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DENSIFICATION STUDIES OF REFRACTORY MATERIALS USING HOT ISOSTATIC PRESSING (HIP) AND TANTALUM CONTAINMENT

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Powders of crystalline rhombohedral boron were HIP processed to near full density at 1500–1800°C and 206.8 MPa. At 1700°C, the densification of boron was independent of particle size in the range of <37 μm to 10 mm. At 1500°C, only the<37-μm powder reached near full density. Silicon and calcium impurities were found to segregate in the grain boundaries during densification. Results indicate that plastic yielding was the dominate densification mechanism. Boron nitride powder with 0.97% oxygen content was pressed to a density of 2.21g/cm^3 at 1800°C and 206.8 MPa. The density of high-purity hot-pressed graphite was increased by 15% to 2.10 g/cm^3 at 2200°C and 206.8 MPa. These results show that refractory metal containers used in hot isostatic pressing significantly expand the availability of high-density–high-purity materials.

1. INTRODUCTION

The use of Hot Isostatic Pressing (HIP) to fabricate materials with improved properties has become a worldwide practice. HIP is attractive for many reasons including better microstructural control and uniformity as well as lower cost through near-net-shape fabrication. Equally important, HIP, has given us the opportunity to explore new materials that otherwise would be unattainable. We believe this is the case with some of the materials currently under study at Lawrence Livermore National Laboratory. The main thrust of this report concerns the hot isostatic pressing of boron, boron nitride, and graphite. Additionally, our HIP program includes work on beryllium oxide, beryllium, boron carbide, metal composites with boron carbide and boron, and graphite bonding. For this high temperature investigation, we have selected tantalum as one of the refractory metals suitable as a HIP container.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

All materials used in this study are commercially available. In characterizing as-received materials, we did not rely entirely on the supplier for basic information. In some cases, we chose to perform our own analyses for chemical purity, phase content, particle density, and porosity.

Our experiments with boron included five particle size ranges. Large particle categories consisted of 0.01–0.1, 0.1–1.0, 1–2, and 1–10 mm sizes from a single source. The smallest size boron was <37 μm from a second source. Powder characteristics are given in Table 1. Mercury porosimetry measurements on the larger particles indicated porosities in the range of 0.2–0.7% with pore sizes of 0.003 to 0.1 mm. Tap densities for all boron powders ranged from 47–58% of the theoretical value.

Table 1. Crystalline boron powder characteristics.

		Large particle sizes	Small particle sizes
Impurities	Fe:	1000–5000 ppm	200 ppm
(spectrochemical	Si:	1000–2000	20
analysis)	Ca, Mn:	200–2000	35
X-ray phase		Rhombohedral	Rhombohedral
He pycnometric density		2.34 g/cm^3	2.34 g/cm^3

Boron nitride powder information was taken directly from that provided by the supplier. Chemical analysis reported 0.5 wt% oxygen, 0.4 wt% carbon, and <0.1 wt% other metals. Screen analysis showed 94.5% through a –325 mesh (44 μm); the surface area was 5 m^2/g. The tap density was 45% of the theoretical value (2.28 g/cm^3).

The graphite was a high-purity hot-pressed material. Supplier information indicated an apparent density of 1.83 g/cm^3 (82% of the theoretical value) with particle and pore sizes of 5 and 0.84 μm, respectively.

2.2 HIP Can Loading

An all-tantalum HIP can design for these experiments is shown in Figure 1. Dimensions were ~3.6-cm i.d. by 5.5-cm ht with a 1.6-mm wall thickness. Cans were thoroughly cleaned and degreased before loading. Powders were either loaded at tap density or prepressed isostatically and machined to fit the can. Powder fill densities were adequate to ensure uniform shrinkage during HIP densification. Cans for boron powders were also lined with a single layer of graphite foil to facilitate sample removal after HIP. Some cans were loaded with one powder only. Other cans were loaded with two to three powders separated by tantalum foil. After all of the material was loaded, a tantalum foil was inserted at the top to facilitate final cleaning of the weld area before inserting the lid. Welding took place inside a high-purity argon glove box. After welding, the assembly was transferred to a pump-out station for evacuation, bake-out, and pinch-off. Prior to pinch-off, samples were baked at 150°C (boron and graphite) and 300°C (boron nitride) and <10 m torr vacuum for 16 hr. After pinch-off cans were leak checked and assigned to an HIP schedule.

