AAEC/E 80

UNCLASSIFIED

AAEC/E 80

AUSTRALIAN ATOMIC ENERGY COMMISSION

RESEARCH ESTABLISHMENT

LUCAS HEIGHTS

A COMPARATIVE STUDY OF TWO GRADES OF BeO

by

K. D. REEVE

E. J. RAMM

Issued Sydney, November 1961

UNCLASSIFIED

AUSTRALIAN ATOMIC ENERGY COMMISSION
RESEARCH ESTABLISHMENT
LUCAS HEIGHTS

A COMPARATIVE STUDY OF TWO GRADES OF BeO

by

K. D. REEVE
E. J. RAMM

ABSTRACT

Pechiney and Brush UOX BeO differ markedly in fabrication behaviour, only Brush UOX being readily sinterable.

A comparative study of the two powders has shown few outstanding differences in powder properties. Both are of high purity but contain free and combined moisture to the extent of about 1.5 per cent. Pechiney BeO has a larger mean crystallite size (0.2 – 0.3μ) than Brush UOX (0.1 – 0.15μ) and a larger range of crystallite size, and both contain a small proportion of crystallites of size 1μ and larger. The tap density of UOX is much lower than that of Pechiney, and its surface area is higher by a factor of two.

UOX BeO can be hot-pressed or cold-pressed and sintered to high densities at temperatures of 1400° and 1500°C respectively, which are approximately 300°C lower than those required for Pechiney. Grain size of fabricated material increases with fabrication temperature in both grades, and at the same temperatures is larger for UOX than Pechiney. However, at comparable densities grain sizes are also comparable for the two materials.

The bend strength at room temperature of hot-pressed Pechiney BeO reaches a maximum of approximately 30,000 p.s.i. when pressed at 1750°C. Above this temperature the strength falls due to increasing crystallite size. Cold-pressed and sintered Brush UOX appears weaker, possibly due to weaker grain boundary cohesion.

Cold-pressed and sintered BeO is considered to be worthy of most intensive study as an irradiation resistant material, and suggestions are given for improving its strength and homogeneity and decreasing its crystallite size.

CONTENTS

TABLES

continued

CONTENTS (continued)

FIGURES

1. INTRODUCTION

Beryllium oxide is of interest in the Australian H.T.G.C. reactor project as a possible moderator and/or fuel matrix material. Ultimate use however, is conditional on the demonstration of satisfactory stability under reactor conditions. As part of the HTGC programme small specimens of fabricated BeO have been and are being irradiation tested to high integrated fast neutron doses in the reactor HIFAR. They were fabricated from two grades of BeO powder; Pechiney nuclear grade and Brush "UOX". Reasons for choosing these materials and the methods used in the preparation of the irradiation specimens are discussed by Reeve and Ramm (1961).

To gain an adequate knowledge of these two materials, a comparative study was undertaken. This study included comparison of powder properties, fabrication behaviour, and as-fabricated properties. The results and their bearing on the problem of BeO irradiation stability are discussed in this report.

2. LITERATURE SURVEY

2.1 Brush UOX BeO

Brush UOX BeO is marketed as a nuclear pure "readily sinterable" powder. The manufacturer's specification states that "the material when cold pressed at 20,000 p.s.i. into a ½ inch diameter x ½ inch high sample shall reach a density of 2.85g/cc minimum (i.e. 95 per cent. theoretical) when fired for two hours in hydrogen at 1600 °C or air at 1500 °C", and that the corresponding shrinkage is 15 – 30 per cent.

Smalley et al. (1959) found that UOX BeO, containing less than 450 p.p.m. cation impurities, could be sintered to 98.5 per cent. theoretical density by suitable physical processing, and sintering for 4 hours in hydrogen at 1650 °C.

The cold pressing and sintering of UOX BeO has been studied recently at the Battelle Memorial Institute, both alone and as a matrix in which UO_2 particles were dispersed (Dayton and Tipton 1960a, 1960b). They concluded that –

(i) 40 w/o BeO plus 60 w/o UO_2 must be sintered at 1750 °C to attain densities in excess of 90 per cent. theoretical.

(ii) Ball-milling of the BeO prior to mixing with the UO_2 for up to one hour broke up aggregates and resulted in better than 95 per cent. theoretical density on sintering the $BeO-UO_2$ at 1650 °C in H_2.

(iii) Addition of 0.01 per cent. MgO increased the sintered density of UOX BeO.

(iv) A pressure of 40,000 p.s.i. resulted in higher densities than 20,000 p.s.i., particularly for conditions where less than 98 per cent. theoretical density was achieved.

The hot pressing of UOX BeO has been studied by McLaughlin and Ballard (1960). Rings of 10½ inch o.d. and 1 inch wall-thickness were hot pressed at a pressure of 1500 p.s.i. at 1400 °C to give mean densities of approximately 96 – 97 per cent. theoretical. Metallographic examination revealed considerable density variations in the products, the areas of highest density containing very dense inclusions measuring up to 0.1 inch across. The starting material for this work had been prepared by hydrostatically pressing dry screened UOX BeO at 22,500 p.s.i. and regrinding to fine powder.

Most of the above information became available only after the completion of the major part of the work described below.

2.2 Pechiney BeO

The hot pressing of Pechiney BeO of total impurity content ≤ 0.04 per cent. has been studied intensively in France. Densities of 98 per cent. theoretical were obtained in discs 3.0 cm in diameter x 0.9 cm thick after pressing in graphite dies at 1600 °C for 30 minutes at a pressure of 2600 p.s.i. (Caillat and Pointud, 1955). By pressing at 1800 °C densities of 99.7 per cent. theoretical could be achieved. In this work the crystallite size near the outer surfaces of pressings was found to be greater than in the interior, and the material contained up to 1 per cent. of free carbon as graphite inclusions introduced during die-loading and pressing.

This technique was subsequently extended to produce dense blocks of size 10 cm x 10 cm x 5 cm (Pointud et al. 1959). In blocks of this size there were slight density gradients unless temperatures of 1800 – 1900 °C were employed. The grade of BeO considered most suitable for this work was prepared by calcining "dense" or "β" $Be(OH)_2$ at 1000 °C for 2 hours, producing a powder of surface area 40 m^2/g. It is stated that 1 – 3 per cent. of an anion added as a beryllium salt to prevent excessive volatilisation during calcination may remain after calcination, but no further details are given. Pointud et al. further observed that $Be(OH)_2$ decomposes only to the extent of 98 – 99 per cent. at 1000 °C, the final 1 – 2 per cent. of water being evolved at higher temperatures.

Irradiation results reported by Elston and Caillat (1958) were based on samples cut from 10 cm x 10 cm x 5 cm bricks. They discuss the inhomogeneity of these blocks, particularly the distribution of graphite inclusions and the variation of density and strength within each block. Strength figures showed wide scatter. Low strength appeared to be closely related to the presence of graphite inclusions, but internal stresses and density and crystallite size variations were also important.

3. POWDER PROPERTIES

To gain a more complete background for the understanding of fabrication behaviour, various tests were carried out on both Brush UOX and Pechiney BeO powders.

3.1 Purity

The manufacturers' specifications on purity and the results of semi-quantitative spectrochemical analyses are compared in Table 1. Where no disagreement with the specification figure was noted, that figure is quoted in the Table.

The results are in general agreement with the specification and in the case of UOX, the purity was better than specification particularly in boron content; copper alone was higher than specified.

McLaughlin and Ballard (1960) reported a spectrochemical analysis of a particular batch of UOX BeO indicating levels of impurities well below those quoted in the specification, particularly for boron (0.4 p.p.m.), Fe (< 4 p.p.m.) and Si (< 5 p.p.m.).

Similarly a spectrochemical analysis, reported by Dayton and Tipton,1960b) indicated levels of impurities well below the maximum in the specification for all except Cu where the amount present was about 15 p.p.m. At the same time it was noted that material sieved through 200 mesh was much purer in most metals than that sieved through 100 mesh. It seems likely that the copper, which is higher than specification in both the present investigation and that of Dayton and Tipton (1960b) was introduced by pickup during sieving.

Qualitative tests for the following ions in both Pechiney and UOX BeO gave negative results:

Carbonate
Sulphate
Chloride
Fluoride
Bromide

Iodide
Acetate
Ammonium
Nitrate
Phosphate

Organic acids.

The most likely foreign anion was considered to be SO_4^{2-}, as $BeSO_4$ is probably an intermediate in the preparation of both oxides. Evidence for its presence was obtained during experiments by the Chemistry Section when compacts were heated to successively higher temperatures up to 1000 °C, and gas samples at each temperature were analysed mass spectrographically. SO_2 was observed in the 800° and 1000°C samples from each oxide. A total SO_3 content (as SO_4^{2-}) of at least 1250 p.p.m. and 2000 p.p.m. respectively for UOX and Pechiney BeO was indicated.

3.2 Weight Loss on Calcination

Samples of both materials were treated in covered alumina boats in a muffle furnace to progressively higher temperatures, cooling and weighing at each step.

The results are shown graphically in Figure 1. The pattern of behaviour was similar for both materials. The total loss was approximately 1.5% in each case. After a small initial loss at temperatures below 200°C (0.4 per cent. for UOX and 0.15 per cent. for Pechiney), no further change in weight occurred up to 600°C. Above this temperature and up to 1350°C a continued loss occurred. The major weight loss in each case was between 600°C and 1350°C, and above 1350°C no further change in weight was observed.

These weight changes are attributed mainly to loss of uncombined moisture (below 200°C) and combined moisture (above 600°C). Retention of up to 2 per cent. of water by $Be(OH)_2$ at temperatures up to 750°C (Quirk, et al., 1957) and 1000°C (Pointud et al., 1959) has been reported. Traces of CO, CO_2, and SO_2 were detected in the chemistry experiment referred to in Section 3.1, but not in sufficient quantities to explain the present results.

The results give some information about the previous treatment of both materials. It appears that UOX has not previously been calcined above 800°C, since above that temperature, further weight loss occurred. Similarly, a calcination temperature of 1000°C for Pechiney BeO as reported by Pointud et al. (1959) is consistent with the weight loss results.

