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IRRADIATION-INDUCED DIMENSIONAL CHANGE IN BORONATED GRAPHITE -- RESULTS OF THE BG-1 (GA-19-1) EXPERIMENT

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SUMMARY

Boronated graphites containing 21 to 35 wt-% boron and fabricated by extrusion or warm-pressing techniques were irradiated at 650 ± 100 C to fast-neutron exposures of 2×10^{21} to 4×10^{21} n/cm² ($E > 0.18$ MeV), which was similar to 2 to 4 year exposure in an HTGR. The specimens were shielded from thermal neutrons so that a B¹⁰ burnup gradient (35 to 80%) developed across the 0.2-in. width of some specimens.

The irradiation caused an increase in the coefficient of thermal expansion and a decrease in thermal conductivity. The flexure strength was unchanged. Dimensional change of the extruded specimen was about 0.7% expansion perpendicular to the extrusion direction and 0.25% contraction in the parallel direction. During irradiation, the warm-pressed and baked material generally expanded 2 to 3% parallel to the pressing direction and either contracted or expanded about 0.5% in the perpendicular direction. Correlation of these experimental results with others showed that dimensional change was relatively insensitive to

B₂O₃ content of the B₄C raw material
Specimen size or B¹⁰ burnup-gradient
Bake temperature (1000 to 2000 C)
B₄C grain size (<400 μm)
Natural boron content in the range 20 to 35 wt-% boron.

Fast-neutron exposure is the parameter that shows the best correlation with irradiation-induced dimensional change. Expansion of boronated graphite in both directions was favored by increasing fast-neutron exposure. Non-boronated warm-pressed graphites contracted more in the perpendicular direction and expanded less in the parallel direction than boronated graphites at the same exposure.

Comparison of nonboronated and boronated warm-pressed graphites showed that the addition of B_4C granules to the graphite matrix produced enhanced expansion at a given exposure even when the B^{10} content of the B_4C was reduced to produce a relatively inert B_4C particle.

It is probable that several mechanisms act to accelerate expansion in boronated graphite. The results of this experiment and evidence in the literature suggest the following possibilities:

1. Swelling of B_4C granules because of fast-neutron damage (effects from the $B^{10}(n,\alpha)Li^7$ reaction being secondary).
2. Enhanced nucleation of fast-neutron radiation damage in the graphite matrix material because of both B^{11} and B^{10} in substitutional solid solution.
3. Complex interaction of the graphite matrix that is attempting to change dimensions around unyielding or swelling granules of B_4C .

In spite of the uncertainties about the mechanisms leading to dimensional change, the absence of a significant size or shielding effect seems well established. Direct use of boronated graphite irradiation data, rather than treating these data in analytical models, would therefore provide the most reliable prediction of absorber dimensional change during HTGR service.

INTRODUCTION

Boronated graphite has shown promise as an economical and effective control material (because of the $B^{10}(n,\alpha)Li^7$ reaction), for the High Temperature Gas-Cooled Reactor (HTGR). This material is made by addition of B_4C granules to a graphite-pitch mixture prior to the forming and baking process. Important design considerations in the long-term use of boronated graphite include changes in dimensions and material properties that result from neutron irradiation. Some irradiation experiments have been conducted to explore radiation effects in boronated graphite (Refs. 1-4). This work revealed the occurrence of changes in thermal and physical properties during irradiation, but the irradiation-induced dimensional change was of primary

concern and showed the greatest variability. In order to predict dimensional changes in the boronated graphite control absorbers of current HTGR design, a calculational model for radiation damage was developed (Ref. 5). To aid in HTGR design, it was desirable to test this model and to gain a better understanding of the factors contributing to dimensional change. An irradiation capsule experiment, designated BG-1, was therefore conducted to provide such information.

Specimens were prepared in the laboratory (1) from raw materials by a warm-press and bake technique or (2) from a neutron absorber material manufactured by an extrusion process for the Peach Bottom HTGR. The laboratory-prepared material was formulated to explore irradiation-induced dimensional change as a function of raw material purity, bake temperature, self-shielding effects, and boron content. The extruded material specimens were included to provide an indication of dimensional change that might be expected in current production materials. There was also the expectation that size effects might be explored at some future time by correlation of experimental capsule data and observed changes in full-sized absorbers in the Peach Bottom HTGR.

SPECIMEN PREPARATION

Warm-Pressed and Baked Specimens

Raw materials used to fabricate specimens are listed in Table 1. A descriptive summary on preparation of the graphite filler and pitch binder is given in the table, but some additional description of the preparation of the B_4C additions is presented here. Boron carbide was prepared either (1) from natural boron (99.5% B) or (2) from B^{10} -depleted boron (98.9% B containing 1.45 at.-% B^{10}) and graphite (material 3685-55-A-2). The powders were blended in a boron to carbon ratio of 3 to 1, placed in a graphite crucible, and lightly compacted. The loaded crucible was placed in a high-temperature vacuum furnace. The furnace was purged (50 μ m to 8 psig) twice with atomic grade helium and then evacuated to a pressure less than 1 μ m. The furnace was then resistance-heated to 2000 C with the pressure maintained at less than 150 μ m. At 2000 C, the furnace was backfilled with helium to 8 psig

Table 1

RAW MATERIALS USED IN PREPARATION OF B₄C GRAPHITE SPECIMENS

Material Number	Description	Preparation	Finished Product Chemical Analysis
3685-55-A-1 (-50 +200 mesh)	Graphitized Wilmington petroleum coke	Crushed in a Stokes Oscillator and sieved into two U.S. mesh size fractions -50 +200 designated A-1 and -200 designated A-2. Graphitized for about 1 hr at 2700°C ± 100 in a graphite resistance furnace filled with helium.	a. Elements detected by emission spectrograph (ppm): <u>A-1</u> : B < 0.5, Ba < 0.5, Mg < 0.5, Si < 10, Ti 2, V 10, Zr 60. <u>A-2</u> : B < 0.5, Ba < 0.5, Cu < 0.5, Mg < 1, Ni 20, Si < 10, Ti 6, V 10, Zr > 1000.
3685-55-A-2 (-200 mesh)			b. Ash content: <u>A-1</u> : None detected < 0.02 wt-%. <u>A-2</u> : 0.13 wt-%. c. Apparent crystallite size, L _c : <u>A-1</u> : 730 to 770 Å. <u>A-2</u> : 1350 to 2000 Å. d. Layer plane spacing, C ₀ : <u>A-1</u> : 6.702 to 6.694 Å. <u>A-2</u> : 6.708 to 6.705 Å.
3685-92-B	Pitch - Barrett No. 30	Sieved and retained -30 U.S. mesh particles. Leached 20 hr at R.T., in 1:1 HCl/H ₂ O solution. Rinsed with distilled water and dried in vacuum (25 mm Hg) oven at 50°C.	a. Elements detected by emission spectrograph (ppm): Mn < 10, Pb 60, Si 40, Al 40, Bi 6, Mo 6, Ni < 4, Ca 60, Fe 20, Na 200, Ti 4. b. Ash content, 0.07 wt-%.
3685-70	Technical grade B ₄ C	Sieved into three size ranges U.S. mesh -40 +50, -50 +70, -70 +140.	B 69, B ₂ O ₃ 1 to 3, C Bal, Fe 0.80 (wt-%).
3685-84	Leached technical grade B ₄ C	B ₄ C (material 3685-70) leached several hr in warm distilled water to remove B ₂ O ₃ . Water leach followed by 48-hr leach in 1:1 HCl/H ₂ O solution to remove Fe. Distilled water rinse and dried in vacuum oven (25 mm Hg) at R.T.	B 69.6, B ₂ O ₃ 0.07, Fe 0.1, C Bal (wt-%).
3685-95	B ₄ ^{nat} C made in laboratory	Blended 99.5% B ^{nat} powder and graphite (3685-55-A-2) in 75:25 ratio by weight. Heated in closed graphite crucible 2 min at 2500°C ± 50 in 1 atm He to fuse (7 separate fusions). Crushed bisque with 1-in. diameter steel Plattner mortar and pestle and laboratory press. Sieved to obtain size fractions -40 +50, -50 +70, -70 +140. Leached in 1:1 HCl/H ₂ O solution 48 hr at R.T. Distilled water rinse and dried in vacuum oven (25 mm Hg) at R.T.	B 69.2, B ₂ O ₃ 0.1, Fe 0.2, C Bal (wt-%).
3685-105	B ₄ ¹¹ C made in laboratory from B ¹⁰ -depleted B	Blended 98.9% B powder from ORNL containing 1.45 at-% B ¹⁰ with graphite (3685-55-A-2) in 75:25 ratio by weight. Processed material the same as 3685-95 except only 3 separate fusions.	B 72.3, B ₂ O ₃ 0.02, Fe 0.1, C Bal (wt-%).

