NEUTRON IRRADIATION EFFECTS IN BORONATED GRAPHITE,
HAINATED GRAPHITE, B_4C , AND HfC

SUMMARY REPORT ON THE BG-1 AND BG-2 EXPERIMENTS

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NEUTRON IRRADIATION EFFECTS IN BORONATED GRAPHITE, HAFNATED GRAPHITE, B_4C , AND HfC

SUMMARY REPORT ON THE BG-1 AND BG-2 EXPERIMENTS

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ABSTRACT

Boronated graphites containing 22 to 43 wt-% boron and fabricated by extrusion or warm-pressing techniques were irradiated at 550° to 850°C to a fast-neutron exposure of $2 \text{ to } 8.8 \times 10^{21} \text{ n/cm}^2$ ($E > 0.18 \text{ MeV}$). The irradiation caused an increase in coefficient of thermal expansion and a decrease in thermal conductivity. The irradiation-induced swelling in the perpendicular and parallel directions was sensitive to anisotropy and B-10 isotope enrichment in the boron addition. Although B_4C swelling during irradiation has been reported elsewhere and also observed in loose granules in the present work (13% density decrease at 100% B-10 burnup), it is suggested that that accelerated dimensional change in the graphitic matrix due to damage from B-10 fission is the dominant dimensional change mechanism. Dimensional change can be reduced by minimizing the amount of B-10 isotope in the graphitic matrix. Boron carbide particle size, in the range 50 to 400 μm , does not influence dimension change during irradiation.

Hafnated graphite containing 90 wt-% hafnium as HfC made by a warm-pressing technique was irradiated at $700^\circ \pm 50^\circ\text{C}$ to a fast-neutron exposure of up to $6 \times 10^{21} \text{ n/cm}^2$ ($E > 0.18 \text{ MeV}$). During irradiation the material expanded 0.25 to 0.29 in the perpendicular direction and 1.09 to 1.55 in the parallel direction and was not sensitive to a bake temperature of 2000° or 2600°C.

Loose granules of HfC were irradiated at $550^\circ \pm 50^\circ\text{C}$ to a fast-neutron exposure of $5.5 \times 10^{21} \text{ n/cm}^2$ ($E > 0.18 \text{ MeV}$). These granules showed no change in visual appearance or microstructure.

1
2
3

CONTENTS

ABSTRACT	iii
1. INTRODUCTION	1
2. EXPERIMENTAL	3
2.1. BG-1 Experiment (Capsule GA-19-1)	3
2.1.1. Specimen Preparation	3
2.1.1.1. Warm-Pressed and Baked Specimens	3
2.1.1.2. Extruded Specimens	7
2.1.2. BG-1 Capsule Design	7
2.1.3. Irradiation History	14
2.1.4. Experimental Results	14
2.1.4.1. Appearance of Capsule Components	14
2.1.4.2. Radioactivity of Specimens	16
2.1.4.3. Dosimetry	16
2.1.4.4. B-10 Isotope Burnup	16
2.1.4.5. Lithium Migration Measurements	24
2.1.4.6. Dimensional Changes	24
2.1.4.7. Microstructure	26
2.1.4.8. Flexural Strength	26
2.1.4.9. Coefficient of Thermal Expansion	35
2.1.4.10. Thermal Conductivity	35
2.1.4.11. Graphite Crystallite Dimensions	36
2.2. BG-2 Experiment (Capsule GA-19-2).	36
2.2.1. Specimen Preparation	36
2.2.1.1. Boronated and Hafnated Graphite	36
2.2.1.2. Piggyback Specimens	38
2.2.2. BG-2 Capsule Design	42
2.2.3. Irradiation History	42
2.2.4. Experimental Results	46

2.2.4.1.	Appearance of Capsule Components	46
2.2.4.2.	Radioactivity of Specimens	53
2.2.4.3.	Dosimetry	53
2.2.4.4.	B-10 Isotope Burnup	53
2.2.4.5.	Lithium Migration	58
2.2.4.6.	Dimensional Change	58
2.2.4.7.	Microstructure	58
2.2.4.8.	Crush Strength	59
2.2.4.9.	Coefficient of Thermal Expansion	66
2.2.4.10.	Thermal Conductivity	66
2.2.4.11.	Graphite Crystallite Dimensions	66
2.2.4.12.	Piggyback Specimens	66
3.	DISCUSSION OF BG-1 AND BG-2 RESULTS	83
3.1.	Boronated Graphite	83
3.2.	Hafnated Graphite	98
4.	CONCLUSIONS	100
	REFERENCES	103

FIGURES

1.	Method of rough-cutting cylindrical compacts to obtain rectangular prismatic specimen sets (types A, B, and C)	6
2.	Method of rough-cutting specimens (types D and E) from Peach Bottom HTGR absorber	9
3.	Capsule configuration and specimen location in the BG-1 (GA-19-1) irradiation experiment	11
4.	Position of specimen in the graphite crucible relative to the thermal-neutron window; Type B specimen, material 3685-111-2000, prior to irradiation	13
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/cm ² (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	15

FIGURES (Continued)

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	17
7.	Specimens irradiated in capsule BG-1 to a fast-neutron exposure of 2×10^{21} to 4×10^{21} n/cm ² ($E > 0.18$ MeV)	18
8.	Neutron exposure profile in capsule BG-1; data points indicate locations at which dosimetry data were obtained	19
9.	Effect of shielding and position in core on B ¹⁰ isotope burnup	22
10.	B ¹⁰ isotope burnup in boronated graphite during irradiation in capsule BG-1	23
11.	Preirradiation microstructure (at two magnifications) of extruded and baked Peach Bottom HTGR type boronated graphite (material 3912-34, 28 wt-% B); the B ₄ C granules appear randomly dispersed in the graphite matrix	27
12.	Preirradiation microstructure (at two magnifications) of warm- pressed and baked boronated graphite made with commercial B ₄ C containing 1 wt-% B ₂ O ₃ (material 3685-111-2000, 22 wt-% B); note differences in microstructure of individual B ₄ C grains and tendency of these grains to align perpendicular to the pressing direction. The large voids in the graphite matrix resulted when B ₄ C grains fell out during metallographic preparation of the specimen	28
13.	Preirradiation microstructure (at two magnifications) of warm- pressed and baked boronated graphite made with commercial B ₄ C that was leached to remove contaminant Fe and B ₂ O ₃ (material 3685-117-1000, 21 wt-% B). The microstructure of this material was not visibly different from that made with unleached B ₄ C (see Fig. 12). Note porosity apparent along the edge of the B ₄ C particle in the 500X photomicrograph; similar appearing porosity became prominent in some B ₄ C grains after irradiation.	29
14.	Preirradiation microstructure (at two magnifications) of warm- pressed and baked boronated graphite containing B ₄ C depleted in B ¹⁰ (material 3685-120-2000, 22 wt-% B, 0.3 wt-% B ¹⁰). Porosity of B ₄ C granules, such as may be noted in these photomicrographs, was common in B ₄ C made in the laboratory from both natural boron and B ¹⁰ -depleted boron	30

FIGURES (Continued)

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/cm ² ($E > 0.18$ 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 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	31
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)	32
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/cm ² ($E > 0.18$ MeV) and B^{10} burnup 35 to 80%; (b) material 3685-111-2000, 22 wt-% B, fast-neutron fluence 3.5×10^{21} to 4.0×10^{21} n/cm ² ($E > 0.18$ MeV) and B^{10} burnup 40 to 66%	33
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/cm ² ($E > 0.18$ 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	34
19.	Typical BG-2 piggyback crucibles and sample.	43
20.	BG-2 specimen assembly	44
21.	Cross section of BG-2 (GA-19-2) capsule showing construction of cells containing either (a) cylindrical or (b) rectangular specimens	45
22.	Inconel-sheathed Chromel/Alumel thermocouples from cell 2 of BG-2	48
23.	Cylindrical specimen of hafnated graphite, $HfC +$ graphite	49
24.	Crucible and specimen No. 4 from cell 2 of BG-2 (material 4065-132-2600)	50

FIGURES (Continued)

25. Warm-pressed boronated graphite (material 3685-124-2000, specimen 4-2-2) made with leached technical grade B_4C (0.52 g natural B/cm ³) baked at 2000°C and irradiated at 700° ± 50°C to a fast-neutron exposure of 7.2×10^{21} n/cm ² ($E > 0.18$ MeV) in capsules BG-1 and BG-2	51
26. Warm-pressed boronated graphite (material 4465-24, specimen 3-5) control rod absorber material containing 0.69 g natural B/cm ³ and irradiated at 700 ± 50°C to a fast-neutron exposure of 5.3×10^{21} n/cm ² ($E > 0.18$ MeV) in capsule BG-2	52
27. Thermal- and fast-neutron exposure profile of capsule BG-2	54
28. B-10 burnup profile for BG-2 specimens	57
29. Microstructure of boronated graphite (B_4C in graphite) manufactured for the Fort St. Vrain control rod absorbers	60
30. Fracture pattern typically observed in B_4C granules of boronated graphite at high B-10 burnup	61
31. Microstructure of boronated graphite (material 4465-24, specimen 4-4) made with 92% B-10-enriched boron powder irradiated in BG-2 at 700°C to a fast-neutron exposure of 4.4 to 4.7×10^{21} n/cm ² ($E > 0.18$ MeV)	62
32. Microstructure of boronated graphite (material 4465-26, specimen 4-7) made with B-10-enriched B_4C (see Fig. 33): (a) Before irradiation, low magnification; (b) preirradiation microstructure of B_4C grains showing excess carbon precipitated within the grain	63
33. Microstructure of boronated graphite (material 4465-26, specimen 4-7) made with B-10-enriched B_4C (see Fig. 32): (a) after irradiation in BG-2 at 700°C to a fast-neutron exposure of 3.8×10^{21} n/cm ² ($E > 0.18$ MeV) and B-10 depletion of 31% (shielded side); (b) postirradiation microstructure of B_4C grains showing fracturing of grain along graphite precipitates which have apparently undergone dimensional change during irradiation, perhaps leading to grain fracture	64
34. Microstructure of hafnated graphite material 4065-132-2000	65
35. Boron carbide (high boron, 76 wt-% boron, material 4065-84, specimen 1-6)	68
36. Boron carbide (technical grade, 70 wt-% boron, material 3685-84, specimen 3-4)	69
37. Spherical B_4C granules (material 3685-4, specimen 11F)	70
38. Boron carbide (material 4465-7, specimen 33F) made from B-10-enriched boron ($B-10/B-11 = 11.5$)	71

FIGURES (Continued)