2.3 HIP Processing

The HIP used in this study was a Model QIH 33 Hot Isostatic Processing System (ABB Autoclave Systems, Inc., 3721 Corporate Drive, Columbus, OH 43229) capable of 2200°C temperature and 206.8-MPa pressure. The workload capacity was 30-cm dia by 68-cm ht, using a graphite resistance furnace. Temperatures were measured with Type C W-5Re/W-26Re thermocouples. Thermocouples were located at the midpoint and extremities of the hot zone. As a check on thermocouple accuracy and drift, the HIP was designed to allow the parallel use of a reference calibrated Type B Pt-6%Rh/Pt-30%Rh located adjacent to the midpoint Type C thermocouple. Checks on millivolt output are made periodically at 1500°C and are compared to the reference thermocouple. After checking, the reference thermocouple is withdrawn and stored. The temperature uniformity in the work zone was ±25°C. In a typical HIP run, the system was equilibrated at 300°C and was cycled between vacuum and a modest argon pressure to ensure a pure inert atmosphere. After this step, an argon prepressure at 300°C was set depending on the desired final test temperature at

206.8 MPa. The temperature was then increased at a constant rate of 20°C/min to the test temperature for all HIP runs. At the end of the soak period, power was terminated to allow system cooling. The cans were removed, and the tantalum was removed from the samples. An example of HIP cans after compaction is shown in Figure 2. The low carbon vapor pressure in the HIP chamber causes a thin gold-colored tantalum carbide layer to form on the surface of the can. Metallographic measurements showed that this carbide layer was ~10-μm thick and that it did not affect the hermetic sealing function of the tantalum can.

3. RESULTS

3.1 Boron

The results of boron HIP experiments at 1500°C and 1700°C and 206.8 MPa are listed in Table 2; microstructures are shown in Figures 3, 4, and 5.

In the experiment at 1500°C, the HIP can was loaded equally with the three powders listed in Table 2. They were loaded in the order listed from the top lid position to the bottom of the can. Only

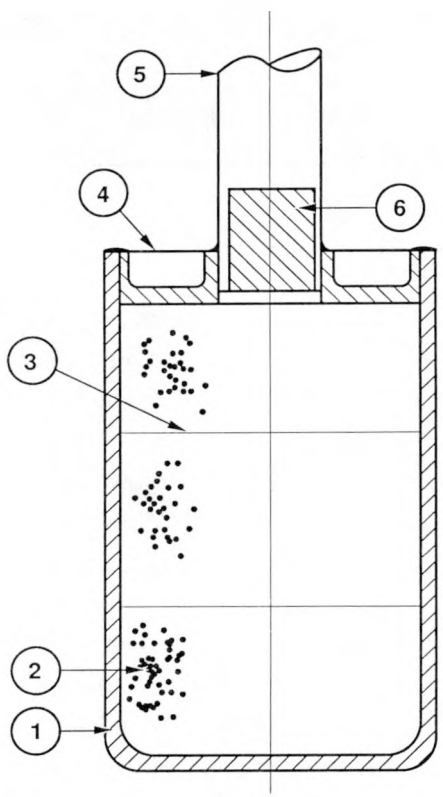

FIGURE 1.
Tantalum HIP container and pump-out tube. (1) can, (2) samples, (3) tantalum foil to separate samples, (4) lid, (5) tantalum pump-out tube (1.3 cm o.d.), and (6) tantalum support insert.