and heated quickly (8 min) to 2500 ± 50 C for 2 min. Power was then shut off and the furnace cooled to room temperature at a rate of 500 C/min. The boron and carbon powders reacted to form B_4C , which partially fused and formed a porous, brittle bisque. The bisque was usually freestanding in the crucible; however, reaction with the crucible was evident in localized places for most of the fusions.

The bisques were crushed with a steel mortar and pestle, and the resultant material was sieved and crushed again until all the material had passed through a 40-mesh screen. Next, the material was leached in a 1:1 HCl/H₂O solution to remove Fe introduced during the crushing process. The crushing and leaching operation was adapted from procedures reported previously (Ref. 6).

Chemical analyses of both natural and depleted boron carbide materials (3685-95 and 3685-105) indicated that boron volatilization and reaction with the crucible were sufficient to lower the boron content from 75 wt-% to about 70 wt-%. The reaction of boron and carbon to form B_4C was assumed to be essentially complete because X-ray diffraction analysis showed only the presence of B_4C and carbon with certainty.

The commercial technical grade B_4C (material 3685-70) had significant quantities of B_2O_3 (1 wt-%), as well as high localized Fe concentrations. To obtain material 3685-84, the B_2O_3 was removed by rinsing the B_4C in warm distilled water (about 80 C) for several hours, and the Fe was removed by soaking in a 1:1 HCl/H₂O solution. After the B_4C had been rinsed in distilled water and dried in a vacuum oven, chemical analysis showed that B_2O_3 and Fe concentrations had been reduced to 0.07 and 0.1 wt-%, respectively.

The warm-pressing and baking technique developed for Peach Bottom HTGR fuel (Ref. 7) was used to fabricate the boronated graphite. The pressing mixtures were prepared by dry-blending the appropriate proportions of graphite filler (3685-55), pitch binder (3685-92B, 15 wt-%), and B_4C . Trichloroethylene was added to the dry blend to dissolve the pitch and form a low-viscosity slurry. The slurry was heated to about 40 C and stirred continuously

until the solvent evaporated and left solid chunks (about 1/8-in. to 1/4-in. in diameter) of the blend. The material was then placed in a vacuum oven at 40 C to complete drying.

Warm-pressing was accomplished at 750 C in a purged helium atmosphere (to minimize oxidation of B_4C). After warm-pressing, the compacts were cut axially with a hardened steel saw to the rough shape of the desired specimens, as shown in Fig. 1. Specimens of types A and B were designed for irradiation in the capsule and for measurement of chemical content, thermal conductivity, thermal expansion, and modulus of rupture perpendicular to the pressing direction. The type C specimens were for measurement of modulus of rupture parallel to the pressing direction. The components of the specimen sets used in the capsule were identified and kept together. The type A specimens were marked so that adjacent faces in the original compact would be adjacent when assembled in the capsule.

After they were rough cut, the specimens were rubbed by hand on 240-grit SiC paper until the desired dimensions were obtained. They were then placed in graphite crucibles and baked 2 hr in a high-temperature vacuum furnace at either 1000 or 2000 C. The furnace was evacuated while the temperature was increasing and was then backfilled with helium at temperature.

The finished boronated graphites had a very granular and coarse appearance because of the B_4C component. The material without a B_4C addition had a relatively fine texture and smooth surfaces when shaped. Table 2 summarizes the capsule specimen materials and the experimental purpose of each.

Extruded Specimens

Three capsule specimens and a complete set of physical and thermal properties specimens were cut from an absorber manufactured for the Peach Bottom HTGR. The absorber was fabricated by blending B_4C granules, graphite filler, and pitch, and then hollow cylinders (2.3 in. OD, 1.3 in. ID by 17 in. long) were formed by extrusion. The extrusions were baked at an unknown temperature for an undetermined time and were then machined to the final shape. Prismatic

Fig. 1. Method of rough-cutting cylindrical compacts to obtain rectangular prismatic specimen sets (types A, B, and C). Final dimensions and intended uses of specimen types are shown.

TABLE 2
B₄C-GRAPHITE SPECIMEN MATERIALS FOR THE BG-1 CAPSULE

Material No.	Bake Temp. (°C)	Boron Conc. (wt-%)	Density ^a (g/cm ³)	B ₄ C Raw Material ^b	Type of Capsule Specimen ^c	Purpose of Material in Irradiation Experiment
3685-111-1000	1000	22	1.77	3685-70	A	1. Provide dimensional change data for B-graphite with significant B ₂ O ₃ in raw B ₄ C. 2. Test model for restraint of dimensional change by shielded material in specimen.
3685-111-2000	2000	22	1.79	3685-70	A	
3685-117-1000	1000	21	1.71	3685-84	B	1. Provide comparison with dimensional change of 3685-111 made with unleached B ₄ C. 2. Determine value of reducing B ₂ O ₃ and Fe content of B ₄ C.
3685-117-2000	2000	21	1.72	3685-74	B	
3685-118-1000	1000	0	1.77	None	A	1. Test model for restraint of dimensional change by shielded material. 2. Comparison of nonboronated and boronated materials made by the same process.
3685-118-2000	2000	0	1.77	None	B	
3685-120-1000	1000	22	1.72	3685-105	B	1. Comparison of dimensional change in material with equal B content but different B ¹⁰ concentration. This material contained about 0.06 times the B ¹⁰ per B ¹¹ atom in natural B ₄ C. 2. Determine if B ¹⁰ fission or merely presence of B can cause significant dimensional change.
3685-120-2000	2000	22	1.72	3685-105	B	
3685-122-1000	1000	23	1.73	3685-95	B	1. Comparison with 3685-120 material. To minimize variables, both B ₄ C additions made in laboratory. 2. Additional dimensional change data for highly boronated graphite.
3685-122-2000	2000	23	1.72	3685-95	B	
3685-124-1000	1000	35	1.71	3685-84	B	1. Comparison of dimensional change between boronated graphites with different B concentration but similar processing.
3685-124-2000	2000	35	1.68	3685-84	B	
3912-34	1000	28	1.60	Peach Bottom HTGR Absorber ^d	D	1. Provide indication of dimensional change in current production material 2. Future correlation between dimensional change in small specimens and actual absorbers in Peach Bottom HTGR.

