PREIRRADIATION CHARACTERIZATION OF
B₄C PELLETS USED IN EXPERIMENTS ON HIGH-WORTH CONTROL RODS

Coordinated by

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EBR-II Project
Argonne National Laboratory
Argonne, Illinois - Idaho Falls, Idaho

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ABSTRACT

Approximately 250 natural-boron B₄C pellets were procured for use in EBR-II. This report characterizes the preirradiation properties of this material: specifically the density, the boron-to-carbon mole ratio, the total boron and carbon assay, the purity, and microstructure. In addition, a very unusual and essentially anomalous density gradient for the pellets, determined by 20-kV X-radiography, was evaluated.

I. INTRODUCTION

Some of the control rods in the EBR-II reactor can be removed and their positions used for inserting experiments with INSAT (Instrumented Subassembly Test Facility) and INCOT (In-core Instrument Test Facility) if the remaining control rods are increased in worth. Experiments were defined to study the effectiveness of high-worth control rods, and enough B₄C pellets to produce two such rods were obtained.

Previous use of B₄C pellets in the EBR-II was in conjunction with the oscillator-rod tests.* These pellets were produced in-house from elemental boron-10 and carbon powders. The required amounts of each constituent were blended and then calcined at 2000°C. The resulting B₄C cake was ground to - 325 mesh and hot-pressed in graphite tooling at 2000 - 2100°C. This material performed satisfactorily in the reactor.

*R. W. Hyndman and R. B. Nicholson, The EBR-II Feedback Function, ANL-7476, (July 1968)

The requirements for specifying the quality of the B_4C to be used in the high-worth control rods were obtained by characterizing the material that was prepared. From this information, a specification was written in March, 1969 (Appendix A).

The specification was intended to characterize a B_4C product that would perform adequately in the EBR-II without over-specifying unimportant parameters that could do little more than increase the cost. Typical of such unimportant parameters were: unnecessarily close dimensional tolerances that would require that the pellets be ground; and an arbitrary specific density requirement above the required minimum density of 2.33 g/cm^3 (93% of theoretical). The specification, therefore, carefully qualifies the B_4C for purity, B/C mole ratio, and ^{10}B content. However, the vendor can select the pellet density over the range from 93 to 100% of theoretical. The pellet diameter will depend on the density attained and will be maximum when the minimum density is obtained. The hot-pressed pellets can be used as is if they meet diameter requirements.

II. CHARACTERIZING B_4C PELLETS PRODUCED

A. Evaluation of Properties Having Specification Requirements

The pellets were produced by CERAC, Inc., Menomonee Falls, Wisc. The outer surfaces were as hot-pressed, but the ends were ground to meet the requirements for end squareness. Figure 1 shows the surface appearance of a group of five pellets typical of those used in the high-worth control rods. CERAC submitted a certificate of analysis based on the starting powder that conformed to the specification (Appendix B).

At ANL, the pellets were inspected to assure compliance with the specification. An incoming-inspection report lists the total pellet-stack length, total weight, and individual pellet diameter (Appendix B). However, the as-pressed diameter of an individual pellet was not uniform, and any diameter recorded would not be valid for comparison with values obtained at another time. Therefore, in only one stack of fourteen

Fig. 1. Typical Appearance of B₄C Pellets Used in High-worth Control Rods L4008S and L4009S

pellets were diameters of individual pellets measured. The results of the incoming inspection indicated that all the pellet stacks were within specified limits for stack length, weight, and diameter.

Results of a separate chemical analysis at Argonne National Laboratory (Appendix B) showed that all analytical requirements were within tolerance limits.

Density was measured by immersion in both water and carbon tetrachloride. The results indicate that pellets exist in at least two levels of densification. One group of three pellets had densities of 92.8 - 95.5% of theoretical, and another group of ten pellets had densities of 98.7 - 99.8% of theoretical. The high-density pellets did not absorb the immersion fluid, and equal densities were observed in either water or carbon tetrachloride. The lower-density pellets had open porosity that would absorb the fluid, and the indicated density increased with time in the fluid. The average density observed for the two groups was 2.38 g/cm^3 for the low-density group and 2.49 g/cm^3 for the high-density group.

