybdenum-bearing bodies showed the highest strengths with moduli of rupture in excess of 20,000 psi.

The graphitic materials produced by hot-working with a dispersed liquid-carbide phase also had high thermal and electrical conductivities in comparison with hot-worked or conventional graphites prepared without additives (Ref. 7). This process of liquid-phase sintering with compressive deformation imposes a greater preferred orientation on the predominantly graphitic material, and the resulting thermal conductivity in the preferred direction of the layer planes is greater than the thermal conductivity of copper or silver.

The process of hot-working with a dispersed liquid carbide was extended to include extruded graphite containing molybdenum metal (Ref. 8). The extruded graphite was easily deformed in compression along the extrusion axis with little risk of fracture providing the hot-working stresses were kept below 3000 psi until the isotropic state was passed. Measurements were made of chemical composition, density, compressive and flexural strengths, thermal and electrical conductivities, and thermal expansivity for a series of these materials hot-worked to various strain levels up to 65% true strain. These properties indicate that a wide range of preferred orientations is attainable, the isotropic state for the extruded material used being attained at a strain level of 20%. The properties of the graphites that were strained only to the isotropic state showed only modest improvements over the properties of conventional graphites. At higher levels of hot-working strain, the characteristic dense, uniform microstructure of graphites hot-worked with a liquid-carbide phase is imposed on the extruded stock.

1.2. RESIN IMPREGNATION

Studies of the furfuryl-alcohol-resin impregnation of hot-pressed graphite-matrix compacts containing fuel particles coated with pyrolytic

carbon were studied briefly (Ref. 9). The results showed a substantial reduction in helium permeability without damage to the coated particles. Compacts with helium permeability levels ranging as low as 3.5×10^{-6} cm²/sec were prepared and used in fission-product release studies to determine the correlation between permeability and fission-product release. The fission-product release studies are summarized in Section 3.1.

1.3. CHEMICAL STUDIES OF PITCH BINDERS

Chemical studies of pitch binders for graphite were conducted to first review the literature and then to ascertain the composition and function of the binders and to derive methods of binder modification for producing graphite matrices of fuel compacts of improved properties.

The general properties, composition, pyrolysis, and effect on graphite bodies of coal-tar pitch were reviewed and published (Ref. 10).

About 5000 different individual compounds are present in pitch in varying amounts, practically all of them in the same class of multiringed aromatic hydrocarbons. The majority of these are compounds of three to seven rings with molecular weights ranging from 170 to 380 and are present as "associated colloids" or loosely bonded aromatic clusters. An insoluble phase similar to carbon black is also present which, although it makes no direct contribution to the binding action, nevertheless influences the properties of both the pitch itself and the graphite products made with pitch.

During the process of producing a graphite body from a filler-pitch-binder mix, the binder undergoes several heat-induced changes. These are very important, even in the early stages, and greatly influence the properties of the final graphite body. They range from melting to partial distillation of the more volatile products to polymerizing and carbonizing to further ordering and graphitizing. As the temperature is increased, sufficient

energy is imparted to the system to cause homolytic-bond fission and free-radical formation. This facilitates polymerization and condensation of the various molecular fragments, which results in the buildup of a network of aromatic-type bonds.

Many of the conclusions on the mechanism of pitch pyrolysis have been confirmed by studies on pure organic compounds known to be present in pitch. These studies include thermal stability, reactivity, differential thermal analysis, coke residue yields, and free-radical affinities. Indications are that the breaking down of these compounds (both pure and as contained in pitch) and their recombining into the larger planar pseudo-graphite structures involve free-radical reactions and polymerization. The relationship of the properties of the finished carbon or graphite body to the ingredients used, particularly the binder, was also reviewed. Generally, the various physical properties of a graphite body could not be related directly to any one single property of the pitch binder, but rather to a combination of its properties. The interaction of filler and binder was also noted as an important variable.

Chemical studies of pitch binders for graphite were conducted to ascertain the composition and function of the binders and the methods by which they could be modified to produce compacts with improved properties (Ref. 11). A solvent-extraction process was established for the separation of pitch into three basic fractions and two subfractions. Liquid-solid elution chromatography was used to effect a further separation of the moltene fraction of pitch into seven groups of compounds. Infrared-spectrographic analyses showed the volatile compounds of pitch were predominantly multi-ringed, aromatic hydrocarbons. The insoluble portion of pitch was shown by microstructural studies to be similar to carbon black.

In studies involving the preparation of graphite compacts with various fractions of pitch used as the binder, it was shown that the asphaltene-carbene fraction produced the best compacts. This is equivalent to using pitch from which the volatile, multiringed hydrocarbons of lower molecular

weight have been removed. The asphaltene fraction was the best binder of the individual fractions. Some 18 pure organic compounds of the type found in pitch were tested as binders for hot-pressed graphite compacts. The best results were obtained with higher-molecular-weight compounds such as β truxene and decacyclene. The best compound, β truxene, produced compacts with a threefold decrease in gas permeability over pitch-bonded compacts and no appreciable decrease in density or strength. A sample of pitch which had been given a "prepyrolysis" treatment was separated and examined. Comparison with the components from untreated pitch indicated that chemical changes had taken place in the pitch during pyrolysis. The use of a free-radical catalyst to upgrade the binding quality of pitch was investigated briefly. X-ray diffraction studies were conducted on samples of whole pitch and pitch insolubles to determine the changes in structural ordering on further heating.

Chemical investigations were made on binders for graphitic bodies to derive methods by which the binders could be modified to produce graphite matrices of improved properties. Tests using pure organic compounds as binders confirmed the superiority of truxene-type compounds in producing compacts of high density and strength. Removal of volatiles from pitch by either solvent extraction or pyrolysis resulted in improvement in the properties of hot-pressed graphite compacts. The material removed by volatilization during prepyrolysis was the same as that removed by petroleum-ether extraction, i.e., the moltene fraction.

A brief investigation of the influence of process variables on hot-pressed graphite compacts revealed the binder concentration and time of pressure application during the heating cycle to be important parameters.

1.4. CATALYTIC GRAPHITIZATION

The use of metallic additives to enhance graphitization below $\sim 2800^{\circ}\text{C}$ was examined as a potential method for increasing the irradiation stability and thermal conductivity of pyrolytic carbons or graphites for nuclear

applications (Ref. 12). A series of metal-doped cokes or coke-pitch compacts were prepared with aluminum, titanium, or zirconium carbide additives and heat treated at 1700° to 2300°C. Aluminum-doped cokes and compacts readily converted to graphite at 2300°C. The volume of graphitic structure produced exceeded the aluminum content by a factor of from 3 to 13 depending on the original metal content in the baked material. The carbon structure was converted to graphite when Al_4C_3 passed through the structure dissolving carbon and rejecting graphite. Conversion of disordered carbon to the graphitic structure was shown to be about 70 to 100% complete in compacts containing 16 to 17 wt % aluminum. Graphite compacts fabricated with aluminum were highly crystalline but had low bulk densities due to the evolution of the aluminum during heat treatment. Titanium was not as effective in converting disordered carbon to graphite below 2300°C because the reaction takes place by solid-state diffusion and, thus, the kinetics of the reaction are slower. Zirconium carbide enhanced the graphitization of needle-coke carbons at 2400° to 2500°C after short heat treatments, but the metal-doped specimens were no better than the control samples after longer heating periods.

