Journal of Nuclear Materials 381 (2008) 249–258

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Fabrication of dense $(Th,U)O_2$ pellets through microspheres impregnation technique

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ARTICLE INFO

Article history:
Received 18 October 2007
Accepted 12 July 2008

PACS:
81.20.Fw
82.70.Gg
66.30.Fq
61.43.Gt
68.37.Hk

ABSTRACT

ThO_2 microspheres were prepared by internal gelation process using a pre-boiled hexamethylenetetramine (HMTA), urea solution. The microspheres were characterized with respect to tap density, specific surface area and pore size distribution. An indigenously designed and fabricated apparatus was used for the impregnation of uranium in thoria microspheres. The loading of uranium was found to vary with the concentration of uranyl nitrate solution, operational vacuum and the time of impregnation. These process conditions were optimized to obtain soft $(Th,U)O_2$ microspheres containing 3–4 mol% of uranium, which are readily amenable for pelletization. The green pellets could be sintered to ~96% of T.D. by heating in air up to 1350 °C for a period of 2–4 h. The polished surface of the fractured pellets showed a smooth surface without any berry structure. The shrinkage behaviour of the pellets was also studied in air using a dilatometer. The SEM studies of the pellets indicated a uniform microstructure with average grain size of 1 μm. The elemental scanning by the EDX method showed the uniform distribution of uranium in the microspheres and pellets.

1. Introduction

Thorium comprises an important component of fuel in India's nuclear power programme and its judicious utilization through the envisaged three stage programme is being pursued. Construction of thorium based 300 MWe advanced heavy water reactor (AHWR) is an important step for this purpose. However there are a few technological problems that need to be settled before starting the large scale use of thorium in $(Th,^{233}U)O_2$ fuel cycle. One of these problems is the radiological toxicity associated with the presence of about 500–2000 ppm of ^{232}U in the ^{233}U fuel. Because of strong radiation, the fuel fabrication flow-sheet should be such that the processes are made in well shielded remote facilities. Alternatively the process should be made fast enough to avoid the accumulation of dose from the daughter nuclides of ^{232}U. This option can be adopted if thoria is that which was received from the fresh mines or cooled for 20 years after reprocessing. If it is easy to automatize and remotize the processes, the fabrication of $(Th,^{233}U)O_2$ can be made by the well established conventional powder pelletization method. However, the conventional method has many mechanical steps such as blending, granulation and pelletization, which make it difficult to do the above improvements to reduce doses. That is to say, the standard powder method is not suitable for fabrication of $(Th,^{233}U)O_2$ fuel. The sol–gel microsphere pelletization (SGMP) technique, which employs free flowing and dust free microspheres as feed material for fabrication of the pellets, offers an alternative option. Several investigations have been made with the aim to develop the gel pelletization technique for the preparation of ThO_2 and $(Th,U)O_2$ pellets [1–5]. As the second option for reducing the time of fuel fabrication, a few alternatives such as the coated agglomerate pelletization (CAP) [6] and the particle/pellet impregnation [7,8] methods have been considered. In CAP process, the ThO_2 microspheres of 1–2 mm ø are prepared from natural ThO_2 powder by way of the extrusion spheronization route. These microspheres are then coated with the desired amount of U_3O_8 containing ^{233}U by blending with the use of suitable chemicals followed by pelletization. The drawback of this process is powder handling. The uniform incorporation of uranium is also a matter of concern. In the pellet impregnation technique, all the pellet fabrication steps can be carried out in an unshielded facility and the shielded facility is needed only for ^{233}U impregnation and sintering. This method is very promising if the green thoria pellets of reproducible morphology can be formed and uranium is successfully impregnated through 10s of mm of capillaries. This process is still under development.

Impregnation of actinides in zirconia matrix through aqueous route has been studied in the work for the burning of minor actinides in reactors and accelerators. Somers and Fernandez [9–11] studied the infiltration of plutonium nitrate solution in the porous yttria stabilized zirconia (YSZ) kernels which were produced in inactive facility. They have demonstrated the feasibility of an

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doi:10.1016/j.jnucmat.2008.07.044

innovative fabrication process for the production of Pu based kernels. For this, YSZ kernels were produced in an inactive facility and infiltrated with a plutonium nitrate solution. In their reports, they mentioned the possibility of the extension of the above process to minor actinide kernels. The microsphere impregnation technique being developed in Fuel Chemistry Division, BARC uses porous thoria microspheres prepared by internal gelation process for impregnation of uranium. The study conducted at ORNL [12] for the preparation of (U,Pu)O_2 microspheres for pelletization showed that the gel microspheres prepared with pre-boiled HMTA, urea enhanced the crystal growth and gave lower tap density and crush strength. Accordingly in the present study, the pre-boiled HMTA, urea solution was used as gelation agent for obtaining thoria microspheres having high porosities. Various feed compositions were tested for the formation of porous thoria microspheres. The process conditions such as the concentration of uranyl nitrate solution, extent of vacuum and time of impregnation were also optimized for the preparation of (Th,U)O_2 microspheres. The obtained microspheres were used for fabrication of high density ThO_2 pellets containing 3–4 mol% of uranium.

2. Experimental

The flow-sheet used for the preparation of (Th,U)O_2 pellets in the present study is shown in Fig. 1. The principal steps involved for the preparation of high density pellets are:

Preparation of feed solution:

- Conversion of feed droplets into solid gel spheres (gelation).
- Washing of gel spheres, heat treatment of the gel spheres to obtain calcined ThO_2 microspheres.
- Impregnation of uranyl nitrate solution into calcined ThO_2 microspheres under vacuum.
- Heat treatment of uranium impregnated ThO_2 microspheres for decomposition of uranyl nitrate to uranium oxide.
- Pelletization and sintering to obtain high density (Th,U)O_2 pellets.

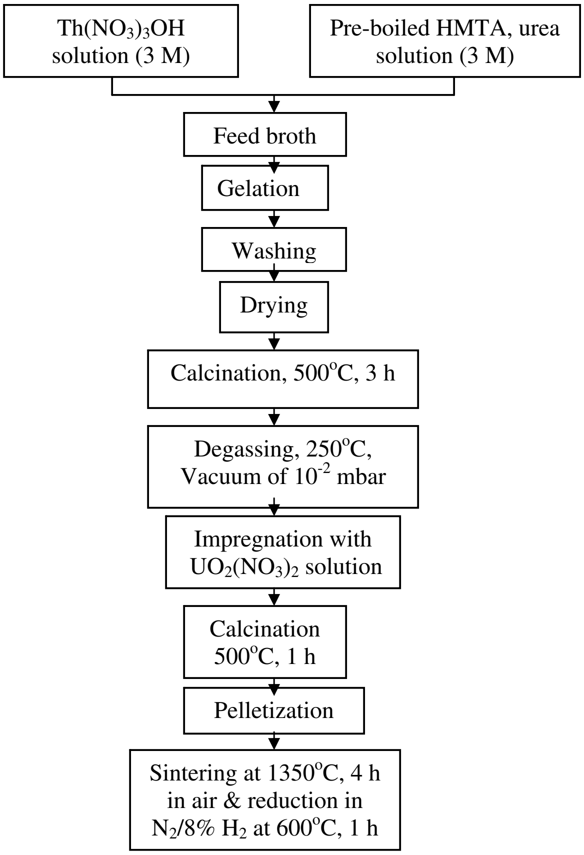

Fig. 1. Flow-sheet for the preparation of (Th,U)O_2 pellets by microsphere impregnation technique.

