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RESEARCH ON DEVELOPMENT AND FABRICATION OF BORON SUBOXIDE SPECIMENS

William H. Rhodes, et al

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RESEARCH ON DEVELOPMENT AND FABRICATION OF BORON SUBOXIDE SPECIMENS

Technical Report AFML-TR-72-159

AVSD-0350-72-CR

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A.J. DeLai

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Air Force Materials Laboratory
U.S. Air Force Systems Command
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13. ABSTRACT

This work describes the processing of dense boron suboxide by hot pressing. Sound billets four inches diameter by three-eighths inch thick were consolidated to a density as high as 99.2% of theoretical. Adjustment of process parameters was very critical as incorrect parameters resulted in either low density, excessive decomposition, or cracked billets. Several process modifications were identified that reduced production costs.

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FOREWORD

This report was prepared by the Materials Sciences Department of the Avco Systems Division under U. S. Air Force Contract No. F33615-71-C-1449. The work was administered under the direction of the Air Force Materials Laboratory, AFSC, with Dr. Robert Ruh acting as Project Manager.

This work was performed during the period 15 March 1971 - 14 March 1972.

This program was under the direction of Dr. W. H. Rhodes at Avco. Mr. M. U. Goodyear was Project Engineer prior to his resignation. Mr. A. J. DeLai continued as Project Engineer and was assisted by the talents of J. Centorino, R. Gardner, C. L. Houck, P. L. Berneburg, P. Foley, E. Vallante, R. Martineau, and G. Ross. Dr. T. Vasilos served as principal consultant and Department Supervisor.

This technical report has been reviewed and is approved.

C. M. Pierce

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Air Force Materials Laboratory

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I. INTRODUCTION

Weight restrictions limit the amount of armor that many military aircraft can carry. Thus, it would be desirable to have a more efficient armor system as more protection could be provided within the available weight allowance. Dense boron suboxide has the potential of providing this improved efficiency because of its low theoretical density and high hardness.

This program was designed to scale-up a hot pressing process for boron suboxide developed by the Ceramics and Graphite Branch of the Air Force Materials Laboratory.[1-3] The intended billet size was 4-inch diameter by 3/8-inch thick. The objective was to hot press sound billets of this size with a uniform microstructure and high density. The principal fabrication problem was cracking during the consolidation cycle; thus, emphasis was given to achieving sound billets together with high density. Attention was also given to reducing the cost of fabrication through process modifications.

II. RESULTS AND DISCUSSION

A. Raw Materials

The raw materials, boron and anhydrous boric acid, were purchased from the same vendor* used to supply the AFML development program. The physical powder characteristics were measured and compared with sample lots of powder used by AFML.

Photomicrographs in Figure 1 illustrate the AFML and Avco anhydrous boric acid powders. The Avco powder appears to be finer than the AFML powder as many of the larger Avco powder grains measure ~½ mm while the larger AFML powder grains measure ~1 mm. However, the powder morphology and shape of both powders seems to be similar. Near the middle of the program, it was decided that the large B_2O_3 particle size was deleterious. Ball milling and precipitation techniques were employed for obtaining finer powder. A 4-8 hour ball milling in toluene using an alumina jar mill produced the particle size shown in Figure 2. The average size was about 200 μm.

The precipitation technique involved preparing a saturated solution of boric acid and methanol and then precipitating the dissolved boric acid by adding toluene and evaporating the methanol. When precipitation appeared complete, the excess liquid was decanted and the powder was vacuum dried at 140°C for approximately 2 hours. This technique produced a fine, fluffy powder, but it was difficult to precipitate all of the boric acid from the liquid. As much as 80% of the powder was lost in processing using this technique, thus this technique was abandoned.

Photomicrographs in Figure 3 illustrate the AFML and Avco amorphous boron powders. Both the photomicrographs and particle size measurements of these two powder samples show the AFML powder to be finer. The average particle size of AFML and Avco boron powder is 0.05 and 0.16 μm, respectively, with powder distribution ranges of 0.01 - 4.0 μm and 0.03 - 6.0 μm. It was thought that these particle size differences had little effect on the consolidation cycle.

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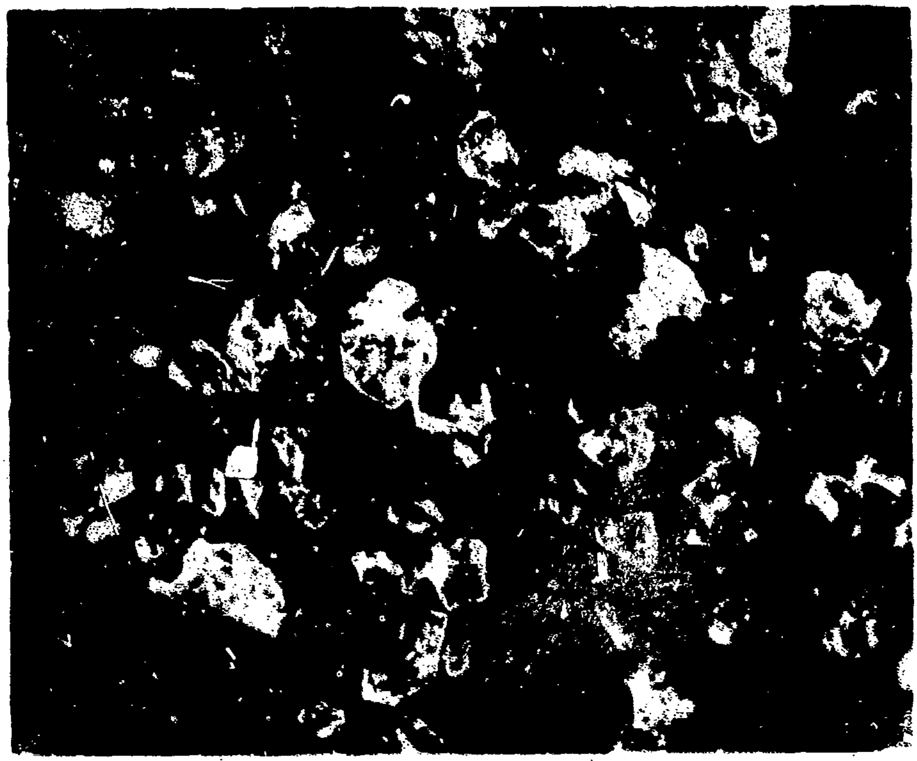
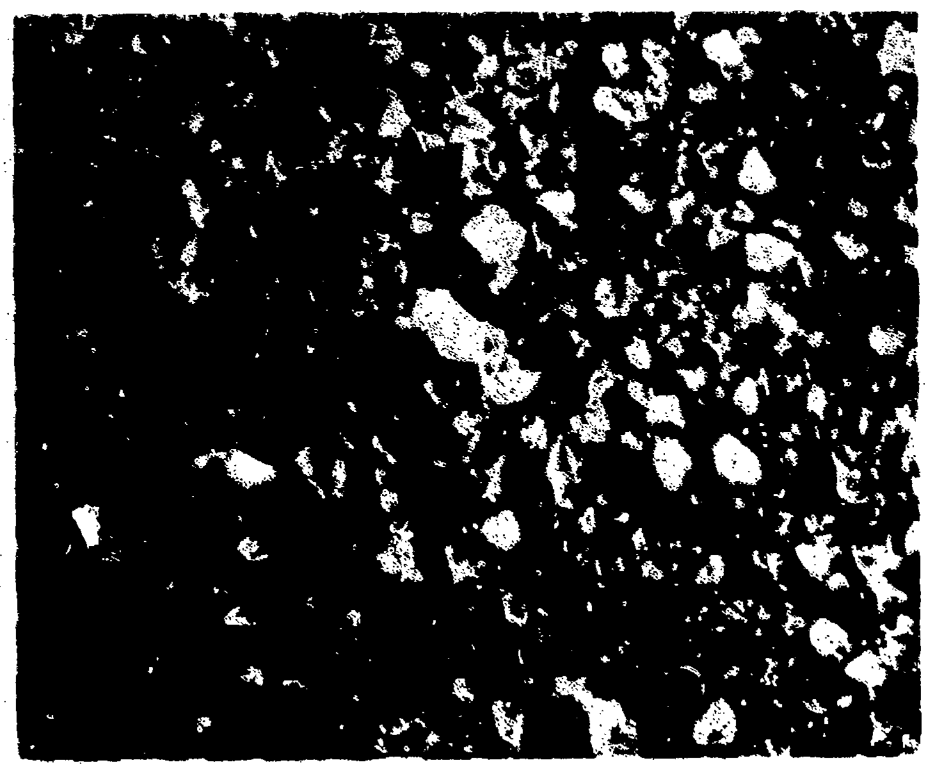
*U.S. Borox



