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GULF GENERAL ATOMIC

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RESEARCH ON GRAPHITE
QUARTERLY PROGRESS REPORT
FOR THE PERIOD ENDING DECEMBER 31, 1971

by

G. B. Engle and R. J. Price

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

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GA-10863 - Quarterly Report for period ending September 30, 1971

ABSTRACT

The results of research on graphite for the period October 1 through December 31, 1971, are reported. No experimental work was performed. Specimens irradiated previously in capsule GE-H-13-18 at 500° to 1400°C up to fluences of 10^{22} n/cm² have been reirradiated to higher fluences in capsule GE-H-13-19.

A review of recent developments in irradiation-induced changes in graphites at high temperatures and high fluences has been initiated. Fundamental changes in the crystallites, dimensional and property changes, microstructural changes, and creep characteristics are covered.

1. INTRODUCTION

The objective of the current program is to develop an understanding of the relationships between the properties, microstructure, and irradiation behavior of graphites required for high-temperature reactors of advanced design.

The postirradiation examination of specimens irradiated in capsule GE-H-13-18* has been completed after irradiation in the range 3.80 to 7.20×10^{21} n/cm² at 1000° to 1430°C. No new experimental work was undertaken during this report period.

Capsule GE-H-13-19,* containing a number of specimens irradiated previously in GE-H-13-18 to fluences of up to 10^{22} n/cm² at 500° to 1400°C plus additional virgin specimens, has completed two cycles of irradiation in the Engineering Test Reactor and was discharged in late January.

A major effort has been made to review current and recent literature concerning high-temperature irradiation behavior of graphites and to summarize the results.

*These capsules are operated by Battelle Northwest Laboratory (BNWL) and the space is shared between BNWL and Gulf General Atomic on a cooperative basis.

2. EXPERIMENTAL WORK

No experimental work was performed during the current quarter. Postirradiation examination of a variety of graphites (described in Tables 1 and 2 of Ref. 1) was completed (Ref. 2) after irradiation in capsule GE-H-13-18. These graphites have now been reirradiated in capsule GE-H-13-19 to higher fluences and will be remeasured for dimensions and properties during the next two quarters. These measurements will complete the program and the project will be closed June 30, 1972. Data will be obtained for the following studies:

1. Effect of crystallite size, crystallite orientation, strength, and original density on dimensional and volumetric changes in graphites
2. Effect of temperature history on dimensional changes of graphites
3. Thermal expansivity changes in graphites
4. Thermal conductivity changes in graphites
5. Irradiation effects in highly oriented carbons and graphites
6. Coke studies

3. REVIEW OF HIGH-TEMPERATURE HIGH-FLUENCE GRAPHITE DATA*

A knowledge of dimensional changes, along with changes in mechanical and thermal properties, that are induced by high-energy neutron irradiation at elevated temperatures and high fluences is important for the design of high-temperature gas-cooled reactors. A knowledge of irradiation-induced creep is also important.

The review of high-temperature high-fluence graphite data undertakes to assemble the pertinent data on the above-mentioned properties from meaningful experiments that have been taken to high fluences ($>10^{22}$ n/cm²). Other books and review articles consider the data prior to 1965 (Refs. 3-7) and, therefore, the present review covers the period from about 1964 to the present.

The assembly of data has been completed and analyses are underway. A very brief description of the findings to date are given below.

3.1. RADIATION DAMAGE

Radiation damage in graphite crystals has been observed in graphite single crystals and highly annealed pyrolytic carbons by electron transmission microscopy. There is general agreement by a number of investigators on the fundamental concepts of radiation damage. High-energy neutrons collide with carbon atoms in the graphite lattice and produce single interstitials and vacancies. Some portions of the vacancies and interstitials are immediately annihilated by recombination, but the remaining may combine

*References have been omitted except to call attention to the various books and previous reviews. A complete bibliography will accompany the topical report.

to form small groups which then move to nucleation sites and form larger clusters. The magnitude of the clusters is dependent upon the irradiation temperature and fluence and the perfection of the graphite crystals. Smaller clusters may also survive depending upon temperature and fluence. The vacancies remaining in the graphite lattice are immobile at low temperatures and remain as point defects. Above about 300° to 500°C the vacancies are believed to become mobile. However, it is speculated that the vacancies can be formed into lines; the lines collapse when they grow to a critical length and then continue to grow by capture of more vacancies at the ends. Interstitial clusters cause crystal growth in the c-axis direction and collapsed vacancies cause lattice shrinkage in the a-axis direction. These mechanisms are responsible for the crystal shape changes.

