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THE VACUUM HOT PRESSING OF BERYLLIUM

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ABSTRACT

The optimum conditions for vacuum hot pressing of Pechiney electrolytic beryllium powder have been established and compacts produced with densities exceeding 99 per cent. of theoretical density; these conditions depend markedly on the geometry of the compact and the oxide content of the powders being pressed. Effects of compact geometry, including low densities in long compacts, are associated with loss of pressure through die-wall friction, particularly where the length-to-diameter ratio of the compacts is greater than 0.5 .

The presence of 2.3 per cent. beryllium oxide as a surface film on the particles reduced the final density attained to less than 97 per cent. of theoretical when pressing with 1500 lb/in² at 1080 °C, whereas this density could be attained in unoxidised powder with only 800 lb/in² for similar conditions. The narrow size range of the oxidised powder may also have contributed to this difficulty in pressing.

CONTENTS

1. INTRODUCTION

Vacuum-hot-pressing of powders to form dense fine-grained beryllium metal is a well-established process for commercial fabrication of beryllium shapes (Beaver 1954). The powder fabrication method is preferred to melting and casting which requires elaborate procedures to obtain a fine-grained structure free from cracks and porosity.

Cold pressing and sintering of powder is suitable for the production of relatively small (< 2-inch dia.) bodies; however, the high compaction pressures necessary (60 – 80 tons/in^2) and vaporisation of beryllium during vacuum sintering are particularly undesirable features of this process (White and Burke 1955). Pressureless sintering has also been investigated (Martin et al. 1961) but non-uniformity in the sintering of various batches of powder and the resulting density variations in the sintered body are objectionable features. The problem of vaporisation also remains.

The limited hot strength of metals suitable for die-making restricts hot-pressing conditions with metallic dies to pressures of less than 25 tons/in^2 at 600 °C or 10 tons/in^2 at 800 °C. On the other hand graphite retains its moderate compressive strength of 1–2 tons/in^2 to high temperatures and dense bodies of beryllium may easily be formed in graphite dies at temperatures of 1050 – 1100 °C using pressures of 1000 – 1500 lb/in^2.

The main purposes of this work were to construct equipment for the hot pressing of cylinders of beryllium 2 inches or 4 inches in diameter and to define the conditions which would allow consolidation of beryllium powder to a high density body (> 99% theoretical density) suitable for subsequ extrusion (Silver 1964). The systematic study of hot-pressing variables was a secondary considerati although an effort has been made to correlate some of the more important aspects of the process and to comment on further work.

2. EQUIPMENT

Two hot pressing arrangements were used. The first, shown in Figure 1, consisted of a fused silica tube 5 inches outside diameter, 4 inches inside diameter, and 18 inches long, forming a vacuum chamber around which was placed the induction heater coil and inside which was placed the graphite die and supports. Pressure was applied to the die plunger through a 1-inch diameter stainless steel ram actuated by a 4-ton hydraulic "Black Hawk" press; the steel ram moved through a Wilson vacuum seal in the brass top plate. The bottom plate with centre hole and spider was placed directly onto the baffle valve of a "Speedivac" mobile high-vacuum pumping system with a model 403 diffusion pump backed by a 150 l/min rotary pump.

This hot-pressing arrangement was limited to a maximum pressure of 400 lb/in^2 on 2-inch diameter cylinders. Higher pressures or larger compacts could not be used because of limitations on the diameter of the silica tube, which thus restricted the allowable die-wall thickness. The use of a silica tube also limited the maximum temperature of the 2-inch diameter cylinders to 1100 °C because of the heat transfer from the die wall. The temperature at a position in the centre of the die wall was recorded using a platinum/platinum-13% rhodium thermocouple attached to glass-to-metal vacuum-tight seals in the bottom plate. Copper tubing was soft-soldered to the top and bottom plates and a high flow of water through this prevented overheating of the neoprene rubber vacuum seals.

A more elaborate apparatus was used in the second arrangement (Figure 2). A cylindrical stainless steel tank 2 ft diameter, 2 ft high, ¼ inch wall thickness, formed the vacuum chamber. The induction heater coil was placed within this chamber. Pressure was again transmitted to the die plungers by a 4-ton hydraulic "Black Hawk" ram for 2-inch diameter compacts and by a 20-ton ram for 4-inch diameter compacts, the load being transmitted by a 1-inch diameter stainless steel ram, passing through a vacuum seal in the centre of the top plate. Pressure on the compacts was measured using a Bourden-type gauge with an accuracy of ± 2 per cent.