#5487-4 a. AFML Anhydrous Boric Acid Powder. 10.75X



#5487-2 b. Avco Anhydrous Boric Acid Powder. 10.75X

Figure 1. Photomicrographs Showing the Anhydrous Boric Acid Powder Used by AFML and Avco to Fabricate B_6O Samples.

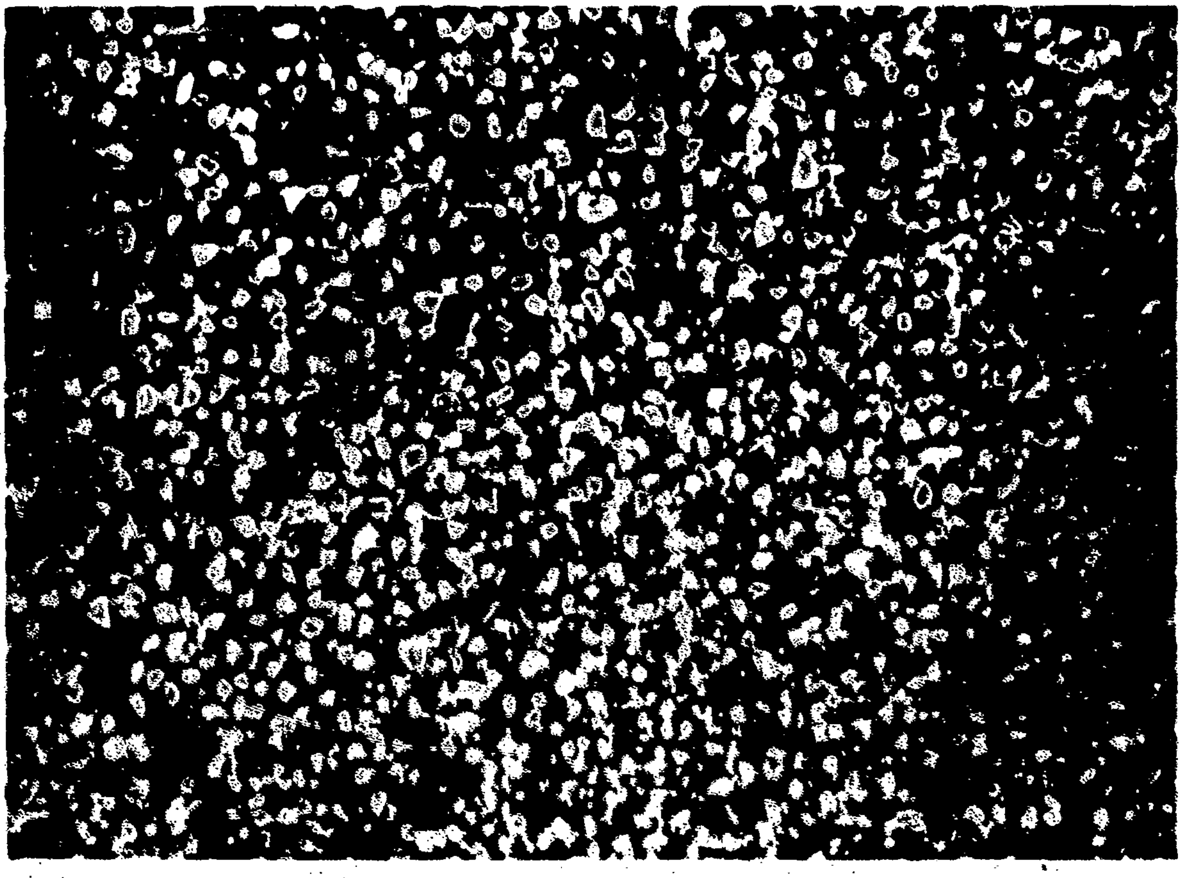


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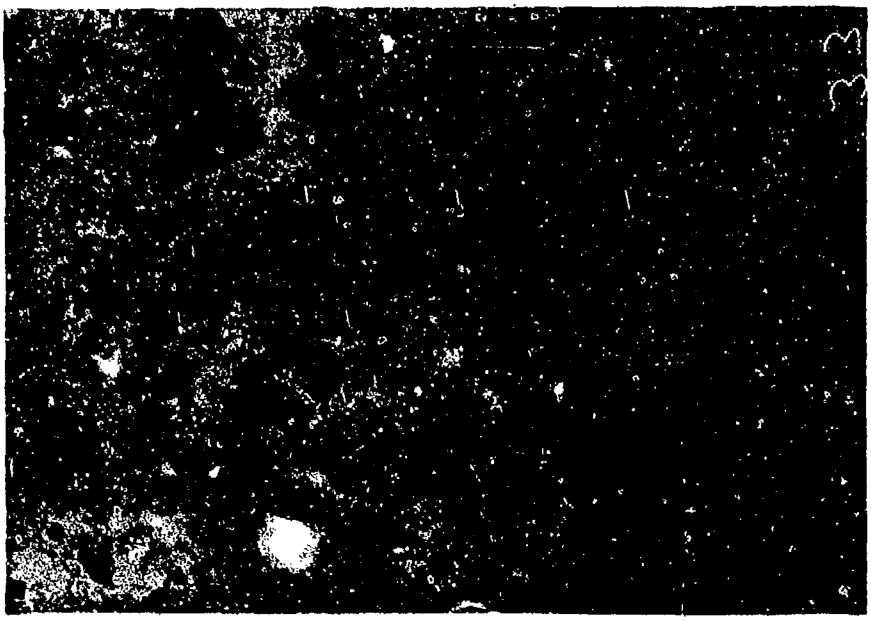
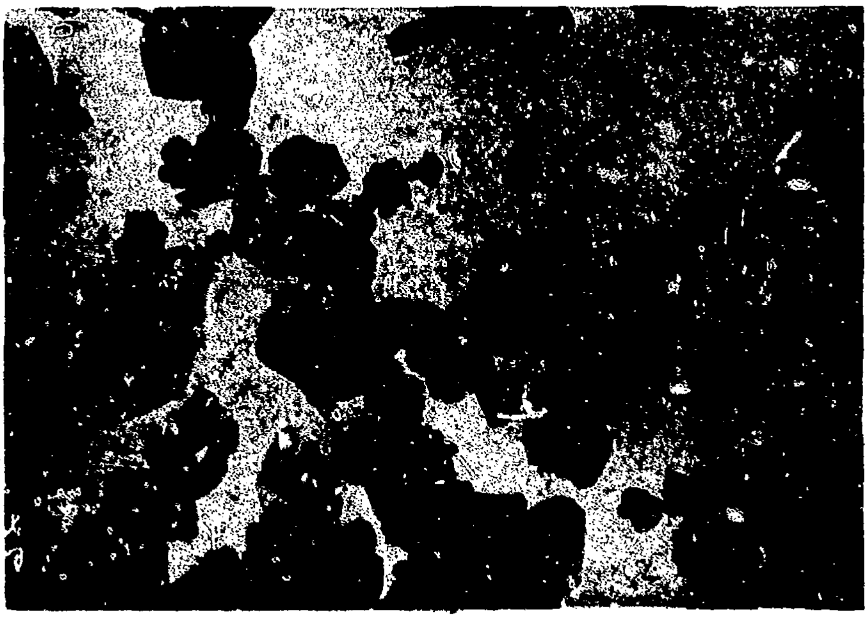
Figure 2. Ball Milled Anhydrous Boric Acid Having Particle Size of About 200 μm.



#71258 a. AFML Amorphous Boron Powder 30,000X



#71300 b. Avco Amorphous Boron Powder 30,000X

Figure 3. Photomicrographs Showing the Amorphous Boron Powder Used by AFML and Avco to Fabricate B_6O Samples.

Compositions between B_6O and $B_{7.5}O$ were dry blended in a paint shaker for 30-45 minutes. Small plastic balls were placed in the container to enhance mixing.

B. Prepressing

Powders for the initial pressing series and many of production pressings were prepressed by an AFML established technique.

The mixed B_6O powder was cold pressed at 1000 psi in the stainless steel prepressing die set-up. To prevent sticking, graphfoil was used on the die wall while tantalum foil discs were used at the piston faces. After cold pressing, the pistons and tantalum discs were removed and ~60 gm of mixed BN-10 w/o B_2O_3 powder was added to each end. The B_2O_3 gave the BN wafer structural integrity. The tantalum discs and pistons were replaced, and the system was prepressed at 1000 psi and 400°C for 15 minutes. This temperature was selected so the B_2O_3 would melt and bond the compact together.

After cooling, the prepressed sample was removed and placed in a dessicator until hot pressed, usually within a couple of days. The B_6O samples were ~¼" thick and the BN wafers were ~3/16" thick at each end.

The temperature was recorded on a thermocouple placed between the furnace wall and die cavity. The compacts were well bonded after prepressing at an apparent temperature of 400°C, but microstructural examination failed to reveal evidence for melting. Temperature calibration runs found that a thermal lag of 200° - 300°C existed due to the steel plungers. The apparent temperature was increased for several runs to as high as 800°C, but the B_2O_3 was still not melted. It was decided that melting was not essential since this occurred early in the hot pressing cycle. Table I gives the prepressing conditions for all runs employing this step. The principal advantage of prepressing was found to be that it gave an easily handleable B_6O/BN assembly that could be loaded in the hot pressing die without contamination or the accidental inclusion of BN, which was used in abundance as a diffusion barrier.

