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GRINDING STUDIES ON BERYLLIUM OXIDE POWDER

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ABSTRACT

Inhomogeneities in Brush UOX beryllium oxide observed in the powder and in cold pressed and sintered specimens have been removed by grinding the powder prior to fabrication. All grinding procedures reduced the densities obtained under standard sintering conditions, but some grain refinement was noted on sintering after short grinding periods. These effects are related to the introduction of alumina and silica impurities during ball milling. There is some indication that short grinding periods improve the strength of sintered specimens.

CONTENTS

1. INTRODUCTION

In the course of sintering studies on beryllium oxide powder it was shown (Reeve and Ramm 1961) that inhomogeneities exist in one grade of Brush UOX BeO powder and that these result in inclusions and non-uniform grain size in the sintered structure. The mechanical properties and irradiation behaviour of such a material are likely to be inferior to those with a structure of more uniform grain-size distribution.

This study was undertaken to investigate ball milling as a method of improving the uniformity of UOX powder prior to fabrication. The results were assessed by changes in powder properties, sintering characteristics, grain size and uniformity, sintered density, and room temperature bend strength. Neutron irradiation experiments were also carried out on both uniform and non-uniform structures, but the discussion of irradiation work is outside the scope of this report.

2. EXPERIMENTAL METHODS.

The main material studied was Brush UOX BeO, lot 87. A second batch of UOX, lot 564, was used only in the bend strength work described in Section 3.5.

This material consists mainly of large (up to 100μ) aggregates of submicron crystallites of BeO. Inhomogeneities are of three types:

- Isolated single crystal particles of BeO of size up to 25μ x 25μ.
- Isolated particles of foreign material.
- Probable impurity and crystallite size differences between aggregates.

To ensure improved homogeneity in the powder by ball milling, the action of the grinding medium should be to break up aggregates, to reduce the size of the foreign material and large single crystal particles to the background size range, and to disperse this ground material in the remainder of the BeO. It was not expected that extensive grinding would be necessary to achieve these aims.

The standard ball-mill container chosen was a one litre porcelain jar, the grinding media were 1 inch diameter alumina balls, and grinding was carried out in either water or alcohol. It was expected that abrasion of balls and jar during milling would introduce a small amount of alumina and porcelain to the BeO, but this was not expected to be a serious problem. However in some experiments a neoprene-lined jar of the same size was used together with BeO cylinders (drilled from hot pressed BeO) as grinding media, so that a ground material containing no foreign cations would be available for comparison with alumina-ground BeO.

Two milling techniques were used. In the first, the jars were placed on ball-mill rolls rotating at 120 r.p.m., and in the second the jars were held in the cradle of a vibroenergy mill (24 cycles/sec).

One hundred grams of BeO powder, 450 grams of grinding balls or cylinders, and 500 ml of water or alcohol were placed in a jar, and grinding was carried out for periods from one to twenty hours. At the end of each grinding period the mill charge was filtered, dried, and submitted for examination.

Powders were examined by transmission optical microscopy, and by transmission electron microscopy. Samples were also taken for chemical analysis and for surface area determination by the BET method using nitrogen gas.

Specimens ½ inch diameter x ½ inch long were cold-pressed hydrostatically at 45,000 p.s.i., without binder addition, and sintered in dry flowing air. The maximum temperature was held for one hour.

Densities of the sintered specimens were determined by loss of weight on immersion in water, and their microstructure was examined by standard metallographic and electron fractographic (replica) techniques.

3. RESULTS

3.1 Powder Properties

3.1.1 Microscopy and surface area

Grinding using alumina balls reduced the number of large crystals even after one hour, with improvement up to 10 hours. The removal of large crystals can be seen by comparing the structures shown in Figure 5a and Figure 4a, which are photomicrographs of polished sections of lightly sintered compacts in which little grain growth has occurred. This technique is useful in recording the uniformity or otherwise of the powders from which compacts were prepared.

The observed degree of aggregation was not noticeably affected by the process presumably because aggregates re-form readily during drying; this was not considered important provided that the original aggregates had been dispersed. As expected, electron microscopy revealed no change in the ultimate BeO crystallite size in the submicron range.

No particles attributed to grinding medium or mill abrasion were detected in BeO powder ground with alumina balls. However grinding with BeO cylinders introduced coarse-grained chips whose concentration increased during grinding. These were attributed to abrasion from the BeO cylinders. They were first detected in ground powder, and in sintered structures gave rise to a duplex grain size distribution (see Section 3.3 and Figure 5b). Any alumina contamination arising from alumina balls was apparently of a much finer particle size.

Surface area-grinding time curves for rotary mill grinding are shown in Figure 1. With alumina balls, surface area first increased and then tended to fall, but the effects were slight. With BeO cylinders, surface area fell significantly as grinding proceeded; this is consistent with the mechanism discussed above in which BeO of low surface area ($< 1\ m^2/g$) is introduced to the high surface area BeO ($15\ m^2/g$) by abrasion from the high-fired BeO cylinders during milling.

3.1.2 Contamination during grinding

The main contaminants arising from alumina-porcelain milling were expected to be Al (from balls and porcelain jar) and Si (from porcelain), and ground powders were therefore analysed for these elements.

Results for Al and Si contamination on vibratory and rotary milling are shown in Figure 2.

Several generalisations may be made from these results:

(i) Alumina was the primary contaminant.

(ii) Contamination was higher for alcohol grinding than for water grinding.

(iii) The pattern of contamination was different in the two types of mill, increasing much more slowly for the vibratory mill.

