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PREPARATION AND PHYSICAL PROPERTIES OF U_3O_8

INTRODUCTION

Fuel tubes for SRP reactors are now made by coextruding aluminum billets containing cast uranium-aluminum alloy cores. The casting process is scheduled to be replaced by a powder metallurgy (P/M) process developed in SRL. Current 300-Area plans are to begin P/M operations in 1987 provided funding is made available in 1985.

The P/M process will require enriched U_3O_8 powder instead of uranium metal as a fuel form. The U_3O_8 can be made by heating UO_3, an intermediate product in the current uranyl nitrate to uranium metal process at Y-12. A feasibility study was requested[1] and was carried out at Y-12 to determine if U_3O_8 powder could be made using a fluid-bed reactor. Information in this report summarizes the conversion data from Y-12 and compares the physical properties of U_3O_8 powder made at Y-12 and SRL.

SUMMARY

Tests have been completed which indicate that near stoichiometric U_3O_8 can be made at Oak Ridge Y-12 for the SRP P/M billet core fabrication process[2]. Oxide conversion will be most likely at 650°C in fluid-bed reactors which are part of the current recycle facility; however, no production runs have been made yet. The

physical properties of U_3O_8 oxide produced at 650°C in flowing nitrogen compare favorably with 800°C fired U_3O_8 produced at SRL in either low grade nitrogen or air atmosphere. It is expected that the Y-12 oxide would behave similar to SRL U_3O_8 during fabrication and irradiation but no tests have been made at this time.

DISCUSSION

Uranyl nitrate solution from 200-Area processing of spent SRP fuel tubes is now sent to Oak Ridge Y-12 for conversion to uranium metal. However, after implementation of the P/M process, U_3O_8 powder will be needed at SRP but not uranium metal. U_3O_8 powder for fabrication and irradiation tests was produced during development of P/M at SRL by firing UO_3, obtained from Y-12, at 800°C for 6 hours in a low grade nitrogen atmosphere. The UO_3 powder was produced by denitration of unsulfated uranyl nitrate solution.

Y-12 Process

The Y-12 system is designed to receive the uranyl nitrate solution and process it into high purity metal. Uranyl nitrate solution is first sent through an organic solvent extraction step. The extraction product is concentrated to molten uranyl nitrate in a thin film evaporator. The evaporator product is then stored in a steam jacketed tank.

Molten uranyl nitrate is next pumped into a stirred-bed, five-inch denitrator to produce UO_3 powder. This UO_3 is in the form of spherical particles with a particle size range predominantly minus 30 plus 100 mesh (US Standard) and is free flowing. As the molten material is continuously pumped into the bed, the UO_3 product in the denitrator overflows into a receiver tank.

Uranium metal is produced by first converting UO_3 to UF_4 "green salt" in a fluid-bed reactor. The UF_4 is reduced to uranium metal by calcium reduction. For the P/M process, it is expected that U_3O_8 can be produced in a fluid-bed but the maximum operating temperature for the existing Y-12 inconel bed is about 650°C. To determine the feasibility of converting UO_3 to U_3O_8 in the fluid-bed, tests were made at Y-12 to define the conversion temperature and physical properties of the U_3O_8 powder[3]. The product was compared with two samples of U_3O_8 powder produced at SRL from Y-12 UO_3. All physical property tests were made at Y-12 using the same analytical techniques.

Oxide Conversion

By decomposing uranyl nitrate, the "orange oxide", UO_3 is obtained; this oxide loses oxygen when heated to form U_3O_8. Studies

by McCoy and Ashman[4] have shown that U_3O_8 is readily obtained by heating any lower or higher oxide of uranium in air at 700°C. To define the lower temperature limit for UO_3 to U_3O_8 conversion, thermogravimetric tests at Y-12 were made at 600, 650 and 700°C in flowing nitrogen. The UO_3 used for the tests had been produced in a previous processing campaign in the Y-12 denitrator from unsulfated uranyl nitrate feed. The isotopic and uranium content of the UO_3 powder is given in Table I. The theoretical uranium content for UO_3 is 0.83145 (gU/g) while the measured value is 0.81827. The difference between these values is primarily due to impurity content.