C. Consolidation

Previous B60 hot pressing studies[2,3] had discovered that carbon reacted with the specimen to form a B_4C reaction zone around the specimen periphery. The differential thermal contraction between the two phases was sufficient to cause cracking if a thick reaction zone formed. The AFML study demonstrated that the reaction zone was minimized by using diffusion barriers consisting of BN and Ta between the sample and the graphite components and by conducting the pressing in a protective atmosphere; preferably vacuum.

It was also discovered that cracking could occur by rapidly traversing the temperature interval where B and B_2O_3 were reacting to form B_6O. The temperature interval for this reaction was 1200° - 1500°C and a heating rate below 5°C/min. was found to be acceptable for 3-inch diameter billets.

The initial pressings were assembled by applying a heavy BN wash to the inside diameter of a grooved 4-inch diameter die body. The circumferential grooves (0.020 x 0.020 in.) helped prevent movement of the BN

TABLE I

Prepressing Conditions*

Run Number	B to O Ratio	Temperature °C	Time mins.
OM-3	6.0	406	15
OM-5	6.0	406	14
OM-8	6.0	406	15
OM-11	6.0	406	15
OM-12	6.0	406	15
OM-14	6.0	406	15
OM-16	6.0	403	15
OM-19	6.75	406	15
OM-25	6.75	406	15
OM-26	6.75	406	15
OM-29	7.50	505	15
OM-31	7.50	800	7
OM-32	7.50	508	60
OM-43	6.75	400	15
OM-46	7.50	400	15
OM-48	7.50	400	15
OM-54	7.00	400	15
OM-79	7.50	400	15
OM-80	7.50	400	15
OM-81	7.50	605	15

*Pressure kept constant at 1000 psi.

during pressing. A 0.010 inch thick tantalum foil liner was then fitted to the inside diameter of the painted graphite die body. The edge of the prepressed B_6O sample was also painted with the BN wash. Tantalum foil discs were used between the prepressed B_6O sample and graphite pistons. This unit was slip-fitted into a graphite susceptor wrapped with graphite felt for insulation. The graphite felt insulation was about 2 inches thick and was contained in a quartz tube. The induction coil was placed over the quartz tube and this system was inserted into the vacuum chamber. The chamber was evacuated overnight before beginning the hot pressing run.