3.3.3 Leaching of soluble material

The filtrates from aqueous and alcohol grinding of UOX in the vibratory mill were analysed in some cases for SO_4^{2-}. The results indicated that up to 340 p.p.m. and 21 p.p.m. SO_4^{2-} respectively had been leached from the material after 20 hours grinding. Even in the first case, the amount of sulphur removed was much less than that known to be present (Reeve and Ramm 1961) indicating that the sulphur was distributed throughout the BeO structure.

3.2 Sintered Density

Specimens were sintered, as described in Section 2, at temperatures of 1520, 1600 and 1660 ° C.

The results are summarised in Figure 3. The most striking observation is that all grinding procedures resulted in a progressive fall in sintered density with increasing grinding time. Any

effects due to variations in pressed density were ruled out by measurements of pressed density on pellets of all types; the values were in the range 1.77 – 1.79 g/cm^3 with no apparent correlation between pressed and sintered densities.

3.3 Uniformity of Grain Size

The uniformity of the sintered compacts increased with grinding time up to approximately 10 hours, for example compare Figure 5a with Figures 4a and 4b. At the same time some trends in grain size were noted; these are shown in Figure 3 and summarised below. A tendency for finer grain size to be associated with higher porosity was expected owing to the grain growth inhibiting effect of porosity. However the possibility of grain growth enhancement or inhibition by other mechanisms was not excluded.

1500 – 1520 °C

Grain size was initially fine (5 – 12μ) and decreased with grinding time corresponding with the decreasing density. In the case of BeO–neoprene milling after 20 hours, areas of coarse grain size appeared (Figure 5b). These presumably arose from the coarse-grained chips introduced during grinding with BeO balls, detected by optical microscopy of the ground material (see Section 3.1.1).

1600 °C

Initial grain size was approximately 15 microns. In the case of water–alumina grinding, grain size fell after grinding without decrease in density, indicating that grinding was having some additional grain refining effect. For alcohol grinding there was an initial fall, associated with decreased density. After longer grinding times grain size increased and finally decreased slightly with further density decrease. The increase in grain size was accompanied by the development of a non–equiaxed structure (Figure 6). A feature of the structure is the presence of twinned grains, also observed by Aitken (1961) in BeO to which small amounts of alumina had been added, and attributed by him to the Al_2O_3 impurity.

BeO ground with BeO cylinders showed equiaxed grains, with a progressive fall in grain size with lower sintered densities.

1660 °C

All grinding procedures gave a similar result, with grain size falling only slightly after 20 hours, accompanying a slight fall in density. All alcohol–ground material showed unequiaxed grain structure, but water–ground showed this only at 10 and 20 hours.

The development of unequiaxed structures at 1600 and 1660 °C after shorter grinding periods in alcohol than in water is consistent with the observed higher contamination levels for alcohol grinding (see Figure 2).

3.4 Grain Refinement Effects

To investigate further the grain size /density relationships and the possibility of grain refinement on grinding, a particular grinding procedure was chosen for more intensive study. This was 3 hours grinding in the vibratory mill using porcelain jar, alumina balls, and alcohol. Under these conditions it had already been observed that:

(i) Sintered density at 1520 °C was not markedly decreased.

(ii) Uniformity was significantly improved.

(iii) Al and Si levels were both moderate at 300 p.p.m.

A further batch of this material was prepared, and specimens made from it by cold–pressing and sintering at temperatures between 1500 °C and 1700 °C. Densities and grain sizes were measured, the latter by a lineal analysis method from either optical micrographs or electron microscope fractographs. At the same time, grain sizes of corresponding specimens sintered from unground powder were measured. Results are shown in Figure 7 and some typical structures of ground material are shown in Figure 8.

Although each curve shows some spread, some conclusions can be drawn:

(i) At or below 2.8 g/cm^3, mean grain sizes of ground and unground UOX are below 3μ, with however a more uniform grain size for ground UOX (compare Figure 5a with Figure 4a).

(ii) At 2.90 – 2.91 g/cm^3 there is a sharp upward trend in each curve; but in the range 2.85 – 2.91 g/cm^3 ground UOX has a significantly finer grain size than unground material (compare Figure 8a with Figure 4b).

(iii) At densities above 2.91 g/cm^3, grain size of both ground and unground material increases rapidly with density, and the grain refinement effect becomes negligible (Figure 8b). This grain size increase is associated with the higher temperatures (of the order of 1700 °C) necessary to achieve densities in this range.

(iv) For ground UOX, grain size can be varied by at least an order of magnitude in the density range 2.90 – 2.94 g/cm^3 with only slight variation in density (see Figures 8a and 8b). This is made possible by the steep slope of the grain size–density curve at these densities (Figure 7), and is achieved by using sintering temperatures between 1500 °C for the smaller and 1700 °C for the larger grain sizes.

3.5 Bend Strength

Evidence that grinding of the powder has a significant effect in improving the strength of sintered UOX was provided by measurements of room temperature bend strength. These were made in 3–point bend over a 0.81 inch span on a Hounsfield tensometer, and they are summarised in Figure 9. It was concluded that grinding prior to fabrication improved the strength of sintered UOX for all the grinding procedures tested and that vibratory grinding in alcohol for three hours or rotary grinding in alcohol for one hour were probably more favourable procedures for producing high strengths at high density than rotary grinding for 10 hours in water.

The mechanism by which this strength improvement occurs is being studied.

