

## Preparation of (U,Pu)O<sub>2</sub> pellets through sol–gel microsphere pelletization technique

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### Abstract

Mixed uranium–plutonium oxide microspheres were prepared by internal gelation process using feed solution of optimized composition. In the feed, total metal concentration was maintained at 1.5 M and hexamethylenetetramine (HMTA)-urea to metal mole ratio (*R*) was kept at 1.0. The gel particles obtained from each batch were dried and heated at 250 °C in air and then calcined in O<sub>2</sub> at 800 °C followed by reduction in 8%H<sub>2</sub>/92%N<sub>2</sub> at 600 °C for 1 h to obtain soft (U,Pu)O<sub>2</sub> microspheres containing 4 mol% Pu. The soft (U,Pu)O<sub>2</sub> microspheres were directly taken for the preparation of pellets. The microspheres were characterized with respect to surface area, tap density, crush strength and O/M ratio. X-ray diffraction analysis of the mixed oxide microspheres was carried out to identify the phases. The mixed oxide pellets were characterized for their density and micro-homogeneity. The sintering behaviour was studied by dilatometric investigations. The green pellets were sintered in 8%H<sub>2</sub>/92%N<sub>2</sub> at 1600 °C for 2 h. The density of the sintered pellet was found to be 10.40 ± 0.05 g/cm<sup>3</sup> with grains in the size range of 3–6 μm with an excellent micro-homogeneity.

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### 1. Introduction

As a consequence of the dismantling of many plutonium based nuclear devices, large amounts of plutonium became available for other applications. Uranium–plutonium mixed oxide pellets containing

plutonium up to 4 mol% is being considered as fuel for thermal reactors for its effective utilization in power production. Fabrication of the pellets of such fuel is usually made by the well established powder oxide pellet (POP) [1–11] route. However, the problems associated with handling of highly radiotoxic plutonium powders call for the development of a technique which would avoid handling of plutonium powders and the accompanying dose related problems. Sol–gel microsphere pelletization (SGMP) technique combines the advantages of

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sol–gel route, which is free from powder handling with an increased amenability to automation, with the proven technology of powder pellet route, thereby offering an excellent solution to these problems. The SGMP technique is particularly attractive for mixed oxide fuel because it gives a high degree of micro-homogeneity of uranium and plutonium in the solution stage. The prolonged ball-milling of oxide powders for achieving good micro-homogenization in the standard powder pellet route is unnecessary. The disuse of the powder mixing step prevents build-up of radioactive dust in the glove box, minimizing the dose related problems to the operating personnel. Gilissen et al. [12] reported the preference of gel-derived microspheres to powder as feed material for pellet pressing. They employed the external gelation process for the preparation of gel microspheres. But they could not obtain good quality sintered pellets. Zimmer et al. [13] and Ganguly et al. [14,15] have demonstrated the preparation of soft  $\text{UO}_2$  and  $(\text{U,Pu})\text{O}_2$  microspheres suitable for gel pelletization by addition of carbon black as pore former. However, the controlled calcination step with low heating rate, necessary for complete and safe removal of carbon, makes the process time consuming. It has been demonstrated by some investigators that by proper choice of process and heat treatment parameters the soft urania and mixed urania–plutonia microspheres suitable for gel pelletization could be prepared without the addition of pore former [16–20]. Mathews and Hart [16] and Tiegs et al. [17] have demonstrated the feasibility of making good quality  $\text{UO}_2$  pellets by gel pelletization from soft  $\text{UO}_2$  microspheres prepared by internal gelation process. They suggested the small  $\text{UO}_2$  microspheres of 50–400  $\mu\text{m}$  as suited for obtaining good quality pellets. However, their production process involves the use of small size capillaries (<0.5 mm) which tend to be clogged. Also the process needs longer time. Under these circumstances, Suryanarayana et al. [18–20] have studied the role of gelation parameters on the properties of  $\text{UO}_2$  microspheres relevant to pelletization and proposed a simplified process flow sheet for gel pelletization without using the step of carbon addition and its subsequent removal. Kumar et al. [21] explored the feasibility of this process for the preparation of soft  $(\text{U,Pu})\text{O}_2$  microspheres.

The present work deals with the extension of the process established for urania to mixed urania–plutonia. During this study the effect of key parameters such as temperature of gelation and

calcination temperature on the crush strength and tap density of the product microspheres was also studied. Both these parameters play an important role in deciding the  $l/d$  ratio ( $l$  = length;  $d$  = diameter of pellet) and final achievable density of the pellet.

## 2. Experimental

### 2.1. Preparation of uranyl nitrate solution

Nearly acid free 3 M uranyl nitrate solution was prepared by dissolving the calculated amount of nuclear grade  $\text{U}_3\text{O}_8$  powder in a deficient amount of concentrated  $\text{HNO}_3$  solution. The addition of the powder was controlled in such a manner that the temperature of the solution does not increase beyond 55 °C. The solution was analysed for uranium content by both gravimetry and volumetry. For gravimetric analysis, an aliquot of the sample solution containing 200–300 mg of uranium was taken in a pre-weighed silica crucible. The sample was first heated gradually to 200 °C till dryness and then to 800 °C in air until a constant weight was obtained. The constant weight of the sample was taken as the weight of  $\text{U}_3\text{O}_8$ .

