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# AUSTRALIAN ATOMIC ENERGY COMMISSION
## RESEARCH ESTABLISHMENT
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## ABSTRACT

A technique for the extrusion and sintering of beryllium oxide to produce high density, fine-grained, high strength material was modified and improved. This resulted in beryllium oxide (250 p.p.m. Fe) which, after extrusion and sintering for 5 hours at 1400°C in nitrogen, had an average grain size of 6 µm, a mean modulus of rupture equal to 34,840 p.s.i. when tested in 4-point bending, and a density range of 2.86 to 2.90 g $cm^{-3}$.

Further modifications reduced the variations in grain size and density of the sintered specimens and increased the mean modulus of rupture. For example, double extruded material, when sintered for 6 hours at 1400°C in nitrogen had an average grain size of 8 µm, a density of 2.92 g $cm^{-3}$ and a mean modulus of rupture of 45,300 p.s.i.

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## 1. INTRODUCTION

In an earlier report (Bardsley and Ridal 1964), the authors described the development of a technique for the extrusion and sintering of beryllium oxide to produce fine-grained material of high density and strength. While satisfactory mean values for these properties of the sintered material were obtained, the range of values in each case was larger than desired. Some of the variations were attributed to the uncontrolled and variable nature of iron contamination; this arose from wear of the mixer blades and extrusion dies. Finely divided iron, particularly in the oxidised state, is known to increase sintering and grain growth rates markedly (Beaver et al. 1964); hence non-uniform iron contamination could have caused the density and grain-size variations. Large pieces of metallic iron were also observed in some sintered specimens, and these probably acted as flaws contributing to the scatter in strength values.

Further development of this process, aimed mainly at reducing and controlling the iron content and at achieving more reproducible properties with less scatter, is described in this report.

## 2. SUMMARY OF EARLIER WORK

The original extrusion process is shown in Figure 1. The resultant material contained a mean of 500 p.p.m. of iron, but the scatter of values of iron content was high. The minimum content found, namely 400 p.p.m, was attributed mainly to wear from the mixer blades. Wear of the extrusion dies introduced iron into surface layers of the extruded material but the amount was not determined.

The best material was produced by sintering for 5 hours at 1350°C in dry nitrogen. The resulting densities were in the range 2.85 to 2.90 g $cm^{-3}$, with a mean modulus of rupture of 34,000 p.s.i. for as-sintered specimens and mean surface and 'core' grain sizes of 9 µm and 5 µm respectively. In this same material three to four times the random number (R) of basal planes were oriented perpendicular to the extrusion direction. The number of planes with this preferred orientation increased to 9R when the material was sintered at 1700°C to a grain size of 45 µm.

## 3. EXPERIMENTAL TECHNIQUE

### 3.1 Raw Materials

The beryllium oxide powder used was sulphate-derived Brush UOX and Table 1 shows results of chemical analyses and surface area measurements on the two batches. The difference in surface area between batches probably arises from variations in the calcination process. Beaver et al. (1964) having stated that during normal production the material is calcined at 1000°C for 10 to 20 hours. This type of powder also contains approximately one volume per cent of BeO single crystal needles up to 150 µm in length.

### 3.2 Iron Contamination

#### 3.2.1 Mix preparation

The mixer used for all this work was of the contra-rotating sigma-blade type. In the original process, beryllium oxide powder, 2 $^{w}/_{o}$ gum tragacanth, 17 $^{w}/_{o}$ water and 10 $^{w}/_{o}$ glycerine were mixed together for four hours. This technique produced a granular material which abraded the iron of the mixer blades. To reduce this abrasion, two different mixing schedules were investigated.

1. 2 $^{w}/_{o}$ gum tragacanth, 17 $^{w}/_{o}$ water and 10 $^{w}/_{o}$ glycerine, plus one quarter of the powder weight, were made into a 'master mix'. Further small additions of powder were made throughout the mixing schedule; the process was complete after about two hours. With this technique iron contamination was limited to about 250 p.p.m.
2. The beryllium oxide powder, 2 $^{w}/_{o}$ gum tragacanth, and 10 $^{w}/_{o}$ glycerine were mixed for 30 minutes with an excess of water (>60 $^{w}/_{o}$) and the mix was then dried under an infra-red lamp to 27 $^{w}/_{o}$ moisture (water plus glycerine). The resultant iron contamination was about 120 p.p.m.