2.1. Preparation of feed solution

The feed solution was prepared by mixing 3 M partially neutralized thorium nitrate solution with 3 M hexamethylenetetramine (HMTA), urea solution. The metal ion concentration ([Th]) in the feed solution was varied from 0.8 to 1.3 M with a step of 0.1 M. For each metal ion concentration the [HMTA, urea]/[Th] ratio (*R*) was varied in a range from 1.1 to 1.8. The thorium nitrate solution was partially neutralized with ammonia so as to have the $[NH_4^+]/\{[NH_4^+] + [Th^{4+}]\}$ ratio close to 0.5 in the final solution. The solution obtained was concentrated to yield 3 M Th^{4+} solution. Pre-boiled 3 M HMTA, urea solution was prepared by heating 3 M [HMTA, urea] solution to boiling in a round bottom flask containing a thermometer and a reflux condenser. The solution was refluxed for 1 h in a round bottom flask equipped with thermometer and reflux condenser. Then, it was cooled to room temperature by placing the flask in tap water. A clear HMTA, urea solution was obtained.

2.2. Preparation of gel microspheres

The gelation assembly used for the preparation of gel microspheres is discussed elsewhere [5]. The equipment mainly consists of a feed tank, gelation column, conveyor belt and wash tank. For the preparation of feed broth, thorium nitrate solution was mixed with pre-boiled 3 M hexamethylenetetramine (HMTA), urea solution in the required proportion. This feed solution was then converted into droplets by forcing the solution through a 1 mm ID SS capillary. For obtaining the droplets of uniform size, the capillary was vibrated at suitable frequency by an electromagnetic vibrator. These droplets were contacted with hot (90 °C) silicone oil fluid (100 cP) in the glass gelation column to obtain solid gel particles. The gel particles were separated from oil by collecting them on a conveyor belt. The gel particles were then washed with carbon tetrachloride (CCl_4) to remove the adherent oil followed by ammonium hydroxide (3 M) to remove HMTA, urea, ammonium nitrate, methylol urea etc. The wet gel microspheres were characterized with respect to their hardness (qualitative), physical appearance and leaching behaviour during ammonia washing. The wet gel particles after the ammonia washing step were first air dried in an oven at 100 °C for 6 h and then at 250 °C for 4 h. The dried microspheres were further calcined at 500 °C for 3 h. The dried product was characterized by measuring size, size distribution, tap density, specific surface area and pore size distribution. The surface area of the samples was determined by multi-point BET method [13] using lower pressure range of adsorption isotherm, i.e. $0.05 \leqslant P/P_0 \leqslant 0.35$, where P is the equilibrium nitrogen pressure and P_0 is the saturation nitrogen pressure using SORPTOMATIC 1990 analyzer of CE instruments, Italy. On the other hand, the whole range of adsorption isotherm was used for pore analysis. To obtain the pore size distribution, the Kelvin equation [14] was used. The pore size distribution was calculated by BJH method [15]. Software supplied by the manufacturer was used for calculations and obtaining graphs such as adsorption isotherms pore size distribution pattern, etc. To check the reproducibility of the morphology of ThO_2 microspheres prepared from a given set of conditions, several batches were prepared for each feed composition keeping all the experimental conditions unchanged.

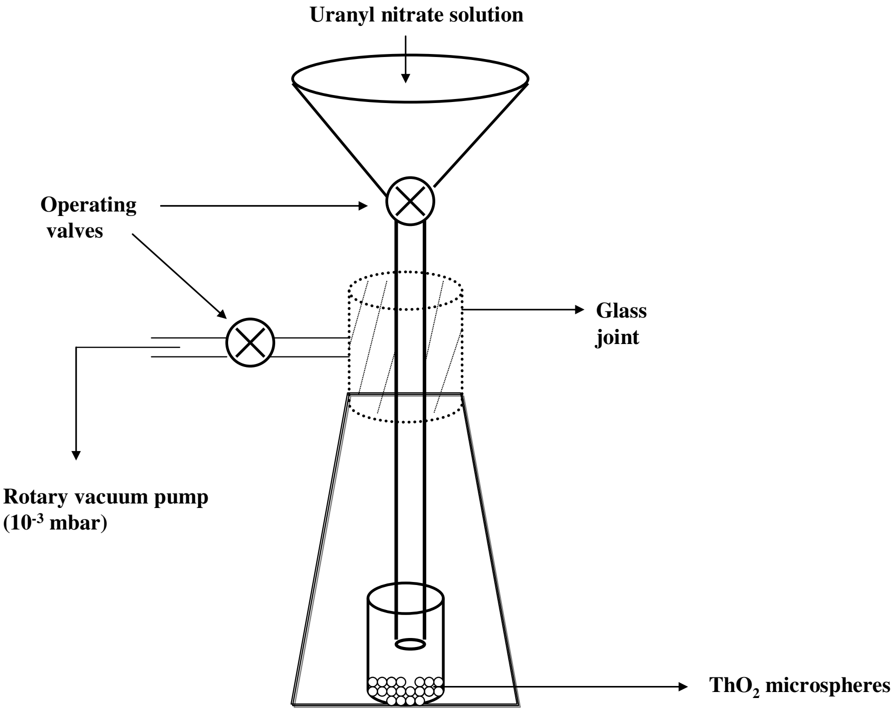

Fig. 2. Apparatus used for impregnation of uranyl nitrate solution in ThO_2 microspheres.

2.3. Impregnation of uranyl nitrate solution into thoria microspheres

Impregnation of uranyl nitrate solution in calcined ThO_2 microspheres was carried out in an indigenously designed glass apparatus. The line sketch of the apparatus is shown in Fig. 2. The apparatus consists of a 1 l capacity conical flask having suitable attachment for attaining the vacuum up to 10^{-3} mbar. For impregnation studies, uranyl nitrate solutions having different concentrations (0.5, 0.75, 1.0, 1.25 and 1.5 M) were used. For each impregnation study around 3 g of ThO_2 microspheres were taken in the sample cell and placed it at the centre of the conical flask as shown in Fig. 2. The flask was then evacuated to different vacuum levels with the highest vacuum of 10^{-3} mbar using a rotary pump. The microspheres were degassed by heating the flask to 250 °C. After degassing, the flask was cooled to room temperature and isolated from the vacuum system followed by introduction of around 5–8 ml of uranyl nitrate solution was introduced into the sample cell from the top funnel. The addition of uranyl nitrate solution was carried out slowly by manipulating the valve, keeping some excess uranyl nitrate solution in the funnel so that the vacuum was not broken. The time of impregnation was varied from 5 to 30 min. Impregnation was terminated by the introduction of air in the system. After impregnation, the microspheres were transferred on a wire mesh and the solution adhered to the spheres was removed in the stream of air jet. The impregnated microspheres were dried at 150 °C and then calcined at 500 °C for 1 h. These microspheres were characterized with respect to XRD and O/M ratio. The uranium content of the $(Th,U)O_2$ microspheres was analyzed by Davies and Grey method [16] and thorium was determined by complexometric titration as discussed elsewhere [5]. To check the reproducibility of U loading, impregnation experiment was performed under similar conditions for selected batches of ThO_2 microspheres.

