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RESEARCH ESTABLISHMENT

LUCAS HEIGHTS

THE PREPARATION OF SPHEROIDAL $UO_2 - ThO_2$ PARTICLES

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ABSTRACT

A self–abradory process is described for the small–scale preparation of 150 – 200 micron spheroidal particles of various UO_2– ThO_2 compositions. The particles can be sintered to high densities before or after dispersion in beryllium oxide. Because of the high compaction pressure used in making particles, they are strong enough to resist abrasion and crushing during mixing with beryllium oxide powder.

After sintering, the particles consist of a $(U,Th)O_2$ solid solution with a small range of composition, but the overall composition does not vary from one particle to another.

The types of porosity observed after sintering are consistent with the occurrence of two competitive mechanisms during spheroidisation, namely particle abrasion and particle build–up.

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1. INTRODUCTION

In a fuel element of the dispersion type, fissile or fissile–fertile material is dispersed in a non–fissile matrix in the form of small, usually dense, particles. Ideally, the fuel particles should be spherical because:

(a) Fission product recoil from a dense particle with attendant matrix damage is proportional to surface area; hence the ideal shape has minimum surface–to–volume ratio, that is, spherical.

(b) Non–equiaxed particles, particularly those with sharp edges and corners, are more likely to fragment into undersized particles during fabrication (see Figure 1).

(c) Non–equiaxed particles can orient themselves with respect to a preferred fabrication direction in processes such as hot–pressing, unidirectional cold–pressing, and extrusion (see Figure 1), and this can lead to anisotropic strength properties in the fuel.

(d) If it becomes necessary to coat individual particles with a layer of fission–product retaining material, this can be achieved more readily with spherical particles. Sharp edges and corners on a particle would make a uniform coating difficult to achieve and would be stress–raisers in the coating.

Particles in the required size range can be produced either by crushing and screening of hot–pressed material to give dense particles, or by crushing and screening of cold–pressed material to yield "green" particles. Green particles may be made dense by processes such as sintering or flash fusion in a plasma jet.

The hot–pressing route has the disadvantages that it is difficult to recycle dense undersize material and still retain an acceptable hot–pressed density, and also that carbon contamination increases as undersize material is reprocessed.

In the present work, 150–200μ particles of $UO_2 - ThO_2$ were produced by crushing, screening, and sintering of cold–pressed material. Particles were required in three different compositions, 25, 50, and 75 molar per cent. UO_2, for incorporation in $BeO–UO_2–ThO_2$ irradiation test specimens. At the outset it was considered that equiaxed but not necessarily spheroidal particles would be adequate for this application, since the relative surface–to–volume ratio, which determines the amount of fission–product recoil producing damage in the matrix, is higher by a factor of only 1.24 for a cube than for an equivalent sphere. However, as it proved possible to produce almost perfect spheres of uniform size by a self–abradory process on screened particles, it was decided to develop the spheroidising process for use in the fabrication of the irradiation test specimens. Since all compositions were finally to contain highly enriched UO_2 but only in small quantities, the developmental work was carried out on a small scale.

Concurrently with this work, similar methods for the production of dense uranium oxide spheroids were developed by Williams (1961) and Hamner and Taylor (1962).

2. METHOD

2.1 Process

The process developed consists of the following steps: mixing of UO_2 and ThO_2 powders; hydrostatic pressing of the mixture; crushing of pressed compacts, and sieving to yield particles of a suitable size range for spheroidising; spheroidising by shaking in an alumina crucible, during which self–abrasion produces rounding of edges and corners; and sintering in hydrogen if required.

Further details of the process follow:

2.2 Mixing

UO_2 powder (Springfields stabilised) and ThO_2 powder (calcined from thorium oxalate at 900 °C), both screened to minus 300 mesh, are ground together dry for 20 – 28 hours in a polythene jar using

alumina grinding cylinders. This mixing operation breaks up aggregates of UO_2 and ThO_2 and redisperses individual UO_2 and ThO_2 particles to give a fine and uniform mixture. The degree of mixing is considered satisfactory if no particles of UO_2 and ThO_2 of more than 10μ in diameter can be distinguished at a magnification of 100, and if the great majority of particles are less than 5μ in diameter. This ensures that the aggregates of up to 40μ diameter initially present have been broken up, and that the required $150 - 200\mu$ diameter particles will consist of a random mixture of $< 10\mu$ UO_2 and ThO_2 particles and will have the same composition in each particle.