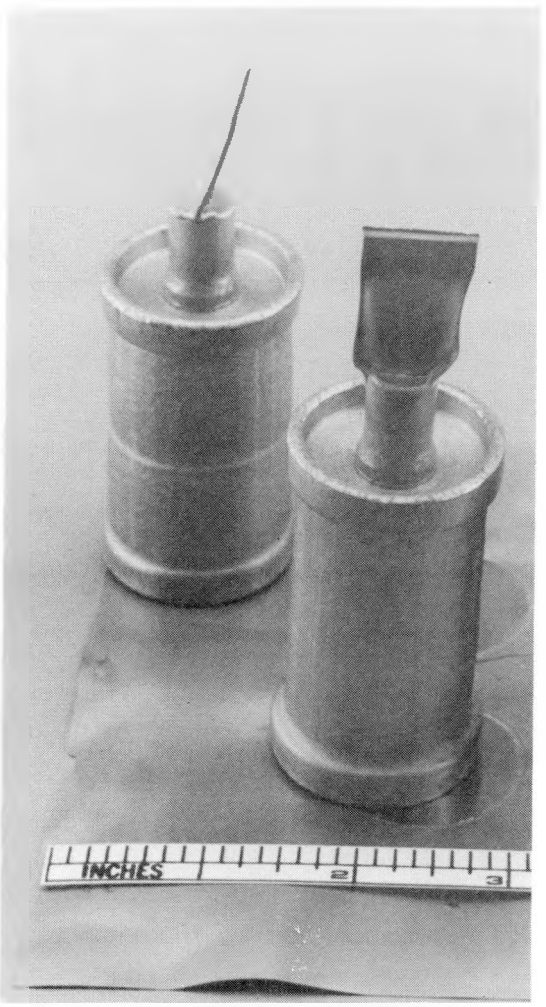

FIGURE 2.
Tantalum HIP cans after HIP processing at 1700°C and 206.8 MPa in argon.

Table 2. Relative density and grain size results from materials loaded in a HIP processed tantalum can.

Material	Initial particle size	Initial % theoretical density	HIP conditions	Final % of theoretical density[f]	Approximate final grain size range (μm)
Boron	<37 μm[a]	62[e]	1700°C/206.8 MPa/2 hr	>99	10–25
Boron	0.01–0.1mm[b]	58	1700°C/206.8 MPa/2 hr	>99	20–80
	0.1–1.0 mm	55		>99	40–300
	1.0–10 mm	47		>99	40–400
Boron	1.0–2.0 mm	47	1500°C/206.8 MPa/2 hr	94	30–300
	0.1–1.0 mm	55		96	30–300
	<37 μm	56		>99	10–25
Boron Nitride	<1.0 μm[c]	84[e]	1800°C/206.8 MPa/4 hr	97	2 × 20
Graphite	Hot pressed[d]	0.81	2200°C/206.8 MPa/2 hr	93	Not measured

[a]Boron from Eagle Picher Inc.
[b]Boron from Herman C. Stark, Inc.
[c]Boron Nitride from Union Carbide Corp.
[d]Graphite from Poco Graphite, Inc.
[e]Isostatic Prepress at 206.8 MPa
[f]Final density determined by Mercury Porosimetry

the small <37-μm powder reached near full density under these conditions. Mercury porosimetry for this sample indicated a porosity of 0.16% with a pore sizes in the 0.003–0.01-μm range. The approximate grain size was 10–25 μm and was close to the original particle size. The density of the larger particle sizes only reached ~95% full density. Both of these samples had 4–6% residual porosity with a pore size in the range of 1–70 μm.

We polished a section cut of the entire 1500°C HIP sample, which extended from the lid to the bottom of the HIP can. Microstructures for the 0.1–1.0 mm and 1.0–2.0 mm sizes are shown in Figure 3. The locations of the Figure 3 microstructures are shown in the section cut schematic (Figure 4). The final grain size range of 30–300 μm shown in Figures 3a and 3b for both samples was similar to that in the starting powder. At 1500°C, there was no apparent grain growth in any of the samples. A polished section view at a center location near the lid is shown in Figures 3d and 3f for the 1.0–2.0 mm boron sample. A polished section from near center of the can is shown in Figure 3c and 3e for the 0.1–1.0 mm sample. Figure 4 shows the location of these views relative to the entire sample. The pore structure in Figure 3f is perpendicular to the direction of isostatic pressure during the final stages of HIP compaction. This structure was typical only for the 1.0–2.0 mm sample in the regions near the can. Remnants of this pore structure are still in evidence at the central location for both the 0.1–1.0 and 1.0–2.0 mm samples. There was a total absence of this type of pore structure in the <37-μm sample, which went to near full density at the bottom location. It is possible that some of the unique pore structure shown is the result of polishing in highly stressed regions.