2.4. Pelletization and sintering

The calcined microspheres were pelletized in a single acting manual press at 200–250 MPa pressure, using 4% stearic acid in acetone as die lubricant. The obtained green pellets were 1.0 cm in diameter and about 0.8 cm in length. The sintering behaviour of the pellets in air was studied using a dilatometer (Netzsch 402 E/7). The bulk sintering of these pellets was studied at 1350 °C for 2–4 h in air. Finally, these pellets were reduced in N_2–8%H_2 atmosphere at 600 °C for 1 h. The density of the sintered pellets was determined by both geometrical method as well as liquid displacement method.

2.5. Microstructural analysis and elemental scanning

For microstructural examination under a scanning electron microscope, a thin layer of gold (~100 Å) was coated on the calcined microspheres and sintered pellets by thermal evaporation in a vacuum coating unit. A vacuum of 3.5×10^{-5} mbar was maintained using a diffusion pump having a rotary backing. A measured quantity of gold wire (99.99% pure) was wrapped on a tungsten wire which in turn was heated to evaporate the gold wire. The coated samples were analyzed by a scanning electron microscope (TESCAN). The elemental mapping of Th and U in the microspheres as well as in the sintered pellets was made by energy dispersive spectrometry (EDS) in order to evaluate the distribution of uranium.

3. Results and discussion

3.1. Preparation of gel microspheres

The wet gel microspheres were white in colour with the texture varying from translucent to opaque. The translucent microspheres were hard, but the opaque ones were either hard or soft. The variation of physical characteristics of the microspheres as a function of feed composition is tabulated as shown in Table 1. It can be seen from the Table 1 that the gelation time, which is defined as the time, required for conversion of liquid droplet into a gel, decreased with increase in R (HMTA, urea to metal ratio) for a given Th metal

Table 1
Characteristics of ThO_2 gel microspheres

Serial no.	Th metal concentration [Th] (M)	(HMTA, urea)/metal (R)	Gelation time (s)	Nature of gel obtained	Leaching during ammonia washing	Nature of dried product
1	0.80[a]	1.50	12	Soft opaque	Yes	Cracked
2	0.80[a]	1.60	10	Soft opaque	Yes	Cracked
3	0.80	1.70	9	Soft opaque	Yes	50% Cracked
4	0.80	1.80	9	Translucent	No	Cracked
5	0.90	1.40	22	Soft opaque	Yes	Survived
6	0.90[a]	1.65	12	Translucent	No	Cracked
7	0.90[a]	1.70	12	Translucent	No	Cracked
8	1.15	1.3	28	Hard opaque	No	Good spheres
9	1.15	1.35	27	Hard opaque	No	Good spheres
10	1.20	1.35	22	Hard opaque	No	Good spheres
11	1.25	1.15	33	Hard opaque	Slight leaching	Good spheres
12	1.25	1.25	29	Hard opaque	Slight leaching	Good spheres
13	1.25	1.35	25	Hard opaque	No	Good spheres

[a] The broth was not stable at room temperature for long. Turned milky in the beaker.

Table 2
Tap density, surface area and cumulative pore volume of ThO_2 microspheres heated at 500 °C in air for 3 h

Composition		Tap density (g/cm^3)	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Pore radius range (Å)
[Th] (M)	R				
1.15	1.30	1.34	12.7	0.0049	10–300
1.15	1.35	1.29	10.3	0.0034	10–100
1.20	1.35	1.43	16.0	0.0288	10–800
1.25	1.15	1.48	21.7	0.0720	10–800
1.25	1.25	1.43	20.4	0.0089	10–100
1.25	1.35	1.45	17.7	0.0159	10–800

concentration in most of the cases. For each of the metal ion concentrations from 0.8 to 1.25 M, spherical gel particles were obtained. Kumar et al. [17] reported that the nature of the gel varied from soft opaque gel particles to hard opaque ones and at last to hard translucent particles, when R was increased in their study to prepare ThO_2 microspheres using $Th(NO_3)_4$ solution denitrated with formaldehyde and un-boiled HMTA, urea solution. They further reported that the minimum metal ion concentration required for obtaining gel particles was 1.0 M. Subsequently, Pai et al. [5] also reported similar results with partially neutralized $Th(NO_3)_4$ solution by ammonia and un-boiled HMTA, urea solution. They restricted the studies to higher metal ion concentrations since they were interested in the preparation of soft thoria microspheres suitable for SGMP. They proposed a mechanism to explain the gelation behaviour of $Th(NO_3)_4$ solution on the basis of the rate of nucleation and growth of hydrolyzed product and recommended the use of high metal ion concentration in the feed broth. In the present investigation where the pre-boiled HMTA, urea solution and ammonia for partial neutralization of $Th(NO_3)_4$ solution are used, gel particles could be made with [Th] of 0.8 and 0.9 M as shown in serial no. 1–7 of Table 1. However, the gel particles were either soft opaque or translucent which were fractured in the heat treatment step. Leaching of metals during the ammonia washing was also observed for such soft gel particles. These were cracked on drying at 100 °C. Soft gel formation is due to incomplete gelation and translucent gel formation is due to fast gelation. In both the cases, gel network is not formed homogeneously throughout the bulk of the particle and a fraction of unhydrolysed metal ion is trapped inside it. This trapped un-gelled material is responsible for cracking in both the cases. The hard opaque gel particles represent the completion of hydrolysis reaction and the development of the uniform gel network throughout the bulk of the particles. This type of gel particles were not obtained at low metal ion concentrations, which suggests that the range of compositions suitable for forming such gel particles is rather narrow. For [Th] of 1.15 M and above gel texture of hard opaque was also obtained in addition to soft opaque and translucent with variation in R for a given [Th]. Since only hard opaque gel survived heat treatment steps, their characteristics are given in Table 1 (serial no. 8–13). The good quality microspheres, which were not fractured in the drying and calcination steps were obtained with [Th] = 1.15–1.25 M and R = 1.25–1.35. These microspheres were used for impregnation study. The average size of the ThO_2 microspheres calcined at 500 °C was 1.60 ± 0.08 mm. The tap density, surface area and cumulative pore volume of heat treated microspheres are listed in Table 2. The tap density increased only marginally with the increase in the Th metal ion concentration from 1.15 to 1.25 M for fixed R at 1.35. But the specific surface area of these microspheres increased from 10.3 m^2/g to 17.7 m^2/g.

3.2. Impregnation of uranium into calcined ThO_2 microspheres

The loading of uranium in the ThO_2 microspheres depends on the morphology of the microspheres, i.e., pore size, shape, volume and their inter connectivity. The defect free microspheres prepared from different feed compositions had micro as well as meso pores. The adsorption–desorption isotherms and pore size distribution curves for ThO_2 microspheres heated at 500 °C are shown in Figs. 3(a) and 3(b) respectively. Also for all the samples (1–4) the adsorption isotherm crosses with the desorption isotherm at certain P/P_0. This may be due to the presence of pores possessed by the sample with wider pore openings than the actual pore radius (below the P/P_0 value where it crosses) which allows more desorption form these pores. The pore size distribution showed that the samples offered more meso porosity (>100 Å). These compositions showed more pore volume also (Table 2). All these microspheres were subjected to the impregnation experiments. The following factors were examined:

(i) Extent of evacuation and degassing achieved before impregnation.
(ii) Time of impregnation.
(iii) Concentration of uranyl nitrate solution used.
(iv) Effect of morphology of the ThO_2 microspheres.

