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PREPARATION OF $^{235}UO_2$-ThO_2 MICROSPHERES BY A SOL-GEL METHOD

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ABSTRACT

A sol-gel technique was used to prepare 210-297-μ-diam $^{235}UO_2$-ThO_2 microspheres in which the Th/U atom ratios were 4.8 and 3.4. The spheres were made from UO_2-ThO_2 sols that were prepared by mixing a UO_2 sol with a ThO_2 sol. Approximately 1 kg of each composition was prepared. The product microspheres had densities of >99% of theoretical and 1-kg crushing strength. The spheres after carbon coating will be irradiation tested in the Dragon Reactor.

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1. INTRODUCTION

The purpose of this report is to describe the preparation of UO_2-ThO_2 microspheres having thorium-to-uranium ratios of approximately 5/1 and 3.5/1 by a sol-gel process. Approximately 1 kg of 210- to 297-μ-diam UO_2-ThO_2 of each composition were prepared. These oxide microspheres were carbon coated with pyrolytically deposited carbon and are presently undergoing irradiation tests in the Dragon Reactor. The carbon coating and preirradiation examination will be reported in a future report.[1] Enriched uranium (97% ^{235}U) was used, and the UO_2-ThO_2 sol preparations consisted of batch preparations in which the total amount of uranium was held at 300 g to achieve criticality control.

The original ORNL sol-gel process[2,3] is limited to uranium compositions in thoria of less than about 10%. Therefore, it was necessary that one of the several methods for making sol-gel UO_2-ThO_2 at higher uranium compositions that are currently being investigated at ORNL be used in this application. A mixed-sol method was selected from other sol-gel methods under current study because it had been evaluated for all UO_2-ThO_2 compositions in small scale (10 to 100 g) laboratory tests.

In the mixed-sol method, a ThO_2 sol is mixed with a UO_2 sol in the correct proportion to give the desired Th-to-U atom ratio. The ThO_2 sol is prepared from steam-denitrated ThO_2[2,3] and the UO_2 sol is prepared by the formate method.[4] For Th/U ratios in the range 3.5 to 5, the (Th + U) concentration is limited to about 1.5 M. At greater concentration, the sols do not have sufficient fluidity.

After the sols are prepared, the sol is formed into gel microspheres in a microsphere forming column using 2-ethyl-1-hexanol containing the surfactants, Ethomeen S/15 (a tertiary amine manufactured by Armour Chemical Co.) and Span-80 (sorbitan monooleate manufactured by Atlas Chemical Co.). The forming column and operating conditions have been described in a previous report.[5] The gel microspheres are dried at low temperatures (100 to 150°C) and are subsequently fired to about 1200°C to achieve high density.

It was required that the Th/U ratios be reasonably close (± 10%) to 5/1 and 3.5/1 and that the values be known accurately. In future studies we plan to determine the accuracy of control on final Th-to-U ratios when preparing mixed oxides by mixed-sol methods.

2. DISCUSSION

Thoria-urania microspheres of 210- to 297-μ-diam and having Th-to-U ratios of approximately 3.5/1 and 5/1 were prepared by a sol-gel method using UO_2-ThO_2 sols that were prepared by mixing a ThO_2 sol with a UO_2 sol. Product specifications for irradiation test specimens were met. Particle densities of >99% of theoretical and carbon contents of <10 ppm were attained.

2.1 Product Specification

The uranium compositions requested were 5/1 and 3.5/1 Th-to-U atom ratios and deviations of ± 10% of the absolute values were permissible. Approximately 1 kg of microspheres of each composition in the size range 210- to 297-μ-diam were required. The particle density required was near theoretical and the carbon content was to be as low as possible. The uranium was to be highly enriched.