In the HIP experiment at 1700°C, all particle size samples went to near full density (see Table 2). The <37-μm sample is listed separately in Table 2 because it was located in a single HIP can. The measured porosity for this sample was 0.1% with pore sizes in the 0.003–0.01 range.

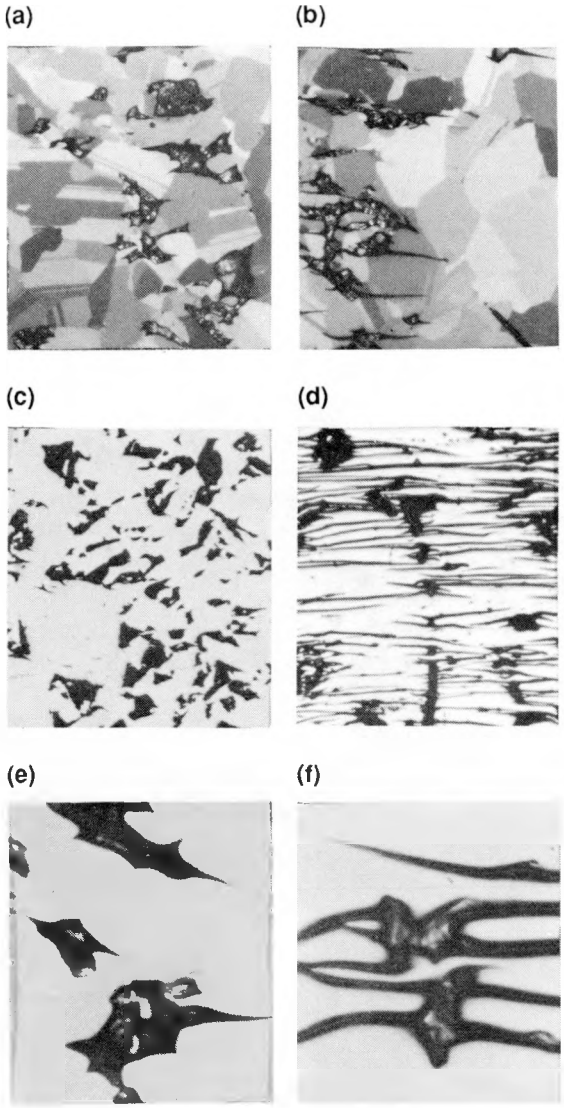

FIGURE 3.
Crystalline boron HIP-processed at 1500°C and 206.8 MPa for 2 hr.

Size: 0.1–1.0 mm	Size: 1.0–2.0 mm
(a) 35× Mag. (polarized light)	(b) 35× Mag. (polarized light)
(c) 13.7× Mag.	(d) 13.7× Mag.
(e) 140× Mag.	(f) 140× Mag.