All dies were made from Reactor Grade B graphite with clearance of 0.001 inch to 0.003 inch between the plunger and die wall. Both the inside die wall and plunger were fine-machined to ensure minimum frictional resistance and maximum pressure transmission to the compact. The dimensions for the 2-inch tooling were 3½ inches o.d. x 2 inches i.d. x 6 inches high, and the 4-inch tooling 6 inches o.d. x 4 inches i.d. x 8 inches high.

A formula given by Roark (1943) was used to determine the maximum allowable axial stre on the compacts; that is:

$$S_2 = P \frac{(b^2 + a^2)}{(b^2 - a^2)} = \text{hoop stress} (lb/in^2) ,$$

where P is the applied pressure (lb/in^2)

a is the inside radius (in)

b is the outside radius (in) ,

assuming hydraulic pressure transmission.

Using the appropriate values of a and b , and a value of 3000 lb/in for S_2, the maximum allowable value of P was determined as 1500 lb/in^2 for 2–inch tooling and 1150 lb/in^2 for 4–in tooling.

A refractory silica tube placed between the graphite die and the induction coil reduced th amount of heat lost to the chamber walls and this was reduced further by a concentric radiation shield of stainless steel placed between the coil and wall. Copper water–cooling pipes were si soldered to the outside wall of the furnace chamber.

The chamber was evacuated through two 4–inch diameter ports by an Edwards 603 B dif pump backed by a 450 l/min rotary pump; a vacuum of 10^{-3} mmHg was readily achieved througho most of the cycle.

A cam–operated device lifted the chamber lid clear of the body flange to a position whe could be pushed clear of the furnace along a pair of rails.

Induction heater coils were readily interchangeable, passing through the base of the cha via brass "lead–in" pieces which were electrically insulated from the furnace chamber by Bake supports. Coils used for the 2–inch and 4–inch diameter compacts were 8 inches high, 6 inche o.d. with 8 turns of ½–inch diameter copper tube, and 8 inches high, 8 inches o.d. with 6 turns ½– diameter copper tube respectively. The refractory silica tubes were a close fit in these coil

A motor–generator set capable of supplying a rated output of 100 kW at 2850 c/s to the cooled induction coils was used. Only 10 kW was required to heat the 2–inch diameter compact 1100 °C and 13.5 kW to heat the 4–inch diameter compact.

3. MATERIALS

Three types of beryllium metal powder were used, differing in particle size distribution, content, and, possibly, degree of strain–hardening. These are listed below and their compositio shown in Table 1.

(a) Pechiney electrolytic beryllium – 200 mesh B.S.S. "as received" with 0.54 per cen weight BeO.

(b) Pechiney electrolytic beryllium –150 +200 mesh B.S.S. oxidised in a fluidised bed 1 hour at 700 °C in an oxygen gas flow (20 p.p.m. H_2O) of 0.2 ft^3/sec to achieve an average BeO content of 2.3 per cent. by weight (P.G. Alfredson, private communicat

(c) Pechiney electrolytic beryllium –200 mesh +300 mesh B.S.S. milled 1 kg at a time i polythene container with beryllium rods in an oxygen atmosphere for 112 hours givin a final oxide content of 1.0 per cent. by weight.

Oxidised powders were included in this investigation in view of the improved corrosion r ance of these materials in carbon dioxide as noted by Smith et al. (1961).

4. OPERATION

The die was loaded by first inserting the bottom plunger into the die to a depth of 1 inch; with the die supported on two steel blocks the powder was then poured into the die body to form a column 4 inches or 6 inches high for the 2-inch and 4-inch diameter compacts respectively. The powder was tamped and vibrated by hand, and was carefully levelled before the top plunger was inserted. Loaded dies were placed centrally in the chamber and supported on mullite bricks; an alumina spacer was placed between the top plunger and the stainless steel ram. The top cover was placed in position and the stainless steel ram inserted through the Wilson seal to contact the alumina spacer. The chamber was then evacuated to a pressure of 10^{-3} mmHg. A light pressur (15 – 100 lb/in^2) was exerted on the plunger to hold the assembly while the die was heated to 1080° This temperature was chosen since the reaction between beryllium and carbon becomes excessive above 1100°C.

