



Investigation of production conditions of $\text{ThO}_2\text{--UO}_3$ microspheres via the sol–gel process for pellet type fuels

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Abstract

The aim of the present study is the preparation of $\text{ThO}_2\text{--UO}_3$ gel microspheres up to 40% UO_3 , suitable as press feed for producing homogeneous and sinterable ThO_2 and thorium based $(\text{Th,U})\text{O}_2$ pellet type fuels using sol–gel process. Without reducing the uranium oxidation state to (IV) and without using any complexing agent, a simple external gelation process was studied taking full advantage of the gelation features of thorium. The source sols used for the processes were prepared by the ammonia addition method where starting thorium and uranium nitrate solutions were heated and partially neutralized by aqueous ammonia under pH control at different pH set and neutralization mode for each uranium mole ratio. Crackfree microspheres suitable for gelation were obtained using a hexone–(10%) CCl_4 mixture as the drop formation medium and ammonia as the gelling agent. The dimensions, sphericity, bulk densities and specific surface area of microspheres were determined. The microspheres were compacted and then the pellets were sintered in a 75% Ar–25% H_2 atmosphere at 1100°C for 150 min. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The sol–gel method is a method for producing high performance and highly reliable ceramics. A shape is produced using the fluidity of a sol such as a liquid after which it is solidified, reaching a gel state without losing the high homogeneity it possessed as a sol. A ceramic is then produced from this gel by sintering. Sol–gel processes have been applied to the fabrication of nuclear fuels since 1960s or earlier. Various methods have been reported in several thorium fuel cycle and sol–gel process symposium proceedings [1–3]. Although sol–gel processes have been mainly developed for production of dense ceramic microspheres of uranium and thorium used as fuel in high temperature reactors (HTRs), the application of sol–gel derived microspheres as feed material also has important production advantages for the pellet type fuel fabrication. Recently, the sol–gel microsphere pelletization (SGMP) process to fabricate high density pellets of ThO_2 and $(\text{Th,U})\text{O}_2$ was studied. Mic-

rospheres being practically dust free, their use as press feed eliminates dust generating steps from the pelleting process. Additionally, the free flowing property of microspheres allows important process line simplifications. Sol–gel microspheres of mixed fuel have a homogeneous composition resulting from coprecipitation of heavy metals. This facilitates the solid solution formation of mixed oxides which is an important prerequisite to obtain good pellets in the sintering step of the process [4–6].

In recent years the sol preparation studies have been focussed on partial neutralization of heated $\text{Th}(\text{NO}_3)_4$ and $\text{Th}(\text{NO}_3)_4\text{--UO}_2(\text{NO}_3)_2$ solutions with ammonia under pH control. The production of crackfree gel spheres depends closely on the sol preparation conditions. For preparing good quality sols suitable for crackfree gelation, source sols have to be high in colloid fraction and large in colloid size. For this purpose, a lot of studies have been made investigating the effects of preneutralization, partial neutralization and pH setting modes on the sol properties [7–12].

In this study $\text{ThO}_2\text{--UO}_3$ sols with uranium contents of 0–40% were prepared by ammonia addition. In order to improve the sphericity and to obtain crackfree gel

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microspheres suitable for pelleting, a method using a hexone–(10%)CCl₄ mixture as sphere forming and gelling medium was developed.

2. Experimental

The initial materials, ADU and commercial thorium nitrate salt were provided by Çekmece Nuclear Research and Training Center. ADU has been produced at Çekmece Nuclear Fuel Pilot Plant with the purification of Salihli-Köprübaşıy Pilot Plant originated yellow-cake. ADU was dissolved in nitric acid and then uranyl nitrate was prepared by successive evaporation–crystallization operation steps.

In this study ThO₂ and (Th,U)O₂ pellets were prepared according to the flow sheet given in Fig. 1.