^aDensity based on volume calculated from linear dimensions and directly measured weight.

^bB₄C size fractions 38%, -40 +50 mesh; 29%, -50 + 70 mesh; 33%, -70 +140 mesh.

^cSee Figs. 1 and 2.

^dB₄C size fraction unknown; approximately 20 to 200 μm size range.

specimens for this experiment were cut with a hardened steel saw from a segment of the absorber about 3 in. from one end. Figure 2 shows the manner in which two types of specimens, types D and E, were taken. The intended uses are also listed. The rough specimens were ground to proper size by hand on 240-grit SiC paper. All specimens were then baked 2 hr in helium at 1000 C to initiate any dimensional change that might take place in the specimens due to thermal relaxation of the stresses possessed by the material segments while in the original absorber. No significant dimensional changes were detected within ± 0.001 in. Table 2 shows the boron content, density, and experimental purpose of this material.

CAPSULE DESIGN

The specimens were held with a loose slip fit in 28 graphite crucibles with inside dimensions of 0.408 in. by 0.408 in. by 0.610 in. long. Two 0.4 in. by 0.2 in. by 0.58 in. specimens (Types A and D) or one 0.4 in. by 0.2 in. by 0.58 in. and two 0.2 in. by 0.2 in. by 0.58 in. specimens (Type B) were placed in each crucible. There was a 0.030-in. gap at the top and a ~ 0.004 in. gap on all sides of the specimens. Seven loaded crucibles were inserted into each of four graphite sleeves, which were then placed in individual Inconel 600 tubes (7/8 in. OD by 5-1/2 in. long). End caps were brazed onto the ends of each of the four Inconel tubes to form cells. The end caps contained the necessary sealed lead-through fixtures for purge gas and four thermocouples. Inconel-sheathed Chromel-Alumel thermocouples monitored the specimen temperature at the center and surface in the fourth crucible in each assembly. The specimen surface temperature in the first and seventh crucibles was also monitored. The cells were placed inside individual aluminum tubes, and the entire assembly was inserted into a stainless steel tube 1.25 in. OD by 26 in. long. Each of the four cells was purged by a separately controlled argon-helium gas mixture to provide an inert atmosphere and temperature control. A fifth argon-helium gas supply purged the space between the four cells and the stainless steel outer tube. The purge gases were passed through a bed of titanium and uranium chips at 720 C to remove oxidants prior to passing through the capsule.

Fig. 2. Method of rough-cutting specimens (types D and E) from Peach Bottom HTGR absorber. Final dimensions and intended uses of specimen types are shown.

Three sides and the top and bottom of each specimen were shielded from thermal neutrons ($E < 0.4$ eV) by gadolinium and cadmium metal sheet. Disks of Gd 0.030 in. thick were placed at the top and bottom of each crucible. A cylinder with a 130° section removed to form a thermal-neutron window was formed from 0.020-in.-thick Cd sheet and positioned adjacent to the inside surface of the outer stainless steel can. The thermal neutrons passing through the 130° window were columnated by 1/4 in. by 4-1/2 in. by 0.060 in. strips of Gd at the crucible surface to produce a 90° neutron window. The specimens were positioned so that their 0.2 in. by 0.58 in. sides were exposed to the neutron window. In crucibles containing two 0.2 in. by 0.2 in. by 0.58 in. specimens, one of the specimens was completely shielded from thermal neutrons by the other specimen and by the metal shielding. Drawings of one cell and of the assembly are shown in Figs. 3(a) and 3(b). Figure 4 is a photograph showing the location of specimens in the crucible relative to the neutron window.

Dosimetry for the capsule consisted of Ni-0.45% Co, Ti, and Fe wires, which were placed at the ends of each cell, centered in the neutron window, and in a shielded position 180° from the window.

IRRADIATION HISTORY

The BG-1 (GA 19-1) capsule was irradiated for four cycles in position F-13-SE in the ETR. Irradiation started in April 1968 with cycle 95 and was completed in November 1968 at the end of cycle 98. A fast-neutron ($E > 0.18$ MeV) exposure of 2.0×10^{21} n/cm² at the ends of the capsule and 4×10^{21} n/cm² near the center was received by the specimens during a total of 2736 hr of reactor operation at a power level above 165 MW. The specimen temperature increased gradually about 50 C during the irradiation. The average surface temperature of most of the specimens was about 600 ± 100 C, while centerline temperatures were 700 ± 100 C. Several of the nonboronated specimens operated about 100 C below these average temperatures. There were no significant malfunctions of the capsule during irradiation. Twenty-seven of the 28 specimen thermocouples operated satisfactorily during the entire irradiation period.

Fig. 3. Capsule configuration and specimen location in the BG-1 (GA-19-1) irradiation experiment: cross section view of (a) entire capsule (Sheet 1 of 2)

Fig. 3. Capsule configuration and specimen location in the BG-1 (GA-19-1) irradiation experiment: cross section view of (b) a single cell (Sheet 2 of 2)

Fig. 4. Position of specimen in the graphite crucible relative to the thermal-neutron window; Type B specimen, material 3685-111-2000, prior to irradiation

One apparently defective thermocouple gave indications of continually decreasing temperature during irradiation.

After it was removed from the ETR core, the capsule was stored for one month and then shipped to GGA. Disassembly was accomplished in the GGA Hot Cell.

EXPERIMENTAL RESULTS

Appearance of Capsule Components

The graphite and metal components of the capsule showed no evidence of corrosion or severe oxidation after irradiation. The Inconel-sheathed thermocouples that were in contact with the specimens appeared slightly discolored. The fact that atmospheric purity had been maintained was shown by the Gd strips, which retained their ductility and could be bent 180° with a 1-in. radius without breaking. Typical thermocouples and bent Gd strips are shown in Fig. 5. The Cd sheet was also ductile. An unsuccessful search was made on components for evidence of a white powder deposit that might indicate the presence of Li, produced by the $B^{10}(n,\alpha)Li^7$ reaction. The specimens were unchanged in visual appearance by the irradiation and were removed from the graphite crucibles with little effort. Figures 6 and 7 show typical specimens of boronated graphite before and after irradiation.

Radioactivity of Specimens

The specimens in a single crucible had a typical radioactivity of about 600 mR β and 160 mR γ at 2 in. The activity probably arose from decay of activated impurities and was low enough that analytical work could be conducted outside the Hot Cell. Two of the materials (3685-122-1000 and 3685-122-2000) had an extremely high radioactivity of about 15 R $\beta+\gamma$ at 1 ft. From a postirradiation measure of the gamma-ray energy spectrum, it was determined that the samples contained activated Ta¹⁸². Further investigations revealed that the boron powder from which the B₄C had been made contained about 2000 ppm of tantalum impurity. These highly radioactive specimens

K239-18, -19, -20, -21

(~2x)

Fig. 5. Thermocouple assembly and gadolinium strips (bent to test the ductility) from cell 1 of capsule BG-1 after irradiation to a fast-neutron exposure of 2×10^{21} to 3.5×10^{21} n/cm² ($E > 0.18$ MeV) at 500° to 750° C. The thermocouples were wrapped with tungsten wire to prevent contact between the Inconel sheath and the carbon crucible.

