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LUCAS HEIGHTS

THE HOT PRESSING OF BERYLLIUM OXIDE WITH ADDITIVES

by

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ABSTRACT

The effect of variations in temperature, pressure, and pressure cycle on the density v grain size relationship was determined for hot pressed, sulphate-derived UOX beryllium oxide: the effects of selected additives on the final grain size using constant hot pressing conditions were also determined.

A single-ended pressing technique, incorporating an incremental build-up in the pressing pressure, was developed to produce hot pressed specimens of near theoretical density with a uniform grain size of 25μ. Smaller grain sizes were not obtained by this technique owing to the onset of discontinuous grain growth at a bulk density of 97 per cent theoretical. However, by introducing a 'dwell' or 'equilibration' time at temperature before the application of the load, a theoretically dense specimen (3.010 g/cm^3) was produced with a uniform 8μ grain size.

<u>ABSTRACT</u> (Continued)

Carbon was the only additive which consistently refined the grain size at all levels of addition. A hot pressed specimen of 99 per cent theoretical density and 2μ grain size was obtained using a standard condition of 1500°C, 250 kg/cm^2 for 25 minutes, 5 volume per cent of colloidal graphite additive.

CONTENTS

1. INTRODUCTION

The degree of irradiation damage and the control of mechanical properties of the potentially useful nuclear reactor material beryllium oxide are known to be influenced by the grain size and density of the fabricated material. Hickman and Pryor (1964) showed that the best resistance to neutron irradiation is obtained with grain sizes of less than 5 microns while Knudsen (1959) predicted that, for ceramics, the highest mechanical properties will be developed by high-density fine-grained material; in addition, a completely non-porous material should have good potential for retaining gaseous fission products. However, the density v grain size relationships achieved by the established cold forming and sintering routes for BeO (for example, Clare 1964, Bardsley and Ridal 1964) show that a grain size of less than 10 microns cannot normally be achieved at densities in excess of 98 per cent theoretical.

For isostatically pressed and sintered BeO, Bannister (1965) predicted that high surface area powders compacted to high green densities were the most likely to sinter to near theoretical densities with a fine grain size. This prediction is difficult to test because high surface area powders are difficult to press to high green densities; green densities greater than 1.7 g/cm^3, even with 10 m^2/g surface area powders, involve the use of very high pressures.

Theoretically-dense, translucent BeO can be produced by a hot pressing route, but unless optimum conditions are accurately determined it is likely to have a grain size of about 30 microns. Johnson (1964) found that grain size in hot pressed specimens was dependent on the hot pressing temperature and on a 'soaking' or 'dwell' time at this temperature before the application of the pressure. Vasilos and Spriggs (1964) showed that grain size at high densities can be effectively controlled during hot pressing by the use of pressures up to 708 kg/cm^2 (10,000 p.s.i.). However, high pressure hot-pressing equipment was not available for the present study and the more conventional graphite dies with a limited maximum pressure of 300 kg/cm^2 (4,300 p.s.i.) were used. It was considered that by close control of the hot pressing cycle, grain sizes much finer than 30μ could be achieved in theoretically dense material, with consequent finer grain sizes at lower densities, even with graphite dies.

An additional method of grain refinement in ceramics is by the use of a second-phase inert additive as proposed by Zener (1949); hot pressing is a suitable technique for investigating this mechanism since any deleterious effects of the additives on sintering rates are minimised due to the faster densification

rates achieved. Langrod (1965) observed considerable grain refinement in hot pressed BeO containing carbon and metal carbides.

The 'stabilised grain size' (that is, the limiting grain size achieved during normal grain growth) in a ceramic oxide containing inert, discrete, uniformly dispersed, uni-sized spherical particles of a second phase can be predicted from a Zener type analysis (Zener 1949). In practice, equations of the type (Woolfrey 1967):

$$D_f = 0.3 \ d/f$$

$$\text{or } D_f^2 = 0.6 \ d^2/f \quad ,$$

are usually applied directly to the non-ideal case where:

D_f = limiting grain size (mean linear intercept $D_L \times 1.5$)

d = mean particle size of second phase.

f = volume fraction of second phase.

In this study the effect of second phase additives (representative of all the available types) on the density $\underline{v}$ grain size relationship established for hot pressed BeO, are examined in an attempt to determine the optimum additive for grain size stabilisation.

2. EXPERIMENTAL TECHNIQUES

2.1 Materials

The BeO used was Brush UOX Lot 200-W-269-P (surface area approximately 10 m^2/g). The powder was ball-milled in water with sintered BeO medium to break up the long needle-like crystals which are present in the powder to the extent of about 1 volume per cent.

Additives were chosen to include three material types, namely oxides, metals, and carbon or carbides. Within these categories actual materials were chosen on the grounds of availability as fine powders. Those used were:

0.015 - 0.020 micron colloidal silica (G. L. Cabot Inc., U.S.A.).

0.004 - 0.007 micron zirconia sol (W. R. Grace Chemical Co., U.S.A.).

0.1 micron gamma alumina (Griffin and George, U.K.).

0.10 - 0.20 micron yttria sol (W. R. Grace Chemical Co., U.S.A.).

1.5 micron tungsten powder.

0.035 - 0.05 micron colloidal graphite (Acheson Colloids Ltd., U.K.).

Additive levels were arbitrarily chosen as 1, 3 and 5 volume per cent for all materials. The required compositions were calculated assuming that BeO and the additives remain as separate phases, each of theoretical density.

2.2 Mixing

The additions were made as an alcohol suspension to an alcohol slurry of the beryllia, and mixed for 1 hour. Alcohol was added during this period to maintain a creamy consistency and to facilitate mixing. The powder was then dried under an infra-red lamp and the dried cake crushed to a powder.

2.3 Hot Pressing

The BeO powders or additive mixtures were poured into 1 inch diameter high-purity graphite dies; the die was tapped to ensure a uniform fill, and the top plunger inserted. The assembled die was then loaded into the hot pressing rig, as shown in Figure 1, and placed on the vertical press; flowing nitrogen was introduced into the insulation to protect the die from excessive oxidation during hot pressing.

The die was heated inductively using a 30 kW R.F. heater and the temperature was measured optically using a graphite sight tube inserted to the centre of the die. Pressure was applied to the die plunger using a 60 ton hydraulic press fitted with air-hydro pumps to allow a pre-determined pressure to be maintained to ± 5 per cent automatically.