B. Evaluation of Other Properties

In addition to the properties examined to determine how the pellets meet specification, three other properties were evaluated: weight loss, sodium compatibility, and density gradient. The weight loss at operating temperature to be expected for the pellets was determined by outgassing four pellets in vacuum at 1100°F for 1 hr. The weight loss was 0.009%. The activity of the pellets for moisture pickup or absorption from the air was considered to be negligible -- of the order of 0.0001 g in 5 min.

The compatibility of the pellets with sodium was not considered significant because the pellets will be used in a helium atmosphere. However, the effect of sodium on the B_4C pellets was evaluated by subjecting a pellet to sodium at 1112°F (cold-trap temperature, 230°F) for a total of eight days. The pellet remained intact but the surface was roughened. The pellet lost 0.11 mg/cm^2 at one-day and 0.41 mg/cm^2 at 2 day exposures.

A very unusual density gradient in some of the pellets was observed by radiographic examination. Evaluation revealed that a phase of high-density material transverse to the longitudinal direction existed in the center portion of most of the pellets. Figure 2 shows a radiograph of three pellets illustrating this phenomenon. In addition, high-density, crack-like lines running longitudinally along the pellets were visible. This radiograph was taken with soft X-rays (20 kV) that greatly intensify this condition. The transverse shadowlike lines at the top and bottom of each pellet are the outline of the tape used to hold the pellets in place during radiography.

This density gradient has been established as being due to a localized concentration of a high-density, second-phase impurity containing mostly iron, as identified by microprobe analysis; this phase occurs as a band around the pellet at the midplane and in longitudinal surface scratches. The results of metallographic examination of a longitudinal section (Fig. 3) show that the band (about 25 mils wide by 9 mils deep) extends around the pellet. Figure 4 shows an enlargement of the structure from the same area. Figure 5 shows the microstructure through a longitudinal section of another pellet at one end. None of the second-phase impurity is present; the sample has been etched to reveal the grain size. The center of the pellet has a coarser grain size and somewhat greater porosity than the ends.

III. FABRICATION

Procedures used to fabricate the pellets are not known in detail because the vendor considered his procedures proprietary. However, we believe that the pellets were produced by hot-pressing B_4C powder at $2100^\circ C$ in graphite tooling, with induction used for heating the tools.

IV. CONCLUSIONS

The quality of the B_4C pellets examined indicate the material is within tolerance limits of the specification and is satisfactory for use in the high-worth control rods in EBR-II.

Fig. 2. Radiograph of B₄C Pellet Showing Segregation of High-density Impurities

Fig. 3. Longitudinal Section of Pellet at Midplane Showing Band of Impurity Phase at Surface of B_4C Pellet

Fig. 4. Enlargement of Area Shown in Fig. 2

**Fig. 5. Longitudinal Section at Pellet End
Showing Grain Structure (Etched)**

APPENDIX A

Specification for Pellets

ARGONNE NATIONAL LABORATORY

Specification No. DW 70-69

Product Specification for Boron Carbide Pellets for
the EBR-II Higher Worth Control Rods

1.0 GENERAL INFORMATION

- 1.1 The Argonne National Laboratory will require a quantity of high-density boron carbide pellets for use in the EBR-II Reactor. The pellets will be used in a closed stainless steel jacket with a helium gas bond. The expected operating temperature will be 980°F.
- 1.2 The pellets are to be produced from boron carbide made from natural boron which contains 18.3 weight percent boron - 10.
- 1.3 The theoretical density of boron carbide shall be used as 2.51 grams per cubic centimeter.
- 1.4 The pellet diameter can vary between a given maximum and minimum value. The diameter will be a function of the final pellet density and the boron content.
- 1.5 Surface Condition
 - 1.5.1 It is intended that the pellets be supplied for use in the as-hot-pressed condition. If die washes are used that become part of the pellet, the extent of this reaction must be cleared with the Argonne National Laboratory before accepting the contract.

2.0 SCOPE

2.1 This specification defines the responsibilities of a vendor to provide boron carbide pellets for the higher worth control rod to be used in the EBR-II.

2.1.1 The vendor must obtain the starting boron carbide powder and characterize it for:

2.1.1.1 Boron content

2.1.1.2 Carbon content

2.1.1.3 Impurity content by spectrographic analyses for Fe, Al, Si, Mg, Ca and other observed impurities.

2.1.1.4 Particle size

2.2 The vendor must develop a manufacturing procedure and establish the parameters required to produce boron carbide pellets that will meet the length, diameter, boron-10 weight, and stoichiometry requirements set forth in this specification.