3.3 Particle Size

3.3.1 Sieve analysis

As received, both powders contain relatively coarse lumps which can be broken up readily by light grinding. Neither powder contains any material which cannot be forced fairly readily through a 240 mesh sieve.

However, as a check on the as–received material, a dry sieve analysis was carried out on each type, only a few very large lumps being broken up. The remainder was lightly shaken through appropriate sieves. The results are given in Table 2; it can be seen that both powders contained a significant proportion of quite coarse lumps. The nature of the coarse fractions is discussed in Section 3.3.2.

3.3.2 Microscopic examination

Minus 200 mesh and plus 44 mesh samples of both powders were mounted in Canada Balsam on glass slides and examined in transmitted light. The observations may be summarised as follows:

Pechiney BeO

(i) The range of particle sizes in the minus 200 mesh material was from 30μ diameter down to submicron sizes.

(ii) There were two different types of larger particles, "cored" (Figure 2) and aggregate particles (Figure 3).

(iii) Under crossed nicols, the cored particles appeared to be composed of submicron crystallites unresolved by the microscope, and the "aggregate" particles were composed of crystallites of dimensions between 1 and 2.5μ.

(iv) A few isolated single crystal needles up to 5μ long were noted.

(v) The 1 – 5μ crystallites represented only a small fraction (~ 1%) of the total volume.

(vi) The plus 44 mesh fraction was generally similar except that occasional plus 44 mesh particles were hard and "gritty" and on examination appeared to be composed almost solely of "aggregate" particles with crystallites of size 1 – 2.5μ.

Brush UOX BeO (See Figure 4)

(i) The range of particle sizes was from irregularly shaped particles 50μ across down to submicron sizes.

(ii) The larger particles appeared to be aggregates of submicron crystallites, unresolved by the microscope.

(iii) Some isolated single crystals of size up to 25μ x 25μ were observed under crossed nicols, and some 1 – 2.5μ crystallites occurred in sharply defined patches in the large aggregate particles.

(iv) The 1 – 25μ crystallites represented only a small fraction (~ 1%) of the total volume.

(v) No differences in fine structure were observed between minus 200 mesh and plus 44 mesh material. The latter appeared to consist of very loose aggregates which broke up during slide preparation.

3.4 Crystallite Size

"Effective" crystallite sizes of as–received powders were determined by the method of Jones (1938). Specimens were prepared by sprinkling BeO powders onto glass smeared with silicone grease, and covering with Milar plastic film.

The instrument used was a Philips x-ray diffractometer fitted with a step-scanning device (steps one minute of arc every minute), a scintillation counter, and a print-out attachment which recorded integrated 60 second counts at each angular position. Copper Kα radiation was used.

The line chosen for study, after preliminary scanning of various lines in the 20 - 165° region of 2θ, was the $300\alpha_1$, which was resolved from the $300\alpha_2$ in all cases. This line occurs at approximately 163° of 2θ.

The standard specimen was prepared by crushing hot pressed BeO to a fine powder. The crystallite size of this material was about 15μ, and as it was lightly crushed and ground, the final crystallite size would be well over 1μ which is quite satisfactory as a standard.

60 second counts were recorded at 1' intervals over the 300 $\alpha_1 - \alpha_2$ lines for the Pechiney, UOX, and standard specimens, and plotted against 2θ. From these graphs line widths at half peak height above background were measured. The "broadening" β was obtained from Jones' curve relating β/B (where B is the width of the "unknown" line) with b/B (where b is the width of the same line in the standard specimen). The apparent crystallite size, which in this case is measured perpendicular to (100) type planes, is then given by the equation

$$t_{\text{apparent}} = \frac{\lambda}{\beta \cos\theta}$$

where λ is the wavelength of the x-rays employed. The results are given in Table 3.

In contrast with these results a BeO powder prepared by calcining Murex $Be(OH)_2$ at 600 °C showed a marked broadening at low angles where it was hardly detectable for Pechiney and UOX. The crystallite size estimated from the (100) line width (2θ = 38.5°) of 0.43° compared with 0.22° for the standard specimen was 0.034μ. Assuming dense spherical particles of this size (which is only an approximation) the surface area would be 60 m^2/g, which is exactly as estimated for this material from the surface area data of Livey et al. (1959).

3.5 Surface Area

Surface areas of as-received Pechiney and UOX BeO were determined by the Chemistry Section by the BET method (N_2 adsorption) after outgassing at 300 °C. The figures obtained were 8.3 m^2/g and 16.9 m^2/g for Pechiney and UOX respectively. Assuming dense spherical particles, of uniform size, calculated particle diameters were 0.23μ and 0.12μ respectively. These values are in fair agreement with those obtained by x-ray methods.

3.6 Electron Microscopy

As-received powders of both materials were suspended in alcohol and a drop of the suspension placed on a carbon grid for examination in transmission with the Siemens electron microscope. Coarser aggregate material was examined at lower magnification.

Examination of the electron micrographs showed that each material consisted principally of submicron crystallites (Figures 5 to 9). In Brush UOX, they ranged in size from 0.05 to 0.3μ, and in Pechiney 0.05 to 0.5μ across. Accurate mean values were not obtained, but Pechiney crystallites were rather larger than Brush UOX, and the crystallite diameters calculated from surface area (viz. 0.23 and 0.12μ respectively) were quite reasonable, and in rather better agreement with observation than the x-ray figures.

Pechiney powder also contained occasional single crystals up to 2μ long (Figure 8), as also observed by optical microscopy, with a larger spread of crystallite sizes than UOX. Large aggregates, at least 30μ across, were observed in both materials. However, as they were too thick to be transparent, no substructure could be seen except at the edges, where their character as aggregates of submicron crystallites was suggested. The "cored" structure of 30μ Pechiney particles, observed optically, could not be detected.

3.7 Tap Density

Tap densities and 1 t.s.i. pressed densities of both powders were measured under various conditions. These are shown in Table 4. Corresponding densities of BeO prepared by calcining Murex $Be(OH)_2$ to various temperatures (Livey et al., 1959) are included. It can be seen that Brush UOX BeO has a very low tap density compared with other materials.

The fairly uniform crystallite size observed with the electron microscope compared to the larger spread of sizes in Pechiney BeO may partly explain the difference in tap density between these two materials, since the more evenly sized particles would pack less efficiently. Another reason may be the character of the large aggregates present in both materials. The cored Pechiney particles, composed of submicron crystallites, appeared much denser under the optical microscope than UOX particles of the same size. The UOX aggregates were therefore possibly much looser and more porous than the Pechiney particles. This explanation is supported by the fact that on compressing to 1 t.s.i. the densities are almost the same, and the fact that by grinding, the tap density of UOX can be raised almost to that of as-received Pechiney material. The consequent large deformation on pressing of as-received UOX to 1 t.s.i. or higher may favourably affect sintering behaviour by exposing a large number of fresh surfaces. The deformation on pressing of Pechiney BeO, which has a higher initial tap density, will be much smaller.

3.8 Discussion of Results of Powder Studies

Both Pechiney and Brush UOX BeO powders are of high purity as far as cations are concerned, but contain uncombined moisture, probably residual $Be(OH)_2$, and traces of other anions e.g. SO_4^{2-}.

Observations of crystallite sizes by x-ray methods and by electron microscopy are in good agreement considering the expected magnitude of sampling errors, and errors inherent in the x-ray method. The crystallite sizes calculated from surface area measurements assuming separate, dense, spherical crystallites of uniform size are in excellent agreement with the electron microscope measurements. Neither grade of powder is completely uniform. Pechiney BeO contains a wide range of crystallite sizes, including 1 - 2.5μ crystallites grouped in aggregates which are difficult to break up. Brush UOX BeO has a more uniform crystallite size in the submicron range but contains a few single crystal particles of 2.5 - 25μ.

Pechiney BeO is understood to be prepared by calcining β-$Be(OH)_2$ at 1000 °C. The weight loss versus temperature curve is consistent with this calcination temperature, but the crystallite size observed, 0.2 - 0.3μ is much higher than the 0.05μ expected from the report of Pointud et al. (1959). The present figure is supported by electron micrographs of the powder so either Pointud's figure is in error or the present Pechiney powder has been prepared under different conditions.

Japanese workers (Katsuzo Kido et al. 1959) state that readily sinterable Brush BeO is prepared by decomposition of $BeSO_4.4H_2O$. The method described by Quirk et al. (1957) developed at Battelle Memorial Institute is on the other hand decomposition of $Be(OH)_2$ at 900 °C, which is the optimum calcination temperature. From the weight loss - temperature curve of UOX, it appears that a temperature not in excess of 800 °C has been used, and since its properties differ markedly from Pechiney, it is suspected that either $BeSO_4.4H_2O$, a different form of $Be(OH)_2$, or another compound was the intermediate. Pointud et al. (1959) give the properties of BeO prepared by calcining $BeSO_4.4H_2O$ at 1000 °C as tap density 0.2g/cc, surface area 18 m^2/g (implying a crystallite size of 0.11μ) and hot pressed density at 1550 °C, 2.79 g/cc. These properties, with the exception of hot pressing behaviour, are close to those of UOX.

The surface area of UOX is higher than that of Pechiney by a factor of 2, and this may partly explain their difference in sinterability. But sinterability is not solely dependent on surface area, and in some cases impurity effects may override surface area effects. For example in the work of Quirk, Mosley, and Duckworth, (1957), the BeO sample of the highest surface area, which was also the most pure, sintered least readily of a series investigated. It is considered that the observed differences in surface area and crystallite size are not sufficient alone to explain the large difference in sinterability of the two materials. Deformation on pressing, which is high in UOX due to low initial tap density, may be an important factor, and of even more importance may be the distribution of impurities. Although overall impurity levels are similar, if impurities are less evenly distributed in UOX than in Pechiney, randomisation by solid solution during sintering could add to the driving force for sintering. A well-known example of such an effect is the enhancement of the sintering rate of ThO_2 by deliberate additions of CaO. These additions have maximum effect if the $CaO-ThO_2$ solid solution is allowed to form during, not prior to, sintering.

4. FABRICATION BEHAVIOUR

4.1 Hot Pressing

4.1.1 Method

Both oxides were hot pressed in high purity graphite dies. The die was heated inductively using a 30kW 400 kc/s valve oscillator set. Pressure was applied to the die plunger using a 60 ton hydraulic press which in the later stages of this work was fitted with air operated pumps allowing a pre-determined pressure to be maintained automatically.