39.	Boron carbide (material 3685-105, specimen 31F) made from B-10-depleted boron ($B-10/B-11 = 0.015$)	72
40.	B-10 burnout profile for B_4C piggyback samples in capsule BG-2	74
41.	Effect of B-10 fission density on the density of B_4C irradiated in piggyback location of BG-2	76
42.	Boron filament (material 3471-122, specimen 23S)	78
43.	Hafnium carbide (4065-111, specimen 2-1-S): (a) unirradiated -48 +200 mesh U.S.; (b) irradiated in BG-2 at $550^\circ \pm 50^\circ C$ to a fast-neutron exposure of $5.5 \times 10^{21} \text{ n/cm}^2$ ($E > 0.18 \text{ MeV}$)	80
44.	Metallographic cross section of hafnium carbide granules (4065-111, specimen 2-7) in an opened piggyback crucible from capsule BG-2 after irradiation at $550^\circ \pm 50^\circ C$ to a fast-neutron exposure of 6.0×10^{21} ($E > 0.18 \text{ MeV}$)	81
45.	Microstructure of HfC (4065-111, specimen 2-1-S) irradiated in capsule BG-2 piggyback location at $550^\circ \pm 50^\circ C$ to a fast-neutron exposure of $5.5 \times 10^{21} \text{ n/cm}^2$ ($E > 0.18 \text{ MeV}$)	82
46.	Irradiation-induced dimensional change in extruded boronated graphite baked at $2200^\circ C$ and irradiated at $700^\circ \pm 50^\circ C$	86
47.	Irradiation-induced dimensional change in a commercially produced warm-pressed boronated graphite (4465-42) containing $0.69 \text{ g boron/cm}^3$, baked at $2000^\circ C$ for 2 hr and irradiated at $700^\circ \pm 50^\circ C$	87
48.	Effect of initial anisotropy on the irradiation-induced dimensional change in warm-pressed boronated graphite baked at $2000^\circ C$ and irradiated at $700^\circ \pm 50^\circ C$	89
49.	Irradiation-induced dimensional change in warm-pressed boronated and nonboronated graphite baked 2 hr at $2000^\circ C$ and irradiated at $700^\circ \pm 50^\circ C$	90
50.	Effect of bake temperature on irradiation-induced dimensional change of boronated graphite	91
51.	Irradiation-induced dimensional change in warm-pressed B-10-depleted, nonboronated, and natural boronated graphite baked at $1000^\circ C$	92
52.	Boronated graphite made with B-10-enriched (91% B-10) boron powder, $0.11 \text{ g boron/cm}^3$ (shielding equivalence $\sim 0.55 \text{ g natural boron/cm}^3$); irradiated at $700^\circ \pm 50^\circ C$ to a fast-neutron exposure of $4.5 \times 10^{21} \text{ n/cm}^3$ ($E > 0.18 \text{ MeV}$)	94
53.	Irradiation-induced dimensional change in B-10-enriched and nonboronated graphite baked at $2000^\circ C$ and irradiated at $700^\circ \pm 50^\circ C$	95
54.	Effect of specimen size and thermal-neutron shielding on irradiation-induced dimensional change	97

FIGURES (Continued)

55. Irradiation-induced dimensional change in hafnated (HfC + graphite) and nonboronated graphite baked at 2000° or 2600°C and irradiated at 700° ± 50°C 99

TABLES

1. Raw materials used in preparation of B₄C graphite specimens 4
2. B₄C-graphite specimen materials for the BG-1 capsule. 8
3. Summary of material properties and irradiation effects in boronated graphite included in the capsule BG-1 experiment. 20
4. Lithium content of specimens and contamination of crucibles and metal components of the cells resulting from the B¹⁰(n,α)Li⁷ reaction 25
5. Raw material used in preparation of BG-2 boronated and hafnated graphite specimens 37
6. Boronated and hafnated graphite materials irradiated in capsule BG-2 39
7. Piggyback samples irradiated in capsule BG-2 41
8. Summary of material properties and irradiation effects in boronated graphite in the BG-2 experiment including prior irradiation in the BG-1 experiment 55
9. Heat capacity of graphite, boron carbide, and boronated graphites assumed for thermal-conductivity measurement 67
10. Summary of BG-2 piggyback specimen results 75

1. INTRODUCTION

Boronated graphite has shown promise as an economical and effective control material for the High-Temperature Gas-Cooled Reactor (HTGR). This material is made by the addition of B_4C granules to a graphite-pitch mixture prior to the forming and baking process. Control in thermal reactors is effected by the capture of thermal neutrons by the $B-10(n,\alpha)Li-7$ reaction. Important design considerations in the use of boronated graphite include changes in dimensions and material properties that result from neutron irradiation.

Some irradiation experiments have been conducted to explore irradiation 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. The literature data have been used to predict dimensional changes in boronated graphite control absorbers of current HTGR design by means of a calculational model for radiation damage (Ref. 5). To aid in HTGR design, it was desirable to test the model and gain a better understanding of the factors contributing to dimensional change. Two irradiation capsule experiments, designated BG-1 and BG-2, were conducted to provide this information.

A control material consisting of hafnium carbide (HfC) granules in graphite has been considered as an alternate to boronated graphite for design conditions of extremely high temperatures. The refractory nature of this material has been shown by other workers (Refs. 6, 7). Reactor control is effected by the capture of thermal neutrons by the Hf-176 to Hf-180 (n,α) chain reaction with the creation of high-cross-section daughter isotopes.

To obtain design data on the irradiation performance of hafnated graphite, samples were included in the BG-2 capsule. In an attempt to gain a better

understanding of combined irradiation effects in the composites of B_4C or HfC in graphite, loose granules of B_4C and HfC were also irradiated in capsule BG-2. These specimens were examined to determine irradiation effects in the granular B_4C and HfC in the absence of carbonaceous matrix material.

Boron filament consisting of vapor-deposited boron on a tungsten wire substrate was also included in BG-2. This material is of interest as a neutron-absorbing reinforcing agent. Complete loss of mechanical integrity of the filament was predicted at the neutron exposures of the experiment, and the filament was irradiated primarily to confirm the prediction.

The materials, capsule design, irradiation history, and experimental results are described in Section 2. Pertinent generalizations and conclusions concerning irradiation effects are then discussed in relation to the results of both experiments.

2. EXPERIMENTAL

2.1. BG-1 EXPERIMENT (CAPSULE GA-19-1)

2.1.1. Specimen Preparation

2.1.1.1. 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 this table, but some additional descriptions of the preparation of the B_4C addition 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 1.5 at. % B-10 ($B-10/B-11 = 0.015$) blended with 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 vacuum cycled (50 μ m to 8 psig) twice with atomic-grade helium in a vacuum furnace and then heated at less than 150 μ m pressure to 2000°C. At 2000°C, the furnace was backfilled with helium to 8 psig and heated quickly (8 min) to 2500° $\pm$ 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 material had passed through a 40-mesh screen. Next, the material was leached in a 1:1 HCl/H₂O solution to remove iron introduced during the crushing process. The crushing and leaching operation was adapted from procedures reported previously (Ref. 8).

Table 1

RAW MATERIALS USED IN PREPARATION OF B_4C 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 $2700^\circ\text{C} \pm 100$ 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_4C	Sieved into three size ranges U.S. mesh -40 +50, -50 +70, -70 +140.	B 69, B_2O_3 1 to 3, C Bal, Fe 0.80 (wt-%).
3685-84	Leached technical grade B_4C	B_4C (material 3685-70) leached several hr in warm distilled water to remove B_2O_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_2O_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 $2500^\circ\text{C} \pm 50$ 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_2O_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_2O_3 0.02, Fe 0.1, C Bal (wt-%).

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 iron 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 iron 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 iron 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. 9) 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

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.

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.

2.1.1.2. 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 (size 100% < 100 mesh, 5% < 325 mesh), 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 2200°C for 30 min in nitrogen and then machined to the final shape. Prismatic 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.

2.1.2. BG-1 Capsule Design

The specimens were held with a loose slip fit in 28 780-S graphite crucibles with inside dimensions of 0.408 in. by 0.408 in. by 0.610 in. long.

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.

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.

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 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. 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.

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 gadolinium 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 cadmium sheet and positioned adjacent to the inside surface of the outer stainless steel can. The thermal neutrons passing through the 130° window were collimated by 1/4 in. by 4-1/2 in. by 0.060 in. strips of gadolinium 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.

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

Dosimetry for the capsule consisted of nickel-0.45% cobalt, titanium, and iron wires, which were placed at the ends of each cell, centered in the neutron window, and in a shielded position 180° from the window.

2.1.3. Irradiation History

The BG-1 (GA-19-1) capsule was irradiated for four cycles in position FE-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 $600^\circ \pm 100^\circ\text{C}$, while centerline temperatures were $700^\circ \pm 100^\circ\text{C}$. 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. 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 Gulf General Atomic. Disassembly was accomplished in the Gulf General Atomic Hot Cell.

2.1.4. Experimental Results

2.1.4.1. 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 gadolinium strips, which retained their ductility and could be bent 180° with a 1-in. radius without breaking. Typical thermocouples and bent gadolinium strips are shown in Fig. 5. The cadmium sheet was also ductile. An unsuccessful search was made on components for evidence of a white

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.

powder deposit that might indicate the presence of lithium, 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.

2.1.4.2. Radioactivity of Specimens. The specimens in a single crucible had a typical radioactivity of about 600 mR/hr β and 160 mR/hr 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/hr $\beta+\gamma$ at 1 ft. From a postirradiation measure of the gamma-ray energy spectrum, it was determined that the samples contained activated Ta-182. Further investigations revealed that the boron powder from which the B_4C had been made contained about 2000 ppm of tantalum impurity. These highly radioactive specimens remained in the Hot Cell, where dimensions were measured and metallographic work was performed.

2.1.4.3. Dosimetry. The fast-neutron ($E > 0.18$ MeV) exposure was determined from analysis of the iron wires activated by the $Fe-54(n,p)Mn-54$ 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 nickel-0.45% cobalt wires activated by the $Co-59(n,\gamma)Co-60$ 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.

2.1.4.4. B-10 Isotope Burnup. Samples were taken for B-10/B-11 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.

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

M-28665-1 (a) 3685-111-1000

0.58
in.

M-28662-1 (b) 3685-111-2000

M-28660-1 (c) 3912-34-1000

0.58
in.

M-28668-1 (d) 3685-118-1000

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.

LC80194

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 RG-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	
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													
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	0	4	4	0	0	0	0	0	0	0	0	3	0
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	650	650 ^c	625	625	625	625	525	575
Surface average	550	550	600	550 ^c	550	600	600 ^c	600	600	600	575	475	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	54 & 43	37 ^d	50 ^d	38	48	50 ^d	50 ^d	(e)	(e)	0	0
Dimensional change during irradi relative to forming direction, %													
Parallel minimum	-0.52	+2.35	+1.50	+1.53	+2.38	+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	6.64	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 (C _{pe} /C _{pe})	1.38	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 (C _{pe} /C _{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 ^b	3300	685	230	595	490	470	310	730	690	(f)	(f)	660	475
Preirradiation perpendicular ^b	1840	995	450	825	930	700	630	1110	1140	(f)	(f)	1100	795
Postirradiation parallel ^b	(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 C_{pa}/C_{pe} (extruded)^hLong axis of test bar parallel or perpendicular to the forming direction

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 B_4C initially depleted in B-10 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. specimens. The companion 0.2 in. by 0.2 in. by 0.58 in. specimens were sampled on the 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

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

(a)

M-28659-2

6X

(b)

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-% boron) with isotopic sample removed from exposed and shielded sides

desired to achieve full simulation of HTGR conditions, but it was considered satisfactory to reveal first-order effects of shielding.

2.1.4.5. 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 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.

2.1.4.6. 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 . 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 are

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

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 reliable because of the ± 0.003 -in. repeatability of the measuring devices, and these changes are not reported.

2.1.4.7. Microstructure. Metallographic examination of all material was conducted before irradiation. After irradiation, selected materials were sectioned and polished 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 of matrix adjacent to the B_4C granules.

2.1.4.8. 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.),

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.

EXTRUSION DIRECTION →

M23756-01

(100x)

M23756-02

(500x)

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 →

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

(a)

(500x)

M28731-5

(b)

(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 3685-111-2000, 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.

2.1.4.9. Coefficient of Thermal Expansion. Prior to irradiation, the coefficient of thermal expansion parallel and perpendicular to the forming direction was determined for all materials between 22° and 1000°C. After irradiation, the expansion coefficient was determined 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,

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.

2.1.4.10. 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.

2.1.4.11. Graphite Crystallite Dimensions. Crystallite dimensions (L_c and C_o) 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 this work are shown in Table 3.

2.2. BG-2 EXPERIMENT (CAPSULE GA-19-2)

2.2.1. Specimen Preparation

2.2.1.1. Boronated and Hafnated Graphite. The raw materials used to manufacture boronated and hafnated graphite compacts in the laboratory are described in Table 5. The B-10-enriched B_4C (4465-7) was prepared by the technique described for preparation of B_4C used in the BG-1 experiment (material 3685-105, Table 1).

Essentially the same warm-pressing and baking technique used in the fabrication of BG-1 specimens was utilized to make the specimens of BG-2. The pressing mixtures were prepared by dry blending the appropriate proportions of graphite filler (4465-2), pitch binder (3685-92), and poison material (3685-53, 4465-7, or 4065-121). The pitch addition was 15% of the total graphite and pitch weight. 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 (less than 1/8 in. in diameter) of the blend.