The effect of these parameters on impregnation is briefly discussed below:

(i) *Effect of extent of evacuation.* During the impregnation experiments, when the vacuum exceeded 10^{-2} mbar, it was found that the microspheres got crumbled irrespective of their

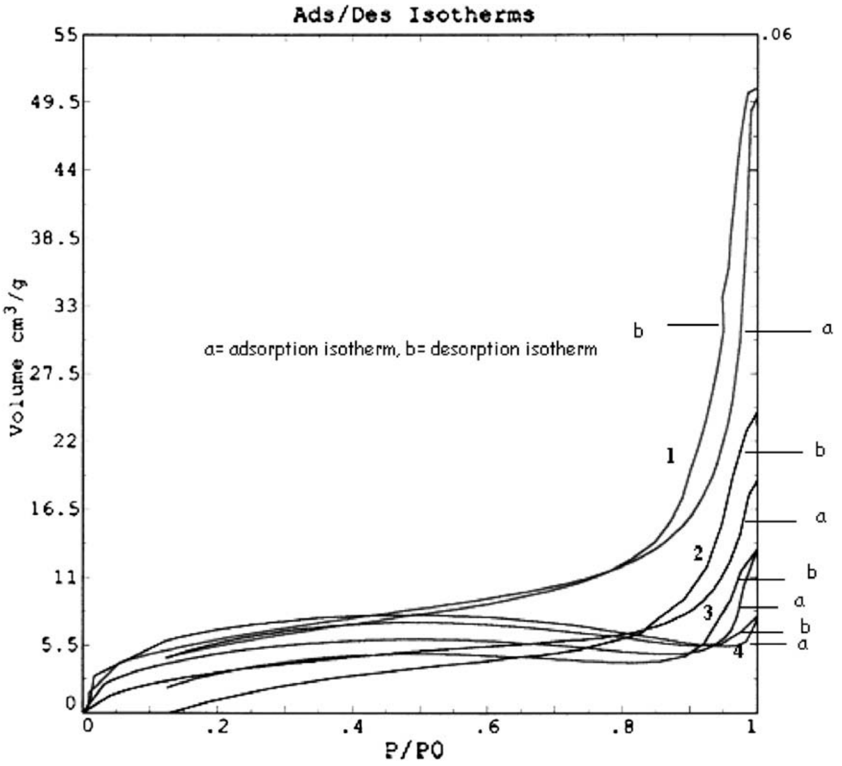

Fig. 3a. Adsorption–desorption isotherms of ThO_2 microspheres prepared by heating at 500 °C.

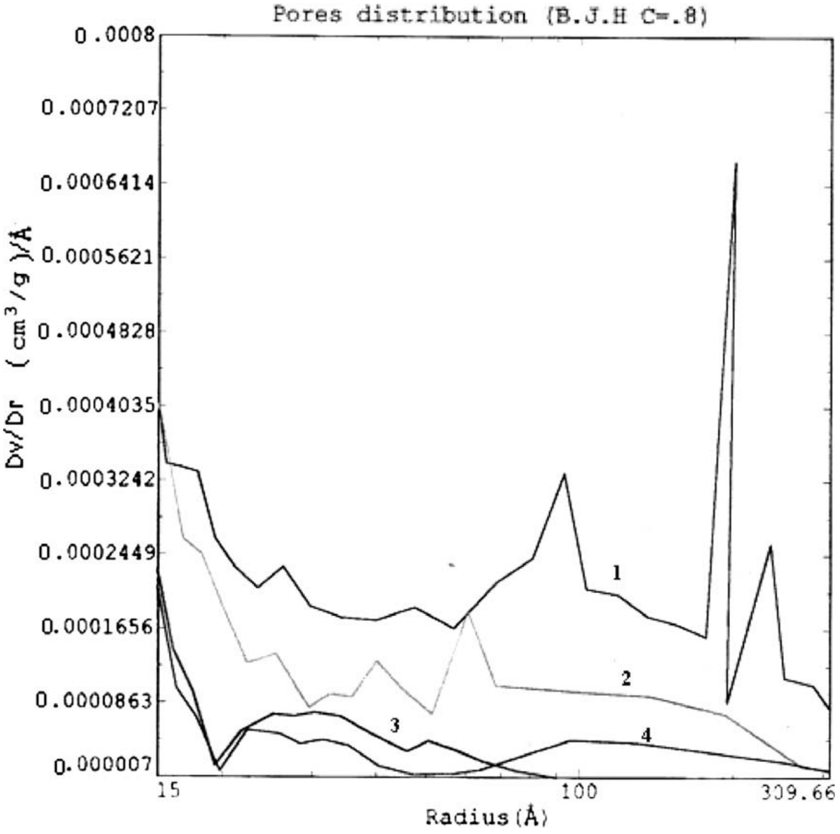

Fig. 3b. Pore size distribution of ThO_2 microspheres prepared by heating at 500 °C.

surface characteristics. This may be due to rapid permeation of uranyl nitrate solution into the pores. With a view to have maximum loading of uranium without damage to the microspheres, 10^{-2} mbar was selected as the operational vacuum.

(ii) *Effect of impregnation time.* The observed loading of uranium in the thoria microspheres was found increasing with the increase in impregnation time. The amount of uranium that could be loaded in ThO_2 microspheres prepared from the feed composition, [Th] = 1.20 M, *R* = 1.35 when impregnated with 1.0 M uranyl nitrate solution in an operational vacuum of 10^{-2} mbar was 3.40, 4.35 and 4.80 wt% when impregnated for 5, 10 and 15 min, respectively. Since the thoria microspheres used for impregnation experiments were those calcined at low temperature (500 °C), leaching of thoria in the uranyl nitrate solution was observed if the impregnation time was longer than 15 min. So the impregnation time of 10 min was chosen as the optimum time in which no leaching of thoria occurs.

(iii) *Effect of the concentration of uranyl nitrate solution.* Table 3 shows the change of the amount of uranium loaded into ThO_2 microspheres for [Th] = 1.25 M, *R* = 1.15 as well as for [Th] = 1.20 M, *R* = 1.35 when the concentration of uranyl nitrate solution was varied. It can be seen that by increasing the concentration of uranyl nitrate solution from 0.5 to 1.5 M, the uranium content in the ThO_2 pellet increased from 0.34 to 4.28 wt% for [Th] = 1.20 M, *R* = 1.35. The loading of uranium was found to be maximum with 1.0 M uranyl nitrate solution. The amount of uranium loaded with 1.5 M uranyl nitrate was comparable. This may be attributed to the higher viscosity of 1.5 M uranyl nitrate solution.

Based on the above observation, the following parameters were used for further impregnation experiments:

Concentration of uranyl nitrate: 1.0 M.
Time of impregnation: 10 min.
Vacuum: 10^{-2} mbar.

Table 3
The amount of uranium loaded in ThO_2 microspheres against uranyl nitrate concentrations

Sample	Molarity of uranyl nitrate (M)	Uranium content (wt%)
[Th] = 1.25 M, *R* = 1.15	0.5	0.34
[Th] = 1.25 M, *R* = 1.15	0.75	1.61
[Th] = 1.25 M, *R* = 1.15	1.0	4.56
[Th] = 1.25 M, *R* = 1.15	1.50	4.28
[Th] = 1.20 M, *R* = 1.35	0.50	1.89
[Th] = 1.20 M, *R* = 1.35	0.75	3.02
[Th] = 1.20 M, *R* = 1.35	1.0	4.35

Table 4
The amount of uranium loaded in ThO_2 microspheres having different surface characteristics

Series no.	Composition	Specific surface area (m^2/g)	Cumulative pore volume (cm^3/g)	Pore radius range (Å)	Uranium content (wt%)
1	[Th] = 1.25 M, *R* = 1.15	21.7	0.0720	10–800	4.56
2	[Th] = 1.20 M, *R* = 1.35	16.0	0.0288	10–800	4.35
3	[Th] = 1.25 M, *R* = 1.25	20.4	0.0089	10–100	1.85
4	[Th] = 1.25 M, *R* = 1.35	17.7	0.0159	10–800	3.79

Concentration of uranyl nitrate solution: 1 M; duration of impregnation: 10 min; vacuum: 10^{-2} mbar.

