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SINTERING STUDIES ON CERAMIC FUEL MATERIALS

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ABSTRACT

Satisfactory dense crack-free dispersions of spheroidal $UO_2 - ThO_2$ particles in BeO can be produced by "co-sintering", a process in which unsintered particles are hydrostatically pressed in BeO and the dispersion is sintered in one step.

The large voids and cracks in dispersions of fully sintered particles in BeO following sintering are related to mismatched sintering shrinkage between the two phases; they are probably indicative of a high interfacial energy between the two phases.

Co-sintering has been used for individual fabrication of specimens for irradiation testing, but is not immediately applicable to large scale fabrication of fuel element shapes. Possible modifications of the method are discussed.

CONTENTS

1. INTRODUCTION

Dispersions of UO_2 or UO_2 plus ThO_2 in BeO are being assessed for their suitability as fuel materials for high temperature gas-cooled nuclear reactors.

Dispersions of UO_2– ThO_2 in BeO have previously been prepared in these laboratories for irradiation testing using hot pressing as the fabrication method (Reeve and Ramm 1960). The disadvantages were:

(i) The particles were highly unequiaxed, and tended to chip to give undersize material during fabrication.

(ii) The preparation of the particles involved successive hot pressing of undersize material, with an undesirable increase in carbon contamination from the hot-pressing die.

(iii) The particles tended to lie in layers with their long axes perpendicular to the hot-pressing direction.

(iv) Hot pressing may not be a favoured production method, at least in small sizes.

The aim of the present work was to develop a method which would allow fabrication of more satisfactory BeO–$(U,Th)O_2$ dispersions by using near-spherical particles (Reeve and Jones 1963) and fabricating by cold-pressing and sintering. The report describes sintering studies on dispersi and the properties of sintered material. It includes discussion on the mechanism of sintering of tw phase fuel dispersions, and on the relation of this work to fuel element fabrication on a larger scal

2. SINTERING STUDIES

2.1 Dense UO_2–ThO_2 Particles in BeO

Dense spheroidal particles of UO_2–ThO_2 were assumed to be the most satisfactory starting material. Particles prepared by the method of Reeve and Jones (1963) were sintered in hydrogen at 1700°C to 95 – 97 per cent. theoretical density (Figure 1). Brush UOX BeO powder (lot 564) was "homogenised" before use by ball-milling in alcohol with alumina cylinders. This treatment was known to introduce between 0.5 and 1.0 per cent. of fine alumina into the BeO. Sintered UO_2–ThO particles were added to the dried powder at 5, 15, and 30 volume per cent. concentrations and the d persion was then mixed by hand as an 80 per cent. acetone – 20 per cent. water slurry until suffici of the acetone had evaporated to give a non-slumping material. The mixture was lightly crushed into 1/4 inch to 1/8 inch pieces to avoid release and subsequent segregation of fuel particles. Th material was then pre-formed to cylindrical shape in a 12 mm diameter steel die and hydrostaticall pressed in rubber tubes at 20 tons/in^2. Sintering was carried out in dry hydrogen at 1500°C to 1600°C, which was found to be the optimum range for sintering similarly treated but unfuelled UOX BeO. The maximum temperature was held for two hours.

Metallographic examination of sintered specimens revealed extensive porosity around partic irrespective of the volume percentage of UO_2–ThO_2 particles added (Figure 2). That these cavitie were not polishing artefacts was shown by the "glazed" appearance of the surface of cavities and their rounded edges; they thus appeared to have formed owing to shrinkage during sintering. Many sintered specimens were cracked on removal from the furnace and metallographic examination show that cracks in these specimens were most pronounced in areas of clumped particles, where voids associated with particles tended to link to form cracks. The cracks were most severe in the $30^{v}/o$ dispersions where the tendency to clump was most marked. In $5^{v}/o$ dispersions, particles were muc more widely spaced and although some voids formed around particles, cracking was rarely seen.

Macro-examination of as-sintered surfaces showed a very uneven texture, with fuel particles raised above the level of the BeO (Figure 3). Cracks had formed in the BeO surrounding the outer fuel particles, giving the impression that a "skin" of BeO had cracked during shrinkage over the particles.

The possible explanations of these effects were:

(i) mismatched shrinkage of particle and matrix during sintering,

(ii) non–uniform pressed density of the matrix in the vicinity of clumps of fuel particles, or

(iii) use of a sintering rate too high to allow the BeO to shrink uniformly around the particles.

Mismatched shrinkage was considered to be the main factor, although the three mechan be somewhat inter–related.