Longer times (24 – 28 hours) are needed in UO_2–rich than in ThO_2–rich compositions (20 – 24 hours), owing to the greater difficulty in breaking up UO_2 aggregates.

2.3 Cold–Pressing

Pellets 1 inch dia. x 1 inch long are pre–formed in a steel die, without binder, to a high enough bulk density to give handling strength. These are then placed in a latex rubber tube closed at one end and de–aired using a water pump. After sealing the open end, the contained pellets are hydrostatically pressed at 20 t.s.i. in glycerine. A pressure of 20 t.s.i. was chosen on the basis of sintering experiments on cold–pressed cylinders of $UO_2 - ThO_2$ mixtures, as these indicated that 20 t.s.i. was necessary for attainment of the required density of 98 per cent. of theoretical.

2.4 Crushing and Grinding

The pressed pellets are crushed carefully by a stepwise process using a hardened steel die as a percussion mortar. Frequent collection (by sieving) of the required size fraction is necessary to avoid production of an excess of undersize material. The process is continued until the whole pellet is reduced to the required size fraction or smaller. The fines are re–pressed and recycled without difficulty. The particles produced from this process are angular but are approximately equiaxed.

The optimum size fraction of angular particles at this stage is that which, allowing for subsequent reduction in size during spheroidising and sintering, will give a maximum yield of sintered $150 - 200\mu$ spheroidal particles. The sintering shrinkage of 16 – 18 per cent. requires a size range of spheroidal particles before sintering of $180 - 244\mu$ or approximately 60 – 85 mesh B.S.S. ($178 - 251\mu$). Since it was found that the 60 – 85 mesh fraction of angular particles gave a better yield of 60 – 85 mesh spheroidised particles in a standard spheroidising operation than did the coarser 44 – 60 mesh fraction (see Table 1), 60 – 85 mesh was chosen as standard both before and after spheroidising. The yield of this required size fraction of angular particles in one crushing operation is about 26 weight per cent.

2.5 Spheroidising

Approximately 30 grams of 60 – 85 mesh angular particles are placed in a round–bottomed alumina crucible, size 2 inches high x 1 inch diameter, fitted with a rubber bung. The crucible is held in a vertical position on a Dynamax flask shaker in such a way that lateral oscillation of amplitude 1 inch at 22 cycles per second can be obtained. It is shaken for about 1½ hours, which is sufficient to produce a yield of 41–45 per cent. of spheroidal particles in the required size range. The spheroidal particles are separated by vigorous sieving.

Combining the yield of spheroidal particles per spheroidising operation, that is 41 – 45 per cent. with that of angular particles of the required size fraction from a pressed block, that is 26 per cent., a yield of spherical particles of 0.26 x (0.41 to 0.45) x 100, that is 10 – 12 per cent. is obtained in one straight–through cycle. This overall yield can be increased by reprocessing reject material, usually fines, from each step. Thus two complete cycles would yield 19 – 22 per cent. and so on.

2.6 Sintering

The fuel particles are sintered by filling small alumina crucibles to a depth of ⅜ inch and heating to 1700 °C for 2 hours in hydrogen. These conditions enable densities of 95 – 98 per cent. of theoretical to be achieved. After sintering, only very light crushing is necessary to break up loose aggregates.

Sintering shrinkage was determined from measurements of cylindrical $UO_2 - ThO_2$ compacts cold–pressed and sintered under the same conditions. Linear shrinkage was found to be 16 – 18 per cent. Therefore, on sintering, the 60 – 85 mesh ($178 - 251\mu$) fraction shrinks to the required range of $150 - 200\mu$.