Alternatively, uranium was also analysed volumetrically in which an aliquot of the solution containing around 200 mg of uranium was first reduced to U(IV) by an excess of Fe(II) in concentrated  $\text{H}_3\text{PO}_4$  medium, followed by selective oxidation of the excess Fe(II) by  $\text{HNO}_3$  in presence of Mo(VI) as catalyst and subsequent titration of U(IV) with standard  $\text{K}_2\text{Cr}_2\text{O}_7$  solution after dilution with 1 M  $\text{H}_2\text{SO}_4$ .

The concentration of  $\text{NO}_3^-$  ion in the solution was determined by redox titration. For this, an aliquot containing 40–60 mg of nitrate was taken in a conical flask to which 25 ml of 0.2 M  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$  solution was added followed by the addition of 5 ml of conc. HCl and 15 ml of conc.  $\text{H}_2\text{SO}_4$ . This mixture was boiled for 5 min and cooled to room temperature. After dilution with 1 M  $\text{H}_2\text{SO}_4$ , the excess Fe(II) was titrated with standard  $\text{K}_2\text{Cr}_2\text{O}_7$  solution using Ferroin (1,10 phenanthroline) indicator.

### 2.2. Preparation of plutonium nitrate solution

$\text{Pu}(\text{NO}_3)_4$  was prepared by dissolving the required amount of plutonium oxide powder in concentrated  $\text{HNO}_3$  solution added with a few

drops of HF. To minimize the nitric acid in the solution, the Pu(IV) nitrate solution was evaporated to dryness at temperatures below 150 °C, and the crystals obtained were redissolved in a minimum quantity of 0.35 M HNO<sub>3</sub>. The Pu content was determined volumetrically [22]. The free acidity was determined by potassium oxalate complexation method [23]. Spectrophotometric analysis of plutonium nitrate solution was carried out using BECKMAN DU-7 spectrophotometer to determine the oxidation states of plutonium in the solution.

### 2.3. Preparation of 3 M hexamethylenetetramine-urea solution

The calculated weights of analytical grade hexamethylenetetramine (HMTA) and urea crystals were dissolved in distilled water to obtain 3 M HMTA-urea solution.

### 2.4. Preparation of (U,Pu)O<sub>2</sub> microspheres containing 4 mol% of Pu

The internal gelation process has been developed for the preparation of soft oxide microspheres containing 4 mol% plutonium, which are subsequently compacted, reduced and sintered into pellets of dioxide. The flow sheet of the process is shown in Fig. 1. The gelation assembly used for the preparation of (U,Pu)O<sub>2</sub> microspheres on a 100 g scale is shown in Fig. 2. The sol-gel assembly consists of an oil tank, gelation column, feed tank, washing equipment, which were housed in one glove box. The furnaces for drying and heat treatments were installed in another glove box. The droplet dispersion assembly has a stainless steel capillary of 0.8 mm diameter mounted on an electromagnetic vibrator. The gelation column was 85 cm in height and 5 cm in diameter through which hot silicone oil was circulated giving a total contact time of 25 s. for feed droplets of 1.6 mm diameter. The gelation medium was controlled within ±1 °C of the set temperature. The feed solution was prepared by adding cold (−2 °C) plutonium nitrate solution to cold (−2 °C) uranyl nitrate solution and mixing it with cold (−2 °C) HMTA-urea solution. In the feed, total metal concentration was maintained at 1.5 M and hexamethylenetetramine (HMTA)-urea to metal mole ratio (*R*) was kept at 1.0. Droplets were prepared by forcing the feed solution to pass through the capillary by application of overhead pressure. The droplets were converted into gel parti-

cles within 20 s. on contact with hot silicone oil circulating through the column maintained at 85 °C. The gel particles were subsequently transferred onto a conveyor wire mesh belt (ASTM size of 12 mesh) along with the hot oil. The oil drains through the openings of the wire mesh belt and was returned back to the oil tank. The gel particles were carried by the conveyor belt and discharged into the wash tank. The gel particles were first washed with carbon tetrachloride to remove the oil on the surface of the gel particles. The particles were then washed with 6% ammonium hydroxide solution to remove the residual chemicals. The gel particles were loaded in a wash column of 7.5 cm diameter and 15 cm height with a stop cock at the bottom to adjust the flow of the wash solution. Ammonium hydroxide solution was filled in the column till the gel particles were submerged. The stop cock was adjusted to give a flow rate of 25 ml/min. The level in the wash column was maintained by adding ammonia solution from a reservoir. A conductivity probe installed in the glove box was used to monitor the progress of ammonia washing by measuring the conductivity of wash effluent. Until the conductivity decreased to the background, the washing was continued. In all the experimental batches, the washing was continued for 1 h (in spite of conductivity attaining background value a little earlier in some cases) so that the wash effluent collected from each experimental batch was equal (1.5 l). As additional experiments, the gelation temperature was changed from 78 °C to 88 °C with all the other conditions kept fixed, to study the effect of gelation temperature on leaching of plutonium in the wash solution. Samples were drawn from the wash effluent collected from each experimental batch for liquid scintillation counting to quantitatively determine the plutonium amount.