4. DISCUSSION

It is suggested that the progressive lowering of sintered density resulting from ball–milling is due to the introduction of increasing amounts of silica and alumina from mill and grinding medium abrasion. This explanation is also consistent with the observations of densities and contamination levels for different grinding methods. For example, for material ground for 10 hours and sintered at 1520 °C, the density decreased, and the alumina content increased, both in the same order: BeO cylinders in water, alumina balls in water, alumina balls in alcohol. The fall in sintered density with BeO cylinders, smaller than that for alumina–porcelain milling, was consistent with the observed fall in surface area under these conditions.

The alcohol–water curves for the vibratory mill are reversed from those for rotary grinding. This is probably due to a difference in grinding action between the two methods. Consistent contamination figures were not obtained for vibratory grinding in water, but those obtained suggested that contamination was higher than for grinding in alcohol. It should be noted that the density–grinding time curves for 1500 – 1520 °C which correspond most closely are alcohol–vibratory and water–rotary and that the corresponding contamination–time curves are also comparable.

The pronounced deleterious effect of ball–mill contamination on sintered densities is at first sight surprising since alumina–silica additives are sometimes employed to increase the sinterability of BeO. It is suggested that in this case, the foreign material is present as very small but dense particles and that these are of a favourable size and distribution for inhibiting densification by physically separating BeO particles, and for inhibiting grain growth by pinning of grain boundaries. It should be noted however that the grain refining effect of the introduced impurities seems to be most pronounced at the lowest levels obtained after the shorter grinding periods, for example 3 hours vibratory grinding in alcohol.

These mechanisms apply only at lower temperatures where there is little reaction between BeO and the impurities. At high temperatures where diffusion rates are higher, it is considered that the

impurities must react with the BeO, and lose their inhibiting effect on grain boundary movement so that densification and grain growth occur rapidly. The results would indicate that this reaction is not effective at 1520 °C where strong inhibition is observed, but becomes rapid in the 1600 – 1660 °C temperature range where there is only slight inhibition of densification and grain growth.

A factor contributing to grain growth inhibition may be the removal of the large crystallites present in unground UOX powder. If present, these can act as centres for exaggerated grain growth, as suggested by comparing Figure 4b with Figure 4a. On their removal by grinding, the onset of rapid grain growth is delayed until a slightly higher overall density has been reached.

5. SUMMARY

The results of this work may be summarised as follows:

(i) The grain size and uniformity of sintered UOX BeO has been markedly improved by grinding the powder with alumina balls in a porcelain jar in alcohol or water for short periods prior to fabrication.

(ii) All grinding procedures reduced the density obtained on sintering UOX BeO at up to 1660 °C in dry air.

(iii) Grinding for 3 hours with alumina balls in alcohol resulted in grain refinement of sintered UOX BeO in the density range 2.85 – 2.91 g/cm³. Grinding for longer periods was not so beneficial.

(iv) Grain size of UOX BeO sintered after grinding could be varied over an order of magnitude with only slight density changes in the range 2.90 – 2.94 g/cm³.

(v) The effects of (ii)–(iv) are due mainly to the introduction of fine alumina particles resulting from mill abrasion during grinding.

(vi) Grinding with BeO cylinders proved unsatisfactory owing to abrasion of coarse–grained chips of BeO from the cylinders during grinding.

(vii) The room temperature bend strength of sintered UOX BeO was improved by most of the grinding procedures investigated.

6. ACKNOWLEDGMENTS

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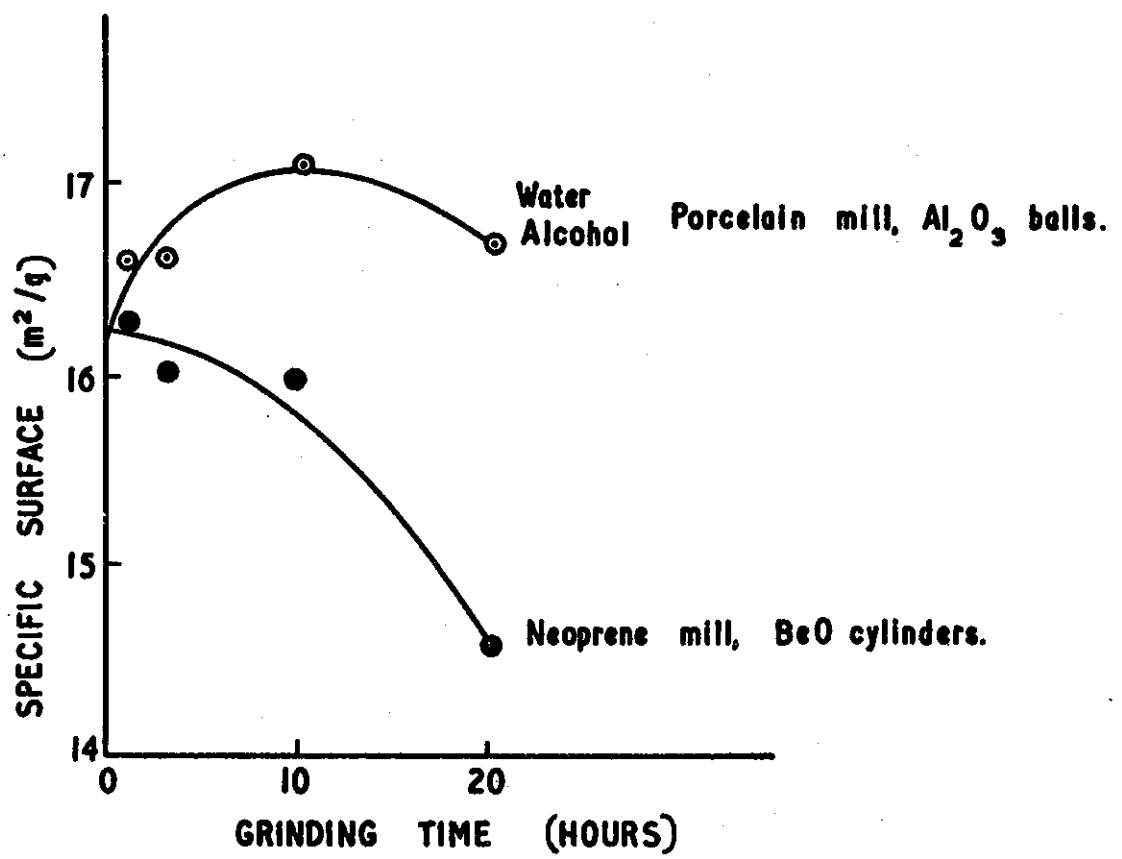