Although at first it was assumed that sintering of particles to as high a density as possible would always be necessary, it was later found that spheroidised particles could be dispersed in BeO powder in the "green" state and the dispersion sintered in one step (Reeve and Jones, unpublished).

3. PROPERTIES

3.1 Macroexamination

Particles after spheroidising usually had a matte surface (Figure 2a) but those richer in UO_2 sometimes had a slightly polished appearance. After sintering, all particles had a smooth reflecting surface (Figure 2b). The colour varied from light green for UO_2/ThO_2 ratio of 1:3 to dark brown–black for a UO_2/ThO_2 ratio of 3:1. Shape throughout a batch was not always uniform, some particles appearing slightly elliptical while others were near–perfect spheres. This point is discussed again in Section 4.

3.2 Microexamination

Photomicrographs of polished sintered particles are shown in Figures 3, 4, and 5.

Figure 3 shows a sample of near–spherical particles from a very dense batch. The grain structure can just be detected in the as–polished condition owing to some residual grain–boundary porosity. Grain size measured on etched specimens was in the range 15 – 25μ, varying from particle to particle.

Figure 4a shows particles which were not of such uniformly high density and which showed two types of porosity. While all particles contained some very fine porosity, others showed large, often crescent–shaped, cavities occupying up to 10 per cent. of the cross–sectional area of the particle. Examination of a number of batches showed that these large cavities were more evident in the near–perfect spheres. This point is discussed further in Section 4. Figures 4a and 4b also show long rectangular shaped particles formed by flaking–off of the compacted layer built up on the walls of the spheroidising container. The sintered flakes are noticeably less porous than most of the sintered spheroidal particles.

3.3 Density

Densities of 98 per cent. of theoretical were achieved on cylindrical compacts of $UO_2 - ThO_2$ pressed and sintered under the same conditions as particles. Density measured on one batch of cavity–free sintered particles was 98.3 ± 0.3 per cent. Sintered particles containing cavities would have a much lower bulk density, although this was not measured.

3.4 Particle Integrity

Both green and sintered particles can be dry–mixed with BeO powder without significant abrasion or fragmentation. Green particles readily break up in contact with water, but are stable in alcohol which can be used satisfactorily in wet–mixing processes. Sintered particles can be wet–mixed with BeO using any convenient liquid. Mixtures of either green or sintered particles with BeO can also be hydrostatically compacted without significant abrasion or fragmentation (Reeve and Jones, unpublished).

The good mechanical strength of green particles is attributed to the high forming pressure, 20 t.s.i., used in making the initial $UO_2 - ThO_2$ compacts. This may be compared with 12 t.s.i. used by Williams (1961) and 7 t.s.i. by Hamner (1962).

3.5 Homogeneity of Fuel Particles

Typical particle batches of three different compositions (25, 50, and 75 per cent. UO_2) dispersed in the green state in BeO and sintered at 1625 °C for 2 hours in H_2, were examined for solid solution formation using an X–ray diffractometer (Cu Kα radiation).

In each case the (444) $(UTh)O_2$ reflection was scanned to cover the positions of possible separate UO_2 and ThO_2 reflections. Two traces are shown in Figure 6 and these have been marked to show where reflections from UO_2 and ThO_2 would appear. It can be seen that while the $(UTh)O_2$ line is very broad in each case, with evidence of splitting, no detectable UO_2 or ThO_2 peaks are present.

If it is assumed that the line broadening is mainly due to the existence of a wide range of solid solution composition in each case, the respective composition ranges calculated from the line widths without allowing for instrumental broadening (and which are therefore pessimistic estimates) are approximately 25 ± 12 per cent. UO_2, 50 ± 16 per cent. UO_2, and 75 ± 16 per cent. UO_2.

Similar particles of UO_2 : ThO_2 ratio 1 : 3 were examined using the X-ray microanalyser technique. The results obtained on 200μ diameter particles indicated that the mean composition varied little from particle to particle but that local variations did exist within particles. However at a resolution of 5 microns the composition within individual particles could be placed with confidence at within ± 5 per cent. for ThO_2 content.

The composition of 200μ particles can therefore be considered to be essentially constant.