M22511-1

(a)

(5x)

M22513-1

(b)

(5x)

Fig. 6. Typical boronated graphite specimens prior to irradiation: (a) type B specimen, material 3685-111-1000, 22 wt-% boron, and (b) types A and D specimens, material 3685-124-1000, 35 wt-% boron

Fig. 7. Specimens irradiated in capsule BG-1 to a fast-neutron exposure of 2×10^{21} to 4×10^{21} n/cm² ($E > 0.18$ MeV): (a) warm-pressed boronated (22 wt-% B) graphite; (b) warm-pressed boronated (22 wt-% B) graphite; (c) extruded boronated (28 wt-% B) graphite; and (d) warm-pressed graphite (0 wt-% B). The appearance of these specimens was typical of all materials having similar boron content.

remained in the Hot Cell, where dimensions were measured and metallographic work was performed.

Dosimetry

The fast-neutron ($E > 0.18$ MeV) exposure was determined from analysis of the Fe wires activated by the $\text{Fe}^{54}(\text{n,p})\text{Mn}^{54}$ reaction. The fast-neutron exposure was the same in both the shielded and unshielded regions. The thermal-neutron ($E < 0.4$ eV) exposure was determined from analysis of Ni-0.45% Co wires activated by the $\text{Co}^{59}(\text{n},\gamma)\text{Co}^{60}$ reaction. The thermal-neutron exposure was about 25% lower in the shielded region than in the neutron window. Figure 8 shows the exposure profile for the capsule. The ratio of fast- to thermal-neutron exposure was about 1.5 in the neutron window and between 2.6 and 3.5 in the shielded regions. The dose received by each specimen is listed in Table 3.

B¹⁰ Isotope Burnup

Samples were taken for B¹⁰-B¹¹ isotopic analysis by scraping the surface of selected specimens with a clean steel file, with precautions taken to avoid cross-contamination. A 0.2 in. by 0.2 in. section about 0.02 in. deep and weighing about 0.020 g was removed from the surfaces that were parallel to the plane of the neutron window. The resulting dust was collected in a plastic vial. Isotopic analysis was performed by mass spectrographic techniques at AVCO Analytical Laboratories, Tulsa, Oklahoma.

Four of the 0.2 in. by 0.4 in. by 0.58 in. specimens that contained natural boron were sampled on both the exposed side and the side opposite the neutron window. One specimen (3685-120-2000) that contained B₄C initially depleted in B¹⁰ was similarly sampled. Two of the 0.2 in. by 0.2 in. by 0.58 in. specimens that contained natural boron and were positioned next to the neutron window were sampled on the exposed surface and at the mid-crucible surface adjacent to the companion 0.2 in. by 0.2 in. by 0.58 in. specimen. The companion 0.2 in. by 0.2 in. by 0.58 in. specimens were sampled on the

Fig. 8. Neutron exposure profile in capsule BG-1; data points indicate locations at which dosimetry data were obtained

Table 3

SUMMARY OF MATERIAL PROPERTIES AND IRRADIATION EFFECTS IN BORONATED GRAPHITE INCLUDED IN THE CAPSULE BG-1 EXPERIMENT

	Extruded and Baked	Warm-pressed and Baked											
	Peach Bottom HTGR Control Rod Absorber	Unleached Commercial B ₄ C in Graphite (low boron content)	Unleached Commercial B ₄ C in Graphite (low boron content)	Leached Commercial B ₄ C in Graphite (low boron content)	Leached Commercial B ₄ C in Graphite (low boron content)	Leached Commercial B ₄ C in Graphite (high boron content)	Leached Commercial B ₄ C in Graphite (high boron content)	Natural Boron Laboratory B ₄ C in Graphite	Natural Boron Laboratory B ₄ C in Graphite	B ¹⁰ Depleted Boron Laboratory B ₄ C in Graphite	B ¹⁰ Depleted Boron Laboratory B ₄ C in Graphite	Nonboronated Graphite	Nonboronated Graphite
Material No	3912 34	3685 111	3685-111	3685 117	3685-117	3685-124	3685-124	3685-122	3685-122	3685 120	3685-120	3685-118	3685-118
Bake temperature, °C	(a)	1000	2000	1000	2000	1000	2000	1000	2000	1000	2000	1000	2000
No of specimens	0	4	4	0	0	0	0	0	0	0	0	3	0
Unshielded, 0.2 x 0.2 x 0.58 in	0	4	4	0	0	0	0	0	0	0	0	3	0
Shielded, 0.2 x 0.2 x 0.58 in	3	4	4	3	3	4	4	3	3	4	4	3	3
Shielded, 0.2 x 0.4 x 0.58 in	3	4	4	3	3	4	4	3	3	4	4	3	3
Boron content, wt-%	28	22	22	21	21	35	35	23	23	22 ^b	22 ^b	0	0
Boron dispersion, g boron/cm ³	0.45	0.38	0.38	0.36	0.36	0.52	0.52	0.40	0.40	0.38	0.38	0	0
Density, g/cm ³	1.60	1.77	1.79	1.71	1.72	1.68	1.71	1.73	1.72	1.72	1.72	1.77	1.77
Fast-neutron exposure (E>0.18 Mev) 10 ²¹ n/cm ²	2.0-2.5	2.5-3.5	3.5-4.0	2.0-2.5	3.5-4.0	2.5-3.0	3.0-3.5	2.5-3.0	2.0-2.5	3.5-4.0	3.5-4.0	3.5-4.0	3.5-4.0
Thermal-neutron exposure (E<0.4 eV) 10 ²¹ n/cm ²	1.5	1.5	2.5	1.5	2.5	1.5	1.5	1.5	1.5	2.5	2.5	2.5	2.5
Specimen irradiation temp, °C													
Surface minimum	500	525	550	500 ^c	525	550	550 ^c	550	550	575	525	450	525
Surface maximum	575	600	625	575 ^c	575	600	600 ^c	625	625	625	625	575	575
Surface average	550	550	600	550 ^c	550	600	600 ^c	600	600	600	600	575	550
Centerline minimum	600 ^c	625	700	600 ^c	675 ^c	675	675 ^c	675 ^c	675 ^c	675 ^c	625	550 ^c	675 ^c
Centerline maximum	675 ^c	750	825	675 ^c	775 ^c	850	850 ^c	825 ^c	825 ^c	700 ^c	700	600 ^c	775 ^c
Centerline average	650 ^c	675	750	650 ^c	700 ^c	750	750 ^c	750 ^c	750 ^c	675 ^c	650	550 ^c	700 ^c
B ¹⁰ isotope burnup, % depletion													
At neutron window	80	80	67 & 66	80 ^d	75 ^d	66	76	80 ^d	80 ^d	(e)	(e)	0	0
Midspecimen	(f)	30	41	35 ^d	35 ^d	35 ^d	35 ^d	35 ^d	35 ^d	(e)	(e)	0	0
Opposite neutron window	37	53	34 & 43	37 ^d	50 ^d	38	48	50 ^d	50 ^d	(e)	(e)	0	0
Dimensional change during irradiation relative to forming direction ±													
Parallel minimum	-0.52	+2.35	+1.50	+1.53	+2.35	+1.76	+0.31	+2.25	+1.72	+1.05	+1.20	+1.23	+0.12
Parallel maximum	-0.03	+2.81	+3.24	+2.65	+3.22	+2.67	+2.23	+2.75	+2.58	+1.87	+2.15	+1.73	+0.91
Parallel average	-0.23	+2.51	+2.35	+2.01	+2.78	+2.20	+1.26	+2.50	+2.12	+1.42	+1.59	+1.40	+0.44
Perpendicular minimum	-0.13	-0.58	1.21	-0.75	-0.37	-0.43	-1.09	-0.25	-0.75	0.68	-1.50	1.21	0.96
Perpendicular maximum	+0.86	+0.91	+0.56	+0.89	+0.92	+1.54	+0.91	0	+0.75	+0.31	+0.17	0.41	0.10
Perpendicular average	+0.69	+0.24	0.19	+0.15	+0.37	+0.44	0.00	0.12	0.12	0.16	0.68	0.80	0.63
Graphite matrix crystallite dimension, Å													
Preirradiation L _c	580	490	675	625	850	675	580	675	770	850	675	850	770
Preirradiation C ₀	6.729	6.719	6.715	6.721	6.721	6.715	6.726	6.736	6.710	6.715	6.710	6.715	6.724
Postirradiation L _c	103	200	119	205	117	210	111	(f)	(f)	170	111	195	200
Postirradiation C ₀	6.820	6.736	6.745	6.739	6.782	6.729	6.758	(f)	(f)	6.742	6.768	6.775	6.756
Coefficient of thermal expansion relative to forming direction from 22° to 700°C, 10 ⁻⁶ in/in-°C													
Preirradiation parallel	3.68	5.57	6.43	7.11	6.60	6.32	5.30	7.05	6.66	6.80	6.18	9.37	9.06
Preirradiation perpendicular	4.70	4.29	3.72	3.40	3.87	4.70	3.82	4.05	4.27	4.26	4.12	4.19	4.01
Ratio (α _{pa} /α _{pe})	1.38 ^e	1.3	1.7	2.3	1.7	1.3	1.4	1.7	1.6	1.6	1.5	2.2	2.2
Postirradiation parallel	(f)	8.17	10.15	8.23	8.44	(f)	(f)	(f)	(f)	(f)	(f)	10.41	10.45
Postirradiation perpendicular	(f)	5.25	6.16	5.08	4.34	(f)	(f)	(f)	(f)	(f)	(f)	(f)	5.51
Ratio (α _{pa} /α _{pe})	(f)	1.6	1.6	1.6	1.9	(f)	(f)	(f)	(f)	(f)	(f)	(f)	1.9
Thermal conductivity perpendicular to forming direction, cal/cm-sec-°C													
Preirradiation 25°C	0.120	(f)	(f)	0.135	0.120	(f)	(f)	0.100	(f)	(f)	(f)	0.170	(f)
Preirradiation 400°C	0.090	(f)	(f)	0.105	0.095	(f)	(f)	0.075	(f)	(f)	(f)	0.110	(f)
Preirradiation 800°C	0.065	(f)	(f)	0.080	0.070	(f)	(f)	0.060	(f)	(f)	(f)	0.090	(f)
Postirradiation 25°C	(f)	(f)	(f)	0.031	0.015	(f)	(f)	(f)	(f)	(f)	(f)	0.027	(f)
Postirradiation 400°C	(f)	(f)	(f)	0.032	0.018	(f)	(f)	(f)	(f)	(f)	(f)	0.033	(f)
Postirradiation 800°C	(f)	(f)	(f)	0.030	0.020	(f)	(f)	(f)	(f)	(f)	(f)	0.035	(f)
Room temperature flexural strength, psi													
Preirradiation parallel ^h	3300	685	230	595	490	470	310	730	690	(f)	(f)	660	475
Preirradiation perpendicular ^h	1840	995	450	825	930	700	630	1110	1140	(f)	(f)	1100	795
Postirradiation parallel ^h	(f)	770	335	575	620	(f)	(f)	(f)	(f)	(f)	(f)	450	600