Loading of BeO into the die was carried out in a specially designed glove box, care being taken that excessive carbon was not introduced during this operation. Pechiney BeO (as-received) could be loaded into the die without difficulty to give a pressing of useful height. Brush UOX BeO on the other hand, due to its lower tap density, presented difficulty in loading a sufficient weight to give a required length of pressing. Both increase in die height, leading to excessive plunger movement, and loading in several stages with compaction at each stage, resulted in excessive carbon contamination. The expedient of precompaction of powder was used to overcome this difficulty. The UOX was compacted hydrostatically at 15 t.s.i. in rubber moulds and then crushed to pass through a 22-mesh sieve. The tap density of this granulated material was 0.79 g/cc approximately, compared with 0.17 for the as-received powder.

After swabbing to remove loose BeO contamination the die was transferred to a ventilated die-loading box and set up ready for hot pressing as shown in Figure 10. Approximately one third full pressure was applied from cold, this being increased to the maximum figure on attainment of maximum temperature. The pressure was reduced to zero just prior to cooling. Temperatures were read optically using a graphite sighting tube inserted to a depth of half an inch into the die body, and are quoted without correction. Typical heating - cooling curves are shown in Figure 11.

Prior to commencement of these studies it was decided, in the light of previous experience and published information, to standardise upon the following conditions:–

Pressure – 1 t.s.i.

Time at maximum temperature – 30 minutes.

Diameter of pressing – 1½ inch – 2 inch

Length to diameter ratio – 0.35 – 0.5

The major part of the work consisted of a study of the effect of maximum temperature, the principal fabrication variable, on the following properties:

(i) Mean pressed density

(ii) Microstructure; mean crystallite size

(iii) Room temperature bend strength as measured in 3–point loading.

4.1.2 Density

The variation of density with hot pressing temperature is shown in Figure 12. It can be seen that UOX BeO consolidates more readily at lower temperatures than Pechiney BeO. For 98 per cent. density, temperatures of 1400 and 1750°C respectively are needed.

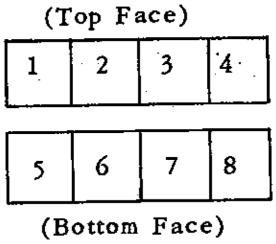
4.1.3 Microstructure

For study of microstructure thin slices of various materials were mounted on Canada Balsam on glass, ground to approximately 0.001 inch thick, and examined under crossed nicols on a petrological microscope. An alternative procedure, used in a few cases, was to polish mounted specimens using standard metallographic procedures, followed by etching in hot 70 per cent. H_2SO_4. The crystallite size was measured in each case using a calibrated eyepiece micrometer. A count was made of the thickness of all grains observed within the area covered by the scale of the eyepiece at several positions over the specimens, observing a minimum of 30 grains, and the arithmetic mean thickness was recorded as the mean crystallite size. The variation of crystallite size with fabrication temperature is shown in Figure 13.

Pechiney BeO

It can be seen from Figure 13 that the mean interior crystallite size of this material increased rather slowly with increasing temperature, and was only 30μ at 1850°C. Within the body of a pressing the grain size did not show excessive spread (see Figure 15) but some "edge" and inclusion effects were noted.

Edge Effects: A 2 inch diameter x ¾ inch high block pressed at 1750°C was sectioned across a diameter, and a thin slice cut parallel to one sectioned face. This slice was cut into 8 pieces in the following way:



Each was polished metallographically and etched. Measurements of mean grain size were made on each specimen with the results given in Table 5. From these it can be seen that specimens 1 and 4, from the outer top of the pressing, were considerably coarser than the remainder. Moreover, a region of even coarser structure extended 1/16 inch to 1/8 inch in from the outer edge of specimens 1 and 4. These effects are shown in Figures 15 to 17, from the interior of specimen 6, interior of specimen 1, and outer edge of specimen 1 respectively. The opposite effect was observed for a different grade of BeO, by Katsuzo Kido et al. (1959) who observed a fine grained skin around the edges of their pressing. The observed effects are apparently particularly sensitive to the properties of the particular BeO powder used.

Inclusion Effects: In many pressings "flecks" of either lighter or darker colour were noted. In a section perpendicular to the pressing these appeared to be circular with diameter up to 1/32 inch, and parallel to the pressing direction they appear as needles oriented perpendicular to the pressing direction (Figure 18). On inspection in transmitted light with crossed nicols, it was seen that these flecks had a coarser grain structure than the surrounding material by a factor of approximately 2. They almost certainly arose from the coarse-grained aggregates discussed in Section 3.3.2. These were originally spherical in shape, but were squashed to flat plates under the influence of pressure. Since the initial crystallite size in the aggregate was coarser than the bulk of the material, it is not surprising that the as-fabricated crystallite size was larger than that of the surrounding areas.

The size of these areas could almost certainly be reduced by using finely sieved material or by fine grinding.

Brush UOX BeO

The interior crystallite size increased much more rapidly above 1400 °C than for Pechiney BeO but at the minimum temperature in each case for a comparable density, the crystallite sizes were also comparable.

No outstanding edge effects were noted. There was however a wide spread of grain size with any selected area and a variation of mean grain size between areas in an apparently non-systematic manner. There were some areas where grain growth was inhibited and more frequent areas where grain growth was excessive (Figure 19). It is considered that these latter resulted from the "single crystals" noted in UOX powder (Section 3.3.2) acting as nucleation centres of grain growth. This was apparent in UOX hot pressed at 1200 °C, where although the bulk of the material was fine (about 1μ) much larger grains were comparatively frequent. This effect can be reduced by fine grinding of the material, but it has not yet been entirely eliminated. The wide spread of grain sizes is consistent with the postulate that the impurity distribution may not be uniform in this material (see Section 3.8), since impurity levels are known to have marked influence on grain growth in ceramic oxides.

4.1.4 Bend strength

Pechiney BeO: Rectangular specimens 1 inch long x 0.24 inch x 0.16 inch were cut from hot pressed blocks of Pechiney BeO, the length being cut perpendicular to the pressing direction. The 10 to 15 specimens from each block were tested at room temperature in 3-point transverse loading with a span of 0.81 inch on a Hounsfield Tensometer.

The relevant crystallite size was measured by selecting a specimen which broke centrally at a load corresponding to a mean strength figure, cutting a thin section from the fracture surface, and examining it petrographically.

The variation of bend strength with crystallite size is shown in Figure 14. Strength figures are remarkably constant for specimens cut from one block as can be seen from Table 6 which gives standard deviations of typical bend strength determinations. The great majority of specimens broke close to the central load point.

The bend strength versus crystallite size curve (Figure 14) shows a rise with decreasing grain size to a maximum of about 30,000 p.s.i. at 15 to 17 microns corresponding to a hot-pressing temperature of 1750 °C. Below this hot-pressing temperature, although the grain size decreases, any increase in strength is precluded by the density beginning to drop significantly below theoretical.

Brush UOX: No bend strength figures were obtained for hot pressed UOX.

4.2 Cold Pressing and Sintering

4.2.1 Brush UOX BeO

As discussed in Section 4.1.1, the low tap density (0.17 g/cc) of this material in the as-received condition made pressing difficult. The tap density has been increased by either precompaction at 15 t.s.i. (0.79) or by fine grinding (0.44 after 35 hours). The former method was chosen for this work. After precompaction as described in Section 4.1.1 the material was formed to a ½ inch diameter pellet by light compaction in a steel die, then hydrostatically pressed at 20 t.s.i. in a rubber mould. The light compaction reduced the tendency of the pellet to narrow in the middle on hydrostatic pressing.

As recommended in the specification (Section 2.1) sintering for one hour in air at 1500 °C was first investigated. The effect of final compacting pressure on sintered and pre-sintered densities is shown in Table 7. A pressure of 20 t.s.i. easily attainable with the equipment available, was chosen as the standard.

Next the effect of maximum sintering temperature on final density and crystallite size was investigated. The graphs of density and crystallite size versus temperature are shown in Figures 20 and 13 respectively.

Density reached 97 per cent. theoretical at 1500 °C. At that temperature the mean crystallite size was 25μ. Both density and crystallite size rose slowly with temperature above this point.

Crystallite size appears to rise very suddenly between 1400 and 1500 °C, which may result from the stage of sintering reached at that point, although it is difficult to see why the same should not occur during hot pressing but at a lower temperature. A grain size at 1500 °C of 5μ, conflicting with the above value was measured in bend test specimens cut from a 2 inch diameter sintered block. It seems possible that the grain-size in this range of temperature was quite sensitive to slight variations in temperature, heating rate, etc. A typical microstructure is shown in Figure 21.

The bend strength figure obtained for this material, 21,250 p.s.i. (standard deviation 1670 p.s.i.), is much lower than the value for hot-pressed Pechiney BeO of similar crystallite size and density (see Figure 14). The explanation proposed is that intercrystalline fracture was more pronounced in the sintered UOX due to weaker grain boundary cohesion. An examination of UOX fracture surfaces on the optical microscope did not resolve this question as the grain size was too small for observation by this method. Electron microscopic examination of fracture surfaces using the replica technique is required.

4.2.2 Pechiney BeO

Specimens were prepared by the methods described for UOX. Results of sintering experiments shown graphically in Figures 13 and 20 indicate that Pechiney BeO can be sintered at 1750 °C to 90 per cent. theoretical density without excessive grain growth. It is expected that further research will discover methods which will give better densities, possibly at lower temperatures. For example, the effect of higher hydrostatic pressures during final compaction on sintered density (Table 7) appears to be considerable. Significantly higher pressures could not be used due to equipment limitations.

5. SUMMARY AND DISCUSSION

The work described above has shown that Pechiney and Brush UOX BeO differ considerably in powder properties, fabrication behaviour, and as-fabricated properties. Direct relationships have been found between powder properties and as-fabricated properties, and between fabrication conditions and as-fabricated properties. Some evidence relating powder properties to fabrication behaviour has been obtained.

The principal observed differences between Pechiney and Brush UOX BeO are as follows:

(i) UOX powder has a higher surface area and a smaller crystallite size than Pechiney BeO. The difference is a factor of two in each case.