The standard cycle, developed from a technique described by Reeve and Ramm (1961), involved rapidly heating the die to 1,000°C and then heating at approximately 800 degC/hour up to the hot pressing temperature. The initial pressure of 50 kg/cm^2 was allowed to leak away until the temperature was 100°C below the required temperature. The pressure was then increased to 100 kg/cm^2, and the full pressure applied at the required temperature. This temperature was maintained to within ± 10°C by manual power adjustment until completion of the time cycle. The power was turned off and the die allowed to cool; the pressure was allowed to leak away for 5 minutes, and was then reduced to 50 kg/cm^2.

Pure BeO was pressed at varying times (1 to 250 minutes), temperatures (1,200°C to 1,700°C), and pressures (100 to 300 kg/cm^2). The temperature-pressure cycle was also varied to examine its effects on grain size and density. A standard condition of 1,500°C and 250 kg/cm^2 for 25 minutes was chosen for powders containing additives.

2.4 Density Determinations

The hot pressed specimens were ground on all surfaces on 280 grit carborundum paper to remove any graphite or beryllium oxide powder adhering to the surface, and the densities were then measured using a water displacement method. The theoretical density of the BeO was taken as 3.010 g/cm^3 while that of the BeO with additives was calculated using the theoretical densities of the components, assuming that no solid solutions or second phases were formed. The accuracy of the density determination was estimated at ± 0.2 per cent.

2.5 Grain Size Measurement

Cut sections of the pressings were metallographically polished, etched and examined under the optical microscope. The reported grain size was the mean linear intercept of a total of 150-200 grains at 10 random positions; the accuracy of the measured grain size was estimated to be $\pm$ 15 per cent.

3. RESULTS AND DISCUSSION

3.1 Beryllium Oxide

Hot pressed specimens were produced using a standard temperature and pressure (1,500°C, 250 kg/cm^2) for times varying from 1-250 minutes. The grain size v porosity and grain size v time relationships of this material are shown in Figures 2 and 3. The distinctive feature of the microstructure was the appearance of a band of larger grain size within the specimen in the bulk density range 97.0 to 99.5 per cent theoretical. Outside this density range the grain size was apparently uniform throughout the specimen. Fully dense BeO produced by this technique had a uniform structure, and a mean grain size of at least 25μ.

The 'banded' grain structure consisted of three distinct regions: a rim of fine grain size, a core of slightly larger size, and between these a region of large grains. The grain size v time relationship (Figure 3) shows that within the fine grain size regions, and also within the uniform structures observed below a density of 97.0 per cent theoretical, grain growth closely followed a cubic law such that the cube of the grain size was proportional to time. At a bulk density of 99.3 per cent theoretical the grain growth became discontinuous, following an almost linear relationship until a bulk density of 99.5 per cent theoretical was achieved. The coarse grained region apparently resulted from the onset of discontinuous grain growth at a low bulk density (approximately 97 per cent theoretical) in a specific region of the specimen, discontinuous grain growth ceased at approximately 20 microns grain size when the growth rate

changed so that the tenth power of the grain size was approximately proportional to time. This implies restricted grain growth, due to impingement effects of equally large grains, as is often found in fully dense metals.

The effects of time, temperature, and pressure on the porosity of hot pressed BeO are shown in Table 1. Bulk density was increased by increasing temperature or pressure, but increasing the hot pressing time beyond 25 min had little effect. Thus to produce the maximum density, both the pressure and temperature should be as high as possible. Accordingly, a beryllium oxide specimen with a measured density of 3.008 g/cm^3 was produced by hot pressing at 1,600°C for 25 minutes at 300 kg/cm^2; the highest density attained previously was 2.995 g/cm^3 (99.5 per cent theoretical).

The investigations into the effect of the pressure cycle on the density·grain size relationships showed that when the full pressure was applied throughout the temperature cycle the density decreased and the microstructure consisted of a coarse-grained rim and fine-grained core. Alternatively, when the pressure was applied after a 'dwell' or 'equilibration' time at the pressing temperature, as advocated by Johnson (1964), the density increased, the mean grain size decreased, and the coarse-grained region moved towards the bottom of the pressing. For one specimen the use of a 'dwell' time of 20 minutes prior to hot pressing at 1,600°C and 200 kg/cm^2 for 80 minutes produced a thin ($\frac{1}{4}$ in) translucent BeO specimen, density 3.010 g/cm^3, with a uniform structure of 8μ mean grain size. Allowing for a possible 0.2 per cent error in measured density, this specimen was at least 99.8 per cent dense and since the microstructure showed it to be almost completely pore-free, the density was assumed to be 100 per cent of theoretical.

No consistent explanation for the appearance of the 'banded' structure has been devised.

3.2 Comparison with Cold Pressed and Sintered BeO

The work of Bannister (1965) on isostatically pressed and sintered sulphate-derived beryllium oxide powders, has shown that sintered grain size G is related to density D, powder surface area S, and green density D_0 by the empirical equation:

$$G = \frac{1.33\ (1-D_0)^{1.25}}{S} \cdot \frac{1}{(1-D)^{1.25}} \qquad \ldots\ldots(1)$$

This relationship was demonstrated to apply for powders with surface area in the range 8-24 m^2/g up to a density of 98 per cent theoretical.

For a powder of surface area 10 m^2/g isopressed to 60 per cent theoretical density (D_0 = 0.60) and sintered to 99 per cent theoretical density (D = 0.99), Equation 1 predicts a grain size of 13μ. This represents the lowest grain size possible for a cold pressed and sintered compact of this density, even if discontinuous grain growth could be completely prevented. A typical hot pressed specimen at this density had a duplex grain size with a range 8 - 20 microns; however, careful selection of the hot pressing technique (that is, using a 'dwell' time at temperature prior to pressing) gave a theoretically dense specimen of uniform 8μ mean grain size.

Equation 1 also predicts that variations in green density within a pressed compact would lead to grain size variations in the compact when sintered and would therefore predict grain size variations in the compacted powder during heating to the hot pressing temperature prior to the final application of the load. These grain size variations may contribute to the 'banded' grain size observed in the hot pressed specimens.