2.1. Sol preparation

ThO₂–UO₃ source sols with uranium contents of 0–40% were prepared starting from mixed nitrate solution of Th(NO₃)₄ and UO₂(NO₃)₂. The concentration of (Th + U) was designed to be 1.6 mol/L before neutralization and to become finally ≈1.0 mol/L. Sols were neutralized up to about 85% of partial neutralization by using NH₄OH, whose concentration was (8.89 – 4.44x) mol/L, where x is the mole ratio of U/(Th + U). The apparatus used for the neutralization is shown in Fig. 2(a). The apparatus consists of a production vessel heated to (100 ± 5)°C with an oil bath, a pH monitoring section cooled at 30°C, a dosimat (Metrohm 665) for injecting ammonia and a titroprocessor (Metrohm 686) for controlling the operation of dosimat according to the pH monitored. For the control, part of sol was circulated from the production vessel to the pH monitoring section and then returned. The ammonia addition was continued when the monitored pH was lower than a preset value, thus the pH increase with ammonia injection and its decrease with conversion into colloids were repeated and the neutralization was advanced stepwise.

2.2. Gelation

The sphericity of microspheres mainly depends on the interfacial tension of the source sol and drop forming medium and on the density difference between both liquids. Interfacial tension acts to minimize the surface area of sol drops to make them spherical and density difference to deform them into flat ellipsoids. The NH₃ solubility in organic solvent is an important parameter which provides necessary prehardening of microspheres before gelation. For this purpose, the survey of organic solvents was made on, interfacial tension, NH₃ solubility and density. Three different media for sol drops formation were investigated:

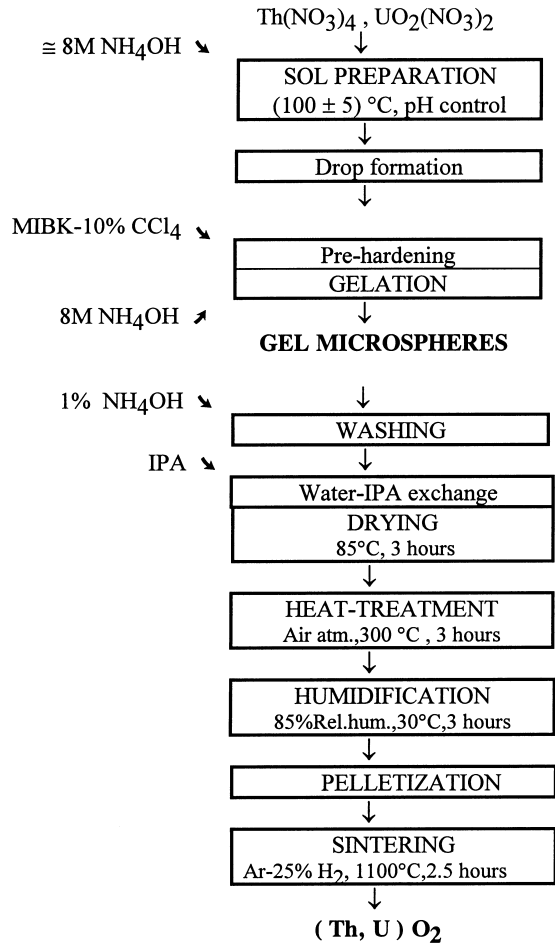


Fig. 1. Flow sheet of the process.

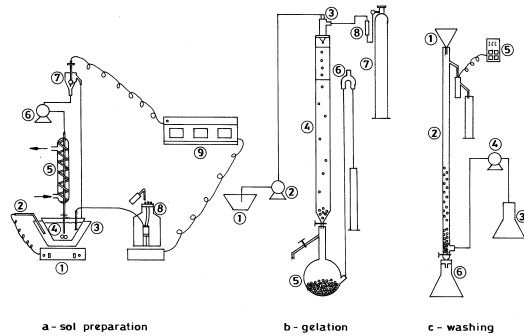


Fig. 2. Apparatus for sol preparation, gelation and washing: (a) sol preparation: 1 – thermostatically controlled heater, 2 – thermocouple, 3 – oil bath, 4 – sol preparation vessel, 5 – cooling tube, 6 – circulation pump, 7 – pH monitoring section, 8 – dosimat, 9 – titroprocessor; (b) gelation: 1 – sol vessel, 2 – peristaltic pump, 3 – nozzle, 4 – gelation column, 5 – reservoir, 6 – adjustment of level, 7 – argon tube, 8 – flow meter; (c) washing: 1 – sphere feed, 2 – washing column, 3 – washing solution, 4 – pulsed pump, 5 – conductivity meter, 6 – reservoir.