(ii) UOX powder has the lower tap density by a factor of three.

(iii) Powder purities differ only slightly. Pechiney contains more SO_3 (2000 p.p.m.) than UOX (1250 p.p.m.).

(iv) Both powders consist mainly of submicron crystallites but UOX contains some crystals up to 25μ and Pechiney some aggregate particles of 1 – 2.5μ crystallites.

(v) UOX can be fabricated by either hot-pressing or cold-pressing and sintering, at temperatures approximately 300 °C below those required for Pechiney BeO for comparable densities.

(vi) For comparable densities, mean as-fabricated crystallite sizes are similar; however UOX is subject to wide random variation in crystallite size and to coarse "inclusions" while Pechiney as-fabricated has a uniform structure except for edge effects and the presence of flecks, both of larger crystallite size. The flecks in Pechiney and the inclusions in UOX result from the observed powder variability (see (iv) above).

(vii) The bend strength of cold pressed and sintered UOX is somewhat lower than that of hot pressed Pechiney of comparable crystallite size and density. It is possible however that this difference is related to fabrication method rather than to differences in the starting material.

The reasons for the difference in sinterability of the two materials have not been completely elucidated, but the following factors are suggested as contributing to the observed behaviour:

(i) Higher surface area of UOX leads to greater driving force for sintering.

(ii) Lower tap density of UOX leads to more deformation on pressing.

(iii) Different impurity distribution may favourably affect diffusion rates during sintering of UOX.

(iv) UOX and Pechiney BeO are probably formed from different intermediates.

X-ray diffraction lattice parameter studies and X-ray micro-analyser studies are expected to throw further light on this question.

This work led to the specification of the following fabrication conditions for the preparation of specimens for irradiation testing (Reeve and Ramm, 1961):

Hot Pressed BeO : Hot press Pechiney BeO for ½ an hour at 1750 °C at 1 t.s.i.

Cold Pressed and Sintered BeO : Press Brush UOX BeO at 20 t.s.i. and sinter for 1 hr and 1500 °C in air.

These conditions were chosen to optimise density, crystallite size, and bend strength. Near theoretical density with a crystallite size as small as possible and with good strength was required. These conditions result in 96 – 99 per cent. theoretical density, crystallite sizes of 15μ and 25μ respectively, and bend strengths of 30,000 and 21,000 p.s.i. respectively. At higher fabrication temperatures, although density increases slightly, crystallite size increases with consequent reduction of bend strengths.

Some comments on these results in relation to the irradiation stability of BeO may be made. While the structure required for most favourable resistance to irradiation damage is not known it is postulated that a mechanically strong BeO would be preferable to a weak one of the same density; that a fine crystallite size, which usually leads to higher strengths, would be preferable to a coarse one at the same density; and that inhomogeneities of any kind would be undesirable.

The present bend strength results would seem to favour hot-pressed Pechiney BeO rather than cold-pressed and sintered UOX, but much more testing is needed before any definite conclusion can be drawn.

The crystallite sizes of Pechiney and UOX BeO fabricated to the same densities are similar. There is the possibility of grain refinement by the use of second phase inclusions to lock grain boundaries. Since both powders consist mainly of crystallites much smaller than 1μ it should be possible to allow considerable grain growth during sintering without exceeding, say, 2μ. However since both powders contain a small proportion of crystallites larger than 2μ, initial fine grinding would be necessary before this end could be achieved.

Fine grinding prior to fabrication is also advocated to ensure removal of inhomogeneities resulting from variations in the powders as received. Hot pressing however introduces inhomogeneities – crystallite size edge effects and graphite pickup – which are inherent in this method.

It is expected that due to the disadvantages of hot pressing already mentioned and to the unsuitability of this method for large-scale production the importance of cold pressing and sintering will increase. Further work in this field will therefore be aimed principally at improving the as-fabricated structure of cold pressed and sintered BeO.

6. ACKNOWLEDGMENTS

The authors wish to thank Dr. L.E. Smythe and the Analytical Chemistry Group for the chemical analyses, Dr. W. Stuart for the analyses of evolved gases, Dr. J. Chute for the electron microscopy, Mr. R. Maughan for assistance in the capacity of vacation student, Dr. M. Cooper for the surface area measurements, and Mr. J.McCracken for the metallography.

7. REFERENCES

Caillat, R., and Pointud, R., (1955) - Sintering of Beryllium Oxide. A/CONF. 8/P/345.

Dayton, R.W., and Tipton, C.R. Jr., (1960a) - Progress Relating to Civilian Applications during July 1960. BMI - 1455.

Dayton, R.W., and Tipton, C.R. Jr., (1960 b) - Progress Relating to Civilian Applications during August 1960. BMI - 1464.

Elston, J., and Caillat, R., (1958) - Physical and Mechanical Properties of Sintered Beryllia under Irradiation. A/CONF.15/P/1159.

Jones, F.W., (1938) - The Measurement of Particle Size by the X-ray Method. Proc. Roy. Soc. A, 166: 16.

Katsuzo Kido, Mitsunobu Abe, Susumi Nishigaki, and Seiichi Imura, (1960) - On the Vacuum Hot-Pressing of High Grade BeO. AEC-tr 4065.

Livey, D.T., Brett, N., Denton, I., and Murray, P., (1959) - The Sintering and Hot-Pressing Characteristics of Beryllia prepared from Beryllium Hydroxide. AERE M/R 2794.

McLaughlin, L.M., and Ballard, A.H., (1960) - A Method for Pressing Large Diameter BeO Rings. Y1302.

Pointud, R., Rispal, Ch., and le Garec, M., (1959) - Fabrication de Frittés de forte densité à base d'oxyde de beryllium. CEA 1234.

Quirk, J.F., Mosley, N.B., and Duckworth, W.H., (1957) - Characterisation of Sinterable Oxide Powders I. BeO. J. Am. Ceram. Soc., 40: 416.

Reeve, K.D., and Ramm, E.J., (1961) - The fabrication of BeO for Irradiation Testing. AAEC/TM 103.

Smalley, A.K., Quirk, J.F., Duckworth, W.H., (1959) - Investigation of Sinterable Powders and BeO Properties. NP-7528 as abstracted in Nuclear Science Abstracts, 13: 14521 (1959).

TABLE 1

COMPARISON OF SPECIFICATION AND ANALYSIS OF BeO POWDERS

Impurity	Specification Maximum Limits (p.p.m.)		Spectrochemical Analysis (p.p.m.)		
	Pechiney	Brush UOX	Pechiney	Brush UOX +200 mesh	Brush UOX – 200 mesh
Si	76	100	76	100	100
Al	<110	100	110	100	100
Fe	110	20	110	20	20
Ca	–	50	50	50	50
B	< 0.3	3	< 0.3	<< 3	<< 3
Cr	–	10	N	N	N
Mg	< 10	50	Present	Present	Present
Mn	–	10	N	N	Present
Na	–	50	> 50	50	50
Ni	–	20	N	N	N
Li	–	1	N	N	N
Cd	–	2	–	–	–
Cu	–	5	> 5	>> 5	>> 5
Co	–	5	N	N	N
F	220	–	–	–	–
Pb	–	–	Present	N	N
Ag	–	–	Present	Present	Present
Zn	–	–	N	Present	N
K, Cs, Sr, Ba, Sn, P, As, Sb, Bi, Au, Hg, Ti, Zr, V, Mo, W, Nb, In, Th	–	–	N	N	N
Loss of weight (110–1000°C)	–	1%	–	–	–
Thermal neutron absorption cross-section	11 mb	From above figures, excluding B, estimated at 10.3 mb	–	–	–

Notes: Present means Present, but levels not stated

N means Not observed

– means Not quoted or investigated

TABLE 2

DRY SIEVE ANALYSES OF BeO POWDERS

Mesh Range	Per cent. by Weight in Range	
	Pechiney	Brush UOX
+44	17.4	19.9
−44+100	18.2	47.6
−100+150	39.7	20.8
−150+200	17.1	8.4
−200+240	0.9	1.0
−240	6.7	2.2

TABLE 3

X–RAY CRYSTALLITE SIZES OF BeO POWDERS

Material	300α Line Width (degrees 2θ)	$t_{apparent}$ (μ)
Standard	0.50	–
Pechiney	0.73	0.18
Brush UOX	0.77	0.15

TABLE 4

TAP DENSITIES OF BeO POWDERS

Material	Tap Density (g/cc)	1 t.s.i. Pressed Density (g/cc)
Pechiney BeO	0.49	1.08
Brush UOX BeO		
as received	0.17	1.02
−240 mesh	0.14	–
finely ground	0.44	–
calcined 900 °C	0.26	–
calcined 1300 °C	0.21	–
Murex BeO		
calcined 500 °C	0.36	0.38
calcined 900 °C	0.29	1.0
calcined 1250 °C	0.49	1.25

TABLE 5

MEAN GRAIN SIZE OF HOT PRESSED PECHINEY BeO IN DIFFERENT AREAS OF THE PRESSING

Specimen No.	Mean Grain Size (μ)
1	45
2	17
3	21
4	37
5	18
6	18
7	20
8	17

TABLE 6

BEND STRENGTH OF HOT PRESSED PECHINEY BeO

Hot Pressing Temperature °C	Bend Strength p.s.i.	Standard Deviation	
		p.s.i.	%
1650	30,250	1,800	5.9
1700	29,900	1,850	6.2
1750	29,680	1,310	4.4
1850	17,260	700	4.1

TABLE 7

EFFECT OF COMPACTING PRESSURE ON BeO POWDERS SINTERED 1 HOUR AT 1500 °C IN AIR

Powder Type	Hydrostatic Compacting Pressure	Pre-sintered density g/cc	Sintered density g/cc
UOX	5.7	1.68	2.81
	11.3	1.71	2.87
	17	1.79	2.89
	20	1.79	2.89
	25.5	1.80	2.89
Pechiney	20	1.78	2.26
	25.5	1.82	2.39