3.3 Effects of Additives

The variations in grain size and density of hot pressed beryllium oxide containing up to 5 volume per cent of the additions investigated are shown in Figure 4. However, the effectiveness of an additive in controlling the grain growth is best considered by comparing the grain size y porosity behaviour with that for pure beryllium oxide, as shown by the dotted lines in Figure 5. Except for tungsten and Y_2O_3 additions, a 'banded' grain structure was not observed in these specimens; the explanation for its occurrence in specimens containing tungsten or Y_2O_3 is not known.

3.3.1 Oxides

At levels of addition of up to 5 volume per cent the oxide additives did not cause grain boundary pinning in BeO. The Y_2O_3 additions apparently reacted with the BeO to form a liquid phase at the grain boundary which caused an increased grain size relative to the density. A liquid phase would not be expected to form at atmospheric pressure between BeO and Y_2O_3 until 1,580°C (Olds and Otto 1964) and the reason for its occurrence at 1,500°C during hot pressing is not known. Al_2O_3 caused unequiaxed grain growth (Figure 1) and no reduction in grain size relative to density. The mechanism of this unequiaxed grain growth has not been explained.

SiO_2 and ZrO_2 had deleterious effects on density but in most cases did not

change the grain size - density relationship from that for pure BeO. The exception was 5 volume per cent SiO_2, where significant grain refinement was observed. Similar effects of SiO_2 have been observed in cold pressed and sintered BeO by Bannister (private communication) who suggested that SiO_2 may dissolve to some extent at BeO grain boundaries. If sintering is controlled by anion diffusion rates, the decreased anion vacancy concentration resulting from the solution of a cation of higher valency would slow densification. A similar explanation may hold for ZrO_2.

These results suggest that oxides may not be suitable grain-refining additives for BeO.

3.3.2 Tungsten

The tungsten additions had little effect on the grain size y density relationship. The slight reduction in density was attributed to segregation of regions of tungsten, probably during mixing, which did not fully sinter under the hot pressing conditions. These regions would be of lower bulk density than originally assumed. The tungsten particle size (5 - 10μ) was probably much too large for grain refinement by a Zener mechanism at the levels used, but this does not preclude the use of refractory metal particles as a grain refining addition provided that they are sufficiently fine and uniformly distributed.

3.3.3 Carbon

At all levels of addition, carbon produced grain refinement (Table 2 and Figure 5); grain size progressively decreased with increasing additive levels while density remained essentially constant. The carbon particles of size 0.5 - 2μ were apparent, Figure 9, and were situated at grain boundaries. No 'banded' structures were observed but some isolated apparently carbon-free regions occurred with 5 - 6 times larger grain size (Figure 10) probably due to inefficient mixing.

Table 2 shows the calculated particle sizes necessary to produce the observed BeO grain sizes using two modified Zener equations due to Woolfrey (1967). The first:

$$D_f = 0.3d/f \quad , \qquad \qquad \ldots\ldots(2)$$

assumes a random distribution of particles, while the second:

$$D_f^2 = 0.6d^2/f \quad , \qquad \qquad \ldots\ldots(3)$$

assumes additive particles situated only at grain boundaries, a condition similar to the observed carbon disposition in these specimens.

Equation 3 yielded a particle size-range (0.77μ to 1.0μ) which is within the observed range and illustrates that the grain refining effects of carbon additions are not inconsistent with a Zener mechanism.

3.3.4 Conclusion on additives

Carbon was the most promising additive investigated for the grain refinement of BeO. However, as tungsten additions had little if any deleterious effect on BeO densification it is probable that any fine, inert, uniformly-distributed refractory particles of metals, or non-metals with the probable exception of oxides, could give the required grain refinement. Those suggested for future assessment are submicron carbon, tungsten, silicon carbide, and tungsten carbide.

4. SUMMARY

4.1 Pure Beryllium Oxide

(1) Hot pressed BeO of density greater than 99.5 per cent theoretical cannot be produced with a uniform grain size less than 25μ when a single ended pressing technique incorporating an incremental build-up of the pressing pressure is used.

(2) This limitation on the uniform grain size arises from the formation of a zone of larger grain size between the rim and the core of the specimen due to localised discontinuous grain growth; this commences at a bulk density of 97 per cent theoretical and persists to 99.5 per cent theoretical density when the grain size again becomes uniform.

(3) The 'banded' microstructure is apparently associated with the application of part or all of the pressure prior to the attainment of the hot pressing temperature. By introducing a 'dwell' or 'equilibration' time at temperature before the application of the load, a theoretically dense specimen of BeO was produced with an 8μ uniform grain size throughout.

4.2 Beryllium Oxide Plus Additives

(1) Carbon was the only additive which consistently refined the grain size at all levels of addition (1 - 5 volume per cent).

(2) SiO$_2$, ZrO$_2$, Al$_2$O$_3$ either adversely affected the densification or caused excessive grain growth. This suggests that oxides may not be satisfactory grain refining agents for BeO.

(3) Effective grain size control may only be possible by the use of inert, fine, uniformly distributed refractory particles, such as submicron carbon, tungsten, silicon carbide or tungsten carbide.

5. REFERENCES

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TABLE 1

EFFECT OF TEMPERATURE, PRESSURE, AND TIME

ON THE POROSITY OF HOT PRESSED BeO

HOT PRESSING TECHNIQUE						Bulk Porosity per cent
Fixed Parameters			Varied Parameter			
Temp. (°C)	Press. (kg/cm^2)	Time (min.)	Temp. (°C)	Press. (kg/cm^2)	Time (min.)	
1500	250	-	-	-	1	6.0
		-	-	-	3	3.5
		-	-	-	5	1.7
		-	-	-	10	1.0
		-	-	-	25	0.7
		-	-	-	50	0.65
		-	-	-	100	0.7
1500	-	25	-	100	-	5.0
	-		-	150	-	1.6
	-		-	200	-	1.2
	-		-	250	-	0.75
	-		-	300	-	0.60
-	250	25	1300	-	-	5.0
-			1400	-	-	2.0
-			1500	-	-	0.7
-			1600	-	-	0.5
-			1700	-	-	0.3