2.2 Sol Preparation

Two UO_2 sols were prepared by the formate method[4] using highly enriched uranium. The isotopic composition of the uranium used was the following:

Mass	Wt %
234	1.04
235	97.69
236	0.21
238	1.06

Two separate preparations of UO_2 sols were required because 300 g of U is the limit that we use for criticality control in batch process for laboratory preparation of UO_2 sols. A stock 3.07 M ThO_2 sol was prepared using steam denitrated thoria.[2,3] The mixed sols were prepared by adding the appropriate amount of the 3.07 M ThO_2 sol to each of the UO_2 sols to give UO_2-ThO_2 sols of Th-to-U atom ratios of 4.94 and 3.46. It was assumed that the UO_2 sols contained 290 g of U because experience[4] had shown over many sol preparations that this was the yield in UO_2 sol production. The error introduced by this assumption would only make an error of 2 to 3% in the absolute value of the Th/U ratio, and in this application ± 10% was permissible. The calculated Th-to-U ratios are compared with those obtained by chemical analysis in Table 1. The chemical analysis agreed very poorly with those calculated by material balance. In each case the Th/U ratio was about 25% lower by analysis than by our original mixing calculations. The thorium analysis on the mixed sol suggested that our analyses on the original ThO_2 sol were in error. However, repeat analysis of the ThO_2 sol gave perfect agreement with the original analysis. Thorium and uranium analysis of the fired microspheres gave values in reasonable agreement with material balance calculations (see Section 2.5). Thus, it was concluded that the thorium analyses of the mixed sols are in error. The uranium analyses on the mixed sol were well within the limit of accuracy of the originally estimated uranium concentration and the measured volume of 3.07 M ThO_2 sol (Table 1).

2.3 Microsphere Forming

The formation of gel microspheres by extraction of water from sol droplets into 2-ethyl-1-hexanol in a countercurrent column has been described in detail in previous reports.[4,5] The column was charged with new 2-ethyl-1-hexanol prior to the forming of the gel microspheres. The initial surfactant concentration was 0.5 vol % Ethomeen S/15. After startup, it was necessary to make incremental additions of both Ethomeen S/15 and Span-80 to the organic solvent to prevent particle coalescence, sticking, and clustering (Table 2). The column operation improved in succeeding runs. It is not known whether this was a result of aging of the organic extractant, operational

Table I. Comparison of Calculated Composition of UO_2-ThO_2 Sols with that by Chemical Analysis

Sol Preparation No.	Volumes (ml)			Calculated Th/U Ratio[b]	Calculated Moles ThO_2 Added	Chemical Analysis							
	3.07 M ThO_2 Sol	Water Added[a]	Final UO_2-ThO_2 Sol			U (M)	Th (M)	U + Th (M)	Th/U	NO_3^-/(U + Th)	U(IV) (%)	Total U (moles)	Total Th (moles)
47-49A-97	1986	1161	4542	4.94	6.097	0.2725	1.1635	1.436	4.27	0.123	83.3	1.2377	5.285
47-27-97	1389	1130	3380	3.46	4.264	0.3665	1.1248	1.491	3.07	0.113	75.2	1.2388	3.802

[a]Water added because dilution to ~1.5 M (Th + U) gives good fluidity.

[b]Calculated from moles of ThO_2 sol added and assuming 290 g of U (1.2336 moles) in the UO_2 sol.

Table 2. Operating Conditions of Microsphere Forming Column

Sol Preparation	Forming Preparation[a]	Surfactant Concentration at Start of Run, Vol % Span 80	Surfactant Concentration at Start of Run, Vol % Ethomeen S/15	Sol Flow Rate (ml/min)	Total Forming Time (min)	Description of Column Operation
47-49A-97	P-2-8-1602	0.0	0.5	4.8	209	At start of the run, there was some sol droplet coalescence; however, this seemed to disappear after adding 0.1 vol % Span 80 after 9 min and an additional 0.1 vol % Span 80 after 40 min. There was some particle clustering in the short tapered section during the entire run. Despite the unusual amount of particles stuck together, most of the particles appeared spherical.
	P-2-9-1525	0.3	0.5	4.8	392	Same operational behavior as above; after 75 min 0.1 vol % Span 80 added and after 170 min 0.1 vol % Ethomeen S/15 added.
	P-2-10-1453	0.4	0.7	4.8	363	For the first 80 min of column operation, the sticking of particles to the short tapered section of the column was same as in above two runs. However, at 110 min operation the sticking on the column walls had almost completely disappeared. The last portion of the run was essentially trouble-free.
47-27-97	P-2-11-1455 P-2-11-1600	0.5	0.7	4.8	342	The column operation was not quite as good as P-2-10-1453 run; however, it was much better than P-2-8 and P-2-9 runs. There was a gradual increase in the amount of sticking during the run, but this did not appear to add a significant amount of misshapen particles to the product. The fluidized material in the column that was collected after the sol feed was shut off was labeled 2-11-1600. These microspheres contained some cherry pits.
	P-2-14-1300 P-2-14-1503	0.5	0.8	4.8	363	Small amount of droplet coalescence during first 5 to 10 min of operation. However, after adding 0.1 vol % Span 80 the operation was essentially perfect. This run was the best of all the runs in this series.