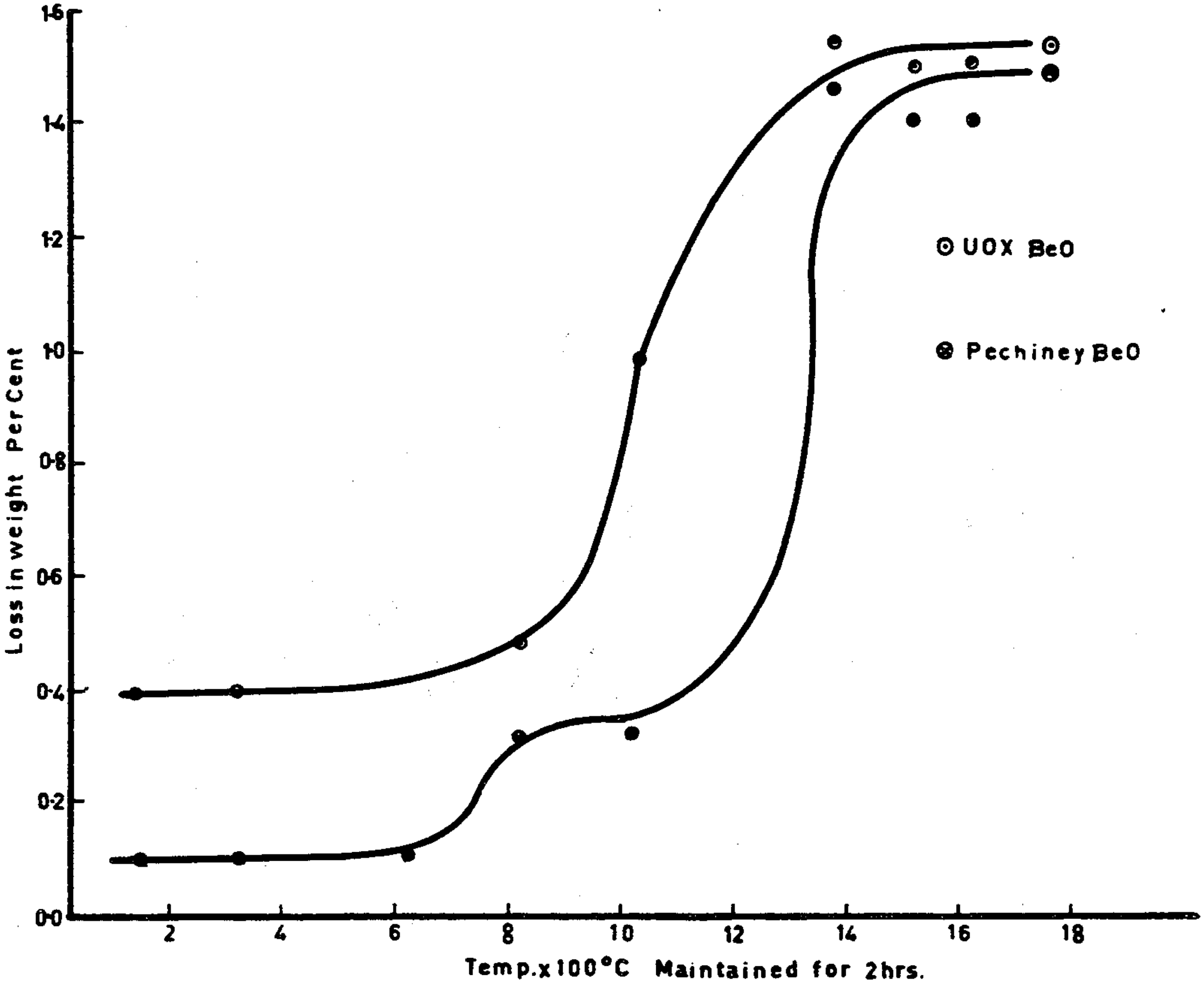


Figure 1 Effect of Calcining Pechiney and Brush UOX BeO Powders

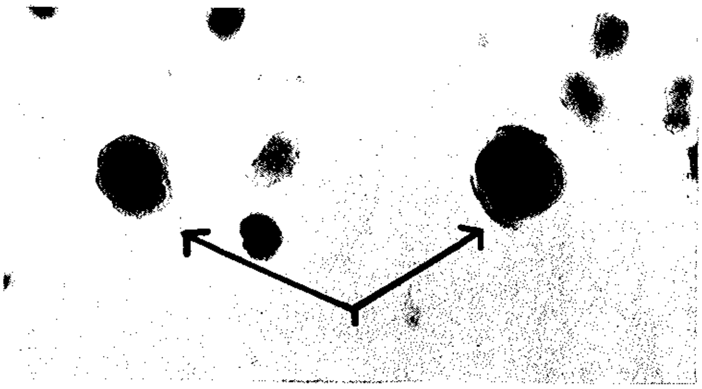


Figure 2 Pechiney BeO Powder Showing "Cored" Particles. (X 200)

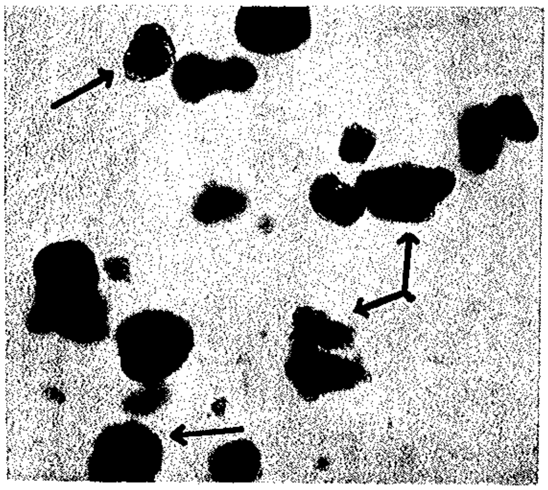


Figure 3 Pechiney BeO Powder Showing "Aggregate" Particles. (X 200)

Figure 4 Brush UOX BeO Powder
(X 200)

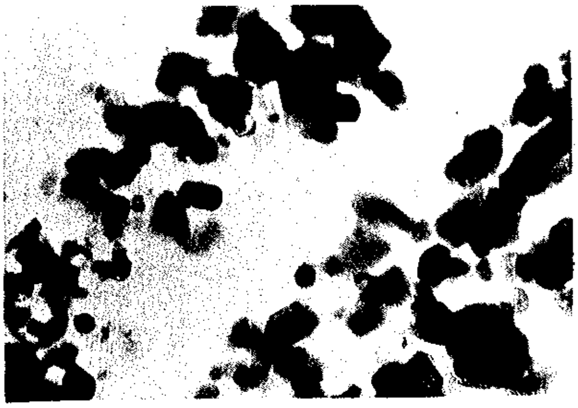


Figure 5 Brush UOX BeO Powder
Electron Micrograph
(X 40,000)

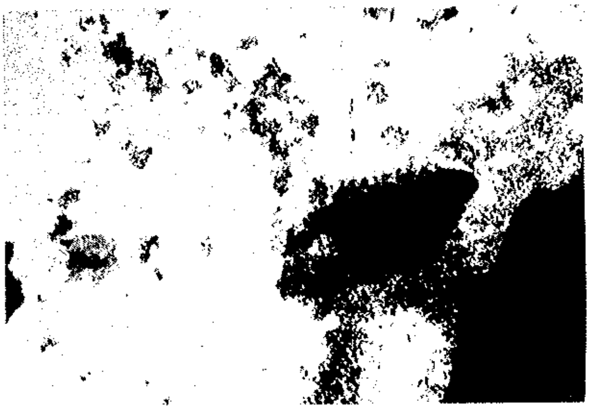


Figure 6 Brush UOX BeO Powder
Electron Micrograph
(X 1500)

Figure 7
(X 40,000)

Figure 8 Showing 1.5 μ Long Crystallite
(X 40,000)

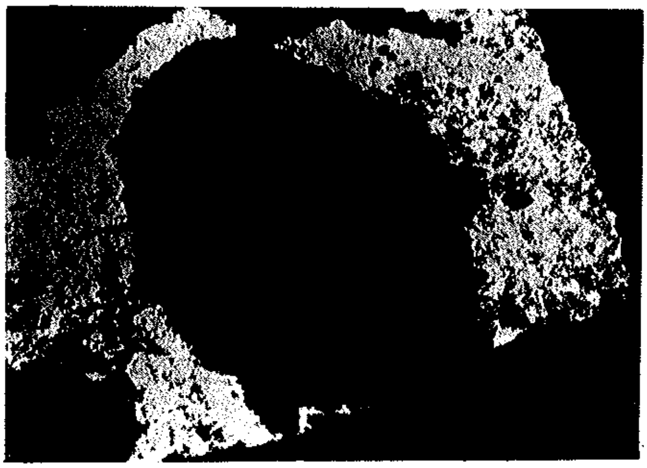


Figure 9 Showing Large Aggregate
(X 1500)