Until recently it was believed that diffusion of interstitial atoms occurred only parallel to the a-axis of the crystallite. However, several authors have recently found evidence for c-axis diffusion where twist boundaries can act as sinks for interstitial atoms.

3.2. DIMENSIONAL AND STRUCTURAL CHANGES

Dimensional and structural changes have been measured on a wide variety of graphites irradiated to fluences of 2 to 3×10^{22} n/cm² ($E > 0.050$ MeV) and to temperatures of up to 1400°C. These experimental data have been generated under programs carried out on the Dragon Project and at Harwell (AERE) in the United Kingdom, KFA at Jülich in West Germany, Petten Laboratory (RCN) in Holland, and Battelle Northwest Laboratory, Oak Ridge National Laboratory, and Gulf General Atomic in the United States.

A large number of conventional graphites, both anisotropic and near-isotropic, manufactured by the traditional binder-filler method with petroleum, pitch, or Gilsonite coke have been irradiated. The bulk dimensional curves for these materials are all similar in shape; the materials shrink initially in all dimensions and then turn around and expand. The rapid expansion results from porosity generation between filler particles. The pores

continue to form until at very high fluences, the material becomes highly expanded and very weak. The initial shrinkage rate is temperature dependent, decreasing up to 800°C and then increasing with increasing temperature up to 1400°C. The rate of expansion after turnaround depends on the graphite microstructure; highly isotropic, strong materials expand at a lower rate than the weaker, anisotropic graphites. The rate of expansion increases with increasing irradiation temperature up to about 1200°C. Above 1200°C there is some confusion, but at least one experiment has shown the rate of expansion to decrease again between about 1200° to 1400°C. If the latter proves correct, the temperature range of greater instability for reactor graphites falls in the range 900° to 1200°C. Other nonconventional materials which do not exhibit a binder phase, such as the PoCo series of materials, show considerably better radiation stability at all temperatures and fluences. These materials are extremely isotropic and strong.

Highly oriented materials which are relatively free of pores and intercrystallite constraints have shown the effect of crystallite size and perfection on irradiation behavior. Above about 500°C there is a pronounced increase in crystallite dimensional change rates with decreasing crystallite size. Other studies with pyrolytic carbons have shown qualitatively that increasing the strength and isotropy of pyrolytic carbons, even with a corresponding decrease in crystallite size, increases the irradiation stability. As mentioned previously, this also appears to hold for reactor graphites.

Several attempts have been made to relate bulk dimensional changes in artificial reactor graphites to structural features and properties such as thermal expansivity, crystallite orientation, and crystallite changes. These models assume the graphite to behave as a single phase. Good agreement with experimental data was obtained when experiments were carried out at low fluences and low temperatures. However, these models failed at higher fluences where break-away expansions have been observed, and modifications have been suggested to account for porosity generation.

2.3. MECHANICAL PROPERTIES AND IRRADIATION CREEP

During the past 6 years, various groups working for the AERE have considered the variations of Young's modulus with heat-treatment temperatures, measurement temperatures, strength levels, etc. A semiquantitative model has evolved that is internally consistent and also accounts for all observed data. The basic features of the model are dislocation pinning within the crystallites and restraint between crystallites as the microscopic voids are closed.

Young's modulus data at irradiation temperatures to 1400°C and from 1.5 to 2.5×10^{22} n/cm² ($E > 0.050$ MeV) have been obtained at Battelle Northwest Laboratory and Euratom. The curves show an immediate hardening followed by a plateau. The plateau terminates with a further sharp increase, followed by a rapid decrease in modulus. The initial hardening can be attributed to dislocation pinning, the plateau to intrinsic crystal shear, the second hardening to locking of the structure, and the final decrease to microfracturing. The theoretical analysis is qualitative only.

Creep coefficients have recently been measured by Euratom and the Russians in the high-temperature regions of interest for HTGRs. The results are consistent with Kennedy's early data at Oak Ridge National Laboratory and demonstrate a rapid increase in secondary creep constant with irradiation temperature in the 600° to 1200°C region. The explanations are qualitative only and involve both neutron and thermal depinning of dislocations. The maximum fluences involved are of the order of 10^{21} n/cm², and data at higher fluences are needed to define the creep limitations as the material structurally degrades.

3.4. THERMAL PROPERTIES

Thermal conductivity and thermal expansivity data have not been analyzed. This task will be undertaken during the next report period.

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