(iv) *Effect of morphology of the ThO_2 microspheres.* ThO_2 microspheres prepared from feed compositions [Th] = 1.25 M, *R* = 1.15 and [Th] = 1.20 M, *R* = 1.35 gave surface characteristics desirable for uranium impregnation. The impregnation experiments were carried out for microspheres having different morphologies using the experimental conditions above. The results for four typical samples are presented in Table 4. The amount of uranium that could be loaded in the microspheres varied between 1.85 and 4.56 wt%. There is no correlation between specific surface area of the microspheres and amount of uranium loaded. But the amount of uranium loaded is largely dependent on the total pore volume of the ThO_2 microspheres. Note that the above dependence is not linear suggesting the influence of pore size distribution on the loading characteristics. Both the total pore volume and size distribution are supposed to exert a

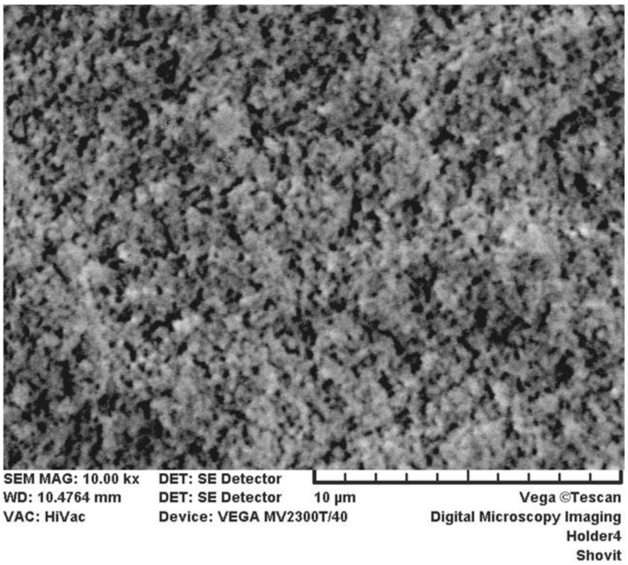

Fig. 4a. Micrograph of fractured ThO_2 microsphere before impregnation.

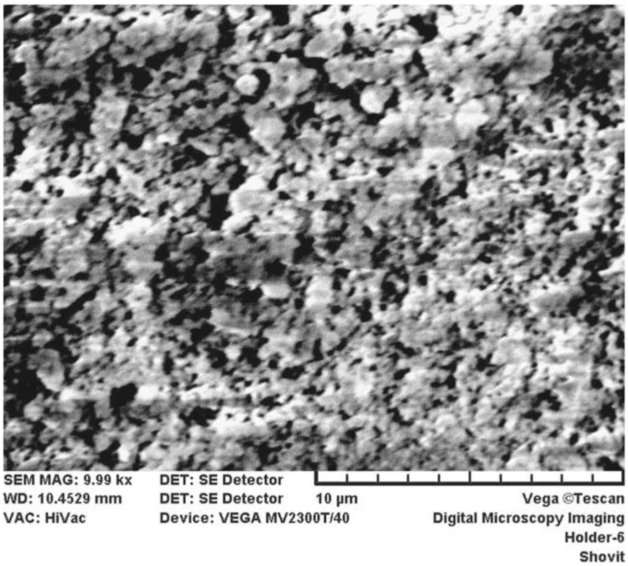

Fig. 4b. Micrograph of fractured ThO_2 microsphere impregnated with 1 M uranyl nitrate solution followed by calcination at 500 °C for 1 h.

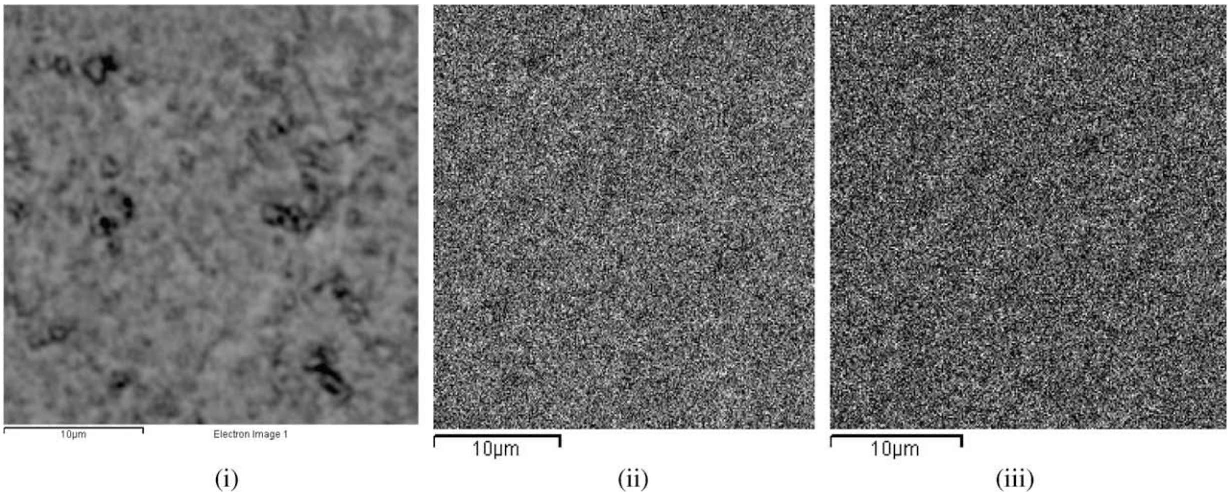

Fig. 5a. Elemental scanning photograph of microsphere sample: (i) secondary electron image scanned; (ii) X-rays from Th; (iii) X-rays from U.

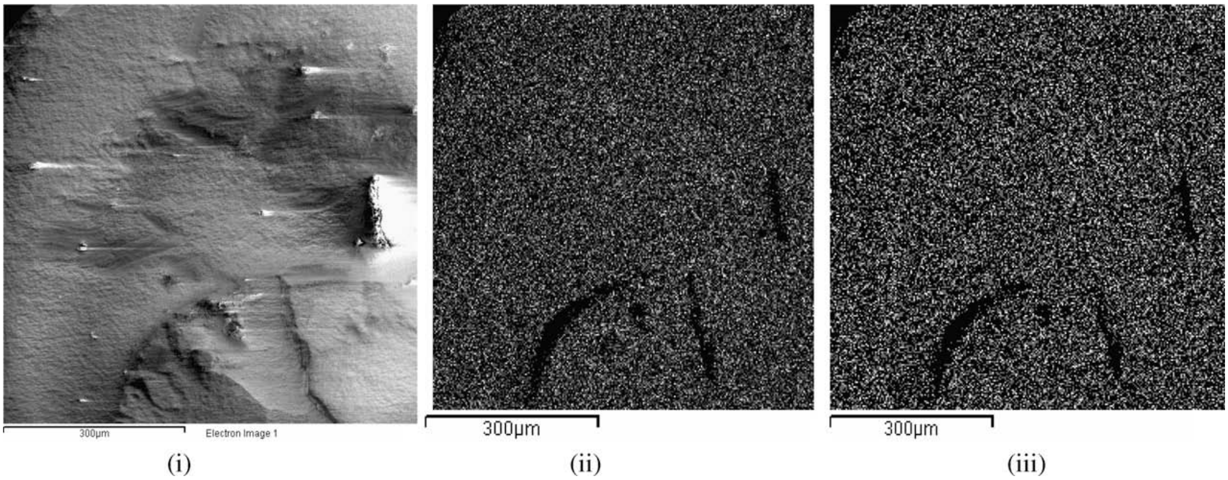

Fig. 5b. Elemental scanning photograph of microsphere sample: (i) secondary electron image; (ii) X-rays from Th; (iii) X-rays from U.

large effect to impregnation in contrast to specific surface area. Detailed studies are now in progress to explain these observations.

