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RADIATION EFFECTS IN BORIDES

Part I — Helium Release and Swelling in Irradiated Borides

By
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February 13, 1962

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February 13, 1962

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INTRODUCTION

This report is the first of a series of three covering the effects of reactor radiation on boron and some binary borides irradiated to boron-10 burnups up to 99%.

Part II will deal with sintering effects observed in some of the borides irradiated as powders, and Part III will report the x-ray diffraction analysis of the crystallographic changes resulting from irradiation.

Interest in boron and borides for control rod applications centers on the $1/v$ high neutron capture cross-section of the B-10 isotope, which comprises one of every five atoms in natural boron. The principal deterrent to the use of borides (or any boron material) in nuclear reactors is associated with the helium and lithium produced when the boron captures neutrons. Each capture event results in the destruction of one boron-10 atom and the creation of one lithium-7 atom and one helium-4 atom. This, in effect, is the replacement of one small atom by two larger ones, and it is not surprising that most boron-containing materials exhibit swelling after appreciable neutron dosage.

Early work on boron carbide by Tucker and Senio⁽¹⁾ in 1954 led them to conclude that at low B-10 burnups the good helium retention of boron carbide was due to the rather open crystal structure of this compound. Later work by Hamman and Schall⁽²⁾ indicated that zirconium diboride (with a relatively close packed structure) was superior to boron carbide in helium retention. Holden⁽³⁾ proposed irradiating a variety of borides in order to assess the relationship of crystal structure to helium retention and structural changes. This was the principal objective of the work being reported.

A secondary objective was to compare the irradiation behavior of powders and dense solids. Another objective was to compare the behavior of borides with similar crystal structures but having metal atoms with vastly different absorption cross-sections, for example, zirconium and hafnium diborides.

MATERIALS AND CHARACTERIZATION

Four different structural classes of borides were selected for irradiation:

1. Boron and boron carbide - rhombohedral structure.
2. Hexaborides - cubic structure.
3. Tetraborides - tetragonal structure.
4. Diborides - hexagonal structure.

The materials used in these irradiations ranged from the rather impure borides that were obtained commercially at the beginning of the study, to the quite pure materials that we later prepared in our laboratory. Borides are now commercially available of much improved quality and with better control of stoichiometry and purity.

The borides that were purchased or prepared as powders were characterized by the following procedures:

1. Composition by wet chemical and spectroscopic analysis.
2. Structure by x-ray diffraction analysis
3. Particle size by electron microscopy and gas sedimentation.
4. Surface area by gas adsorption measurements.

The powder characteristics as determined by these methods are listed in Table I.

In general, the borides used were prepared by reacting the metal oxide with boron at temperatures above 1500 C. The commercial rare earth boride powders that had been prepared in hydrogen gave very broad x-ray diffraction peaks, comparable to those obtained with crystallites smaller than 1000 angstroms. Both adsorption type surface area measurements and examination by electron microscopy failed to show particles small enough to broaden the x-ray lines. We found that heating the powders to above 1700 C in vacuum resulted in sharpening of the x-ray peaks without change in lattice parameters.

Analysis of the gases removed during the high temperature treatment showed mainly hydrogen. It appears that the hydrogen was responsible for the observed line broadening, either by producing lattice strains or plastic deformation. ⁽⁴⁾ It is interesting to note that only a small amount of hydrogen was removed by the high temperature vacuum treatment, even in the case of powders outgassed at 2200 C. Larger amounts of hydrogen were found to have been released from some of these same borides during irradiation and/or during post-irradiation heating.

TABLE I
BORIDE POWDER CHARACTERISTICS

Mat'l	Source	Chemical Analysis	Spectroscopic Analysis	X-Ray Diffraction	Particle Size Microns	Surface Area m ² /gm
BN	C	97.5% BN 2.4% B ₂ O ₃ 0.3% other oxides		Hexagonal BN	50% < 10μ	6.07
B (Enr.)	A	97.2% B 0.88% C 0.16% Fe	(93.3% B-10 by mass spec.)	Rhombohedral B	50% < 70μ	0.27
B (Nat.)	B	99.6% B	< 0.1% Mg, Fe, Cu, Ca < 0.01% Al, Si, Cr	Rhombohedral B	< 1μ	4.79
TiB ₂	D	69.0% Ti 29.6% B	< 1.0% Fe < 0.1% Al, Cr < 0.01% Mg, Si, Cu, Ca	Hexagonal TiB ₂	50% < 10μ	< 1
ZrB ₂	D	81.2% Zr	< 0.01% Al, Ca, Mg Si, Fe, Cr, Cu	Hexagonal ZrB ₂ + Monoclinic ZrO ₂	50% < 6μ	< 1
HfB ₂	D	87.1% Hf 11.2% B	< 1% Mg, Fe < 0.1% Si, Cr, Ca < 0.01% Ti, Mn, Cu	Hexagonal HfB ₂ + Cubic HfO ₂	50% < 12μ	0.25
B ₄ C	E	72.2% B	< 1% Fe < 0.1% Al, Sn, Mg, Cu < 0.01% Zn, Mo, Ti	Rhombohedral B ₄ C + Graphite	50% < 10μ	< 1
YB ₄	D	25.6% B	< 1.0% Si, Al < 0.1% Fe, Mg < 0.01% Ca, Cr, Cu	Tetragonal YB ₄ + Cubic YB ₆	50% < 16μ	< 1
YB ₆	D	37.93% B	< 1% Mg, Al < 0.1% Si, Fe < 0.01% Ca, Cr, Cu	Cubic YB ₆ Tetragonal YB ₄ Cubic YB ₁₂	50% < 9μ	< 1
CaB ₆	D	52.3% B	"	Cubic CaB ₆ + Ca ₃ (BO ₃) ₂	50% < 10μ	< 1
SmB ₆	D	30.3% B	< 0.1% Mg, Al < 0.01% Si, Fe < 0.001% Cu, Cr, Ca	Cubic SmB ₆ + Hexagonal SmBO ₃	50% < 10μ	< 1
EuB ₆	D	30.3% B	"	Cubic EuB ₆	50% < 10μ	< 1
DyB ₄	F	21.2% B	< 0.01% Al, Ni, Cr, Ca	Tetragonal DyB ₄	50% < 20μ	--
DyB ₆	F	31.6% B	"	Cubic DyB ₆ + Tetragonal DyB ₄	50% < 20μ	--