- Toluene-(10, 20, 30, 40 vol.%) isoamyl alcohol mixtures,
- Hexone (methyl isobutyl ketone),
- Hexone-(10 vol.%)CCl₄ mixture.

In order to improve the sphericity and to obtain crackfree microspheres a method using a hexone-(10%)CCl₄ mixture as a sphere forming medium was developed. Gelation was carried out in the apparatus shown in Fig. 2(b). A stainless steel nozzle with an inner diameter of 0.60 mm was used for sol drops formation. The nozzle was adapted into a system giving permission to inner passage of sol which is dispersed into droplets by external air flow. The sol drops system was vertically placed at the top of the gelation column. Sols were added to the system at various feed-rates using a peristaltic pump. The gelation column contains two phases. The upper phase is water immiscible and is composed of 90% hexone and 10% CCl₄ to provide prehardening. The lower phase where the microspheres are gelled completely is 8M NH₄OH. The resulting gel microspheres are collected in a reservoir connected to the bottom of the column.

2.3. Washing

The formed gel microspheres were placed in a column and washed by diluted NH₄OH (1% v/v) to remove NH₄NO₃ formed from the precipitation reaction which causes serious problems in the further heat-treatment steps. For a good contact of microspheres with washing solution, ammonia is added from the bottom of the column to form a fluidized bed, using a pulsed pump (Fig. 2(c)). It was found that NH₄NO₃ is completely removed by washing with a washing solution about 15 fold excess volume of microspheres.

2.4. Drying, heat-treatment and humidification

To obtain soft microspheres for easy pelletization, the water in the gel microspheres was replaced by isopropyl alcohol (IPA) until the water content of the IPA in the gel microspheres was lowered to less than 1 wt%. These microspheres were put to form a monolayer on a sieve of stainless steel and IPA was then removed by heating in a dryer at 85°C. The effect of heat-treatment and humidification on the green and sintered pellet densities were investigated.

The dried microspheres were heat-treated at 300°C for 3 h. The specific surface area of the heat-treated microspheres was measured by the BET method using a high speed surface area analyser (Micrometric 2200 model). For the determination of the dimension and sphericity of the microspheres, images obtained through optic microscope and video camera were analysed using the image analysis instruments Optomax V and Vids III. To determine the sphericity, 10 microspheres for each U

ratio were chosen randomly; the maximum and minimum diameters were measured; the mean values and sphericity were calculated. Equivalent diameters were calculated from the equation

$$\text{Eq } \phi = [(\phi \text{ max})^2(\phi \text{ min})]^{1/3}. \quad (1)$$

The bulk density of the heat-treated microspheres was calculated from the equivalent diameter and the sol concentration as % of the theoretical density of (Th,U)O_{2+x}. The theoretical density of (Th,U)O_{2+x} for each U/(Th+U) mol% has been determined from the data of *x* value and lattice constant of standard (Th,U)O_{2+x} equilibrated in air at 1200°C, in a previous study [6].

The moisture content of the heat-treated microspheres was calculated to be 3–4 wt% from the thermal analysis data using a Shimadzu Thermal Analyser(TGA-30) heating them at 750°C. The microspheres were humidified in a humidification chamber under 85% relative humidity during 3 h at 30°C. In this case the moisture content of microspheres was ≥ 18 wt%.

2.5. Pelletizing and sintering

The microspheres were compacted in a hydraulic press with a floating die system and double pressing action was used. The maximum achievable green pellet densities for each group of microspheres including 0–35% UO₃ that their bulk densities are considerably different from each other, were obtained by arranging only the press stroke height. The geometric densities of green pellets were measured and then the pellets were sintered in 75% Ar–25% H₂ atmosphere at 1100°C for 150 min. The sintered pellet densities, open and closed porosities were calculated from application of m-xylene buoyancy method based on the Archimedes principle, by weighing the dry pellets in air and then weighing the m-xylene impregnated pellets in air and m-xylene [13]. The X-ray diffraction diagrams of the (Th,U)O₂ sintered pellets were taken using a Perkin–Elmer model diffractometer.