TABLE 2

GRAIN REFINING EFFECTS OF CARBON IN HOT-PRESSED BeO

Additive Fraction (f)	Observed BeO Grain-size (D_L x 1.5) (μ)	Calculated Addition, Size d Assuming Limiting Grain Size Achieved (μ)	
		Equation 2	Equation 3
0.01	6	0.20	0.77
0.03	4.5	0.45	1.00
0.05	3	0.50	0.86

D_L = mean linear intercept grain size

Brass Ram Guide — Ram

Mullite Spacer — Rubber Packing

Brass Plunger Guide — Gas Outlet Tube

Sindanyo Top — Graphite Sight Tube

Graphite Seal — Silica Tube filled with Alumina Bubble

Alumina Thermocouple Sheath — Graphite Die

Graphite Plungers — BeO Powder

Alumina Gas Inlet Tube — Graphite Base

Graphite Stool — Sindanyo Base

Water Cooled Induction Coil — Steel Load Distribution Plates

Mullite Base — Rubber Packing

Mullite Bricks — Steel Press Base

FIGURE 1. HOT PRESSING RIG
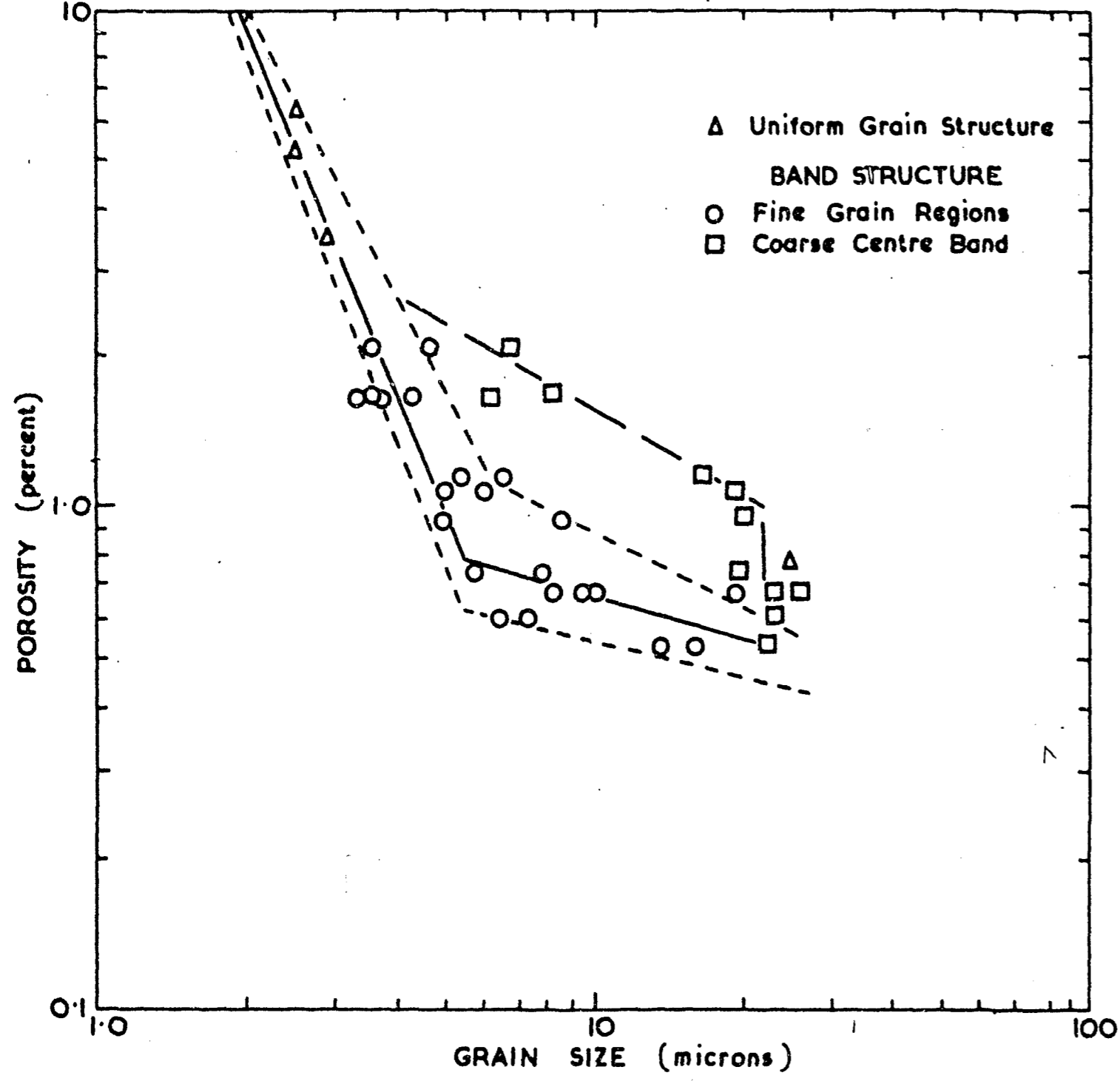
P1420

FIGURE 2. POROSITY v. GRAIN SIZE RELATIONSHIP FOR HOT PRESSED BeO
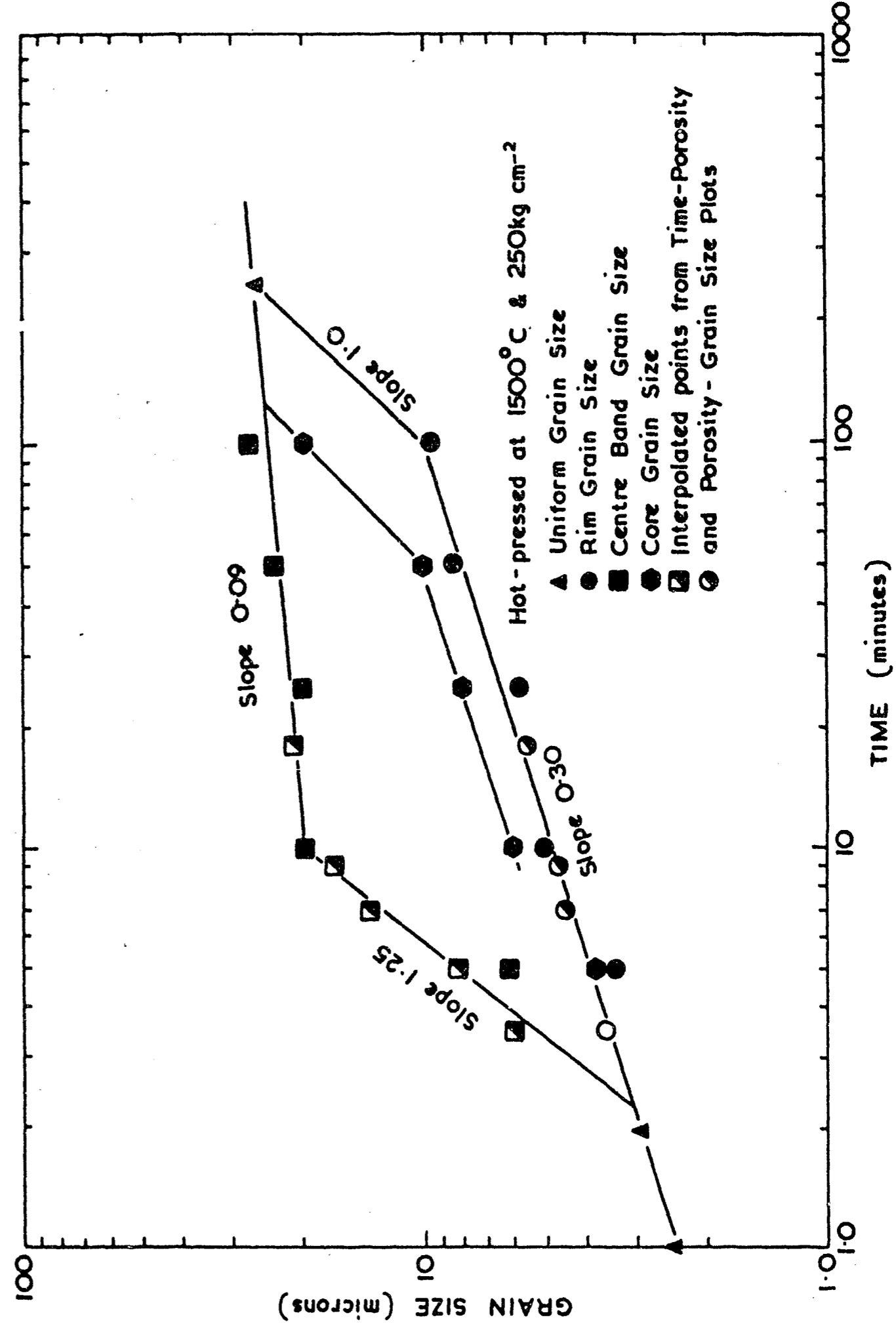
P1420

FIGURE 3. GRAIN SIZE v. TIME RELATIONSHIP FOR HOT PRESSED BeO
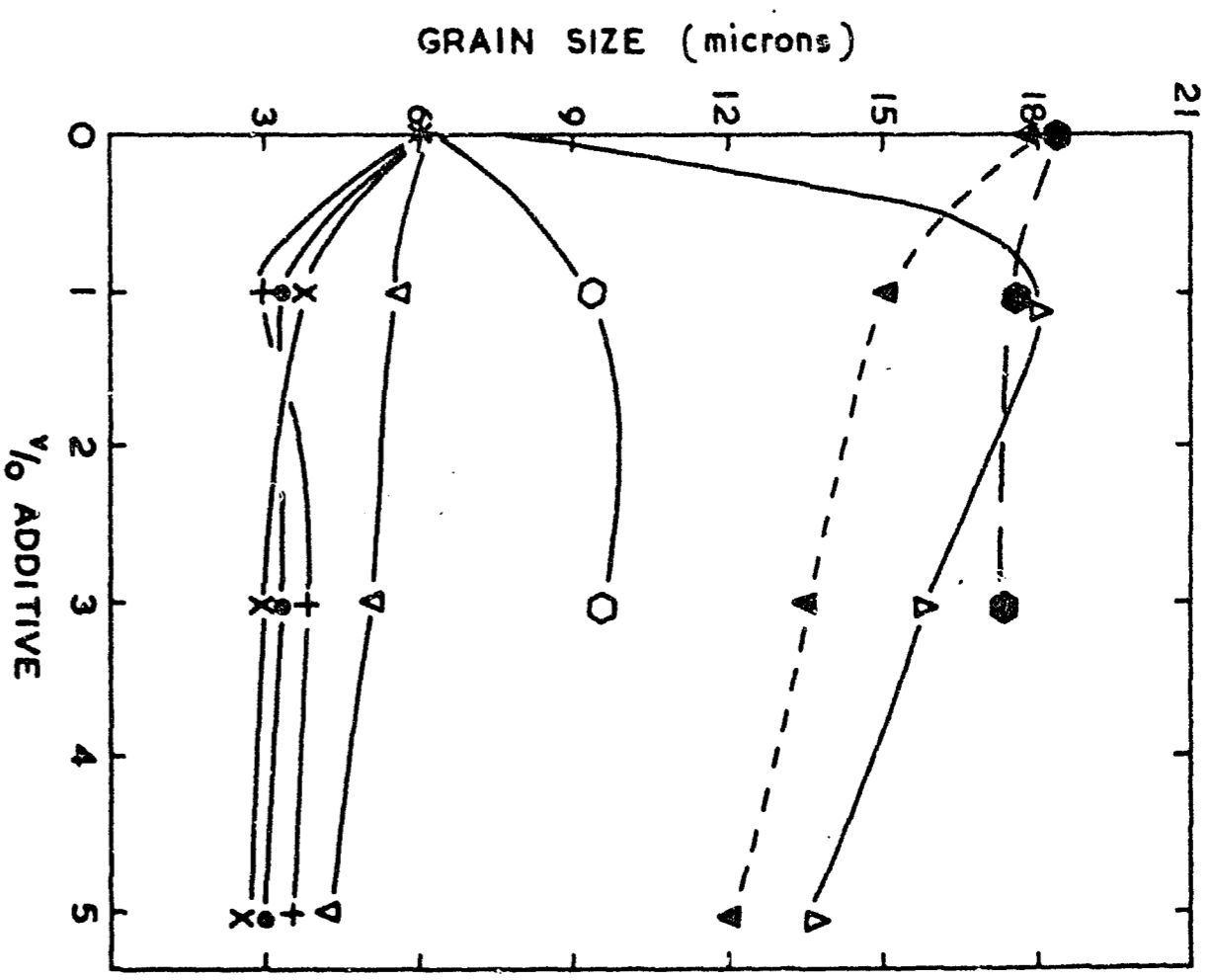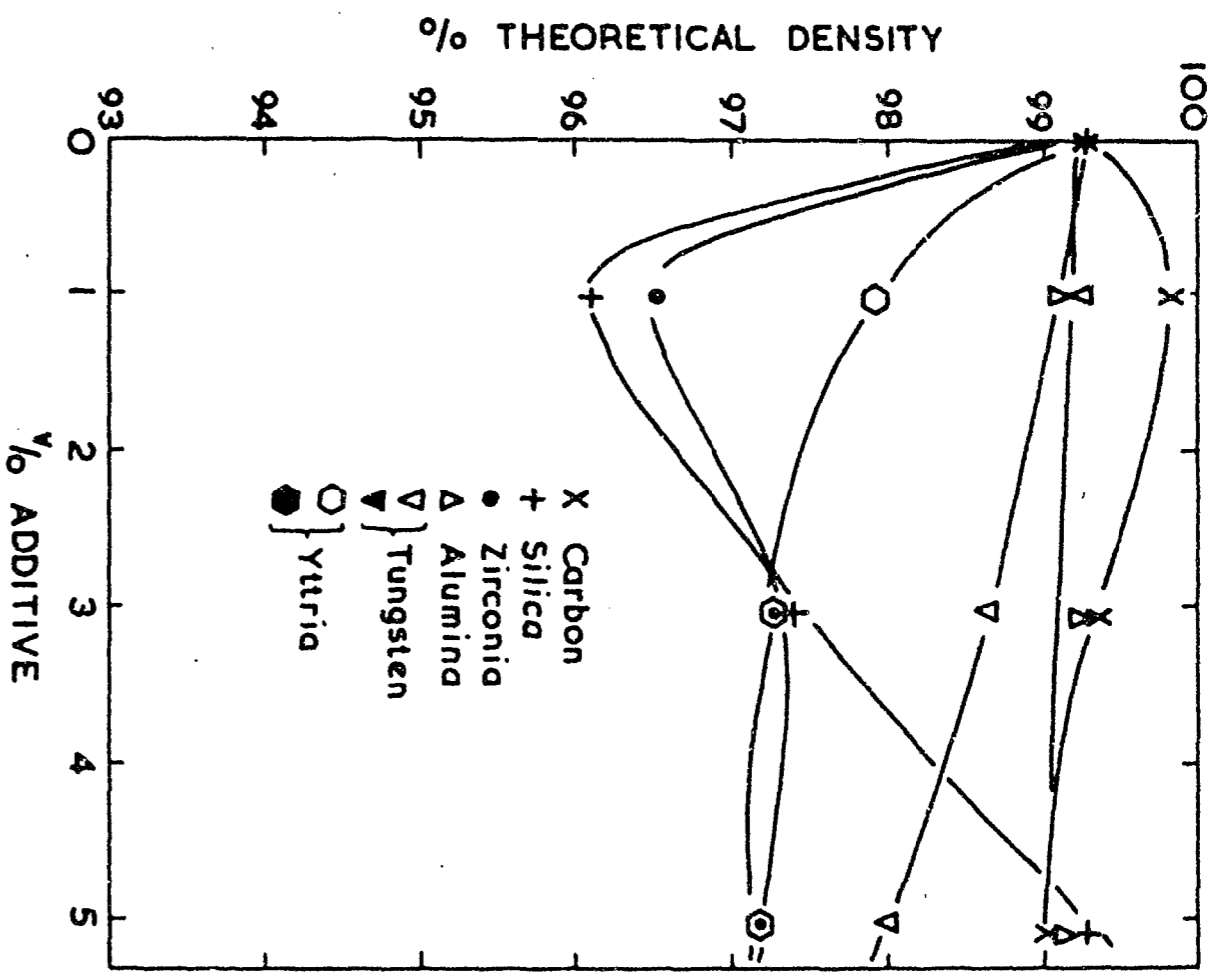
P1420