### 2.5. Heat treatment of gel microspheres

The gel particles after completion of ammonia washing were transferred into a shallow silica boat and initially heated in an air oven at 100 °C for 8 h and then at 250 °C for 4 h to obtain dried microspheres of UO<sub>3</sub> · xNH<sub>3</sub> · yH<sub>2</sub>O (where *x* and *y* are dependent on preparation conditions) [24,25] and hydrated PuO<sub>2</sub> [26]. The dried microspheres obtained were characterized for surface morphology prior to further heat treatment. The dried microspheres were heat treated on a 100 g scale. The dried microspheres were loaded in two alumina boats and

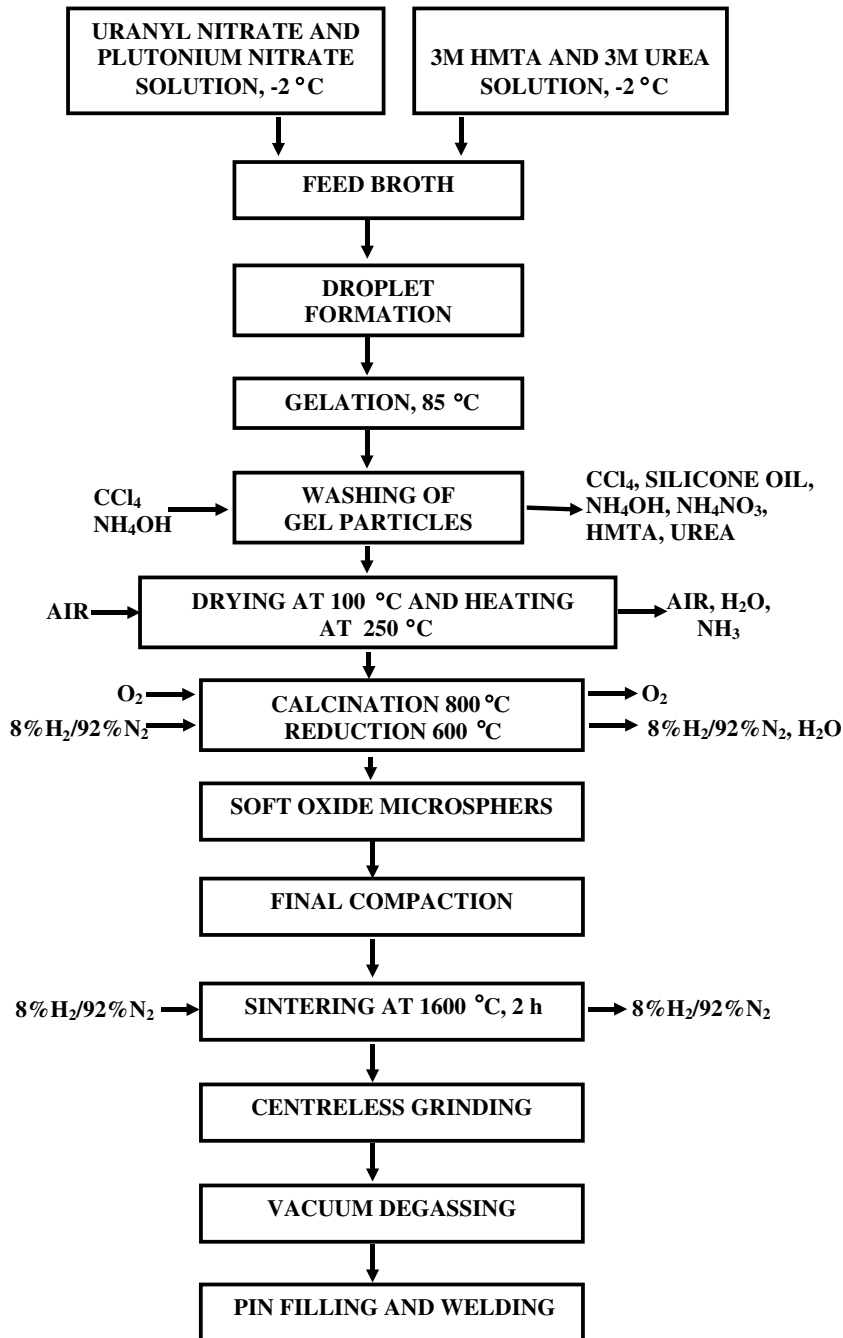


Fig. 1. Flow sheet of SGMP technique for the fabrication of mixed oxide pellets.