2. CHARACTERIZATION OF MICROSTRUCTURE AND CARBONIZATION STUDIES

2.1. MESOPHASE STUDIES

Micrographic studies were undertaken to investigate the reaction mechanisms and structural transitions involved in the carbonization and graphitization of the carbonaceous materials employed in the manufacture of nuclear graphites (Refs. 13, 14). Observations by polarized light of the microstructures formed during the pyrolysis of coal-tar pitches used in the fabrication of graphitic artifacts directed attention to the narrow range of temperature during which the carbonizing liquid exists as a liquid crystal called the carbonaceous mesophase. It was shown that 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 of the extinction contour pattern observed by crossed polarizers are the nodal points and centers of crosses, which do not move when the plane of polarization is rotated. These features were identified as four types of linear defects in the stacking of the aromatic layer molecules. Fine insoluble particles were segregated by the mesophase transformation, and the effect of graphitic substrate particles was 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. RELATION OF PHYSICAL PROPERTIES OF GRAPHITIC MATERIALS TO MICROSTRUCTURE

The principal efforts in this investigation were directed to the relation between preferred orientation and properties such as thermal expansion and dimensional changes under neutron irradiation.

Expressions were derived for the thermal expansion coefficient of polycrystalline graphite in terms of the single-crystal coefficients and the preferred crystallite orientation of the sample (Ref. 15). Thermal expansion and preferred orientation measurements showed such expressions adequately represent the behavior of several different graphites over a range of temperatures, provided the "accommodation" of a part of the c-direction crystallite expansion by microcracks is taken into account. The amount of c-direction accommodation is a function of preferred orientation and the direction of measurement.

It was shown that a model similar to the one used for thermal expansion may be used to express the irradiation-induced dimensional changes in polycrystalline graphite in terms of the preferred orientation of the sample: a contraction in the crystallite a-direction and an expansion in the crystallite c-direction which is partially accommodated by microcracks. The model, termed a single-phase model, was found to be in reasonable agreement with published irradiation data for a number of graphites. Samples having different degrees of preferred orientation were cut from the wall of an extruded graphite tube and irradiated at temperatures between 540° and 1060°C to provide data to test the model.

The irradiation data were used to test the single-phase model with another published single-phase model derived from thermodynamic considerations (Ref. 16). The results reported in Ref. 17 showed the data agreed more closely with the thermodynamically derived model.

It should be noted that information obtained later in the program (Section 4.8) shows both single-phase models to break down at higher temperatures and higher fluences.

In other work (Ref. 18), expressions were derived to express Young's modulus of an anisotropic aggregate of hexagonal crystallites in terms of the single-crystal elastic constants and functions of the preferred orientation, assuming either a constant tensile strain or a constant tensile stress throughout the aggregate. Measurements of Young's modulus and

preferred orientation on a number of pyrolytic carbons with different anisotropies showed that the "constant stress" model represents the behavior of these materials to a good approximation. Young's modulus of polycrystalline nuclear graphite whose dislocations have been pinned by a low-temperature neutron irradiation agreed with the same model.

2.3. MICROSTRUCTURAL CHARACTERIZATION OF GRAPHITE

A need for detailed micrographic information, beyond that provided by conventional metallography, was recognized in several areas of the research and development program. In the initial period of this program, principal efforts were devoted to applying electron microscopy in combination with optical metallography to define the microstructural components of impregnated compacts, development and application of methods for the quantitative definition of preferred orientation in polycrystalline graphites, micrographic recognition of the filler and binder constituents in fuel-matrix graphite, replication electron microscopy on hot-worked graphite, and observations of the fracture characteristics of hot-worked graphite (Refs. 9, 19).

In connection with studies of flow mechanisms of graphite crystals at temperatures in the hot-working range, techniques were developed for the observation of dislocations in thin flakes by electron transmission microscopy (Ref. 19). A chemical method in which the kinetics of oxidation by a hot dichromic acid solution are measured manometrically was developed for measuring the degree of graphitization of graphite materials in order to follow structural changes in carbonaceous materials during heat treatment and in graphite materials during irradiation (Ref. 20). Electron replication micrography utilizing a cathodic etching device was employed to study the structures existing in graphitic materials (Ref. 20).

Micrographic studies were made on binder-filler artifacts which were molded at 120°C, baked at 500°C, and heat-treated to temperatures between 550° and 900°C (Ref. 21). The results showed that the microstructural characteristics of a graphite body are established early in the manufacturing process. The pitch binder phase develops an optical response below 550°C. Bodies

prepared with calcined needle-coke filler showed little pitch phase external to the filler grain, suggesting that a major portion of the pitch is absorbed by the porosity of the calcined coke grains.

2.4. CHARACTERIZATION OF DEGREE OF GRAPHITIZATION

The overall objective of this work was to separate and identify the various structural states of the carbons that comprise conventional binder-filler artifacts and to apply the knowledge to the irradiation behavior of these materials. During the initial phase of the work, the apparatus and procedure for determining the structural and density distributions in carbons and graphites were developed (Ref. 22). A sink-float technique employing a density-gradient separation column was selected and experiments were performed to test the feasibility and thoroughness of the separation. A relationship between crystallinity and apparent liquid density was shown.

Densimetric separations were performed on a wide variety of anisotropic and isotropic artificial graphites, and the apparent crystallite sizes of the density fractions were measured (Ref. 23). Anisotropic porous artificial graphites were shown to consist of semigraphitic regions coexisting with highly graphitic regions. The transition of the structure from semigraphitic to highly graphitic was smooth, and the apparent crystallite size could be correlated with the apparent density of the fractions. The isotropic graphites had semigraphitic structures and were more uniform in apparent crystallite size than the anisotropic graphites. The mean apparent crystallite size $\bar{L}_c$ of the graphites showed a systematic correlation with the anisotropy factor, thermal expansivity, and unirradiated strength of the graphites. Graphites that are nearly isotropic had the highest thermal expansivities, the smallest apparent crystallite sizes, the smallest range of crystallite sizes, and the highest strength, whereas those fabricated with needle-coke that were anisotropic had low thermal expansivities, relatively large mean apparent crystallite sizes, a wide range of apparent crystallite sizes, and were relatively weak.

These characteristics and correlations were utilized in explaining irradiation behavior as described in Section 5.3.

3. FUEL PARTICLE AND FUEL COMPACT STUDIES

3.1. FISSION-PRODUCT RELEASE

The fission-product release of spherical monogranular UC_2 particles was studied by postirradiation annealing of neutron-activated samples and by exposing samples to a steady rate of photofission (Ref. 24). The release of the several fission products studied appeared to follow the kinetics and temperature-dependence of an activated diffusional process. The anomalous fast release of a portion of the Xe-133 in annealing experiments may be interpreted as being due to release of attached or trapped xenon atoms by a process not following Fick's law.