- A. A.E.C.
B. Cooper Metallurgical Associates
C. Carborundum Company
D. Technical Research Group
E. Norton Company
F. Vallecitos Atomic Laboratory

PREPARATION AND ENCAPSULATION OF SAMPLES

Borides were irradiated as fine powders, as dense self-bonded polycrystalline bodies, and in one case as a single crystal.

The powders were prepared for irradiation by dry compacting in a metal die at pressures of approximately 50,000 psi. The powder compacts were then inserted into the aluminum holders and finally into the aluminum capsule. The capsule used in the powder irradiations is shown in Figure 1.

Before the final closure weld was made the capsules containing the materials to be irradiated were given a final outgassing treatment under vacuum at 400 C for 16 hours. The capsules were then stored in an argon atmosphere or vacuum until making the final closure weld. The final weld was made in an argon filled welding box. After holding 16 hours in 100 psi helium the welded capsules were then tested for leak tightness using a mass spectrometer leak detector.

The dense solids were prepared by hot pressing the powders in vacuum⁽⁵⁾ at temperatures ranging from 1900 to 2300 C. Spectroscopic analysis of the borides after hot pressing showed a considerable reduction in the more volatile impurities. For example, the change in impurity levels in boron carbide is shown in Table II.

The surfaces of the hot pressed solids were prepared by grinding and polishing with a diamond wheel. Encapsulation followed the same procedure outlined for the powders.

A segment of a single crystal rod of titanium diboride, grown by an arc fusion process,⁽⁶⁾ was encapsulated as above. However, a slightly modified capsule design was used for this sample as well as some of the later irradiations of the hot pressed solids. The modified capsule design is shown in Figure 2. In this design the sample is under no mechanical restraint other than the slight pressure of the spring.

IRRADIATION

All of the capsules were irradiated in the General Electric Test Reactor (GETR) for several cycles (approximately 22 days/cycle). The capsules were stacked vertically in standard GETR aluminum irradiation baskets and cooling was provided by the downward flow of water through a capsule-basket annulus of 1/8 inch. Water inlet and outlet temperatures were approximately 40 C and 50 C, respectively.

TABLE II

SPECTROSCOPIC ANALYSIS OF BORON CARBIDE
BEFORE AND AFTER HOT PRESSING IN VACUUM AT 2500°K

<u>Element</u>	<u>As-Received</u>	<u>After Vacuum Hot Pressing</u>	
Ba	50	--	
Mg	500	50	
Mn	2000	10	
Si	2000	2000	
W	10	--	
Fe	10000	1000	
Ni	2000	500	
Al	2000	500	
Cu	300	50	
Ag	--	--	
Cd	--	--	All data in parts per million (ppm)
Co	--	--	
Na	50	50	
Be	--	--	
Mo	--	--	
In	--	--	
Cr	2000	100	-- = Not detected (< 1 ppm)
Bi	--	--	S = Major constituent
Ga	--	--	* = Interference
Ti	50	10	
Pb	50	--	
Sb	--	--	
As	--	--	
Sn	1000	10	
Ta	--	--	
Ru	--	--	
Th	--	--	
Hf	--	--	
V	100	--	
B	S	S	
Ca	*	*	
Li	--	--	
Zn	--	--	
Cb	--	--	
Pt	100	1	
Zr	--	--

Figure 1. IRRADIATION CAPSULE - TYPE I

Figure 2. IRRADIATION CAPSULE - TYPE II

High flux inner core positions were selected in order to achieve maximum B-10 burnup rates. The average unperturbed thermal flux in these positions was 1.5×10^{14} nv, with an average peak of 2.3×10^{14} nv, and a maximum of 2.9×10^{14} nv at the start of cycle. Burnup rates changed during each cycle as a result of the axial shift of the peak flux from beginning to end of cycle, and varied from cycle to cycle in many samples as capsule positions were adjusted to accommodate other experiments. For the high burnup samples, irradiation times ranged from 7 to 12 cycles or 137 to 226 days. Radiochemical analysis of the Al - 0.01% Co flux wires, which were irradiated with the test capsules, revealed integrated thermal neutron flux values of 1.3×10^{21} to 2.3×10^{21} nvt, and time-averaged fluxes of 8×10^{13} to 1.9×10^{14} nv. Fast fluxes were not monitored; however, the fast (> 0.18 Mev) to thermal flux ratio in the test positions used was estimated to be 1.3.