were calcined in an electrical resistance furnace housed inside a glove box at temperature 600, 700 or 800 °C for 1 h in a continuous flow of oxygen ( $\sim 17 \text{ cm}^3/\text{s}$ ). The microspheres were then reduced at 600 °C using 8% $\text{H}_2$ /92% $\text{N}_2$  gas mixture for 1 h. After cooling to room temperature, the product microspheres were stabilized by passing commercial

nitrogen gas (impurities: oxygen = 400–500 vppm, moisture = 10 vppm,  $\text{CO}_2$  = 50 vppm and hydrocarbon = 5 vppm) at room temperature for 1 h. The reduced product was characterized with respect to tap density, crush strength, surface area, O/M ratio [27]. X-ray diffraction analysis of the mixed oxide microspheres was carried out to identify the



Fig. 2. Gelation assembly used for the preparation of (U,Pu)O<sub>2</sub> microspheres.

phases while chemical analysis was made for the determination of the O/M ratio. The XRD patterns of the oxides were recorded on a DIANO X-ray powder diffractometer using CuK<sub>α</sub> radiation ( $\lambda = 1.5406 \text{ \AA}$ ) with a graphite monochromator. The applied voltage was 45 kV and the current was 30 mA.

#### 2.6. Pelletization of (U,Pu)O<sub>2</sub> microspheres

The microspheres were converted into pellets of 10 mm and 15 mm diameters having the *l/d* ratios ranging from 0.9 to 1.0. The compaction pressure was varied from 150 to 300 MPa. For die wall lubrication, 4% stearic acid in acetone was used. The green density of the pellets was determined by geometric measurements. The absence of cracks was ascertained by subjecting the green pellets to acetone dip test.

#### 2.7. Sintering of the green pellets and characterization

The green pellets were sintered in an environment of 8%H<sub>2</sub>/92%N<sub>2</sub> gas mixture. The pellets were heated at a rate of 5 °C/min to 1600 °C and sintered for 2 h at that temperature. They were then cooled at a rate of 5 °C/min down to 400 °C after which it followed the natural cooling down to room

temperature. The density of the sintered pellets was measured by geometric method consisting of measuring the diameter and height of the pellet with a micrometer (accuracy  $2 \times 10^{-3} \text{ cm}$ ), and the mass with an analytical balance (accuracy  $10^{-4} \text{ g}$ ). Sintered pellets were characterized by measuring *l/d* ratio, micro-homogeneity and observing micro-structure. The sintering behaviour was studied by measuring the shrinkage in axial direction using a push rod type dilatometer (Netzsch 402 E/7). For the dilatometric studies, the sample used was in the form of pellet of 10 mm diameter and 9 mm length. The pellet was prepared using mixed oxide microspheres obtained after heat treatment (calcination at 800 °C, reduction at 600 °C and stabilization at room temperature). The bulk density of this pellet was 4.95 g/cm<sup>3</sup>. The sample supporter, measuring unit and displaceable furnace of the dilatometer were mounted horizontally. The length change measurements were made by Linear Voltage Differential Transformer (LVDT), which was maintained at a constant temperature by means of water circulation from a constant temperature bath. The accuracy of the measurement in length was within  $\pm 0.1 \text{ }\mu\text{m}$ . The temperature was measured using a calibrated thermocouple which was placed closely above the sample. A small force of 0.2 N was applied to the sample through the push rod. The experiments were carried out in high purity Ar (impurities: oxygen

and moisture = 4 vppm, CO<sub>2</sub> and CO = 1 vppm, N<sub>2</sub> = 10 vppm, hydrocarbon = 1.5 vppm) with a flow rate of 300 ml/min. The heating rate was 7 °C/min. Correction was applied to the expansion of the system by taking a run under identical conditions using a standard sample (POCO graphite, NIST).

Homogeneity of the sintered MOX pellets was studied by alpha auto-radiography. For this a 'Mylar film' sandwiched between two thin aluminum foils (~12 μm thick to cut off α rays falling on the film at an angle) was exposed over the sintered MOX pellet. The Mylar film was then taken out from the aluminum foils and was first cleaned with soap water followed by washing with distilled water. The film was then etched using NaOH solution to develop the alpha tracks.

### 3. Results and discussion

#### 3.1. Preparation of mixed oxide microspheres

The gelation experiments carried out at various temperatures showed that the optimum temperature was 85 ± 2 °C for complete gelation of 1.6 mm droplets in falling down the length of the gelation column. At higher temperature (88 °C), the gel net work formed seemed to be harder than the gel net work formed at lower temperature (78 °C). This was supported by the leaching studies conducted. It can be seen from Table 1 that, the amount of plutonium leached into the wash solution decreased with increasing gelation temperature. The microspheres obtained below 80 °C were comparatively softer, and eroded microspheres were found to form after drying. As a compromise between particle softness and erosion of particle due to plutonium leaching during ammonia washing, a gelation temperature of 85 ± 2 °C was used for preparation of mixed oxide microspheres. The 250 °C heated product was smooth surfaced and crack free with a tap

Table 1  
Plutonium leached during ammonia washing as a function of gelation temperature

Gelation temperature (°C)	Plutonium leached (mg/l)
78	5.51 × 10 <sup>-2</sup>
82	3.68 × 10 <sup>-2</sup>
84	2.55 × 10 <sup>-2</sup>
88	2.35 × 10 <sup>-2</sup>

density of 1.2 g/cm<sup>3</sup>. The microspheres were found to be in the ASTM sieve range between -16 mesh and +18 mesh, indicating the average size to be around 1100 μm.