^aOriginal bake temperature unreported (<2450°C), specimens baked 2 hr at 1000°C in the laboratory after shaping^bBoron depleted in B¹⁰ (1.45 at-% B¹⁰, remainder B¹¹)^cEstimated temperatures based on indicated temperatures of adjacent specimens^dEstimated B¹⁰ burnup based on measured burnup of specimens nearby^eBurnup of B¹⁰ not detectable because of initial low B¹⁰ content and probable cross-contamination of specimens^fNot measured^gRatio α_{pa}/α_{pe} (extruded)^hLong axis of test bar parallel or perpendicular to the forming direction

side opposite the neutron window. A standard sample was also prepared from unirradiated material (3685-111-2000) using the technique described above.

The isotopic analysis of the material made with B^{10} -depleted B_4C (3685-120-2000) indicated a B^{10} increase of 27% on the exposed surface and a burnup of 56% on the shielded surface. This unlikely result was probably caused by slight cross-contamination from samples containing natural boron. The initial low level of B^{10} concentration (1.5 at.-% total boron) made these specimens extremely sensitive to B^{10} contamination. The primary value of the isotopic analysis was to confirm the low B^{10} content relative to specimens containing natural boron.

The results of the B^{10} isotopic analysis are shown in Table 3. The accuracy of the analytical technique was sufficient to allow calculation of burnup to within $\pm 1\%$. Specimens not sampled were assumed to have a burnup similar to that of the nearest specimen that was sampled.

The effect of position in the capsule and shielding on B^{10} burnup is shown in Fig. 9. There was no consistent trend in B^{10} burnup relative to axial position in the reactor core; however, a significant burnup gradient was measured across the specimens from the exposed to the shielded surfaces, as shown in Fig. 10. The burnup gradient obtained was not as great as desired to achieve full simulation of HTGR conditions, but it was considered satisfactory to reveal first-order effects of shielding.

Lithium Migration Measurements

The lithium content of selected specimens was determined by atomic absorption techniques. Samples were taken by scraping fragments from either the exposed or shielded surfaces of the specimens. Some unirradiated samples were also analyzed.

The extent of lithium migration out of the specimens was investigated by rinsing the thermocouples and end caps of two cells in nitric acid and analyzing the acid residue for lithium by emission spectrograph. One cell

Fig. 9. Effect of shielding and position in core on B^{10} isotope burnup

Fig. 10. B^{10} isotope burnup in boronated graphite during irradiation in capsule BG-1: (a) burnup gradient across specimens; and (b) irradiated specimen (3912-34; 28 wt-% B) with isotopic sample removed from exposed and shielded sides

contained specimens with no boron or boron depleted in B^{10} . The other cell contained specimens with natural boron. In addition, one graphite crucible that had contained a boronated specimen was scraped on both the inside and outside at the neutron window position; these two samples were separately analyzed for lithium by emission spectrograph. A similar analysis was conducted on a crucible that had contained a boronated specimen with B^{10} -depleted boron. The results are shown in Table 4.

Dimensional Changes

The dimensions of specimens were measured prior to irradiation on a Bausch and Lomb optical gage (precision ± 0.00001 in.). After irradiation, the dimensions of specimens that could be manually manipulated were measured by means of a mechanical-dial bench micrometer (precision ± 0.0001 in.) that was calibrated with the optical gage. Dimensions of the highly radioactive samples (3685-122-1000) were measured remotely in the Hot Cell in a micrometer device (precision ± 0.001 in.). Although the precision of the measuring devices was high, the rough and granular nature of the surfaces of the specimens limited the repeatability of the measurements to ± 0.003 in. Length and width dimensions were measured at multiple locations. At each location, the average of three measurements was recorded and the dimensional change computed. The dimensional change for each type of material was determined from the average of the computations.

The dimensional changes measured for each material in the direction perpendicular and parallel to the pressing or extrusion direction is shown in Table 3. The reported dimensional changes in the perpendicular direction were determined only from the 0.4-in. depth. Changes measured in the 0.2-in. width were not as reliable because of the ± 0.003 -in. repeatability of the measuring devices.