The time required for conversion from UO_3 to U_3O_8 at temperature was determined by measuring the theoretical weight loss of 1.843% from the thermogravimetric data. Test results are given in Table II. The initial weight loss during heating is caused from loss of water and nitrate impurities. Complete conversion to U_3O_8 occurred after 6 hours at 650°C. At 700°C, conversion was completed in about 1 hour.

Batch or tray tests were also made at Y-12 by heating approximately 1 Kg of UO_3 in an electrical resistance tube furnace at 650, 700, and 800°C from 6 to 3 hours depending on temperature. The oxide powder was ∿1/2-inch deep in the trays. The UO_3 powder was converted to approximate theoretical U_3O_8 composition in flowing nitrogen at temperatures greater than 650°C as indicated by the gU/g data in Table III.

At SRL, U_3O_8 was produced by heating UO_3 obtained from Y-12 in an electrical resistance box furnace at 800°C. Two samples were sent to Y-12 for analysis. One sample was heated 6 hours in a low grade nitrogen atmosphere and the other sample was heated 2 hours in air.

Physical Properties of U_3O_8

The stoichiometry, particle size distribution, surface area and density of the Y-12 and SRL powders were measured. A comparison was then made between SRL U_3O_8 produced at 800°C in nitrogen and in air and U_3O_8 produced at Y-12 at other heating temperatures.

Stoichiometry

Based on the isotopic content and stoichiometry, the theoretical uranium content for complete conversion to U_3O_8 oxide (gU/g) is 0.84732. The measured values as shown in Tables III and IV were less than theoretical for the Y-12 and SRL oxides produced from UO_3 by heating in either flowing nitrogen or a nitrogen/air mixture. Non stoichiometric compositions of U_3O_8 have been reported.[5,6] The oxygen to uranium ratio (o/u) for the U_3O_{8-z} phase is a

function of the conversion temperature and partial pressure of oxygen in the gas passing over the sample. In air at temperatures below about 700°C, the oxide is oxygen rich giving o/u values greater than 2.6667 theoretical while at higher temperatures, oxygen deficient compositions occur with o/u values less than 2.6667.[5] Calculated o/u values for Y-12 and SRL oxides, given in Table V, show that all samples converted in flowing nitrogen or nitrogen/air atmospheres are oxygen rich. Note also that the Y-12 samples heated below 800°C in flowing nitrogen had compositions that were not as rich in oxygen as SRL oxides. The Y-12 U_3O_8 sample reheated at 800°C in nonflowing nitrogen was oxygen deficient (o/u = 2.6370).

Particle Size

The particle size distributions for the SRL and Y-12 U_3O_8 powders are shown in Table VI. The distribution is also given for one SRL UO_3 sample; it was not measured for other powders used in the tests. For the SRL sample, the average particle size of UO_3 was about 350 μm compared to about 330 μm for U_3O_8 converted at 800°C in the low grade nitrogen gas. The size difference of 6% after heating may be due to sampling and/or sintering of the oxide powder. These powders were furnace cooled and removed after reaching 300°C so thermal shock would not fracture oxide particles. The SRL U_3O_8 powders are coarser than Y-12 U_3O_8 having an average particle size of about 350 μm (45 mesh) compared to about 240 μm (60 mesh), respectively. This difference is understandable because the particle size distribution of the denitrated UO_3 powder varies somewhat from lot to lot.

Surface Area

The particle surface area was determined by BET analysis using krypton gas. The surface area of the Y-12 U_3O_8 powder decreased when heated in flowing nitrogen from 1.410 $\frac{m^2}{g}$ at 650°C to 0.538 $\frac{m^2}{g}$ at 800°C. One must assume that the decrease in surface area was due to a decrease in particle size or open particle porosity which is a function of the heating temperature because neither the particle size distribution nor surface area of the initial UO_3 powder samples was reported. At 650°C, the surface area of a U_3O_8 sample decreased an additional 25% when heated 22.5 hours.

The measured surface areas for the two SRL U_3O_8 powders were 0.09 and 0.17 $\frac{m^2}{g}$ when heated at 800°C in a flowing low grade nitrogen or air atmosphere, respectively. About 75% of the difference in surface area is due to the larger average particle size for the two powder samples. The remaining difference is due to either atmospheric effects during heating or particle porosity.

