GEAP-3743

(PART II)

RADIATION EFFECTS IN BORIDES

Part II. Fission Sintering of Boride Powders

By

E. W. Hoyt

D. L. Zimmerman

February 15, 1962

Vallecitos Atomic Laboratory
General Electric Company
San Jose, California

DISCLAIMER

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

DISCLAIMER

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

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

This report has been reproduced directly from the best available copy.

Printed in USA. Price \$0.50. Available from the Office of Technical Services, Department of Commerce, Washington 25, D. C.

RADIATION EFFECTS IN BORIDES
PART II - FISSION SINTERING OF BORIDE POWDERS

By

E. W. Hoyt
D. L. Zimmerman

U. S. ATOMIC ENERGY COMMISSION
CONTRACT NO. AT(04-3)-189
PROJECT AGREEMENT NO. 4

February 15, 1962

APPROVED:

A. N. Holden
Manager, Metallurgy and Ceramics

B. Weidenbaum
Project Scientist

Atomic Power Equipment Department
Vallecitos Atomic Laboratory
General Electric Company
San Jose, California

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

TABLE OF CONTENTS

	<u>Page</u>
LIST OF FIGURES	iv
LIST OF TABLES	iv
INTRODUCTION	1
BORIDE POWDER CHARACTERISTICS	2
PREPARATION OF POWDERS FOR IRRADIATION	2
IRRADIATION	2
POST-IRRADIATION EXAMINATION	5
DISCUSSION	6
REFERENCES	18

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1.	Irradiation Capsule	9
2.	YB ₆ Powder Compact Before and After Irradiation to 91% B-10 Burnup	10
3.	EuB ₆ Powder Compact Before and After Irradiation to 68% B-10 Burnup	11
4.	Illustration of Technique Used to Prepare Metallographic and Burnup Samples	12
5.	B ₄ C Powder Compact Before and After Irradiation to 85% B-10 Burnup	13
6.	YB ₄ Powder Compact Before and After Irradiation to 99% B-10 Burnup	14
7.	Comparison of Microstructures of Unirradiated and Irradiated YB ₄ Powder Compacts	15
8.	ZrB ₂ Powder Compact Before and After Irradiation to 99.8% B-10 Burnup	16
9.	HfB ₂ Powder Compact Before and After Irradiation to 93% B-10 Burnup	17

LIST OF TABLES

<u>Table</u>		<u>Page</u>
I	Boride Powder Characteristics	3
II	Boride Powder Irradiation Data	4

INTRODUCTION

This is the second of a series of three reports describing the effects of reactor radiation on elemental boron and some binary borides.

The earlier report, Part I,⁽¹⁾ outlined the objectives of the irradiation study and presented an analysis of the helium release and swelling data obtained from samples of irradiated borides.

During the post-irradiation examination of the borides it was discovered that the samples which had been irradiated as powders had sintered into firmly bonded bodies. This radiation sintering occurred at temperatures hundreds of degrees below that required to produce similar interparticle bonding by the application of heat alone. This report discusses the results of the post-irradiation examination of some of these borides which were irradiated as powders and compares the results of our observations with the reports of similar radiation sintering occurring in other materials.

BORIDE POWDER CHARACTERISTICS

The boride powders irradiated were all obtained commercially and were the highest purity obtainable at the time. The as-received powders ranged in size from 5 to 200 microns as determined microscopically. To ensure uniformity of starting material, those powders showing large particle size were ground to less than 20 micron average diameter in a jet pulverizer.

The powders were then characterized as follows:

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.

PREPARATION OF POWDERS FOR IRRADIATION

The boride powders were compacted without a lubricant at 50,000 psi in a steel die. The resulting compacts (3/8" dia. x 1/8" thick) were 50 to 70% dense and rather fragile. After weighing and measuring, the compacts were placed in the recessed half of the aluminum sample holders, covered, and inserted into the irradiation capsules. A sketch of the capsule assembly is shown in Figure 1.

After outgassing at 400 C in vacuum to remove residual water and gases, the capsules were sealed by welding in an argon atmosphere.

IRRADIATION

All of the samples were irradiated in high flux (average thermal 1.5×10^{14} nv) positions of the General Electric Test Reactor. Details of the irradiation have been discussed in Part I of this report. ⁽¹⁾

The irradiation data for these samples are summarized in Table II.