2.3 The vendor must establish a formal quality control and assurance program that will assure acceptable quality levels of the requirements listed below:

2.3.1 Pellet diameter

2.3.2 Fourteen pellet stack length

2.3.3 Boron-10 weight per fourteen pellet stack

2.3.4 Boron to carbon mole ratio

2.3.5 Boron carbide assay and purity

- 2.4 The vendor must establish packing and shipping procedures that will prevent damage or deterioration of the pellets from rough handling or moisture pick-up.

3.0 BORON CARBIDE PELLET REQUIREMENTS

3.1 Size (see drawing No. EB-1-39935A)

- 3.1.1 Individual pellets must have a diameter no larger than 0.549 inches, nor smaller than 0.534 inches. The pellet length must be 1.0 inch such that fourteen pellets will make a stack 14.00 ± 0.03 inches long.

3.2 Boron-10 weight per fourteen pellet stack $18.04 \pm .50$ grams.

3.3 Stoichiometry: The boron to carbon mole ratio must be from 3.9/1 to 4.1/1.

3.4 Boron carbide assay must be at least 98.0 weight percent boron and carbon.

3.5 Total impurity content must not exceed 2.0 weight percent.

3.5.1 Individual impurities must not exceed the following limits:

Fe 0.3 Max.
Al 0.5 Max.
Si 0.3 Max.
Mg 0.5 Max.
Ca 0.2 Max.
All others 0.2 Max.

3.6 Pellet Ends Condition

- 3.6.1 The pellet ends must be flat, parallel, and square with the sides within 0.002 inches.

4.0 PACKAGING

4.1 Groups of fourteen pellets which passed all the requirements of this specification shall be packaged and identified as a stack.

4.2 Characterization of the stacks

4.2.1 Each stack must be characterized for:

4.2.1.1 Total length

4.2.1.2 Total pellet weight (gms)

4.2.1.3 Total boron-10 weight (gms)

-----APPENDIX B

Analyses and Tests

Certificate of Analysis

October 7, 1969

To . . . Argonne National Laboratory
Argonne, Ill.

Order No. . . 658453

BORON CARBIDE PELLETS

Drawing EB1-39935A

1. Boron carbide powder, lot no. 21-091-991. B = 78.04%.
2. Boron carbide powder, lot no. 21-091-991. C = 21.28%.
3. Boron carbide powder, lot no. 21-091-991.

a) Semi-quantitative spectrographic analysis.

Si	0.1%	Fe	0.04%
Cu	0.001-0.01	Al	0.05-0.5
Mg	0.0001		no others visible

b) Calculated boron-to-carbon mole ratio, 4.06/1.

c) Boron + carbon total weight % = 99.68.

4. Each pellet has passed thru a "go, no-go" gauge of diameter 0.550" at the upper limit and 0.534" at the lower limit.

5. Final stacks have the following characteristics, using the values for boron-10 as follows:

19.78 atom %

18.31 wt. %

Ervin Colton

by Dr. Ervin Colton
Chief Chemist

Certificate of Analysis

Page 2

To . . . Argonne National Laboratory
Argonne, Ill.

Order No. . . 658453

<u>stack no.</u>	<u>stack length, in.</u>	<u>no. of pellets</u>	<u>total pellet wt/stack, gm.</u>	<u>total boron-10 wt/stack, gm.</u>
1	14.015	14	125.8	18.03
2	13.975	14	129.0	18.48
3	14.006	14	125.7	18.01
4	13.978	14	126.1	18.07
5	14.015	14	126.3	18.09
6	14.005	14	126.9	18.18
7	13.976	14	125.5	17.98
8	13.985	14	125.6	17.99
9	13.982	14	129.4	18.54
10	13.992	14	127.0	18.19
11	13.975	14	128.2	18.37
12	14.004	14	126.4	18.11
13	14.002	14	128.7	18.44
14	13.992	14	129.3	18.52
15	14.005	15	129.4	18.54
16	14.005	15	129.4	18.54
17	13.990	16	130.9	18.76
18	13.982	16	131.2	18.80

