MASTER

GULF GENERAL ATOMIC

RECEIVED BY DTIC NOV 18 1971

Gulf-GA-A10507

IRRADIATION-INDUCED MICROSTRUCTURAL CHANGES
IN A TWO-PHASE BINDER-FILLER GRAPHITE

by

G. B. Engle

September 17, 1971

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

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

GULF GENERAL ATOMIC

Gulf-GA-A10507

CONF-711030--1

IRRADIATION-INDUCED MICROSTRUCTURAL CHANGES IN A TWO-PHASE BINDER-FILLER GRAPHITE

by
G. B. Engle

This is a preprint of a paper to be presented at the 24th Annual Pacific Coast Regional Meeting of the American Ceramic Society, October 30 - November 3, 1971, Anaheim, California.

Work sponsored by the U. S. Atomic Energy Commission, Contract AT(04-3)-167, Project Agreement No. 12.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Gulf General Atomic Project 271

September 17, 1971

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

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ABSTRACT

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). 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.

1. INTRODUCTION

The microstructure of binder-filler graphites consists of carbon structures and pores (Ref. 1). The crystallite size, perfection, and orientation can vary within a single specimen of commercial graphite depending upon the raw materials and processing. Isotropic graphites are relatively uniform with apparent crystallite sizes L_c ranging from 400 to 600 Å, whereas in anisotropic materials such as needle-coke graphites L_c ranges from 350 to 1600 Å (Ref. 1). Above about 500°C, the rate of dimensional change of the crystallites in carbonaceous materials is sensitive to the apparent crystallite size (Ref. 2). Materials with small crystallites, 20 to 140 Å, change rapidly while near-single crystals are more stable even at irradiation temperatures of 1200°C. The densification or expansion of the solid materials (i.e., crystallites) in binder-filler graphites will depend upon the behavior of each of the various carbon structures present, but the bulk volume changes will depend upon interactions among the various crystallites, their interaction at boundaries between the different structures, and internal accommodation of these changes.

The data presented in Ref. 1 indicate the complexity of binder-filler graphites. In material of such complexity it is difficult to observe discrete changes in each phase because there is a continual gradation from one structure to another and boundaries between structures are not readily distinguishable. An attempt is made in this study to overcome this difficulty by fabricating in the laboratory under controlled conditions a binder-filler graphite with two distinct structures, namely, pyrolytic carbon with small crystallites and a petroleum coke with large well-ordered crystallites.

These carbon structures vary widely in their apparent crystallite sizes, crystallite orientation, and pore morphology. Because of the

variance in their structure, their high-temperature irradiation behavior should be quite different. The pyrolytic carbon, needle-coke structures, and large open pores can easily be distinguished by light microscopy and, therefore, microstructural changes that take place during high-temperature irradiation can be observed in each of the materials when they are combined with a binder to form a binder-filler graphite. Changes in porosity within each carbon phase can be determined by density measurements.

2. PREPARATION OF GRAPHITE COMPACTS

A filler coke was prepared by coating calcined needle-coke particles with a low-temperature isotropic pyrolytic carbon. The coke was crushed to pass a 200-mesh screen, and the flour was thoroughly mixed with 25 wt-% Barrett No. 30 coal-tar pitch. Porous binder-filler compacts were formed by warm-molding at 800°C and 5400 psi. The compacts had densities of about 1.48 g/cm³. The open pores of the compacts were impregnated with additional pitch from the same source as the binder, at 200°C and 140 psi for 3 hours, heated to 900°C to carbonize the binder, and finally heated to 2800°C. The heat-treated material consisted of a two-component filler, each of different density and crystallite sizes, plus the residue coke from the binder and impregnant (see Table 1). Photomicrographs of the raw materials and compacts are shown in Fig. 1 and in Figs. 2a and 2b, respectively.

TABLE 1
COMPOSITION AND PROPERTIES OF GRAPHITE COMPACT

Composition (wt %)			Thermal Expansivity $\alpha \times 10^6, ^\circ\text{C}^{-1}$ at 400°C		BAF ^(a)
Filler Coke		Binder-Impregnant Coke			
Pyrolytic Carbon	Needle Coke		Parallel	Perpendicular	
34.5	53	12.5	5.62	3.37	1.35
			5.21	3.20	

(a) Measured by technique described by Bacon (Ref. 3).

M32379-1

(a)

M32670-2

(b)

Fig. 1. Photomicrographs of raw materials. (a) Needle-coke as-coated with pyrolytic carbon, and (b) flour made from comminuting to <75 microns

M28566-2

(a)

M28566-6

(b)

M32378-1

(c)

M32378-2

(d)

Fig. 2. Effect of irradiation on microstructure of graphite. (a) and (b) Unirradiated, and (c) and (d) irradiated at 1300°C to 4×10^{21} n/cm²

3. EXPERIMENTAL METHODS

Dimensional measurements, physical property measurements, and irradiation techniques* have been described elsewhere (Ref. 4). Density measurements were made on the graphite by measurement of dimensions and weight (bulk), immersion of the bulk in a liquid (apparent bulk), and comminution of the graphite to a powder of <38 microns and immersion in a liquid (mean apparent density of powder). The apparent bulk density of the needle-coke filler, the binder carbon, and the impregnant carbon collectively, and the pyrolytic carbon, was measured in situ by the technique of lineal analysis. The mean apparent density of the needle-coke filler (heated to 2800°C) after comminution to <38 microns and of the bulk pyrolytic carbon was measured by immersion in liquid as independent components prior to fabrication (Refs. 1, 5, 6).