Although Technique (2) gave a lower and less valuable iron pick-up, control of the moisture content was extremely difficult and this caused variations in the extrusion load and green bulk density. Hence Technique (1) was adopted as the mixing technique.

The mix, granular in appearance, was de-aired in the container of the press by evacuating at a pressure of less than 1 mm of mercury. This step was essential to remove entrapped air; otherwise longitudinal cracking of the extruded sections occurred. A moisture loss of 1 per cent was normal in this process and was allowed for in the preparation of the mix.

#### 3.2.2 Die construction

Surface iron contamination, resulting from abrasion of the mild steel dies during extrusion, contributed to the larger sizes of surface grains in those extruded and sintered specimens whose average grain size was less than 20 µm. To eliminate this contamination, a modified extrusion die (shown in Figure 2) was developed and used in all experiments described in this report. It consisted of a sintered beryllium oxide insert, set in a mild steel adaptor, a polythene washer protecting those metal surfaces which would otherwise be exposed to the beryllium oxide mix.

### 3.3 Extrusion Technique

The modified process is shown in Figure 3.

The original technique consisted of extruding the de-aired plastic mass through shear dies (180° included angle) with a reduction in area of 45:1. This produced material which after baking, had a green bulk density of 1.5 $g\ cm^{-3}$. However, sintered specimens had larger than desirable variations in density and grain size; Figure 4 shows a typical microstructure with a mainly large grain-size area interspersed with regions of small grain size and high porosity. These could have been caused by the non-uniform iron contamination leading to areas of low sintered density within the specimen; microanalyser scans across these regions showed them to be of low iron content.

Variation in green density within a specimen also leads to variation in sintered density and grain size (Bannister 1965). In an attempt to improve the uniformity of the green density within a specimen, a double extrusion technique involving coiling and immediate re-extrusion of the initial product was investigated; we had observed, for 1-inch diameter single extrusions, a reduction in green bulk density from 1.45 to 1.4 $g\ cm^{-3}$ when the surface of the extruded specimen was removed. However, the green bulk density of the double extruded material remained unchanged at 1.5 $g\ cm^{-3}$. Variations in green density within each specimen were not measured directly but indirect evidence (Section 4) suggested that some improvement had been achieved.

### 3.4 Sintering

Sintering studies during the development programme used an induction heated alumina tube furnace capable of a maximum temperature of 1700°C; a pure dry nitrogen (less than 100 p.p.m. moisture) atmosphere could be maintained in the furnace. However, the maximum capacity of this furnace was 15 specimens per sintering run and minor variations in sintering conditions from batch to batch may have contributed to the large variations in sintered density and properties which were observed (see Section 4). To reduce these variations to a minimum, a Super-Kanthal heated muffle furnace was modified to allow 50 specimens to be sintered at the same time. An alumina muffle was placed inside the work space of the furnace and the nitrogen atmosphere was introduced through an alumina tube at a flow rate of 10 $ft^3\ h^{-1}$. The moisture and oxygen content of the nitrogen atmosphere was no longer so closely controlled and the nitrogen entering the furnace could contain up to 1000 p.p.m. moisture. However no change was observed in the density range of the sintered material (2.86 to 2.90 g $cm^{-3}$).

### 3.5 Preferred Orientation

The preferred orientation was determined on sintered specimens using a Siemens two-circle texture goniometer. The type and degree of texture was determined by comparing the X-ray intensity reflected by the basal plane at any orientation with that reflected by a randomly oriented specimen.

### 3.6 Microstructure

The grain sizes were determined by the mean linear intercept method; reported grain sizes were the mean linear intercept of 150-200 grains at a total of 10 random positions. The accuracy of the measured grain size was estimated to be ± 15 per cent

### 3.7 Mechanical Properties

The moduli of rupture for as-sintered specimens 0.25 inches in diameter by 1.75 inches long were determined in 4-point bending, with a gauge length of 0.75 inches and a span of 1.5 inches.