Metallography

Metallographic examination of all material was conducted before irradiation. After irradiation, selected materials were sectioned and polished

TABLE 4
LITHIUM CONTENT OF SPECIMENS AND CONTAMINATION
OF CRUCIBLES AND METAL COMPONENTS OF THE CELLS
RESULTING FROM THE $B^{10}(n,\alpha)Li^7$ REACTION

Cell No.	Crucible No.	Description of Material	Irradiation Temp. (C)	Location of Sample	B^{10} Isotope Burnup (%)	Calculated Li Content Based on B^{10} Burnup and No Migration (wt-%)	Measured Li Content (Atomic Absorption Technique) (wt-%)	Remarks
None	None	3685-118-1000 0 wt-% B	None	Surface	None	0	None detected <16 ppm	Unirradiated standard sample
None	None	3685-124-1000 35 wt-% B	None	Surface	None	0	None detected <11 ppm	Unirradiated standard sample
1	6	3685-111-1000 22 wt-% B	600 ± 100	1/2 specimen, including surface exposed to thermal neutrons	50 to 80	2.20	0.50	-----
				1/2 specimen, including surface shielded from thermal neutrons	30 to 50	1.70	0.54	-----
3	4	3685-120-2000 22 wt-% B^{11}	600 ± 100	Surface exposed to thermal neutrons	Not detectable, assume 50%	0.15	0.22	B^{10} -depleted sample
				Surface shielded from thermal neutrons		0.15	0.24	
				Graphite crucible adjacent to exposed surface of specimen	0	0	0.0193	Crucible containing specimen
				Graphite crucible, outer surface of exposed side	0	0	0.0100	
3	6	3685-118-1000 0 wt-% B	525 ± 75	Surface	0	0	None detected <15 ppm	Irradiated standard sample
4	4	3685-124-1000 35 wt-% B	700 ± 150	Surface exposed to thermal neutrons	66	4.6	0.25	Highly boronated graphite
				Surface shielded from thermal neutrons	38	2.7	0.25	Highly boronated graphite
				Graphite crucible, adjacent to exposed surface of specimen	0	0	0.42	Crucible containing specimens
				Graphite crucible, outer surface of exposed side	0	0	0.08	Crucible containing specimens
3	All	Acid rinse of thermo-couples and end cap	600 ± 100	-----	0	0	2 µg/10 ml	From cell containing very little B^{10}
4	All	Acid rinse of thermo-couples and end cap	700 ± 150	-----	0	0	80 µg/10 ml	From cell containing highly boronated graphite

for metallograph examination. Photomicrographs of typical microstructures before and after irradiation are shown in Figs. 11 through 18. The most obvious effect of irradiation on the boronated graphite microstructure was the formation of voids at the grain boundaries of B_4C . Fine cracks were also seen penetrating into some grains. No evidence of B_4C swelling could be detected in the microstructures.

Flexural Strength

The flexural strength for each of the thirteen materials was determined prior to irradiation. After irradiation, strength was determined for six materials. The bend-specimen dimensions were about 0.6 in. by 0.2 in. by 0.1 in., with the long axis either parallel or perpendicular to the forming direction. Three-point loading was employed with two supports separated by 0.4 in. and midspan loading at 0.005 in./min on an Instron Model TTCM-1 testing machine. Either three or four specimens were tested in both directions for each material. The flexural strength was calculated using the following expression:

$$\text{Flexural Strength} = \frac{3p\ell}{2bh^2} ,$$

where p = load at failure, in lb,

ℓ = distance between supports (0.4 in.),

b = width (0.2 in.), and

h = thickness in the direction of loading (0.1 in.).

An average flexural strength was calculated for each material; the results are shown in Table 3.

Coefficient of Thermal Expansion

Prior to irradiation, the coefficient of thermal expansion parallel and perpendicular to the form direction was determined for all materials between 22 and 1000 C. After irradiation, the expansion coefficient was determined

Fig. 11. Preirradiation microstructure (at two magnifications) of extruded and baked Peach Bottom HTGR type boronated graphite (material 3912-34, 28 wt-% B); the B_4C granules appear randomly dispersed in the graphite matrix

PRESSING DIRECTION →

M28157-1

(100x)

M28157-03

(500x)

Fig. 12. Preirradiation microstructure (at two magnifications) of warm-pressed and baked boronated graphite made with commercial B_4C containing 1 wt-% B_2O_3 (material 3685-111-2000, 22 wt-% B); note differences in microstructure of individual B_4C grains and tendency of these grains to align perpendicular to the pressing direction. The large voids in the graphite matrix resulted when B_4C grains fell out during metallographic preparation of the specimen.

PRESSING DIRECTION →

M23754-01

(100x)

M23754-02

(500x)

Fig. 13. Preirradiation microstructure (at two magnifications) of warm-pressed and baked boronated graphite made with commercial B_4C that was leached to remove contaminant Fe and B_2O_3 (material 3685-117-1000, 21 wt-% B). The microstructure of this material was not visibly different from that made with unleached B_4C (see Fig. 12). Note porosity apparent along the edge of the B_4C particle in the 500X photomicrograph; similar appearing porosity became prominent in some B_4C grains after irradiation.

PRESSING DIRECTION →

31

M28162-1

(100x)

M28162-03

(500x)

Fig. 14. Preirradiation microstructure (at two magnifications) of warm-pressed and baked boronated graphite containing B_4C depleted in B^{10} (material 3685-120-2000, 22 wt-% B, 0.3 wt-% B^{10}). Porosity of B_4C granules, such as may be noted in these photomicrographs, was common in B_4C made in the laboratory from both natural boron and B^{10} -depleted boron.

M28727-2

(100x)

M28727-5

(500x)

Fig. 15. Postirradiation microstructure (at two magnifications) of warm-pressed and baked boronated graphite made with commercial B_4C that had been leached to remove contaminant Fe and B_2O_3 (material 3685-117-1000, 21 wt-% B); fast-neutron exposure was 2.0×10^{21} to 2.5×10^{21} n/cm² ($E > 0.18$ MeV), and B^{10} burnup was 35 to 80%. Intergranular voids were common in the B_4C after irradiation but were not observed prior to irradiation. The appearance of voids was not influenced by the extent of B^{10} burnup in the range of 35 to 80% B^{10} depletion. The constant width of the voids between the grains suggests that there was preferential removal of material at the grain boundary during polishing, rather than mechanical separation of the grains.

M28731-2

(100x)

M28731-3

(500x)

Fig. 16. Postirradiation microstructure (at two magnifications) of warm-pressed and baked boronated graphite made with commercial B_4C containing 1 wt-% B_2O_3 (material 3682-111-2000, 22 wt-% B); fast-neutron exposure was 3.5×10^{21} to 4.0×10^{21} n/cm² ($E > 0.18$ MeV), and B_{10} burnup was 40 to 66%. Both intergranular and intragranular cracks or voids were observed in some B_4C granules after irradiation, but these were not detected prior to irradiation. The presence or absence of B_2O_3 did not influence the microstructure appearance of the boronated graphites studied in BG-1. The crack pattern shown in the 500X magnification was not typical, but it may represent a condition that could lead to dimensional change of boronated graphite through swelling of B_4C granules.