The specimens were warm-pressed at 750°C in an Incoloy 800 die with ATJ graphite punches, under a pressure of 5000 psi. After about 5 min at 750°C, the specimens were ejected hot into a container purged with argon, where they cooled to room temperature. The specimens were then placed in graphite

TABLE 5

RAW MATERIAL USED IN PREPARATION OF BG-2 BORONATED AND HAFNATED GRAPHITE SPECIMENS

Material No.	Description	Preparation	Chemical Composition
4465-2	GP-38 graphite flour ($<48\ \mu\text{m}$)	Used as received from manufacturer	C 99.88 wt-%, Fe 400 ppm, V 100 ppm, Si 400 ppm, ash -0.10 wt-%
3685-92	Coal tar pitch	Crushed and sieved to retain -30 mesh (U.S.) particles. Leached 20 hr in 1:1 HCl/H ₂ O solution at R.T. Distilled water rinse	C 99.96 wt-%, Ash 0.07 wt-%
3685-53	B ¹⁰ -enriched (92 wt-% B ¹⁰) amorphous boron powder ($<10\ \mu\text{m}$)	Used as received from ORNL isotope supply	B 94.3 wt-%, C 2 wt-%, Cu 1 wt-%, O 0.9 wt-%, H ₂ O 0.1 wt-%, Ni 0.9 wt-%, K 0.6 wt-%, Na 0.1 wt-%
4465-7	B ₄ C made in laboratory from 92% B ¹⁰ enriched boron powder. Particle Size (U.S. mesh) Fraction -48 +65 0.42 -65 +150 0.35 -150 +200 0.08 -200 0.15	Blended 3685-53 and 4465-2 in 3:1 weight ratio. Heated in closed graphite crucible 3 min at 2500°C in He to fuse. Crushed bisque with 1-in. platner mortar and pestle and laboratory press. Sieved to obtain -48 mesh size fraction. Leached 1 hr in 1:1 HCl/H ₂ O solution at 80°C. Distilled water rinse.	B 69 wt-%, C ~31 wt-%, B as B ₂ O ₃ <0.01 wt-%, Ni 2000 ppm, Fe 200 ppm
4065-121	HfC ($<38\ \mu\text{m}$)	Used as received from manufacturer	Hf 91.4 wt-%, Zr 1.5 wt-%, C 5.7 wt-%, Ti 0.5 wt-%, Ni 0.4 wt-%

crucibles and baked at 2000° or 2600°C (hafnated only) for 2 hr. In each case the furnace was evacuated while being heated to 2000°C and was then back-filled with helium.

In this way cylindrical specimens 0.40 in. in diameter and 0.58 in. long were made for the capsule. Capsule specimens were identified with a number scribed on the side. Before being baked, some of the capsule and crush strength specimens had a 0.082-in.-diameter hole bored with either a tungsten carbide or diamond-tipped drill along the center line for passage of capsule thermocouples. A groove 0.1 in. wide by 0.040 in. deep was cut on the surface of all the cylindrical capsule specimens parallel to the axis to allow them to be pinned in place in the capsule.

Some specimens were taken from vendor-produced boronated graphite absorber compacts made from GP-38 and B_4C with coal tar pitch. These specimens were made by diamond core drilling along the axis of the absorber to produce a solid cylinder within the core drill. The cylinders of boronated graphite were then machined to 0.40 in. in diameter by 0.58 in. long and baked 2 hr at 1000°C in helium.

Selected specimens irradiated in the BG-1 experiment were also placed in the BG-2 capsule. The specimens were rectangular in cross section, being either 0.58 x 0.40 x 0.20 in. or 0.58 x 0.20 x 0.20 in. These specimens occupied all of cell No. 1 of BG-2, while the specimens discussed previously occupied the other three cells. A complete description of boronated and hafnated graphite specimens is given in Table 6.

2.2.1.2. Piggyback Specimens. The boronated and hafnated specimens described above were contained in graphite crucibles. Holes were drilled in the crucible walls parallel to the axis and along the specimen center line to accommodate thermocouples, but not all of these holes contained thermocouples. Into those holes not required for thermocouples were inserted graphite crucibles (0.081 in. in diameter by 0.60 or 0.45 in. long) containing samples of loose B_4C , HfC granules, or boron fibers.

TABLE 6
BORONATED AND HAFNATED GRAPHITE MATERIALS IRRADIATED IN CAPSULE BG-2

Cell No.	Crucible No.	Specimen No.	Specimen Description	Purpose of Material in Irradiation Experiment
1	1	1-1-1, 1-1-2	Peach Bottom HTGR absorber material (28 wt-% B), irradiated in capsule BG-1 (material 3912-34)	Continuation of irradiation from BG-1 to a total exposure of about 4×10^{21} n/cm ² ($E > 0.18$ Mev) to obtain further irradiation data on commercially available material; correlation of dimensional change in capsule specimens and full-sized HTGR absorbers may eventually be possible.
1	2	1-2-1 (3 specimens)		
1	2	4-1-2,	Warm-pressed boronated graphite (35 wt-% B), baked at 2000°C, irradiated in capsule BG-1 (material 3685-124-2000).	Continuation of irradiation from BG-1 to a total exposure to 5×10^{21} n/cm ² ($E > 0.18$ Mev) to obtain irradiation data on high boron material at significant portion of HTGR life for control rods; study the effect of bake temperature, boron content, and B ¹⁰ burnup gradient on irradiation effects in warm-pressed and baked compacts.
1	3	4-2-1, 4-2-2 (3 specimens)		
1	4	4-3-1, 4-3-2 (2 specimens)	Warm-pressed boronated graphite (35 wt-% B), baked at 1000°C, irradiated in capsule BG-1 (material 3685-124-1000).	
1	5	3-6-1, 3-7-1 (2 specimens)	Warm-pressed graphite (0 wt-% B), baked at 1000°C, irradiated in capsule BG-1 (material 3685-118-1000).	
1	6	1-4-2, 1-4-3, 1-5-2, 1-5-3 (4 specimens)	Warm-pressed boronated graphite (22 wt-% B), baked at 1000°C, irradiated in BG-1 (material 3685-111-1000).	
1	7	3-2-1, 3-2-2 (2 specimens)	Warm-pressed boronated graphite (22 wt-% B), baked at 1000°C, made with B ₄ C depleted in B ¹⁰ , irradiated in capsule BG-1 (3685-120-1000).	
2	1,4,7	2-1, 2-4, 2-7 (3 specimens)	Warm-pressed hafnated graphite (90 wt-% Hf), baked at 2600°C; particle size <325 mesh (4065-132-2600).	Determine dimensional stability of hafnated graphite as a function of bake temperature.
2	5,6	2-5, 2-6 (2 specimens)	Warm-pressed hafnated graphite (90 wt-% Hf), baked at 2000°C; particle size <325 mesh (4065-132-2000).	
2	2,3	2-2, 2-3 (2 specimens)	Warm-pressed graphite (0 wt-% B, Hf), baked at 2000°C (4465-21-2000).	Determine irradiation effects in matrix material used for warm-pressed hafnated and boronated graphites baked at 2000°C.
3	1,2	3-1, 3-2 (2 specimens)	Peach Bottom HTGR absorber material (28 wt-% B), cut from same absorber as specimens in BG-1 (material 3912-34).	New sample of same material as irradiated in BG-1; results from BG-2 irradiation will be correlated with BG-1 results.
3	3,4,5,6,7	3-3, 3-4, 3-5 3-6, 3-7	Vendor-produced warm-pressed absorber (43 wt-% B) (4465-42).	Determine irradiation effects in material; correlation of dimensional change in capsule samples and full sized HTGR absorbers may eventually be possible.
4	1	4-1 (6 specimens)		
4	2,3,4	4-2, 4-3, 4-4 (3 specimens)	Warm-pressed graphite with 7 wt-% B (91% B ¹⁰ -enriched) added as an amorphous powder, baked at 2000°C (4465-24).	Determine irradiation effects using amorphous B ¹⁰ -enriched boron powder in graphite to achieve a refractory, low-density absorber material with nuclear worth equivalent to boronated graphite containing ~40 wt-% B.
4	5,6,7	4-5, 4-6, 4-7 (3 specimens)	Warm-pressed boronated graphite with 10 wt-% B ₄ C made from 91% B ¹⁰ -enriched boron, baked at 2000°C (4465-26).	Determine if use of B ¹⁰ -enriched B ₄ C results in less dimensional change than was observed in compacts of equivalent worth made with amorphous B ¹⁰ powder.

The primary purpose of these specimens, which were called piggyback specimens, was to determine the extent of irradiation-induced volumetric change possible in unrestrained granules of B_4C and HfC . Because of the thermal neutron shielding, the effect of various degrees of B-10 burnup at constant fast-neutron exposure could be determined. Correlation with dimensional changes observed in the compact of boronated or hafnated graphite should allow a determination of the influence of particle swelling on the dimensional change of the composite. Boron filaments were included to explore the irradiation stability of a potential structural reinforcement material with neutron-absorbing qualities.

Piggyback specimens of five different B_4C batches, representing various B-10 enrichments and microstructures, were prepared. Sink-float density determination techniques were used for separating out one density range fraction from random samples of the B_4C particles. The fractions with well determined density were then washed with acetone and dried at room temperature in air.

An HfC sample was included in the experiment without density determination. Boron filaments (0.004 in. in diameter on a 0.0005-in. tungsten core) were cut into pieces about 0.3 in. long and radiographed to allow measurement of diameter before and after irradiation.

Two piggyback crucibles loaded with boron filaments, 33 loaded with B_4C granules, and five loaded with HfC granules were prepared. The weight of sample in each crucible was about 0.002, 0.015, and 0.070 g for boron filaments, B_4C , and HfC , respectively. A graphite plug was inserted into the 3/64-in.-diameter bore of each crucible, where it was cemented in place with a thin film of furfuryl alcohol catalyzed with maleic anhydride and cured by heating at 100°C for 1 hr in air. The crucibles were then placed in a vacuum furnace evacuated to about 20 μ m Hg and backfilled twice with helium. They were then heated in helium to 1000°C and held at temperature for 30 min. A description of the piggyback specimens and the purpose of each are given in Table 7. Typical piggyback specimens are

TABLE 7
PIGGYBACK SAMPLES IRRADIATED IN CAPSULE BG-2

Material No.	Description	Particle Size Range (mesh size)	Density Range of Samples (g/cm ³)	Major Impurities	Reason for Irradiation
4065-84	B ₄ C, high purity (76 wt-% B)	-48 +140	2.434-2.500	0.1 wt-% Fe, 1 wt-% B ₂ O ₃ ; Trace elements (ppm): Al 200, Ca 300, V 300, Zr 400	Determine effect of B content on volumetric change
3685-84	B ₄ C, technical grade (70 wt-% B)	-50 +140	2.495-2.557	0.1 wt-% Fe, 0.2 wt-% B ₂ O ₃	
3685-4	B ₄ C, spherical from ORNL (82 wt-% B)	-210 μ m +149 μ m	2.304-2.526	Trace elements (ppm): Cu 200, Al 100, Fe 10, V 200, Si 600	Make correlation between volume change determined by radiograph (diameter measurement) and volume change inferred from density change
4465-7	B ₄ C, made from B ¹⁰ enriched boron (92% B ¹⁰), 69 wt-% B	-48 +200	2.33-2.36	0.03 wt-% B ₂ O ₃ ; trace elements (ppm): Ni 2000, Si 400, Ca 400, Fe 200	Determine effect of B ¹⁰ enrichment on dimensional change in B ₄ C
3685-105	B ₄ C, made from B ¹⁰ depleted boron (1.5 at-% B ¹⁰), 72 wt-% B	-50 +140	2.436-2.547	0.1 wt-% Fe, 0.06 wt-% B ₂ O ₃	
4065-11	HfC, low Hf 90 wt-%, high Zr 2.8 wt-%, large particle size	-48 +65	Not determined	Spectrographic analysis (ppm): Al 225, Cr 500, Fe 1800, N 824, Ni 200, O 1900, Ti 1000	High radioactivity level prevents detailed analysis of irradiated particles. Gross effects such as sintering, cracking of container, dusting of large granules examined.
3471-122	Boron filament, vapor-deposited boron on tungsten-wire substrate	0.004-in. diam. on 0.0005-in. tungsten substrate $\sim$ 3 in. long	Not determined	Not determined	Evaluate irradiation stability of high-strength, high-modulus reinforcing material with neutron-absorbing properties

shown in Fig. 19, and an assembly of boronated graphite, piggyback specimens, and a crucible ready for insertion in the capsule are shown in Fig. 20.