3. Results and discussion

ThO₂ and ThO₂–UO₃ sols suitable for gelation into microspheres have been studied previously. These sols have to be high in colloid fraction and large in colloid size. It is well known that these properties closely depend on partial neutralization, preneutralization and pH setting modes. U is more difficult in its conversion into colloid than Th and once colloid forms, it tends more to coagulate into precipitates [11,12]. So, in this study parameters influencing colloid fraction and colloid size were arranged according to the U content of sols. For obtaining good quality sols at high U content, it is necessary to increase its colloid fraction as high as possible

and to keep the limit of partial neutralization attainable without precipitation. It was observed that at higher pre-neutralization, the decrease of pH to its setting value take shorter time and this means easier conversion into colloid. For this purpose the preneutralization ratios were taken as 50%, 55%, 65% for 0%, 5–10%, $\geq 20\%$ U contents, respectively.

In the preliminary studies, it was seen that at the low partial neutralization ratio the sols were unsuitable for gelation and gel-sphere failure occurred. The failure was a crack for 0%, 5% U and a hole for higher U contents. The preset pH was fixed at a single value in the case of U content $>20\%$ to obtain more colloid and in the case of U content $\leq 20\%$ it was changed after the neutralization being sufficiently repeated at the first preset pH. The 2nd stage neutralization was executed by a single ammonia injection to reinforce colloids. The neutralization rate was 2%/min in early steps in both cases. The rate was lowered to 0.15% in the 2nd stage of two-stage neutralization. At the higher neutralization rates pH increase became too rapid to keep the pH around the setting value and unpeptizable precipitations occurred. Table 1 summarizes the best conditions for each set of U. It was determined that good sols with (0–35%) U content suitable for gelation into microspheres were produced. Although the partial neutralization reached to a low value (69.2%) for the source sols with 40% U, unacceptable precipitations occurred and the gelation

behaviour of these microspheres was bad. The microspheres produced from these sols could not to be compacted.

For sol drops formation three different media were investigated. Taking into consideration a previous study [14] where 50% toluene and 50% isoamyl alcohol have been used as the drop formation medium, toluene-(10,20,30,40%) isoamyl alcohol mixtures pretreated with 8 M ammonia solution were tested. Due to the high NH_3 solubility in the $>10\%$ mixtures of toluene-isoamyl alcohol, sol drops were gelled suddenly unless necessary pre-hardening was carried out, resulting in intolerable deformations. Additionally, the high NH_3 causes plugging of nozzles. With the mixture toluene-(10%) isoamyl alcohol, the shape of gelled microspheres was like a lentil. In the case of hexone as a drop formation medium, the gelled microspheres were slightly ellipsoid in shape. In both cases NH_3 solubility is above the level (0.3 mol/L) sufficient for gelation. The deformation of gel microspheres is attributed to the insufficient interfacial tension. The interfacial tension of the CCl_4 -water system is 46.5 mN/m at 20°C which is about four times larger than that of the hexone-water system but the NH_3 solubility is lower than that of hexone. For the purpose of improving the sphericity, it was thought that the utilization of CCl_4 and hexone by mixing in a convenient ratio would provide sufficient interfacial tension, NH_3 solubility and decreased density difference between

Table 1
Production conditions and gelation behaviour of ThO_2 and $\text{ThO}_2\text{-UO}_3$ sols

U/(Th + U) (mol%)	0	5	10	20	30	35	40
(Th + U) conc. (mol/L)	1.6	1.6	1.6	1.6	1.6	1.6	1.6
NH_4OH conc. (mol/L)	8.89	8.67	8.45	8.00	7.56	7.34	7.11
Preneutralization (%)	50	55	55	65	65	65	65
Max. pH	2.95	3.05	3.00	3.01	2.95	2.95	2.95
1st stage neutralization							
pH set	2.75	2.75	2.75	2.75	2.90	2.90	2.95
Neutralization rate (%/min)	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Max. pH	2.85	2.85	2.83	2.83	2.93	2.95	3.09
Heating time (min)	310	170	155	115	180	180	210
Final step interval (min)	35	35	30	30	30	30	100
Partial neutralization (%)	77.0	62.0	57.8	69.2	70.6	74.0	69.2
(Th + U) conc. (mol/L)	1.03	1.11	1.13	1.07	1.06	1.04	1.07
2nd stage neutralization							
pH set	3.05	3.20	3.05	3.05	–	–	–
Neutralization rate (%/min)	0.15	0.15	0.15	0.15	–	–	–
Max. pH	3.15	3.20	3.06	3.05	–	–	–
Heating time (min)	50	100	145	65	–	–	–
Partial neutralization (%)	85.0	70.6	74.5	76.4	–	–	–
(Th + U) conc. (mol/L)	1.00	1.06	1.04	1.03	–	–	–
Precipitation ^a	A	A	A	A	A	B	B
Gelation behaviour ^b	①	①	①	①	①	①	②

^a Volume (%) a week after preparation: A(0), B(<0.2), C(>0.2).