M28727-3

(500x)

M28731-5

(500x)

Fig. 17. Postirradiation microstructure of B_4C granules in warm-pressed and baked boronated graphite: (a) material 3685-117-1000, 21 wt-% B, fast-neutron exposure 2.0×10^{21} to 2.5×10^{21} n/cm² ($E > 0.18$ MeV) and B^{10} burnup 35 to 80%; (b) material 3685-111-200, 22 wt-% B, fast-neutron fluence 3.5×10^{21} to 4.0×10^{21} n/cm² ($E > 0.18$ MeV) and B^{10} burnup 40 to 66%. The cracks in single grains of B_4C that developed during irradiation apparently nucleated at the grain surface or grain boundary and then progressed into the grain. The termination of some cracks in the grain suggests that crack propagation may not have proceeded in a brittle manner.

M29193-2

(100x)

M27193-8

(1000x)

Fig. 18. Postirradiation microstructure (at two magnifications) of warm-pressed and baked boronated graphite containing B_4C depleted in B^{10} (material 3685-120-2000, 22 wt-% B, 0.3 wt-% B^{10} ; fast-neutron exposure was 3.5×10^{21} to 4.0×10^{21} n/cm² ($E > 0.18$ MeV), and B^{10} burnup was not detectable. The void pattern in both porous and relatively dense B_4C was similar to that in B_4C containing 16 times more B^{10} per B^{11} atom but with the same total boron content and neutron exposure. However, there was less material removed at the grain boundary during polishing than with irradiated natural B_4C . Porosity at the grain boundaries rather than a continuous void was evident at high magnification. The porosity that developed may have been caused by migration and coalescence of helium, by the $B^{10}(n,\alpha)Li^7$ reaction, from within the grain.

for six selected materials. The measurements were made with a vitreous-silica differential dilatometer in which the expansion of the sample was sensed by a linear differential transformer. The sample temperature was monitored by a Pt/Pt - 10 Rh thermocouple that touched the specimen. Dimensions were 0.6 in. by 0.2 in. by 0.1 in. for parallel specimens and 0.4 in. by 0.2 in. by 0.1 in. for perpendicular specimens; the thermal expansion was measured along the long axis. The measurements were made with a programmed heating rate of about 15 C/min.

The mean coefficient of linear thermal expansion σ was calculated from the expression

$$\sigma = \frac{\Delta l}{l_0} (t - t_0) ,$$

where t = final temperature,

t_0 = initial temperature,

l_0 = initial length of specimen, and

Δl = change in length in the temperature range $t - t_0$.

The mean coefficients of expansion are shown in Table 3. Some of the irradiated specimens started to contract rapidly perpendicular to the pressing direction when they were heated above 700 C (near the irradiation temperature), so expansion coefficients are reported for the temperature range zero to 700 C.

Thermal Conductivity

Thermal conductivity was determined between room temperature and 800 C for six materials prior to irradiation and three materials after irradiation. The xenon flash method (Ref. 8) was employed with specimens 0.30 in. in diameter by 0.060 in. thick, shaped so that the direction of measurement was perpendicular to the forming direction. Neumann and Kopp's additivity rule for specific heat of B_4C and graphite was used in calculating the heat capacities (Ref. 9). These results are shown in Table 3.

Crystallite Dimensions

Crystallite dimensions (L_c and C_0) of the graphitic phase of each material were measured by X-ray diffractometer techniques before and after irradiation. Powdered samples were held between transparent tape during the X-radiation exposure. Results of that work are shown in Table 3.

DISCUSSION

The flexural strength of the warm-pressed material was highly variable and considerably less than that of the extruded boronated graphite, which had strength comparable to that of nonboronated conventional graphites (Ref. 10). The strength perpendicular to the pressing direction or parallel to the extrusion direction was 50 to 100% greater than in the other direction. The postirradiation strength of selected warm-pressed materials showed both increase and decrease in strength. No systematic trend was evident.

The strength values measured in a flexure test are sensitive to surface flaws. The coarse texture of the material resulting from the large B_4C grain size produced a highly flawed surface. Small changes in strength that may have resulted from irradiation could have been masked by the random influence of surface defects.

The measured thermal conductivities of selected boronated materials prior to irradiation were much alike; with increasing temperature (room temperature to 800 C), these values decreased 25 to 40%. Thermal conductivity of the material that contained no B_4C had a temperature dependence similar to that of boronated graphite, but the value was somewhat higher over the same temperature range. After irradiation, the thermal conductivities measured in two boronated and one nonboronated graphite at room temperature were alike, each 75 to 90% lower than before irradiation. Heating to 800 C caused little change in thermal conductivity of the irradiated specimens.

Prior to irradiation the coefficient of thermal expansion (CTE) in all thirteen materials perpendicular to the forming direction varied in a relatively

narrow range (3.4×10^{-6} to 4.7×10^{-6} in./in.-°C). Parallel to the forming direction, the coefficient varied greatly between 3.68×10^{-6} in./in.-°C for the extruded boronated graphite and 9.37×10^{-6} in./in.-°C for the nonboronated warm-pressed graphite. The ratios of CTE in the two directions, which varied from 1.3 to 2.3, gave an indication of anisotropy in the materials. The extruded and most of the warm-pressed boronated graphites were of comparable anisotropy (1.3 to 1.7), while the nonboronated graphites and one boronated graphite were of somewhat higher anisotropy (2.2 to 2.3). After irradiation, the CTEs of selected materials were measured and found to be 10 to 60% higher than before irradiation. The boronated graphite made with 1% B_2O_3 impurity in the B_4C and baked at 2000 C (3685-111-2000) showed the largest increase in CTE in both the perpendicular and parallel directions. There was no other consistent correlation of change in CTE or anisotropy with material properties or process parameters.

The crystallite properties of the graphite filler material were measured in terms of crystallite height L_c and layer spacing C_0 . The crystallite height decreased with neutron exposure and the average layer spacing increased, but there were no correlations of these effects with boron content or with the bake temperature of the materials. When boron is taken into solution in the graphite lattice, the lattice spacing tends to decrease (Ref. 11). In this work the nature of the material was such that there were considerable variations in C_0 ; if boron were taken into solution, its effect was not detectable.

In each specimen containing B^{10} there was lithium production by the $B^{10}(n,\alpha)Li^7$ reaction. There was considerable migration of lithium out of the highly boronated specimens. Evidence of this was the fact that when B^{10} burnup was significant, the measured lithium content (0.05 to 0.25 wt-%) was much lower than the value estimated from B^{10} burnup. On the other hand, when B^{10} burnup was slight, as in the B^{10} -depleted samples (3685-120-2000), the estimated lithium content was in better agreement with the measured values.

The fact that the lithium was mobile at the irradiation temperature was also shown by the lack of a lithium concentration gradient in the specimens

in which a steep B^{10} gradient was detected. The lithium apparently migrated from the relatively hot specimens to the cooler crucibles and metal components. When the specimen temperature was high (about 700 C), the lithium concentration in the cooler graphite crucible became higher than in the highly boronated sample that was the source of lithium (see Table 4). For example, in one case, 3685-124-1000, the lithium content of the specimen was 0.25 wt-%, whereas in the adjacent graphite crucible wall the lithium content was 0.42 wt-%.

In similar irradiation experiments with boronated graphite at 500 C, the migration of lithium was determined to be insignificant (Ref. 1). From this work it appears that above 500 C migration of lithium can be significant.

No attempt was made to determine helium retention of the specimens. It was assumed that helium that escaped from the B_4C granules could diffuse out of the specimens. In experiments with 5 to 7 wt-% boronated graphite, other workers have estimated a 60% retention of helium in boronated graphite after irradiation at 500 C to 50% of B^{10} burnup (Ref. 1). Release of helium may have been greater in the BG-1 experiment because of the higher operating temperature.