None of the test capsules were instrumented for temperature monitoring, consequently sample operating temperatures were calculated. These calculations were based upon the following:

1. Heat generation consisted of the B-10 (n, α) Li-7 reaction energy of 2.5 Mev and an average gamma heating of 7 watts/gm in the sample and capsule parts. Activation product decay heat was neglected, except in the case of europium.

Because of frequent shifting of capsule positions from cycle to cycle and flux shifts during cycle, heat generation rates varied quite extensively during irradiation. Consequently an average heat rate was calculated from the total B-10 burnup and total irradiation time.

The highest average sample heat generation rate was 360 BTU/hr.

2. All heat was assumed to be transferred through both of the flat sample surfaces, and radially through the aluminum holder and capsule wall in the case of the Type I Capsule. In the case of the Type II Capsule, all sample heat was assumed to be transferred through the flat surface in contact with the capsule wall. Uniform heat transfer through the capsule wall to the flat top surface and upper 1/4 inch cylindrical surface of the capsule was assumed.

3. The contact coefficients of conductivity across the gaps were calculated to be 900 - 1000 BTU/hr-ft²-°F, and the water film coefficient to be 3000.
4. Temperature drops through the samples were based upon uniform gamma heating in the sample and surface heat generation from the (n,α) reaction. Thermal conductivity values were available for only three boride compounds (ZrB₂, TiB₂, and B₄C) and these ranged from 14 to 15 BTU/hr-°F-ft. Consequently, a value of 15 was assumed for all of the solid boride compounds. In the case of the powders, a single conductivity value was calculated on the basis of experimental data on the thermal conductivity of powders reported by Deissler and Eian.⁽⁷⁾ They found that the conductivity of 58% dense MgO powder in an argon atmosphere was 1.7% that of solid MgO at 260 C. This fraction was applied to the conductivity value assumed for the solid borides to obtain an approximate value for the powders.

The calculated operating temperature of the boride powders varied from 350 C to 550 C and of the solids from 200 C to 450 C.

POST-IRRADIATION EXAMINATION PROCEDURES

Following completion of irradiation, the test capsules were transferred to the Radioactive Materials Laboratory for examination. The examination and test procedures used are described below.

A. Gas Release Measurements

Before disassembly, each capsule was punctured and the released gas was sampled and quantitatively analyzed for helium and hydrogen. The sampling and analysis procedures are described as follows:

1. Sampling Procedure

The capsule is placed in a small open-ended cylindrical chamber with the capsule puncture diaphragm end at the chamber opening. An O-ring seal is then made between the chamber flange and the puncturing mechanism head which is connected to an out-of-cell vacuum and gas aliquoting system. After evacuating the capsule chamber, puncture head, vacuum lines, and aliquoting system to

a pressure of $< 10^{-2}$ Torr the capsule is punctured by hydraulically driving a hardened steel pin through the puncture diaphragm. The released gas is allowed to diffuse through the entire system until an equilibrium pressure is obtained as determined by a Zimmerli gauge. Four aliquots, amounting to 5-10% of the total released gas are then transferred from the pre-calibrated system volume to evacuated glass containers by means of a mercury aliquoting burette. Details of the sampling system are described in a report by Womack.⁽⁸⁾

2. Helium Analysis

Each gas aliquot is quantitatively analyzed for helium and hydrogen by gas chromatography as described below:

The glass container is connected to a Consolidated Electro-Dynamics Corporation chromatograph and the air in the glass tubulation and stop-cock bores is flushed out with argon. The gas sample is then introduced into the chromatograph with argon carrier gas. The gas passes through a molecular sieve and thence through a thermal conductivity cell. The change in conductivity resulting from He or H₂ in the gas flowing through the cell is recorded on a strip chart recorder. Total gas volumes are then determined by peak area correlation with calibration curves.

The over-all error in the gas release determination arise primarily from errors in sampling and chromatographic analysis. Of the two error sources, analysis is the larger contributor. The sampling error of the gas collection system has been previously determined by Womack⁽⁸⁾ and found to be $\pm 5\%$. This was based on a statistical analysis of the results of several fission gas release determinations made by Kr⁸⁵ counting. This error actually includes the Kr⁸⁵ counting error, so that the true sampling error is less than $\pm 5\%$. A check of the analytical error was made by introducing a known quantity of He into the gas aliquoting system, collecting aliquots of the introduced He, and analyzing the aliquots chromatographically.

This was done using several different known quantities of He. A comparison of the known volumes with those determined chromatographically revealed an analytical error of $\pm 10\%$. The total error of the He determination is therefore estimated to be less than $\pm 15\%$.

B. Capsule Disassembly

Following the gas release determination the capsules were cut open for removal of the flux wire and sample. After end cap removal, it was observed that the cylindrical aluminum sample holder had become stuck in nearly every Type I Capsule (Figure 1), thereby necessitating further cutting of the capsule body to extract the holder. Sticking of the holders was observed to be the result of sample swelling, which also caused the samples to become stuck in the holders. An attempt was made to mechanically remove one sample from its holder, but this resulted in extensive fragmentation of the sample. Consequently, it was decided to leave the samples undisturbed in their holders, and when necessary for other operations, remove them by dissolution of the holder in a caustic solution.