TABLE I
BORIDE POWDER CHARACTERISTICS

Material	Source	Chemical Analysis	Spectroscopic Analysis	X-Ray Diffraction	Particle Size Microns	Surface Area m^2/gm
BN	C	97.5% BN 2.4% B_2O_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	1 μ	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	< 1% Mg, Al < 0.1% Si, Fe < 0.01% Ca, Cr, Cu	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	< 0.1% Mg, Al < 0.01% Si, Fe < 0.001% Cu, Cr, Ca	Cubic EuB ₆	50% < 10μ	< 1

A. A.E.C.
B. Cooper Metallurgical Associates
C. Carborundum Company

D. Technical Research Group
E. Norton Company

TABLE II

BORIDE POWDER IRRADIATION DATA

<u>Sample</u>	<u>Initial Density % Theoretical</u>	<u>% B-10 Burnup</u>	<u>Fission Density fissions/cm³ x 10²¹</u>	<u>Maximum Operating Temperature °C</u>
B (Nat)	54	90 *	12.5	550
B-10 (93%)	65	15 *	12.5	500
HfB ₂	59	93	7.4	500
TiB ₂	67	99 *	10.3	450
VB ₂	64	96	9.6	400
ZrB ₂	58	99	7.5	400
YB ₄ -1	62	94	9.3	500
YB ₄ -2	70	99 *	11.3	450
YB ₄ -3	63	98	10.1	450
B ₄ C	70	85	13.0	400
CaB ₆	67	96	10.9	350
EuB ₆ -1	61	60	6.8	550
EuB ₆ -2	53	65 *	5.7	500
SmB ₆	60	63 *	6.4	350
YB ₆	67	91	10.6	500

* Not analyzed - calculated value.

POST-IRRADIATION EXAMINATION

Visual examination of the samples after removal from the capsules revealed that all of the samples but one (EuB_6 -1) were stuck in the holder as a result of the swelling (5-7 v/o) which occurred during irradiation.⁽¹⁾ An attempt was made to remove the B_4C sample from its holder by probing with a sharp scribe. This operation revealed that the sample had been converted from a soft, friable powder compact, to a hard solid body. All of the other samples were subsequently checked in the same manner and, with the exception of the natural and enriched boron (which showed only slight evidence of sintering), were found to have undergone the same change. Further evidence of sintering is illustrated in Figure 2, which shows the yttrium hexaboride sample after it had fractured during an attempt to remove it from its holder by sectioning.

Figure 3 shows the appearance of one of the EuB_6 samples. This was the only sample to come free of its aluminum holder. The white material on the surface of this sample is believed to be lithium oxide.⁽¹⁾ Material of this type was also found on the surface of other samples.

Selected samples were prepared for metallographic examination by mounting in epoxy resin and sectioning with an abrasive cut-off wheel as shown in Figure 4. The sectioned samples were then prepared for microscopic examination by grinding through 600 grit silicon carbide and then polishing with $1\ \mu$ diamond on a nylon cloth covered rotating lap.

Attempts to prepare the EuB_6 -2 sample were unsuccessful. Large portions of the surface continually eroded away during preparation. This erosion indicates that the sample was in a much softer condition than the B_4C , YB_4 , HfB_2 , and ZrB_2 samples which were processed successfully.

Figure 5 shows the pre- and post-irradiation appearance of the boron carbide powder compact. It can be seen from the cross-section view that the compact has swelled beyond the top surface of the holder. The photomicrograph clearly shows the inter-grain bonding that had occurred. It is also significant that the cracks are trans-granular.

Figures 6 and 7 show the macro and microscopic appearance of the yttrium tetraboride compact before and after irradiation. It can be seen from Figure 7 that in addition to intergrain bonding, extensive micro-cracking and a general rounding of the grain corners had occurred.

An excellent example of "necking" and grain boundary disappearance can be seen in the zirconium diboride photomicrograph. (Figure 8).

The photomicrograph (Figure 9) of the hafnium diboride shows a nearly continuous network of interparticle bonds.

Because of the highly porous nature of these samples, attempts to measure micro-hardness were not successful.