Analysis of the data obtained gave the following diffusion coefficients for krypton, tellurium, iodine, xenon and barium in UC_2 (in cm^2/sec):

$$D_{Kr} = (6.2 \times 10^{-5}) \exp \left(- \frac{44,000}{RT} \right) \text{ from steady-state release}$$

$$D_{Te} = (1.26 \times 10^{-5}) \exp \left(- \frac{67,000}{RT} \right) \text{ from annealing experiments}$$

$$D_I = (4.1 \times 10^{-8}) \exp \left(- \frac{53,300}{RT} \right) \text{ from annealing experiments}$$

$$D_{Xe} = (4.6 \times 10^{-6}) \exp \left(- \frac{68,000}{RT} \right) \text{ from the "slow" component}$$

$$D_{Ba} = (2.0_4 \times 10^{-7}) \exp \left(- \frac{49,000}{RT} \right) \text{ from annealing experiments}$$

The diffusion coefficient for xenon in UC_2 was in agreement with the diffusion coefficient for xenon in UO_2 . A negative activation entropy (-13 eu) for diffusion was indicated.

Studies of the kinetics of fission-product release from single-crystal UC_2 particles mentioned above were extended to investigate the effect of UC_2 particle size on the rate of release. In general, the rate of release decreased with increasing particle size over the range 150 to 300 μm .

Fission-product release studies were also performed on a series of fuel compacts that had been impregnated to various levels of permeability (see Section 1). No apparent correlation could be found between the fission-product release and the permeability of the compacts. Hot-working was found to improve the retention of xenon, tellurium, and iodine by the graphite-matrix compacts. However, absolute release rates were still high.

A diffusion coefficient of $1.0 \times 10^{-9} \text{ cm}^2/\text{sec}$ was obtained for barium in granular-type pyrolytic carbon at 1400°C . This was in excellent agreement with results obtained for the diffusion of Ba-140 perpendicular to the layer planes in pyrolytic carbon.

The steady-state release of short-lived fission gases between 1100° and 1700°C from high-density ThC_2 (150 to 250 μm) showed the release mechanism to be similar to that of monogranular UC_2 (179 to 210 μm). The inclusion of about 5% UC_2 in the high-density ThC_2 improved the fission-gas retention by a factor of 2 to 10.

4. PYROLYTIC CARBONS AND MODEL MATERIALS

The studies of pyrolytic carbons were extensive covering a number of subjects. The work is reviewed by presenting summaries and abstracts from the numerous reports on the subject.

4.1. FABRICATION AND STRUCTURE

A variety of pyrolytic-carbon deposits produced in fluidized beds were categorized according to their structure (Ref. 25). For a given coater configuration and flow rate, the structures of the deposits were found to vary systematically with the bed temperature, gas composition, and bed surface area.

The structures were divided into three groups according to their microstructures, i.e., laminar, isotropic, or granular. The structural data, together with kinetic measurements and published results on related processes, suggested the following deposition mechanisms for these structures:

1. The low-temperature laminar structures are considered to be built from large planar molecules that form in the gas phase, dehydrogenate, and, when deposited, align themselves parallel to each other and to the substrate.
2. The isotropic low-density structures are considered to be formed at conditions where general gas-phase nucleation of droplets and soot occurs in the bed.
3. The high-density granular structures are considered to be structures formed when there is orderly growth over relatively large distances. The conditions that favor this structure are low gas-phase supersaturation, high surface mobility, and a temperature gradient between the substrate and the gas phase.

Each of the structures was characterized further by measuring its density, crystallite size, and degree of preferred orientation.

The structures of representative laminar, isotropic, and granular carbons were studied in more detail using X-ray scattering techniques to determine the concentration of amorphous carbon and misaligned single layers in each (Ref. 26). It was found that significant quantities of amorphous carbon can be present in carbons deposited at 1400°C and that the amount present increases with the deposition rate. The concentration of misaligned single layers in these carbons varied from 23% in the low-density carbon deposited from 5% methane to less than 2% in the high-density anisotropic carbon deposited from 40% methane. This decrease in the concentration of single layers with methane concentration occurred regardless of a concomitant increase in deposition rate.

Carbons deposited at 1650°C and above had no detectable amorphous carbon in their structures. The low-density, isotropic carbon deposited at a very high rate at 1650°C was found to contain about 10% single misaligned layers compared with 1% to 2% in the carbons deposited at 1900° and 2000°C.

Pyrolytic carbon deposits were also produced in a fluidized bed between 1900° and 2400°C from a carrier gas containing between 1% and 15% methane (Ref. 27). The carbons had either a granular or an isotropic microstructure. Formation of granular carbon occurred at high temperatures, low methane partial pressures, and low bed surface areas. Increasing the deposition temperature decreased the metallographic grain size and increased the density, X-ray apparent crystallite size, and preferred orientation of the granular deposits, and increased the crystallite size and density of the isotropic and transition deposits. The elastic moduli and fracture stresses of the granular carbons deposited from 3% methane rose from 1.5 to 1.8×10^6 psi and 18 to 32×10^3 psi, respectively, as the deposition temperature was increased from 1900° to 2400°C. The isotropic and transition carbons had fracture stresses of $\sim 30 \times 10^3$ psi and elastic moduli that decreased from ~ 2.2 to $\sim 1.6 \times 10^6$ psi over the deposition temperature range of 1900° to 2400°C.

The carbons had thermal conductivities in the range of 1 to 4×10^{-2} cal/cm-sec-°C perpendicular to the deposition plane. The conductivities were highest for the isotropic carbons and lowest for the most highly oriented granular carbons.

4.2. DEFORMATION AND FRACTURE

An investigation (Ref. 28) was undertaken to relate the mechanical properties of fluidized bed pyrolytic carbons to their structure, which in turn depends on the deposition conditions and subsequent heat treatment. Carbons deposited from methane between 1350° and 1925°C were characterized according to their density, degree of preferred orientation, apparent crystallite size, and micrographic appearance (laminar, isotropic, or granular). Stress-strain curves to fracture were obtained from room-temperature three-point bend tests on planar samples and the mode of fracture was investigated by optical microscopy and electron microfractography. Both the elastic modulus and the fracture stress decreased in progressing from laminar to isotropic to granular structures, whereas the fracture strain was highest in the isotropic deposits. Annealing at temperatures between 1700° and 2800°C was found to change greatly the properties of only the high-density laminar structures deposited from high methane concentrations, where the elastic modulus and fracture stress were reduced by annealing. The variations in the mechanical properties of the various carbons were interpreted in terms of the structural variations with deposition conditions as well as those brought about by annealing.

4.3. DIFFUSION OF URANIUM

This work was undertaken to study the diffusion of uranium and thorium in pyrolytic carbon as a function of temperature, temperature gradient, and the structure of the carbon.