4. EXPERIMENTAL RESULTS

Specimens from the center of the compacts were irradiated at 1300°C to 4×10^{21} n/cm² ($E > 0.18$ MeV). Dimensional, volumetric, and density changes are given in Table 2. Photomicrographs of the unirradiated and irradiated compact are shown in Fig. 2.

The filler particles of needle coke were highly aligned by the forming process with the major portion of their c-axes parallel to the molding direction. This orientation resulted in large contractions perpendicular to the molding direction (a-axis direction) and only small contractions or expansions in the parallel direction (c-axis direction). The perpendicular specimens probably have passed through a maximum contraction at some fluence $< 4 \times 10^{21}$ n/cm² and have begun to expand. This behavior is typical

*The specimens were irradiated in the Engineering Test Reactor in capsules designed and operated by Battelle Northwest Laboratory.

TABLE 2
IRRADIATION DATA
(FLUENCE, 4×10^{21} N/CM²; TEMPERATURE, 1300°C)

Component	Density (g/cm ³)						Specimen No.	Bulk Changes (%)		
	Bulk		Immersion in Liquid							
			Bulk		Particles					
	Unirradiated	Irradiated	Unirradiated	Irradiated	Unirradiated	Irradiated		Dimensional	Volumetric	
Compact	1.60	2.04	1.89	2.12	2.06	2.08	1	0	-9.95	-19.90
Needle coke	-1.85 ^(a)	2.10 ^(a)	--	--	2.22 ^(b)	2.15 ^(b)	2	-1.65	-10.16	-21.97
							3	0	-11.91	-23.82
							4	-0.83	-11.13	-23.10
							5	-2.07	-10.55	-23.17
Pyrolytic carbon	1.78 ^(a)	1.98 ^(a)	1.85 ^(c)	2.00 ^(d)	--	--	10	+0.83	-9.95	-19.07
							12	-0.83	-11.53	-23.89
							13	0	--	--
							14	-1.65	-9.57	-20.79
							15	-2.48	--	--

(a) By lineal analysis, needle-coke filler, binder carbon, and impregnant carbon were treated together.

(b) From Ref. 5.

(c) From Refs. 6 and 7.

(d) From Ref. 8.

of other highly aligned graphites when irradiated under similar conditions (Refs. 3, 9, 10).

Volume changes measured by the lineal analysis technique indicate apparent bulk volume changes and include all micropores within a filler, whereas those measured by liquid immersion indicate an apparent volume change that excludes all pores which are open to the wetting liquid. The pyrolytic carbon phase showed approximately the same behavior whether measured in situ by lineal analysis or by liquid immersion external to the binder-filler compact. The porosity within the pyrolytic carbon is closed to the wetting liquid and the pyrolytic carbon densifies by the removal of extremely small pores or structural defects. In contrast, the behavior of the needle-coke phase was quite different. The needle-coke grains consist of a considerable volume of porosity that can be eliminated when the needle coke is comminuted. The total porosity or structural defect remaining after comminution of the needle coke is less than that of the pyrolytic carbon and probably of a different morphology due to differences in crystallite sizes and orientation.

Upon irradiation the bulk density of the needle-coke grains increases by the elimination of porosity. This is the same porosity that can be eliminated by comminution. Concurrently the volume of the crystallites and associated defects is expanding. The bulk volume of the binder-filler graphite contracts during irradiation. The open porosity, i.e., the pores visible in the photomicrographs in Fig. 2, is disappearing.

Density distribution curves for the components and compacts are shown in Fig. 3. In the unirradiated state the two filler phases are separate and distinct and each has a narrow distribution of densities. After irradiation the curve for each component has shifted in accordance with the volume changes of each material. These curves are based on density measurements of each carbon component external to the composite. The curve for the unirradiated composite shows one distinct broad peak located near the

Fig. 3. Density distributions in unirradiated and irradiated binder-filler composite and its individual carbon components. (a) Separate pyrolytic carbon and needle coke

Fig. 3. Density distributions in unirradiated and irradiated binder-filler composite and its individual carbon components. (b) Binder-filler composite

pyrolytic carbon peak, between the pyrolytic carbon and needle-coke peaks, and a high-density tail extending into the needle-coke region. Remeasurement after irradiation produces a composite curve with two distinct peaks that more closely approximate the peaks of the irradiated pyrolytic carbon and needle coke. However, the distribution of densities is wider and the peaks are still not as sharp as the individual-phase peaks.