FIGURE 1.

SPECIFIC SURFACE VERSUS GRINDING TIME FOR VARIOUS PROCEDURES. UOX BeO (ROTARY GRINDING)

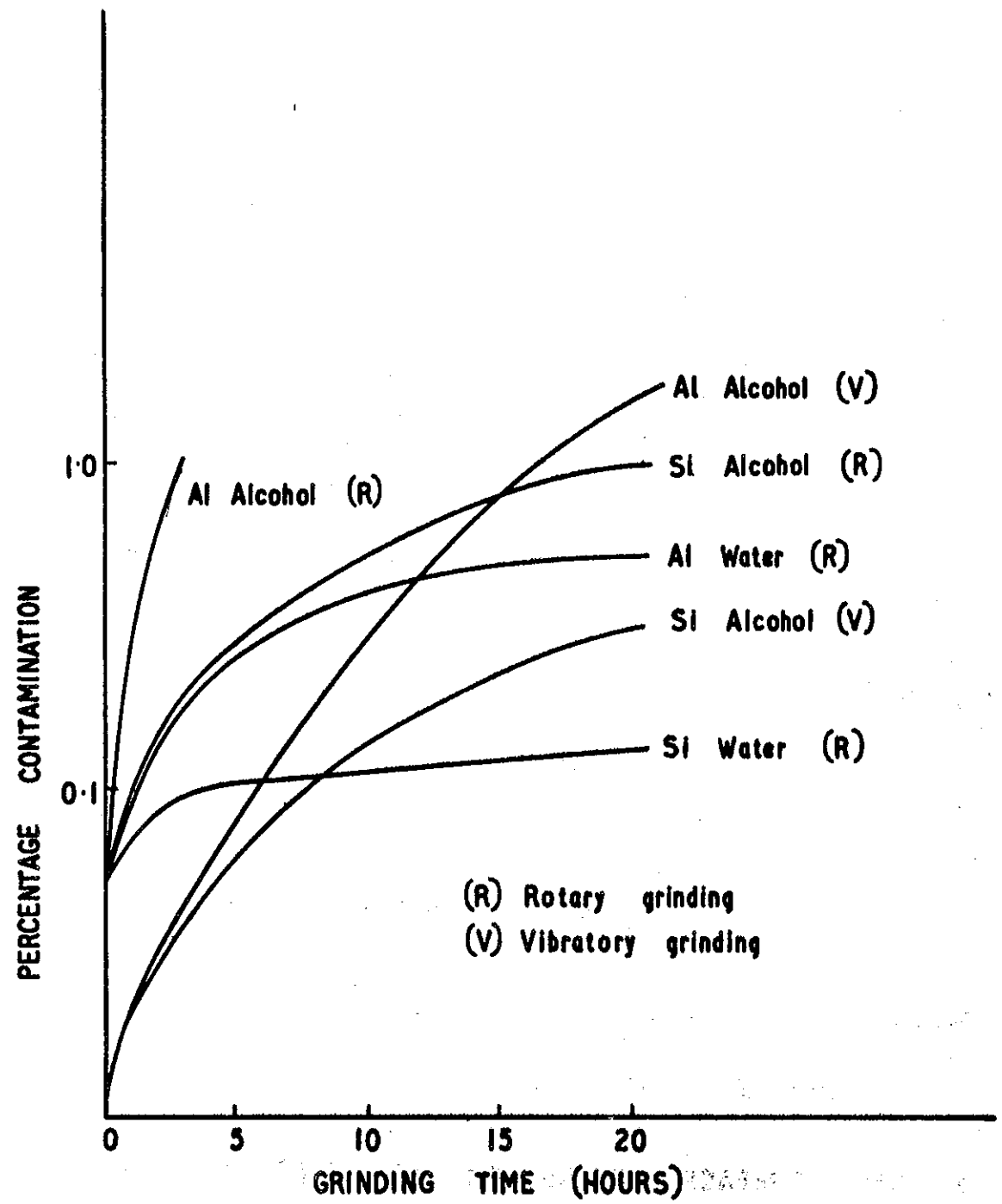


FIGURE 2.