DISCUSSION

In addition to our own observations, a number of workers⁽²⁻⁵⁾ have reported interparticle welding or sintering in irradiated materials containing a fissionable isotope (U-235 or B-10). There is some evidence that non-fissionable materials, such as Al_2O_3 , also sinter under the influence of ionizing radiation.⁽⁶⁾ We shall refer to the special case of the radiation sintering of fissionable material as "fission sintering".

Sintering has been defined⁽⁷⁾ as "the pore shape change, pore shrinkage, and grain growth which particles undergo during heating". Normally this process leads to shrinkage and densification of the aggregate mass. However, in the case of fission sintering there is the competing process of gas generation and swelling which undoubtedly masks any attempt to measure "sintering" in terms of macroscopic increase in density.

Four principal mechanisms of thermal sintering have been postulated. Sintering in most pure materials can be explained (and in some cases predicted) on the basis of one or more of these mechanisms. The four common mechanisms of sintering postulated are:

1. Bulk diffusion.
2. Plastic flow.
3. Vapor transport.
4. Surface diffusion.

Aitken⁽⁸⁾ has recently reviewed the manner in which radiation might influence the four modes of sintering as follows:

1. "Radiation can enhance diffusion rates by producing an increased concentration of vacancy-interstitial pairs and enhancing migration to suitable sinks by displacement."

2. "Radiation can alter the number and location of sinks for vacancies to migrate."
3. "Through recoil processes radiation can cause atoms to vaporize and recondense."
4. "Radiation can cause enhanced surface mobility."

In addition, in the special case of fissionable materials, the internal production of a fission product species such as lithium, strontium, or barium might act as a liquid phase additive which can also enhance sintering.

Details regarding the possible mechanisms of energy and material transport during irradiation have been indicated in the work of Silsbee,⁽⁹⁾ Noggle and Steiger,⁽¹⁰⁾ and Gibson, Coland, Milgran and Vineyard.⁽¹¹⁾ At the present time, however, the theories growing out of this work can only suggest controlled experiments or material-radiation interactions simpler than those which were considered.

In thin film work on UO_2 , Noggle and Steiger concluded that the principal mechanism of energy transfer from the fission fragment to the solid was by electron excitation and ionization. In this case the electric field associated with a moving charge can excite all electrons moving more slowly than it moves. The authors estimate that 85-90% of the fragment energy is transferred to the solid in this fashion. The remaining energy is transferred by nuclear encounters. They show that at a free surface the fragments dig a furrow through the solid, thereby displacing a considerable volume of material. This displacement probably does not occur within the bulk of the material because of the constraint offered by the surrounding solid.

Vineyard⁽¹²⁾ (working with computer calculations) has likened the agitation in the wake of an energetic knock-on to the production of locally high temperatures. Immediately after the most violent stages of a displacement event individual atoms appear to have agitations sufficiently chaotic to constitute thermal energy for intervals of $\sim 3 \times 10^{-13}$ sec. However, almost all excited atoms have cooled down to ambient by 10^{-12} sec. This kind of a thermal spike could conceivably produce enough material transport to effect or enhance localized welding of adjacent particles.

It is likely that no single mechanism can explain fission sintering. It is probable that several mechanisms are operative to some extent. The work of Noggle and Steiger suggests that surface mobility may be the dominant mechanism, although vaporization - condensation in the neighborhood of a fission event - may be equally important.

In order to gain a clearer understanding of the process of fission sintering, controlled irradiation experiments need to be done. Some of the parameters that should be examined for their relative importance might be as follows:

Radiation Variables

1. Fission rate.
2. Fission density.

Powder Variables

1. Particle size.
2. Surface area.
3. Stoichiometry.

A systematic study of the effects produced by these variables, preferably by electron microscopy techniques, should be helpful in getting a better understanding of the mechanism of fission sintering.

ACKNOWLEDGEMENT

The authors are indebted to R. E. Smith for performing the metallographic preparation of the samples.

Figure 1. IRRADIATION CAPSULE

M199

7X

Before Irradiation

V15088

5X

After Irradiation. Sample cracked during attempts to remove it from aluminum holder.