3.3. Characterization of gel microspheres by SEM

The first purpose of calcination at 500 °C was to get rid of the residual chemicals from the pores, which causes to have clean porous matrix for impregnation. The second was to enhance the chemical stability of ThO_2 gel microspheres towards uranyl nitrate solution. The SEM images of fractured surface of the microspheres of compositions before impregnation and after impregnation followed by calcination are given in Figs. 4(a) and 4(b), respectively. It can be seen that sub micron size pores are distributed uniformly across the fractured surface of the microspheres. These pore structures get modified due to impregnation of uranyl nitrate followed by calcination (Fig. 4(b)). This is attributed to the strain imparted in the pore structure due to the decomposition of uranyl nitrate solution during the calcination step.

The homogeneous distribution of uranium in the calcined microspheres is very important since these microspheres will be used for pellets production. Figs. 5(a) and 5(b) show the energy dispersive spectrometry (EDS) elemental mapping in the impregnated microspheres with two different magnifications. In Figs. 5(a) and 5(b), (i) represents the image of secondary electron beam scanned over the microspheres. (ii) and (iii) represents the energy dispersive X-rays coming out of the scanned portion from Th and U respectively. By overlapping the portions (ii) and (iii) the distribution of Th and U over the portion scanned could be determined. By this procedure, the distribution of uranium was observed to be very uniform in the microspheres. For different areas of the microspheres scanning was repeated, and the result confirmed the uniform distribution of uranium. These data show that uranyl nitrate has penetrated into the pores having interconnectivity which result in formation of the uniform distribution of uranium in the microspheres.

3.4. Study of reproducibility of uranium loading

As discussed in Section 3.2, the feed solutions of [Th] = 1.25 M, *R* = 1.15 and [Th] = 1.20 M, *R* = 1.35 gave the best results in the various compositions tested. The next step is to ascertain that such conditions reproducibility yields the microspheres of controlled morphology, loaded with a fixed quantity of uranium. Table 5 lists the characteristics of microspheres for three batches of same feed composition [Th] = 1.20 M, *R* = 1.35. The microspheres of all three batches (denoted as IMPC-1, IMPC-2 and IMPC-3) were prepared

Table 5
Characteristics of ThO_2 microspheres of different batches of the same feed composition [Th] = 1.20 M, $R = 1.35$ under taken for consistency studies

Batch no.	Specific surface area (m^2/g)	Cumulative pore volume (cm^3/g)	Nature of pores	Uranium loaded (wt%)
IMPC-1	28.05	0.0327	Micro and meso	3.91 4.09
IMPC-2	28.45	0.0388	Micro and meso	3.99 3.81
IMPC-3	29.47	0.0348	Micro and meso	4.17 3.84
Mean value				3.97 ± 0.12

by using the identical process conditions for gelation, washing, drying and heat treatments. It can be seen that the specific surface areas of IMPC-1, IMPC-2 and IMPC-3 are quiet close ($28.05\ m^2/g$, $28.45\ m^2/g$ and $29.47\ m^2/g$, respectively). The adsorption-desorption curves for IMPC-1, IMPC-2 and IMPC-3 calcined at 500 °C for 3 h in air are presented in Fig. 6(a). The cumulative pore volume of these samples varied from 0.0327 to $0.0388\ cm^3/g$ (Table 5). Fig. 6(b) shows the pore size distribution of these three batches. This figure clearly shows that for all three batches the particles have micro as well as meso porosities in them. Table 5 lists the amount of uranium loaded in these microspheres for the optimum set of impregnation conditions. For each batch, the impregnation experiments were carried out in triplicate. The average uranium content of the $(Th,U)O_2$ microspheres analyzed by Davies and Gray method was found to be 3.97 ± 0.12 wt% of $(Th,U)O_2$ in all the samples.

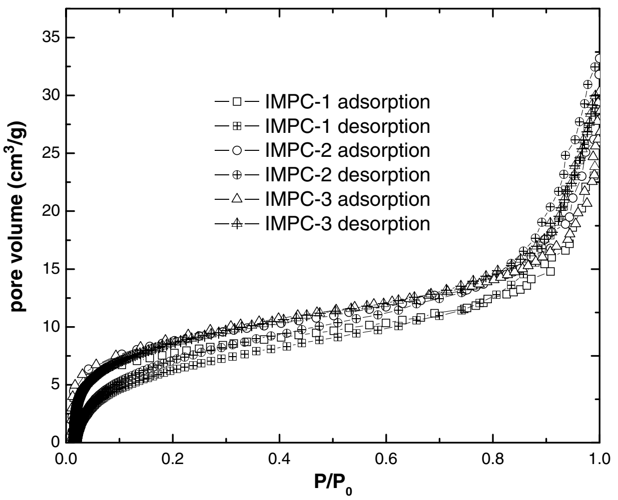

Fig. 6a. Adsorption–desorption isotherms for IMPC-1, IMPC-2 and IMPC-3.

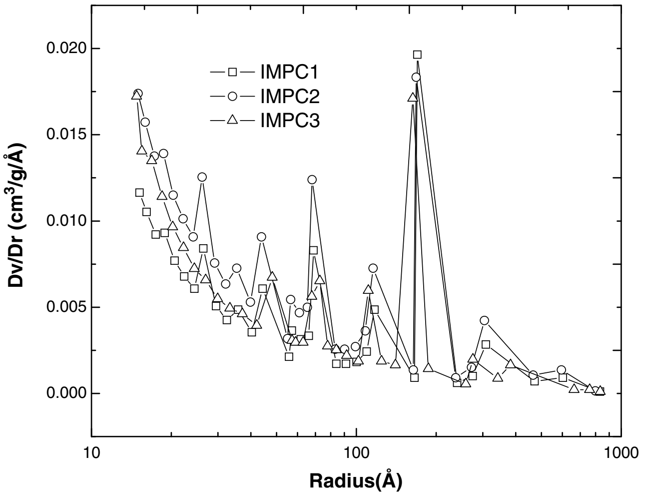

Fig. 6b. Pore size distribution for IMPC-1, IMPC-2 and IMPC-3.