When the temperature reached about 700°C the die and contents evolved gases which led to an increased chamber pressure; in most pressings the pumping system was able to maintain the chamber pressure below 10^{-3} mmHg. Gas evolution was most marked when a new graphite die was used and a separate degassing stage was introduced for new dies.

The temperature in the centre of the die wall was measured with a platinum/platinum–13% rho thermocouple, and confirmed by measurements on an optical pyrometer focused on the top of the die through a quartz glass window in the furnace cover. When the temperature reached the desired leve (1070 – 1080°C) the power was reduced and the temperature held constant for 15 minutes to enable the interior of the compact to attain constant temperature. The pressure was then increased slowly to the desired values, ranging from 50 – 1500 lb/in^2, and held for times ranging from ½ to 3 hours. The power was then switched off and the compact allowed to cool to room temperature.

The die and compact were removed from the chamber and the compact removed from the die by applying a light pressure; the thermal expansion coefficient of beryllium (18 x 10^{-6} in/in deg C) is greater than that of graphite (4 x 10^{-6} in/in deg C) and the finished piece was smaller than the die cavity.

Above a temperature of 700°C beryllium reacts with graphite (Clare 1958) and reaction rates at 1000 – 1100°C are high enough to cause a small amount of beryllium carbide to form on the working faces of the graphite die and plungers. Carbide formation was greatest on the die wall coinciding with the top and bottom faces of the compact. By carefully scraping this formation away with a sharp metal scraper and refitting the plungers a die could be used for as many as six pressings. This die life is reasonable on experimental equipment but die costs are high and improvement in die utilisation is most desirable. Most of the carbide formed on the graphite side of the interface; the thin film of carbide (0.005 – 0.020 inch) on the beryllium compact was machined off to give a clean product.

The density of the compacts was calculated from the ratio of weight in air to volume.

5. RESULTS

5.1 Hot Pressing of "Standard" Powder

This powder is defined as Pechiney "electrolytic" powder –200 mesh B.S.S. containing 0.5 – 0.6 per cent. BeO, present as a coating on each particle rather than as free BeO particles.

The following conditions were suitable for consolidation of this powder into 2-inch diamete compacts weighing 150 – 200 g and attaining a density of 99.3 ± 0.3 per cent. of theoretical (1.85 g/c

Temperature	1080°C
Pressure	1200 lb/in^2
Time	1 – 2 hours .

These agree with conditions published for Brush Beryllium Company Q.M.V. grade powder (Whit and Burke 1955) where 2½-inch diameter compacts required 1000 lb/in² pressure at 1075 °C for consolidation.

The variations in density with compact diameter, weight, pressure, and time are shown Figure 3; marked effects were noted as compact weight and size were varied. The effect of com weight for 2-inch diameter compacts was most marked at pressures below 500 lb/in² and a redu in compact weight from 200 g to 130 – 140 g achieved an increase in density of 5 – 10 per cent. these conditions. Similarly 4-inch diameter compacts containing 700 – 1100 g powder were rea consolidated to > 98 per cent. of theoretical density at pressures of 800 lb/in² or 400 lb/in² lo than required for the 2-inch compacts.

These effects were attributed to the reduced wall friction losses applying on the compac with low length-to-diameter ratios. These ratios were 0.7 and 1.2 for the 2-inch compacts co ing 140 g and 200 g powder respectively, and 0.4 for the 4-inch compacts containing 700 g pow

The rate of approach to final density was followed by noting the ram position at various during pressing. After times in excess of 40 – 50 minutes the density approached theoretical, a reproducibility of these measurements was poor. However results suggest that negligible comp occurred after this time and it is therefore doubtful that any significant difference in behaviour attributed to compacts pressed for one and three hours, particularly where final densities above cent. of theoretical were achieved.

5.2 Hot Pressing of "Oxidised" Powder

Two grades of oxidised beryllium powders were hot-pressed.

(i) Pechiney "electrolytic" beryllium –150 +200 mesh B.S.S. oxidised in a fluidised be 1 hour at 700 °C to achieve an average BeO content of 2.3 per cent.