C. Visual Examination

After capsule disassembly, each sample was visually examined and photographed with a Kollmorgen periscope at magnifications up to 5X. In some cases, a Bausch & Lomb Stereo Viewer was used for additional examination.

D. Dimensional Measurements

Sticking of the samples in their holders precluded direct micrometer measurement of sample dimensions. Therefore, these measurements were made with a cathetometer, which was accurate to ± 0.002 inch, and/or by photography of the sample together with a 0.01 inch division scale at 5X magnification. Dimensions could then be measured from the photograph to within ± 0.003 inch. Thickness measurements were made on only those samples which were prepared for metallographic examination. Volume changes were calculated from the pre- and post-irradiation

dimensional measurements. In cases where post-irradiation thickness measurements could not be made, the thickness increases were assumed to be proportional to diameter increases for purposes of obtaining an approximate volume value.

E. Metallographic Examination

All of the samples selected for metallographic examination were first potted in Hysol epoxy resin. Thirty v/o alumina powder filler was added to the resin to reduce shrinkage during curing. Orientation of the sample is shown in Figure 3. Vacuum impregnation was used to ensure good penetration of the resin into any spaces between the sample and holder and into sample cracks. This was accomplished by the following procedure:

The sample was placed in a bakelite mold and the mold filled with liquid resin and placed in a vacuum chamber. The chamber was evacuated, held under vacuum for a few minutes, and returned to atmospheric pressure. This cycle was repeated several times. The resin was then allowed to harden at room temperature and atmospheric pressure.

After complete curing of the resin, the mounts were sectioned by means of a silicon carbide cut-off wheel using water as a coolant. The cuts were made along the sample diameters, thereby producing one-half for metallographic examination, and one-half for other experimental work (Figure 3). Following sectioning, the specimens were ground successively on 240, 400, and 600 grit SiC abrasive papers with water as a lubricant. Polishing was performed on a rotating cloth covered lap with a Buehler Automet sample holder. Only one stage was necessary to attain a final polish: Linde B alumina on nylon cloth.

F. Hardness Measurements

Microhardness tests were performed on the polished metallographic specimens by means of a modified Tukon Tester. All tests employed the Vickers diamond pyramid indenter. Loads varied from 50 to 200 grams, depending upon the hardness of the particular samples tested and the tendency of some grains to fragment under the higher loads.

Figure 3. ILLUSTRATION OF TECHNIQUE USED TO PREPARE SAMPLES FOR METALLOGRAPHY, He EVOLUTION DETERMINATIONS AND BURNUP ANALYSIS.

Figure 3. ILLUSTRATION OF TECHNIQUE USED TO PREPARE SAMPLES FOR METALLOGRAPHY, He EVOLUTION DETERMINATIONS AND BURNUP ANALYSIS.

G. Elevated Temperature Gas Evolution Measurements

Several samples were selected for measurement of helium and hydrogen evolution at elevated temperatures.

The experimental procedures employed in these measurements are described below:

Sample Preparation

All but two of the selected samples were also used for metallographic examination, thereby necessitating cutting of these samples into two halves. Details of this operation are described in Section E and illustrated in Figure 3. Separation of the specimens from the plastic mounts and aluminum holders was accomplished by dissolving the holder in a sodium hydroxide solution and the resin mount in methylene chloride. The freed specimens were then cleaned in dilute nitric acid, followed by water and acetone rinses. The two samples (B_4C , TiB_2) not mounted for metallography were freed by caustic dissolution of their holders. Prior to heating, each specimen was visually inspected and photographed to ensure that all of the resin was removed from the surface, and to provide a comparison for detecting changes in specimen appearance. Lastly, specimen densities were determined as described in Section II.

Heating and Gas Analysis

Sample heating runs were carried out in a specially designed in-cell resistance heated vacuum furnace.⁽⁸⁾ The Inconel-X furnace tube was connected to the out-of-cell vacuum and gas aliquoting system described in Section A. Furnace temperatures were recorded and maintained by means of a chromel-alumel thermocouple located between the sample and furnace tube wall and a potentiometer type recorder-controller. Temperature control limits ranged from ± 8 C at 300 C to ± 5 C at 1000 C.

Samples were contained in a stainless steel can which was vented with a small hole to permit release of the evolved gases. At the start of a heating run the furnace and associated vacuum system were evacuated to $< 10^{-2}$ Torr (static vacuum). The rate of air leakage into the

system was determined prior to making any runs by measuring the system pressure rise while operating the furnace at 1000 C. The pressure rise was found to be 10^{-4} Torr/min. indicating a leak rate of approximately 0.005 cm^3 (STP)/hr for the entire system.

Each sample was heated from room temperature to 1000 C under static vacuum. Temperatures were held at 300, 500, 750, and 1000 C for periods of 4 to 12 hours at each temperature. Total heating times ranged from 28 to 48 hours. Heating rates varied from 30 C/min. in the room temperature -300 C range, and 6 C/min. in the 750 C-1000 C range.