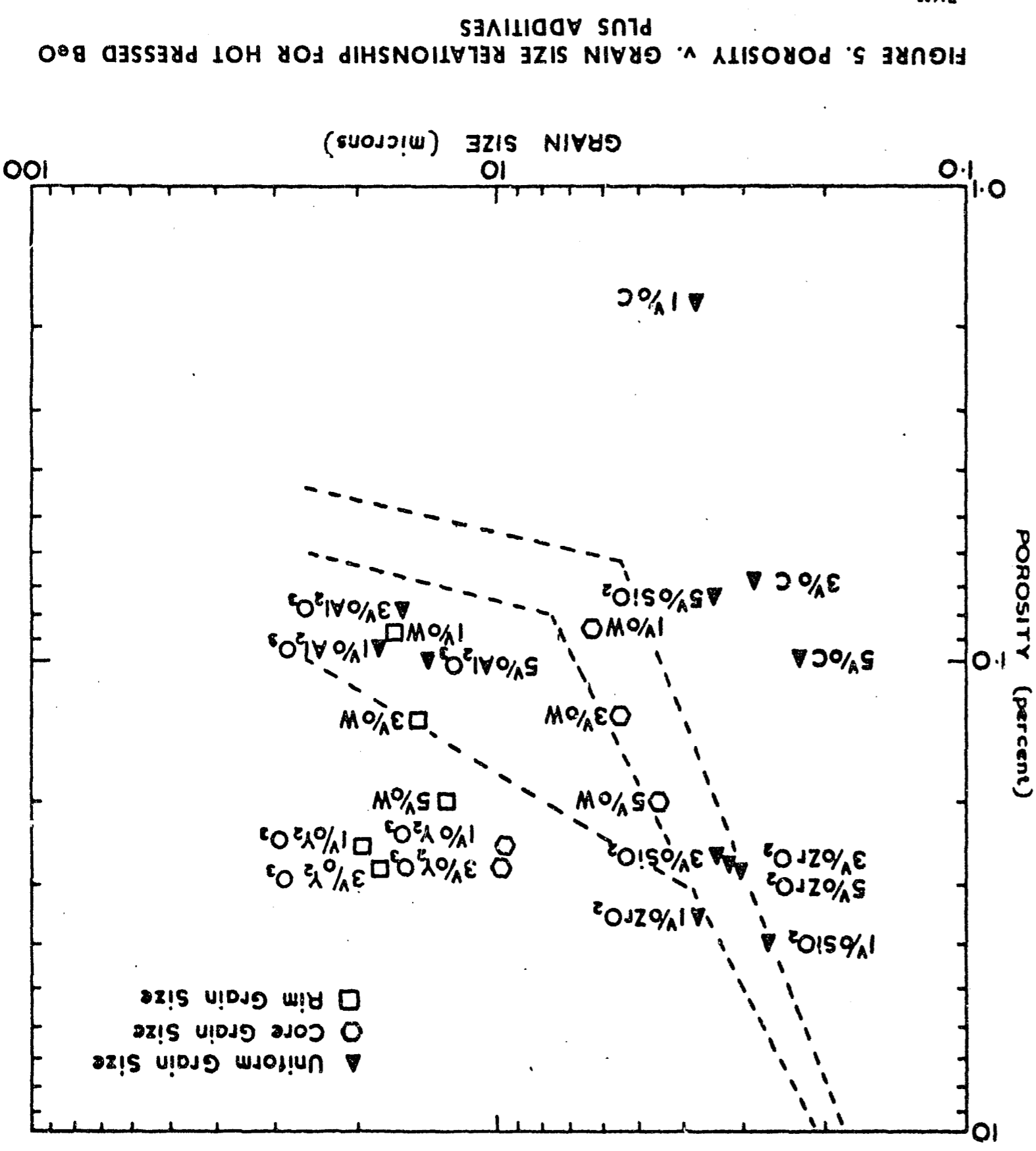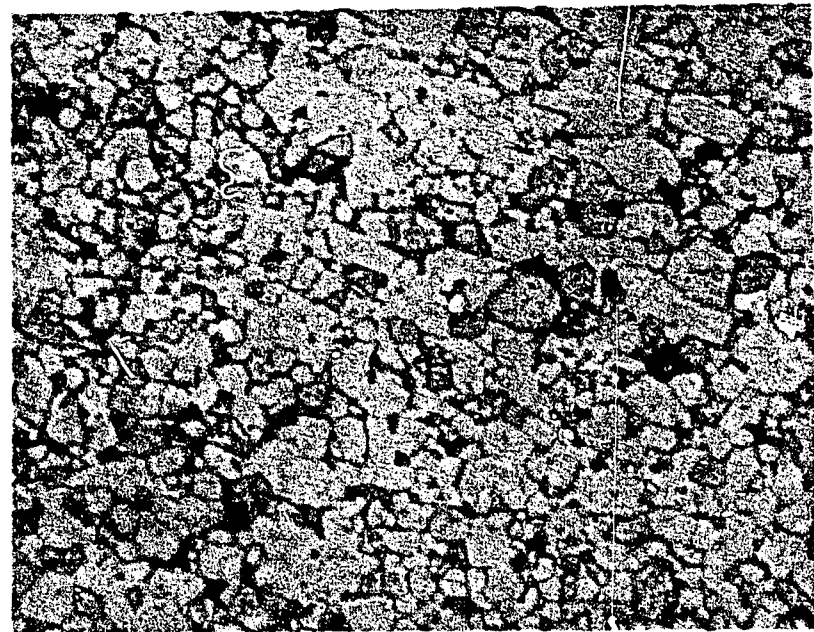FIGURE 4. EFFECT OF ADDITIVES ON HOT PRESSED DENSITY AND GRAIN SIZE OF BeO

% THEORETICAL DENSITY

% ADDITIVE

X Carbon
+ Silica
• Zirconia
△ Alumina
▽ Tungsten
● ○ } Yttria

GRAIN SIZE (microns)

% ADDITIVE

P1420

FIGURE 5. POROSITY v. GRAIN SIZE RELATIONSHIP FOR HOT PRESSED BeO PLUS ADDITIVES

GRAIN SIZE (microns)

POROSITY (percent)