#### 3.2. Heat treatment of microspheres

The objective of the heat treatment is to obtain the (U,Pu)O<sub>2</sub> microspheres which are soft enough to be crushed easily but have reasonable tap densities to give a desired *l/d* ratio. The effect of calcination in air on the densification of UO<sub>3</sub> particles was reported by Suryanarayana et al. [20]. Similar heat treatment scheme was adopted in the present study; calcination was carried out at 600, 700 or 800 °C in a batch furnace. In all the cases, the reduction treatment was subsequently made at 600 °C in 8% H<sub>2</sub>/92% N<sub>2</sub> atmosphere for 1 h ensuring completion of reaction with minimum sintering of the product. Completion of the reaction was confirmed by XRD analysis. The XRD pattern of the gel particles calcined at 800 °C and then reduced at 600 °C for 1 h and stabilized in commercial N<sub>2</sub> at room temperature is shown in Fig. 3. A comparison of the XRD pattern of (U,Pu)O<sub>2</sub> microspheres with that of UO<sub>2</sub> microspheres clearly indicates that under

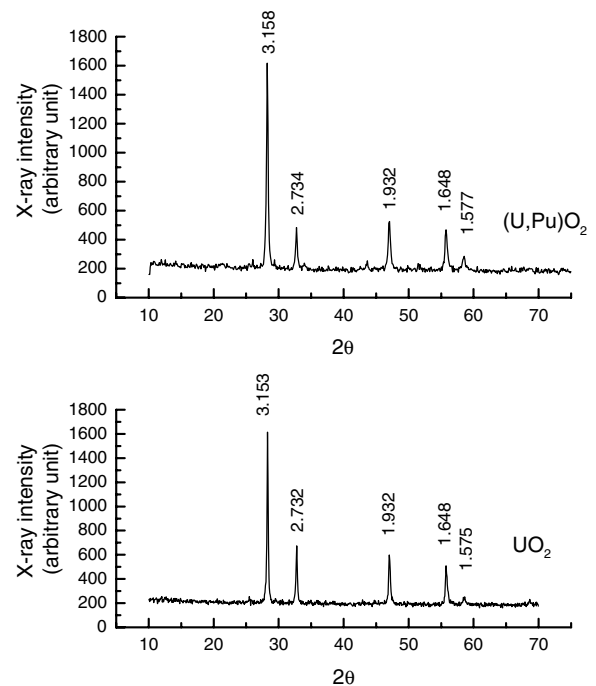


Fig. 3. XRD pattern of UO<sub>2</sub> and (U,Pu)O<sub>2</sub> microspheres calcined at 800 °C in air and reduced at 600 °C.



Table 2

Change of tap density, crush strength and specific surface area of uranium–plutonium mixed oxide microspheres as a function of calcination temperature

Calcination temperature (°C)	Tap density (g/cm <sup>3</sup> )	Crush strength (N/particle)	Specific surface area (m <sup>2</sup> /g)
600	1.43	2.2	8.3
700	1.57	2.2	6.7
800	1.65	2.3	5.5

Reduction temperature: 600 °C; heating time = 1 h.

these conditions U<sub>3</sub>O<sub>8</sub> had completely converted into UO<sub>2</sub>. The tap density, crush strength and specific surface area of mixed oxide microspheres are listed in Table 2 as a function of calcination temperatures. The table shows that the obtained microspheres were soft, with crush strengths around 2.2 N/particle, for all the products heated at 600, 700 and 800 °C. However, the tap density was low and specific surface area was high for the microspheres calcined at 600 °C. To obtain green pellets of 50% TD from the 600 °C calcined microspheres, high compaction (*l/d*) ratios were required which often resulted in formation of defective compacts. Sintering characteristics of the obtained green pellet were also not good because of higher specific surface area which tends to give chipping, cracking and other defects. (U,Pu)O<sub>2</sub> microspheres obtained by calcination at 800 °C and reduction at 600 °C gave better compacts which yielded good quality sintered pellets.