Gas evolution rates were monitored by taking periodic pressure measurements of the vacuum system with a Zimmerli gauge which was connected to the out-of-cell portion of the system. No temperature corrections were applied to the measured pressures because the furnace volume was only 15% of the total system volume. The fraction of the total gas which was evolved at each temperature was taken to be the fraction of the total pressure rise which was observed from the time a given temperature increase was started to the time the next increase was started.

After the completion of each heating run, the furnace was cooled to room temperature and aliquots of the evolved gases were taken and quantitatively analyzed for helium and hydrogen by gas chromatography as previously described in Section A.

Following gas sampling, the test specimens were removed from the furnace for visual examination and density measurements.

H. Density Measurements

Densities of the samples selected for post-irradiation heating experiments were determined by weighing them in air and in carbon tetrachloride. Penetration of small cracks and surface irregularities with the CCl_4 was ensured by vacuum impregnation prior to weighing. All of the samples were quite small ($< 1 \text{ gm}$), thereby limiting the precision of the measurements to ± 2 percent. In some cases the available sample fragments were so small ($\sim 100 \text{ mg}$) that reliable measurements could not be made.

I. Boron-10 Burnup Analysis

The fractional burnup of B-10 atoms in the boride samples was determined by mass spectrometric measurements of B-10/B-11 ratios. Since the concentration of the B-11 isotope does not change during irradiation, the depletion of the B-10 isotope can be determined by comparing the B-10/B-11 ratios before and after irradiation.

The analytical procedure used for this determination is as follows: the sample is first reduced to a fine powder by pulverizing in a Spex Industries Mixer Mill. It is then converted to sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$) by fusing with sodium carbonate. The sodium tetraborate is purified by converting to methyl borate which is distilled into a sodium hydroxide solution. Reaction with the sodium hydroxide converts the methyl borate back to sodium tetraborate. The purified tetraborate is deposited on a filament and run on a single stage surface ionization-type mass spectrometer. An intense Na_2BO_2^+ ion beam is produced in the mass spectrometer which allows the B-10/B-11 ratio to be measured at mass positions 88 and 89. The B-10 burnup is then calculated by means of the following equations:

$$\% \text{ B-10 burnup} = (1 - R_1/R_2) \cdot 100\%$$

$$\begin{aligned} \text{where: } R_1 &= \text{B-10/B-11 ratio of irradiated material} \\ R_2 &= \text{B-10/B-11 ratio of unirradiated material} \end{aligned}$$

Two natural boron standards were analyzed and the average B-10 concentration was found to be $19.8 \pm 0.1\%$ which is in precise agreement with the value reported by Brookhaven National Laboratory.⁽⁹⁾ This value was consequently used to calculate an R_2 value of 0.247 which was used in the burnup calculations of samples containing natural boron.

All of the samples were not analyzed because in many cases the amount of sample available for analysis after other tests were performed was so small that it was not considered to be representative of the entire sample. For those samples that were not analyzed, burnup values were calculated using the ratios of the integrated flux values (obtained from the Al-Co flux wires) of analyzed and unanalyzed samples.

RESULTS

A. Gas Release

Tables III, IV, and V show the results of the post-irradiation gas release and swelling measurements made on the borides.

The results obtained on the powders (Table III) indicate that the diborides are superior to the tetra and hexaborides in helium retention. The results obtained on the solids shows the same relative pattern, both during irradiation (Table IV) and on subsequent heating (Table V).

The relative fractional helium release, during irradiation, for the powders and solids are compared in Figure 4. The much greater relative release from the powders can be attributed to recoil of the helium to free surfaces and subsequent escape.

Table V shows the fractional helium release values obtained by heating segments of eight of the irradiated solid samples. The table also includes the fractional release during irradiation and the cumulative total. Hydrogen was also evolved from all samples during heating, and the amount remaining in the system after heating is expressed in terms of the mass of the sample (column 6). In all cases this number was lower than the actual amount of hydrogen released because some was lost through permeation of the Inconel heating chamber. This was verified analytically. Gas samples taken at 750 C contained more hydrogen than those at 1000 C.

Figure 4-A is a plot of percent helium release (cumulative) versus temperature for the eight borides that were heated following irradiation.

We had hoped to be able to determine helium diffusion rates during post-irradiation heating of these borides. However, lack of coherent geometry in the samples, concomittant helium and hydrogen evolution, and permeation of the hydrogen through the wall of the steel heating chamber, introduced large uncertainties into any attempt to make diffusion calculations on the basis of gas pressure measurements alone. The high temperature points on the curves represent the total amount of helium as determined by analysis. The intermediate points were obtained by calculation on the basis of pressure by assuming that the determined hydrogen to helium ratio was constant throughout the run.