3.5. Pelletization and sintering

It was found during pelletization that the microspheres after impregnation become softer and therefore can readily be converted into good quality pellets. In the recent development study of $(U,Pu)O_2$ kernels by internal gelation process at ORNL [12], the use of pre-boiled HMTA, urea solution has been reported. This solution yielded porous calcined kernels that could be used as a direct-press feed for fabrication of Fast Breeder Reactor fuel. Controlled crystal growth was seen in the microspheres formed

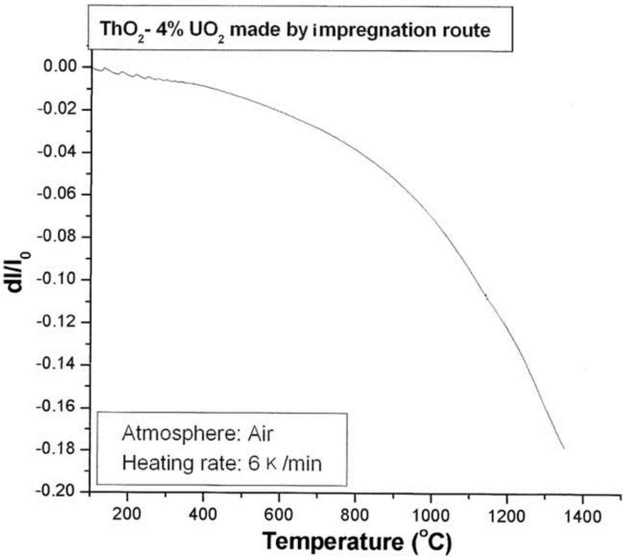

Fig. 7. Shrinkage behaviour of $(Th,U)O_2$ pellet containing 4 mol% uranium.

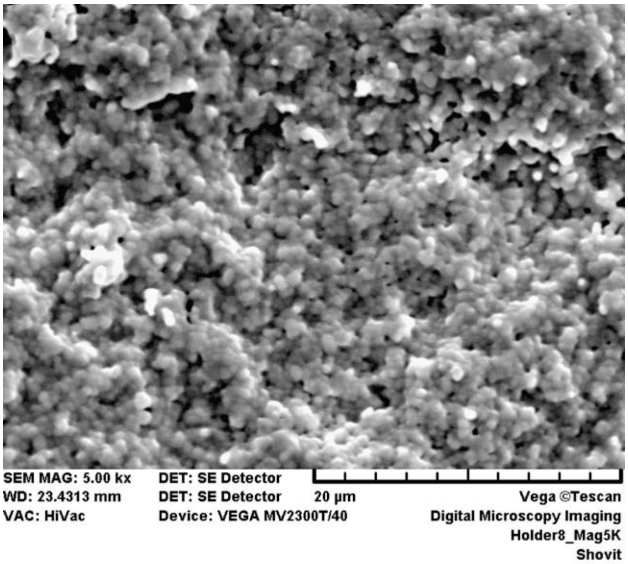

Fig. 8. Microstructure of ThO_2 pellet containing 0. 34 wt% uranium sintered in air at 1350 °C for 4 h (sintered density = 90% of T.D.).

by use of the HMTA, urea solution pre-boiled for 60 min or less. On gel formation it renders big crystallites in the microspheres which modify the pore characteristics favorably. Similar results were obtained in this study for thoria gels prepared by pre-boiled HMTA, urea solution. Another reason for obtaining a soft product may be the decomposition of uranyl nitrate solution, followed by the escape of residual gases during calcination step which resulted strain in the gel matrix, thus making it further softer. The green pellets prepared had densities in the range of 4.5–5 g/cm^3 when pelletized by a uni-axial press using a compaction pressure of ~225 MPa.

The shrinkage behaviour of the pellet studied using a dilatometer in air atmosphere is shown in Fig. 7. From the figure it is clear that shrinkage process started at around 250 °C, which is much lower temperature at which shrinkage could be observed due to sintering. Ananthasivan et al. [18] systematically studied the sintering characteristics of thoria doped with group VB elements. They reported the formation of pellets with a sintered density of 97% T.D. below 1300 °C using the powder synthesized from wet chemical route. A close look of Fig. 7 also reveals the existence of three different slopes in the shrinkage pattern. In the temperature region 250–600 °C the shrinkage was very less. In the temperature range of 600–1200 °C the shrinkage attained to around 50% of total shrinkage observed. The shrinkage observed in the temperature region 1200–1350 °C amounts to around 30% of the total shrinkage.

The green pellets sintered in air at 1350 °C for duration of 4 h which contained less than 2 wt% of uranium, could not be sintered to higher than 90% of T.D. The pellets containing higher amount of uranium (>3 wt%) could be sintered to ~ 96% T.D. under the similar conditions. Figs. 8–12 show the SEM photographs of sintered pellets having uranium in the range of 0.34–4.5 wt%. From Figs. 8 and 9, it is seen that a large porosity still remains in these pellets whereas the pellets containing ~4 wt% of uranium was found to

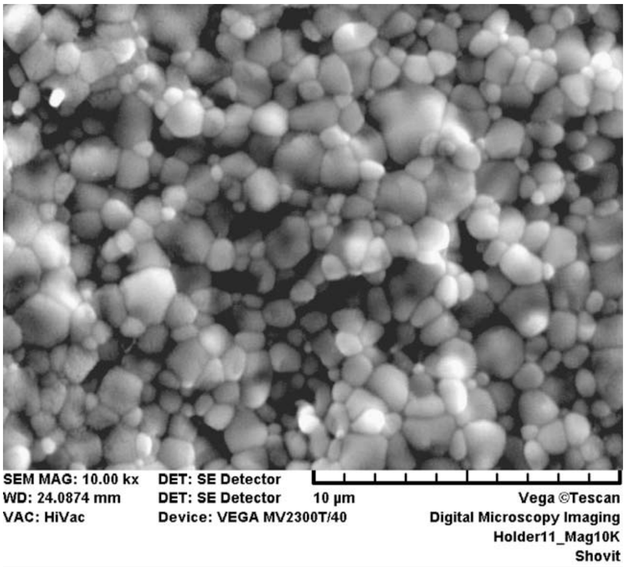

Fig. 9. Microstructure of ThO$_2$ pellet containing 1.61 wt% uranium sintered in air at 1350 °C for 4 h (sintered density = 93% of T.D.).

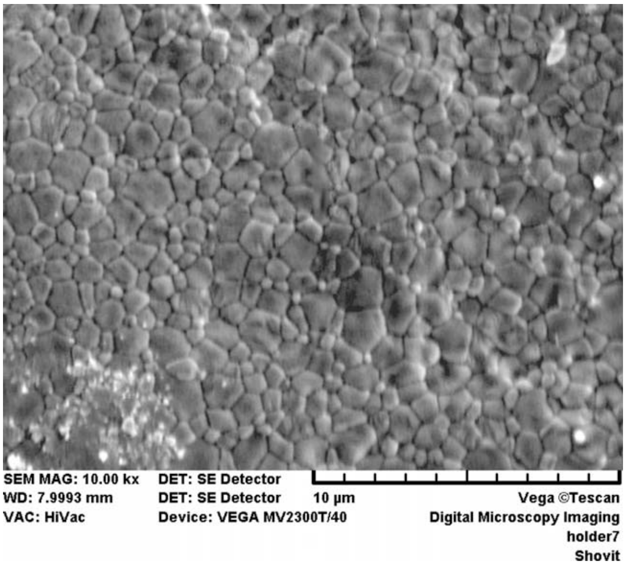

Fig. 10. Microstructure of sintered ThO$_2$ pellet containing 4.5 wt% uranium sintered in air at 1350 °C for 4 h (sintered density = 96% of T.D.).