To test the effect of pressure, a lubricant (1/2^{w}/o stearic acid in chloroform) was adde powder before pressing, and lower pressures (5 and 10 tons/in^2) were used, in an attempt to r possible as–pressed density variations in the BeO. No improvement resulted. However some ment was obtained by pre–compacting the BeO powder at 20 tons/in^2 and granulating to –100 before mixing the fuel particles; this was presumably due to improvement in packing propertie powder, but extensive void formation still occurred on sintering. To test the effect of sinteri the time of rise to maximum temperature was increased from 4 hours to 7 hours; no significant ment was observed. Hence mismatched shrinkage between matrix and particles appeared to b main cause of the observed void and crack formation.

2.2 Unsintered Particles in BeO

Experiments showed that the shrinkage during sintering of UO$_2$–ThO$_2$ and of BeO com when hydrostatically pressed at 20 tons/in^2 and sintered at 1630 °C in H$_2$ was about 15 linea cent. in each case, suggesting that unsintered UO$_2$–ThO$_2$ fuel particles in BeO could be "co with the BeO to minimise void formation and cracking in the dispersion. The sintering temper 1630 °C in hydrogen was chosen to fall between the optimum sintering temperatures of the two (1500 – 1600 °C for UOX BeO, and approximately 1700 °C for UO$_2$–ThO$_2$).

Careful mixing of the unsintered fuel particles with BeO by hand in an alcohol slurry in negligible fragmentation. The slurry was dried under an infra–red lamp, lightly broken up Section 2.1), pre–formed in a 12 mm diameter steel die, hydrostatically pressed at 20 tons/in^2 sintered at 1630 °C in hydrogen for two hours.

Sintered specimens of 5 – 30 ^{v}/o dispersions showed no macroscopic cracking; the bu densities were in the range 98.0 ± 0.5 per cent. of theoretical as measured by a water displac technique. Examples of the macro– and micro– structure are shown in Figures 4 and 5.

Figure 4 shows that the distribution of fuel particles was not ideal, but was quite sat considering the limitations of the mixing method. Particle shape ranged from almost perfect s to elongated spheroids whose size was substantially in the preferred range 150 – 200 μ diame There was little evidence of particle fragmentation but some particles had broken into approx equal halves during fabrication.

Figure 5 shows that there was good particle–to–matrix contact and complete absence large voids observed when sintered particles were used.

The BeO microstructure consisted of large unequiaxed crystallites of size up to 100 μ by 20 – 30 μ wide. Twinning was common. This type of structure is known to occur in BeO Al$_2$O$_3$ or other impurities (Aitken 1961), and its occurrence in this case was assumed to be du Al$_2$O$_3$ pickup, amounting to about 1 per cent., during ball–milling. The UO$_2$–ThO$_2$ structure considerable inter– and some intra–granular porosity and a variable grain size in the range 10

For maximum irradiation stability and minimum fission product release from a fuel mat the BeO should be dense with no open porosity and fine (< 5μ) grain size, while the UO$_2$–T should be dense with no open porosity. It is apparent that neither condition was achieved in material shown in Figure 4. This is an example of an inherent disadvantage of co–sintering, one particular sintering condition, not necessarily the optimum for both phases, must be chosen. In this case, the conditions caused grain growth in the BeO while not allowing elimination of grain boundary (and open) porosity in the UO_2–ThO_2. If co-sintering is to achieve the optimum structure in both phases, the surface properties of the two powders should be adjusted, for example by calcination, fine grinding, or use of additives before sintering, so that a particular sintering temperature an time is the optimum for both phases.

2.3 Partly Sintered Particles in BeO

The use of particles partly sintered under conditions which impart some mechanical strength with very little densification would offer a possible solution to problems of mechanical mixing of the two phases, and should allow uniform sintering shrinkage as with unsintered particles. The inherent disadvantage of co-sintered particles in the choice of one optimum sintering condition for both phases would however still be present.

This possibility was not explored in detail in the present work.

2.4 Improved Uniformity of Dispersion

The dispersion obtained by mechanical mixing of fuel particles in the beryllia tends to conta some particles in near contact; in a dilute fuel, this may not significantly affect fuel lifetime or integrity but the minimum number of particle near-approaches in a concentrated fuel would be most desirable.