2.2.2. BG-2 Capsule Design

The design of capsule BG-2 was similar to that of BG-1 (described in detail in Section 2.1.2 and shown in Fig. 3). However, in BG-2 the cadmium thermal-neutron shield was 0.060 in. thick rather than 0.020 in., and no longitudinal gadolinium strips were employed to border the thermal-neutron window. These design changes in BG-2 were made to increase thermal-neutron shielding for 270° of the specimen circumference. The objective was to achieve a greater B-10 burnup gradient than in BG-1. Another design difference in BG-2 was in specimen shape. Cell one contained prismatic specimens previously irradiated in capsule BG-1, but the three other cells contained unirradiated cylindrical specimens. Cross sections of the capsule showing the design modifications from BG-1 are shown in Fig. 21.

A design feature of the BG-2 capsule that did not influence the experimental work reported here was a fifth cell which contained an experiment designed to determine the effect of irradiation on thermocouple performance. That work has been reported elsewhere (Ref. 10).

2.2.3. Irradiation History

The BG-2 (GA-19-2) capsule was inserted in ETR position F-13-NW and started irradiation in July 1969 (cycle 103) at temperatures of 600° to 700°C. The capsule remained in the ETR through cycle 106 (4 cycles) and was removed in May 1970. A fast-neutron ($E > 0.18$ MeV) exposure of 3.5×10^{21} n/cm² at the ends and 6×10^{21} n/cm² at the middle of the capsule was received in a period of 4332 hr of reactor operation at a power level above 165 MW. The time-averaged surface temperature of specimens of boronated and hafnated graphite varied from 450° to 630°C, while the time-averaged center-line temperatures were maintained at 700°C.

Fig. 19. Typical BG-2 piggyback crucibles and sample. The sample in the upper photograph is B_4C depleted in B-10 (3685-105); the lower photograph shows boron filaments (3471-122)

BORONATED
GRAPHITE
4465-42

780-S
GRAPHITE
CRUCIBLE

PIGGYBACK
SPECIMENS

2X

BORONATED
GRAPHITE
SPECIMEN

PIGGYBACK
SPECIMEN

ROD HOLE

THERMOCOUPLE
HOLE

780-S GRAPHITE
CRUCIBLE

5X

Fig. 20. BG-2 specimen assembly. The upper photograph shows a side view of the specimen disassembled; the lower photograph is a top view of the assembled specimen. A 90° thermal neutron ($E < 0.4$ eV) window is centered about the piggyback specimen nearest the scale so that each piggyback specimen receives a different thermal-neutron dose (scale in inches).

Fig. 21. Cross section of BG-2 (GA-19-2) capsule showing construction of cells containing either (a) cylindrical or (b) rectangular specimens. See Fig. 3 for additional details.

Twenty-two of the 23 monitoring thermocouples operated satisfactorily during the entire irradiation period. The only thermocouple failure occurred in cell 2 after 1840 hr of irradiation, resulting in maladjustment of purge gas mixtures and an overtemperature condition which lasted for 18 hr with a maximum center-line temperature of $\sim 1350^{\circ}\text{C}$ (Inconel M.P. $\sim 1350^{\circ}\text{C}$) for 11 hr. The overtemperature condition was assumed to apply to all specimens in cell 2, which were hafnated graphite and piggyback samples containing all the HfC and boron filaments.

After it was removed from the ETR core, the capsule was stored for one month and then shipped to Gulf General Atomic. Disassembly of the capsule was accomplished in the GGA Hot Cell starting in June 1970.

2.2.4. Experimental Results

2.2.4.1. Appearance of Capsule Components. The graphite and stainless steel components of the capsule showed no evidence of corrosion or oxidation after irradiation. The Inconel-sheathed thermocouples which were within or adjacent to the specimens appeared black.

The gadolinium wafers placed between specimens as thermal-neutron shields showed evidence of severe corrosion in cells 1, 2, and 4. In cells 1 and 3, a white powder deposit was observed on graphite components that had been near the purge gas inlet and adjacent to the metal walls of the cell. A sample of the powder taken from cell 1 was examined by X-ray diffraction and found to be Li_2CO_3 .

Apparently the cells had been purged with gas containing oxidant which attacked the gadolinium wafers, carbon, and lithium produced by the $\text{B-10}(n,\alpha)\text{Li-7}$ reactions. The source of the oxygen in the cells was not determined. Helium leak detector inspection of the purge lines during shutdown between the last two cycles at the ETR had not revealed a leak. Observations during disassembly did not reveal evidence of water leakage into the system from the ETR coolant.

The Inconel-sheathed Chromel/Alumel thermocouples and the tungsten wire wrapping did not show signs of severe oxidation or other corrosion with the exception of the single thermocouple at the center of cell 2. That thermocouple had failed about half-way through the irradiation experiment, and a subsequent operator error caused the cell temperature to approach the melting point of the Inconel sheath ($\sim 1350^{\circ}\text{C}$) for a period of 11 hr. About 1/2 in. of the tip of that thermocouple had the appearance of having been melted and about 1/8 in. was missing, as shown in Fig. 22. Metallographic examination revealed large grain size and apparent plastic deformation of the metal, confirming that the sheath had been near the melting point. The tungsten wire wrap had been pressed into the softened Inconel with no apparent chemical reaction.

A qualitative indication of the room-temperature ductility of the Inconel sheath material on the thermocouples was obtained by bending the thermocouples about 180° with a 3/8-in. radius. No brittle cracking of the sheath was observed, which is consistent with the expected compatibility of the nickel-base alloy with boronated graphite at high B-10 burnup at reactor service conditions.

The visual appearance of the specimens was unchanged from the unirradiated appearance except for black lines on the surfaces corresponding to positions which had been adjacent to discontinuities in the crucible. Examples of hafnated graphite specimens before and after irradiation are shown in Figs. 23 and 24, and boronated specimens taken from BG-2 are shown in Figs. 25 and 26.

The specimens in cell 3 (see Table 6) did not slide freely from the crucibles as did specimens in the other cells. Cell 3 specimens could be removed from a graphite crucible only by cutting the wall longitudinally at a thermocouple hole and splitting the crucible in half. The continuation of irradiation-induced radial shrinkage of the graphite crucible and expansion in the specimens caused the observed interference. There was an initial diametral gap of 0.005 to 0.007 in. between specimens and the crucible wall. A radial shrinkage in the crucible of $<1\%$ at 5 to $6 \times 10^{21} \text{ n/cm}^2$ ($E > 0.18 \text{ MeV}$) and $\sim 500^{\circ}\text{C}$ would have been sufficient to cause contact with the specimens,

K-367-60

Fig. 22. Inconel-sheathed Chromel/Alumel thermocouples from cell 2 of BG-2. The central thermocouple tip had apparently been melted and about 1/8 in. was missing from the end. Three other thermocouples in the cell performed satisfactorily throughout the experiment. Tungsten wire was wrapped on the thermocouples to prevent intimate contact with the graphite and specimens. Note where tungsten wire produced grooves in the central thermocouple near the tip.

M29813-19

4X

Fig. 23. Cylindrical specimen of hafnated graphite, HfC + graphite
(material 4065-132-2600), before irradiation in capsule BG-2

K-367-76

Fig. 24. Crucible and specimen No. 4 from cell 2 of BG-2 (material 4065-132-2600). Specimen contained 90 wt-% hafnium (HfC + graphite) and was irradiated to a fast fluence of about 5.9×10^{21} ($E > 0.18$ MeV) at a center-line temperature of 700°C . A piggyback crucible can be seen in one of the holes in the crucible wall.

M33607-1 (Side)

M33607-2 (Top)

Fig. 25. Warm-pressed boronated graphite (material 3685-124-2000, specimen 4-2-2) made with leached technical grade B_4C ($0.52 \text{ g natural B/cm}^3$) baked at 2000°C and irradiated at $700^\circ \pm 50^\circ\text{C}$ to a fast-neutron exposure of $7.2 \times 10^{21} \text{ n/cm}^2$ ($E > 0.18 \text{ MeV}$) in capsules BG-1 and BG-2

M33621-1

(Side)

M33621-2

(Top)

Fig. 26. Warm-pressed boronated graphite (material 4465-24, specimen 3-5) control rod absorber material containing $0.69 \text{ g natural B/cm}^3$ and irradiated at $700 \pm 50^\circ\text{C}$ to a fast-neutron exposure of $5.3 \times 10^{21} \text{ n/cm}^2$ ($E > 0.18 \text{ Mev}$) in capsule BG-2

which expanded 0.62% to 1.00% in the radial direction. Specimens in other cells had more initial diametral clearance and/or less positive dimensional change than cell 3 specimens experienced during BG-2 exposure. The gap between the specimens and the crucible wall had been minimized in BG-2 design to optimize temperature distributions and heat transfer.

2.2.4.2. Radioactivity of Specimens. The radioactivity of boronated graphite samples was typically 350 to 750 mr/hr $\beta+\gamma$ at 2 in. The hafnated graphite specimens had a much higher activity of 90 to 120 R/hr $\beta+\gamma$ at 2 in.

2.2.4.3. Dosimetry. The profile of fast- and thermal-neutron fluence experienced along the length of capsule BG-2 is shown in Fig. 27. The fast-neutron exposure ($E > 0.18$ MeV) was determined from analysis of iron wires activated by the $\text{Fe-54}(n,p)\text{Mn-54}$ reaction with a 51.2-mb cross section. The fast-neutron exposure was the same in both the shielded and unshielded region of the specimens. The thermal-neutron exposure ($E < 0.4$ eV) was determined from analysis of nickel-0.45% cobalt wires activated by the $\text{Co-59}(n,\gamma)\text{Co-60}$ reaction with a 36.8-b cross section. The thermal-neutron exposure, as defined here, was two to three times lower in the shielded portion than in the unshielded portion of the specimens. The neutron exposure received by each specimen is shown in Table 8, which is a summary of results for all specimens of boronated and hafnated graphite in BG-2.