1%C

3%C

5%C

5%SiO₂

1%W

5%Al₂O₃

3%Al₂O₃

3%W

5%W

1%Y₂O₃

3%Y₂O₃

5%Y₂O₃

3%SiO₂

5%SiO₂

1%ZrO₂

3%ZrO₂

5%ZrO₂

1%SiO₂

□ Rim Grain Size
○ Core Grain Size
▽ Uniform Grain Size

FIGURE 6. HOT PRESSED BeO + 3 VOL. PER CENT Y_2O_3
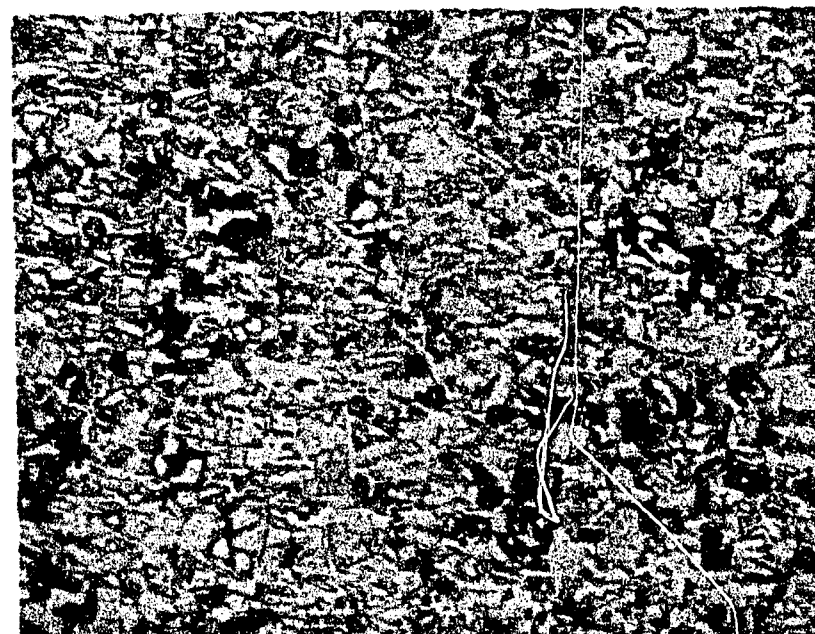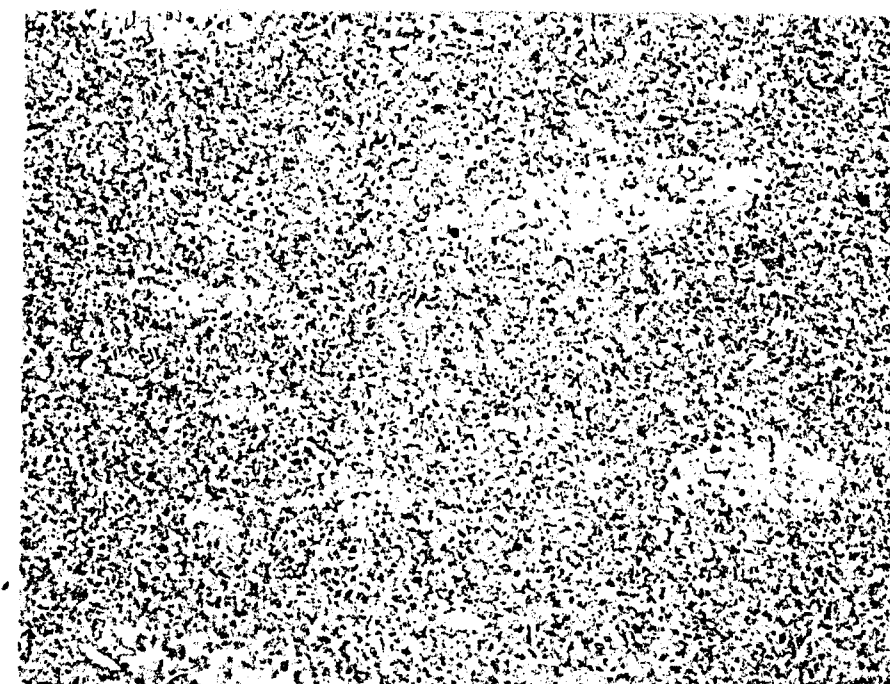

FIGURE 7. HOT PRESSED BeO + 3 VOL. PER CENT Al_2O_3
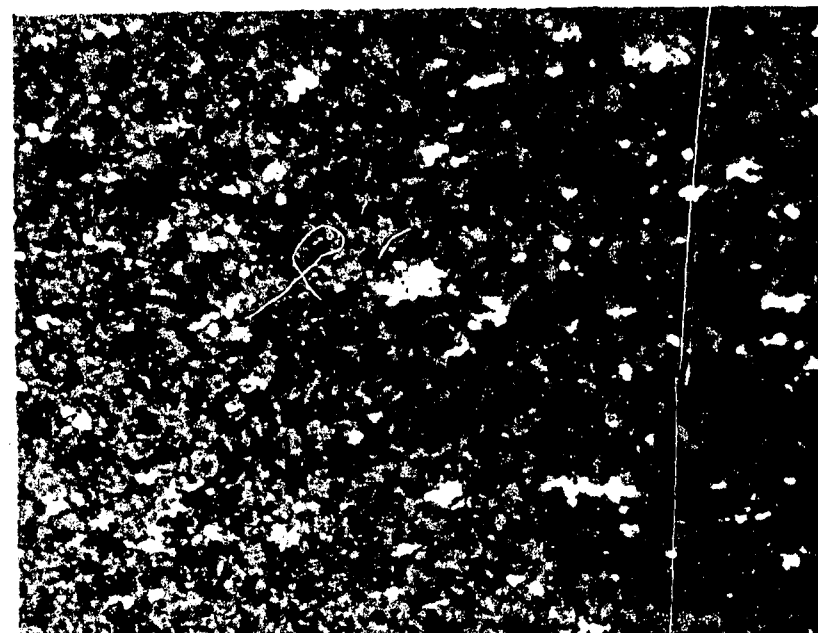
FIGURE 8. HOT PRESSED BeO + 3 VOL. PER CENT TUNGSTEN
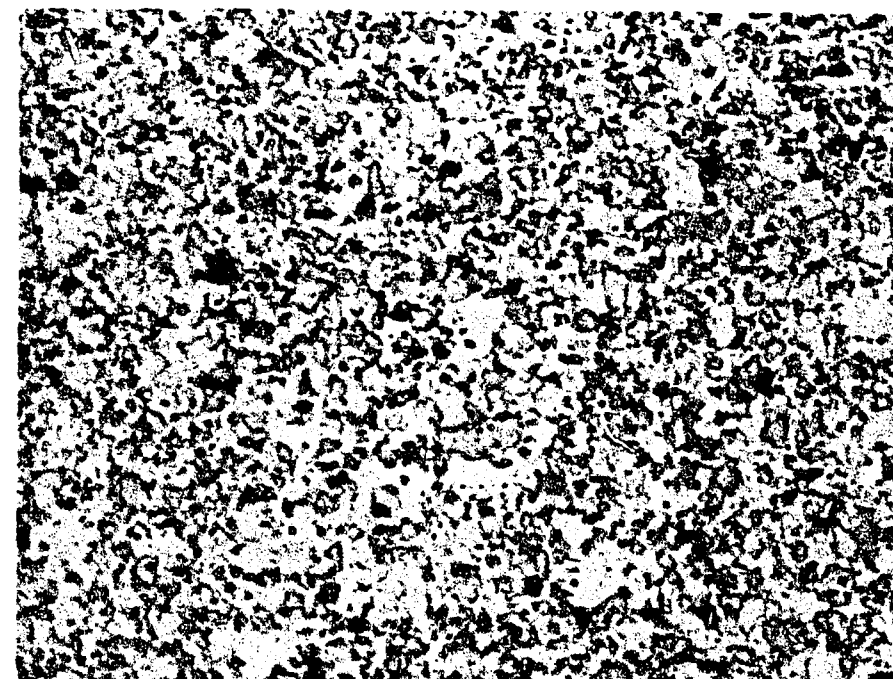
FIGURE 9. HOT PRESSED BeO + 5 VOL. PER CENT CARBON

FIGURE 10. HOT PRESSED BeO + 5 VOL. PER CENT CARBON