Figure 2. YB₆ POWDER COMPACT BEFORE AND AFTER IRRADIATION TO 91% B-10 BURNUP

M199

7X

Before Irradiation

V15079

5X

After Irradiation. Sample removed from holder. White surface deposit believed to be lithium oxide.

Figure 3. EuB_6 POWDER COMPACT BEFORE AND AFTER IRRADIATION TO 68% B-10 BURNUP.

Sample and holder vacuum potted in epoxy resin and sectioned along sample diameter.

Figure 4. ILLUSTRATION OF TECHNIQUE USED TO PREPARE METALLOGRAPHIC AND BURNUP SAMPLES

M199

7X

Before Irradiation.

V8324-1

8X

Cross-section A-A After Irradiation.

V8324-4

500X

Microstructure After Irradiation. As polished.

Figure 5. B_4C POWDER COMPACT BEFORE AND AFTER IRRADIATION TO 85% B-10 BURNUP.

A
↑

A
↑

M199

7X

Before Irradiation.

V8325-1

8X

Cross-section A-A After Irradiation.

V8325-3

500X

Microstructure After Irradiation. Gray phase is YB_6 .

Figure 6. YB_4 POWDER COMPACT BEFORE AND AFTER IRRADIATION TO 99% B-10 BURNUP.

M3180

1000X

Unirradiated

V8325-10

1000X

Irradiated

Figure 7. COMPARISON OF MICROSTRUCTURES OF UNIRRADIATED AND IRRADIATED YB₄ POWDER COMPACTS.

A
↑

M199

7X

Before Irradiation

A
↑

V8323-1

8X

Cross-section A-A After Irradiation

V8323-3

1000X

Microstructure After Irradiation. As polished.

Figure 8. ZrB_2 POWDER COMPACT BEFORE AND AFTER IRRADIATION TO 99.8% B-10 BURNUP.

Before Irradiation

Cross-section A-A After Irradiation.

Microstructure After Irradiation.
Gray phase is HfO_2 . As polished.

Figure 9. HfB_2 POWDER COMPACT BEFORE
AND AFTER IRRADIATION TO 93% B-10 BURNUP.

REFERENCES

1. Hoyt, E. W. and D. L. Zimmerman, "Radiation Effects in Borides", GEAP-3743, Part I - Helium Release and Swelling in Irradiated Borides.
2. Barney, W. K., et al, "Reactor Technology Report ND-8 Metallurgy", KAPL-2000-5, March 1959.
3. Barney, W. K. and B. D. Wemple, "Metallography of UO_2 Containing Fuel Elements", KAPL-1836, June 15, 1958.
4. Riehl, N., W. Marth, and R. Sizmann, "Effects of High Energy Radiation at the Surface of Solids". Transactions of the Fourth International Symposium on the Reactivity of Solids. D. Van Nostrand, Inc. (1961).
5. Ewing, R. A., D. N. Sunderman, "Effects of Radiation Upon Hafnium Diboride", BMI-1521, June 14, 1961.
6. Baskin, M. L., A. A. Semerchan, "Growth and Joining of Crystals Under the Influence of Ionizing Radiation", Vestnik Akademik Nauk SSSR, 28, 69 (1958).
7. Coble, R. L., "Sintering Crystalline Solids", I. Intermediate and Final Stage Diffusion Models, GE 60-RL-2594M, December 1960.
8. Aitken, E. A., "Sintering Characteristics in a Radiation Environment". Paper presented at the ASTM Symposium on "Radiation Effects in Refractory Fuel Compounds", Atlantic City, New Jersey, June 29, 1961.
9. Silsbee, R. H., "Focusing in Collision Problems in Solids", Journal of Applied Physics, Vol. 28, No. 11, November 1957.
10. Noggle, T. S. and J. O. Stieger, "Fission Fragment Tracks in UO_2 ". Paper presented at the ASTM Symposium on Radiation Effects, Atlantic City, New Jersey, June 1961.
11. Gibson, J. B., A. N. Goland, M. Milgrom, and G. H. Vineyard, "Dynamics of Radiation Damage", Physical Review, Vol. 120, No. 4, November 15, 1960.
12. Vineyard, G. H., "Discussion on Radiation Effects in Inorganic Solids". The Faraday Society (April 11-12, 1961).