2.2.4.4. B-10 Isotope Burnup. Samples were taken for B-10 - B-11 isotope analysis by scraping the surface of selected boronated graphite samples with a clean steel file, with precautions taken to avoid cross-contamination. A section 0.2 in. square, 0.02 in. deep, and weighing about 0.020 g was removed from the specimen surfaces exposed in the thermal-neutron window and from the shielded side. Some cylindrical specimens also had samples removed by drilling at the center on the bottom. Isotopic analysis was performed by mass-spectrographic techniques at AVCO Analytical Laboratories, and the results of this work are shown in Table 8. The profile of B-10 burnup along the length of the capsule is shown in Fig. 28. The B-10 burnup within the specimens in the neutron window was about two times that in the middle and

Fig. 27. Thermal- and fast-neutron exposure profile of capsule BG-2

TABLE 8
SUMMARY OF MATERIAL PROPERTIES AND IRRADIATION EFFECTS IN BORONATED GRAPHITE
IN THE BG-2 EXPERIMENT INCLUDING PRIOR IRRADIATION IN THE BG-1 EXPERIMENT

	Extruded and Baked			Warm Pressed and Baked																
	Peach Bottom HTGR Control Rod Absorber			Non-Boronated Graphite Control Samples			Unleached Commercial B ₄ C in Graphite		Leached Commercial B ₄ C in Graphite				B-10 Depleted Boron Laboratory B ₄ C in Graphite		B-10 Enriched Boron in Graphite (91% B-10 Enriched)	B-10 Enriched Boron Laboratory B ₄ C (91% B-10 Enriched)	Fort St. Vrain HTGR Control Rod Absorber (Commercial)	Hafnated Graphite		
																		Low Temp Bake	High Temp Bake	
Material No.	3912-34			3685-118-1000			4465-21-2000	3685-111-1000		3685-124-1000		3685-124-2000		3685-120-1000		4465-24	4465-26	4465-42	4065-132-2000	4065-132-2600
Bake Temperature (2 hours), °C	2200 (30 min)			1000			2000	1000		1000		2000		1000		2000	2000	2000	2000	2600
Boron Content, wt-%	28			0			0	22		34		34		22 ^(e)		7.1	7.5	43	0	0
Boron Density, g B/cm ³	0.45			0			0	0.38		0.52		0.52		0.38		0.11	0.14	0.69	0	0
Hafnium Content (wt-%)	0			0			0	0		0		0		0		0	0	0	90	90
Hafnium Density (gm Hf/cm ³)	0			0			0	0		0		0		0		0	0	0	24	5.19
Bulk Density, g/cm ³	1.60			1.72			1.98	1.77		1.68		1.68		1.72		1.70	1.91	1.60	5.81	5.76
Irradiation Experiment	BG-1	BG-2	BG-2	BG-1	BG-2	BG-2	BG-1	BG-2	BG-1	BG-2	BG-1	BG-2	BG-1	BG-2	BG-1	BG-2	BG-2	BG-2	BG-2	BG-2
No of Specimens:																				
Prismatic 0.2 x 0.2 x 0.58 in.	0	0	0	6	0	0	8	4	0	0	0	0	0	0	0	0	0	0	0	0
Prismatic 0.2 x 0.4 x 0.58 in.	3	3	0	3	2	0	4	0	4	2	4	3	4	2	0	0	0	0	0	0
Cylindrical 9.4 DIA x 0.58 in.	0	0	2	0	0	2	0	0	0	0	0	0	0	0	0	3	3	6	2	3
Total Fast Fluence (E>0.18 Mev), 10 ²¹ n/cm ²	2.0-2.5	5.6-6.1	6.0	3.5-4.0	8.25	5.5	2.5-3.5	7.5	2.5-3.0	7.3	3.0-3.5	7.0-7.3	3.5-4.0	8.8	4.36-4.66	3.76-4.19	4.80-5.87	6.0	5.5-6.0	
Total Thermal Fluence (E 0.4 ev), 10 ²¹ n/cm ²	1.5	3.5	3.0	2.5	4.5	2.8	1.5	3.7	1.5	3.5	1.5	3.5	2.5	4.8	2.0	1.8	2.0-2.7	3.0	2.7-3.0	
Specimen Irradiation Temp, °C:																				
Minimum	600(a)			550(a)			625		675		675(a)		675(a)		675		725	725 ^(g)	725 ^(g)	
Maximum	675(a)	675	790	600(a)	725	725	750	700	850	725	850(a)	725	700(a)	625	725	725	730	700	700	
Average	650(a)	650	700	550(a)	700	700	675	675	750	700	750(a)	700	675(a)	575	700	700	700	700	700	
B-10 Isotope Burnup, % Depletion																				
At Neutron Window	80	62 ⁽ⁱ⁾	92	0	0	0	80	(b)	66	73 ⁽ⁱ⁾	76	(b)	(f)	(b)	76	66	80	(b)	(b)	
Mid Specimen	(b)	(i)(b)	(b)	0	0	0	30	(b)	35 ^(d)	(b)	35 ^(d)	(b)	(f)	(b)	30	37	32	(b)	(b)	
Opposite Neutron Window	37	58 ⁽ⁱ⁾	53	0	0	0	53	(b)	38	76 ⁽ⁱ⁾	48	(b)	(f)	(b)	36	31	40	(b)	(b)	
Dimension Change During Irrad. Relative to Forming Direction, %:																				
Parallel Minimum	-0.52	-0.51	-0.21	+1.23	+4.14	+1.76	+2.35	+5.21	+1.76	+5.34	+0.31	+4.10	+1.05	+4.29	+9.24	+6.08	+1.72	+1.41	+0.87	
Parallel Maximum	-0.03	+0.35	-0.52	+1.73	+4.30	+1.93	+2.81	+7.57	+2.67	+6.10	+2.23	+4.65	+1.87	+4.63	+13.61	+6.42	+2.17	+1.69	+1.29	
Parallel Average	-0.23	-0.05	-0.37	+1.40	+4.22	+1.84	+2.51	+6.65	+2.20	+5.72	+1.26	+4.29	+1.42	+4.46	+11.32	+6.22	+1.88	+1.55	+1.09	
Perpendicular Minimum	-0.13	+1.43	+0.62	-1.21	-1.34	-2.78	-0.58	+1.53	-0.43	(b)	-1.09	+0.418	-0.68	+0.255	-1.50	-0.13	+0.37	+0.25	+0.25	
Perpendicular Maximum	+0.86	+1.76	+0.62	-0.41	-1.67	-2.78	+0.91	+3.04	+1.54	(b)	+0.91	+0.585	+0.31	+0.587	-2.25	-1.01	+1.00	+0.25	+0.37	
Perpendicular Average	+0.69	+1.57	+0.62	-0.80	-1.50	-2.78	+0.24	+2.41	+0.44	+1.60	0.00	+0.502	-0.16	+0.421	-1.88	-0.543	+0.68	+0.25	+0.29	
Graphite Matrix Crystallite Dimension, Å:																				
Preirradiation L _c	580	103	580	850	195	625	490	200	675	610	580	111	850	170	770	625	540	(b)	(b)	
Preirradiation C ₀	6.729	6.820	6.724	6.715	6.775	6.717	6.719	6.736	6.715	6.729	6.726	6.758	6.715	6.742	6.727	6.729	6.730	(b)	(b)	
Postirradiation L _c	103	(b)	(b)	195	(b)	147	200	(b)	210	(b)	111	(b)	170	(b)	(b)	131	96	(b)	(b)	
Postirradiation C ₀	6.820	(b)	(b)	6.775	(b)	6.767	6.736	(b)	6.729	(b)	6.758	(b)	6.742	(b)	(b)	6.762	6.782	(b)	(b)	
Coef. of Thermal Exp. Relative to Forming Direction (22° to 700°C), 10 ⁻⁶ in./in. °C:																				
Preirradiation Parallel (α _{pa})	3.68	3.68	3.68	9.37	9.37	8.01	5.57	5.57	6.32	6.32	5.30	5.30	6.80	6.80	8.84	7.76	4.83	5.19	5.09	
Preirradiation Perpendicular (α _{pe})	4.70	4.70	4.70	4.19	4.19	4.19	4.29	4.29	4.70	4.70	3.82	3.82	4.26	4.26	2.11	2.23	4.58	4.01	4.52	
Ratio (α _{pa} /α _{pe})	1.3(c)	1.3(c)	1.3(c)	2.2	2.2	3.5	1.3	1.3	1.3	1.3	1.4	1.4	1.6	1.6	4.2	3.5	1.1	1.3	1.1	
Postirradiation Parallel (α _{pa})	(b)	5.04	5.34	10.41	12.32	12.41	8.17	8.54	(b)	7.14	(b)	9.01	(b)	8.98	12.49	10.02	6.78	(b)	(b)	
Postirradiation Perpendicular (α _{pe})	(b)	6.62	5.70	(b)	5.87	2.87	5.25	3.76	(b)	4.60	(b)	4.84	(b)	5.71	3.93	3.09	6.56	(b)	(b)	
Ratio (α _{pa} /α _{pe})	(b)	1.3(c)	1.1(c)	(b)	2.1	4.3	1.6	2.3	(b)	1.5	(b)	1.9	(b)	1.6	3.2	3.2	1.0	(b)	(b)	
Thermal Conductivity Perpendicular to Forming Direction, cal/cm-sec-°C:																				
Preirradiation 25°C	0.120	(b)	0.120	0.170	0.027	0.320	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	0.175	0.054	(b)	(b)	
Preirradiation 400°C	0.090	(b)	0.090	0.110	0.033	0.225	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	0.175	0.333	(b)	(b)	
Preirradiation 800°C	0.065	(b)	0.065	0.090	0.035	0.175	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	0.130	0.020	(b)	(b)	
Postirradiation 25°C	(b)	(b)	0.009	0.027	(b)	0.045	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	0.020	0.008	(b)	(b)	
Postirradiation 400°C	(b)	(b)	0.012	0.033	(b)	0.050	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	0.025	0.012	(b)	(b)	
Postirradiation 800°C	(b)	(b)	0.012	0.035	(b)	0.046	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	0.023	0.012	(b)	(b)	
Room Temperature Crush Strength, Loaded Parallel to Forming Direction, psi:																				
Preirradiation	(b)	(b)	5500	(b)	(b)	5400	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	4050	7050	6000	3780	4780	
Postirradiation	(b)	(b)	5120	(b)	(b)	8050	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	2630	4225	3807	4500	7000	

(a) Estimated temperatures based on indicated temperatures of adjacent specimens.
(b) Not measured.
(c) Ratio (α_{pa}/α_{pe}) for extruded specimens.
(d) Estimated B-10 burnup based on measured burnup of adjacent specimens.
(e) Boron depleted in B-10 (1.45 at % B-10; remainder B-11).

(f) Burnup of B-10 not detectable.
(g) An 11-hour period was spent at ~1175°C because of temperature control error.
(h) Only one specimen suitable for + measurement.
(i) Unexplained anomaly in measured B-10 burnup.

Fig. 28. B-10 burnup profile for BG-2 specimens

on the shielded side. Results from isotopic analysis of two specimens (material 3912-34 and 3685-124-1000) described in Table 8 were not included in Fig. 28 because of unexplained anomalous behavior. In both cases the extent of B-10 burnup was less than anticipated and did not decrease from the window to the shielded side.

2.2.4.5. Lithium Migration. No measurement of lithium migration was attempted in the BG-2 samples.

2.2.4.6. Dimensional Change. The dimensions of boronated graphite specimens were measured before and after irradiation on a bench dial micrometer (precision ± 0.0001 in.). The highly radioactive hafnated graphite was measured remotely after irradiation in the Hot Cell on a micrometer with a precision of ± 0.001 in. The surface textures of specimens in cell 1 (previously irradiated in BG-1) was rough and granular, as fabricated, so that repeatability was ± 0.003 in. In the other specimens repeatability of a measurement on the same area was ± 0.001 in.

The diameter of specimens was measured at the mid-section. One indication of bow was obtained by rotating the specimens on the flat stage while measuring the apparent diameter with the dial micrometer. An additional bow determination was made by measuring the specimen length at 90° intervals on the circumference.

At each measuring location, two measurements were taken. The average of all measurements in one direction for a single material type was then used to compute the dimensional change values which are given in Table 8.

2.2.4.7. Microstructure. The microstructure of the boronated graphite specimens was similar to that observed after irradiation in capsule BG-1. The B-10 burnup gradient which should have existed in the specimens was not evident in the microstructure. Some cracking of B_4C granules appeared to occur during irradiation, but it was as prevalent on the side exposed to thermal neutrons as on the shielded side. An example of boronated graphite

microstructure before and after irradiation is shown in Fig. 29. A high-magnification view of a cracked B_4C granule is shown in Fig. 30.

The boronated graphite made with B-10-enriched boron powder (4465-24) showed irregular granules of porous B_4C in a matrix of graphite. The B_4C was formed in situ from boron powder and graphite matrix. The microstructure of the B_4C was unchanged by irradiation. An example of the microstructure is shown in Fig. 31. This observation, along with the low volume loading of B_4C (<7%), was taken as evidence that the observed irradiation-induced dimensional change in this material was due primarily to damage in the graphite matrix rather than swelling of the B_4C .

The boronated graphite made with B-10-enriched B_4C (4465-26) showed a change in microstructure during irradiation. Before irradiation the B_4C was laced with carbon precipitates. After irradiation the B_4C granules appeared to have fractured along the precipitates. In addition, the remaining carbon within the B_4C showed high optical anisotropy and gave the appearance of having expanded in one direction to cause cracking of the B_4C . There was an accompanying shrinkage in the opposite direction, which is consistent with the expected irradiation performance of graphite. An example of this kind of microstructure is shown in Figs. 32 and 33.