4. DISCUSSION

Sintered particles show two types of porosity, the first fine and fairly evenly distributed, the second in the form of large concentric circumferential cavities. Some particles show both types (Figure 4a). The types of porosity bear close relationship to two particle shapes, the almost perfect spheres tending to contain the large cavities while the more angular or elliptical particles contain only evenly distributed porosity.

This effect was also pointed out by Williams (1961) who observed similar types of voids in UO_2 spheroids after sintering. He overcame the problem of the large voids by re-pressing green particles hydrostatically in rubber powder at 12 t.s.i. before sintering. He suggested that the large voids were due to a combination of grinding and sintering effects and were closely connected with the geometry of the particle.

Hamner and Taylor (1962) attributed Williams' large voids to the occurrence of a spheroidisation process competitive with that involving abrasion. In the competitive process, particles are built up from fine material produced during abrasion. Variations in "green" density in built-up particles then lead to non-uniform shrinkage with the formation of large internal voids. Hamner and Taylor eliminated particle build-up by continuous removal of fine material during the process. The photomicrographs in Figures 4 and 5 supply strong evidence for the operation of such a build-up mechanism in the present work. The built-up layers, exemplified by the outer skin of particles with large voids (Figure 5a) and by rectangular chips from a hard layer which builds up on the wall of the crucible during the process, sinter to a much lower porosity than does the material as originally pressed. This is presumably due to a higher "green" density in built-up layers, the high density being achieved by repeated impaction by other particles. The build-up process produces much more nearly spherical particles than does abrasion, as shown in Figures 5a and 5b particularly.

Additional evidence that particle build-up can occur by the method described here is obtained from the results given in Table 1. The 60-85 mesh fraction of angular particles, after a spheroidising treatment for 1½ hours, showed 13.0 per cent. of 44-60 mesh spheroidised particles, that is, 13.0 per cent. were larger than the starting material.

In the present work where the particles were to be used for preparation of $BeO-UO_2-ThO_2$ irradiation specimens, the cavity problem was overcome by dispersing green particles in BeO powder, and hydrostatically pressing and sintering the mixture. Metallographic examination of sintered dispersions showed no evidence of fissures in the fuel particles. (Reeve and Jones, unpublished).

The degree of solid solution attained at 1625°C after 2 hours in H_2, while surprisingly good, is still incomplete. Since solid solution formation occurs by a two-way process of diffusion of uranium ions into ThO_2 and thorium ions into UO_2, the homogeneity of solid solution can be improved, if required, by increasing the sintering temperature, increasing the sintering time, or by improving the intimacy of mixing in the original powder.

5. SUMMARY

(1) Near spherical particles of UO_2-ThO_2 in the composition range 25 - 75 per cent. UO_2 and size range 178 - 251μ diameter have been produced by cold-pressing blocks at 20 tons per square inch, crushing, collecting sized angular particles, and spheroidising the latter in a self-abradory process.

(2) The yield in one series of operations was 10 – 12 per cent.; this yield can be increased by recycling.

(3) Particles may be consolidated to 98 per cent. of theoretical density by sintering in H_2 for two hours at 1700 °C, when the size range reduces to 150 – 200μ.

(4) Sintered particles consist of (U, Th)O_2 solid solution and are effectively of the same overall composition although minor variations in composition exist within particles.

(5) Unsintered particles have sufficient strength to be mixed with BeO powder without crushing or abrasion.

(6) Some particles are spheroidised by a building up process from "fines"; large voids which occur in some of these particles on sintering are related to the non-uniform build-up of these particles during the spheroidising process.

(7) Voids do not form in particles if unsintered particles are mixed with BeO powder and cold pressed and sintered as a dispersion.

6. ACKNOWLEDGMENT

The authors wish to thank Dr. D.G. Walker and members of the Physical Metallurgy Group for the X-ray diffraction and X-ray microanalyser results, and for the metallography and photomicrography.

7. REFERENCES

Hamner, R.L. (1962). – Private Communication.