## 4. RESULTS

### 4.1 Sintering

In the original process, extruded material (500 p.p.m. Fe) was sintered for 5 hours at 1350°C in a nitrogen atmosphere to produce densities in the range 2.85 to 2.90 g $cm^{-3}$. Table 2 shows the changes in densification behaviour for material containing 250 p.p.m. Fe produced by the modified technique (Figure 3). The reduction in the iron contamination from 500 p.p.m. to 250 p.p.m. caused an increase from 1350°C to 1400°C in the 'sintering temperature' at which a density in the range 2.85 to 2.90 g $cm^{-3}$ could be attained in 5 hours. All standard material produced by the modified technique, including that produced by double extrusion, was sintered for 5 hours at 1400°C in nitrogen. However, the density range achieved was now 2.86 to 2.89 g $cm^{-3}$, and for double extrusion, 2.88 to 2.89 g $cm^{-3}$.

A limited number of experiments used both nitrogen/6%-hydrogen and vacuum rather than dry nitrogen as the sintering atmosphere. The lower densities attained particularly after sintering for 5 hours at 1400°C in nitrogen/6%-hydrogen (see Table 3), show that non-reducing atmospheres are necessary during sintering if the enhanced sinterability produced by the iron contamination is required.

### 4.2 Preferred Orientation

The results of the preferred orientation determinations are summarised in Table 4. For sintered specimens of average grain size 6 μm the extent of the preferred orientation increased from 4R to 6R when the powder batch was changed from Lot 216 to Lot 266. It further increased from 6R to 8R when the double extrusion technique was used.

### 4.3 Microstructure

For the high strength specimens produced by the original extrusion technique and sintered for 5 hours at 1350°C the microstructure exhibited a fine-grained core (typical mean 5 μm) and a coarser grained rim (typically 9 μm mean). Material produced by the modified extrusion technique and sintered for 5 hours at 1400°C differed only in that the rim was a non-uniform region consisting of areas of 6 μm and 9 μm mean grain size. However, material produced by the modified technique but including the double extrusion technique was of 6 μm mean grain size throughout, although individual grains up to 20 μm in size were still present (Figure 5).

### 4.4 Mechanical Properties

A comparison of strength and density of material produced by these techniques is shown in Table 5. For extruded material using Lot 216 UOX BeO, produced by the modified technique and sintered for 5 hours at 1400°C the average modulus of rupture was 34,840 p.s.i., which increased to 38,400 p.s.i. when Lot 266 UOX BeO was used as the powder feed. This further increased to 43,500 p.s.i. when a double extrusion technique was incorporated into the fabrication process. The highest average strength was developed by double extruded Lot 266 powder, sintered for 6 hours at 1400°C to a density of 2.92 to 2.93 g $cm^{-3}$ with average grain size of 8 μm.

## 5. DISCUSSION

### 5.1 Extrusion Technique

As expected from previous results, reduction of the iron content from 500 to 250 p.p.m. by use of the modified technique reduced the sinterability of the material. Whereas 5 hours at 1350°C was sufficient to produce densities in the range 2.85 to 2.90 g $cm^{-3}$ from material containing 500 p.p.m. of iron, the lower iron content material required a sintering temperature of 1400°C to achieve these densities in the same time. The lower densities obtained using a nitrogen/6%-hydrogen atmosphere suggest that iron oxides are responsible for this enhanced sinterability.

These results produced no evidence of the relative effect of variations in green density or iron contamination on the relationship between grain size and density for extruded material. Considering only the 'standard density' range 2.86 to 2.90 g cm$^{-3}$ and single extruded specimens, surface grain size changed from a fairly uniform 9 μm to a non-uniform 6 μm and 9 μm banded structure when beryllium oxide instead of mild steel extrusion dies were used. This suggests that surface iron contamination was partly responsible for the larger grain size. However, the complete absence of a large surface grain size in double extruded specimens produced by the modified technique suggests that variations in green bulk density within the specimen were also partly responsible.

The increased preferred orientation obtained when the powder batch was changed from Lot 216 to 266 is tentatively attributed to a slightly increased 'needle' content in the UOX Lot 266 although this was not apparent on metallographic examination.

### 5.2 Properties

Considering only the 'standard' density range (2.86 to 2.90 g cm$^{-3}$) the apparent increase in average strength of single extruded material (34,840 p.s.i. for Lot 216 to 38,400 p.s.i. for Lot 266) was shown to be significant at the 95 per cent confidence level; however, no obvious explanation for this increased strength is available. Double extruded material was also significantly stronger at the 95 per cent confidence level than single extruded material of the same density and from the same batch. The reason for this increase is probably that at any density a small and uniform grain size is being stressed instead of the irregular and large grain size previously obtained. Fryxell and Chandler (1964) showed that preferred orientation does not affect the strength of beryllium oxide unless more than 60 per cent of the basal planes are preferentially oriented. The effect of preferred orientation can therefore be ruled out in the present case where a much lower degree of orientation was obtained.