CONTAMINATION RESULTING FROM VARIOUS GRINDING PROCEDURES

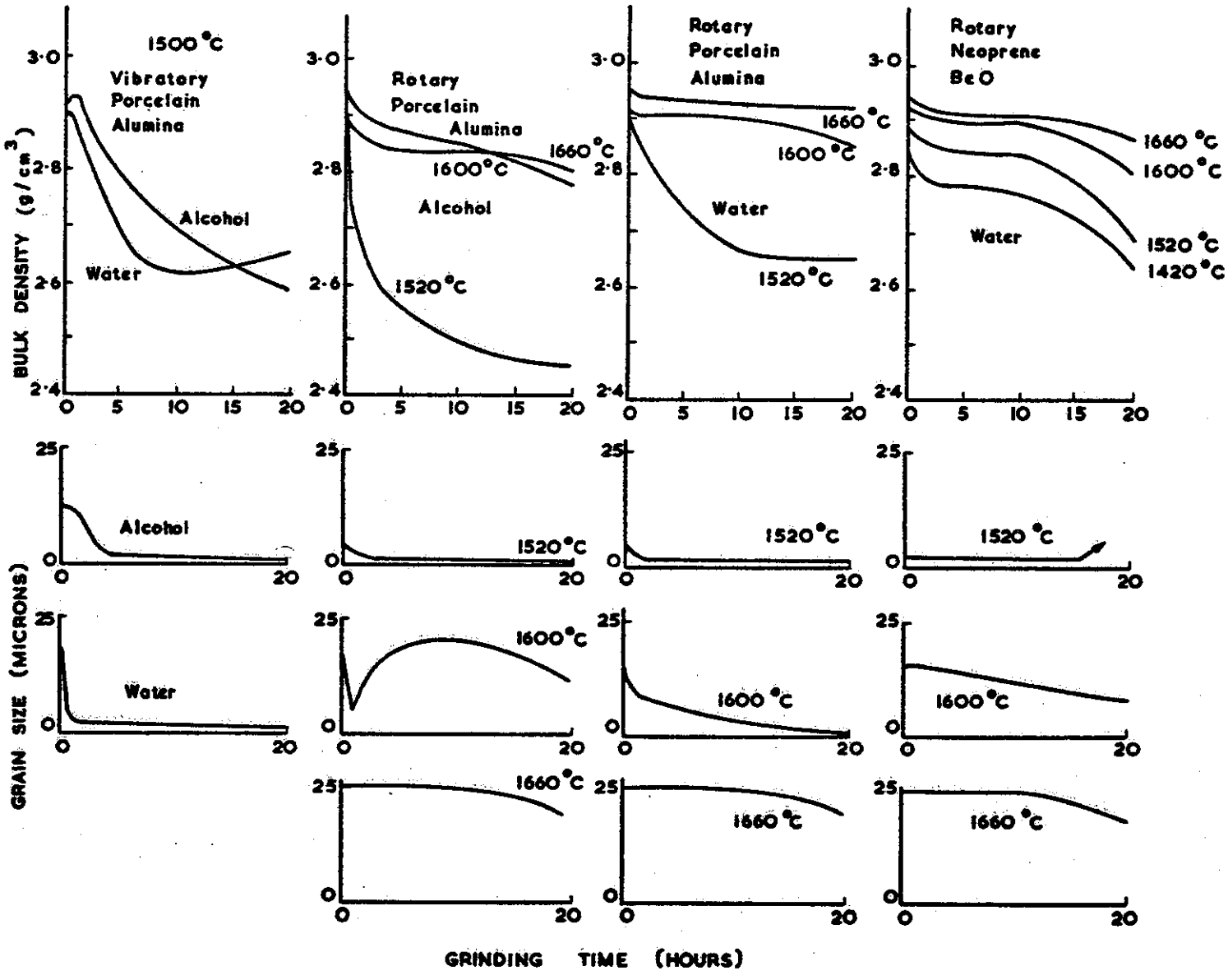
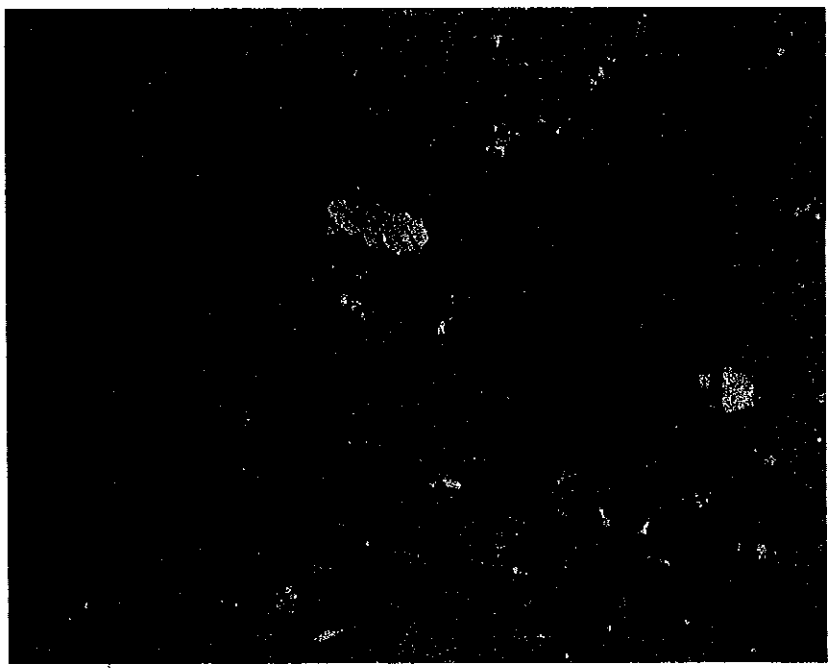


FIGURE 3.