In a preliminary investigation of one particular method of achieving this, unsintered UO_2–Th particles were coated with a porous layer of UOX BeO by shaking the particles for up to 30 minutes loose BeO powder in a plastic phial. The equipment used was a flask shaker operating at 22 cycles with an amplitude of two inches. The thickness of the porous coating obtained varied from particle t particle between $30\,\mu$ and $100\,\mu$, as measured by the increase in particle diameter. The coated but unsintered particles were then dry-mixed with BeO, hydrostatically pressed at 20 tons/in², and sintered at 1630 °C in hydrogen for 2 hours. Dry mixing, found to be unsatisfactory for dispersing uncoated particles in BeO, owing to considerable settling-out of the denser particles from the BeO, was satisfactory here since the overall bulk density of the thickly coated particles was quite low.

Some of the coated particles were sintered in hydrogen at 1625 °C and polished to show coatin thickness and structure. Figure 6 shows such particles and Figure 7 shows a sintered dispersion of 15 volume per cent. UO_2–ThO_2 in BeO made using unsintered UO_2–ThO_2 particles with porous BeO coatings. No crack or void formation occurred in the dispersion and the coatings merged into the ma to become indistinguishable from it. However the technique had the desired effect of reducing the nu of particle-to-particle contacts, as can be seen by comparing Figures 4 and 7, and is considered a p ising method of achieving this more uniform structure. Similar results for alumina and graphite matri dispersions of coated UO_2 particles have been described by Smalley and others (1962).

2.5 Uniformity of Particles

X-ray diffraction and X-ray microanalyser studies of similar co-sintered specimens (Reeve and Jones 1963) showed that the UO_2:ThO_2 ratio did not vary significantly between particles; the UO_2 and ThO_2 were present almost entirely as a solid solution which was of variable composition presumably owing to incompleteness of inter-diffusion in the time allowed during sintering. The uniformity and degree of solid solution were considered satisfactory in the present investigation of sintering methods, and probably would be satisfactory for fuel element service. The degree of solid solution would be slightly increased if fully sintered particles were used, as they would be heat treated again during sintering of the dispersion. Significant improvement in co-sintered structures could be obtained by increasing the intimacy of the original UO_2–ThO_2 mixture, for example, by using a co-precipitation method for UO_2–ThO_2 preparation. Other means such as sintering at highe temperatures and for longer times would almost certainly lead to undesirable grain growth in the BeO

3. DISCUSSION

The void formation which occurs during sintering of dispersions in BeO of fully sintered particles of UO_2–ThO_2 is almost certainly related to the mismatched shrinkage between fuel pa and matrix. When shrinkages are matched by using unsintered particles the whole body shrinks uniformly, the fuel particles behaving as if they were holes in the BeO.

As a basis for discussion, two possible mechanisms (A and B) for void formation in dispe of sintered UO_2–ThO_2 particles in BeO are proposed. In mechanism A, variations are assumed pressed density in the body such that the density is lower in the areas between closely spaced icles. In these areas, large unstable pores, which tend to grow outwards, can be formed by the ism discussed by Coble (1959). The criterion for the formation of growing pores is that the rati their diameter to the surrounding grain size exceeds a critical value. A characteristic of such u pores is the convex inward curvature of their surfaces. In mechanism B, surface and interfacial considerations are assumed to decide the form of the BeO–$(U,Th)O_2$ interface and it is suggeste the BeO–$(U,Th)O_2$ interfacial energy is unfavourably high.

The stages in development of porosity expected from each mechanism are shown in Figu In mechanism A an unstable pore commences to grow from a point midway between two closely s particles until it reaches the particles. In B, surface energy considerations dictate that the Be UO_2 surfaces separate to form lens-shaped pores. If such pores form around two closely space particles they may grow to the final configuration shown for mechanism B.

An examination of Figure 2 and other polished sections provided no evidence of any of t stages visualised for mechanism A. On the other hand Figure 2 shows structures very like the result for B, and many examples of the second stage, that is, lens-shaped pores, could be foun even around apparently isolated particles.

It is concluded therefore that the interfacial energy between presintered UO_2–ThO_2 and is unfavourably high, and this brings about separation of the two phases during sintering; if uni sintering of both phases can occur, for example, by the use of unsintered particles, the interfac contact area is reduced during sintering, and free energy requirements are satisfied without voi formation.