For extruded and sintered specimens with grain sizes up to 10 μm and tested in the as-sintered condition, the moduli of rupture (Table 5) show that strength increases as density increases up to 2.93 g cm$^{-3}$. However, the large scatter in strength values makes any definite conclusion difficult; this large scatter may be associated with variations in surface finish of the 'as-sintered' specimens. Detailed investigations using a standard test procedure are necessary to determine how grain size, density, pore morphology, preferred orientation and surface condition actually affect the moduli of rupture.

## 6. SUMMARY

1. A modified process produced extruded and sintered beryllium oxide (250 p.p.m. Fe contamination) of 6 μm average grain size, 34,840 p.s.i. mean modulus of rupture, and a density range of 2.86 to 2.90 g cm$^{-3}$. The sintering conditions were 5 hours at 1400°C in dry nitrogen.

2. A significant increase in the average modulus of rupture values to 43,500 p.s.i. was obtained with one powder batch by introducing a double extrusion process. This increased strength has been attributed to the greater uniformity of the grain size (mean 6 μm) and the smaller density range (2.88 to 2.89 g cm$^{-3}$) of the specimens.
3. Although the scatter in values of the moduli of rupture was large, the apparent trend was an increase in strength with increase in density for grain sizes less than 10 μm; double extruded material sintered for 6 hours at 1400°C had a grain size of 8 μm, a density of 2.92 g cm$^{-3}$, and an average modulus of rupture of 45,300 p.s.i.
4. The modifications introduced into the basic process reduced the large variations in grain size previously observed, and results indicate that these variations are due to both non-uniform contamination by iron and variations in the green bulk density of the extruded material. Sintered specimens produced by the double extrusion process had a uniform matrix grain size of 6 μm, interspersed with a few larger grains up to 20 μm diameter.
5. For sintered material with a grain size of 6 μm, the preferred orientation of the basal planes increased from 4R to 6R when the powder feed batch was changed from Lot 216 to Lot 266; this was tentatively attributed to an increased BeO single crystal needle content.

## 7. ACKNOWLEDGEMENTS

Mr. B. G. Breadner was concerned in much of the development work and Mr. K. Watson made the preferred orientation determinations.

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## TABLE 1

## ANALYSIS OF THE POWDER BATCHES USED FOR EXTRUSION STUDIES

| Element | UOX Lot 200-W-216-P (p.p.m.) | UOX Lot 200-W-266-P (p.p.m.) |
|---|---|---|
| Na | 30 | 35 |
| Mg | 45 | 60 |
| Ca | 35 | 20 |
| Al | 70 | 35 |
| Si | 45 | 50 |
| Fe | 35 | 25 |
| S | 900 | 740 |
| F | 5 | 5 |
| C | 210 | 310 |
| Surface Area | 11.4 $m^2$ $g^{-1}$ | 9.5 $m^2$ $g^{-1}$ |

## TABLE 2

## SINTERED DENSITIES SHOWING EFFECTS OF POWDER BATCH AND IRON CONTENT

| Powder Batch (UOX Lot) | Extrusion Method | Iron Content (p.p.m.) | Sintering Times (hours) | Density (g $cm^{-3}$) | |
|---|---|---|---|---|---|
| | | | | 1350°C | 1400°C |
| 216 | Original (Single) | 500 | 4 | 2.85 | 2.90 |
| | | | 5 | 2.90 | 2.90 |
| | | | 6 | 2.90 | 2.90 |
| 216 | Modified (Single) | 250 | 4 | - | 2.85 |
| | | | 5 | 2.68 | 2.88 |
| | | | 6 | 2.80 | 2.91 |
| 266 | Modified (Single) | 250 | 4 | 2.46 | 2.82 |
| | | | 5 | 2.60 | 2.88 |
| | | | 6 | 2.68 | 2.92 |