EFFECT OF VARIOUS GRINDING PROCEDURES ON SINTERED DENSITY AND GRAIN SIZE OF UOX BeO



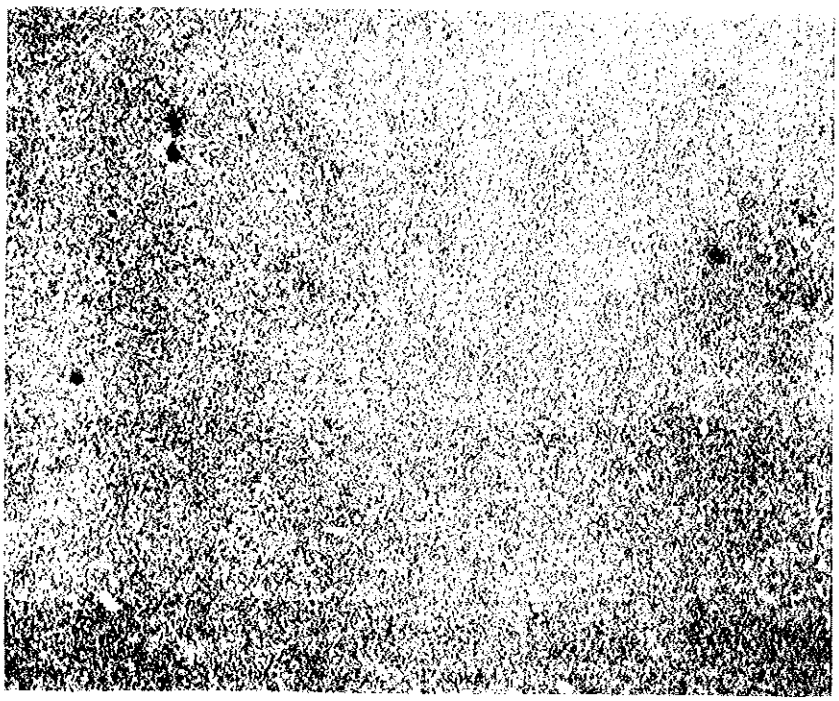
x 250

(a) 1200 °C 75% dense

x 250

(b) 1600 °C 97% dense

FIGURE 4 MICROSTRUCTURE OF UOX BeO SINTERED AS RECEIVED



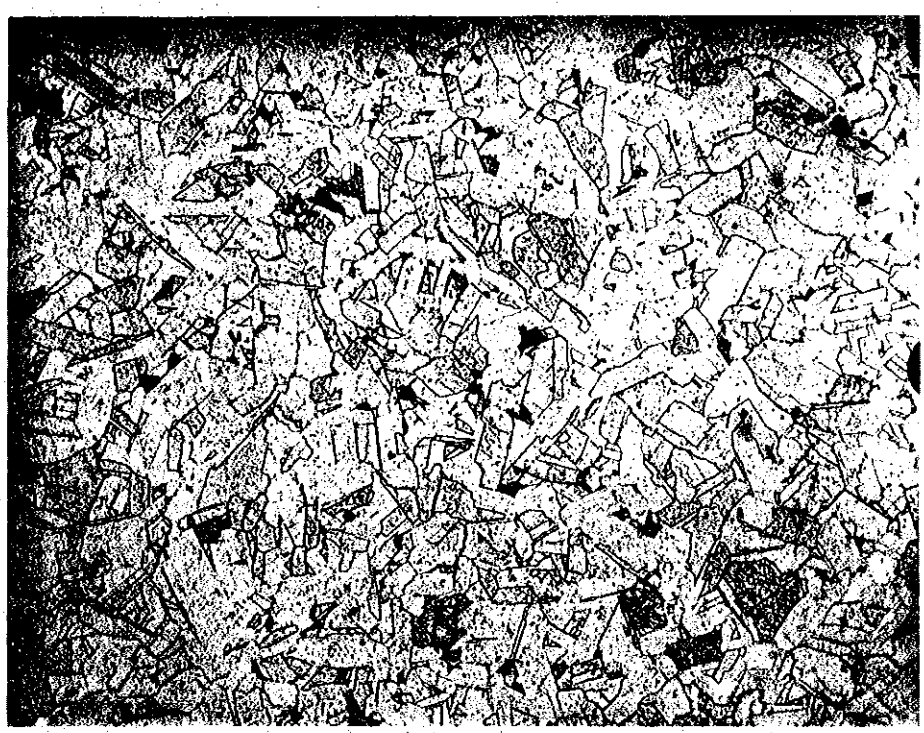
x 250

(a) Al_2O_3 Balls (10 hours)
1600 °C 93% dense

x 250

(b) BeO Cylinders (10 hours)
1520 °C 89% dense

FIGURE 5 MICROSTRUCTURE OF UOX BeO
GROUND BEFORE SINTERING



x 250

FIGURE 6 MICROSTRUCTURE OF UOX BeO GROUND WITH ALUMINA BALLS (3 hours in alcohol); sintered 1550°C 98% dense