The contact angle ϕ between the two phases at each end of the lens-shaped voids in Fi approximates 180°, that is, the tangent to the curved BeO surface at the point of contact is coi with the particle surface. The interfacial energy may therefore be estimated using the equation

$$\gamma_{s(U,Th)O_2} = \gamma_{BeO-(U,Th)O_2} + \gamma_{s(BeO)} \cos \phi \quad .$$

Surface energies of UO_2, ThO_2, and BeO at 0°C were estimated by Livey and Murray (1956) as 530, and 1420 ergs/cm² respectively. Taking a value of 600 ergs/cm² for $(U,Th)O_2$ and assumin temperature coefficient of −0.1 ergs/cm²/°C in each case (Livey and Murray 1956), then for 16

$$\begin{aligned}\gamma_{BeO-(U,Th)O_2} &= (410 - 1230 \cos 180)\text{ergs/cm}^2 \\ &= 1640\ \text{ergs/cm}^2 \ .\end{aligned}$$

This estimated value of interfacial energy is not necessarily the equilibrium value, sinc times used in sintering were relatively short. The high figure obtained in this way however tenc confirm a previous report (Reeve and Murray 1959) that no solid state reactions or solid solution occur between BeO and $(U,Th)O_2$ phases; such reactions would tend to lower the interfacial en and cause "wetting", which is not observed.

If this value of interfacial energy is applicable to sintered structures, there will be littl bonding between fuel and matrix even where there is no actual gap, and therefore the fuel partic will not contribute to the strength of the body. Any reduction of interfacial energy, for example means of an additive, should result in higher strength in the dispersion. These points will be s in more detail.

4. FUEL ELEMENT FABRICATION METHODS

The work discussed above has shown that "co-sintering" of BeO-$(U,Th)O_2$ dispersions, hydrostatically pressed without binder, is a satisfactory method of producing dense, crack-free structures. It necessitates individual fabrication of each specimen and is ideal where small numbe of specimens of differing compositions are required, for example, for irradiation testing. The use fully sintered particles under these conditions is likely to cause void and crack formation.

Since fuel material prepared by this method has behaved well under irradiation (B.S. Hickm private communication), it is worth while examining how the method would have to be modified for fabrication of large numbers of fuel element shapes of identical composition.

Fuel element shapes would probably be fabricated either by cold-pressing and sintering o by extrusion and sintering. In the first process, an intimately mixed binder and lubricant would be necessary to allow for automatic pressing and handling, and in the second, a plasticiser would be added to the powder prior to extrusion. In both processes, the mechanical action required to mix the powders and binders may cause fragmentation of unsintered particles; during extrusion, high shear stresses on unsintered particles may also tend to cause fragmentation. The method describe in this report is therefore not immediately applicable to the fabrication of fuel element shapes by these large scale processes.

The following relevant conclusions may however, be drawn from the present work:

(i) Matching of particle and matrix shrinkages as closely as possible is likely to be beneficial; wide mismatching may result in voids and cracks. If sintered particles cause cracking, the use of partly sintered particles may be an advantage.

(ii) When shrinkages are mismatched, less severe problems should be experienced in dilute dispersions (for example, those of less than 15 volume per cent. fuel) than in concentrated dispersions. Uniform distribution of the fuel phase is also an advantage in preventing cracking.

(iii) Uniform green density may be an advantage in minimising the risk of formation of "growing voids". The highly plastic mix used in extrusion may be beneficial in this respect.

(iv) The use of fully sintered particles may be allowable where impurities or additives are present in either the BeO or fuel phase, and where these decrease the BeO-$(U,Th)O_2$ interfacial energy or allow more rapid achievement of equilibrium interfacial energy conditions during sintering.

(v) Where fully sintered particles are used, even if cracking and void formation can be avoided, the surfaces of sintered dispersions will probably contain fuel particles raised above the BeO matrix level. The smaller the mismatching the smaller will be this difference in levels.

5. SUMMARY

(i) Dispersions of dense $150\,\mu$ $(U,Th)O_2$ particles hydrostatically pressed and sintered in UOX BeO without binder showed extensive void and crack formation, particularly at 15 and 30 volume per cent. levels of addition.

(ii) Dispersions of unsintered spheroidal UO_2-ThO_2 particles in UOX BeO were cold pressed and "co-sintered" to high densities without evidence of void formation.

(iii) Improved uniformity of dispersion of $150\,\mu$ particles in BeO was obtained by coating unsintered particles with porous BeO prior to fabrication.

(iv) Evidence is presented to show that void formation occurs in dispersions of dense $(U,Th)O_2$ particles in BeO owing to a high interfacial energy, which may be as high as 1640 $ergs/cm^2$.

(v) The apparently high interfacial energy supports an earlier report (Reeve and Murray 1959) of the absence of solid state reactions between BeO and $(U,Th)O_2$.

(vi) If co-sintering is used, properties of the BeO and UO_2–ThO_2 powders should be adjusted so that under the chosen sintering conditions the required density and grain size is obtained in each phase.

(vii) Use of fully sintered particles may be allowable under certain conditions, for example in dilute dispersions, or where interfacial energy is reduced owing to the presence of impurities.