## TABLE 3

## EFFECT OF ATMOSPHERE ON SINTERED DENSITY

| Time (hours) | Temperature (°C) | Atmosphere | Density (g $cm^{-3}$) | Extrusion Method |
|---|---|---|---|---|
| 5 | 1400 | Vacuum | 2.86 | Modified Double |
| 5 | 1400 | $N_2$ | 2.89 | " |
| 5 | 1400 | $N_2/6\%\ H_2$ | 2.70 | Modified Single |
| 5 | 1400 | $N_2$ | 2.86 - 2.89 | " |

## TABLE 4

## EFFECT OF POWDER BATCH AND EXTRUSION METHOD ON PREFERRED ORIENTATION

| Extrusion Method | Powder Batch (UOX Lot) | Density (g $cm^{-3}$) | Grain Size (μm) | Degree of Texture R = Random |
|---|---|---|---|---|
| Modified Single | 216 | 2.90 | 6 | 4R |
| Modified Single | 266 | 2.90 | 6 | 6R |
| Modified Double | 266 | 2.92 | 6 | 8R |

## TABLE 5

## EFFECT OF DENSITY, GRAIN SIZE, EXTRUSION METHOD AND POWDER BATCH ON MODULUS OF RUPTURE

MODIFIED SINGLE EXTRUSION

| Time Hours | Temperature (°C) | Powder Batch | Density (g cm$^{-3}$) | Grain Size (µm) | Modulus of Rupture (p.s.i.) | | | Standard Deviation (p.s.i.) |
|---|---|---|---|---|---|---|---|---|
| | | | | | Number | Range | Average | |
| 4 | 1400 | 266 | 2.80 - 2.85 | 3 | 10 | 26,800-38,600 | 31,250 | 3,900 |
| 5 | 1400 | | 2.86 - 2.90 | 6 | 10 | 33,250-48,350 | 38,400 | 4,875 |
| 6 | 1400 | | 2.91 - 2.93 | 10 | 10 | 30,550-40,600 | 37,200 | 3,250 |
| 5 | 1400 | 216 | 2.86 - 2.90 | 6 | 100 | 26,300-43,200 | 34,840 | 4,400 |

MODIFIED DOUBLE EXTRUSION

| Time Hours | Temperature (°C) | Powder Batch | Density (g cm$^{-3}$) | Grain Size (µm) | Number | Range | Average | Standard Deviation (p.s.i.) |
|---|---|---|---|---|---|---|---|---|
| 4 | 1400 | 266 | 2.85 - 2.86 | 3 | 15 | 28,500-52,600 | 40,800 | 7,560 |
| 5 | 1400 | | 2.88 - 2.89 | 5 | 10 | 36,100-50,250 | 43,500 | 4,550 |
| 6 | 1400 | | 2.92 - 2.93 | 8 | 15 | 37,400-52,000 | 45,300 | 4,410 |