[a]In order of runs. The column was started up with new 2-ethyl-1-hexanol and the same alcohol was used throughout.

experience, or proper adjustment of the surfactant concentrations. The gel products from all runs appeared to be acceptable, with only small amounts of clusters or cherry pits.

2.4 Microsphere Drying

The drying conditions that were used were essentially those reported for previous UO_2 or ThO_2 microspheres.[3,4] The gel microspheres were dried in argon at 120 to 140°C using drying times of 15 to 20 hr. The last five microsphere preparations were dried in argon at room temperature prior to heating for time periods of 20 to 90 hr (Table 3). There were not any observable differences in the microspheres as a result of different total drying times.

2.5 Firing of Gel Microspheres and Product Properties

The dried gels were fired to excellent microspheres (Table 4). The spheres have very high density (10.15 to 10.16 g/cm^3), good crushing strengths, and essentially "geometric" surface area. X-ray diffraction measurements showed that solid solution was achieved. The only impurity introduced in the firing was 100 ppm alumina. Carbon analyses were <10 ppm in all cases. The Th-to-U ratios are in good agreement with those calculated from the amounts of UO_2 and ThO_2 that were mixed. We estimate that the accuracy of our mixing technique gave an accuracy of $\pm 3\%$ in the Th/U ratio (Section 2.2). Residual gases after firing were about 0.01 cc/g* and were composed primarily of hydrogen. The spheres produced by the 1400°C firing in H_2 were amber-colored and transparent, which is an effect that was not produced in the 1100°C firings in Ar-4% H_2. Photomicrographs of typical metallographic sections are shown in Fig. 1.

A number of interesting color effects were noted throughout the course of the firings. After the 1100°C firing, the microspheres were not transparent and were

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*Determined by heating to 1200°C in vacuum.

Table 3. Drying of Microspheres

Sol Preparation	Forming Preparation	Drying Conditions Temp. (°C)	Time (hr)	Wt of Dried Gel
47-49A-97	P-2-8-1602	25-70	1.5	450
		70-84	2.5	
		84-120	2.5	
		120-136	9	
	P-2-9-1525	25-60	1	810
		60-70	3	
		70-115	3	
		115-150	8	
	P-2-10-1453	25	80	750
		25-120	10	
		120-140	22	
47-27-97	P-2-11-1455	25	72	521
		25-100	2.5	
		100-120	13.5	
	P-2-11-1600	25	90	209.3
		25-120	2	
		120-140	19	
	P-2-14-1300	25	20	286.0
		25-120	3	
		120-130	18	
	P-2-14-1503	25	42	487.6
		25-100	3.5	
		100-115	19.5	

Table 4. Analyses on UO_2-ThO_2 Microspheres (97.69% ^{235}U) After Firing

Firing Procedure: First Firing - Fired to 1100°C and reduced for 2 hr in Ar-4% H_2; cooled to 25°C in Ar

Second Firing - The 210-297 μ fraction from the first firing was fired to 1400°C and reduced 4 hr in H_2; cooled to 25°C in Ar