TABLE III

GAS RELEASE AND SWELLING OF BORIDE POWDERS DURING IRRADIATION

<u>Sample</u>	<u>Density % Theo.</u>	<u>% B-10 Burnup</u>	<u>Fission Density F/cm³x10²¹</u>	<u>% He Released</u>	<u>H₂ Released cm³/gm Sample</u>	<u>% Volume Increase</u>	<u>Maximum Operating Temp. °C</u>
B(Nat'l)	54	90*	12.5	69	--	6 **	550
B-10 (93%)	65	15*	12.5	75	--	6 **	500
HfB ₂	59	93	7.4	13	--	7	500
TiB ₂	67	99*	10.3	2.7	--	7 **	450
VB ₂	64	96	9.6	27	33	7 **	400
ZrB ₂	58	99	7.5	9	--	7	400
YB ₄ -1	62	94	9.3	28	2.0	6 **	500
YB ₄ -2	70	99*	11.3	17	--	6 **	450
YB ₄ -3	63	98	10.1	22	--	7 **	450
B ₄ C	70	85	13.0	18	--	6	400
CaB ₆	67	96	10.9	60	--	6 **	350
EuB ₆ -1	61	68	6.8	61	--	5 **	550
EuB ₆ -2	53	65*	5.7	64	--	6	500
SmB ₆	60	63*	6.4	60	210	6 **	350
YB ₆	67	91	10.6	47	--	6 **	500

* Sample not analyzed - calculated value

** Thickness not measured

TABLE IV

GAS RELEASE AND SWELLING OF BORIDE SOLIDS DURING IRRADIATION

<u>Sample</u>	<u>Density % Theo.</u>	<u>% B-10 Burnup</u>	<u>Fission Density F/cm³x10²¹</u>	<u>% He Released</u>	<u>H₂ Released cm³/gm Sample</u>	<u>% Volume Increase</u>	<u>Maximum Operating Temp. °C</u>
B (Nat'l)	100	31*	8.1	2.2	--	32 ^a	200
B-10 (93%)	100	10*	12.0	89	--	38 ^a	250
BN	97	99*	9.9	84	(3.4% N ₂)	14 ^a	250
HfB ₂	83	87	10.1	0.3	0.9	15	250
TiB ₂	97	67*	9.8	1.1	--	40 ^a	250
TiB ₂ ‡	100	23	3.5	2.7	--	Fragmented	450
VB ₂	90	50	8.1	7.9	0.4	19	200
ZrB ₂	85	83*	9.1	3.6	--	25	200
B ₄ C	100	37*	8.1	11	--	36 ^a	250
YB ₄	95	62	9.5	4.9	3.5	23	250
DyB ₄	86	44*	5.5	39	--	Fragmented	300
DyB ₆	87	43*	6.3	82	--	Fragmented	300
EuB ₆	87	37	5.7	19	4.3	7	250
SmB ₆	86	44	6.4	18	--	15	250
YB ₆	92	42	6.7	14	--	12	200

‡ Single Crystal

* Sample not analyzed - calculated value

a Thickness not measured

TABLE V

GAS RELEASE OF IRRADIATED BORIDE SOLIDS DURING HEATING

<u>Sample</u>	<u>% B-10 Burnup</u>	<u>% Helium Release</u>			<u>Hydrogen Release (cm³/gram)</u>	
		<u>During Irradiation</u>	<u>After Heating to 1000°C</u>	<u>Total</u>	<u>During Irradiation</u>	<u>After Heating to 1000°C</u>
HfB ₂	87	0.3	31.3	31.6	0.9	1.31
TiB ₂	67	1.1	33.6	34.7	--	41.5
VB ₂	50	8	35	43	0.4	3.35
B ₄ C	67	11.4	33.3	44.7	--	145.0
YB ₄	62	4.9	51.0	55.9	3.5	13.1
EuB ₆	37	19	51.3	70	4.3	8.42
SmB ₆	44	18	82	100	--	3.06
YB ₆	42	14	86	100	--	6.24

Note Added In Press

In studying the curves showing the helium released as a function of temperature (Figure 4A), B. Weidenbaum pointed out that if one plots the points for the helium release and irradiation temperature obtained on the powders, these points also fall very near the curves for the solid samples. This suggests that the helium release from the powders may have been determined more by temperature than particle size. Although the latter cannot be ignored, especially in the case of boron which had a very small particle size.

Figure 4. FRACTIONAL RELEASE OF HELIUM FROM ELEMENTAL BORON AND BORIDE POWDERS AND SOLIDS DURING IRRADIATION.

Figure 4a. HELIUM RELEASED FROM BORIDES DURING POST-IRRADIATION HEATING

The data presented show a clear correlation between boride structure type and helium release. It appears that the open and/or badly damaged⁽¹⁰⁾ crystal structure of the irradiated hexaborides permits essentially complete release of the helium at 1000 C.

Nearly every investigator who has made gas release measurements from irradiated borides has observed hydrogen in some cases. The source or sources of this hydrogen remains to be adequately explained, although several possibilities exist.

As mentioned earlier, x-ray evidence suggests that the hydrogen may become tied up within the crystal lattice during preparation or processing in hydrogen. Another possibility is that the observed hydrogen was produced as a result of a reaction of the borides with adsorbed water. It has been reported⁽¹¹⁾ that the radiolytic decomposition of water is greatly enhanced in the presence of boron carbide. Another less likely probability is the decomposition of organic impurities to yield hydrogen.

B. Changes in Volume and Appearance

All of the irradiated borides had swelled to some extent, with low porosity solids exhibiting much larger changes in volume than the powder compacts. Column 7 of Tables III and IV show the measured volume changes. In general, the amount of swelling appears inversely related to the fraction of helium released and to the volume fraction of porosity available to accommodate the helium.