The hot pressing conditions and results are summarized in Table II. Runs OM-3 - OM-16 were conducted in vacuum throughout. Vacuum breakdown and coil arcing was a problem at high temperatures, thus subsequent runs were conducted by swtiching from vacuum to argon at about 1800°C.

The recorded temperatures are optical sightings on the side of the die body at the sample level. It is recognized that these are apparent temperatures and not readily translatable from one experimental construction to another; although it is noteworthy that AFML recommended 1950°C - 2000°C as an appropriate apparent hot pressing temperature. The bulk of the pressings in this program were conducted between 1975°C and 2000°C.

Pressings OM-3 - 8 were performed at too low a temperature to reach high density. Pressings OM-11 - 16 were conducted at higher temperatures, but full density was still not achieved. Figure 4 illustrates the rough edge and small periphery porous pockets obtained on OM-11. These pockets were larger on samples pressed in excess of 2000°C. A typical porous pocket extracted from OM-14 was identified by X-ray diffraction techniques as B_6O and B. Thus, it appears that the pockets were formed by decomposition and volatilization of B_6O. An effort was made to find an acceptable hot pressing cycle close to or below 2000°C.

AFML researchers had found that compositions with boron ratios in excess of B_6O underwent more rapid densification. Free B was sometimes found in the product, but this was judged acceptable and vastly superior to having free B_2O_3 which would be subject to leaching. Increased B was added to pressings OM-19 - 29 which were conducted under a variety of conditions, but with a maximum density of only 94.2%. Thus, it was judged that some other variable was limiting density.

Up to this point the progress of densification was thought to initiate with melting of B_2O_3 at 294°C. As the temperature increased it was speculated that the B_2O_3 flowed throughout the predominantly B compact forming an intimate mixture for final reaction to B_6O between 1300°-1500°C. At about 1800°C, rapid densification began and the pore structure collapsed.

Metallographic examination of OM-5 and OM-19 (Figure 5) showed the existence of 60-100 μm pores scattered throughout the structure. The large pores were found to correlate with the spacing of the original B_2O_3 particles. They were smaller than the original B_2O_3 particles. This suggested that the cavity formed by the melting and flow of B_2O_3 was somewhat stable and only partially collapsed during the consolidation cycle. Pressing OM-31 was the initial pressing conducted with the ball milled B_2O_3 described in Section IIA, and it is thought highly significant that this was the densest sample obtained to this point in the program.

Table II

SUMMARY OF HOT PRESSING RUNS FOR 4-INCH B_6O BILLETS

Run No.	B to O Ratio	Heating Rate °C/min.	Hot Pressing Temp. °C	Hot Pressing Pressure psi	Time at Temp. and Pressure mins.	Final Comp. Rate mil/15 min.	Density g/cm³	Density % of Theo.	Atmosphere	Visual Appearance or Remarks	Post Machining* NDT Check
OM-3	6.0	10.7	1925	4000	15	29	2.07	79.5	150 µ	Sound	
OM-5	6.0	7.5	1925	4000	60	9	2.21	85.2	70 µ	Sound	
OM-8	6.0	11.6	1920	4000	-	-	2.07	79.5	Run terminated due to arcing problems.		
OM-11	6.0	13.8	2000	4000	15	20	2.45	94.2	.01 µ	Sound	
OM-12	6.0	10.8	2000	4000	15	11	2.42	93.2	50 µ	Sound	Cracks on 1 side
OM-14	6.0	8.2	2040	4000	15	24	2.50	96.2	Argon	Edge Crack	Cracked
OM-16	6.0	10.8	2060	4000	15	33	2.45	94.2	40 µ	Sound	Cracked
OM-19**	6.75	7.7	1975	4000	15	24	2.35 2.45***	90.3 94.2	Argon	Cracked	
OM-25	6.75	8.1	1975	4000	60	33	2.41	92.7	Argon	Sound	3 Small Cracks
OM-26	6.75	7.6	2010	5000	15	30	2.42	93.2	Argon	Sound	High Density Zones
OM-29	7.50	8.7	2010	5000	15	33	2.43	93.5	Argon	Sound	
OM-31	7.50	10.9	2010	4000	60	0	2.57	98.9	Argon	Sound	
OM-32	7.50	12.9	1975	4000	35	0	2.56	98.4	Argon	Sound	
OM-36	6.75	9.8	1975	4000	60	21	2.42	93.2	Argon	Center Sound; ¼" cracked off rim.	
OM-43	6.75	9.7	1980	4000	60	1	2.49	95.8	Argon	Sound	Cracked
OM-45	7.5	12.9	1980	4000	60	4	2.51	96.6	Argon	Sound	Some small inclusions
OM-46	7.5	16.5	1995	4000	60	15	2.53	97.3	Argon	Cracked	
OM-47	7.5	6.4	2000	4000	60	8	2.52	96.9	Argon	Center sound; ½" edge crack on one side.	Sound
OM-48	7.5	19.0	2000	4000	90	2	2.58	99.2	Argon	Sound	
OM-54	7.0	16.5	1975	4000	90	1.5	2.55	98.1	Argon	Edge cracks	Surface cracks
OM-55	7.0	16.5	1975	4000	90	1.5	2.50	96.2	Argon	Edge cracks	Cracked; high density zones
OM-56	7.0	20.5	1950	4000	120	2.0	2.36	90.8	Argon	Sound	
OM-57	7.5	12.1	2000	4000	60	3.0	2.48	95.4	Argon	Cracked	
OM-59	7.5	17.9	1975	4000	60	0	2.48	95.4	Argon	Cracked	
OM-60	7.5	14.6	1975	4000	90	0	2.49	95.8	Argon	Slight edge reaction; edge cracks.	Cracks one side; center more porous.