Figures 7 – 9

Pechiney BeO Powder, Electron Micrographs

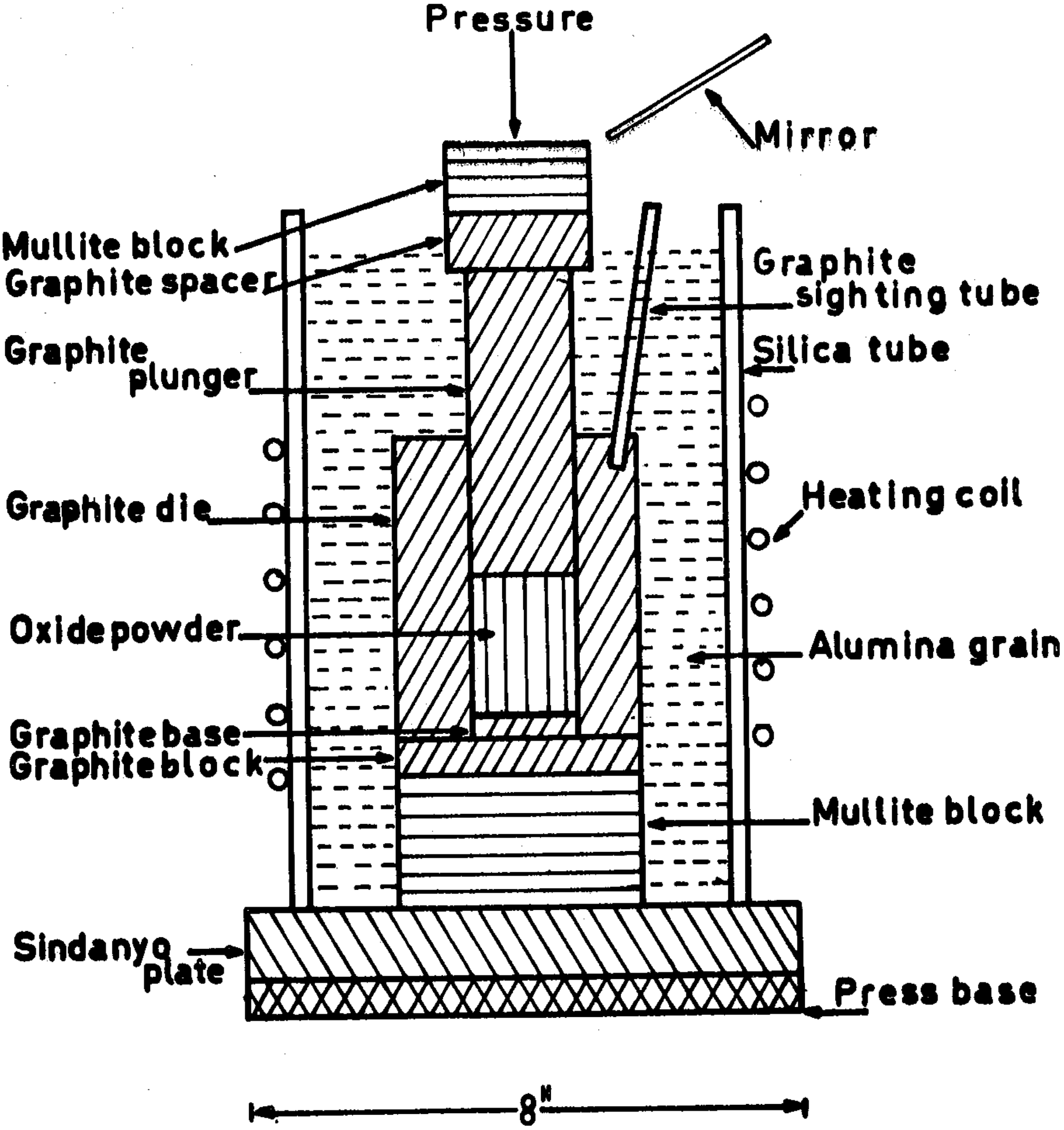


Figure 10 BeO Hot Pressing Assembly

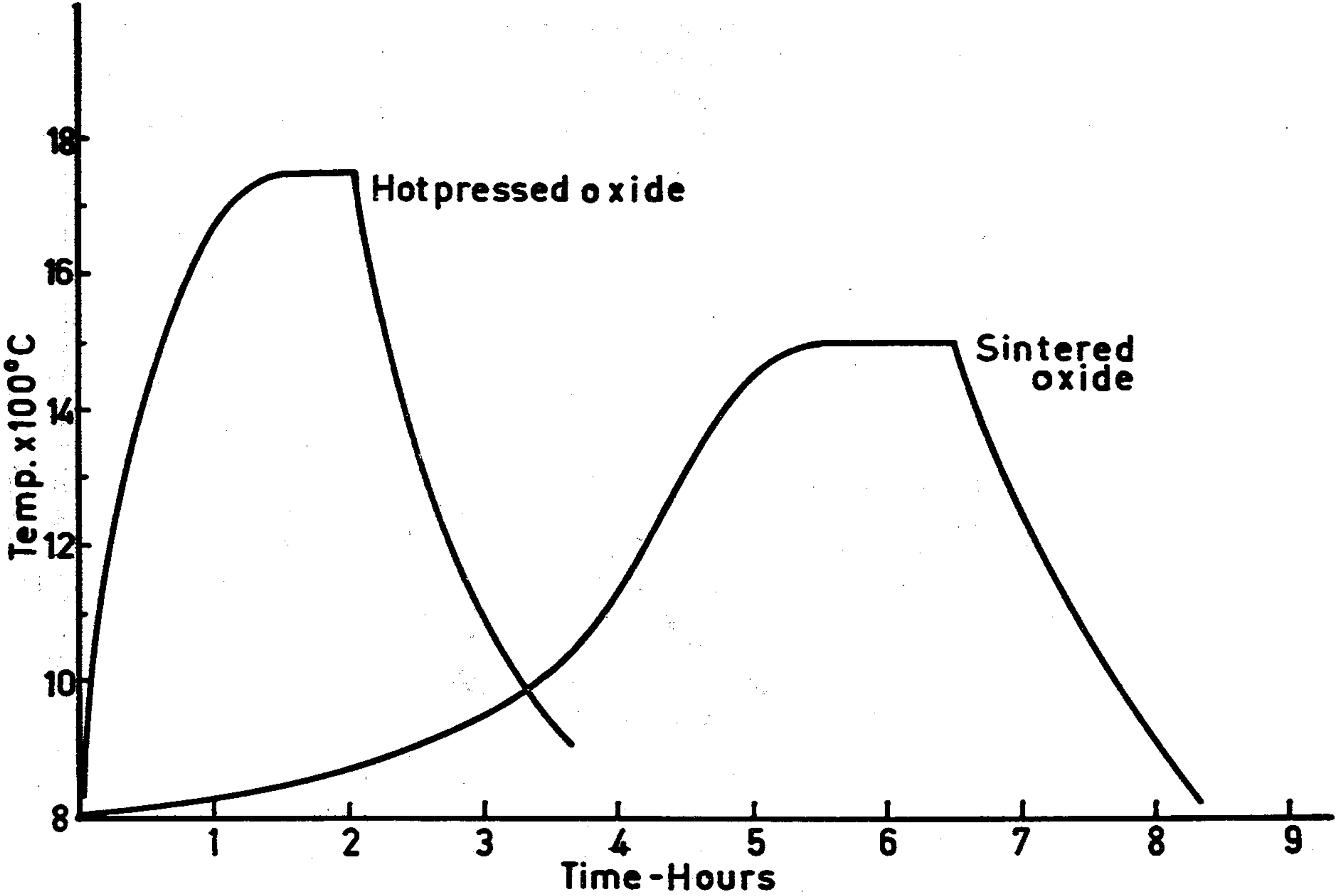


Figure 11 Heating Cooling Curve for BeO Hot Pressing and Sintering

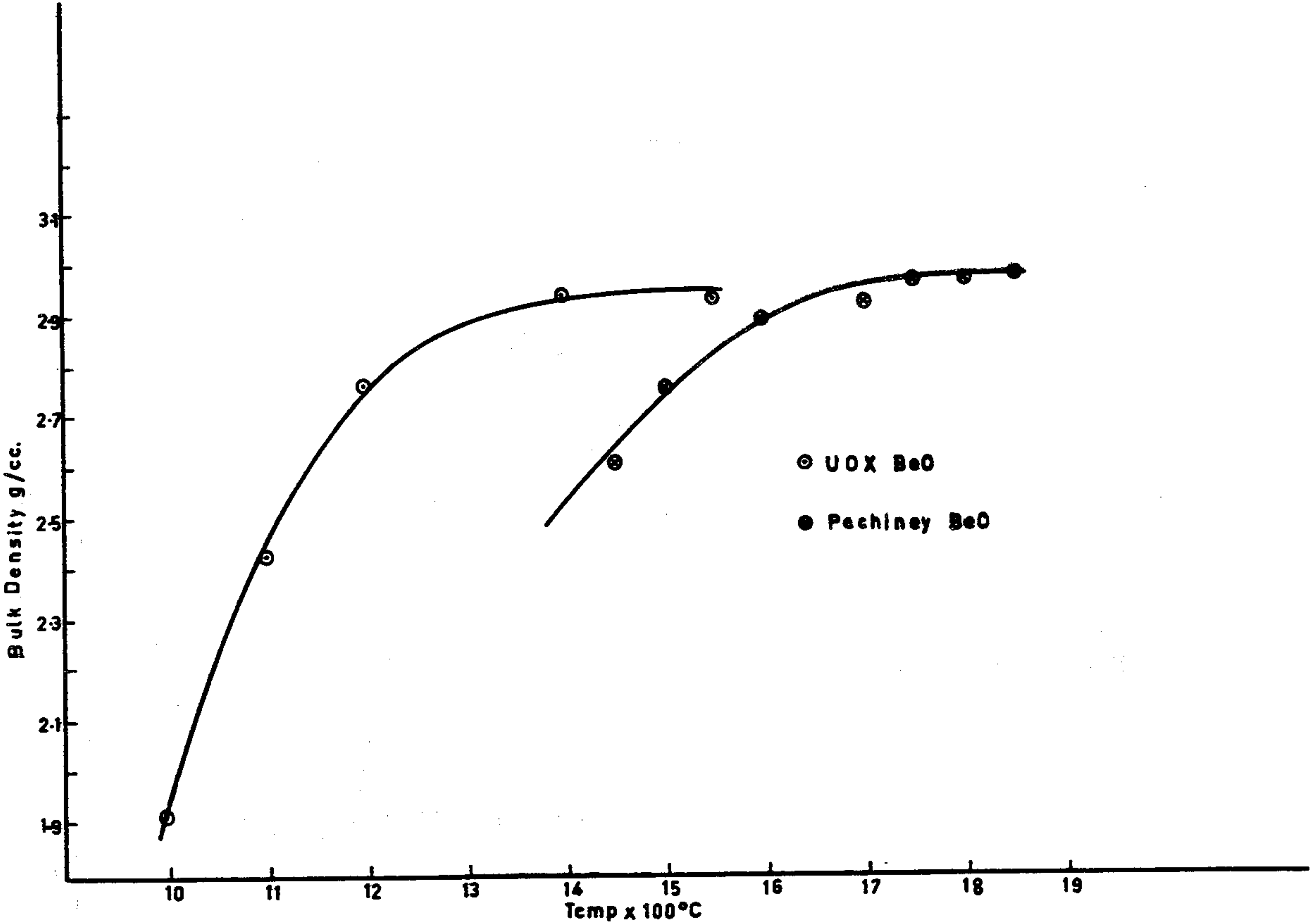


Figure 12 Effect of Hot Pressing Temperature on Hot Pressed Density for Pechiney and Brush UOX BeO