Tracer-level diffusion studies using Th-228 were conducted on laboratory-prepared samples of pyrolytic carbons of widely divergent microstructure (Ref. 29). These samples were well characterized and contained no exposed

layer-plane edges. Diffusion coefficients were measured perpendicular to the plane of deposition over the temperature range 1600° to 2000°C. The diffusion coefficients were found to have a significant dependence on microstructure, the diffusion coefficient in a highly oriented laminar pyrolytic carbon being more than an order of magnitude smaller than that in either isotropic or granular carbons. The diffusion coefficient D , in cm^2/sec , of thorium perpendicular to the plane of deposition in granular, isotropic, and laminar pyrolytic carbons was found to be

$$\begin{aligned} D &= 7.1 \times 10^4 \exp(-152,000/RT) && \text{(granular)} \\ D &= 15.5 \exp(-114,000/RT) && \text{(isotropic)} \\ D &= 1.2 \times 10^4 \exp(-157,000/RT) && \text{(laminar)} \end{aligned}$$

The tracer-level diffusion coefficients for thorium in the laminar pyrolytic carbon were substantially smaller than the values reported by others for diffusion in highly anisotropic, columnar pyrolytic carbon. Microstructural parameters, such as apparent crystallite size and anisotropy factor, were useful in correlating the above results but of limited value in quantitatively rationalizing the large variations in diffusion coefficients.

Measurements of the tracer-level diffusion coefficient of thorium in a polycrystalline graphite were also performed.

4.4. FISSION-RECOIL DAMAGE

Fission products that recoil from the fuel kernel and travel into the carbon coating are expected to cause damage as a result of both the displacement of carbon atoms from their lattice position and the accumulation of the fission-product atoms in the lattice. The nature of the damage to carbon coatings caused by 2×10^{18} to 3×10^{18} fission recoils/ cm^2 at temperatures between 1200° and 1300°C and the dependence of the damage on the structure of the carbon coating were studied in two fission-product irradiations (Ref. 30).

In the first experiment, a high-density isotropic carbon was irradiated at 1200°C. The total calculated fission-product fluence was about 3.0×10^{18} fission recoils/cm². The irradiation damage was so severe that reliable quantitative data on dimensional change could not be obtained.

In the second irradiation experiment, specimens of a low-density isotropic carbon and a high-density granular carbon were irradiated at about 1300°C to a fast-neutron fluence of 6×10^{20} n/cm² ($E > 0.18$ MeV) and a fission-product fluence of 2×10^{18} fission recoils/cm². The damage to the high-density granular pyrolytic carbon was very severe, while the damage to the low-density isotropic pyrolytic carbon was less severe. In all cases, however, the degree of damage clearly showed carbon used as a coating for nuclear fuel particles must be shielded from fission recoil.

4.5. THERMAL EXPANSION

The relation between preferred orientation and the thermal expansion coefficient was investigated for a wide variety of pyrolytic carbons, including materials used for free-standing bodies as well as those used for coating nuclear fuel particles (Ref. 31). Over most of the range of preferred orientations studied, the data deviated from the simple Bacon relation (Ref. 32), indicating that a portion of the crystallite c-axis expansion was accommodated. The amount of accommodation was found to depend on the density of the carbon. A high-temperature lattice parameter determination established that intercrystalline elastic restraints do not contribute significantly to the accommodation. The accommodation is therefore attributed to porosity. The thermal expansion coefficients of a variety of carbons used as coatings for nuclear fuel particles were found to be insensitive to neutron irradiation at 890° to 1060°C to exposures of 2.2 to 2.4×10^{21} n/cm² ($E > 0.18$ MeV).

4.6. THERMAL CONDUCTIVITY

Analysis of thermal conductivity measurements of high-temperature isotropic (HTI) pyrolytic carbons (Ref. 33) showed that for carbons with L_c

greater than $\sim 100 \text{ \AA}$, the conductivity was always reduced by irradiation. The reduction tended to saturate with increasing fluence and was less for higher irradiation temperatures. Carbons with smaller L_c values experienced either an increase or decrease in conductivity, depending on the irradiation conditions. The temperature dependence of the thermal conductivity was analyzed by Kelly's model (Ref. 34) for thermal conduction in defected graphite crystals. The analysis indicated high values (80 to 180) for the porosity-tortuosity factor and values of ~ 0.5 to $1 \text{ \mu m}$ for the phonon mean free path between scattering boundaries. These values are reasonable if conduction takes place through the oriented "skins" of the spherules from which isotropic pyrolytic carbons are built up.

4.7. ANNEALING

A series of isochronal annealing experiments were conducted on irradiated pyrolytic carbon specimens to learn the extent to which irradiation-induced property changes are recoverable by annealing at temperatures up to 3000°C .

A variety of pyrolytic carbons irradiated with fast neutrons to 1.5 to $2.4 \times 10^{21} \text{ n/cm}^2$ ($E > 0.18 \text{ MeV}$) at 540° to 1060°C were annealed at 100°C temperature increments between 400° and 3000°C (Ref. 35). 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. 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 distributions of activation energies for the annealing processes were calculated, assuming a single-valued pre-exponential factor. The calculations indicated an apparent activation energy of 5 to 5.5 eV for the earliest annealing steps, and a peak in the distribution function at $\sim 8.5 \text{ eV}$.

Another series of experiments were performed using titanium-bearing specimens to evaluate metals as a graphitization catalyst. Isochronal 1-hr anneals were conducted on a laminar pyrolytic carbon deposited at 1225°C containing 6.7 wt % titanium, an isotropic pyrolytic carbon deposited at 2200°C containing 9.7 wt % titanium, and titanium-free companion carbons (Ref. 36). Changes in layer spacing, apparent crystallite size (L_c), density, electrical resistivity, and microhardness were followed. Heterogeneous recrystallization to graphite started in the titanium-doped isotropic carbon at 2300°C and was completed at 2500°C. The titanium-doped laminar carbon did not show catalytic recrystallization. The undoped isotropic carbon was not responsive to annealing. 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 begin until ~1800°C. The dimensional changes induced by fast-neutron exposures up to $\sim 8 \times 10^{21}$ n/cm² at ~600° to 1250°C were measured and found to be lower by a factor of 3 to 10 in a catalytically graphitized pyrolytic carbon than in an as-deposited carbon with the same degree of preferred orientation.

4.8. IRRADIATION

A variety of pyrolytic carbons with laminar, isotropic, or granular microstructures, deposited from methane in a fluidized bed between 1400° and 2000°C, were irradiated at temperatures between 540° and 1060°C to fast neutron exposures of 1.5 to 2.4×10^{21} n/cm² ($E > 0.18$ MeV) (Ref. 37). Changes in linear dimensions, density, and crystallite size were measured. The data showed the irradiation-induced dimensional changes in the pyrolytic carbons depended sensitively on their structure. At ~1000°C the dimensional changes depended primarily on the degree of preferred orientation with a secondary dependence on the density of the carbon. The changes calculated for the crystallites were independent of the crystallite size L_c in the range 30 to 145 Å, but the changes were less for larger L_c values. At ~600°C the dimensional changes depended on L_c , density, and the degree of preferred orientation. At this temperature the calculated crystallite changes were

very sensitive to variations in L_c in the range 30 to 200 Å. At all temperatures the irradiation caused the carbons to densify. The irradiation tended to increase the L_c value of carbons with initially small L_c values and to decrease those of carbons with initially high L_c values.