6. ACKNOWLEDGMENTS

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7. REFERENCES

Aitken, E.A. (1961). – J. Nuclear Materials 3 : 302.

Coble, R.L. (1959). – Kinetics of High Temperature Processes, p.147, Wiley.

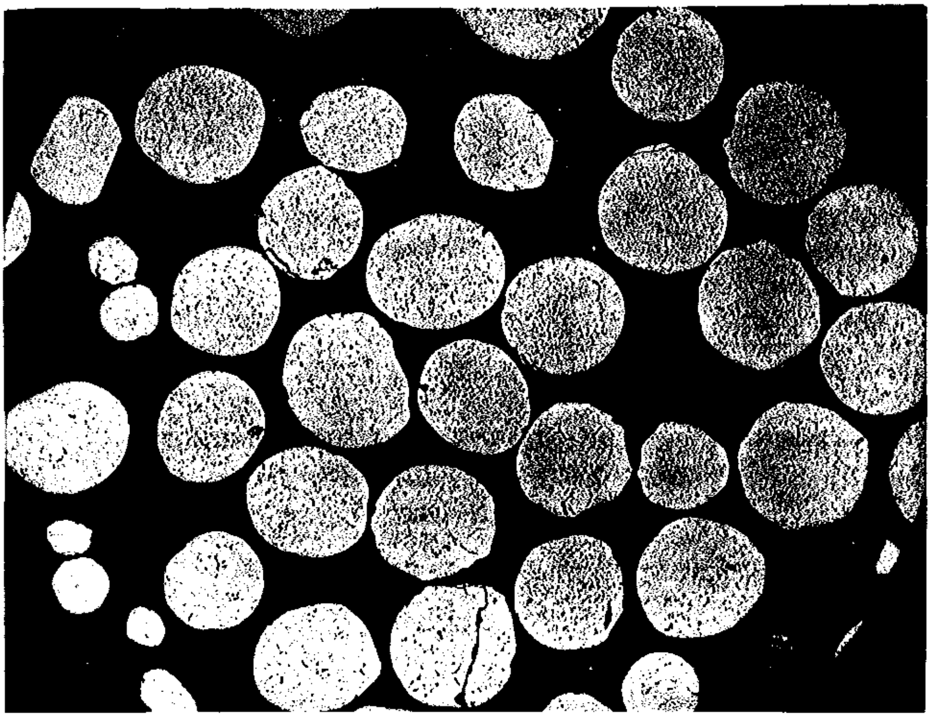
Livey, D.T., and Murray, P. (1956). – AERE M/R 1846.

Reeve, K.D., and Jones, K.A. (1963). – AAEC/E 104.

Reeve, K.D., and Murray, P. (1959). – Trans. Brit. Ceram. Soc., 58 : 387.

Reeve, K.D., and Ramm, E.J. (1960). – AAEC/TM 51.

Smalley, A.K., Brockway, M.C., and Duckworth, W.H.(1962). – BMI–1579.