The microstructure of the boronated graphites showed angular B_4C granules dispersed in a continuous matrix of graphite and carbonized binder. In the warm-pressed materials the long axes of B_4C granules tended to be aligned perpendicular to the pressing direction. Before irradiation, the polished surfaces of most B_4C granules were porous or featureless. After irradiation, material in the grain boundaries in large B_4C granules was removed during polishing, which rendered the grain boundaries visible as apparent open voids. Fine cracks radiated from some grain boundaries into the individual grains. Figures 16 and 17 show examples of this phenomenon at high magnification. The fact that the cracks did not propagate through the grains suggests the B_4C may have possessed a degree of plasticity at the time the cracks developed, presumably during irradiation. The ability of B_4C to deform plastically at low temperature in a neutron flux has been reported (Ref. 12).

The cracks in grains and the voids that delineated grain boundaries in the B_4C may have been the result of helium and lithium production in the granules. Migration of microporosity (present before irradiation, see Figs. 11 and 13) to grain boundaries during irradiation, however, cannot be discounted as a potential source of voids. There was no apparent effect of thermal-neutron shielding such as might be expected if B^{10} fission were important to the observed void formation at grain boundaries. The granules at the centers of specimens exhibited the cracks as frequently as granules fully exposed to thermal neutrons. On the other hand, the B_4C made with B^{10} -depleted boron exhibited somewhat reduced void volume at grain boundaries (see Fig. 18), indicating that B^{10} fission and helium or lithium formation may be important in the observed effect.

Whatever the cause of the cracks and voids, their presence suggests that the individual grains of B_4C may have expanded. Such expansion could have contributed to the observed expansion of the irradiated materials; however, the presence of cracks is not necessary for significant volume expansion of B_4C to have occurred. Up to 30 vol-% expansion in 200 μm diameter B_4C spheres has been observed at 78% B^{10} burnup without evidence of extensive crack formation (Ref. 13).

Dimensional change of boronated graphite during irradiation was the most important determination of the experiment. The observed dimensional change of the extruded boronated graphite (material 3912-34) perpendicular and parallel to the extrusion direction is shown in Fig. 19 as a function of fast-neutron exposure. Other reported values for irradiation-induced dimensional changes in extruded boronated graphite are also shown for comparative purposes. There is a lack of agreement in the data. The boron content, neutron energy spectrum, and irradiation temperature differed for each source of the data shown in Fig. 19, and these differences probably contributed to the lack of agreement between experimental results of various workers.

Experimental error must also contribute to the lack of agreement among dimensional change data. The percentage changes shown in Fig. 19 for the

Fig. 19. Effect of fast-neutron exposure on dimensional change in extruded and baked boronated graphite

most part represent measured changes of 0.005 in. or less. This is about the lower limit of detectability because of the coarse texture of the measured surface. In spite of the uncertainties involved, the data on extruded boronated graphite show that dimensional change will be relatively small under conditions of the irradiation experiments conducted to date.

The irradiation-induced dimensional change in the warm-pressed and baked material was not dependent on specimen size or B^{10} burnup gradient. Dimensional changes exhibited by shielded and nonshielded specimens of two boronated and one nonboronated graphite are shown in Fig. 20. The B^{10} burnup gradient experienced by the specimens was shown in Fig. 10. There were three to four specimens of each type, and they had the same amount of dimensional change within the repeatability ($\pm 0.5\%$) of the measurements of the specimen lengths (± 0.003 in.). The dimensional changes in nonboronated specimens were less than in the boronated graphite specimens.

Irradiation-induced dimensional change data for all warm-pressed and baked boronated and nonboronated graphite specimens are shown in Fig. 21 as a function of fast-neutron exposure. The results of the BG-1 experiment and other available data in the literature were included. Bands are drawn to enclose most of the data points, to indicate the trend.

With one exception, the boronated graphites of other workers, which were made with B_4C particle size less than 20 μm , showed irradiation-induced dimensional change comparable to the BG-1 boronated graphites, which contained only 100 to 400 μm diameter B_4C particles.

The BG-1 specimens containing no boron and those containing B_4C made with B^{10} -depleted boron showed a tendency to expand less in either direction than most of the materials that contained natural boron. This observation would seem to indicate that B^{10} content might influence dimensional change; however, with similar exposure, a set of specimens containing 35 wt-% natural boron also showed much less expansion in the parallel direction than other boronated graphites. The dimensional change of the B^{10} -depleted boronated

Fig. 20. Effect of specimen size and thermal-neutron shielding on irradiation-induced dimensional change; all specimens were irradiated in the BG-1 experiment

Fig. 21. Effect of fast-neutron exposure on dimensional change of warm-pressed boronated and nonboronated graphites; the boron content for each specimen, in wt-%, is indicated beside each data point

graphite may therefore have been within the range of experimental variation in dimensional change of all boronated materials in this work.

With one notable exception, the nonboronated graphite contracted more in the perpendicular direction and expanded less in the parallel direction than did the boronated graphite. The exception in this generalization was a set of specimens in the BG-1 experiment baked at 1000 C. It appears that much of the variation and scatter in irradiation-induced dimensional change data in both boronated and nonboronated graphites must result from undetected differences either in material properties or irradiation conditions.

An examination of the data from this experiment and previous work (Figs. 20 and 21) suggests several generalizations that can be made. Irradiation-induced dimensional change in boronated graphite was not sensitive to the following:

- B₂O₃ content of the B₄C raw material in the range 0 to 1 wt-% B₂O₃
- Specimen size or B¹⁰ burnup gradient
- Bake temperature (1000 to 2000 C)
- B₄C particle size (less than 400 μm)
- Natural boron content in the range 20 to 35 wt-% boron

These results are contrary to predictions that might be made on the basis of the boronated graphite dimensional change model (Ref. 5) for the relatively small specimens that were irradiated.

Fast-neutron exposure is the parameter that shows the best correlation with irradiation-induced dimensional change. This is the result predicted (Ref. 5) by the model for large neutron absorbers. Therefore, the size or shielding effects must be minimal.

The observation that B₄C particle size did not effect dimensional change shows that localized graphite matrix damage from B¹⁰ fission fragments is not important. The reduction in dimensional change achieved when B₄C was

not present in the graphite matrix, however, implies that B_4C in some manner enhanced the expansion of boronated graphite.

Boron (both B^{11} and B^{10}) in solution in graphite single crystals can produce accelerated nucleation of irradiation damage and dimensional change (Ref. 14). Small amounts of boron in the graphite matrix, therefore, might make it more sensitive to fast-neutron damage than nonboronated graphite.

Swelling of B_4C granules because of fast-neutron damage is a second possible mechanism for the observed dimensional change (Ref. 13). Normally, only the $B^{10}(n,\alpha)Li^7$ reaction is considered when damage in B_4C is discussed. In view of the results of this work, a determination of the importance of fast-neutron damage in B_4C expansion is warranted.

A third mechanism that might contribute to dimensional change is the complex interaction of the graphite matrix (itself subject to considerable variation in properties) with the dispersed B_4C granules. Dimensional change of both components could produce a situation in which the graphite matrix would attempt to shrink down around the unyielding or expanding B_4C granules.

In spite of the uncertainties about the mechanisms leading to dimensional changes in boronated graphite, the absence of a significant size or self-shielding effect makes possible the direct application of irradiation data rather than model predictions to estimate neutron absorber dimensional change during HTGR service.

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