(ii) Pechiney "electrolytic" beryllium –200 +300 mesh B.S.S. milled for 112 hours in an atmosphere of oxygen giving a final oxide content of 1.0 per cent. BeO.

The results for these grades of powder are shown in Figure 3 and Table 2. A marked de tion in compaction behaviour was noted with the fluidised material containing 2.3 w/o BeO. For diameter compacts containing 140 g Be, the final density was 5 – 10 per cent. less than that att on unoxidised "standard" powder and this effect may be associated with either the presence o oxide or the narrow particle size range and larger particle size of the powder used. (More unifor ditions in the fluidised bed were attained with the narrow range of large particles than with stan material). A lower final density was also noted for the milled powder containing 1 per cent. Be (–200 +300 mesh) pressed in either 2-inch or 4-inch diameter compacts, although in this case effect was much smaller and densities equivalent to those for standard powder could be achieve pressures 200 – 300 lb/in² above those for "standard" powder.

6. DISCUSSION

To achieve compacts of uniform density the die arrangement and pressing conditions are important. Considerable loss of pressure within a compact occurs owing to die-wall and partic particle friction (Train and Hersey 1960); these frictional forces oppose the transmission of app pressure in some areas, and the unequal distribution of pressure within the compact produces wi variations in density. Ideally pressure should be applied isostatically to achieve a uniform den but reasonable conditions may be achieved by pressing from both ends of the die; in this way a of high density with length-to-diameter (L/D) ratio of about one can be formed. When pressing one end only, under the same conditions of pressure, temperature, and time, the ratio is usually less than unity.

In the present investigation a small amount of bottom pressing was attained by the "floa die" principle described in Section 4. Frictional forces between the powder and die prevented die from falling over the bottom plunger. When pressure was applied in one direction the powde particles agglomerated to form a coherent mass and frictional forces between the powder and die

were greater than forces between plunger and die wall. On further compression the die was therefor forced downwards over the lower plunger which was solidly supported. The compression of powder and densification of the compact therefore progressed in a similar manner from both ends. This was confirmed by the presence of a low-density band in the centre of compacts (particularly where the mean densities were below 90 per cent. theoretical); these compacts can be regarded as two single-end pressed compacts, one being the mirror image of the other.

In all compacts with L/D ratios above 0.5, the geometry of the compact is a major factor in determining the mean density and the variations in density within the body; for compacts with large values of L/D, the relationships between mean density and pressing conditions are meaningless unless the pressures at all points throughout the compact are greater than the opposing frictional forces. The total pressing load required is thus the sum of the "inherent" pressure required for consolidation of the powder under ideal ("frictionless") conditions and the pressure required to overcome powder and die-wall friction. The friction term increases with the L/D ratio of the compa

This effect was noted in the present work (Figure 3) where the pressure required to consolid "standard" powder to 99 per cent. of theoretical density increased approximately as follows:

L/D	Pressure Reqd. (lb/in^2)
0.4	670
0.7	900
1.1	1200

Thus with larger L/D values a larger pressure must be applied to ensure the centre of the compact achieves minimum pressing conditions. Extrapolation of these conditions to low L/D ratios suggest that the "frictionless" stress required to consolidate beryllium at 1080 °C is about 400 lb/in^2 which is consistent with the required stress for creep at this temperature.

The hot-pressing process has been studied previously (see for example, Williams 1954; McClelland and Smith 1961) and there is general agreement that densification proceeds primarily by a plastic (or viscous) flow mechanism; diffusion effects have been noted but do not appear to be the rate-determining factor except possibly at densities near to theoretical where particle-particle contact is extensive and grain boundary rearrangement or recrystallisation is proceeding. The variations in pressing behaviour noted between the "standard" and "oxidised" powders should thus be associated with the plastic flow behaviour of these materials. The presence of an oxide film may tend to retard the process of hot-pressing by restricting movement of particle-particle interfaces, particularly in the first stages of consolidation where particle rearrangement is proceeding; alternatively the oxide particles (or broken film) may increase the yield stress by dispersion hardening, and at high densities the oxide may reduce diffusion across the original particle boundaries. The relative importance of these effects has not been established.