The difference in the measured surface area between SRL and Y-12 samples heated at 800°C in nitrogen is 0.448 $\frac{m^2}{g}$. About 63% of

this difference can be attributed to the larger particle size of the SRL powder. Particle photomicrographs are shown in Figure 1 for SRL U_3O_8 heated at 800°C for 6 hours in low grade nitrogen and for Y-12 U_3O_8 heated at 650°C for 6 hours in pure flowing nitrogen. Both SRL and Y-12 U_3O_8 oxides are made up of smaller agglomerated and sintered particles but the substructure for the Y-12 oxide is much smaller than for SRL oxide as shown at 5000x magnification. The size difference of the substructure may account for the remaining difference in measured surface area because smaller particles would give a larger surface area.

Particle Density

The particle density of the U_3O_8 powders was measured using a helium displacement pycnometer and for the SRL U_3O_8 samples, the density was also measured using a toluene pycnometer. Results are shown in Tables III and IV for Y-12 and SRL U_3O_8, respectively. The measured density of Y-12 U_3O_8 at 650°C and 700°C fired in flowing nitrogen was about the same, 7.5 g/cc while at 800°C the density was slightly less, 7.4 g/cc. By heating U_3O_8 from the previous 800°C test, the particle density increased to 7.5 g/cc after 4 hours at 800°C in nonflowing nitrogen. For SRL fired U_3O_8, the particle density was found to be about 7.0 g/cc for powder heated for 6 hours in low grade nitrogen and about 7.3 g/cc for powder heated 2 hours in air. The toluene displacement technique gave slightly lower densities.

HBP:dwb

REFERENCES

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4. McCoy, H. N. and Ashman, G. C., The Preparation of Urano-uranic Oxide, U_3O_8, and a Standard of Radioactivity, Am. Jour. Sci., Fourth Series, Vol XXVI, No. 156, December 1908.

5. Dhaswadkar, S. R. and Chandrasekharaiah, M. S., Nonstoichiometry of the U_3O_8 Phase at High Temperature, High Temperature Science. 5, 5-7, pp 5-7, 1973.

6. Ackermann, R. J. and Chang, A. T., Thermodynamic Characterization of the U_3O_{8-z} Phase, J. Chem. Thermodynamics, 5, pp 873-890, 1973.

TABLE I

UO_3 FEED MATERIAL - TGA AND TRAY TESTS

gU/g = 0.818270

Assay:	U-234	- 0.33%
	U-235	- 39.80%
	U-236	- 0.75%
	U-238	- 59.12%

TABLE II

THERMOGRAVIMETRIC ANALYSES IN FLOWING N_2 FOR Y-12 UO_3

Run	Temp. °C Segment	% Weight Loss	Time Required for Constant Temperature for Conversion
1. 25 to 800°C	25 to 500	0.894	
	500 to 685	0.321	
	720 to 803	1.99	
		3.18	
2. 600°C Constant Temp.	25 to 600 at 600	1.23	Greater than 17 hours. About 37 hours calculated from rate. UO_3 particles remaining after 17 hours.
		0.78	
		2.01	
3. 650°C Constant Temp.	25 to 650 at 650	1.27	
		1.843	5.75 hours
		3.09	
4. 700°C Constant Temp.	25 to 700 at 700	1.298	
		1.843	0.94 hours
		3.12	

TABLE III

DATA FROM TRAY TESTS IN FLOWING N_2

Run No.	Feed Mat'l	Temp. (°C). at Time (Hrs)	Analyses gU/g	Surface Area[a] M^2/g	Particle Density[b] (g/cc)	Other
1	UO_3	650 6	0.844960	1.410	7.51	250 ppm NO_3
1A	U_3O_8 from run 1	650 22.5	0.845480	1.050	7.48	
2	UO_3	700 5	0.844560	1.260	7.54	
3	UO_3	800 3	0.846480	0.538	7.43	
3A	U_3O_8 from run 3	800 in N_2 but no flow 4	0.848760	0.539	7.50	

(a) Analytical method - BET using krypton.
(b) Analytical method - Micromeretics, helium displacement automatic pycnometer.

TABLE IV

Y-12 ANALYSES OF SRL U_3O_8

Sample	SRL Description	gU/g	Surface Area[a] M^2/g	Particle Density (g/cc) He Disp.[b]	Toluene[c]
E-191B	U_3O_8, 800°C 6 hrs in N_2	0.84364	0.09	6.99	6.87
E-193B	U_3O_8, 800°C 2 hrs in air	0.84397	0.17	7.30	7.26

(a) Analytical Method - Same as (a) Table III
(b) Analytical Method - Same as (b) Table III
(c) Analytical Method - Toluene displacement - manual pycnometer.