Diameter measurements made on the compacted powder samples revealed that swelling had proceeded to the point where the original diametrical clearances were closed and further expansion was restrained by the holders. When an attempt was made to remove the powder samples from their holders, it was discovered that they had changed from loose friable powders (before irradiation) to firm solids. These "radiation sintered" solids showed no evidence of cracking or fragmentation. At this point, this effect was investigated by metallographic analysis. The results of this investigation are described in Part II⁽¹²⁾ of this series of reports.

Examination of the hot pressed samples showed a definite effect of degree of restraint on the amount of swelling that occurred. It could be seen that the maximum swelling occurred in the direction of least restraint, that is, in the direction along the axis of the capsule, (Figure 1). The capsule wall acted as an effective restraining barrier to limit radial expansion.

Figures 5 and 6 show the pre- and post-irradiation appearance of the natural boron carbide and boron samples. Considerable swelling and some cracking has occurred.

Figure 7 shows the pre- and post-irradiation appearance of the enriched boron sample. It is interesting that this sample exhibited such a large volume increase at low burnup, especially since most of the damage would be expected at the surface.

Figure 8 shows the pre- and post-irradiation macroscopic appearance of three solid borides irradiated in Capsule Type II (Figure 2). This capsule was designed to minimize mechanical restraint and permit free expansion of the sample. The three unrestrained samples were severely fragmented.

This observed difference in behavior of the restrained and unrestrained samples is in agreement with the previous observations. Barney, Sehmel, and Seymour⁽¹³⁾ reported that boron carbide can undergo appreciable burnup if it is "firmly held". On the other hand, Valovage⁽¹⁴⁾ found extensive fragmentation of a boron carbide disk that was irradiated unrestrained.

Table VI lists the results of density measurements made on the segments of the solid samples that were heated following irradiation. For comparison the pre-irradiation densities and the measured post-irradiation volume changes are also listed. In general, there was good agreement between the post-irradiation density values and volume change measurements. The observed increase in density following heating can be attributed to the loss of lithium, hydrogen, and helium.

The pre- and post-heating appearance of some of the sample segments are shown in Figures 16 and 17.

TABLE VI

BORIDE DENSITY CHANGES

<u>Sample</u>	<u>Density-gm/cm³</u>			<u>Pct. Vol. Change During Irrad.*</u>	<u>Pct. Change in Density</u>	
	<u>Pre-Irrad.</u>	<u>Post-Irrad.</u>	<u>Post Heating</u>		<u>During Irrad.</u>	<u>During Heating</u>
HfB ₂	9.23	7.86	8.42	+ 15	- 15	+ 7
TiB ₂	4.37	**	**	+ 40	--	--
VB ₂	4.60	3.95	4.04	+ 19	- 14	+ 2
B ₄ C	2.54	**	**	+ 36	--	--
YB ₄	4.25	3.59	3.53	+ 23	- 16	- 2
EuB ₆	4.30	3.79	4.29	+ 7	- 12	+ 13
SmB ₆	4.33	3.58	4.09	+ 15	- 17	+ 14
YB ₆	3.46	3.03	3.11	+ 12	- 12	+ 3

* Based on dimensional measurements of entire sample.

** Sample segment too small for accurate density measurement.

C. Lithium Migration

A white deposit (probably lithium oxide) was evident to some extent on all of the boride surfaces examined after irradiation. It was also observed on the adjacent surfaces of the aluminum holders. In general, the white material was more pronounced in the case of the powders; however, large amounts were observed on the surface of the hot pressed boron-10 sample after some days following removal from the capsule (Figure 7). Close inspection of the surface showed what appeared to be columns of white material being extruded to the surface from micro cracks and pores. Assuming that the lithium collects at free surfaces, it would be oxidized in air and the pressure created by the volume change would force it out of the body. To determine how much of the generated lithium was located at the sample surfaces, fragments from the dysprosium tetra- and hexaboride samples (Figure 8) were collected and leached with distilled water at room temperature for twenty-four hours. Chemical analysis of the leach solution showed that 21% of the lithium generated in the dysprosium tetraboride and 19% of the lithium generated in the dysprosium hexaboride was leached from these samples. A small amount of the white material was scraped from one of the sample holders and analyzed by x-ray diffraction. However, the results of this analysis were inconclusive.

D. Metallography

Figures 9, 10, and 11 show the pre- and post-irradiation macroscopic and microscopic appearance of the irradiated diborides of hafnium, vanadium, and zirconium. Following irradiation, the hexagonal vanadium diboride showed a rather marked loss of optical activity when viewed under polarized light. As can be seen from the pre- and post-irradiation photomicrographs (Figure 10) the irradiated surface appears nearly isotropic. Figure 12 shows the pre- and post-irradiation macroscopic and microscopic appearance of the tetragonal yttrium tetraboride.

Figures 13, 14, and 15 show the pre- and post-irradiation appearance of the cubic hexaborides of yttrium, samarium and europium. The steep burnup gradients can be seen in the cross-sectional views of all these samples in Section AA (pages 38-40). The marked increase in porosity in the higher burnup peripheral regions can be seen in the 100X photomicrographs.

E. Hardness Changes

The pre- and post-irradiation hardness measurements made on two diboride and two hexaboride samples are compared in Table VII. These data reveal that the borides undergo pronounced softening during irradiation. The fact that the outer surface regions underwent significantly greater decreases in hardness than the central region shows that this effect is directly related to the amount of B-10 burnup. This is in agreement with x-ray diffraction data which show the radiation damage of the boron compounds is greater at the surface than in underlying zones.