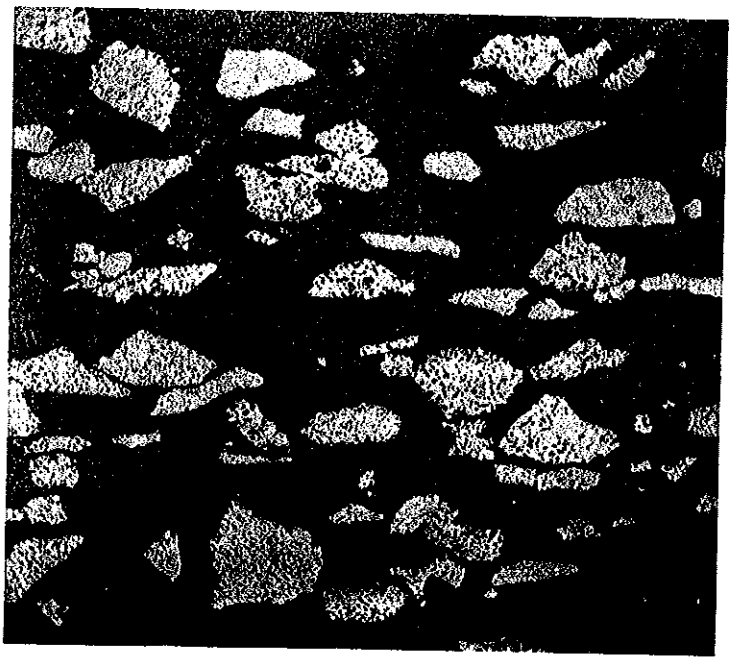
Hamner, R.L. and Taylor, A.J. (1962). – O.R.N.L. 3302, page 256.

Williams, N.R. (1961). – AERE-M888.

TABLE 1

INITIAL AND SPHEROIDISED SIZE FRACTIONS

Initial Size Fraction (mesh)	Per cent Spheroidised Particles in Various Size Fractions after 1½ Hours' Spheroidising Treatment
44 – 60	15.8 in –85 mesh 58.0 in 44 – 60 mesh 26.2 in 60 – 85 mesh
60 – 85	42.5 in –85 mesh 13.0 in 44 – 60 mesh 44.5 in 60 – 85 mesh