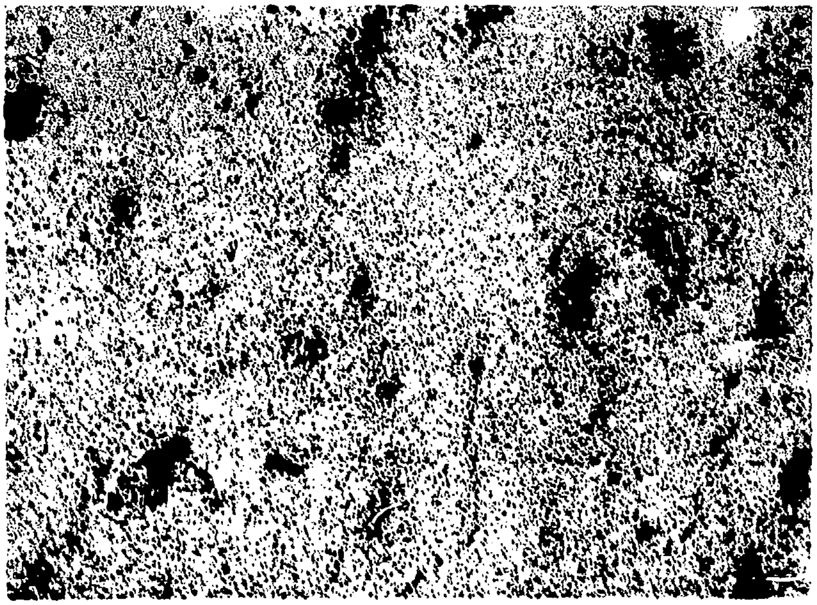
Table II concluded

Run No.	B to O Ratio	Heating Rate °C/min.	Hot Pressing Temp. °C	Hot Pressing Pressure psi	Time at Temp. and Pressure mins.	Final Comp. Rate mil/15 min.	Density g/cm³	Density % of Theo.	Atmosphere	Visual Appearance or Remarks	Post Machining* NDT Check
OM-61	7.5	14.3	1990	4000	90	0	2.57	98.9	Argon	Edge cracks	Cracked
OM-62	7.5	12.0	1980	3100	60	5	2.42	93.2	Argon	Slight edge reaction and cracks.	Severe crack; porous zones.
OM-63	7.5	18.5	1975 2040	4000	60	0	2.57	98.9	Argon	Cracked	Cracked
OM-69	7.5	18.6	1975	4000	60	0	2.50	96.2	Argon	Cracked	
OM-76	7.5	9.2	1975	4000	50	0	2.55	98.1	Argon	Cracked	
OM-79	7.5	8.4	1975	4000	50	5	2.33	89.6	Argon	Sound	
OM-80	7.5	9.2	1975	4000	45	19	2.44	93.9	Argon	Edge cracks	Cracked
OM-81	7.5	9.2	1975	4000	90	2	2.59	99.6	Argon	Cracked	
OM-82	7.0	10.0	2000	4000	15	13	2.56	98.4	Argon	Sound	Sound
OM-83	7.0	8.9	2000	4000	15	24	2.58	99.2	Argon	Sound	Sound

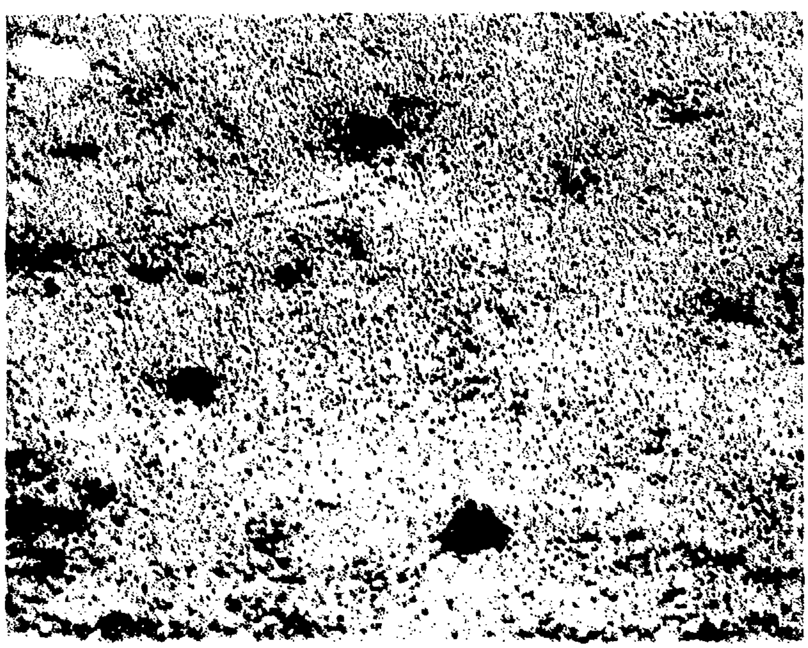
*Performed at AFML
**Graphite piston broke during run.
***Density of densest portion corresponding to uncracked portion of billet.

#5500-1 1X

Figure 4. Photograph of Billet OM-11, Hot Pressed at 2000°C - 4000 psi - 15 min. at Temperature and Pressure. Density is 2.45 g/cm^3 = 94.5 percent. Note reaction or decomposition zones on circumferential edge.



5488-1 (a) As-Polished 100X



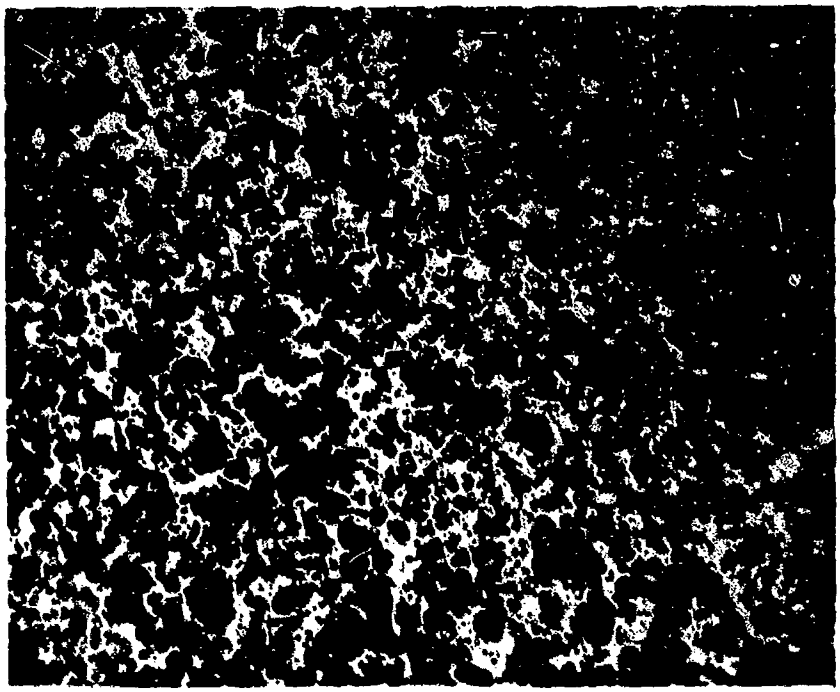
5639-1 (b) 100X

Figure 5. Photomicrogra[illegible] [illegible]owing (a) Microstructure of 85% Dense Billet [illegible] [illegible]nd (b) 94% Dense Billet CM-19.