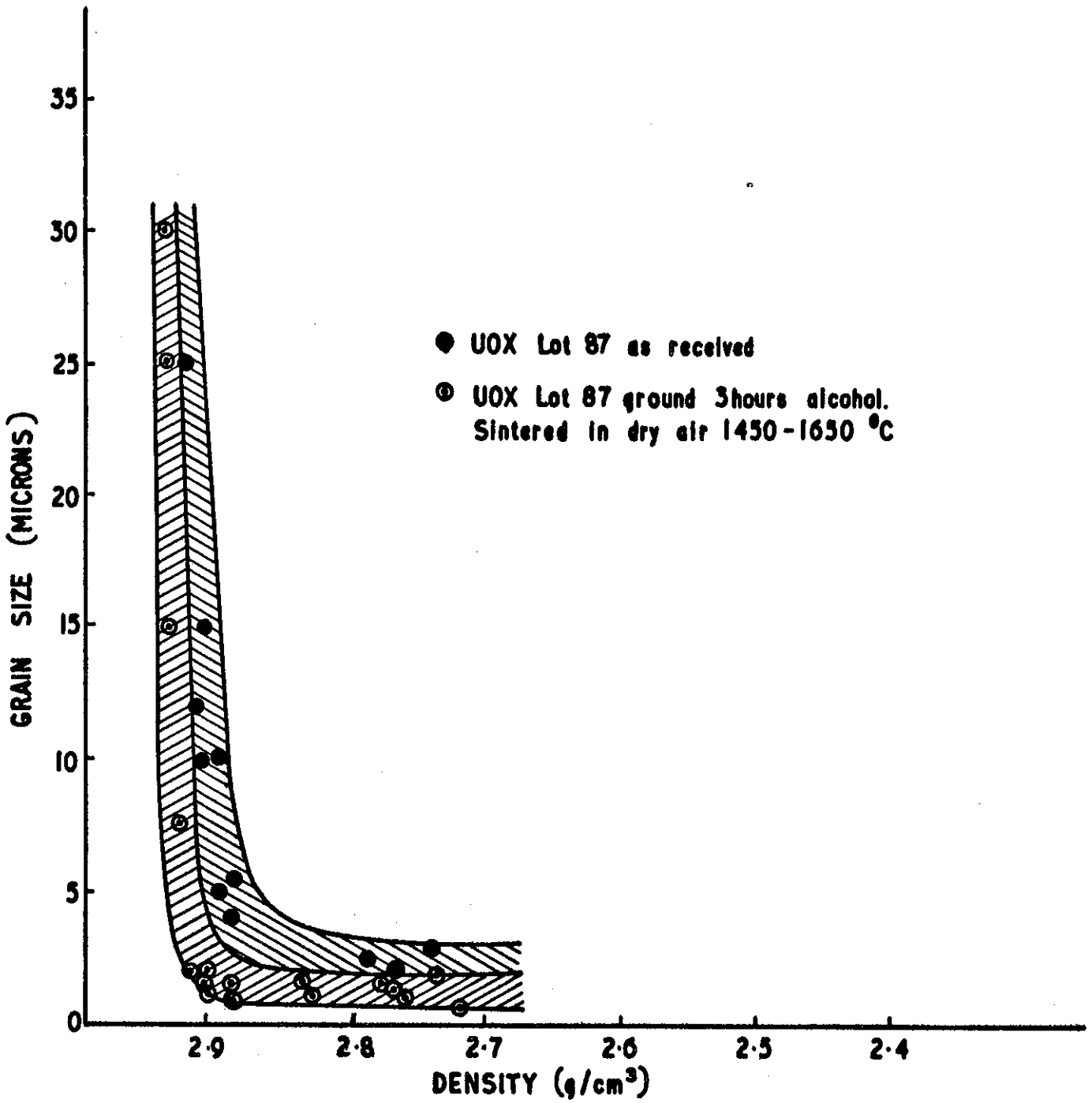
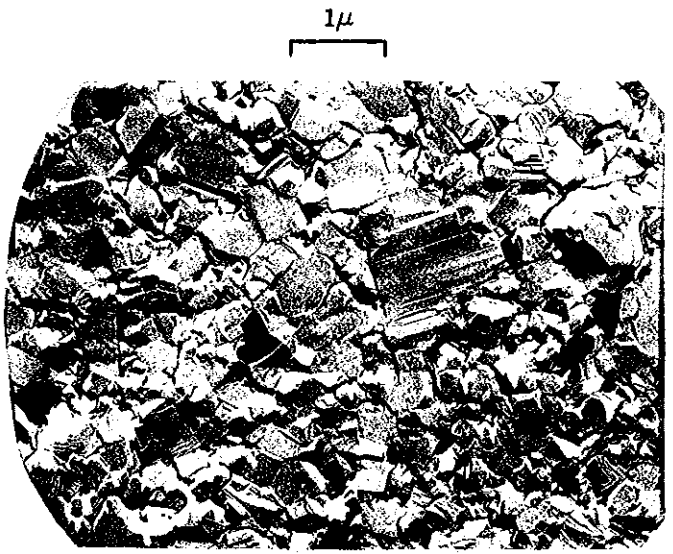
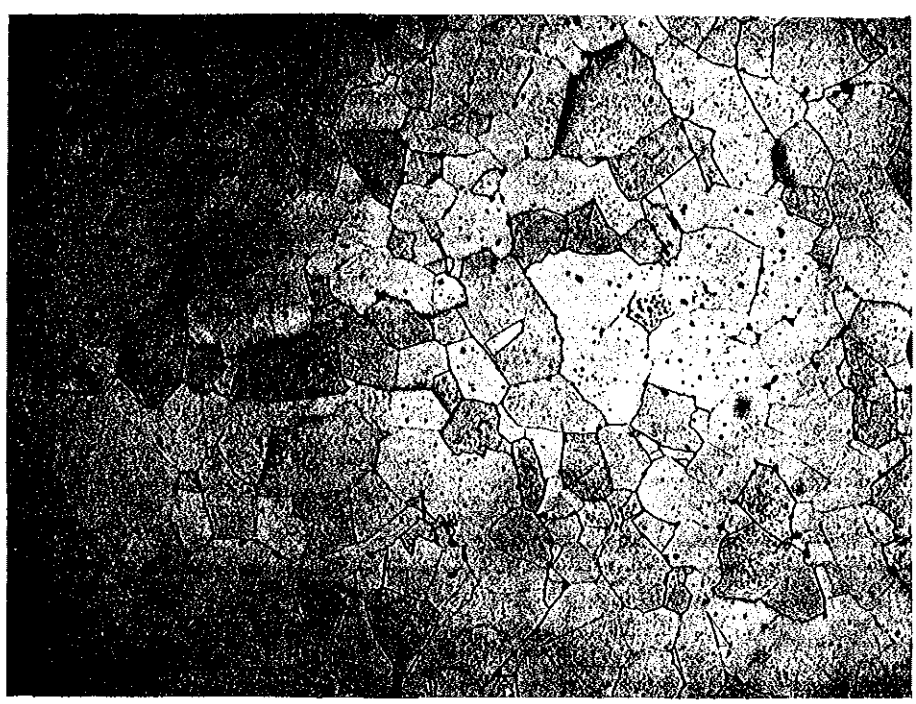