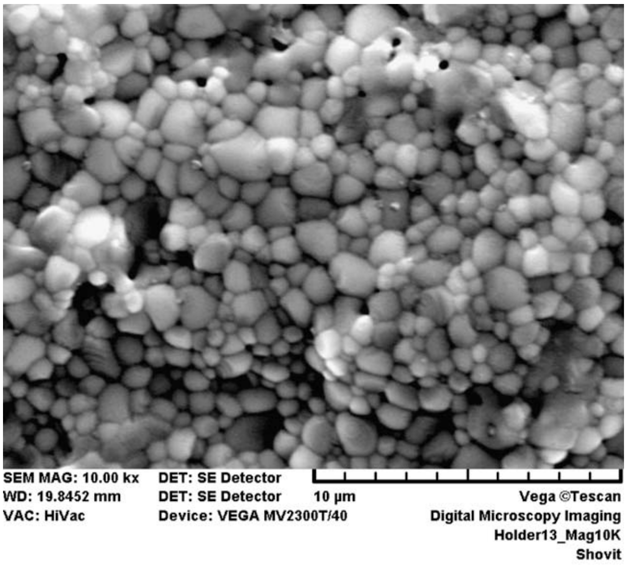

Fig. 11. Microstructure of sintered ThO$_2$ pellet containing 4.2 wt% uranium sintered in air at 1350 °C for 4 h (sintered density = 94.1% of T.D.).

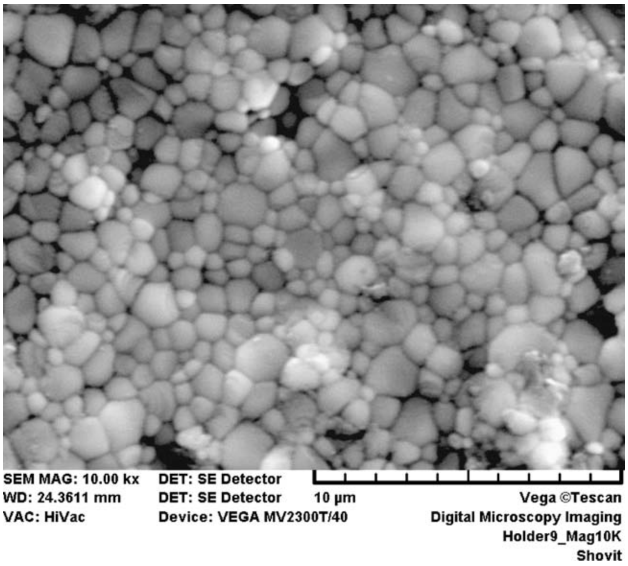

Fig. 12. Microstructure of sintered ThO$_2$ pellet containing 4.35 wt% uranium sintered in air at 1350 °C for 4 h (sintered density = 95.2% of T.D.).

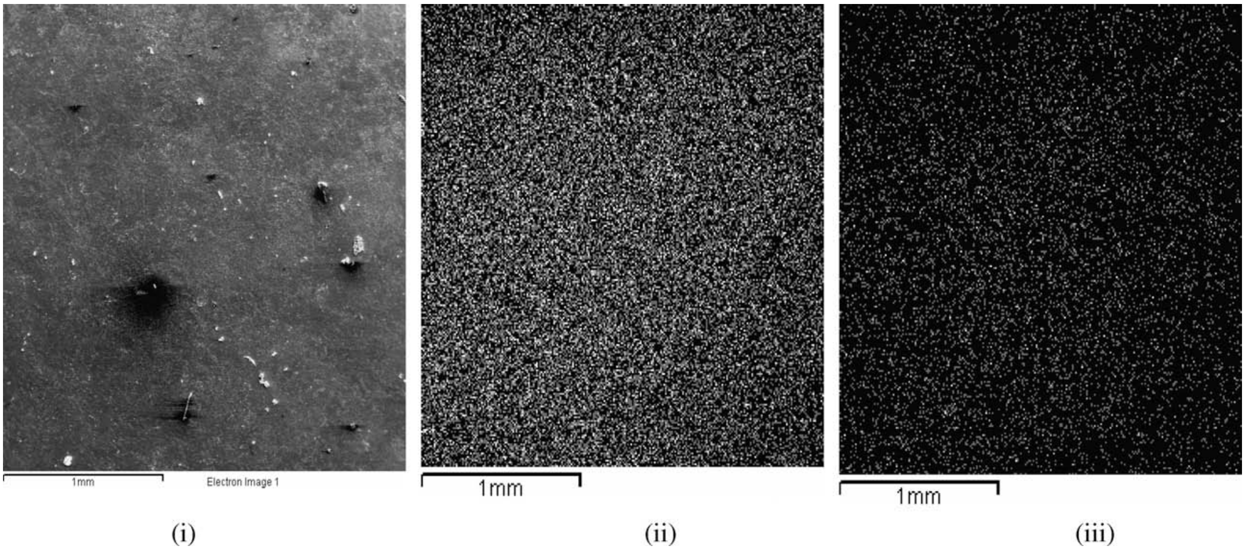

Fig. 13. Elemental scanning photograph of sintered pellet sample: (i) secondary electron image; (ii) X-rays from Th; (iii) X-rays from U.

be more dense (Figs. 10–12). The sintering temperature required to attain a 96–97% of T.D. dense $(Th,U)O_2$ pellet in reducing atmosphere [3] was much higher compared to the sintering temperatures in the present study. It is well known that the addition of aliovalent cations accelerates the sintering of thoria [19,20]. In the present case during sintering in air, uranium exists in higher oxidation state ($>4^+$). The presence of uranium in higher oxidation state in UO_{2+x} matrix is known to incorporate cationic vacancies in the matrix, which is responsible for the enhanced cation diffusivity [21]. The pellets originated from the same composition loaded with 0.34, 1.61 and 4.5 wt% of uranium have sintered densities 90%, 93% and 96% of T.D., respectively (Figs. 8–10). The pellets prepared from different compositions which contained more than 4 wt% of uranium also could be sintered to higher than 94% of T.D. (Figs. 11 and 12).

The distribution of uranium in the sintered pellets was evaluated with the help of energy dispersive spectrometry as evaluated in microspheres. Fig. 13. shows the elemental mapping for Th as well as for U in a sintered pellet. This confirmed a homogeneous distribution of uranium across the pellet. Since the pellet is prepared from microspheres having a uniform distribution of uranium, homogeneous distribution of uranium across the pellets was also expected.

4. Conclusions

Internal gelation process has been standardized for the preparation of porous ThO_2 microspheres suitable for reproducible and uniform loading of about 4 wt% of uranium. The morphology of the ThO_2 microspheres significantly depends on the composition of the feed solution and pre-treatment of HMTA, urea solution. Loading of uranium was studied as a function of vacuum, concentration of uranyl nitrate solution, duration of impregnation and the morphology of the ThO_2 microspheres. The extent of uranium loaded depends on pore volume and pore size distribution of the ThO_2 microspheres rather than their specific surface area. Using the standardized process flow-sheet for the preparation of ThO_2 microspheres and impregnation of uranyl nitrate solution, homogeneous loading of uranium within 3% of the desired value could be obtained. Use of pre-boiled HMTA, urea as well as an intermediate calcination step was found to give the microspheres which could be easily pelletised even at 225 MPa pressure. The pellets containing >3 wt% of uranium could be sintered to ~96% T.D. by heating at 1350 °C in air for 4 h. The elemental mapping showed that uranium was distributed in the microspheres as well as in the pellets homogenously.

Acknowledgements

The authors are thankful to Dr S.K. Aggarwal, Head, Fuel Chemistry Division for his keen interest and support in the work. The authors sincerely thank Shri. T.V. Vittal Rao, FCD, BARC for surface area and pore size measurements and Dr T.R.G. Kutty for his kind help in processing the dilatometric data.

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