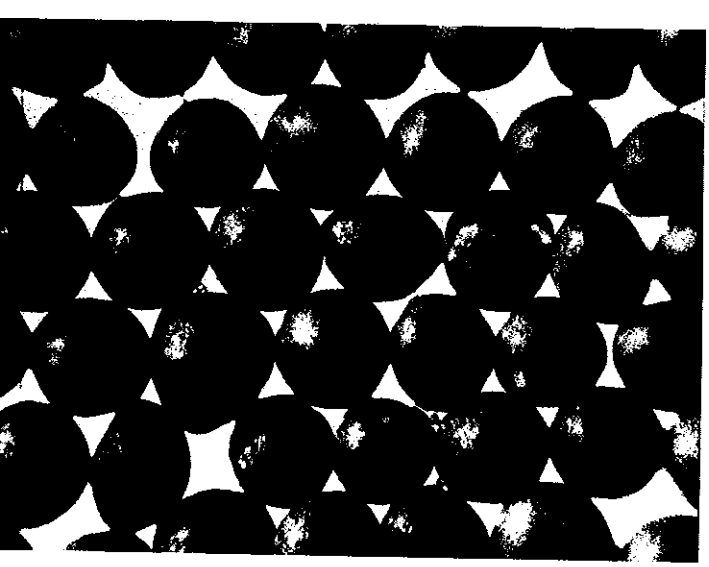


Hot pressing directio

x 100

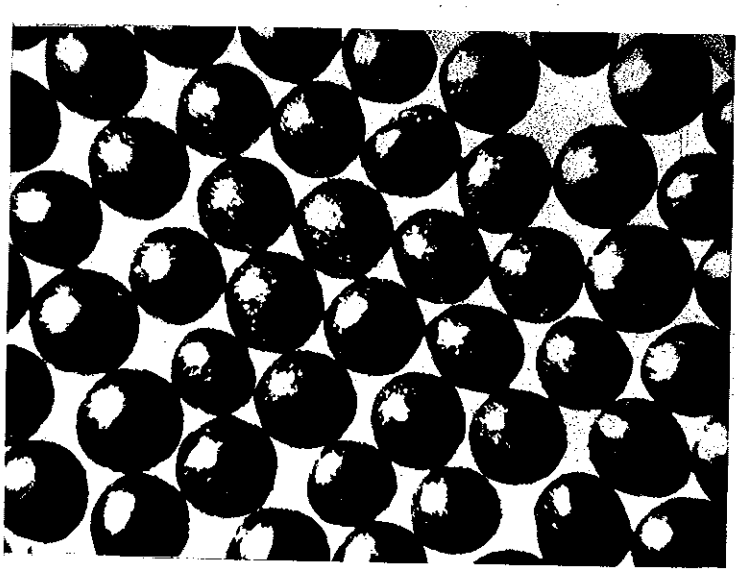
FIGURE 1 $UO_2 - ThO_2$ PARTICLES PREPARED BY HOT PRESSING; HOT PRESSED IN BeO :

Showing: Unequiaxed particles, particle fragmentation, and particle orientation during hot pressing.