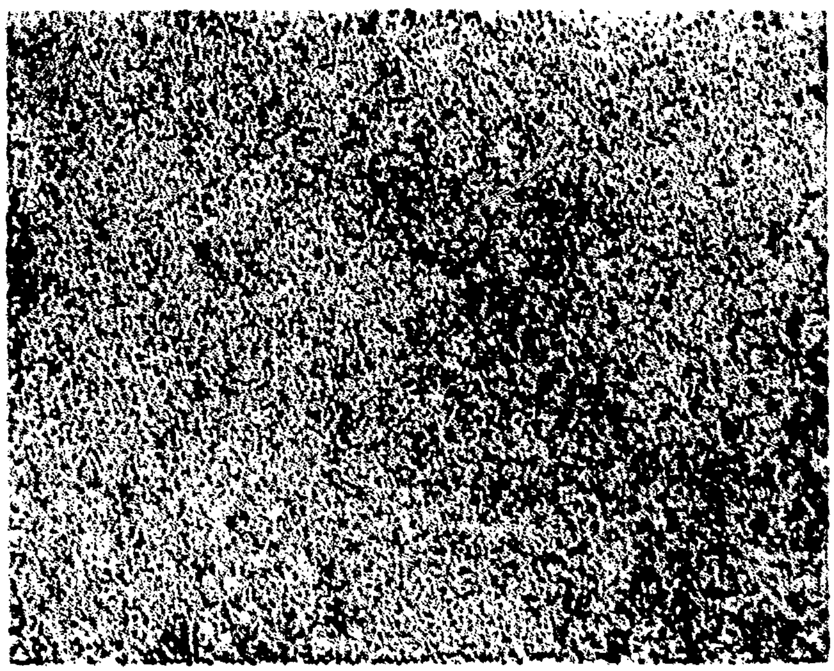
Several process modification experiments were conducted in an effort to eliminate process steps and therefore manufacturing costs. Run OM-36 was conducted without the prepressing step and without the use of a Ta diffusion barrier. A $\frac{1}{4}$-inch wide rim cracked and separated cleanly from the center of the billet. The central section was sound. Metallographic examination, Figure 6, showed the outer rim to be of low density, Figure 6a, but it did not appear to be two-phase or even a different phase from the center. The center, Figure 6b, had a uniform, moderate density structure with no evidence for a second phase. The absence of free B was noteworthy. The cracked rim was a negative point for the run, but the fact that a moderately high density and good looking central section was fabricated lends promise to this concept. The moderate density of 93.4% may be due to the reduced B content although the change in processing procedure also has to be considered an explanation. Prepressing was eliminated for OM-45, but in this run the Ta foil diffusion barrier was again employed. The billet was 96.6% dense and was visually sound with only very slight edge cracks. Small inclusions were found by NDT techniques and these may have resulted during loading the powder into the graphite die. A $\frac{1}{2}$-inch wide segment broke away from the next sample hot pressed without prepressing (OM-47). Examination of the fractured edge revealed a $\frac{1}{4}$-inch diameter inclusion which, from appearance only, was identified as BN. This sample was 96.9% dense and otherwise sound. Thus, it appeared from a densification standpoint that prepressing was unnecessary. The main advantage was that contamination was prevented. By exercising increased operator care during powder loading, four (4) inclusion-free samples were consolidated without prepressing (OM-60, OM-61, OM-62, and OM-63). Eight (8) other samples (OM-55, OM-56, OM-57, OM-59, OM-69, OM-76, OM-82, and OM-83) were produced without prepressing. These were not examined by NDT for possible inclusions.

Pressings OM-36 and OM-45 demonstrated the importance of maintaining the Ta diffusion barrier at both the die inside diameter and the punch faces. Pressings OM-82 and OM-83 employed 0.005 inch thick Mo on the die inside diameter while the punch face material remained Ta. The edges appeared to have an equivalent appearance to pressings employing Ta only, leading to the conclusion that Mo was an equally suitable diffusion barrier.

Cracking and variable billet density continued to be a problem until the last few pressings of the program. Figure 7 illu ates the temperature-time-deflection profile for OM-54. Many of the runs conducted after OM-31, where it was learned that ball milled B_2O_3 must be employed, were conducted with a process cycle very similar to OM-54. The heating rate was about 8°C/min. during the reaction phase of the cycle and densification became very rapid at about 1700°C. The long (90 min.) soak time at 1975°C was characterized by continued apparent densification. It was decided to significantly alter the process conditions for run OM-82 using a slightly higher hold temperature (2000°C) and a very short (15 min.) hold time. These conditions resulted in both a sound and high density body, so the conditions were repeated for OM-83. The temperature-time-deflection plot, Figure 8, illustrated a markedly different deflection behavior from OM-54. The heating rate during the reaction portion of the cycle was only 5.9°C/min. accompanied by nil apparent densification. At about 1800°C, rapid densification began and apparently continued right through the hold phase of the cycle. There is nothing in the deflection plot to indicate an approach to full density, but the final density for this billet was 99.2% of theoretical.



5577-2 (a) 100X



5577-1; (b) 100X

Figure 6. As-Polished Structure of OM-36 Showing (a) Porous $\frac{1}{4}$-Inch Wide Edge, and (b) Dense Central Section.