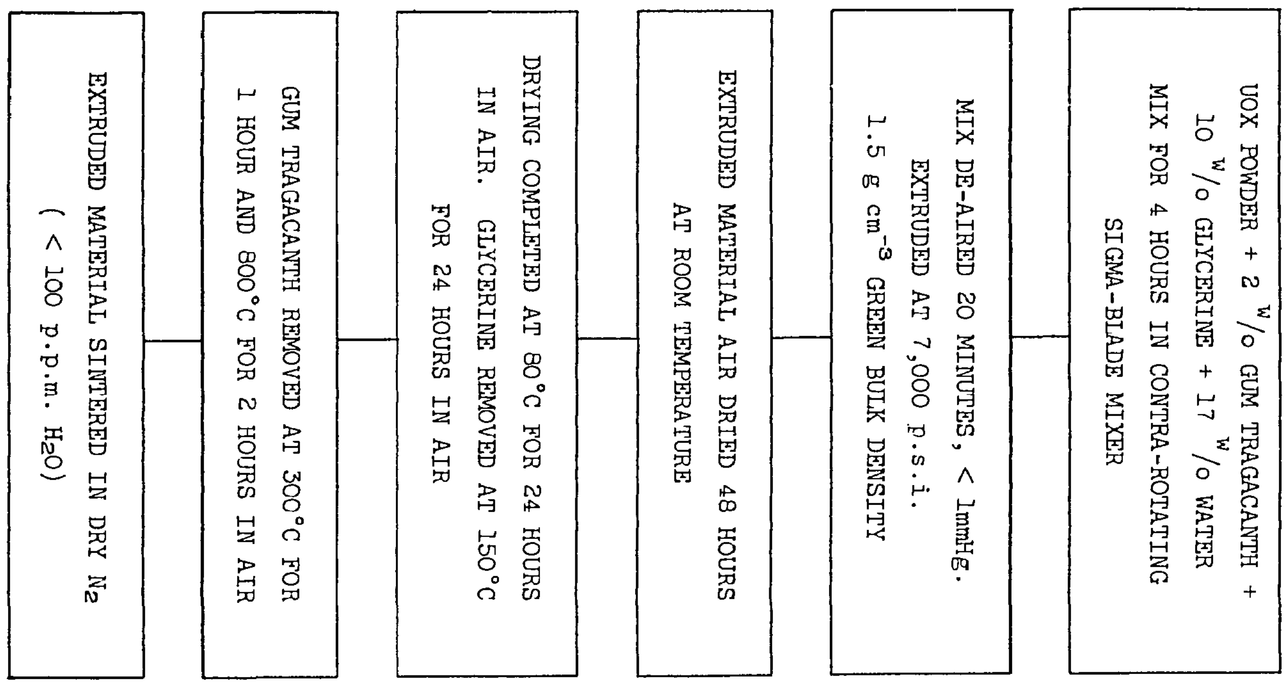

FIGURE 1. ORIGINAL EXTRUSION PROCESS

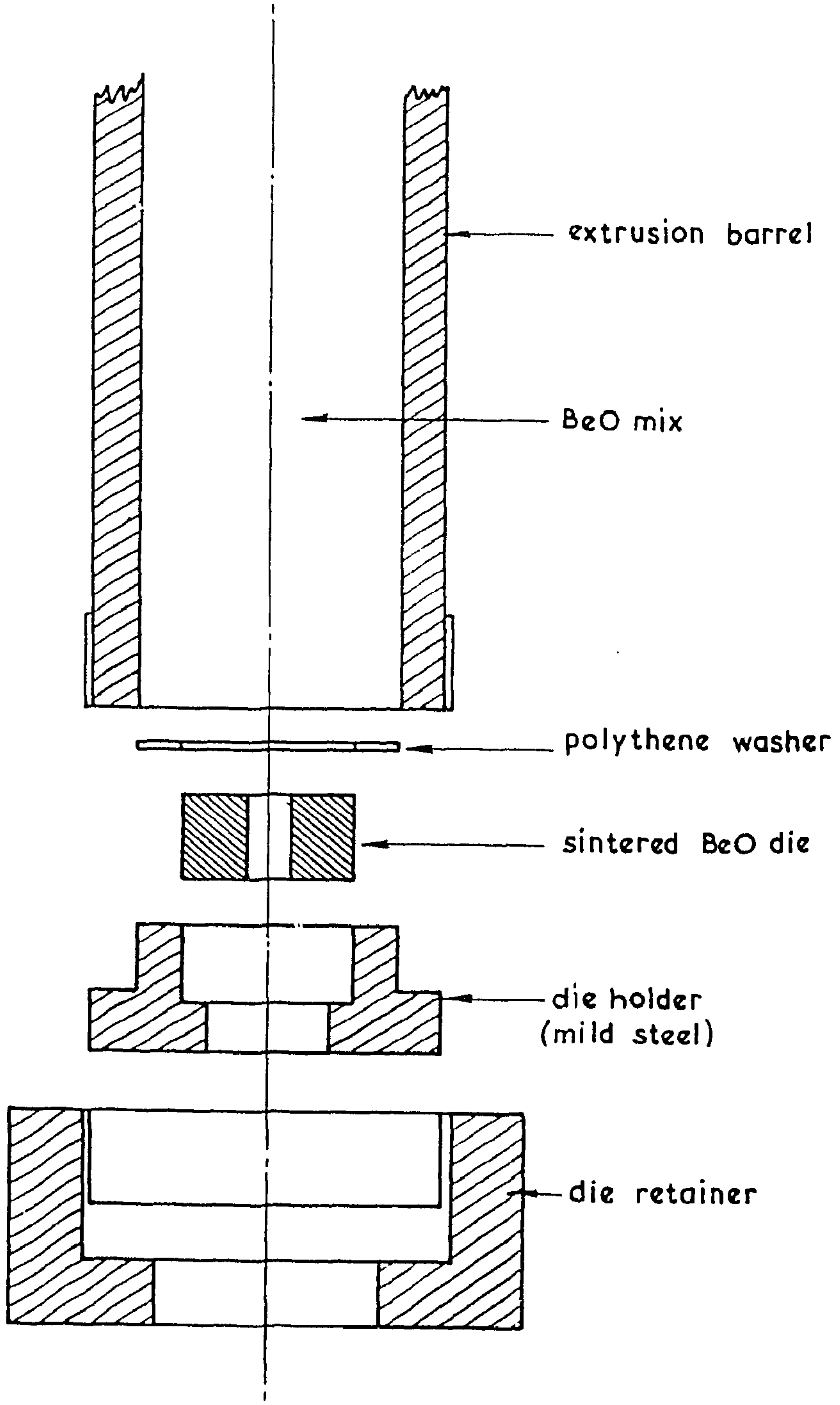