x 75

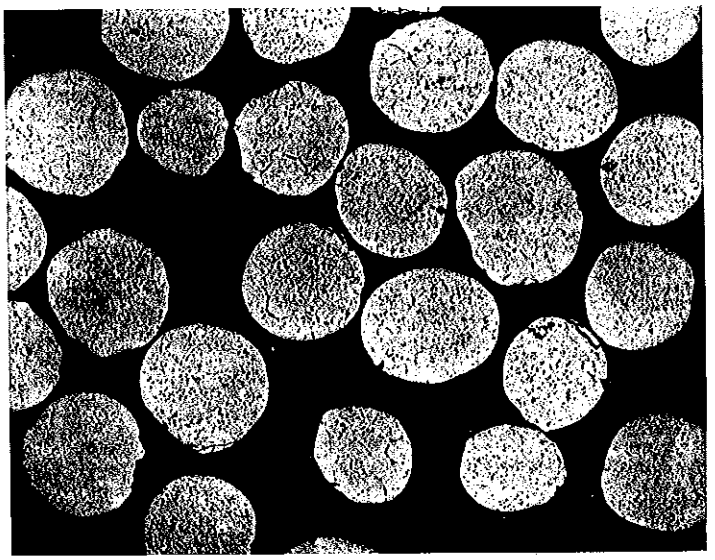
(a) UNSINTERED



x 75

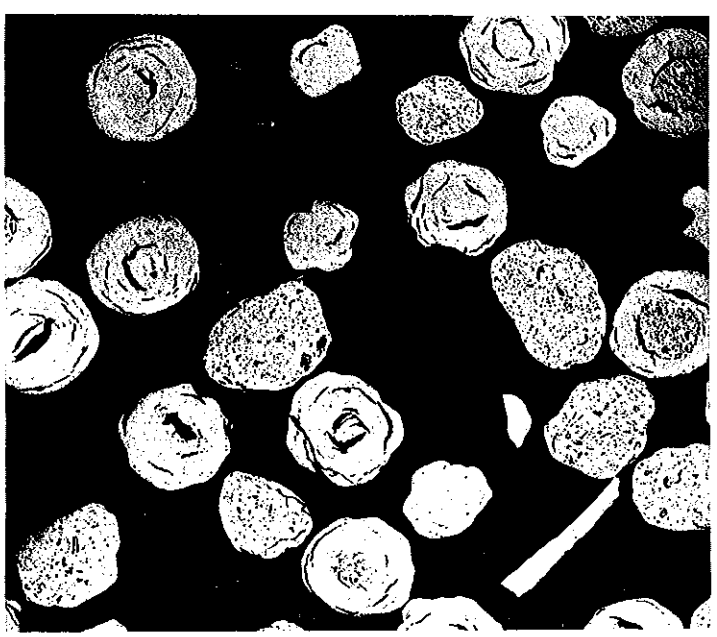
(b) SINTERED

FIGURE 2 $UO_2 - ThO_2$ PARTICLES



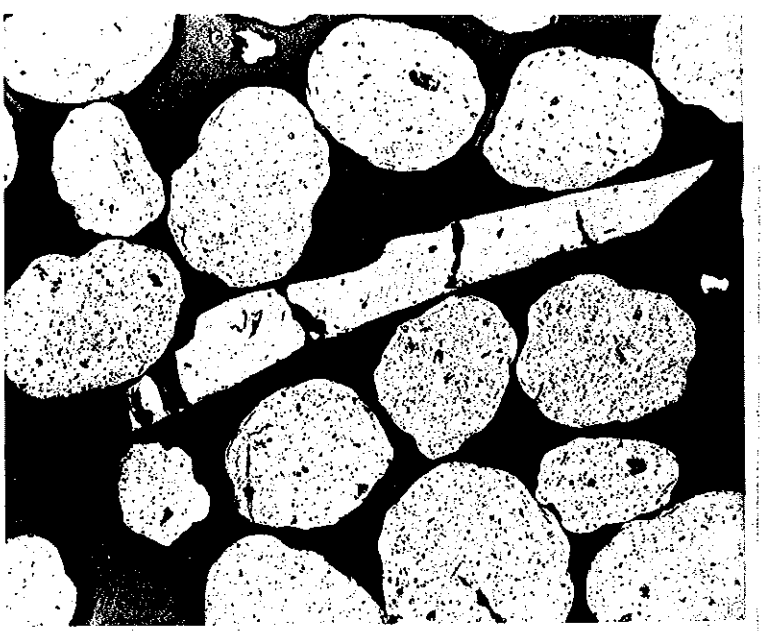
x 100

FIGURE 3 SINTERED $UO_2 - ThO_2$ PARTICLES



x 100

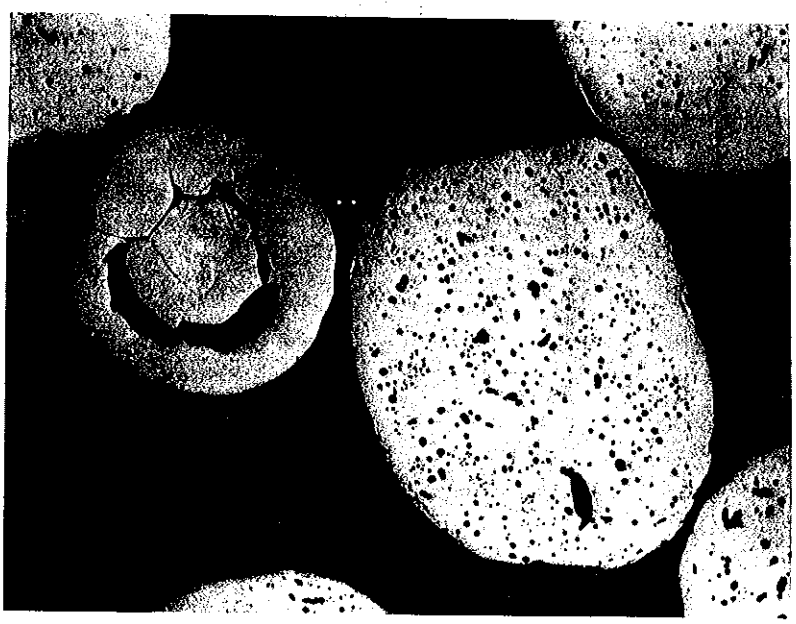
(a)



x 250

(b)

FIGURE 4 SINTERED $UO_2 - ThO_2$ PARTICLES SHOWING TYPES OF POROSITY



x 250

(a)

x 250

(b)