X 100

FIGURE 1 SINTERED UO_2 - ThO_2 PARTICLES

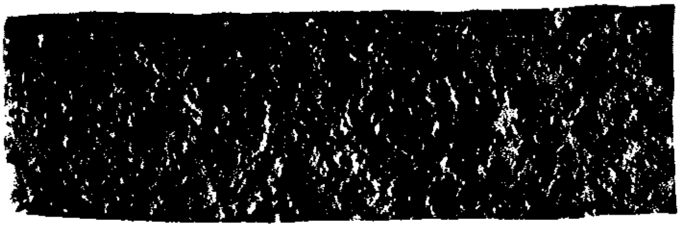
X 100

(a) 15 $^{v}/o$

X

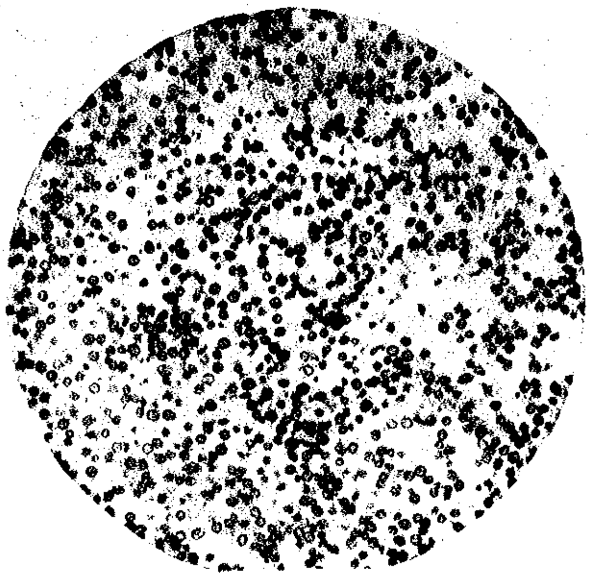
(b) 15 $^{v}/o$

FIGURE 2 SINTERED DISPERSIONS OF SINTERED $UO_2 - ThO_2$ PARTICLES IN BeO



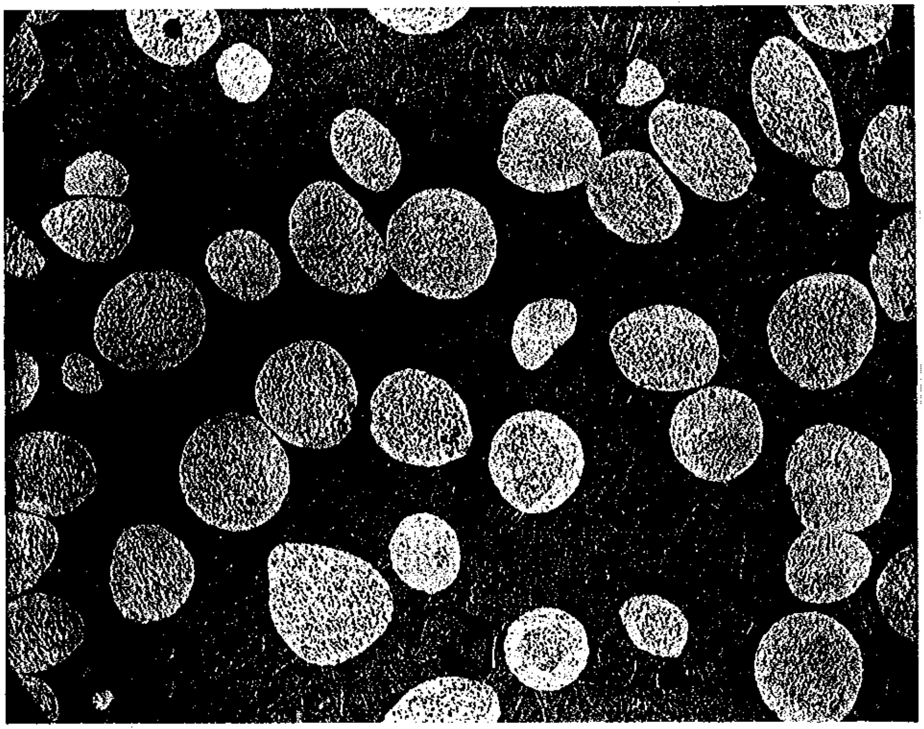
X7.5

FIGURE 3 SURFACE OF SINTERED DISPERSION OF DENSE $UO_2 - ThO_2$ PARTICLES IN BeO (15 $^{v}/o$)