5. DISCUSSION AND CONCLUSIONS

It is evident, from the curve for the unirradiated composite in Fig. 3 and the bulk density of the composite from Table 2, that comminution has removed the large open pores which result from fabrication but not all of the smaller ones. It is not possible in binder-filler artifacts to completely liberate the various carbon structures by comminution, but only to approach complete liberation (see Ref. 1). However, due to differences in the volume changes of the various carbon structures during irradiation, i.e., densification of the pyrolytic carbon, bulk densification of the needle coke, and expansion of the solid structure of the needle coke, internal cracks can form that enhance cleavage at the interfaces between these various structures and improve the liberation of the phases, as shown by the curve for the composite after irradiation.

Although the two carbon structures present in the compact represent an extreme example of a binder-filler composite with widely different carbon phases, it is not unlike a typical binder-filler graphite that often has a smoothly varying spectrum of carbon structures such as those described in Ref. 1.

The internal rearrangements that take place within the microstructure are complex and depend sensitively upon the original density and structure of the various carbon components and the morphology of the pores that result from fabrication. However, from this experiment and the work in Ref. 1, a general picture emerges concerning microstructural changes in a binder-filler graphite during irradiation at low fluences and high temperatures.

The filler component of highest density is usually more graphitic than the low-density components; i.e., the needle-coke particles show bulk densification concurrent with expansion of the solid material. Apparently these two mechanisms concurrently consume and produce pores of different morphology and in different size domains within a filler particle due to crystallite shape changes, i.e., c-axis expansion filling pores along their basal planes while pulling the structure apart along the a-axis at the crystallite edges. Independent of this reaction, the low-density components densify by the removal of microdefects which may be in yet a third domain with respect to size. Still an additional source of crack formation in a composite can be at the interfaces between regions with different carbon structures and densities. Cracks may form at these interfaces if the volume change rates or the crystallite orientations of the coinciding regions are different. An example in this case may be the interface regions between the pyrolytic carbon, needle-coke, or binder carbon structures. Since all components are connected, the net effect on the bulk dimensions and volume results from the sum of the components with allowances for interactions among the components. Further complicating the microstructure is the network of pores created during fabrication, which lies between the various particles of the carbon filler particles. These pores are usually consumed at low fluences as a result of the densification or expansion of the various components and their internal structural rearrangements as described above.

As the irradiation continues to higher fluences, the cracks formed earlier at the boundaries between different structural regions begin to grow at an accelerated rate and account for the large volume expansions observed at high fluences.

It should be recognized, however, that the strength at the various interfaces discussed above and consequently the irradiation-induced creep that can occur in graphites will also influence the degree and rate of crack formation. The effects of strength and irradiation creep of graphites are discussed in more detail in Ref. 11.

ACKNOWLEDGMENTS

The author gratefully acknowledges the help of J. Pontelandolfo for preparation of the specimens and L. Bailey for density and property measurements. The aid of W. Gray of Battelle Northwest Laboratory for irradiation of the specimens is also gratefully acknowledged.

REFERENCES

1. Engle, G. B., "Density and Structural Distributions in Artificial Graphites," Carbon 8, 485 (1970).
2. Bokros, J. C., G. L. Guthrie, and A. S. Schwartz, "The Influence of Crystallite Size on the Dimensional Changes Induced in Carbonaceous Materials by High-Temperature Irradiation," Carbon 6, 55 (1968).
3. Bacon, G. E., "A Method for Determining the Degree of Orientation of Graphite," J. Appl. Chem. 6, 477 (1956).
4. Engle, G. B., "Irradiation Behavior of Nuclear Graphites at Elevated Temperatures," to be published in Carbon.
5. Engle, G. B., "The Influence of Pitch-Binder Coke Content on the Properties and Irradiation Behavior of Molded Graphite," to be published in Carbon.
6. Bokros, J. C., and K. Koyama, "Interpretation of Dimensional Changes Caused in Pyrolytic Carbon by High-Fluence Neutron Irradiation," J. Appl. Phys. 41, 2146 (1970).
7. Bokros, J. C., "Structure of Pyrolytic Carbon Deposited in a Fluidized Bed," Carbon 3, 17 (1965).
8. Bokros, J. C., G. L. Guthrie, R. W. Dunlap, and A. S. Schwartz, "Radiation-Induced Dimensional Changes and Creep in Carbonaceous Materials," J. Nucl. Mater. 31, 25 (1969).
9. Cox, J. H., Jr., and J. W. Helm, "Graphite Irradiations 300°-1200°C," Carbon 7, 319 (1969).
10. Henson, R. W., A. J. Perks, and J. W. Simmons, "Lattice Parameters and Dimensional Changes in Graphite Irradiated Between 300° and 1350°C," Carbon 6, 789 (1968).
11. Engle, G. B., and J. C. Bokros, "Interpretation of High-Temperature Irradiation Effects in Carbons and Graphites," paper presented at the Tenth Biennial Conference on Carbon, June 27 - July 2, 1971, Lehigh University, Bethlehem, Pennsylvania.