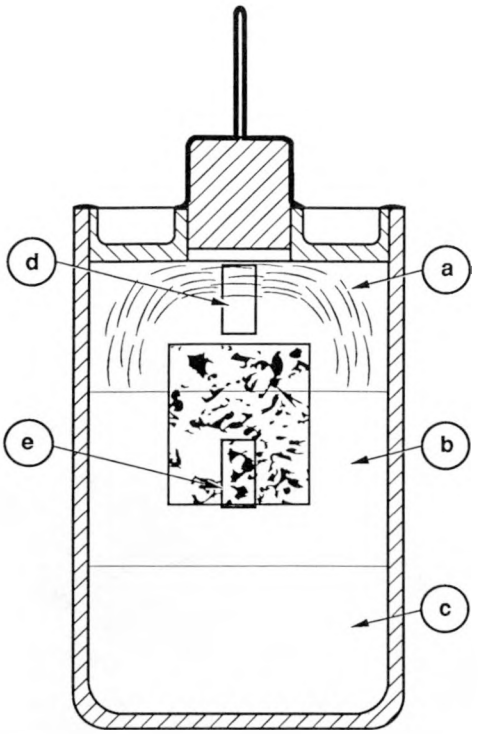

FIGURE 4.
Overall section view of 1500°C HIP experiment showing powder locations and pore structures at edge and central locations in the HIP can.
(a) 1.0–2.0 mm powder (6% porosity)
(b) 0.1–1.0% powder (4% porosity)
(c) <37-μm powder (<1% porosity
(d) Ref. area in Figs. 3d and 3f
(e) Ref. area in Figs. 3c and 3e.

Final grain sizes were 10–25 μm. The larger particle size samples were in a single can and are listed in Table 1 according to location from the top lid position to the bottom. Mercury porosimetry measurement for all samples indicated 0.3–0.5% porosity with pores in the 0.003–0.02 μm size range. Final grain sizes ranged from ~20–400 μm. The grain structure for all samples is shown in Figures 5a to 5d. The 1.0–10.0 mm sample was also analyzed with an electron microprobe to look for impurity distribution. These results are shown in Figures 5e and 5f. There was a clear concentration of impurities in the grain boundaries. Silicon and calcium were dominate in these locations. Trace amounts of Si, Ca, Fe, and Mn were also found within the grains.

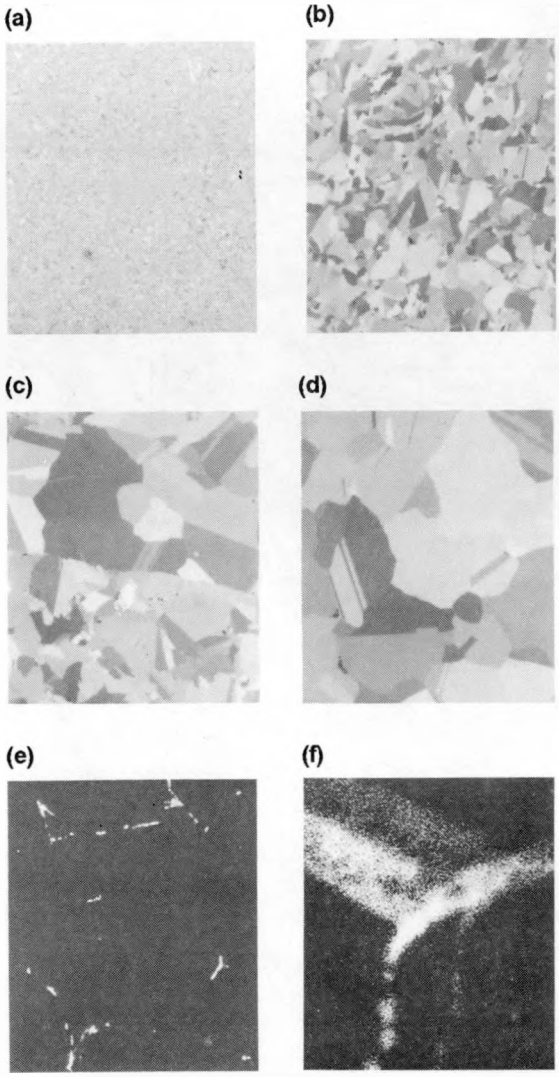

FIGURE 5.
Crystalline boron HIP-processed at 1700°C and 206.8 MPa for 2 hr.

Initial Size (35× Mag.–polarized light.)
(a) <37 μm (b) 0.01–0.1 mm
(c) 0.1–1.0 mm (d) 1.0–10.0 mm

BSE Image for Ca and Si
(e) 70× Mag. (f) 700× Mag.