TABLE V

CALCULATED O/U RATIOS FOR Y-12 AND SRL OXIDES IN HIGH AND LOW GRADE NITROGEN

	O/U Ratio*	
Firing Temp. °C	Y-12	SRL
650	2.7155	---
700	2.7238	---
800	2.6840	2.7428/2.7360 (Air)

*Stoichiometric U_3O_8 o/u = 2.6667

TABLE VI

U_3O_8 SCREEN ANALYSES

Screen Mesh Size	Screen Fraction - wt % Y-12 U_3O_8 Run 1 (See Table III)	SRL Oxide Sample E-191B U_3O_8	Sample E-193B UO_3	 U_3O_8
+20	---	0.26		0.25
-20 +30	0.2	11.12	12.63	8.96
-30 +40	5.7	41.67	32.50	37.95
-40 +50	28.5	32.55	35.00	33.67
-50 +60	22.9	9.19		11.77
-60 +70	19.5	3.44		4.63
-70 +80	8.3	1.02	18.75	1.46
-80 +100	10.7	0.25	0.50	0.49
-100 +140	2.9	0.11	0.25	0.30
-140	1.4	0.40	0.37	0.52

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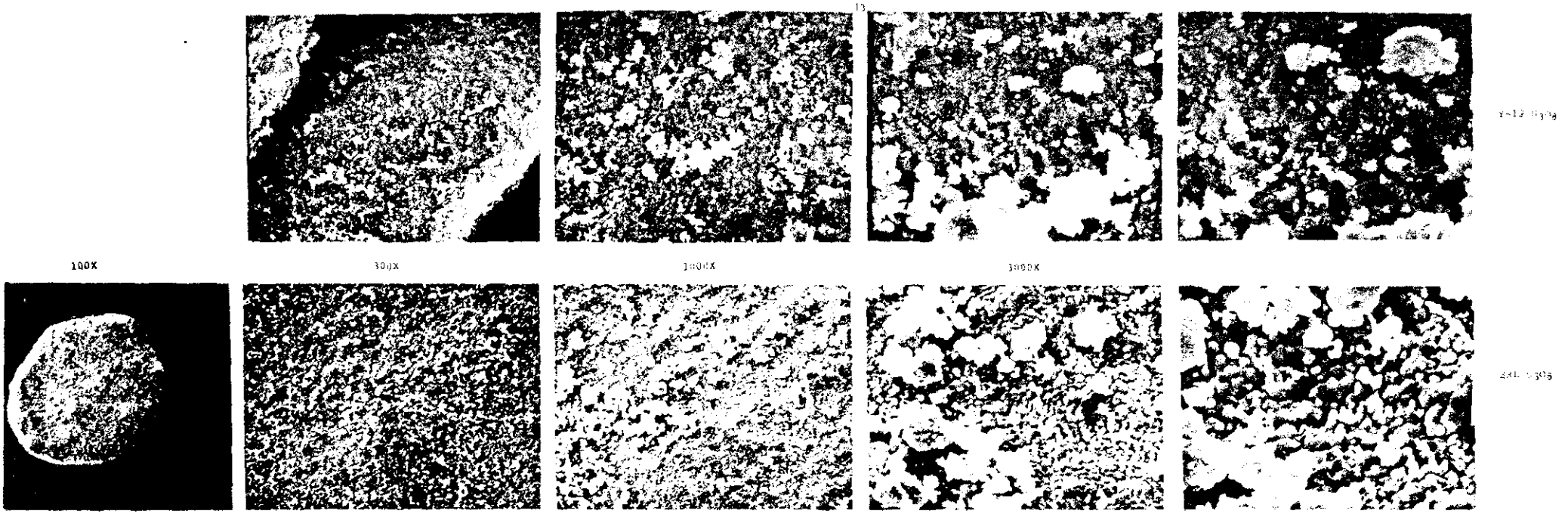

FIGURE 1. SEM photomicrographs of Y-12 U_3O_8 made by heating at 650°C for 6 hours in flowing nitrogen and SRL U_3O_8 made by heating at 800°C for 6 hours in a low grade nitrogen atmosphere.