Ervin Colton

by Dr. Ervin Colton
Chief Chemist

ARGONNE NATIONAL LABORATORY

9700 South Cass Avenue

Argonne, Illinois 60439

REPORT ON CHEMICAL ANALYSIS

Date Received: 10/24/69

Sample: Boron Carbide

Source: D. Walker

YOUR NUMBER	OUR NUMBER	% Boron	% Carbon	Total
525-1	19106	77.43 } 77.50 77.58 }	21.62 } 21.72 21.82 }	99.22
525-2	19107	77.51 } 77.62 77.74 }	21.94 } 21.96 21.99 }	99.58
		<u>Mole Ratio</u>	<u>%B+C</u>	
525-1		B/C = 3.96	99.22	
525-2		B/C = 3.93	99.58	
<p>Note: Material bought to our Spec. DW 70-69 for higher worth control rods for EBR-II vendor: CERAC</p>				

Reported by: R. W. Bane

Date: 11/24/69

Copies to: D. Walker

Analyst: R. Telford
I. Fox

ANL Spectrochemical Analysis Report

1						2					
Our No. 50016			Your No. 525-1			Our No. 50017			Your No. 525-2		
Material B ₄ C						Material B ₄ C					
ELE- MENT	1	2	ELE- MENT	1	2	ELE- MENT	1	2	ELE- MENT	1	2
Ac			Eu			Nd			Sm		
Ag	---	---	Fe	VFT	W→M	Ni	---	---	Sn	---	---
Al	---	VFT	Ga	---	---	Np			Sr	---	---
Am			Gd			Os			Ta	---	---
As			Ge			P	---	---	Tb		
Au	---	---	Hf	---	---	Pa			Tc		
B	VS	VS	Hg			Pb	---	---	Te		
Ba			Ho			Pd	---	---	Th	---	---
Be	---	---	In	---	---	Pr			Ti	---	---
Bi	---	---	Ir			Pt	---	---	Tl	---	---
Ca	VFT	FT	K			Pu			Tm		
Cd	---	---	La			Ra			U	---	---
Ce			Li			Rb			V	---	---
Co	---	---	Lu			Re	---	---	W	---	---
Cr	---	---	Mg	---	VFT	Rh	---	---	Y		
Cs			Mn	---	---	Ru	---	---	Yb		
Cu			Mo	---	---	Sb	---	---	Zn	---	---
Dy			Na			Sc			Zr	---	---
Er			Nb	---	---	Si	VW→W	W			

RESULTS REPORTED IN FOLLOWING UNITS

☐ parts per million

☒ per cent

☐ micrograms per ml.

☐ micrograms in total sample

☐

SYMBOL	MEANING	APPROX. CONC.
VS	very strong	100% to 10%
S	strong	1% to 10%
M	moderate	1% to 0.1%
W	weak	0.1% to 0.01%
VW	very weak	0.01% to 0.001%
T	trace	0.001% to 0.0001%
FT	faint trace	< 0.0001%

SYMBOL	MEANING
L	less than
G	greater than
	element not investigated
—	element not detected
e	interference
()	accuracy uncertain
?	presence uncertain

<p>Remarks</p> <p>Specification DW 70-69 requires purity of 98.0%; calls for the following elements to be checked.</p> <p>Al } Ca } All in specification Fe } Mg } Si }</p>	<p>ESTIMATED ACCURACY OF RESULTS</p> <p>☒ order of magnitude</p> <p>☐ factor of two</p> <p>☐ —% of amount present</p> <p>☐</p> <p>Plate No. <u>23875</u></p> <p>By: <u>J. Lech</u></p> <p>Date <u>11-4-69</u></p>
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Submitted By: D. Walker Location: 212 - G241 Date Received: 10-24-69

Reports To: D. Walker

ISOTOPIC ANALYSIS FOR ^{10}B

<u>Mass No.</u>	<u>Ratio To Ref.</u>	<u>Mole Percent</u>	<u>Weight Percent</u>	<u>"Internal" Precision</u>	
				<u>Std Error</u>	<u>95 Percent Conf Lim</u>
10	.2493914	19.963981	18.484552	.224590	.440196
11	.9998155	80.036021	81.515450	.176274	.345498
Your No. Boron 525-1		Our No. 9-9649	Sec 11-24-69	Page 2234	

<u>Mass No.</u>	<u>Ratio To Ref.</u>	<u>Mole Percent</u>	<u>Weight Percent</u>	<u>"Internal" Precision</u>	
				<u>Std Error</u>	<u>95 Percent Conf Lim</u>
10	.2525669	20.166954	18.675992	.050940	.099843
11	.9998132	79.833047	81.324008	.039864	.078135
Your No. Boron 525-2		Our No. 9-9650	Sec 11-25-69	Page 2235	