Our early experiments clearly indicated that boron could be successfully processed in tantalum containers. A programmatic need for large high-density boron-sputtering targets motivated an attempt to fabricate a larger boron sample. A combination of large size boron (0.01–10.0 mm) was loaded into a tantalum can (10 cm dia × 10 cm ht) to a tap density of 62.2% of the theoretical value. The can was baked as before for the smaller cans and was HIP processed at 1800°C and 206.8 MPa for 4 hr. The entire sample was removed from the can with no visible cracks. The sample was sliced and ground into targets like the one shown in Figure 6. Mercury porosimetry of a

representative fragment showed a uniform 0.7% porosity throughout the sample. Metallographic examination at the outer boron-tantalum interface indicated an ~200-μm penetration of tantalum into the boron.

3.2 Boron Nitride

Boron nitride powders were isostatically prepressed to 82% of the theoretical density before HIP processing. After HIP processing (at 1800°C and 206.8 MPa for 4 hr), the bulk density of the machined cylinder shown in Figure 7 was 2.21 g/cm^3 [97% of the theoretical value for hexagonal BN (2.28 g/cm^3)]. These results are shown in Table 2. The microstructure consisted of dense assicular crystals of ~2 × 20 μm. Phase analysis by x-ray diffraction showed only hexagonal BN. Spectrochemical analysis showed: Ti (1000 ppm), Fe (100 ppm), Ca and Si (each 30 ppm). Analysis by neutron activation indicated 0.97 ± 0.04% oxygen. Chemical analysis for boron gave 43.20 ± 0.27% (the theoretical value is 43.6%). Vickers microhardness measurements were taken on the tantalum can after HIP. Hardness values using a 200-g load varied from 568 to 526 kg/mm going from the BN interface to a 50-μm carbide layer at the outer surface. The grain size of the tantalum varied from 200–600 μm.

3.3 Graphite

The graphite sample was HIP processed at 2200°C and 206.8 MPa for 2 hr. The bulk density of a machined sample was 2.10 g/cm^3 [93% of the theoretical value (2.26 g/cm^3)]. Mercury porosimetry measurements from two locations showed a porosity range of 5.8–6.5% (94% of the theoretical value). Pore sizes were in the range of 0.003 to 0.118 μm with a mean of 0.07 μm. In this experiment, the porosity and pore size were reduced by 68% and 92%, respectively. We believe that additional pore reduction could have been achieved with longer hold times at 2200°C.

4. DISCUSSION

4.1 Boron

HIP temperatures of 1700–1800°C at 206.8 MPa for 2 hr hold periods were more than sufficient to achieve near full density crystalline boron regardless of the particle size. The remaining 0.3–0.5% porosity could have been the result of small amounts of residual gas even though these samples received a thorough bake-out. This gas would have made the total elimination of porosity difficult. At 1500°C and 206.8 MPa for 2 hr, only the small <37-μm particle size powder achieved near full density. Large-particle samples still retained 5–6% porosity under these conditions. Again we believe that longer times at 1500°C and 206.8 MPa would have yielded higher densities for the larger particle sizes.

In consideration of the densification mechanisms that apply to these boron experiments we refer to the work A. S. Helle et al.[1] They reviewed plastic yielding, diffusion from interparticle boundaries, Nabarro-Herring and Coble creep, and pore separation and grain growth as possible mechanisms for hot-isostatic densification. We believe that plastic yielding was the dominate mechanism in the HIP densification of boron. In plastic yielding, densification is dependent on particle contact area and the yield stress of the material. During HIP, the effective contact area increases until the yield stress is reached, halting further densification. At this point, the effective pressure at particle

boundaries is equal to the HIP pressure. To our knowledge, the yield stress as a function of temperature for boron has not been determined. Finlay[2] reports a bending strength of 524 MPa for boron but does not give the source of his information. For many ceramics, the yield stresses are reduced to very low levels at T/T_m ratios <0.6. In our experiments at 1500–1700°C, the homologous temperatures (T/T_m) were 0.75 and 0.84, respectively, for a melting point of 2350 ± 50°K. We believe that in our experiments the HIP pressures and the effective pressure on powder compacts were well above the yield stress for boron. One reason for the lack of mechanical property data on boron is the difficulty of fabricating monolithic specimens. This is now possible using HIP processing.