The effect of using large particles with a restricted size range is to decrease the loose packed density and a larger strain is therefore required to consolidate the particles to a high density The effect on compacting pressure would be small, however, unless the metal tended to work-harden under these strains. At 1080 °C, beryllium will work-harden at high strain rates, such as achieved i extrusion, but these rates could only be expected at the positions of point contact of powders; the volume of metal subject to these high strain rates is therefore small. On the other hand, the yield strength of dispersion-hardened structures is particularly sensitive to both strain and strain rate, and the yield strength of these oxidised powders may vary with strain and hence reflect an effect of particle size.

7. STRUCTURE OF THE COMPACTS

The preparation of the billets described in this report was an intermediate stage in fabricatio all billets were subsequently extruded by the techniques detailed by Silver (1964). Extensive invest gation of the hot-pressed structures in relation to pressing conditions was thus impractical since the yield on extrusion would be drastically reduced. A small number of billets was examined, however, with results as discussed below.

Figure 4 shows a typical structure from a billet of "standard" powder hot pressed at 108 under 1200 lb/in² to achieve a mean density of > 99 per cent. of theoretical; this sample was ta from the centre of the top face, that is, directly under the moving plunger, and the sectioned face perpendicular to the pressing direction. The mean grain size measured on Figure 4 is 20 micron a range of 4 – 80 microns. The particle size of the powder was less than 76 microns, with a me of 20 – 25 microns and thus the extent of grain growth was negligible.

Although the measured density on the billet was > 99 per cent. of theoretical, a number o were noted in the section; final pore removal is probably quite difficult at 1080 °C if diffusion a boundary migration are operative as discussed previously.

The oxide film originally present on the "standard" powder was broken and dispersed b pressing but was still present at the grain boundaries; this undoubtedly contributed to the stabi the grains and prevented extensive grain growth.

The "oxidised" powder billets (containing 2.3 w/o BeO) showed a similar grain size and ture to those noted for the "standard" powder but there was more porosity as anticipated from th density measurement of 96 per cent. The oxide was again dispersed to the grain boundaries.

8. CONCLUSIONS

1. The "standard" Pechiney beryllium powder containing 0.5 – 0.6 per cent. oxide may hot–pressed to densities greater than 99 per cent. of theoretical at temperatures of 1050 – 1080 but the pressure required depends on the compact geometry (length:diameter ratio) and the press arrangement. Compacts with L/D ratios of 0.4 were consolidated under pressures of 650 – 700 l whereas compacts with L/D ratios of 1.1 required applied pressures of 1200 lb/in². These diff are attributed to the loss of pressure by die–wall and particle–particle friction.

2. The presence of 1 per cent. oxide introduced by ball milling has only a small effect u the pressing behaviour of Pechiney powder but powder with 2.3 per cent. oxide is particularly di icult to press to a high density; a narrow particle size range in this powder may also contribute the problem.

3. There was no evidence of significant grain growth under the pressing conditions use this work and the oxide film on the original powder tended to be broken and dispersed at grain b aries.

9. ACKNOWLEDGMENTS

The large scale pressing unit was partly designed and wholly constructed by Mr. R. Ro Mr. J.M. Silver and Mr. P.G. Alfredson assisted in powder preparation.

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TABLE 1

SPECTROGRAPHIC ANALYSIS OF BERYLLIUM POWDERS

Type of Powder	p.p.m. by Weight									% by Weight Beryllium Oxide
	Fe	Al	Si	Mn	Cr	Ca	Na	Mg	Cl	
"Standard"	550	280	350	< 20	40	65	40	65		0.54
Oxidised in fluid bed	450	285	375	< 20	< 40	< 50	40	30	20	2.3
Oxidised by ball mill-ing	,,	,,	,,	,,	,,	,,	,,	,,	,,	1.0