^b ①: good, ②: bad

sol and drops forming medium to improve the sphericity.

It was determined that the hexone–(10%) CCl_4 mixture provides sufficient interfacial tension and NH_3 solubility necessary to obtain crackfree microspheres having good sphericity. In comparison with the other methods previously reported which use hexone and CCl_4 , this method seems to be advantageous for the sphere forming medium.

For the purpose of investigating the effect of heating temperature on sintering, dried microspheres of ThO_2 were heat-treated at 200°C, 300°C, 400°C and 450°C for 3 h in air. The microspheres were compacted into pellets at a pressure of 200 MPa and then green pellets were sintered at 1100°C for 3 h in air. The green and sintered densities of ThO_2 pellets derived from as-dried and as heat-treated microspheres is given in Fig. 3. The failed pellets are indicated by a closed symbol. As seen, green pellet densities increase with increasing temperature. Although the green pellets were intact, the sintered pellets derived from 400°C and 450°C heat treatment were cracked. The crack is attributed to the low compactability. The ratio of green pellet density ρ_g to source microsphere density ρ_m is a measure of the compactability. The compactability of microspheres is plotted against the heat treatment temperature in Fig. 4 where the ρ_g/ρ_m ratio is seen to decrease with increasing temperature. The decrease at 400 and 450°C is very sharp.

ThO_2 microspheres heat treated at 300°C were humidified to different water contents and compacted into

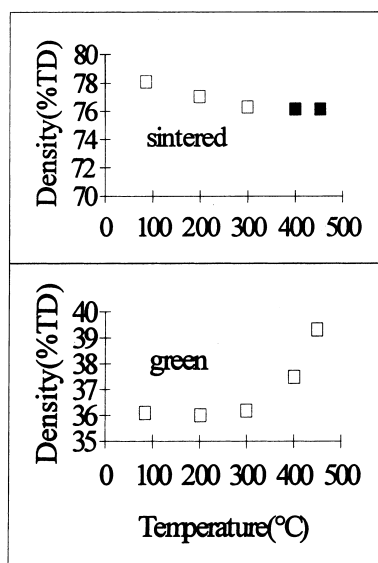


Fig. 3. Green and sintered densities of pellets derived from as-dried and as-heat-treated microspheres. (The open or closed symbol indicates the success or failure in obtaining satisfactory pellets, respectively.)

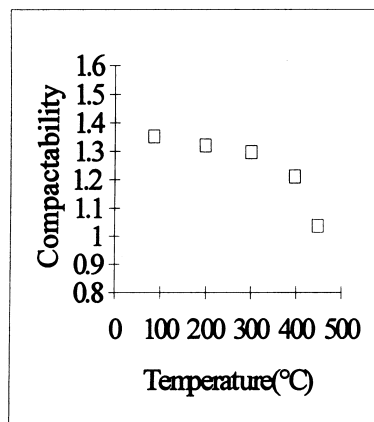


Fig. 4. Compactability of as-dried and as heat-treated microspheres.

pellets at 300 MPa and then sintered at 1100°C for 3 h in air. The effect of included moisture on green and sintered densities of the pellets is given in Fig. 5. As seen, the green pellet density increases with increasing moisture and reaches a maximum at 15% humidification. Three beneficial effects of the adsorbed moisture may be considered. First, the moisture facilitates the compaction and seems to act as a lubricant between and within microspheres. Second, the moisture behaves as a binder on compaction. This effect is clearly seen in Fig. 5. For the <10% humidification green pellet failure occurred, for higher humidification no pellet failure was observed. The third effect of humidification is to aid the densification during sintering. In the >15% humidification, nearly the same sintered density was attained in spite of the decrease of green density with increasing the adsorbed moisture.