The microstructure of the hafnated graphite was unchanged by irradiation. An example of a microstructure typical for both materials (4065-132-2000 and 4065-132-2600) is shown in Fig. 34.

2.2.4.8. Crush Strength. The crush strength of cylindrical samples of materials in BG-2 was determined before and after irradiation. The specimens were loaded axially at a cross-head speed of 0.005 or 0.01 in./min in an Instron Model TTCM-1 testing machine. Three to six unirradiated and one to four irradiated specimens were crushed to determine their strength at room temperature. The cross-sectional area of the thermocouple hole on the center line of some samples was not included in calculating strength, and the presence of the hole was assumed not to significantly affect the ultimate strength. The results of this work are shown in Table 8.

M29982-6

(a)

(75x)

M367-142

(b)

(75x)

Fig. 29. Microstructure of boronated graphite (B_4C in graphite) manufactured for the Fort St. Vrain control rod absorbers; (a) before irradiation, (b) after irradiation to 4.80 to 5.87×10^{21} n/cm^2 ($E > 0.18$ MeV) at $700^\circ \pm 50^\circ C$ in thermal-neutron window of capsule BG-2. Note wide variation in B_4C microstructure before irradiation; after irradiation some B_4C granules were fractured.

M367-143

(500x)

Fig. 30. Fracture pattern typically observed in B_4C granules of boronated graphite at high B-10 burnup; material 4465-42; fast-neutron exposure of 4.80 to 5.87×10^{21} n/cm^2 ($E > 0.18$ MeV) at $700^\circ \pm 50^\circ C$ in capsule BG-2

M367-121

(a)

75X

M367-124

(b)

200X

Fig. 31. Microstructure of boronated graphite (material 4465-24, specimen 4-4) made with 92% B-10-enriched boron powder irradiated in BG-2 at 700°C to a fast-neutron exposure of 4.4 to 4.7×10^{21} n/cm² ($E > 0.18$ MeV). The area shown (a) is from the side of the specimen exposed to thermal neutrons and had a B-10 burnup of 76%. Irregular inclusion shown at higher magnification (b) was apparently B_4C converted in situ from matrix and boron powder during 2000°C heat treatment. No change in microstructure of the matrix or inclusions were detected as a result of irradiation.

M29736-1

(a)

75X

M29736-4

(b)

500X

Fig. 32. Microstructure of boronated graphite (material 4465-26, specimen 4-7) made with B-10-enriched B_4C (see Fig. 33): (a) Before irradiation, low magnification; (b) preirradiation microstructure of B_4C grains showing excess carbon precipitated within the grain

M367-107

(a)

75X

GRAPHITE
PRECIPITATE
INFERRED
FROM
OPTICAL
ANISOTROPY

M367-95

(b)

500X

Fig. 33. Microstructure of boronated graphite (material 4465-26, specimen 4-7) made with B-10-enriched B_4C (see Fig. 32): (a) after irradiation in BG-2 at $700^\circ C$ to a fast-neutron exposure of 3.8×10^{21} n/cm^2 ($E > 0.18$ MeV) and B-10 depletion of 31% (shielded side); (b) postirradiation microstructure of B_4C grains showing fracturing of grain along graphite precipitates which have apparently undergone dimensional change during irradiation, perhaps leading to grain fracture (note areas showing graphite precipitates inferred from optical anisotropy)

M29627-1

500X

M367-267

500X

Fig. 34. Microstructure of hafnated graphite material 4065-132-2000: (a) before irradiation showing HfC grains in a graphite matrix; (b) after irradiation in BG-2 at 700°C to a neutron exposure of 3.0 to 6.0×10^{21} n/cm² ($E > 0.18$ MeV), exposed side, showing no obvious change during irradiation

2.2.4.9. Coefficient of Thermal Expansion. Prior to irradiation, the thermal expansion parallel and perpendicular to the forming direction was determined for all materials between 22° and 700°C. After irradiation, the thermal expansion was measured over the same temperature range in all specimens except the highly radioactive hafnated graphite. Measurements were made in prismatic samples from the BG-1 capsule and cylindrical specimens irradiated in BG-2 using the apparatus and technique described for the BG-1 experiment.

The mean coefficients of expansion are shown in Table 8.

2.2.4.10. Thermal Conductivity. The thermal conductivity of four materials was determined between room temperature and 800°C before and after irradiation in capsule BG-2. The xenon flash method (Ref. 11) was employed with specimens 0.30 in. in diameter by 0.060 in. thick, shaped so that the direction of measurements was perpendicular to the forming direction. Neuman and Kopp's additivity rule for the specific heat of B_4C and graphite (as shown in Table 9) was used in calculating the heat capacity (Ref. 12). The results of thermal conductivity measurements are shown in Table 8.

2.2.4.11. Graphite Crystallite Dimensions. Crystallite dimensions (L_c and c_o) of the graphitic phase of all boronated materials were measured by X-ray diffractometer before irradiation and in three materials after irradiation. The powdered samples were held between transparent strips of tape during the X-radiation exposure. The results of that work are shown in Table 8.

2.2.4.12. Piggyback Specimens

Boron Carbide. The boron carbide piggyback specimens are described in Table 7. Not all of the granular samples could be examined after irradiation because of the small amount of material retrieved from the graphite crucibles. However, a sample of each material was obtained, and preirradiation and post-irradiation photographs of the various samples are shown in Figs. 35 through 39.

TABLE 9
HEAT CAPACITY OF GRAPHITE, BORON CARBIDE, AND BORONATED
GRAPHITES ASSUMED FOR THERMAL-CONDUCTIVITY MEASUREMENT

Temp (°C)	Graphite	Heat Capacity (cal/g-°C)			
		B ₄ C	Boronated Graphite (wt-% B ₄ C)		
			10	28	43
25	0.174	0.225	0.180	0.188	0.196
100	0.223	0.255	0.226	0.232	0.237
200	0.279	0.285	0.280	0.281	0.282
300	0.325	0.330	0.326	0.326	0.327
400	0.360	0.345	0.359	0.356	0.354
500	0.388	0.375	0.387	0.384	0.382
600	0.410	0.400	0.409	0.410	0.406
700	0.426	0.425	0.426	0.426	0.426
800	0.439	0.450	0.440	0.442	0.444

M33891-1

(a)

22X

M33894-1

(b)

22X

Fig. 35. Boron carbide (high boron, 76 wt-% boron, material 4065-84, specimen 1-6): (a) before irradiation; (b) after irradiation in BG-2 at $500^{\circ}\text{C} \pm 50^{\circ}$ to a fast-neutron fluence of $4.8 \times 10^{21} \text{ n/cm}^2$ ($E > 0.18 \text{ MeV}$) and B-10 burnup of 61%

M33888-1

(a)

22X

M33897-2

(b)

22X

Fig. 36. Boron carbide (technical grade, 70 wt-% boron, material 3685-84, specimen 3-4): (a) before irradiation; (b) after irradiation at $500^{\circ} \pm 50^{\circ}\text{C}$ to a fast-neutron fluence of 5.8×10^{21} n/cm^2 ($E > 0.18$ MeV) and a B-10 burnup of 94%

M33887-1

(a)

22X

M33893-1

(b)

22X

Fig. 37. Spherical B_4C granules (material 3685-4, specimen 11F): (a) before irradiation; (b) after irradiation as loose granules in BG-2 at approximately $450^\circ \pm 50^\circ C$ to a fast-neutron fluence of $3.4 \times 10^{21} \text{ n/cm}^2$ ($E > 0.18 \text{ MeV}$) and B-10 burnup of 76%

M33889-1

(a)

22X

M33897-1

(b)

22X

Fig. 38. Boron carbide (material 4465-7, specimen 33F) made from B-10-enriched boron ($B-10/B-11 = 11.5$): (a) before irradiation; (b) after irradiation in BG-2 at $500^\circ \pm 50^\circ\text{C}$ to a fast-neutron exposure of $5.9 \times 10^{21} \text{ n/cm}^2$ ($E > 0.18 \text{ MeV}$) and B-10 burnup of 94%. Much of the irradiated sample was apparently turned to fine powder and lost. The largest granule in (b) was a piece of graphite debris from the crucible.

M33890-1

(a)

22X

M33896-2

(b)

22X

Fig. 39. Boron carbide (material 3685-105, specimen 31F) made from B-10-depleted boron ($B-10/B-11 = 0.015$): (a) before irradiation; (b) after irradiation in BG-2 at $500^\circ \pm 50^\circ\text{C}$ to a fast-neutron fluence of $6.0 \times 10^{21} \text{ n/cm}^2$ ($E > 0.18 \text{ MeV}$) and a thermal fluence estimated at approximately 3×10^{21} ($E < 0.4 \text{ eV}$)

The original shapes of both the granular and spherical particles were maintained, although there was evidence of fracturing and reduction in grain size of the B-10-enriched B_4C (4465-7).

Isotopic analysis for B-10 and B-11 was obtained for selected samples, and the B-10 depletion of all samples was estimated from the relationship shown in Fig. 40. The density distribution of granules of irradiated and unirradiated B_4C samples was measured in a liquid-density-gradient column made from a mixture of benzene and methylene iodide. The two liquids were added to a graduated burette so that a stable, approximately linear decrease in liquid density with increasing height in the burette was created.

Glass beads with known densities from 2.00 to 2.59 g/cm³ were dropped into the liquid column to calibrate the system. The granular B_4C samples containing 50 to 200 grains were then added individually and allowed to come to rest at the column height containing the same liquid density as the B_4C grain. The individual grains were then counted, and their density was recorded so that a maximum, minimum, and mean B_4C density could be determined. A new liquid column was used for each sample. The results of this work are shown in Table 10.

The results of the work showed that density decrease during irradiation was not dependent on the stoichiometry of the B_4C or fast-neutron exposure. The decrease in density of all samples could be correlated with B-10 depletion or B-10 fission density. With natural boron the density decreased approximately linearly with B-10 fission density as shown in Fig. 41.

A simple linear regression fit of the natural-boron B_4C data predicts a maximum of 13% decrease in density at 100% B-10 depletion. With B_4C made from B-10-enriched boron, the decrease in density apparently saturates or decreases slowly after a fission density of about 2×10^{22} B-10 fissions/cm³ B_4C is exceeded. The density decrease observed in this work is less than would be predicted on the basis of work reported previously (Ref. 13) in which a 30 vol-% increase took place in unrestrained B_4C spheres irradiated