TABLE 2

DETAILS OF VACUUM HOT PRESSINGS

VHP No.	Type of Powder	Weight (g)	Diam. (in)	Temp. (°C)	Time (h)	Pressure (lb/in^2)	% Theoretical	
							Compact	Ext
1	Standard	140	2	1080	1	50	70.5	9
5	,,	140	2	1080	2	100	73.0	9
2	,,	140	2	1080	1	100	75.0	9
3	,,	140	2	1080	1	140	73.5	10
6	,,	140	2	1080	1	250	92.4	10
15	,,	120	2	1070	1	750	88.0	–
16	,,	120	2	1070	1	750	97.4	–
17	,,	140	2	1080	1	750	94.5	10
7	,,	200	2	1080	1	250	77.0	–
8	,,	200	2	1080	1	400	78.5	–
14	,,	190	2	1070	1	500	85.5	–
26	,,	200	2	1080	2	1300	99.5	10
27	,,	200	2	1070	2	1200	98.9	–
28	,,	200	2	1080	2	1200	99.5	10
41	,,	835	4 *	1080	½	1000	92.0	–
42	,,	1170	4	1080	3	800	98.5	–
46	,,	680	4	1080	3	800	99.5	–
19	2.3% BeO	140	2	1080	2	800	88.1	–
20	,,	140	2	1080	2	1350	93.4	10
21	,,	120	2	1080	2	1500	96.5	–
22	,,	130	2	1080	2	1500	97.0	–
44	,,	400	4	1080	3	800	82.0	–
45	,,	400	4	1080	3	800	87.0	–
23	1% BeO	140	2	1080	½	1500	99.8	10
24	,,	140	2	1080	2	1500	99.5	10
25	,,	140	2	1070	2	1500	99.6	–
43	,,	300	4	1080	3	800	98.0	–