The same pyrolytic carbon specimens were used for mechanical property measurements (Ref. 38). The elastic modulus, flexural strength, and fracture strain were determined for unirradiated and irradiated samples. Irradiation creep behavior was studied by measuring the strain in composite samples consisting of pyrolytic carbon and polycrystalline graphite in which the differential neutron-induced contraction caused the carbon to be strained in tension during irradiation. Irradiation increased the elastic moduli of the carbons by 30 to 100%, the increases being greatest in the isotropic and granular carbons with low initial moduli. The flexural strength of the laminar carbons was not changed by irradiation, but that of the isotropic and granular carbons increased by up to 60%. The creep specimens of granular and high-density isotropic carbons withstood tensile creep strains of up to 3.3% without cracking. The steady-state creep constant was of the order of $\sim 1 \times 10^{-7} \text{ (psi)}^{-1} (10^{20} \text{ n/cm}^2)^{-1}$.

In another series of experiments (Ref. 39) a variety of pyrolytic carbons with various densities, anisotropies, and microstructures, but with similar crystallite sizes, were irradiated at 600°, 1180°, 1330°, and 1650°C to fast neutron exposures of 1.9, 2.6, 3.1, and $3.3 \times 10^{21} \text{ n/cm}^2$ ($E > 0.18 \text{ MeV}$), respectively. Changes in linear dimensions, density, apparent crystallite size, layer spacing, and anisotropy were measured.

Significant changes in preferred orientation resulting from irradiation temperatures above 1100°C were measured. The Bacon anisotropy factor for many specimens increased more than 20% due to the irradiation.

The kinetics of densification at 600°C were found to be first order with respect to the density defect and independent of the microstructural appearance of the carbon. At irradiation temperatures above 1100°C, the

densities of the carbons with initial densities less than about 2.06 g/cm^3 were increased by the irradiation, but the densities of those with initial densities greater than this value were decreased.

The crystallite dimensional changes, $\Delta X_c/X_c$ and $\Delta X_a/X_a$, produced by irradiation were derived from the measured dimensional changes parallel and perpendicular to the deposit and compared with the crystallite dimensional changes previously published for carbons and graphites with crystallite densities above 2.0 g/cm^3 . The data showed no dependence on crystallite size below $\sim 500^\circ\text{C}$, where the mobility of radiation-induced point defects is low. Above $\sim 500^\circ\text{C}$, where the mean diffusion distance of the displaced atoms is large compared with the crystallite size, dimensional change rates were higher for carbons with smaller crystallite sizes.

A model was derived to describe the dimensional behavior of pyrolytic carbon during irradiation by fast neutrons (Ref. 40). The model used crystallite averaging methods to describe the anisotropic distortion of the bulk in terms of its preferred orientation and the shape change of the individual crystallites. The densification, a simple first-order rate process, was assumed to be independent of the shape change and superimposed isotropically on it. The predictions of the model agreed with experimental observations.

Strain rates calculated from the model were used to estimate the suitability of various carbon structures for use as coatings on an unyielding support. For example, using a creep constant of $1 \times 10^{-27} (\text{n/cm}^2\text{-psi})^{-1}$ at 1200°C , the model predicted that a carbon with a Bacon anisotropy factor (BAF) of 1.2 and apparent crystallite sizes L_c in the range 120 to $155 \text{ \AA}$ would not fail due to neutron-induced dimensional changes if its original density were greater than 2.0 g/cm^3 . Similarly, carbons with the same crystallite size but with $\text{BAF} = 1.0$ would not fail under the same conditions if their original densities were greater than 1.7 g/cm^3 .

Results from the carbons irradiated showed that in the temperature range 500° to 1000°C , the densification constant k_d for carbons with L_c

parameters in the range 25 to 45 Å was independent of temperature and equal to $3.3 \times 10^{-22} \text{ (n/cm}^2\text{)}^{-1}$. When L_c was relatively large (155 to 175 Å), k_d was also independent of temperature and equal to $1.1 \times 10^{-22} \text{ (n/cm}^2\text{)}^{-1}$. The value of k_d increased with temperature for carbons with intermediate values of L_c .

The values of k_d for isotropic carbons were 1.0×10^{-22} , 1.4×10^{-22} , and $2.8 \times 10^{-22} \text{ (n/cm}^2\text{)}^{-1}$ at irradiation temperatures of 520°, 670°, and 1000°C, respectively (Ref. 41). The activation energy obtained from the temperature dependence of k_d for isotropic carbons was about 0.2 eV, suggesting a process involving the thermal motion of single displaced interstitial carbon atoms.

To further clarify the relation between neutron-induced dimensional changes and the crystallite size of carbonaceous materials, specimens of four uniformly crystalline materials (natural graphite, annealed pyrolytic carbon, catalytically graphitized carbon, and turbostratic carbon) were irradiated at temperatures below 1300°C (Ref. 42). The data showed the existence of a minimum rate for all but the natural crystals. This minimum rate occurred at a temperature which increased with increasing crystallite size. For the largest crystallite sizes (natural crystals), the rate decreased monotonically with temperature to the maximum of the study (1300°C). For large crystallites (>200 Å) and low irradiation temperatures (~200°C), the distortion rate was insensitive to crystallite size. The distortion rate became increasingly dependent on crystallite size as the irradiation temperature was increased. At temperatures near 1200°C, the rate varied by over two orders of magnitude for the various crystallite sizes used in the study. The functional dependencies noted from the data were qualitatively consistent with the Reynolds and Thrower model (Ref. 43) involving the temperature-dependent heterogeneous nucleation of widely spaced interstitial clusters.

Data from further irradiation experiments carried to higher neutron exposures (Ref. 44) showed that the irradiation-induced densification familiar at low exposures was replaced by an expansion process at high exposures.

It was suggested that the expansion resulted from porosity generated by intercrystalline irradiation creep. When the expansion process became apparent at high exposures, the shape changes of all the carbons taken as a group departed from the relations predicted by crystallite averaging methods. The nearly isotropic carbons behaved as if either the crystallite's shape change rate was enhanced by the irradiation itself or that the expansion caused by the new porosity generated at high exposures was directed perpendicular to the original deposition plane. The data also showed that, for turbostratic carbons with apparent crystallite size $L_c = 120$ to $200 \text{ \AA}$, an irradiation at $\sim 600^\circ\text{C}$ to $\sim 1 \times 10^{21} \text{ n/cm}^2$ did not influence the neutron-induced dimensional changes that occurred in a subsequent irradiation at $\sim 900^\circ\text{C}$.