FIGURE 2. SCHEMATIC DIAGRAM OF CERAMIC INSERT EXTRUSION DIE

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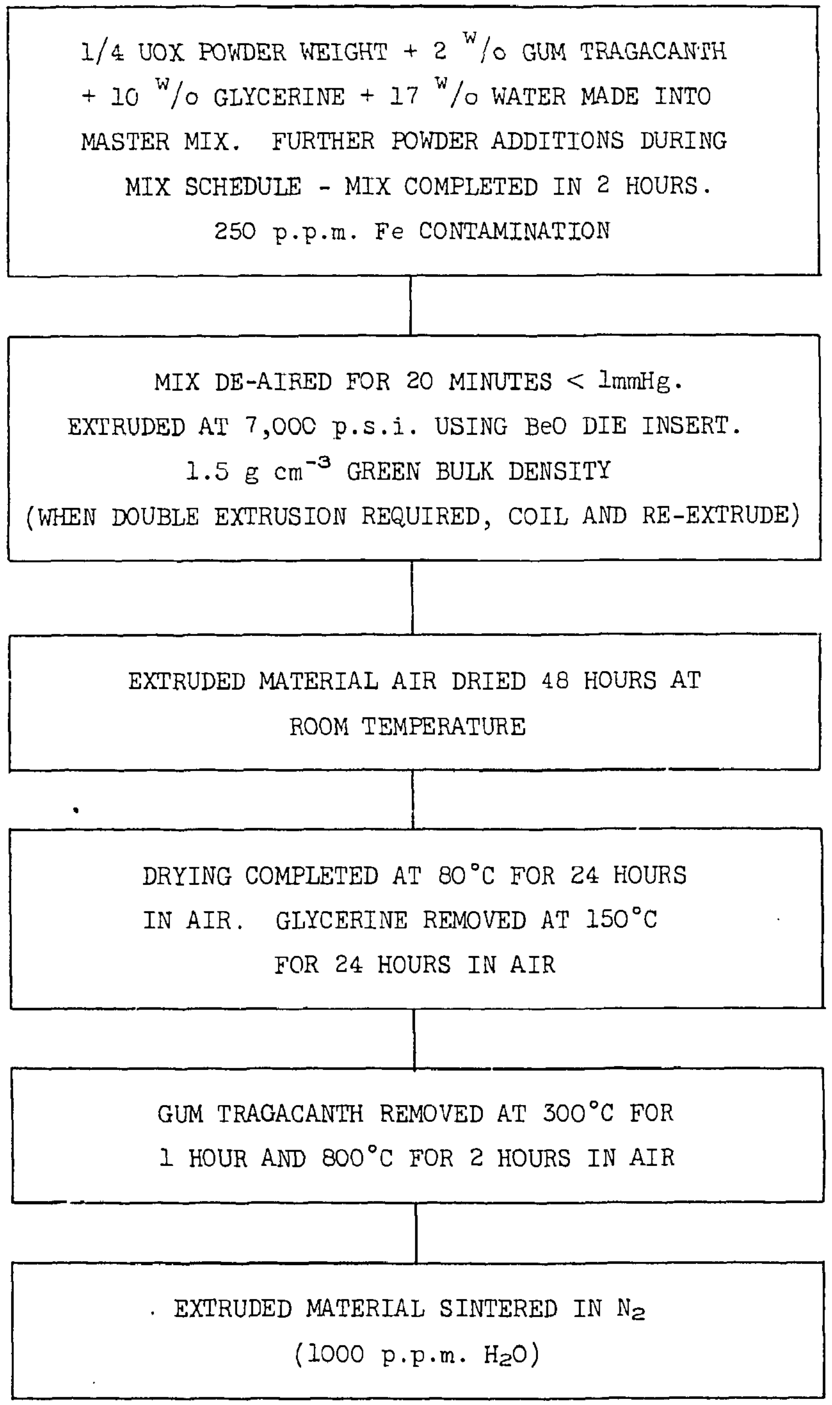