Sample No. [a]	3371-78-1400 [b]	3371-80-1400	3371-82-1400
Sol Preparation No.	47-27-97	47-27-97	47-49A-97
Th/U atom ratio [e]	3.41	3.41	4.79
U, %	10.95	10.95	8.18
Th, %	37.3	37.3	39.2
Hg Porosimetry:			
Density, g/cc	10.13	10.17	10.11
Density, % theoretical	99.3	99.7	99.6
Porosity, %	<1	<1	<1
Crushing Strength, g	1152	1008	907
Surface area, [c] m^2/g	0.004	0.003	0.004
X-ray crystallite size, A	1537	1280	1348
Lattice Parameters	5.5679	5.5680	5.5679
Carbon, ppm	<10	<10	<10
Aluminum, ppm	100	110	110
Gas Release to 1200°C in vacuum:			
Total vol, cc/g	0.011	0.007	0.007
Composition, vol %			
H_2	91.4	68.8	81.1
H_2O	0.69	5.24	2.16
N_2 + CO	7.92	13.4	16.2
Ar	-	0.26	0.27
CO_2	-	12.0	0.27
O_2	-	0.26	-
Weight of 210-297 μ fraction, g	439.2	539.3	1295.1
Screen Analysis, [d] wt %			
+297 μ	20.6	9.2	15.5
249-297 μ	65.9	74.9	69.0
210-249 μ	0.6	1.7	3.2
-210 μ	12.9	14.2	12.2

[a] All analyses on 1400°C-fired material except as indicated.

[b] Contained some cherry-pitted spheres.

[c] Calculated geometric surface area of 210-297 μ spheres is $2.0\text{-}2.8 \times 10^{-3}$ m^2/g.

[d] After 1100°C firing.