Additional experimental data for turbostratic carbons taken to high fast neutron exposures and irradiation temperatures where irradiation behavior departed from that established at lower exposures again showed that after an initial densification, which is first order with respect to the density defect, the densification ceased and the material expanded (Ref. 45). Concomitantly, the rate at which the material changed shape increased. The acceleration of the rate of dimensional change was thought to be the result of the autocatalytic influence of radiation-generated defects and irradiation-induced increases in anisotropy. The new porosity responsible for the expansion at high doses was thought to be associated with large intercrystalline strains that are relaxed by radiation creep.

Measurements of the macroscopic creep strains (Ref. 45) indicated that strains of at least about 2, 3, and 6% per 10^{21} n/cm^2 ($E > 0.18 \text{ MeV}$) could be accommodated at 600° , 900° , and 1200°C , respectively, and total strains of about 10% in tension were possible. These measurements, together with the dimensional change behavior of isotropic carbon coatings for nuclear fuel particles, showed that for survival to high neutron exposures, the density must be chosen so that coatings will not fail early in life due to densification and so that intolerable anisotropic behavior will not be

encountered late in life. The data suggested that, for the designs most commonly used, the optimum densities for isotropic carbons were in the range 1.5 to 1.8 g/cm³.

Comparison of the data for turbostratic carbons and data for graphitic materials showed that at ~1200°C the dimensional change rate can vary by two orders of magnitude with crystallinity. The influence was considerably less at ~600°C.

Irradiation-induced dimensional changes in a variety of pyrolytic carbons at 900° to 1000°C and at 1200° to 1300°C showed an acceleration in the rate at which the specimens changed dimensions during the irradiation (Ref. 46). The accelerations were most pronounced in dense, isotropic carbon and were accompanied by the generation of pores in the structure, which caused a volume expansion. The data obtained at the lower irradiation temperatures (~900°C) suggested that the accelerations were due primarily to a degradation in crystal structure that enhanced the instability of the crystallites. At the higher irradiation temperatures, increases in anisotropy contributed significantly to the accelerations. The volume expansions, the degradation of the crystal structure, and changes in thermal conductivity were all less for irradiations above 1200°C than at 1000°C. These observations, together with the increases in anisotropy, were believed to be manifestations of the fact that the intercrystallite irradiation creep rate is substantially higher at irradiation temperatures above 1200°C than at 1000°C. High creep rates provide an effective mechanism which relaxes the stresses generated between adjacent, misaligned crystallites during irradiation.

Comparative dimensional data from irradiation experiments that included both high-temperature isotropic (HTI) and low-temperature isotropic (LTI) carbons showed that at high fluences the volume expansion and accelerations in the dimensional change rates were considerably more pronounced for HTI carbons than for LTI carbons (Ref. 47). Alloying LTI carbons with up to 15 wt % silicon enhanced the dimensional stability slightly at ~600°C but had no effect on the behavior in irradiations at higher temperatures. For

HTI carbons the effects of the alloying additions were more pronounced. However, the improvements were not thought to be of practical importance in either case. Data from both multiple irradiations at different temperatures and irradiations in which the temperatures were programmed down during the course of the irradiation showed that prior irradiation at high temperature markedly enhanced the dimensional changes that occurred in subsequent irradiations at lower temperature.

An investigation was made of the dimensional behavior of unrestrained and spherically restrained isotropic carbons deposited at both high temperatures ($>1500^{\circ}\text{C}$; HTI carbons) and low temperatures ($<1500^{\circ}\text{C}$; LTI carbons) during irradiation at 600° , 1000° , and 1250°C to fast-neutron fluences near $2 \times 10^{21} \text{ n/cm}^2$ ($E > 0.18 \text{ MeV}$) (Ref. 48). The investigation covered, in particular, the effect of the initial density on the unrestrained dimensional changes and on the total strain accommodated without fracture in the spherically restrained specimens. For isotropic carbons (Bacon anisotropy factor <1.1), the unrestrained dimensional changes were primarily those due to irradiation-induced densification, and the strain accommodated consisted mostly of irradiation-induced creep strain. The largest dimensional changes and highest total strains accommodated were in low-density carbons. At 1000°C the accommodated strain rates were 0.04 per 10^{21} n/cm^2 and 0.05 per 10^{21} n/cm^2 for LTI and HTI carbons, respectively. At 600°C the respective accommodated strain rates were 0.028 per 10^{21} n/cm^2 and 0.025 per 10^{21} n/cm^2 . At 1250°C both an upper and a lower limit on the density of the restrained LTI carbons that survived irradiation were observed. The lower density limit apparently revealed the maximum densification strain rate that can be tolerated.

A large number of experiments were carried out in which natural crystals and annealed massive pyrolytic carbon were irradiated at high temperatures (Ref. 49). The natural crystals were chosen to represent the more nearly perfect crystallites. The degree of crystallinity represented by the natural crystals is almost never found in artificial graphite, but the dimensional behavior of the crystals provides a fundamental reference

point for theoretical interpretations. The crystallinity of the annealed pyrolytic graphite, on the other hand, is representative of that of the crystallites in most needle-coke graphites.

At low fluences, the rates of c-axis growth for the natural crystals were found to be consistent with the values predicted by Reynolds and Thrower (Ref. 43) from direct observations of the size and distribution of interstitial loops in natural crystals irradiated to low fluences at 1200°C. At higher fluences, however, the c-axis growth rates were higher (especially at 1200°C and above), and the higher rates were accompanied by a volume increase. This effect was ascribed to either an accumulation of uncollapsed vacancy loops (Ref. 50) or to interlayer cracking and was most pronounced in the less crystalline annealed material. The accelerations in the rates at high fluences were believed to be the result of an accumulation of irradiation-produced defects which act as heterogeneous nucleation sites.

Inferences about the dimensional behavior at high fluences of polycrystalline graphite from the behavior of materials with near single-crystal anisotropy must be made with caution since the behavior of crystallites in aggregates is likely to be modified by interaction stresses between adjacent misaligned crystallites.

Irradiation of model materials was continued to fluences of 1.8×10^{22} n/cm² at 1000° to 1250°C (Ref. 33). These studies showed maximum irradiation stability in carbonaceous material to result from perfectly isotropic structures. The rate of crystallite dimensional changes was higher at 1250°C than at 1000°C. At high fluences the dimensional changes accelerated continuously with increasing density. At 1000° and 1250°C, the initial densification in carbon structures was followed by expansion until all carbons reached the same density. If mechanical strength of the carbon is high, it will not enter the expansion phase as quickly as a weaker material. The information developed on the model carbons indicated that artificial graphites should be isotropic and have intermediate densities and high mechanical strength, which implies an intermediate crystallite size.

5. IRRADIATION STUDIES OF ARTIFICIAL REACTOR GRAPHITES AND CARBONS

5.1. IRRADIATION EFFECTS ON HIGHLY ORIENTED CARBONS AND GRAPHITES

Irradiation data from samples of highly oriented carbons and graphites of various crystallite sizes provide direct information on the dimensional change rates of crystallites without the complications of gross porosity and crystallite interactions inherent in data from polycrystalline graphites.