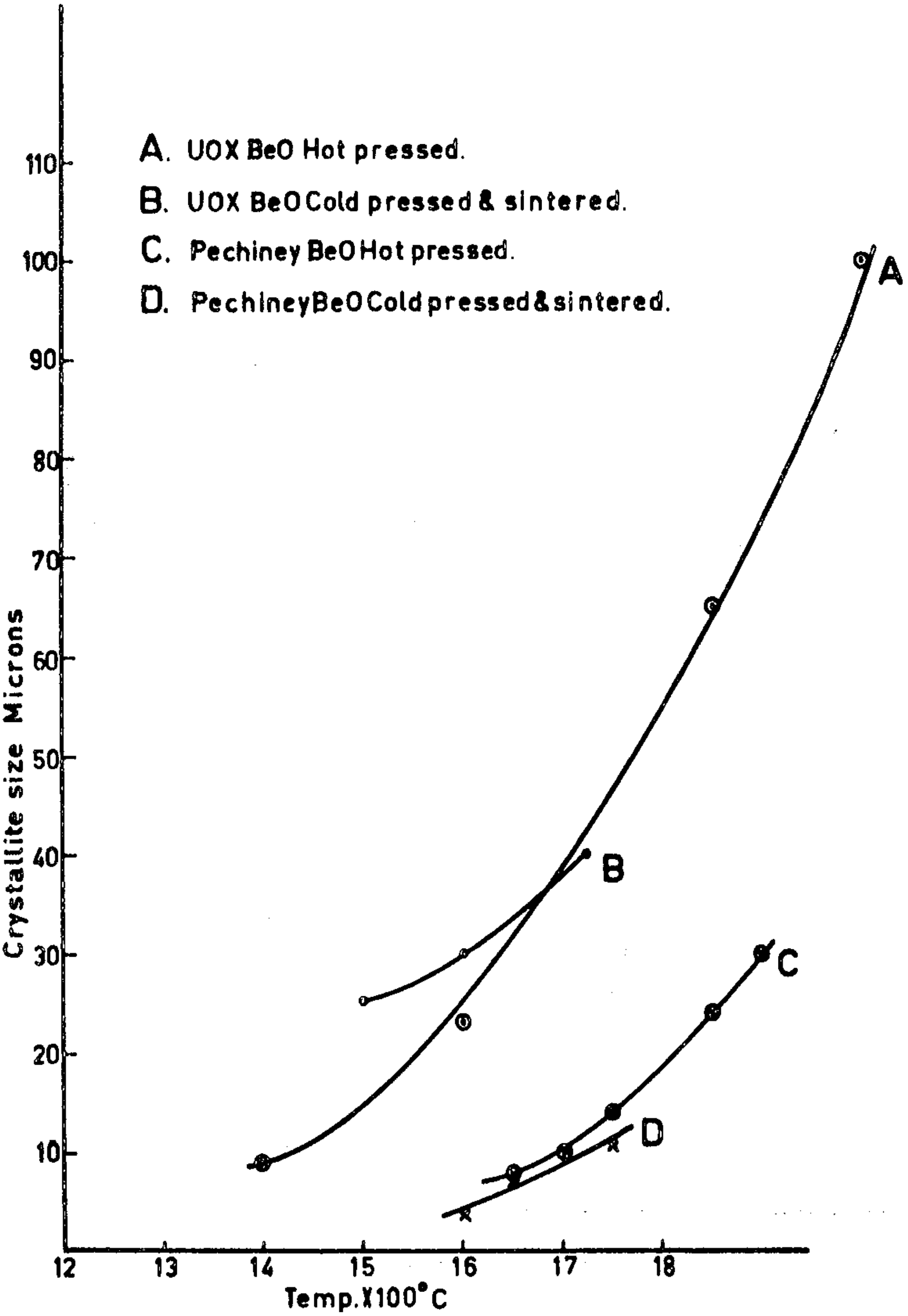


FIGURE 13 EFFECT OF FABRICATION TEMPERATURE ON CRYSTALLITE SIZE OF PECHINEY AND BRUSH UOX BeO

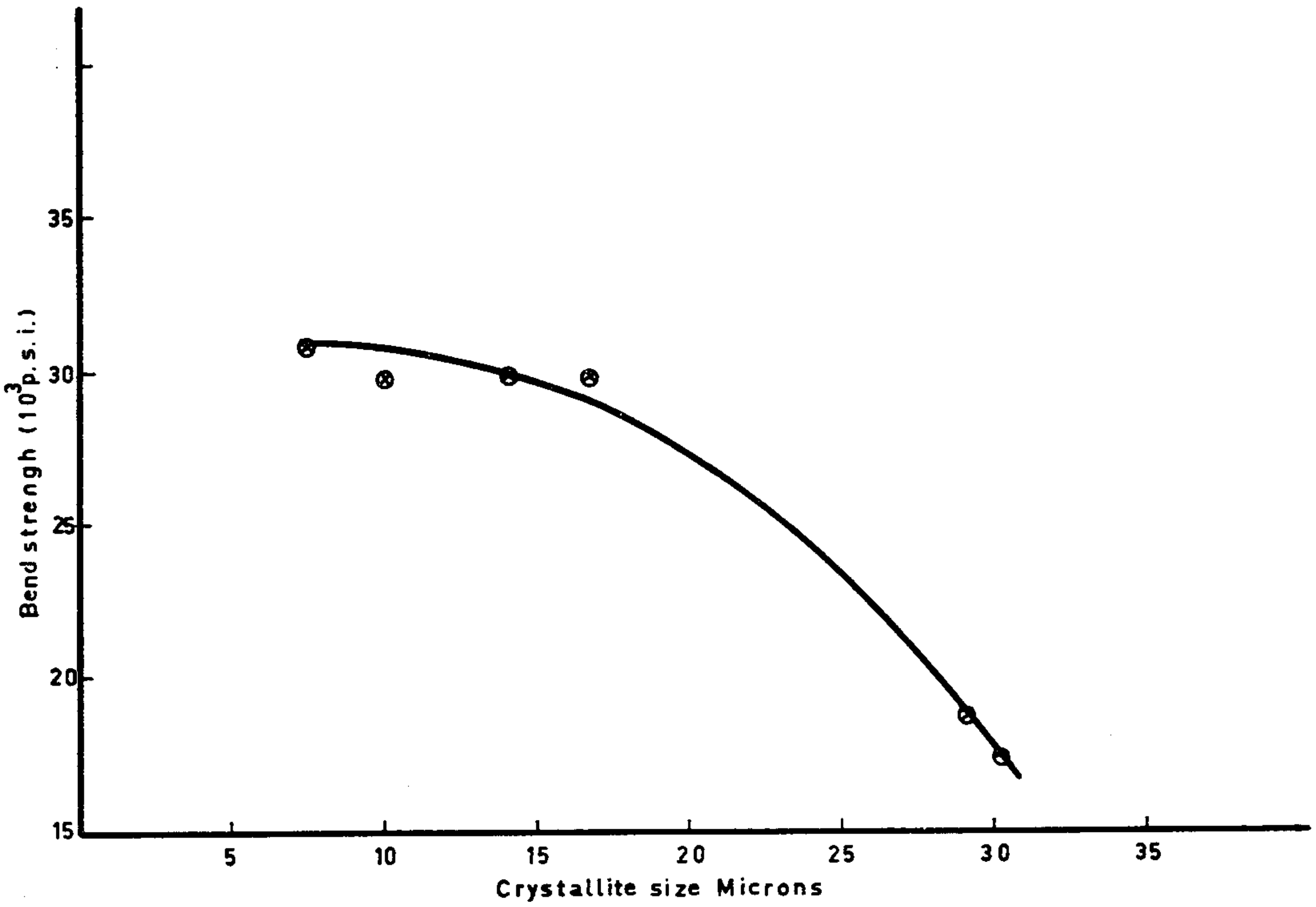


Figure 14 Effect of Crystallite Size on Bend Strength of BeO
(Hot pressed Pechiney)

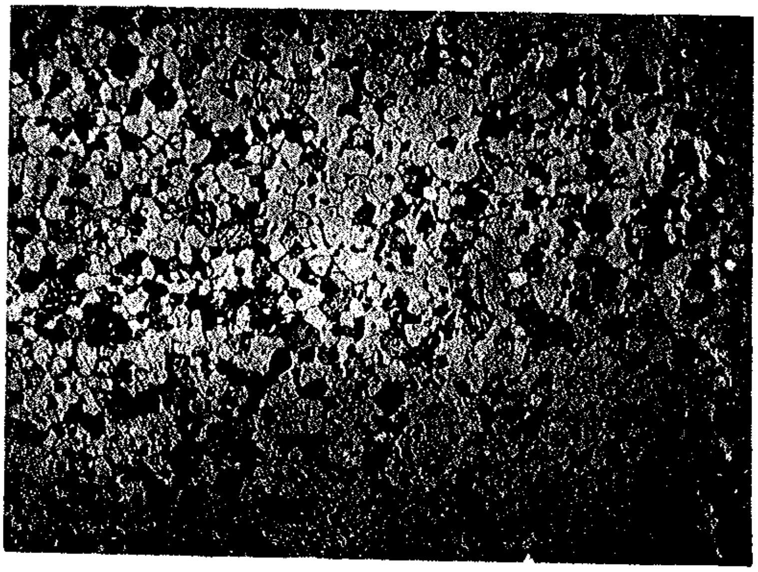


Figure 15 Interior of Specimen

Figure 16 Near Outer Edge

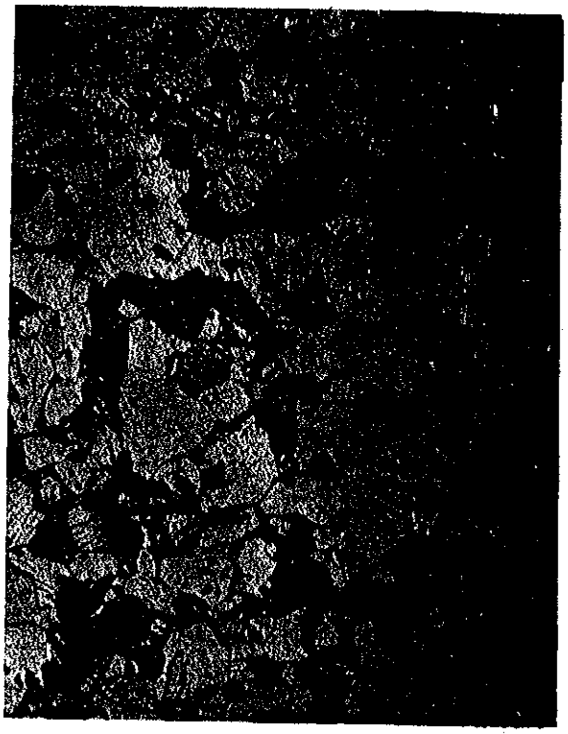


Figure 17 Outer Edge

Figures 15 - 17

Pechiney BeO Hot Pressed at 1750 °C,
Showing Crystallite Size Variation from
Interior of Specimen to Outer Edge.
(X 200)