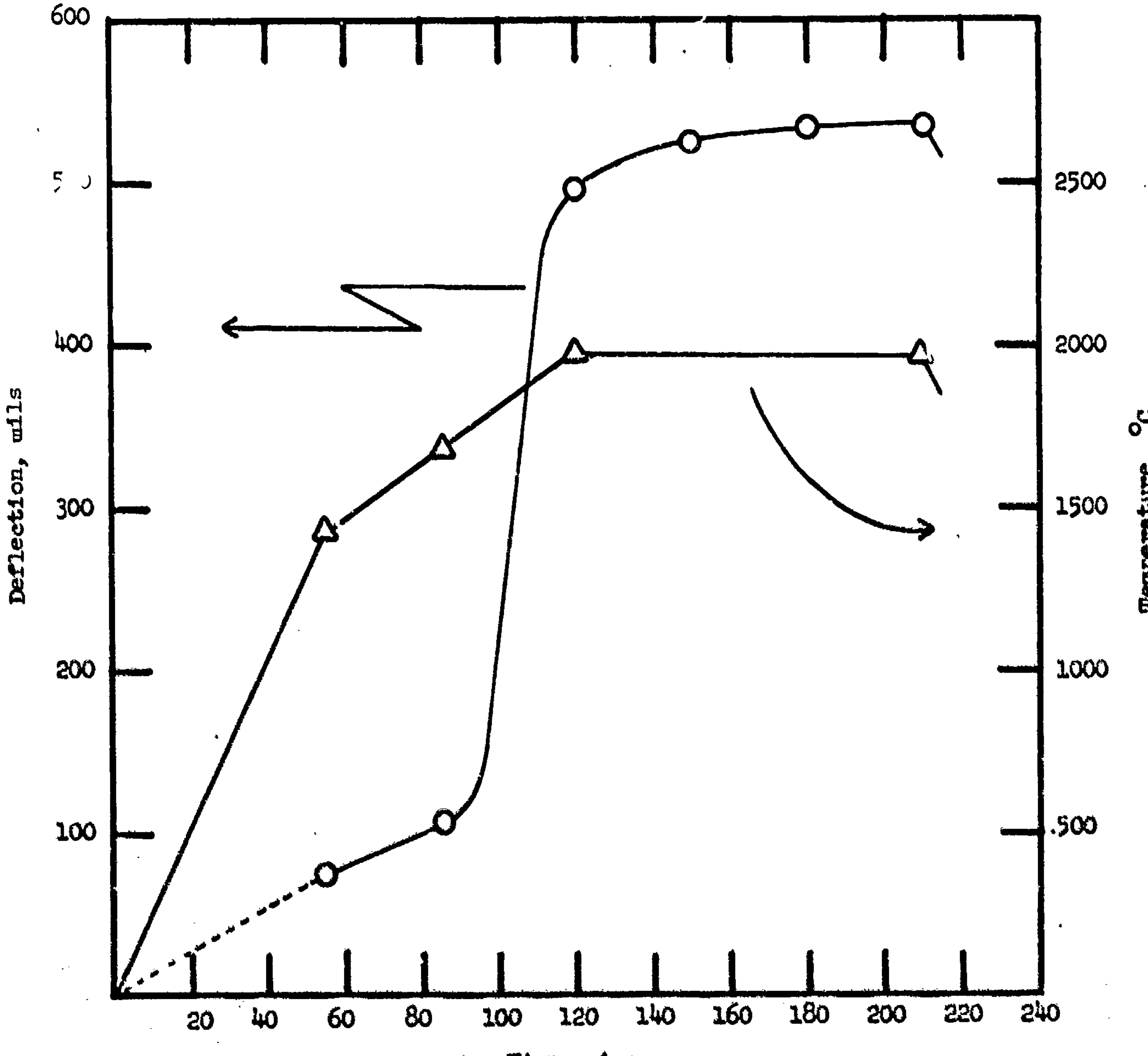


Figure 7. Densification-Time Plot for ON 54 - 1975°C - 90 mins.

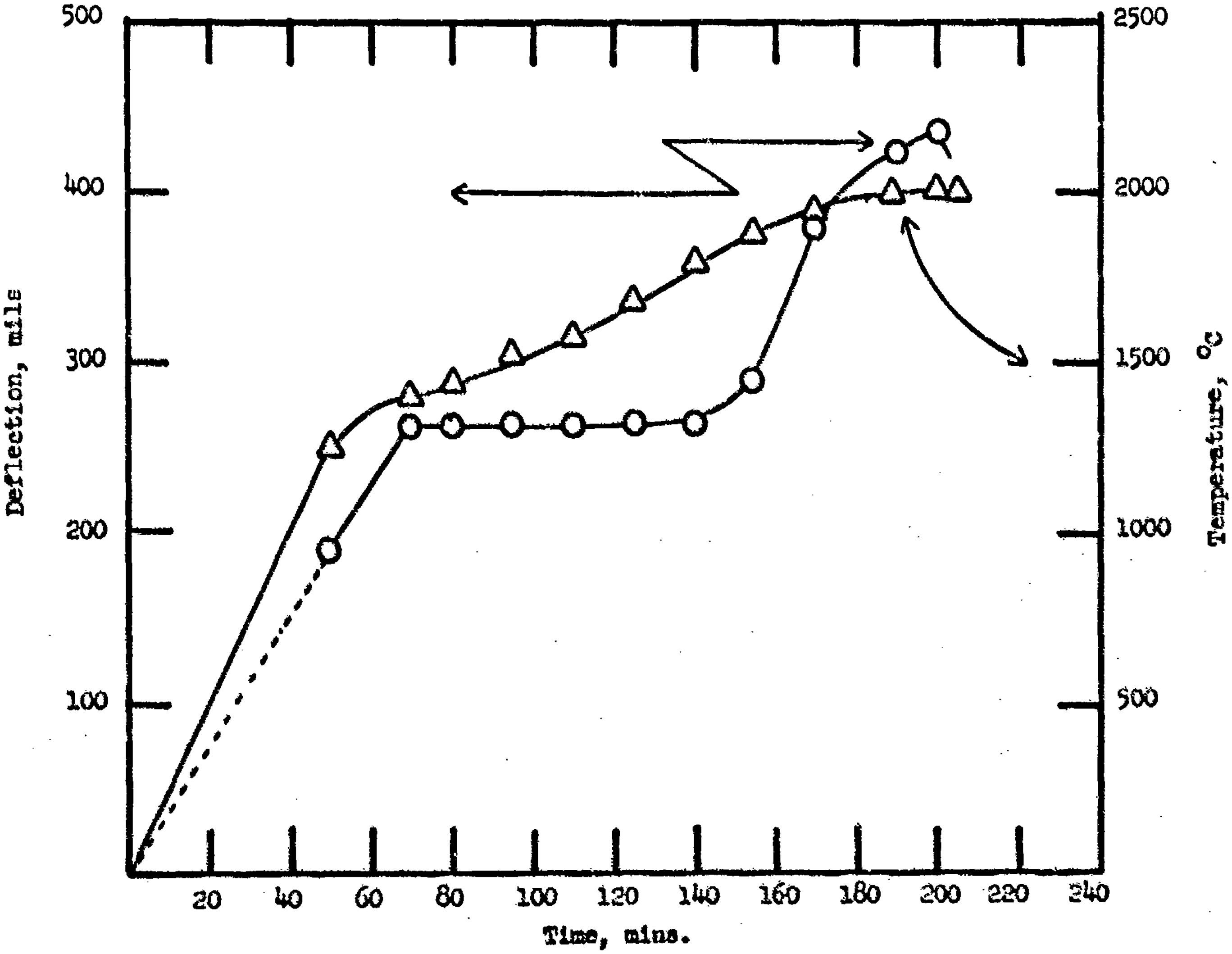


Figure 8. Densification-Time Plot for OM 83 - 2000°C - 15 mins.

The elements of this latter process cycle that are thought to be responsible for its success are:

1) Excess B for improved densification,
2) Ball milled B_2O_3 for small pore cavities than can collapse,
3) Heating rate of about 5^oC/min. during the reaction phase to reduce strains and cracking,
4) 2000^oC pressing temperature for rapid densification, and
5) 15 minute hold at temperature for reduced reaction and/or decomposition which contribute to cracking.