[e] Analysis on coated particles

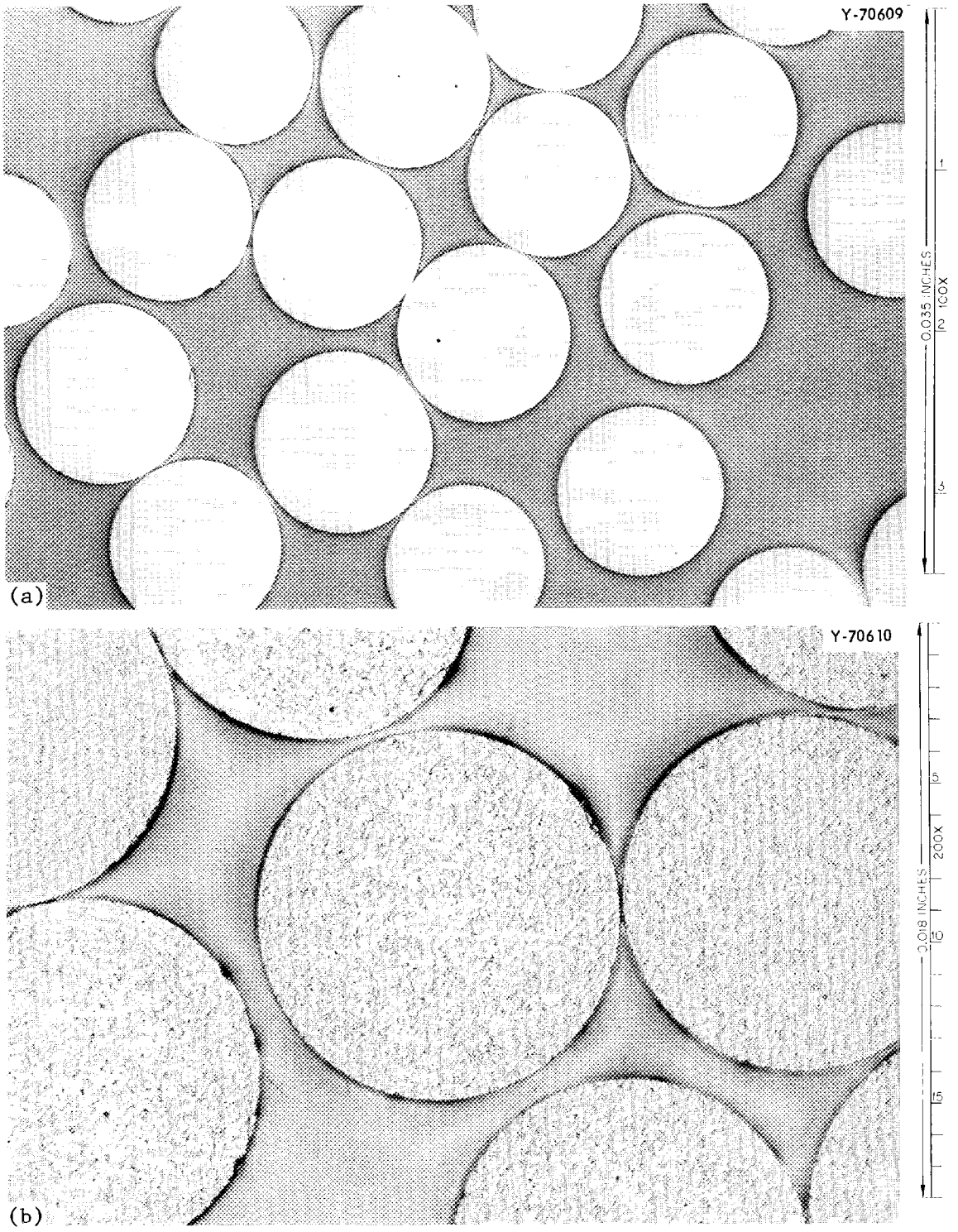

Fig. 1. Metallographic Sections of Sol-Gel UO_2-ThO_2 Preparation 3371-82-1900. a) 100X, as polished, the halos are light effects from the transparent spheres. b) 200X, etched with H_3PO_4-HF: grain structure is visible.

composed of about equal numbers of pale green-colored and black-colored microspheres. The density was 97 to 98% of theoretical, and the oxygen-to-uranium ratio was <2.006. These values are acceptable. However, it was decided to refire the spheres in pure hydrogen in case the color difference was due to minor variations in the oxygen-to-uranium ratio among the individual spheres. A test sample was fired to 1150° in H_2 and held for 4 hr, and three different colors of spheres resulted. In addition to the blacks and pale greens, there were amber-colored, transparent spheres which composed about one-half of the total. All of the material was then refired to 1400°C in H_2, and all of the spheres were converted to the amber-colored, transparent type. The phenomenon of the conversion to the amber-colored, transparent spheres is not understood. For some purposes the multicolored spheres that are obtained in the 1100°C-firing may be superior, since these spheres are factors of 2 to 3 stronger and only slightly less dense than the amber, clear spheres (Table 5).

Table 5. Firing of UO_2-ThO_2 Microspheres to 1100°C

Reduced 2 hr at 1100°C in Ar-4% H_2

	47-49A-97 (Th/U ~5/1)						47-27-97 (Th/U ~3.5/1)			
Firing Code	3371-50-1100	3371-50-1150[a]	3371-52-1100	3371-54-1100	3371-58-1100	3371-60-1100	3371-62-1100	3371-64-1100	3371-66-1100	3371-68-1100
Forming Code	P-2-8-1602	P-2-8-1602	P-2-9-1525	P-2-9-1525	P-2-10-1453	P-2-10-1453	P-2-11-1600	P-2-11-1455	P-2-14-1300	P-2-14-1503
Initial Gel Wt (g)							209.3	521.0	286.0	487.6
Final Fired (g)	397.3	396.6	517.9	230.7	456.5	236.8	189.1	479.0	259.2	449.6
% Wt Loss on Firing							10.7	8.78	10.3	8.45
Screen Analysis										
+297 μ	-	7.67	10.67	35.30	9.42	31.56	2.55	27.76	5.25	11.54
250-297 μ	-	73.95	73.12	55.08	73.81	56.10	51.07	71.68	93.22	64.43
210-250 μ	-	4.74	3.46	3.02	2.43	1.96	1.72	0.21	1.31	1.89
-210	-	13.59	12.76	6.60	14.33	10.37	44.67	0.34	0.21	22.27
Prod. Anal.(wt %)										
Density (pour)	9.35	10.25	10.14	9.90	10.2	9.96	10.25	10.13	10.29	10.01
Density (Hg)								9.97		9.92
Crush (g)	>1788	1265	>1695	>2200	~1760	>1860	>1450	>2200		
BET Surface Area (m^2/g)	-	-	-	-	-	-	-	0.109	-	0.151

[a]Refire of 3371-50-1100 to 1150°C.

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