X7.5

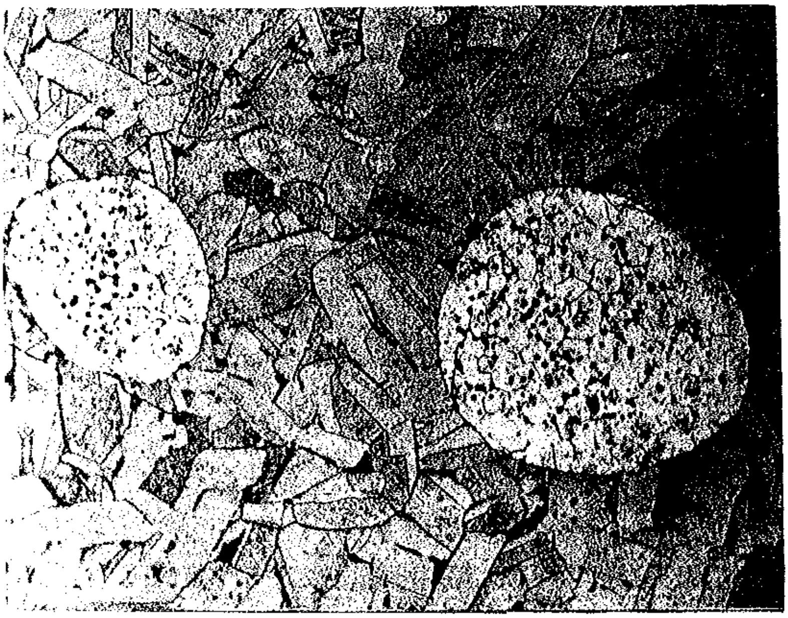
(a) 15 v/o



X 100

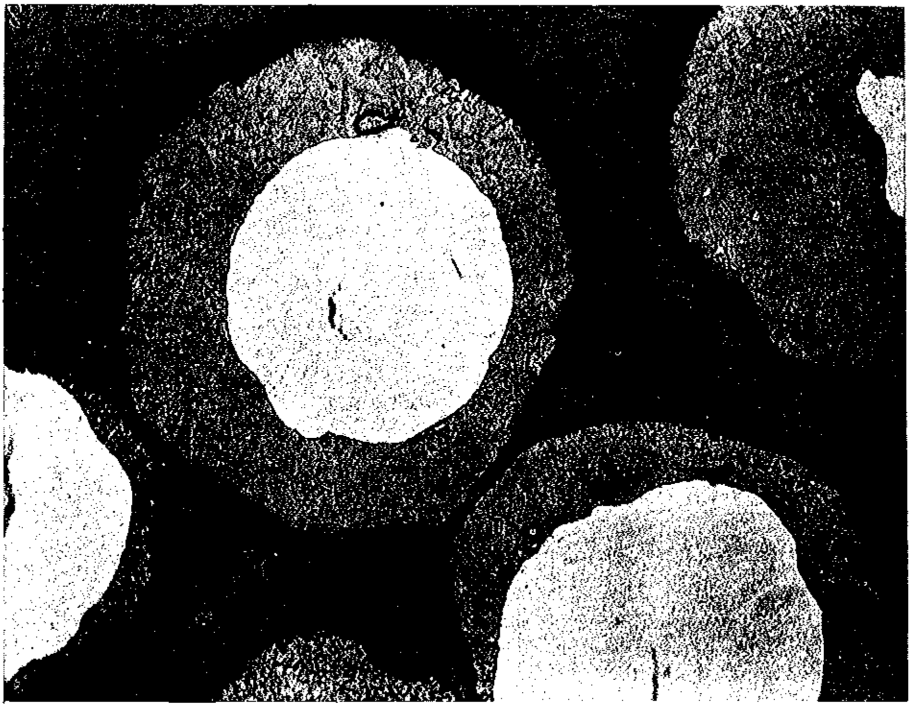
(b) 15 v/o

FIGURE 4 SINTERED DISPERSIONS OF UNSINTERED $UO_2 - ThO_2$ PARTICLES IN BeO



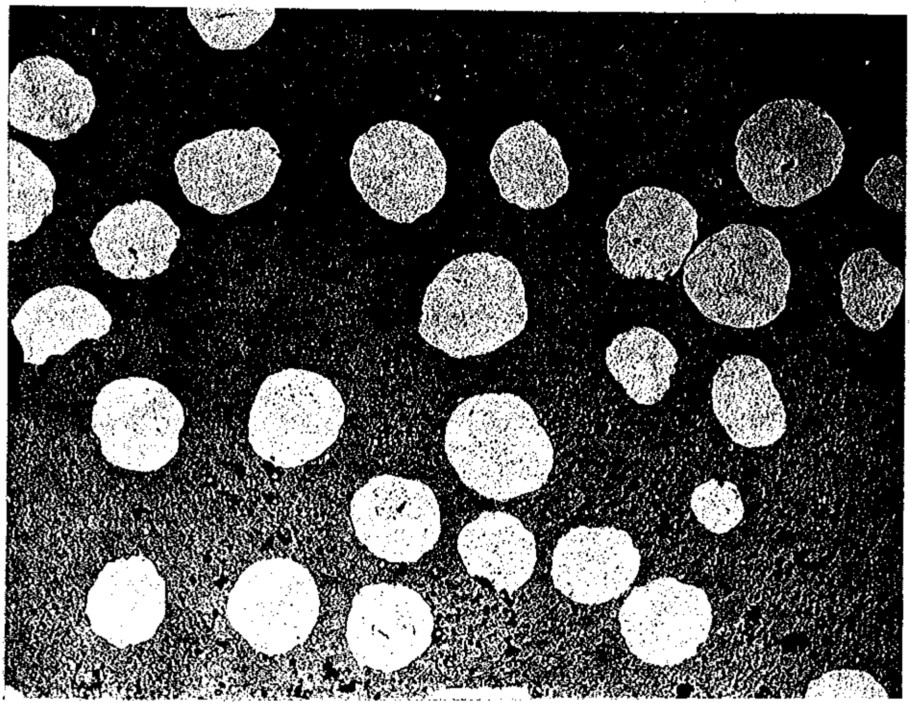
Etched, X 250

FIGURE 5 SINTERED DISPERSION OF UNSINTERED $UO_2 - ThO_2$ PARTICLES IN BeO