The role of impurities in boron densification is uncertain. There is little doubt that large quantities of silicon and calcium have segregated at grain boundaries during compaction as is shown in Figures 5e and 5f. These elements most likely formed borides early in the HIP process, and it is difficult to understand how they could have segregated in the absence of significant grain growth. However, there remains the possibility that the diffusion of these elements to grain boundaries may be an indication that a diffusion mechanism may have also contributed to densification.

The photomicrographs (Figures 3c through 3f) of boron in the final stages of densification demonstrate clearly the isostatic nature of HIP pressure imparted to the powder compact. Besson and Abouaf[3] have studied the numerical simulation of ceramic powders processed by HIP, and the effects of "hard and soft" containers and their shapes. High strength steel, for example, can impart

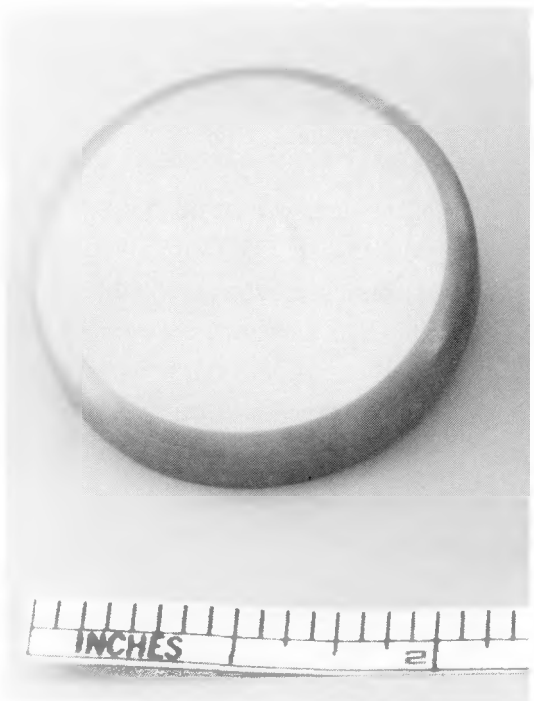

FIGURE 6.
Boron sputtering target ground from a monolith HIP processed at 1800°C and 206.8 MPa.

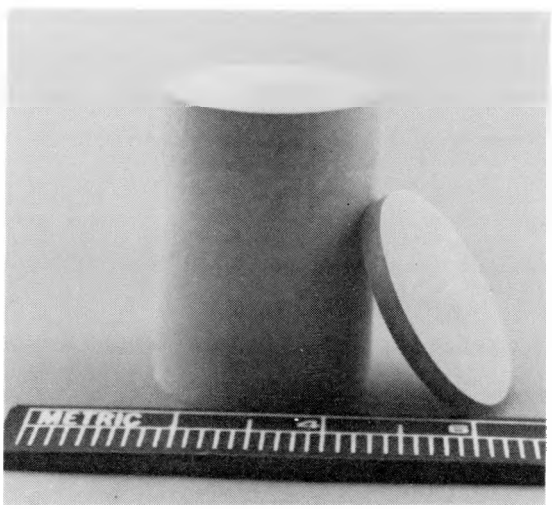

FIGURE 7.
Hexagonal boron nitride HIP processed at 1800°C And 206.8 MPa to a density of 2.21 g/cm^3.

significant residual stress to ceramic HIP samples as can sharp corners in the container. In our experiments, tantalum acted as a soft container, and our samples did not appear to contain any residual stress.

4.2 Boron Nitride and Graphite

Our experiments with both these materials were exploratory in nature. We did not study the particle size effects on HIP densification. The hexagonal boron nitride material prepared with a density of 2.21 g/cm^3 and 0.97% oxygen was a significant improvement over commercially available material. Likewise, the reductions in porosity and pore size of commercial high-purity graphite produced a material with improved performance for our applications.

5. CONCLUSIONS

The use of refractory metal containers like the tantalum can increase the material options available using hot isostatic pressing. The potential availability of high-density–high-purity boron, boron nitride, and graphite has been significantly expanded as a result of this work. In the case of boron, the HIP temperatures and pressures used are suitable for achieving near full density for several particle sizes. The results indicate that densification is dominated by a plastic yielding mechanism.

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