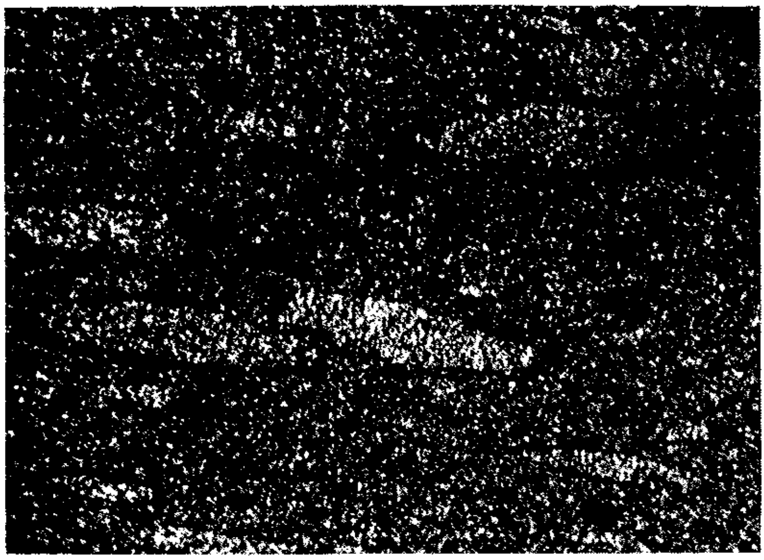


Figure 18 Pechiney BeO Hot Pressed at 1750°C Showing "Flecks" (X 50)

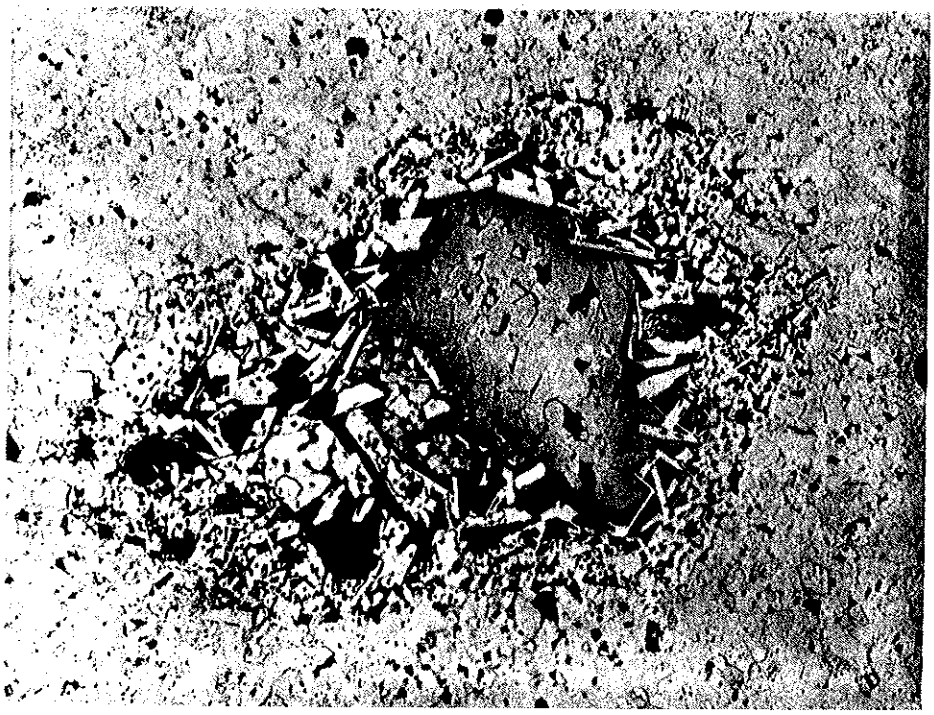


Figure 19 Brush UOX BeO Hot Pressed at 1400 °C Showing Interlocking Grain–growth.

(X 250)

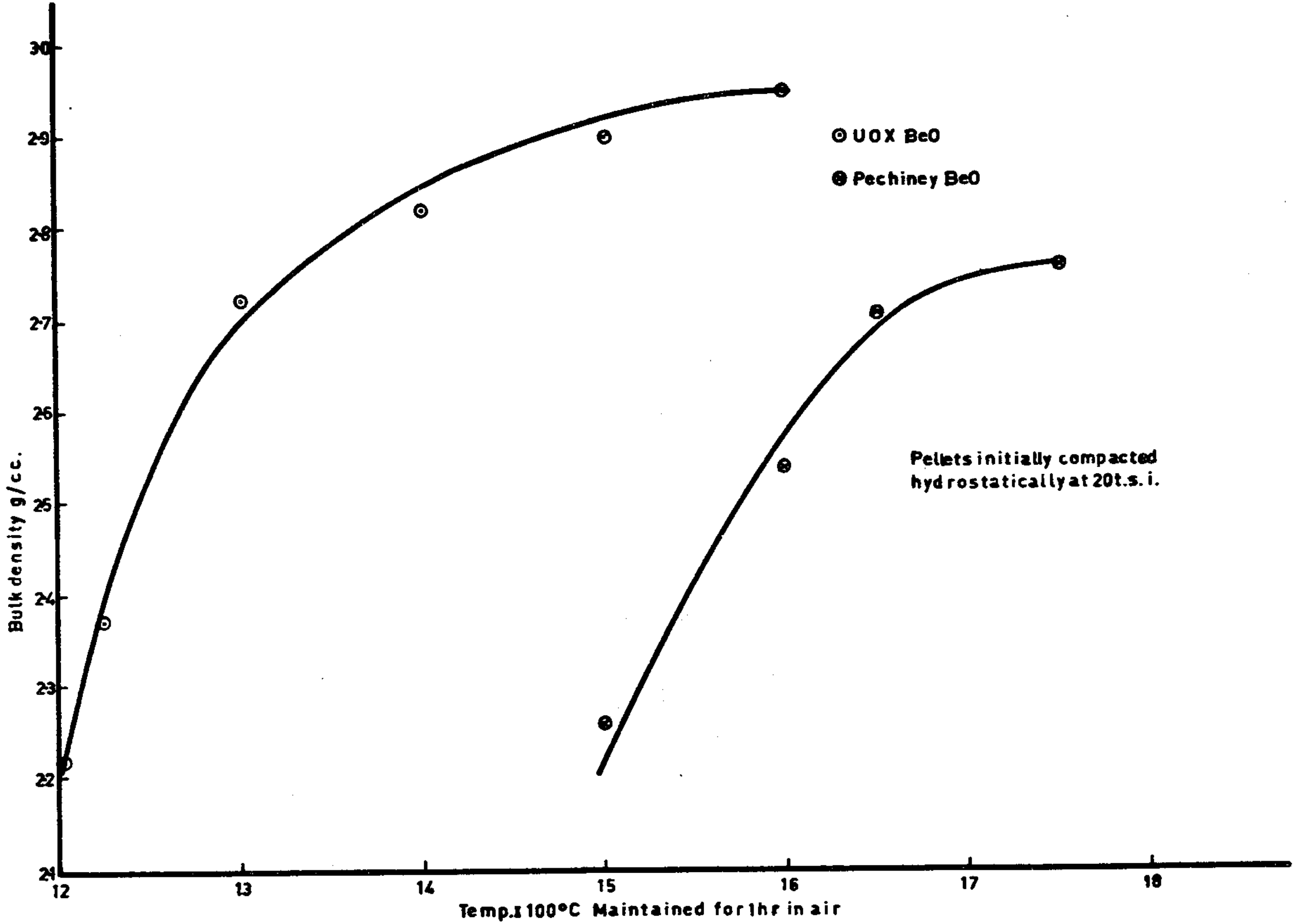


Figure 20 Effect of Sintering Temperature on Sintered Density for Cold Pressed Pechiney and Brush UOX BeO

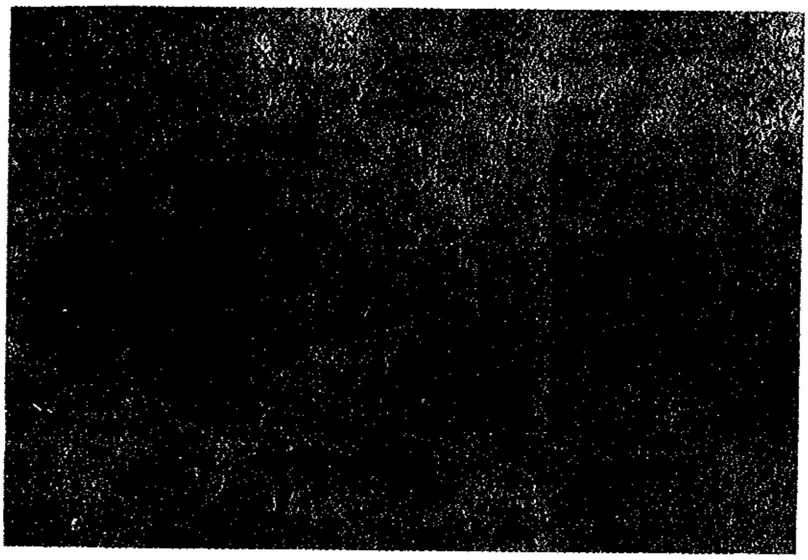


Figure 21 Sintered Brush UOX BeO
(X 250)