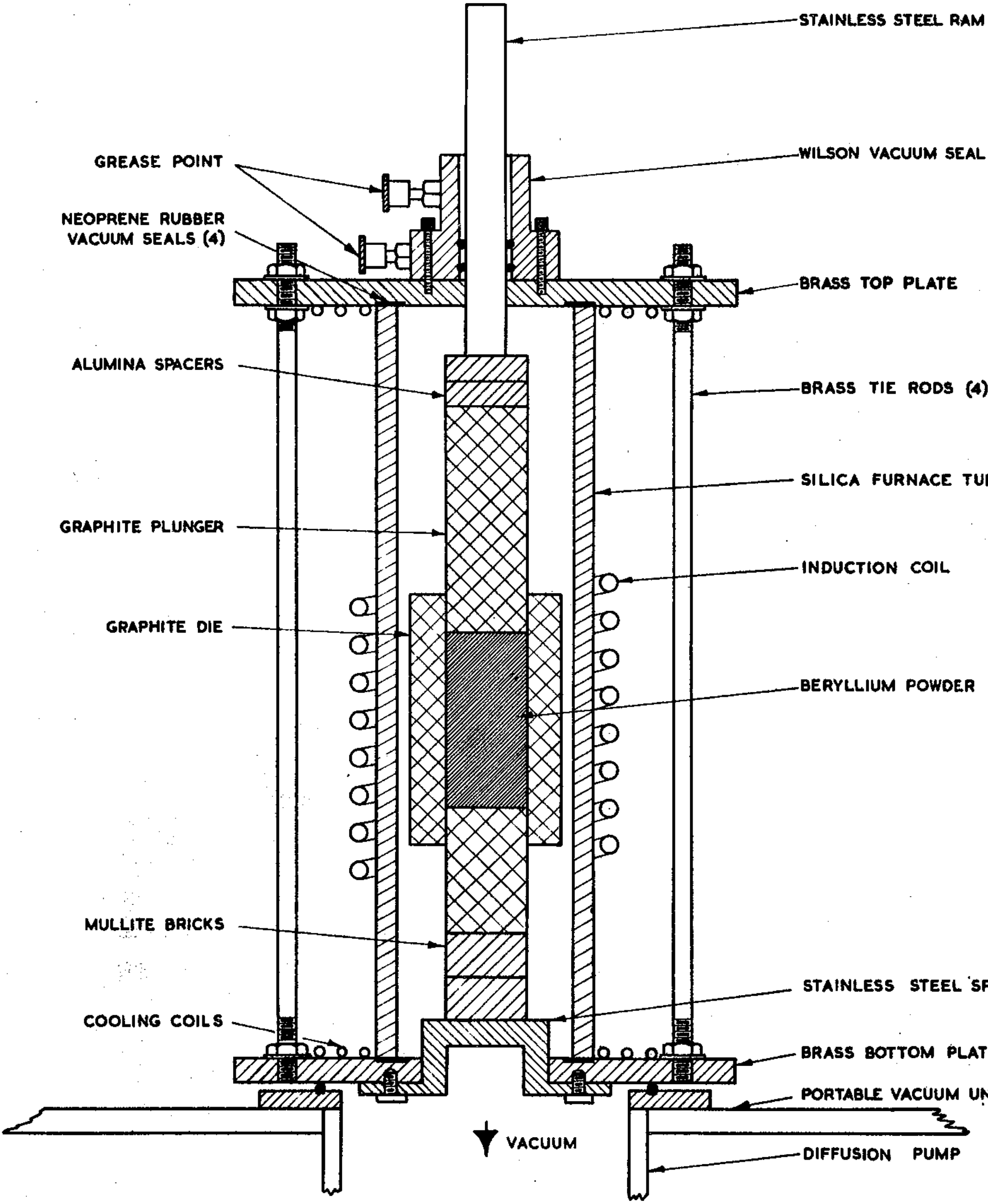
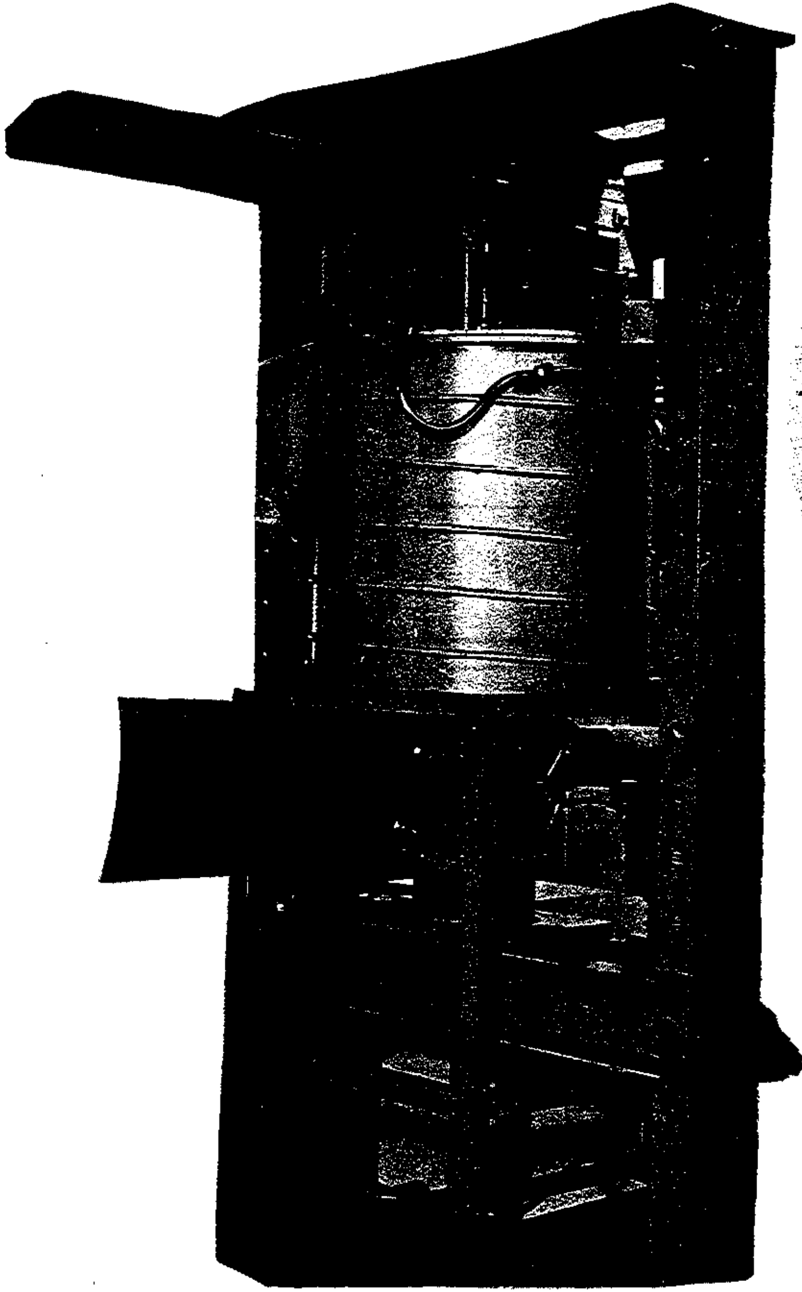