Taking into consideration heat-treatment and humidification effects on the green and sintered pellet densities, the microspheres which will be used in this process were heat treated at 300°C in air for 3 h and then humidified to a moisture ratio $\geq 18\%$.

Dimension and sphericity of heat-treated microspheres at 300°C were determined using Image Analyser. The results are given in Table 2. The differences between the diameters of microspheres for each U ratio are mainly related to the variations in the drop formation system, and as a result considerable differences in bulk density were obtained (13–28%).

The bulk densities of the heat-treated microspheres at 300°C calculated from the equivalent diameter and the sol concentration are given in Table 3. As seen, the BET specific surface area of these microspheres are very high. The surface of these spheres had a brittle pattern including very small pores. In comparison to powders, the microspheres had a very different pelleting and sintering behaviour. For a good sintering it is desired that the

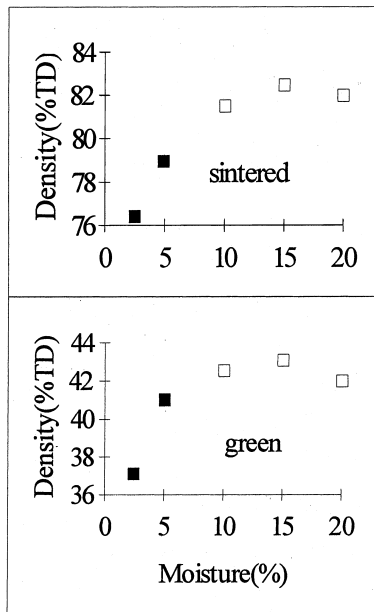


Fig. 5. Effect of included moisture on green and sintered pellets derived from 300°C heated microspheres. (The open or closed symbol indicates the success or failure in obtaining satisfactory pellets, respectively.)

green density of the pellet reaches about 55% of the theoretical density. The densities of green pellets produced via sol-gel are considerably lower (32–41%TD) than the

Table 2
The dimension and sphericity of heat-treated microspheres

U (mol%)	Mean value			
	Max ϕ (μm)	Min ϕ (μm)	Eq. ϕ (μm)	Sphericity
0	1184.4	1098.2	1154.9	1.078
5	1292.4	1161.4	1247.7	1.112
10	1138.0	1023.6	1098.5	1.111
20	1248.5	1042.5	1175.3	1.197
30	1667.2	1504.9	1611.2	1.107
35	1485.5	1211.5	1387.8	1.226
40	1438.8	1335.4	1403.4	1.077

Table 3
Some physical data of microspheres and derived pellets

U%	ρ_m (TD%)	ρ_g (TD%)	ρ_g/ρ_m	ρ_s/ρ_g	ρ_s (TD%)	^a SSA (m^2/g)
0	28.20	41.35	1.46	1.96	81.04	140
5	17.05	32.59	1.91	2.22	72.33	170
10	25.96	39.25	1.51	2.04	79.89	144
20	23.55	36.59	1.55	2.11	77.22	154
30	12.24	24.25	1.98	2.81	68.17	190
35	16.79	32.42	1.96	2.19	71.15	178

^a Specific surface area values of heat-treated microspheres at 300°C.

ρ_m : Bulk densities of heat-treated microspheres at 300°C, ρ_g : Green pellet densities, ρ_g/ρ_m : Compactibility, ρ_s/ρ_g : Sinterability, ρ_s : Sintered pellet densities.

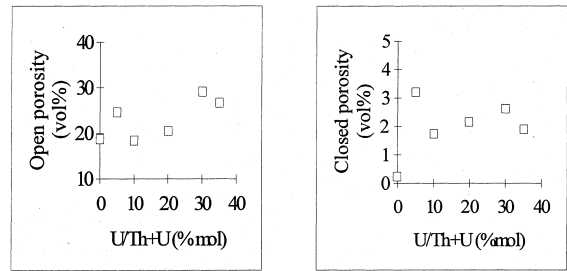


Fig. 6. Open and closed porosity of sintered pellets.