Fig. 40. B-10 burnout profile for B_4C piggyback samples in capsule BG-2

TABLE 10
SUMMARY OF BG-2 PIGGYBACK SPECIMEN RESULTS

Sample Material Number	Description	Cell	Crucible	Position	Fast-Neutron Exposure $\times 10^{21}$ (E>0.18 MeV)	Irrad Temp ($^{\circ}\text{C}$ ± 50)	Fraction B-10 Depletion (a)	B-10 Fission Density [(B-10 Fission/cm ³ B ₄ C) $\times 10^{22}$]	Density (g/cm ³) (b)		
									Min.	Max.	Mean
3685-105	B ₄ C granules depleted in B-10 $\left[\frac{\text{B-10}}{\text{B-11}} = 0.015\right]$	--	--	Unirrad	0	--	--	0	2.42	2.56	2.50
		3	1	(c)	6.0	500	(d)	0	2.40	2.51	2.47
		3	1	(e)	6.0	500	(d)	0	2.43	2.51	2.46
		3	1	(f)	6.0	700	(d)	0	2.44	2.52	2.48
		4	1	(c)	4.8	600	(d)	0	2.42	2.50	2.45
		4	1	(e)	4.8	600	(d)	0	2.40	2.50	2.45
3685-4	Spherical B ₄ C Natural boron 82 wt-% B	--	--	Unirrad	0	--	--	0	2.39	2.54	2.48
		1	1	(e)	3.4	450	0.45(g)	1.0	2.12	2.38	2.30
		1	1	(c)	3.4	450	0.76(g)	1.7	2.05	2.31	2.19
		1	2	(c)	3.8	450	0.77	1.7	2.22	2.37	2.32
		1	2	(e)	3.8	450	0.48	1.1	2.13	2.31	2.23
		1	3	(e)	4.2	550	0.48(g)	1.1	2.19	2.36	2.29
		1	3	(c)	4.2	550	0.81(g)	1.8	2.11	2.28	2.25
		3	6	(c)	5.6	500	0.93	2.1	2.10	2.26	2.18
		4	6	(c)	4.0	500	0.84	1.9	2.15	2.35	2.24
		--	--	Unirrad	0	--	0	0	2.43	2.52	2.50
3685-84	B ₄ C granules Natural boron 70 wt-% B	3	2	(c)	5.9	500	0.95(g)	1.8	2.09	2.21	2.14
		3	2	(e)	5.9	500	0.38(g)	0.7	2.32	2.42	2.37
		3	4	(c)	5.8	500	0.94	1.8	2.12	2.18	2.15
		3	5	(c)	5.8	500	0.93	1.8	2.09	2.21	2.15
		4	2	(c)	4.6	600	0.88(g)	1.7	2.05	2.25	2.15
		4	2	(e)	4.6	600	0.74(g)	1.4	2.10	2.28	2.18
		4	2	(f)	4.6	700	0.28(g)	0.5	2.36	2.46	2.41
		4	4	(c)	4.3	550	0.85	1.6	2.12	2.24	2.21
		4	5	(c)	4.2	550	0.84	1.6	2.15	2.26	2.20
		--	--	Unirrad	0	--	0	0	2.43	2.52	2.49
4065-84	B ₄ C granules Natural boron 76 wt-% B	1	4	(c)	4.4	500	0.82	1.7	2.15	2.35	2.29
		1	5	(c)	4.6	500	0.84	1.7	2.09	2.22	2.16
		1	6	(c)	4.8	500	0.61(g)	1.2	2.11	2.27	2.22
4465-7	B ₄ C granules Boron enriched in B-10 $\left[\frac{\text{B-10}}{\text{B-11}} = 11.5\right]$	--	--	Unirrad	0	--	0	0	2.27	2.36	2.35
		3	3	(c)	5.9	500	0.94	8.1	1.90	2.07	2.00
		3	3	(e)	5.9	500	0.64(g)	5.6	2.04	2.18	2.13
		3	3	(f)	5.9	700	0.24(g)	2.1	2.07	2.15	2.09
		4	3	(c)	4.5	550	0.84	7.3	2.03	2.21	2.08
		4	3	(e)	4.5	550	0.56	4.9	2.01	2.13	2.09

(a) Estimated B-10 depletion from Fig. 40 except where noted as measured.

(b) Determined by liquid density gradient column.

(c) Unshielded, front of crucible.

(d) Not measured but assumed to be approximately zero.

(e) Partially shielded side of crucible.

(f) Completely shielded center of boronated graphite sample.

(g) Measured B-10 depletion.

Fig. 41. Effect of B-10 fission density on the density of B_4C irradiated in piggyback location of BG-2; a simple linear regression fit of the data for B_4C containing natural or depleted boron is shown

at 500°C to a B-10 burnup of 78%. Other irradiation results with large hot-pressed shapes of B_4C resulted in greater expansion than observed here (Ref. 14).

The density change measured in this work by liquid displacement would represent a minimum value because of liquid penetration of cracks created during irradiation. A measure of the change in apparent volume including voids of the B_4C particles would yield data more comparable to literature values. An attempt was made to gather such data by measuring the diameter of 130 and 147 particles in microradiographs of unirradiated and irradiated specimens of spherical B_4C (3685-4). The irradiated B_4C had experienced a fast-neutron exposure of 3.4×10^{21} n/cm² ($E > 0.18$ MeV) and a B-10 depletion of 76% of original B-10. This work showed that the average in the distribution of particle volumes increased about 21% at a B-10 fission density of 1.7×10^{22} fissions/cm³ B_4C . This magnitude of volume change is more consistent with literature values, but the rather wide range in both irradiated and unirradiated particle sizes (1 standard deviation ~20 vol-%) makes further speculation hazardous.

Boron Fibers. The boron fiber piggyback specimens are described in Table 8. In the BG-2 capsule the fibers were irradiated at $550^\circ \pm 50^\circ\text{C}$ to a B-10 burnup of about 65%. The fibers fragmented, and very few remnants of the original samples were recovered. Photographs of unirradiated and irradiated boron fibers are shown in Fig. 42. Portions of the tungsten substrate could be seen in some fragments. The predicted poor performance of the fibers at extremely high B-10 burnup was confirmed.

Hafnium Carbide. The material (4065-111) irradiated in capsule BG-2 was HfC granules, 200 to 300 μm in diameter, containing 90 wt-% hafnium and 2.8 wt-% zirconium, with the remainder being carbon. The description of the material is given in Table 6. The samples were irradiated at $550^\circ \pm 50^\circ\text{C}$ to a fast-neutron exposure of 5.5 to 6.0×10^{21} n/cm² ($E > 0.18$ MeV). After irradiation the samples were retrieved remotely (radioactivity about 100 R/hr at 2 in.) from the graphite crucibles by breaking the crucible top off and pouring the granules out. Most granules remained packed in the graphite crucibles.

M33892-1

(a)

22X

M33896-1

(b)

22X

Fig. 42. Boron filament (material 3471-122, specimen 23S); 0.004-in.-diameter vapor-deposited boron on 0.0005-in.-diameter tungsten wire

However, a portion did pour out and the individual grains showed no sign of agglomeration or change, other than a darkening, from the unirradiated state as shown in Fig. 43. A polished cross section of one of the crucibles is shown in Fig. 44. No damage was observed in the graphite crucible. A typical microstructure of HfC before and after irradiation is shown in Fig. 45. No change in morphology was detectable from the unirradiated state. A distinctive second phase existed in the grain boundaries of some HfC granules. Electron microprobe examination of these areas in unirradiated HfC showed that they were relatively high in iron, chromium, and nickel content and probably represented a low-melting-point impurity phase rejected from the HfC.

M28858-1

(a)

25X

S367-5

(b)

20X

Fig. 43. Hafnium carbide (4065-111, specimen 2-1-S): (a) unirradiated -48 +200 mesh U.S.; (b) irradiated in BG-2 at $550^{\circ} \pm 50^{\circ}\text{C}$ to a fast-neutron exposure of $5.5 \times 10^{21} \text{ n/cm}^2$ ($E > 0.18 \text{ MeV}$). Before irradiation sample was screened to -48 +65 mesh U.S. (~ 200 - to $300\text{-}\mu\text{m}$ size range). During irradiation there was darkening and loss of reflectivity; no other changes were evident.

S367-7

7X

Fig. 44. Metallographic cross section of hafnium carbide granules (4065-111, specimen 2-7) in an opened piggyback crucible from capsule BG-2 after irradiation at $550^{\circ} \pm 50^{\circ}\text{C}$ to a fast-neutron exposure of 6.0×10^{21} ($E > 0.18 \text{ MeV}$). Top was broken off and contents were poured out before mounting. No damage was evident in either top or bottom portion of graphite crucible.

M367-252

200X

M267-250

500X

Fig. 45. Microstructure of HfC (4065-111, specimen 2-1-S) irradiated in capsule BG-2 piggyback location at $550^{\circ} \pm 50^{\circ}\text{C}$ to a fast-neutron exposure of $5.5 \times 10^{21} \text{ n/cm}^2$ ($E > 0.18 \text{ MeV}$). No change was detected in grain morphology during irradiation; white intergranular phase was identified in unirradiated samples as having high iron, chromium, and nickel concentration.

3. DISCUSSION OF BG-1 AND BG-2 RESULTS

3.1. BORONATED GRAPHITE

The flexural strength of the warm-pressed material (Table 3) was highly variable and considerably less than that of the extruded boronated graphite, which had strength comparable to that of nonboronated conventional graphites (Ref. 15). 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 an increase and a decrease. No systematic trend was evident.

Crush strength measurements (Table 8) showed less variation between materials than the flexural strength, probably because the former test method is less sensitive to surface flaws, which were prevalent. The crush strength of boronated graphite decreased with irradiation, while nonboronated and hafnated graphite strength increased.

The perpendicular thermal conductivities of boronated materials (Tables 3 and 8) were similar with the exception of 4464-42 (Table 8), which had a thermal conductivity one-half to one-sixth of that of the other boronated materials. The low conductivity of 4464-42 was a result of high porosity in the matrix, which produced a low bulk density (1.60 g/cm^3) in spite of the high B_4C loading ($0.69 \text{ g boron/cm}^3$).

Prior to irradiation the thermal conductivity was more temperature-dependent than after irradiation. After irradiation the thermal conductivity was less than before irradiation.

The thermal expansion was measured in both directions in the specimens, and the ratio of parallel-to-perpendicular coefficients (CTE) was taken as a measure of anisotropy. The most highly anisotropic materials were the

nonboronated graphites. Graphites made with GP-38 (4465-21-2000) were more anisotropic than those made with graphitized Wilmington coke (3685-118-1000). However, the boronated material with the least anisotropy (4465-42) was made commercially using GP-38. The fabrication process obviously played an important part in determining the degree of anisotropy in the specimens.

The crystallite properties of the graphite filler material were measured in terms of crystallite height L_c and layer spacing C_o (Tables 3 and 8). 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. 16). In this work the nature of the material was such that there were considerable variations in C_o ; if boron was 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 (Table 4). 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 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 these experiments because of the higher operating temperature.

The dimensional change of boronated graphite during irradiation was the primary material property being monitored in BG-1 and BG-2. The experimental results are given in Tables 3 and 8.

The extruded boronated graphite (3912-34) contracted slightly in the parallel direction and expanded in the perpendicular direction as shown in Fig. 46. The change in dimension was linear with fast-neutron exposure when specimens irradiated first in BG-1 and then in BG-2 are considered. The perpendicular (radial) expansion of specimens irradiated only in BG-2 was restrained by the crucible as discussed earlier, so the data do not represent the radial expansion on unrestrained specimens. The best estimate of radial dimensional change is represented by the line drawn through the data points for the unrestrained specimens.

The parallel dimensional change of specimens in BG-1 and BG-2 agreed well with data from full-sized control rod absorbers of the same material (3912-34) in reactor service (Ref. 17).

The only other material in BG-2 which had some specimens under radial restraint for part of the time was 4465-42, a commercially made boronated graphite. One specimen out of six was not restrained radially during irradiation, and the data point from that material was weighted by drawing a straight line through it to the origin to represent the expected unrestrained radial dimensional change. These data are presented in Fig. 47.

Fig. 46. Irradiation-induced dimensional change in extruded boronated graphite baked at 2200°C and irradiated at 700° ± 50°C

Fig. 47. Irradiation-induced dimensional change in a commercially produced warm-pressed boronated graphite (4465-42) containing 0.69 g boron/cm³, baked at 2000°C for 2 hr and irradiated at 700° ± 50°C. Seven specimens were irradiated but six became restrained in the (I) direction during irradiation, and a line representing the best estimate of unrestrained swelling was drawn through the data for the unrestrained specimen, shown as a weighted data point.

The other warm-pressed boronated graphites with a 2000°C bake temperature changed dimensions as shown in Fig. 48. Expansion in both the parallel and perpendicular directions was observed to be sensitive to initial anisotropy. The boronated graphite sample from a Fort St. Vrain HTGR absorber (4465-42) was the most isotropic of materials tested and showed less parallel expansion but greater perpendicular expansion than material made in the laboratory. Warm-pressed nonboronated graphite made from graphite fillers and pitch binder similar to those used in the boronated graphites showed less irradiation-induced parallel expansion and more perpendicular contraction, as illustrated in Fig. 49. Clearly, not all the difference in the irradiation performance of nonboronated and boronated graphite can be ascribed to the B_4C content. Some of the difference in performance was due to differences in the degree of preferred orientation (anisotropy) of graphite crystallites as revealed by differences in the coefficient of thermal expansion in the two principal directions.