### 3.3. Pelletization and sintering

The results of the pelletization experiments are given in Table 3. The compaction pressures applied were 150–350 MPa. At 150–225 MPa, low density green pellets with rough surfaces were obtained which had berry-like structure with large open pores as shown in Fig. 4. This indicates that the microspheres still keep their shape to some extent in the

Table 3

Properties of green pellets as a function of compaction pressure

Compaction pressure (MPa)	Average green density (g/cm <sup>3</sup> )	Observation of pellets
150–225	4.75	Rough surface (Black berry-like structure)
225–270	4.95	Good quality pellets
270–350	5.20	Laminated pellets

pellets. On the other hand, if the pressure is higher than 270 MPa, the pellets started to give laminar cracks although the green density increased. Good quality green pellets free from external cracks and end chipping were obtained at the pressures in a range 225–270 MPa. These pellets were shown to have sufficient mechanical strength. Table 3 indicates that the density of the green pellet increases from 4.75 g/cm<sup>3</sup> for 150–225 MPa to 5.20 g/cm<sup>3</sup> for 270–350 MPa with increasing compaction pressure.

The green pellets were sintered in a flow of 8%H<sub>2</sub>/92%N<sub>2</sub> reducing gas at 1600 °C for 2 h. The product pellets were intact, free from cracks and surface defects. The density of the sintered pellet was 10.40 ± 0.05 g/cm<sup>3</sup> (94–95% TD). Fig. 5 shows a typical microstructure of sintered MOX pellet. The microstructure photograph reveals grains of the sizes ranging from 3 to 6 μm with uniformly distributed pores across the pellet. The alpha autoradiographic studies of sintered MOX pellet showed that the distribution of plutonium was completely uniform without any plutonium rich areas as shown in Fig. 6. The good uniformity is considered to be caused by mixing of plutonium and uranium in solution. The characteristics of (U,Pu)O<sub>2</sub> microspheres and pellets are given in Table 4.

### 3.4. Shrinkage behaviour of (U,Pu)O<sub>2</sub> pellets

The densification pattern obtained from dilatometric studies is shown in Fig. 7, where  $dl/l_0$  is the change in length divided by the initial length. The results of the sintering studies show that the shrinkage of the pellets starts at a very low temperature of 655 °C. A sharp shrinkage occurs between 655 and 980 °C. Around 42% of the total shrinkage was observed even below 1000 °C. It can be seen from the figure that there is a slight swelling in the curve in the initial part in spite of applying correction using a standard sample. The probable reason could be due to the thermal expansion of the sample due to the presence of nano pores which is normally seen in sol–gel derived materials. Such a type of swelling was also observed in thoria–urania sample prepared by similar route [28]. In the temperature range 980–1215 °C, the sintering was sluggish, but thereafter another sharp shrinkage occurred up to 1600 °C. The first large shrinkage cannot be attributed to densification of materials, otherwise it should have continued beyond 1000 °C without an arrest between 1000 and 1200 °C. Further, this can not

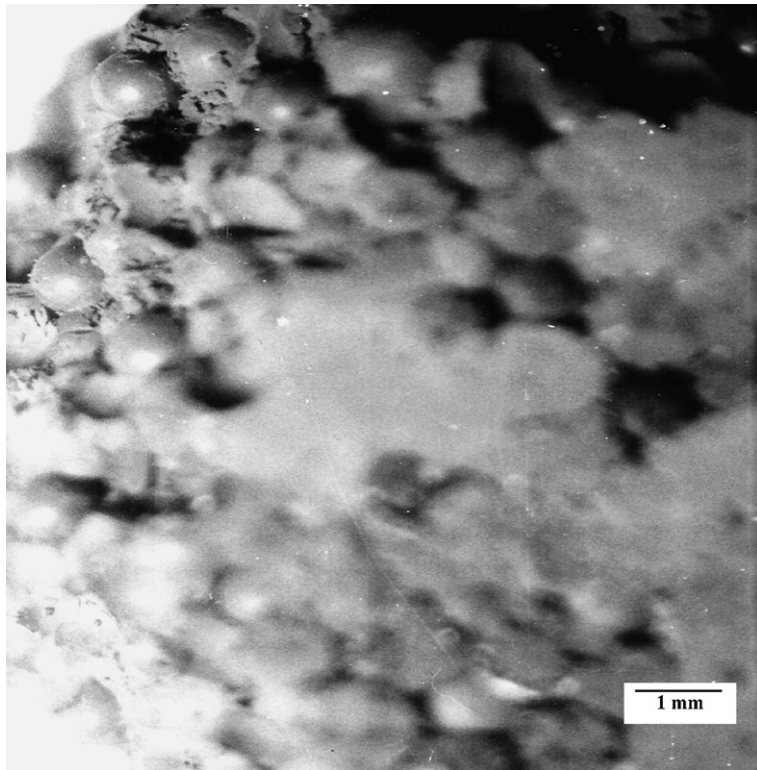


Fig. 4. Pellet with berry-like structure obtained at low compaction pressure (<225 MPa).