TABLE VII
HARDNESS CHANGES IN IRRADIATED BORIDES

<u>Sample</u>	<u>Average Hardness - VHN</u>		
	<u>Pre-Irradiation</u>	<u>Post-Irradiation</u>	
		<u>Surface</u>	<u>Center</u>
ZrB ₂	1600 (c)	600 (c)	700 (c)
VB ₂	1400 (a)	650 (b)	1050 (b)
YB ₆	3000 (a)	1150 (b)	1400 (b)
SmB ₆	2200 (b)	1100 (b)	1700 (b)

(a) 50 gm load

(b) 100 gm load

(c) 200 gm load

DISCUSSION AND RECOMMENDATION FOR FUTURE EXPERIMENTS

Helium release in irradiated borides appears to be a structure sensitive phenomenon. The close packed crystal structures retain more helium than the more open crystal types. At the macroscopic level this generalization also appears valid. Those borides having the least porosity were superior in helium retention, providing they were under some mechanical restraint. Those borides of low porosity, such as the vacuum hot pressed polycrystalline solids and the arc fused titanium diboride single crystals, that were irradiated unrestrained showed extensive fragmentation. Furthermore, the fragmented samples gave much higher helium release values than borides with similar structures irradiated under restraint.

It is apparent from the work on borides and from similar observations on UO_2 ⁽¹⁵⁾ that mechanical restraint is an important parameter in limiting both swelling and/or fragmentation in these refractory fissionable materials. What is not yet clear is the influence of restraint on gas release. One experiment that is indicated is to irradiate a single crystal under mechanical restraint (say imbedded in a metallic matrix) and observe whether swelling and/or gas release is inhibited thereby. Another experiment that is indicated is the irradiation of a polycrystalline diboride with varying percentages of closed porosity.

The following relationship between the amount of swelling, helium retained, closed porosity, and mechanical restraint, seems to exist in irradiated borides:

$$\text{Swelling} \propto \frac{\text{helium retained}}{\text{closed porosity and mechanical restraint}}$$

The question of the mechanism whereby these brittle refractory materials can deform plastically at low temperatures is one that deserves study. Some measure of understanding might be gained by making pre- and post-irradiation texture analyses of those materials exhibiting radiation-deformation. By varying the amount of initial preferred orientation and mechanical restraint during irradiation one might hope to learn something of the deformation process.

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Figure 5. B₄C BEFORE AND AFTER IRRADIATION TO 37% B-10 BURNUP.

5X
After Removal From Al Holder

Figure 6. NATURAL BORON AFTER IRRADIATION TO 31% B-10 BURNUP.

M1391

5 X

Pre-Irradiation

R15978

5 X

Post-Irradiation. Shortly after capsule was opened.

R17133

5 X

Two weeks after capsule was opened.
Note formation of white Li compound

**Figure 7. ENRICHED BORON (93% B-10) BEFORE
AND AFTER IRRADIATION TO 10% B-10 BURNUP**

Figure 8. BORIDES BEFORE AND AFTER IRRADIATION. SAMPLES UNRESTRAINED DURING IRRADIATION (See Fig. 2)

M902

5X

M929

250X

Pre-Irradiation

R13465

5X

R11897

250X

Post-Irradiation

R11818

Section A - A

5X

Figure 9. HfB_2 BEFORE AND AFTER IRRADIATION TO 87% B-10 BURNUP. ALL MICROS AS POLISHED.

M902

5X

M855

Polarized Light

250X

Pre-Irradiation

R15180

5X

R8329-4

Polarized Light

250X

Post-Irradiation

R8329-1

5X

Section A - A

Figure 10. VB_2 BEFORE AND AFTER IRRADIATION TO 50% B-10 BURNUP.

Figure 11. ZrB_2 BEFORE AND AFTER IRRADIATION TO 83% B-10 BURNUP. ALL MICROS AS POLISHED.

Figure 12. YB_4 BEFORE AND AFTER IRRADIATION TO 62% B-10 BURNUP. ALL MICROS AS POLISHED.

Figure 13. YB_6 BEFORE AND AFTER IRRADIATION TO 42% B-10 BURNUP. ALL MICROS AS POLISHED.

M 902

5 X

Pre-Irradiation

R13477

5 X

Post-Irradiation

R 8331-1

5 X

Section A - A

Post-Irradiation

R 8331-3

100 X

Figure 14. SmB_6 BEFORE AND AFTER IRRADIATION TO 44% B-10 BURNUP.

M902 Pre-Irradiation 5X

R13456 Post-Irradiation 5X

R11824 Section A - A 5X

Figure 15. EuB_6 BEFORE AND AFTER IRRADIATION TO 37% B-10 BURNUP.

Before

After

R13644

5X

R13667

5X

Yttrium Tetraboride

R13668

5X

R13639

4X

Yttrium Hexaboride

R13477

5X

R13671

5X

Samarium Hexaboride

Figure 16. IRRADIATED TETRA AND HEXABORIDE SAMPLES
BEFORE AND AFTER HEATING TO 1000°C

Figure 17. IRRADIATED DIBORIDE SAMPLES BEFORE AND AFTER HEATING TO 1000°C

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