Bake temperature affects the irradiation-induced dimensional change of boronated graphite as shown in Fig. 50. A final bake temperature of 2000°C resulted in significantly less expansion in both directions than observed in boronated graphite baked at 1000°C. Also, as shown in Figs. 49 and 50, the presence of B_2O_3 in the B_4C addition (3685-111-1000 and 3685-111-2000) caused no significant difference in dimensional change relative to the other materials.

The effect of B-10 content in graphite on irradiation-induced dimensional change was explored by irradiating graphites containing B_4C or boron powder made from B-10-depleted, and B-10-enriched boron powders (see Table 7). With the B-10-depleted B_4C , the total boron content of boronated graphite was kept about the same as in boronated specimens containing natural boron. The dimensional changes which took place upon irradiation are shown in Fig. 51. The boronated graphite containing B-10-depleted B_4C underwent much less expansion in both directions than graphite containing natural boron. In fact, the parallel-direction dimensional change was similar for nonboronated and the B-10-depleted boronated graphite. In the perpendicular direction the B-10-depleted (B-10/B-11 = 0.015) graphite showed slight swelling, whereas

Fig. 48. Effect of initial anisotropy on the irradiation-induced dimensional change in warm-pressed boronated graphite baked at 2000°C and irradiated at $700^\circ \pm 50^\circ\text{C}$

Fig. 49. Irradiation-induced dimensional change in warm-pressed boronated and nonboronated graphite baked 2 hr at 2000°C and irradiated at 700° ± 50°C; dashed lines are drawn through laboratory-produced boronated graphite shown in Fig. 48.

Fig. 50. Effect of bake temperature on irradiation-induced dimensional change of boronated graphite; data points for material with 1000°C bake show consistently more expansion than that baked at 2000°C (shown in Fig. 48, and shown here by dashed line)

Fig. 51. Irradiation-induced dimensional change in warm-pressed B-10-depleted, nonboronated, and natural boronated graphite baked at 1000°C; irradiated at 550° to 750°C (graphitized coke filler C₀ 6.694 to 6.750 Å, L_c 730 to 2000 Å)

the nonboronated graphite underwent shrinkage of 1.5% at 8.25×10^{21} n/cm² ($E > 0.18$ MeV). Therefore, it appears that the incorporation of B₄C granules into graphite results in increased volume expansion during irradiation. However, the volume expansion is reduced if the B₄C is relatively inert by virtue of being depleted in the B-10 isotope.

Another series of graphites contained B-10-enriched (B-10/B-11 = 11.5) boron either as boron powder or as B₄C made from the B-10-enriched boron. These were baked at 2000°C and irradiated in BG-2. They showed a marked tendency to bow. The bow was caused by the accelerated axial expansion of that portion of the specimen exposed to thermal neutrons. For example, the specimens made with B-10-enriched boron powder (see 4465-24, Table 8) expanded axially about 13% on the surface in the thermal-neutron window and 9% on the opposite shielded side. This effect was present but less pronounced in the specimens made with B-10-enriched B₄C. They expanded 7% on the surface exposed in the thermal-neutron window and 5% on the shielded side. A photograph of one specimen displaying the bowing effect is shown in Fig. 52. The average dimensional change due to irradiation of these specimens is shown in Fig. 53. The graphite containing B-10-enriched B₄C or boron powder showed much larger dimensional changes than were observed with nonboronated or boronated graphite containing natural or B-10-depleted boron. The dimensional changes in the B-10-enriched boronated graphite showed the same anisotropic character as the changes in the nonboronated material.

This observation suggests that the dimensional change in the boronated graphite was probably controlled by accelerated change in the graphite matrix rather than swelling of randomly oriented B₄C or boron particles. Boron atoms in solution in graphite have been shown to produce accelerated dimensional change during irradiation (Ref. 18). However, swelling of B₄C granules during irradiation has also been demonstrated here and elsewhere (Ref. 13).

Generation of helium gas bubbles and other damage within the B₄C crystal lattice lead to volume swelling (Ref. 14) proportional to B-10 fission density. However, irradiation-induced change in dimension of graphite precipitated at the grain boundaries in B₄C containing excess carbon is suggested here as

M33626-1

SIDE

M33626-2

TOP

Fig. 52. Boronated graphite made with B-10-enriched (91% B-10) boron powder, 0.11 g boron/cm³ (shielding equivalence ~ 0.55 g natural boron/cm³); irradiated at $700^\circ \pm 50^\circ\text{C}$ to a fast-neutron exposure of 4.5×10^{21} n/cm³ ($E > 0.18$ MeV). Note the specimen bow showing greater expansion on the side with the highest B-10 burnup; material 4465-24, specimen 4-4 (scale 0.1 in./div.)

Fig. 53. Irradiation-induced dimensional change in B-10-enriched and nonboronated graphite baked at 2000°C and irradiated at 700° ± 50°C (filler GP-38 graphite powder <48 μm, C₀ 6.73 Å, L_c 770 Å)

a potential source of B_4C dimensional change. This mechanism (represented in Fig. 33) could contribute to the observed tendency of boronated graphite (natural boron) to swell during irradiation independent of the B-10 burnup gradient. Dimensional changes exhibited by shielded and nonshielded specimens of two boronated and one nonboronated graphite from BG-1 are shown in Fig. 54. The B-10 burnup gradient experienced by the specimens is shown in Fig. 10 and the average dimensional change in Table 3. There were three or 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.). Observations of cylindrical specimens of boronated graphite containing natural boron in BG-2 revealed no bowing and were consistent with the results of BG-1.

Swelling of boronated graphite due to B-10 fission fragment damage in the matrix has been postulated (Ref. 19). In the materials used here, the B_4C size range was 50 to 150 μm in 3912-34 and 100 to 400 μm in the other boronated graphites containing natural boron. No accelerated swelling rate was observed in the material with the small particle size range, so the proposed mechanism is not important in the B_4C size range used here.

There was no apparent gradient in microstructural effects in B_4C due to thermal-neutron shielding such as might be expected if B-10 fission were important to the observed void and crack formation in B_4C . The granules at the centers of boronated graphite specimens exhibited cracks as frequently as granules fully exposed to thermal neutrons.

These results seem to conflict with the swelling of B_4C expected from the observations that B_4C made with B-10-depleted boron exhibited reduced void volume at grain boundaries (see Fig. 18). In addition, piggyback samples of B_4C showed definite density decrease with increasing B-10 fission density independent of fast-neutron exposure (see Table 10 and Fig. 41).

The above observations suggest that at least two mechanisms for dimensional change in boronated graphite compete. It would seem that dimensional

Fig. 54. Effect of specimen size and thermal-neutron shielding on irradiation-induced dimensional change; all specimens were irradiated in the BG-1 experiment

change in boronated graphite can be minimized by fabrication processes which minimize both the quantity of B-10 atoms in solution in the graphite matrix and the volume loading of B_4C . For example, saturating the matrix with B-11 atoms prior to the introduction of B-10-enriched B_4C might be a process capable of yielding a desirable control material with irradiation properties very similar to those of nonboronated graphite.

3.2. HAFNATED GRAPHITE

The hafnated graphite specimens were unchanged in appearance by the irradiation. Dimensional change measurements were made on the specimens in the hot-cell facility because of the high radioactivity of the specimens (~ 250 R/hr, $B + \gamma$ at 6 in.). While the appearance of the specimens was unchanged from the unirradiated condition, the abrasion resistance was relatively low and under the pressure of the micrometer anvil some chipping and crumbling was observed. However, the crush strength was relatively high. The results of the dimensional change measurements are given in Table 8 and shown graphically in Fig. 55. It can be seen that the higher-temperature bake had a slight effect in reducing axial expansion during irradiation. The hafnated graphites expanded axially less than the nonhafnated graphite. However, the hafnated graphites experienced a net volume expansion, whereas the nonhafnated graphite showed a net volume contraction. A complicating feature in comparing the performance of the hafnated and nonhafnated graphite is the difference in anisotropy as shown by the coefficient of thermal expansion. The nonhafnated graphite had a much more anisotropic structure than the hafnated graphite, and that condition as well as the addition of HfC could be expected to influence the relative dimensional changes during irradiation. The results of this work show that hafnated graphite can be expected to perform satisfactorily under HTGR conditions.

Fig. 55. Irradiation-induced dimensional change in hafnated (HfC + graphite) and nonboronated graphite baked at 2000° or 2600°C and irradiated at 700° ± 50°C

4. CONCLUSIONS

The primary conclusions derived from the BG-1 and BG-2 irradiation experiments are summarized below.

1. Extruded boronated graphite of the type in the Peach Bottom HTGR (28 wt-% boron) expands perpendicular to the extrusion direction and contracts parallel to the extrusion direction when irradiated at $700^{\circ} \pm 100^{\circ}\text{C}$ to fast-neutron exposures up to $6.1 \times 10^{21} \text{ n/cm}^2$ ($E > 0.18 \text{ MeV}$).
2. Warm-pressed boronated graphite of the type to be used in the Fort St. Vrain HTGR (22 to 43 wt-% boron) expands in both the radial and perpendicular directions when irradiated at $700^{\circ} \pm 100^{\circ}\text{C}$ to fast-neutron exposures up to $7 \times 10^{21} \text{ n/cm}^2$ ($E > 0.18 \text{ MeV}$).
3. Dimensional change during irradiation of boronated graphite exhibits a direct correlation with fast-neutron exposure.
4. The magnitude of expansion or contraction in either direction becomes greater with increasing anisotropy of the boronated graphite.
5. In boronated graphite containing B_4C made with natural boron (19.8 at.-% B-10), B_4C particle size greater than $50 \mu\text{m}$ (325 mesh), and bake temperatures of 1000° to 2200°C , the dimensional change is not influenced by the B-10 isotope burnup gradient or specimen size.
6. Boronated graphite baked at 2000°C undergoes less dimensional change during a given irradiation than material baked at 1000°C .

7. The presence of up to 3 wt-% B_2O_3 in the B_4C addition to boronated graphite caused no difference in irradiation-induced dimensional change relative to boronated graphite made with leached B_4C .
8. The amount of B_4C in boronated graphite has no significant effect on dimensional change in the range 22 to 43 wt-% boron.
9. The use of boron enriched in B-10 isotope in boronated graphite causes increased volume expansion during irradiation relative to graphites containing natural boron of equal B-10 isotope content.
10. Boronated graphites made with B-10-enriched boron powder expands more during irradiation than graphite with the same B-10 isotope content in the form of B_4C granules.
11. Irradiation-induced dimensional change in boronated graphite is not sensitive to B_4C particle size in the B_4C size range 50 to 400 μm .
12. Loose granules of B_4C swelled during irradiation ($\sim 13\%$ decrease in density at 100% B-10 depletion) due to the internal generation of helium and swelling of graphite precipitates at B_4C grain boundaries. However, dimensional change in boronated graphite is not sensitive to B_4C swelling since B_4C content and B-10 burnup did not correlate with dimension change.
13. Irradiation-induced dimensional change in boronated graphite can be reduced by the use of fabrication techniques which minimize the amount of B-10 isotope in solution in the graphite matrix.
14. Control of anisotropy of boronated graphite and amount of B-10 isotope in solution in the graphitic matrix offers the most effective means to control the irradiation-induced dimensional change properties of boronated graphite.

15. Neutron irradiation causes a decrease in thermal conductivity and an increase in the coefficient of thermal expansion in boronated graphite.
16. Hafnated graphite is satisfactory for HTGR service.
17. Hafnated graphite (90 wt-% hafnium) expanded in both directions during neutron irradiation. The expansion in the perpendicular direction was less than 1.7% after irradiation at $700^{\circ} \pm 50^{\circ}\text{C}$ and fast-neutron exposure up to $6 \times 10^{21} \text{ n/cm}^2$ ($E > 0.18 \text{ MeV}$).
18. Loose granules of HfC irradiated at $550^{\circ} \pm 50^{\circ}\text{C}$ to a fast-neutron exposure of $5.5 \times 10^{21} \text{ n/cm}^2$ ($E > 0.18 \text{ MeV}$) showed no change in visual appearance or microstructure.

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