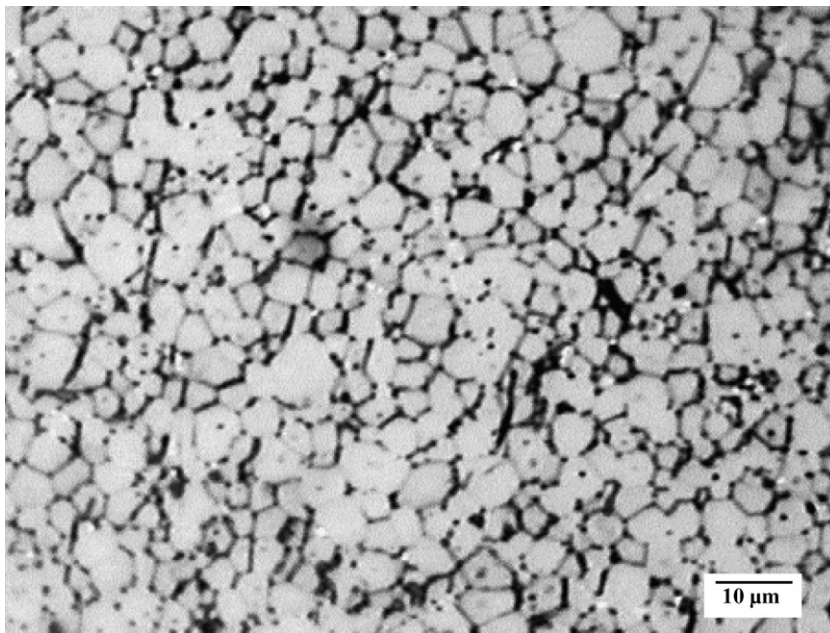


Fig. 5. Microstructure of sintered (U,Pu)O<sub>2</sub> pellet.

be due to any phase change either because the expected change of O/M from 2.08 in the starting material to 2.00 or less will always result in

expansion of lattice rather than contraction. Another possible reason for this shrinkage is the collapse of pores in this temperature range. Kumar



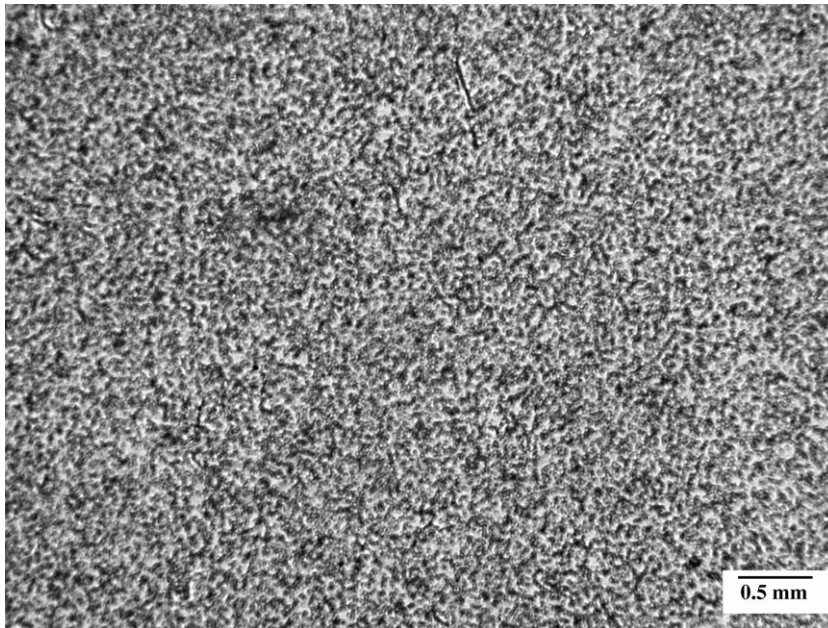


Fig. 6. Alpha radiography of MOX pellet showing uniform distribution of plutonium.

Table 4  
Physical properties of 250 °C heated, heat treated<sup>a</sup> mixed oxide microspheres, green pellets and sintered<sup>b</sup> MOX pellets

Characteristics	Observation
Average size of 250 °C heated microspheres	1100 μm
Tap density of 250 °C heated microspheres	1.2 g/cm <sup>3</sup>
Average size of heat treated microspheres <sup>a</sup>	900 μm
O/M ratio <sup>a</sup>	2.08 ± 0.03
Average green pellet density <sup>a</sup>	4.95 g/cm <sup>3</sup>
Sintered pellet density <sup>b</sup>	10.40 ± 0.05 g/cm <sup>3</sup>
Sintered pellet <i>l/d</i> <sup>b</sup>	0.9–1.0
Sintered pellet grain size <sup>b</sup>	3–6 μm

<sup>a</sup> Calcination in O<sub>2</sub> at 800 °C followed by reduction in 8% H<sub>2</sub>/92% N<sub>2</sub> at 600 °C for 1 h.

<sup>b</sup> Heated in 8% H<sub>2</sub>/92% N<sub>2</sub> at 1600 °C for 2 h.