In this work, (Ref. 4) the specimens consisted of highly oriented hot-worked graphite, massive pyrolytic carbon deposited at about 2200°C, and massive pyrolytic carbon annealed at 2900° to 3300°C. Apparent crystallite sizes ranged from 220 to 1660 Å. The materials were irradiated to a maximum fluence of 2×10^{22} n/cm² at 1225° to 1290°C.

The parallel and perpendicular dimensional changes increased linearly with neutron exposure except for the hot-worked graphite irradiated at ~1250°C, which had lower dimensional change rates for fluences beyond 6×10^{21} n/cm². This indicates that high strength, and not isotropy, is the important factor in inhibiting breakaway growth in polycrystalline graphites at high fluences.

Crystallite change rates increased 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 explained by an increase in intercrystallite restraint at high damage levels.

Metallographic examination of as-deposited massive pyrolytic carbon irradiated at $\sim 1250^{\circ}\text{C}$ showed that macroscopic delamination cracks started to form at about $4 \times 10^{21} \text{ n/cm}^2$. No visible change in the microstructure of hot-worked graphite was observed.

5.2. INFLUENCE OF PITCH BINDER-COKE CONTENT

Variations in microstructure and properties due to variation of the relative amount of binder coke and the corresponding effects in neutron-induced dimensional and property changes were studied.

A series of molded compacts were prepared with uncalcined coke, calcined coke, or natural flake graphite and pitch binder contents of 0, 15, and 25 wt % (Ref. 51). The carbonization of the binder-filler artifacts was studied by micrographic examinations; thermal expansivity, preferred orientation, electrical resistivity, modulus of rupture, density, porosity, apparent crystallite size, and lattice parameters were measured on samples that had been heat treated to 2600°C .

Volume shrinkages of about 30% were observed after carbonization and graphitization of compacts prepared with uncalcined coke. These volume changes were accompanied by decreases in electrical resistivity and increases in the strength of the compacts that contained a pitch binder. The strength of the compacts without binder was low.

During baking, the carbonization of the pitch binder occurred predominantly in locations between the filler particles, and the filler particles developed a significant crack structure. Relatively few cracks were formed in the filler grains of compacts that contained no binder. In the case where calcined coke was used as filler, a large portion of pitch binder apparently carbonized within the pores of the filler particles. These compacts were relatively weak and fragile.

The addition of pitch binder in the green mix altered the microstructure, porosity, and properties of the compacts that were heat treated to 2600°C .

Increasing the pitch content reduced the total porosity but increased the closed porosity. These alterations in structure produced attendant changes in the anisotropy of the compacts; higher pitch contents produced a more isotropic material.

The molded compacts were irradiated in the range 400° to 1450°C (Ref. 52). Compacts prepared with uncalcined coke showed decreasing anisotropy in linear dimensional contractions with increasing pitch content when irradiated at 915° or 1450°C. A dimensional contraction of 9% was observed in the perpendicular direction of compacts prepared without a pitch binder after irradiation at 1450°C and $3.25 \times 10^{21} \text{ n/cm}^2$ ($E > 0.18 \text{ MeV}$).

Optical micrography and electron micrographs showed a significant closure of the crack structure that was located parallel to the basal planes in the filler particles of the unirradiated material. The changes in the microstructure were accompanied by changes in both bulk and pycnometric densities. Thermal expansion coefficients increased for samples without pitch binder and showed little or no change in those with pitch binder. The micrographic evidence suggested that c-axis expansion is absorbed by basal-plane cracks in the particles during high-temperature irradiation. The microporosity, which decreased during irradiation in samples that contained pitch-binder carbon, may also absorb c-axis growth.

The electrical resistivity increased slightly in uncalcined-coke samples irradiated at 950°C but was unchanged in samples irradiated at 1450°C.

In later work, a series of needle-coke graphites were prepared with calcined coke and various fractions of pitch-binder coke in the range 5.5 to 14.2 wt % (Ref. 53). The specimens were irradiated to $9.70 \times 10^{21} \text{ n/cm}^2$ ($E > 0.18 \text{ MeV}$) at 1225°C. Apparent bulk density and apparent crystallite size L_c were dependent on the binder-coke content. Crystallite orientation and thermal expansivities were not affected. Dimensional and volumetric changes were sensitive to binder-coke content; specimens deficient in binder

coke showed volumetric turnaround at lower fluences and higher expansion rates at high fluences. Specimens of 5.5 wt % binder coke expanded 20 vol %, whereas those of 11.7 wt % binder coke expanded only 4 vol %. Thermal expansivity increases closely followed the volume changes and were large in specimens deficient in binder coke.

Unbonded coke particles expanded at three times the rate of coke particles bonded with pitch. The needle-coke particles were restrained by the binder coke during expansion at high fluences. Large cracks formed between filler particles during expansion and were responsible for the large volume expansions.

5.3. REACTOR GRAPHITES

5.3.1. Dimensional and Structural Changes

A number of anisotropic and isotropic graphites have been under irradiation for several years. The graphites were characterized for properties and structure prior to irradiation; these studies are described in Section 2.4 and Ref. 23. The graphites were irradiated to fluences of up to 2.0×10^{22} n/cm² at 1175° to 1290°C (Refs. 54-56).

The volume expansions of needle-coke graphites ranged from 25 to 70%, whereas those of Gilsocoke graphites were only about 15%. The needle-coke specimens were weak and distorted and had passed the point of being useful as structural members of a reactor core, whereas the Gilsocoke material was considerably better. The needle-coke graphites entered net expansion at about 4 to 6×10^{21} n/cm² in the c-axis direction of preferred orientation at 1175° to 1290°C, while the Gilsocoke graphites did not show net expansion until fluences of 8 to 11×10^{21} n/cm². Photomicrographs of the graphites after irradiation to 2×10^{22} n/cm² showed that large pores continued to develop between the filler-coke particles by disintegration of the binder-carbon bridges. This effect was considerably more pronounced in the anisotropic needle-coke materials than in the near-isotropic Gilsocoke graphite.

A qualitative interpretation of the relationships between dimensional and structural changes in the reactor graphites was given (Ref. 55). The maximum volume contraction of each material was shown to correlate with the mean apparent crystallite size $\bar{L}_c$ and the crystallite size distribution of the graphites provided they had similar crystallite orientations. Pores, located between crystallite clusters, were eliminated during densification by the crystallite c-axis expansion. The rate of elimination of these pores increased with increasing irradiation temperature. In contrast to the behavior of the bulk, the crystallite clusters (as measured by sink-float densitometry) did not densify but expanded, and their expansion was more dependent on crystallite orientation than on the original strengths of the various materials. Larger pores were observed to form between filler particles during the expansion phase at high fluences, accounting for the large volume expansions of the graphites. The ease of formation of these pores and cracks and the expansion rate after turnaround were found to be dependent on the volume percent of highly graphitic (low-strength) material in the structure.