FIGURE 7.
GRAIN REFINING EFFECT OF GRINDING UOX BeO POWDER PRIOR TO FABRICATION (FOR DENSITIES UP TO 97% THEORETICAL)



x 6000

(a) 2.91 g/cm³ ; 1550 °C ; 1 – 2μ



x 250

(b) 2.94 g/cm³ ; 1670 °C ; 30μ

FIGURE 8 TYPICAL MICROSTRUCTURES OF UOX BeO
Ground before sintering (3 hours alcohol)

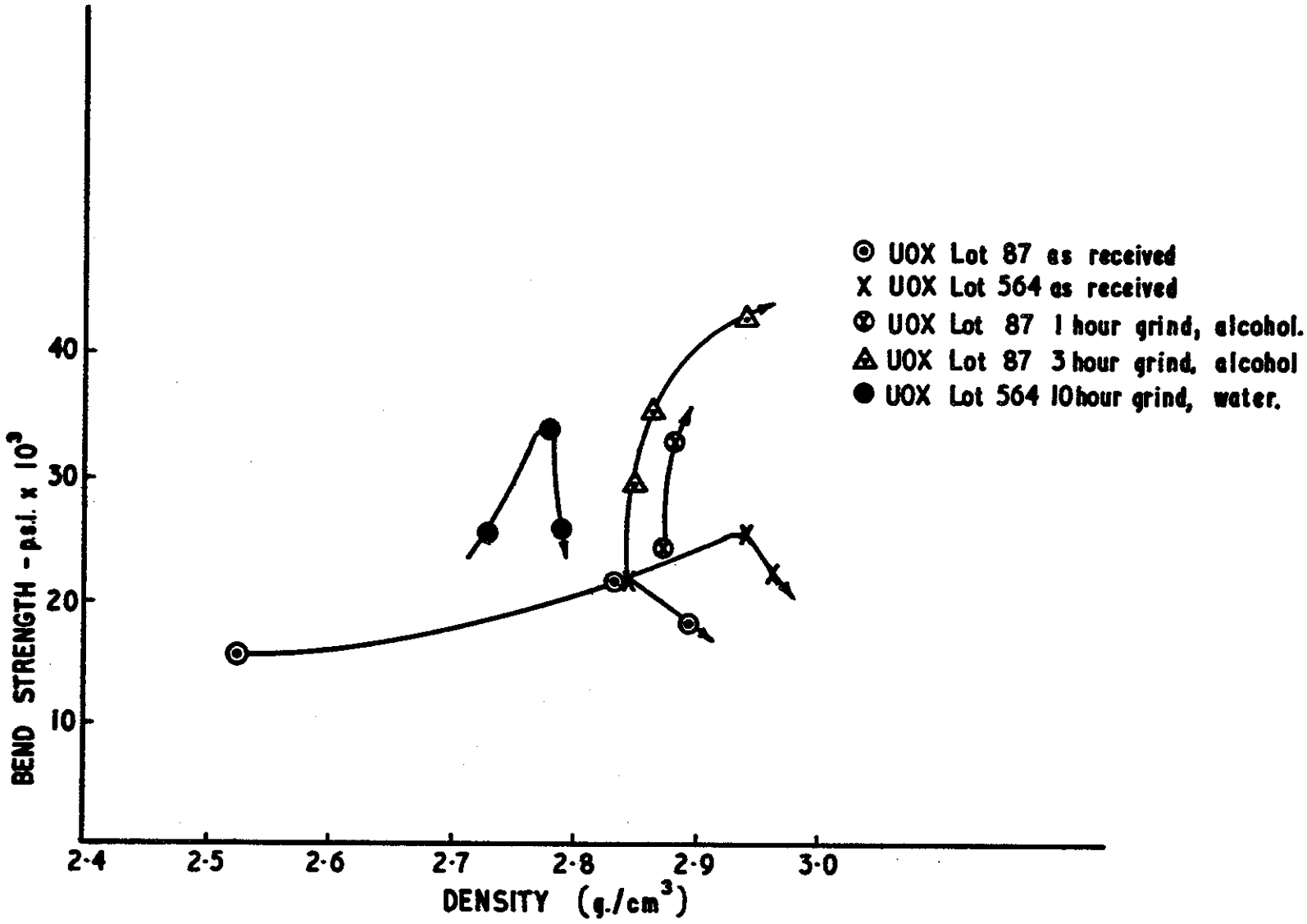


FIGURE 9.

BEND STRENGTH VERSUS DENSITY FOR VARIOUS TREATMENTS OF UOX BeO