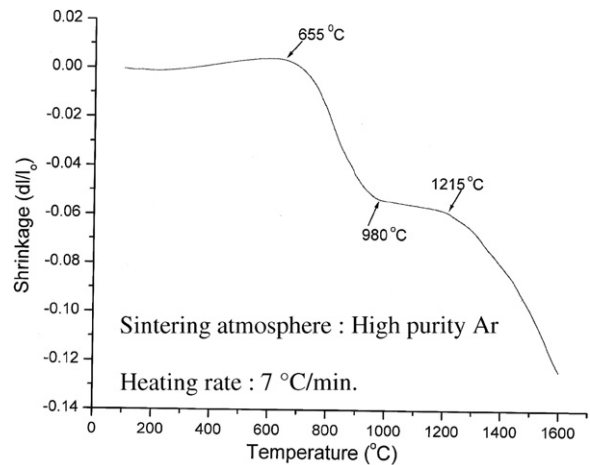


Fig. 7. Dilatometric curve of sintering MOX pellet.

et al. [27] investigated the morphology of uranium oxides using SEM and BET analyses and reported that when UO<sub>3</sub> microspheres were calcined to U<sub>3</sub>O<sub>8</sub> at 800 °C in air, a large amount of closed nano pores of 10–20 Å size were uniformly trapped throughout the bulk of the particles. Fig. 8 shows the pore size distribution curve and specific pore volume of intact particles (outer surface) and fractured particles (inner surface), where  $Dv/Dr$  is the ratio of change in specific volume at two different partial pressures of nitrogen gas to difference in radius of pores at those pressures. When the oxide was further reduced to UO<sub>2</sub> at 600 °C there was

no significant change in its morphology. The UO<sub>3</sub> + PuO<sub>2</sub> microspheres, with UO<sub>3</sub> as major constituent is expected to behave in a similar fashion. Also, these nano pores must be responsible for limiting the maximum achievable green density of the pellets to a relatively lower value. Since the shrinkage initiates at 650 °C, which is by 150 °C lower than the calcination temperature of 800 °C, the probable reason for this shrinkage could be strains either developed during its reduction to UO<sub>2</sub> at 600 °C or caused to form on compaction into

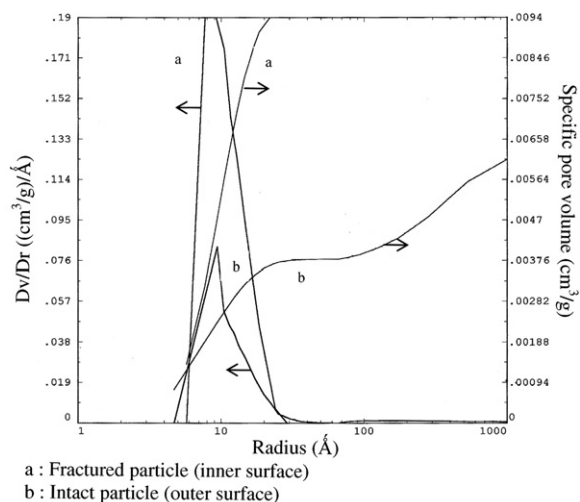


Fig. 8. Pore size distribution of outer and inner surface of calcined  $U_3O_8$  microspheres (figure taken from Ref. [27]).

pellets. Normally, coalescence and release of such large porosity in a narrow temperature range may be detrimental to the integrity of the pellet. However, in the present case no such damage was observed in the sintered pellets. This may be attributed to the isotropicity of the shrinkage due to narrow size distribution range of the pores and their uniform distribution throughout the bulk of the material.

#### 4. Conclusion

The process parameters of  $[U,Pu] = 1.5$  M,  $R = 1.0$  and gelation temperature of  $85^\circ\text{C}$  yielded good quality mixed oxide microspheres. The dried mixed oxide microspheres on calcination at  $800^\circ\text{C}$ , reduction at  $600^\circ\text{C}$  in  $8\%H_2/92\%N_2$  atmosphere and stabilization in commercial nitrogen at room temperature results in formation of soft  $(U,Pu)O_2$  microspheres with crush strength of around  $2.3$  N/particle, tap density of  $1.65$  g/cm<sup>3</sup>, O/M ratio of  $2.08$  and surface area of  $5.5$  m<sup>2</sup>/g, which are suitable for obtaining good quality pellets. A compaction pressure of  $250$  MPa was found to be optimum for obtaining  $45\%$  TD green pellets without defects. The green pellets heated in a flow of  $8\%H_2/92\%N_2$  reducing gas at  $1600^\circ\text{C}$  resulted in formation of defect free sintered pellets having a density of  $94\%$  TD. The microstructure showed grains in the size range of  $3\text{--}6$   $\mu\text{m}$ . The alpha auto-radiography of the sintered  $(U,Pu)O_2$  pellet revealed an excellent micro-homogeneity of plutonium. The good sin-

tered density, coupled with optimum grain size and excellent micro homogeneity indicate that the pore former free sol-gel microsphere pelletization process (SGMP) has emerged as a suitable alternative to the conventional powder oxide pellet (POP) route for the fabrication of MOX fuel.

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