ones produced from powders. But during sintering, suitable properties of microspheres such as, small particle size, homogeneity, sphericity and shrinkage capability between and within microspheres eliminate this disadvantage. Although the utilization of lubricant and binder have no significant effect, the humidification is a very important factor inevitable to obtain intact and high density pellets. The sintered pellet densities are increasingly depending on green pellet densities. The same relation is observed between green pellet densities and bulk densities of microspheres. The bulk densities of microspheres prepared at different U content principally depend on the final sol concentration, sol drop diameter and microsphere diameter after heat-treatment. The different shrinkage of the microspheres diameters during the heat-treatment is related with the colloid fraction and colloid size of the sols prepared under various conditions. The particle sizes in the microspheres are approximately their source sols colloid size (4–10 nm).

It was observed that sintering realized in 75% Ar–25% H₂ atmosphere at 1100°C during 150 min is not sufficient for the closure of the pores in a desirable level. During sintering densification had occurred mainly within the microspheres and not so much between them. This is in agreement with the high open porosity (Fig. 6) measured. In this case the sintered densities also were low. In spite of absence of suitable sintering conditions to obtain high density pellets, the formation of the solid solution takes place in all of the obtained mixed-oxides

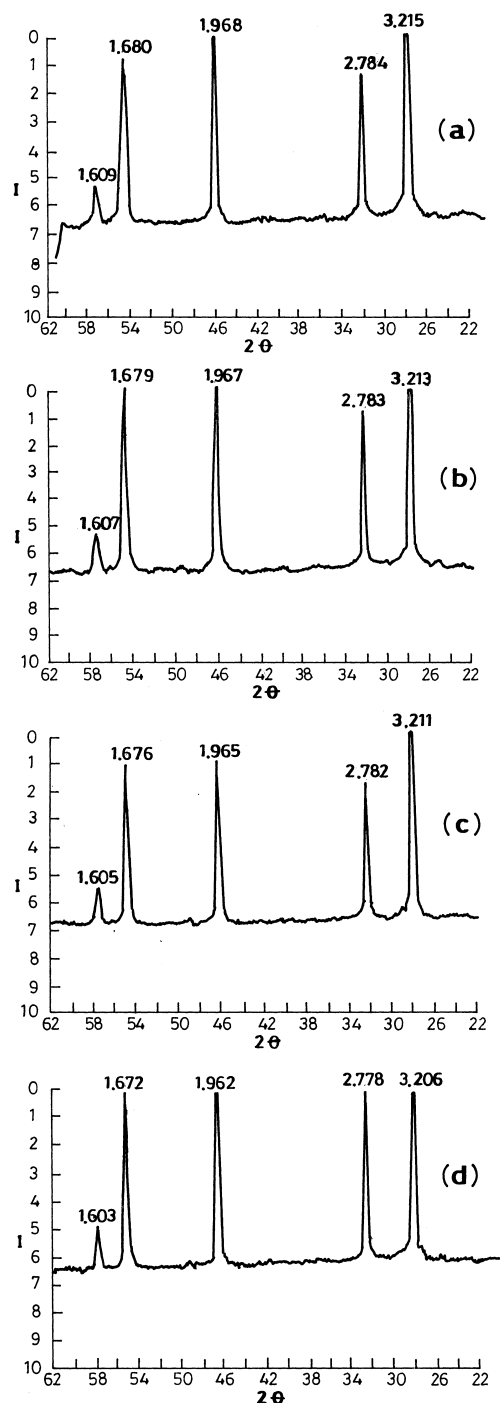


Fig. 7. XRD diagrams of (Th,U)O₂ pellets with U content of 5–35% (a) 5%, (b) 10%, (c) 20%, (d) 35%.

(Fig. 7). Sol-gel microspheres have a homogeneous composition resulting from coprecipitation and this facilitates the solid solution formation. In comparison with the mixed oxide pellets prepared via coprecipitation

of Th and U oxalates in our previous study [15], the results are similar in view of the solid solution formation facility and maximum attainable sintering densities at the same sintering temperature (1100°C). But in this method, the use of microspheres as press feed possesses undoubtedly important advantages in comparison with the classical powder techniques, where the dust generation and flowability problems necessitate supplementary precautions in view to minimize the exposure of personnel to radiation and this means more operation steps which complicate the process.

It is necessary to investigate the sintering conditions in order to reach high densities.

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