An experiment was carried out to verify the above observations. A binder-filler graphite with two distinct carbon structures, needle coke and pyrolytic carbon, was irradiated at 1300°C to 4×10^{21} n/cm² ($E > 0.1$ MeV) (Ref. 57). The volume change of the composite binder-filler was determined by density and dimensional measurements, and the volume change of each carbon structure and the gross porosity were followed by lineal analysis. The volume change of each carbon structure was also determined external to the composite by density measurements. The bulk compact densified by the elimination of pores between the carbon and graphite filler particles and by elimination of pores and density defects within the needle-coke and pyrolytic carbon filler particles. Concurrently, during bulk densification of the composite, microcracks began to form immediately within the needle-coke particles. These results confirmed in a qualitative way the observations on the reactor graphites.

A number of production-grade needle-coke and Gilsocoke graphites were irradiated at 600° to 1280°C to maximum fluences of about 13×10^{21} n/cm²

($E > 0.18$ MeV) (Ref. 58). The needle-coke graphites behaved similarly and showed marked anisotropy in dimensional changes. At temperatures from 900° to 1280°C , they contracted in the perpendicular direction to a maximum shrinkage of about 1.5% at an exposure of 3 to 5×10^{21} n/cm², and then expanded upon further irradiation. In the parallel direction, they contracted rapidly with irradiation to $\sim 10\%$ shrinkage after fluences of 8 to 10×10^{21} n/cm², and then the contraction rate slowed. In contrast, the Gilsocoke material showed near-isotropic behavior in dimensional changes when irradiated at 1000° to 1250°C to a fluence of 11×10^{21} n/cm². No differences in dimensional changes were observed between edge-cut and center-cut specimens from one 18-in.-diameter production log of needle-coke graphite. This contrasted to other data obtained on a similar 18-in.-diameter production log where variations of up to 25% were observed in the radially cut specimens from edge to center (Ref. 1).

The effect of irradiating graphite initially at a high temperature followed by irradiation to higher fluences at a lower temperature was studied (Ref. 2). When reactor graphites, of the same type as those discussed in Refs. 54 and 55, were irradiated initially to fluences of about 3 to 5×10^{21} n/cm² at T_1 of 1200° or 1000°C and then to higher fluences at T_2 of about 1000° or 800°C , respectively, the dimensional changes coincided with the isothermal curve for irradiation at T_1 , the higher temperature.

A number of the graphites mentioned above plus additional materials were irradiated further at 500° to 1430°C to 8×10^{21} n/cm² and reexamined to explore the effect of crystallite size and orientation, original strength, and density on their irradiation behavior (Ref. 1).

Structural features of the graphites were again determined by metallographic examination, by the scanning electron microscope (SEM), and by X-ray diffraction to measure the mean apparent crystallite size $\bar{L}_c$ and the distribution of crystallite sizes.

Detailed structural examination of a number of the moderator graphites mentioned above showed these materials to vary from extremely fine-grained isotropic structure to highly heterogeneous aggregates consisting of a wide range of crystallite sizes. This result was shown in considerably more detail in this work than in the previous work in Ref. 23. The various structural components within the aggregates were identified by SEM and related to the microstructures of their coke precursors.

Structural correlations showed the following. As the mean apparent crystallite size $\bar{L}_c$ values increased, the range of L_c values also increased. There was a strong correlation between anisotropy and $\bar{L}_c$, the material becoming more anisotropic with increasing $\bar{L}_c$. Modulus of rupture also decreased as $\bar{L}_c$ increased.

Thermal expansivity (CTE) data were correlated previously with the mean apparent crystallite size L_c (Ref. 23). There were also correlations between thermal expansivity and anisotropy factor (α_c/α_a) and to some degree strength (modulus of rupture).

Additional correlations were also sought between the initial dimensional and volume contraction and the rate of expansion after turnaround of the graphites. The initial dimensional and volumetric changes of the graphites correlated strongly with the original strength of the graphites. Original strength was again found to be important in the prevention of volumetric expansion after turnaround.

Thermal expansivity changes depended strongly on the original CTE values and microstructure. The thermal expansivity of anisotropic needle-coke structures increased with fluence, whereas isotropic structures decreased. A needle coke heavily impregnated with isotropic carbon showed no change.

5.3.2. Thermal Conductivity

Thermal conductivity was reduced rapidly and saturated at relatively low fluences when graphites were irradiated at high temperatures (Refs. 13,

59, 60). The fractional change in thermal conductivity decreased with increasing irradiation temperature in the range 300° to 1200°C at fluences up to 3×10^{21} n/cm² when measured at room temperature. However, when the measuring temperature was raised to the irradiation temperature, there was little or no dependency on irradiation temperature.

Further irradiation of graphite from 3 to 8×10^{21} n/cm² at 1000° to 1200°C showed no further degradation of thermal conductivity, but irradiation to 2×10^{22} n/cm² where the graphites exhibit large volume expansions showed an additional degradation of thermal conductivity to about 0.02 cal/cm-sec-°C.

A new series of needle-coke and Gilsocoke graphites were measured for thermal conductivity changes after irradiation to 1.5 to 8.5×10^{21} n/cm² at 500° to 1430°C (Ref. 3). A strong effect of irradiation annealing above 800°C was observed; specimens irradiated at 1430°C showed only a minimal decrease in thermal conductivity.

The partial removal of irradiation defects by thermal annealing during measurement was accomplished in the range 1100° to 1400°C. When postirradiation measurements were made at the specimen irradiation temperatures, the fractional reduction in thermal conductivity ranged from about 80% at 300°C to 0% at 1250° to 1500°C (Ref. 59). When measurements were made at room temperature, the values ranged from 85% for specimens irradiated at 300°C to about 35% for those irradiated at 1250° to 1500°C.

Irradiation defects in the anisotropic needle-coke graphite started to anneal at 1200°C, and a fractional change in thermal conductivity of only 3% remained after heating to 1500°C. A fractional change of 15% remained in an isotropic Gilsocoke graphite after heating to 2000°C, and all defects were not removed until annealing temperatures were taken to 2300° to 2600°C.

5.3.3. Creep

Irradiation-induced deformation or creep affects stresses in graphite components that are exposed to temperature or flux gradients and is therefore an important property to measure for the purpose of reactor design.

Graphites currently under consideration for HTGRs were irradiated in the Dragon Reactor to 2×10^{21} n/cm² at 875° to 1235°C (Ref. 13). The experimental arrangement provided for dumbbell specimens, restrained by pad materials that changed dimensions at a different rate than the dumbbells. 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°C and confirmed preirradiation 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 $K = 6.7 \times 10^{-7}$ (psi)⁻¹ (10^{-20} n/cm²) for all materials, which is in excellent agreement with data for Dragon graphites (Ref. 61).

6. CONCLUSIONS AND INTERPRETATION OF MODEL CARBON AND GRAPHITE IRRADIATION STUDIES

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 high-density, high-strength isotropic 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. High-density, high-strength graphites, as mentioned previously, are current examples of materials that approach the ideally stable graphite.

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