FIGURE 5 SINTERED $UO_2 - ThO_2$ PARTICLES SHOWING LARGE CIRCUMFERENTIAL VOIDS IN NEAR-SPHERICAL PARTICLES

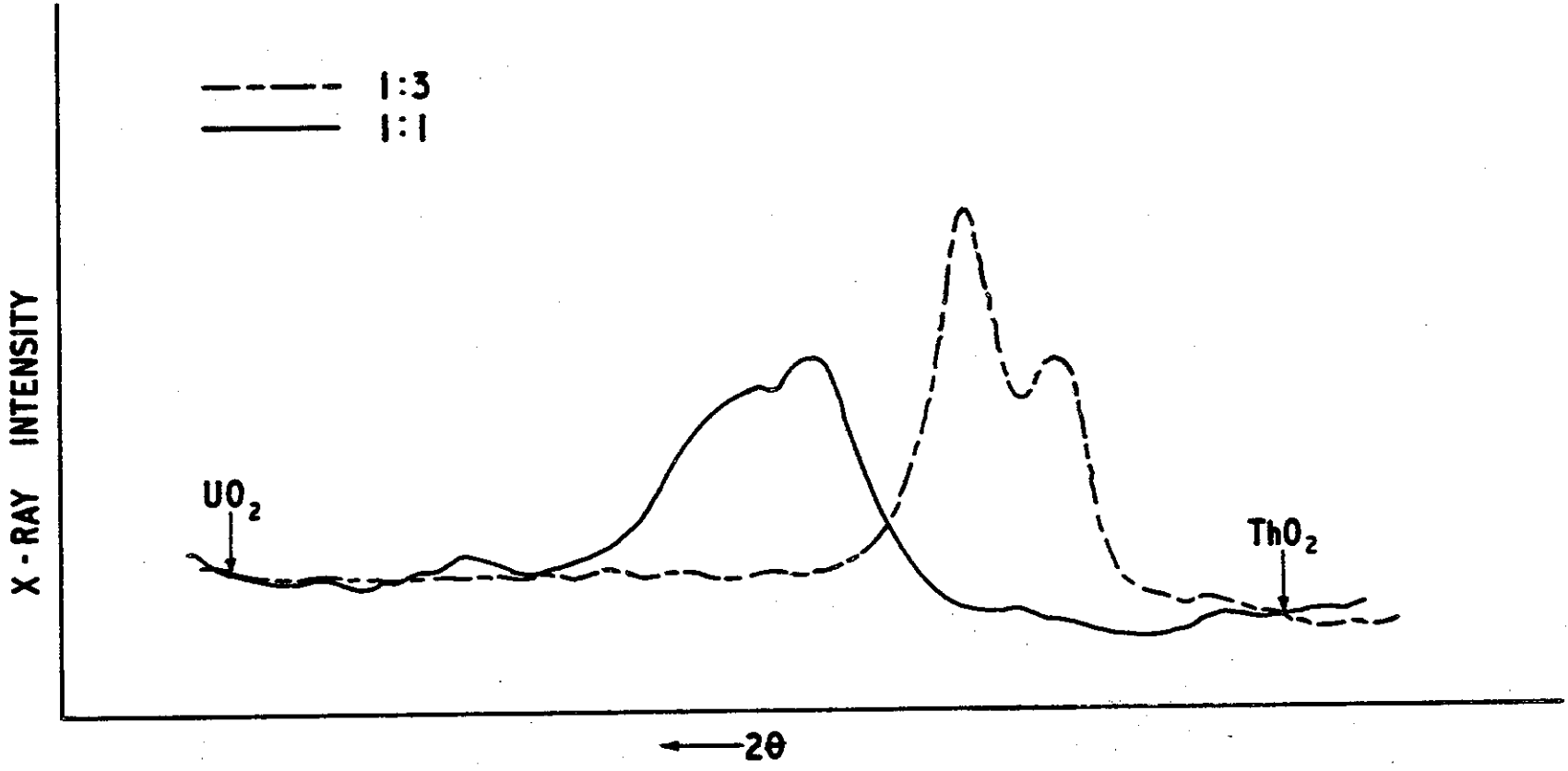


FIGURE 6.
DIFFRACTOMETER RECORDS OF SINTERED UO_2 - ThO_2 PARTICLES