D. Microstructure

Figure 9 illustrates several typical "as-polished" structures for 95.4% dense OM-57 and 97.3% dense OM-46. The high reflectivity phase is thought to be free B. In general, the porosity is very finely distributed. Several pore clusters are visible. These may be caused by large particle size B_2O_3 as discussed with reference to Figure 5. The as-polished microstructure of 98.9% dense billet OM-31 is shown in Figure 10. The porosity is very fine and a small concentration of free B is evident.

Metallographic examination of a peripheral section on 98.4% dense OM-32 (Figure 11) revealed 80 µm patches of a high reflectivity phase. A microhardness measurement of this phase gave an average value of 2566 Knoop. Associated with this phase were microcracks which appear to result from a thermal expansion mismatch. This structure was restricted to a zone within 0.350 inch from the outer periphery. A similar zone was noted on Billet OM-76. This zone may well have been present on other billets that were not checked metallographically. It is noteworthy that the zone does not extend from the top or bottom surfaces beyond this zone toward the center of the billet. X-ray analysis of this zone detected poorly crystalline B and a possible trace of H_3BO_3 as well as B_6O. Thus, judging by the Knoop hardness and X-ray analysis, the bright spherical phase is identified as B. The B containing zone apparently was caused by the initiation of B_6O decomposition. The existence of this zone may have contributed to the edge cracking noted in Table II.

Grain sizes were not measured on these billets, but based on previous work[2,3], the size is estimated at 1 µm.

III. SUMMARY

1. Sound 4-inch diameter by 3/8-inch thick boron suboxide billets can be fabricated by reaction hot pressing.

2. Boron suboxide is quite susceptible to cracking in fabrication; thus, close process control is required.

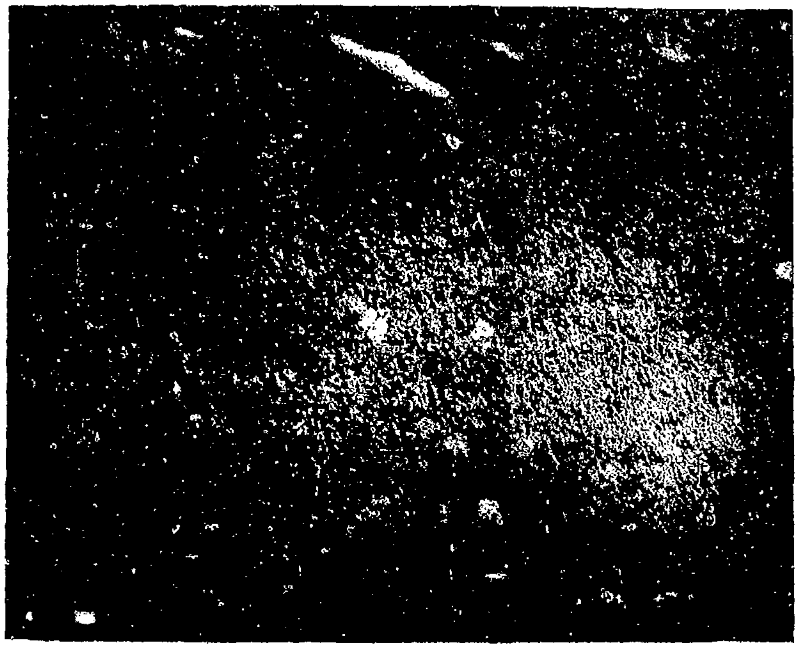
3. Tantalum or molybdenum foils plus a boron nitride wash are required as a diffusion barrier to prevent the diffusion of carbon from the die to the boron suboxide sample.

4. Vacuum or inert atmosphere pressing conditions are required to prevent the diffusion of gaseous forms of carbon into the sample cavity.

5609-3 (a) 100X

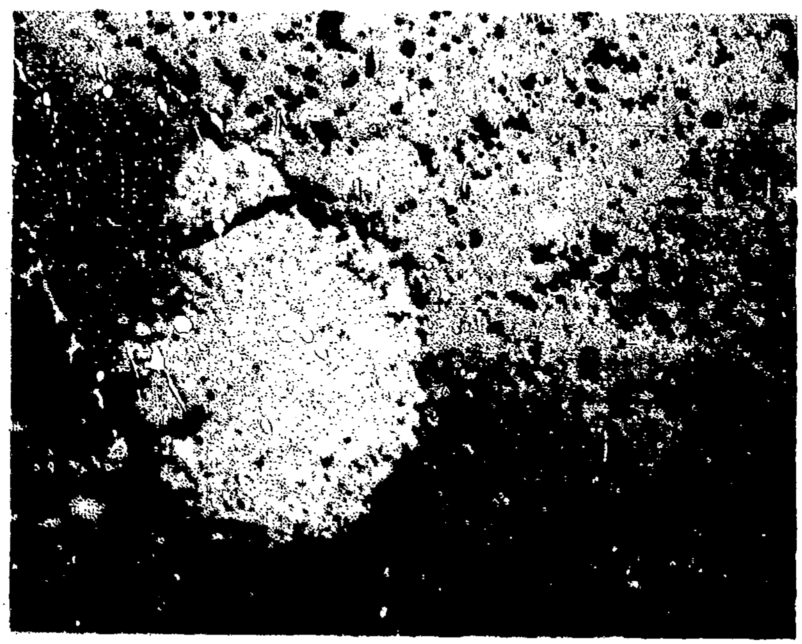
5624 (b) 100X

Figure 9. As-Polished Structure of (a) 95.4% Dense OM-57, and (b) 97.3% Dense OM-57.



5550-1 100X

Figure 10. As-polished structure of 99.1% dense billet OM-31.



5550-4 500X

Figure 11. As-polished structure of OM-32 showing microcracks associated with phase thought to be boron.

5. The anhydrous boric acid should have a particle size of 200 μm or below to prevent the formation of uncollapsible pore cavities.

6. No critical relationship between fabricability and amorphous boron particle size was found, so the 0.16 μm particle size used was judged acceptable.

7. A composition with boron ratio in excess of B_6O and near B_7O gives improved densification and microstructure compared with a stoichiometric composition or an excessively high boron content ($B_{7.5}O$) may be too high).

8. Prepressing avoids contamination problems, but by exercising care in powder loading, this step can be eliminated.

9. The heating rate should be held to about 5°C/min. above 1200°C to reduce strains and possible cracking.

10. The pressing temperature should be below the temperature where edge decomposition problems become serious. This was an apparent temperature of 2000°C for the experimental apparatus used in this program.

11. A very short (15 minute) hold time at temperature is all that is required even though deflection measurements indicate otherwise. The short hold time minimizes reaction and/or decomposition which, if allowed to proceed, contribute to cracking.

12. A pressing pressure of 4000 psi is adequate.

IV. REFERENCES

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