X 250

FIGURE 6 $UO_2 - ThO_2$ PARTICLES WITH SINTERED BeO COATINGS



15 $^{v}/_{o}$ X 75

FIGURE 7 SINTERED DISPERSION USING BeO-COATED $UO_2 - ThO_2$ PARTICLES

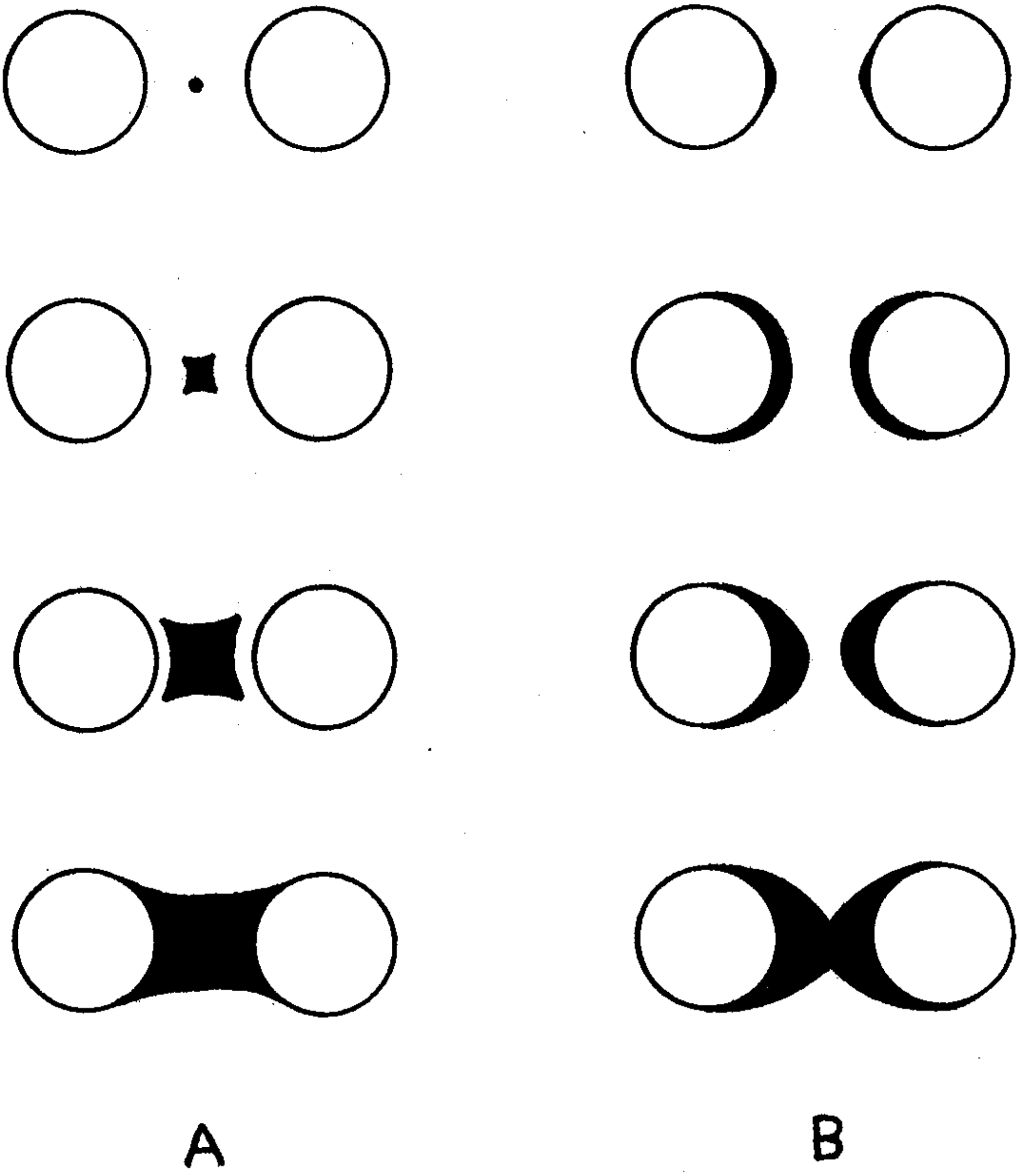


FIGURE 8 STAGES OF VOID FORMATION BY TWO HYPOTHETICAL MECHANISMS