1/4 UOX POWDER WEIGHT + 2 $^{w}/_{o}$ GUM TRAGACANTH + 10 $^{w}/_{o}$ GLYCERINE + 17 $^{w}/_{o}$ WATER MADE INTO MASTER MIX. FURTHER POWDER ADDITIONS DURING MIX SCHEDULE - MIX COMPLETED IN 2 HOURS. 250 p.p.m. Fe CONTAMINATION

MIX DE-AIRED FOR 20 MINUTES < 1mmHg. EXTRUDED AT 7,000 p.s.i. USING BeO DIE INSERT. 1.5 g $\text{cm}^{-3}$ GREEN BULK DENSITY (WHEN DOUBLE EXTRUSION REQUIRED, COIL AND RE-EXTRUDE)

EXTRUDED MATERIAL AIR DRIED 48 HOURS AT ROOM TEMPERATURE

DRYING COMPLETED AT 80°C FOR 24 HOURS IN AIR. GLYCERINE REMOVED AT 150°C FOR 24 HOURS IN AIR

GUM TRAGACANTH REMOVED AT 300°C FOR 1 HOUR AND 800°C FOR 2 HOURS IN AIR

EXTRUDED MATERIAL SINTERED IN $N_2$ (1000 p.p.m. $H_2O$)

FIGURE 3. MODIFIED EXTRUSION PROCESS

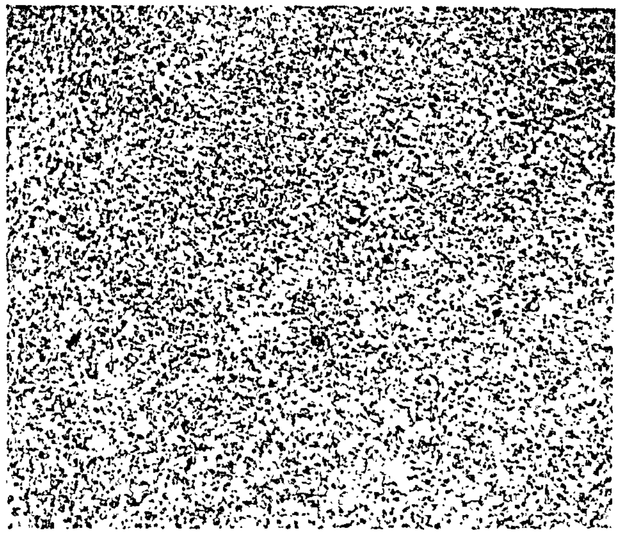

FIGURE 4. MICROSTRUCTURE SHOWING VARIABLE GRAIN SIZE AND DENSITY

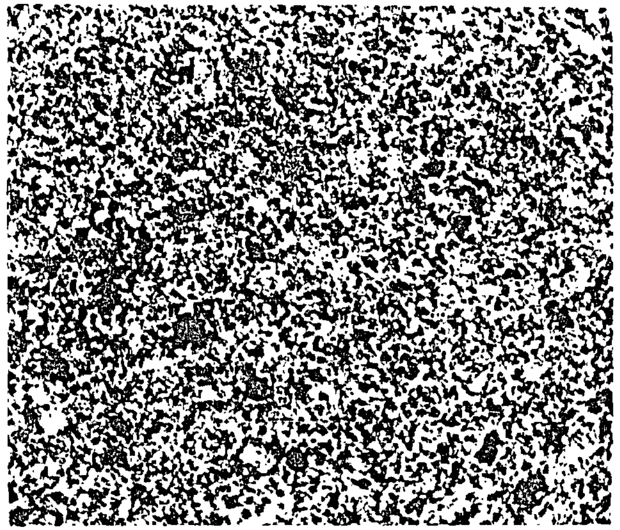

FIGURE 5. DOUBLE EXTRUDED AND SINTERED SPECIMEN 5 HOURS, 1400°C, $N_2$

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