FIGURE 1

CROSS-SECTIONAL VIEW OF SMALL HOT PRESSING ARRANGEMENT



(a) General arrangement

(b) Transducer [illegible]

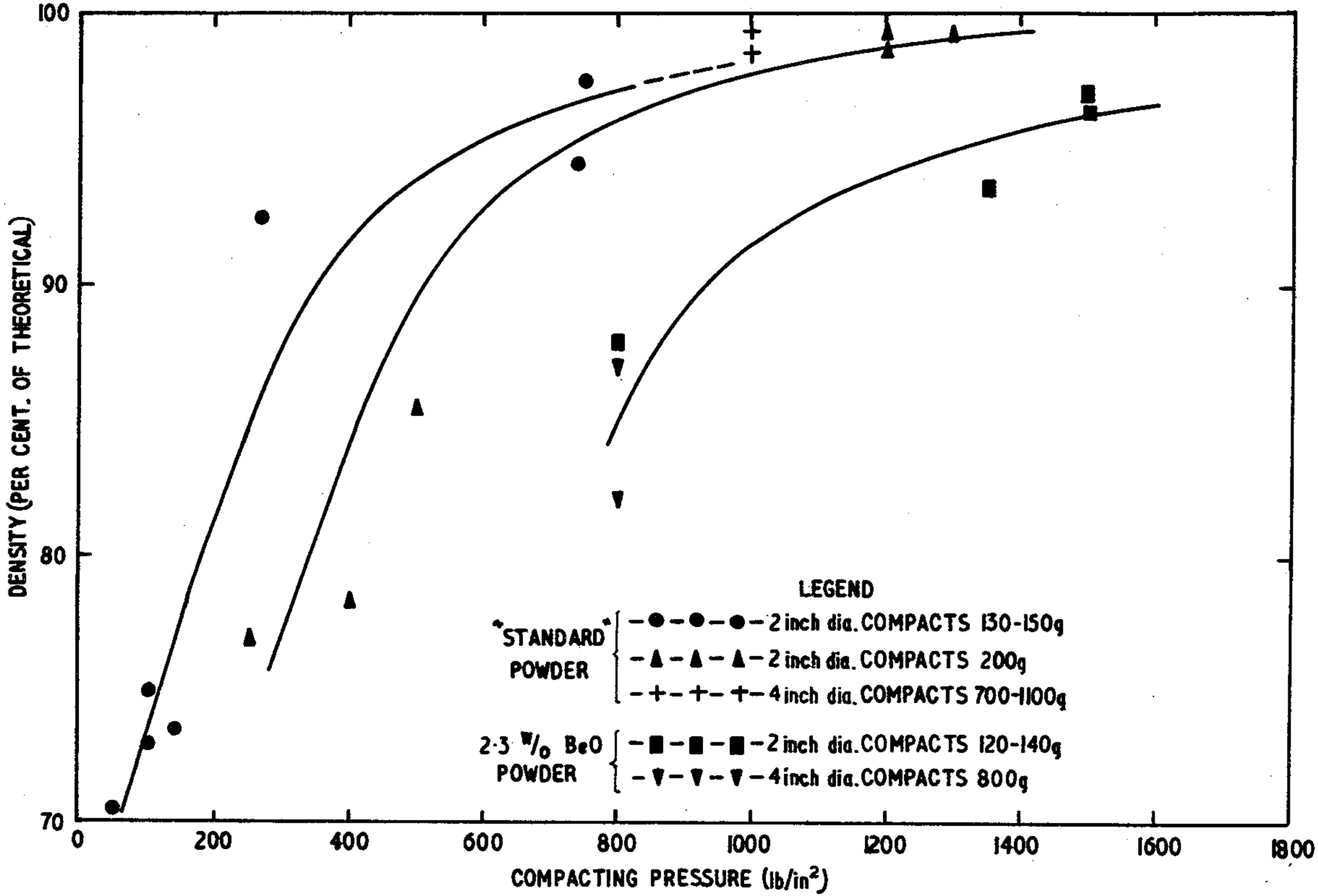


FIGURE 3 SUMMARISED RESULTS OF HOT PRESSING CONDITIONS

X 250

FIGURE 4 TYPICAL STRUCTURE FROM A BILLET OF 'STANDARD' BERYLLIUM POWDER HOT-PRESSED AT 1080°C UNDER 1200 lb/in²