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ALUMINA COATING OF UO_2 SHOT BY HYDROLYSIS
OF ALUMINUM CHLORIDE VAPOR

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ALUMINA COATING OF UO₂ SHOT BY HYDROLYSIS OF ALUMINUM CHLORIDE VAPOR

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Uniform, dense coatings of alumina about 5 to 150 μ thick were applied to uranium dioxide particles 44 to 350 μ in diameter by hydrolysis of aluminum chloride vapor in a fluidized bed of the particles at 1830 F. The coated particles were resistant to nitric acid leaching, to oxidation in 1830 F air, and to thermal cycling from 600 to 2500 F. After low neutron exposures, the coated particles showed excellent fission-gas retention at temperatures up to 2400 F in inert gas. Although not optimized in the study, the coating process appears to have commercial feasibility.

INTRODUCTION

Uranium dioxide particles individually coated with a dense, impervious ceramic coating and dispersed in a suitable matrix have several potential advantages in high-temperature fuel-element applications. Coatings can retain fission products, prevent oxidation of the UO₂, and prevent both fission-recoil damage to the matrix and UO₂-matrix reactions. The composite particle also has important mechanical advantages. The coated particle is small, so stress and thermal gradients in the coating are minimized. Optimizing the ratio of coating thickness to particle size, as determined by the fission-product retentivity of the coating and the quantity of coating material permitted by fuel-loading requirements, is one of the important problems in applying this fuel concept.

During recent years, the coating of individual fuel particles by chemical vapor deposition has received considerable study. Use of such coating materials as carbon, chromium, molybdenum, niobium, niobium-vanadium alloys, tantalum, tungsten, zirconium, chromium carbide, silicon carbide, and the oxides of aluminum, chromium, vanadium, yttrium, and zirconium has been investigated. (1, 2) A striking general characteristic of these coatings is a dense, fine-grained structure. The high density and microcrystallinity is related to the frequent and energetic collisions between particles during the coating process.

The fluidized-bed technique is preferred at Battelle for coating fuel particles up to 400 microns in diameter. Workers at NUMEC^(3, 4) have successfully coated particles agitated on vibrating trays or in rotary kilns. Several other coating processes have been described.

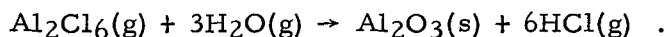
In the present program, dense coatings of alpha Al₂O₃ showing excellent oxidation resistance were applied to UO₂ particles by the vapor-phase hydrolysis of aluminum chloride in a fluidized bed of the UO₂ particles. This coated particle is under investigation at Battelle as part of Sanderson & Porter's fuel-element program for the Pebble-Bed Reactor.

(1) References at end.

In the course of preparing several lots of Al₂O₃-coated UO₂ powder for this program, some information has been gained on the effect of process variables on the properties of the coating, although a systematic study of this system has yet to be made. Thus, the conditions used up to now may be far removed from optimum. However, in view of the very promising fission-gas retention exhibited by these coatings, and the interest that has been generated on the subject, it was thought that the preliminary results should be reported.

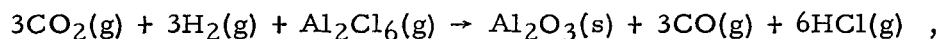
EQUIPMENT AND PROCEDURE

The chemical vapor-deposition reaction used in the present work to coat UO₂-powder particles with Al₂O₃ was the direct hydrolysis of aluminum chloride vapor:



Aluminum chloride was chosen as the volatile halide to be hydrolyzed because of its low cost and commercial availability. Although this reaction yields a promising product, it may not be the best, and other reactions such as hydrolysis or oxidation of the bromide, iodide, acetylacetonate, or alkyls should be studied.

In the present work, hydrolysis of the chloride by a mixture of carbon dioxide and hydrogen,



was explored initially. This reaction has been long known as a method of coating extended surfaces with Al₂O₃⁽⁵⁾, where the slow kinetics of the "water-gas" reaction, CO₂ + H₂ → H₂O + CO, prevents hydrolysis of the Al₂O₃ before the reactants reach the heated surface. However, in the present work with the CO₂-hydrogen feed, incomplete hydrolysis of the aluminum chloride was observed at 1830 C. This led to the use of water vapor as the hydrolyzing agent. The aluminum chloride and water vapor were fed separately to prevent premature reaction, mixing being permitted to occur within the fluidized bed. This procedure is appropriate for the small fluidized-bed reactors used in the experimental work. However, in scaling up the process, the problem of providing proper mixing by means of multiple vapor injectors may be sufficiently formidable to make it worthwhile to reconsider use of the water-gas reaction.

Data on the fluidization characteristics of UO₂ powder have been reported.⁽²⁾ The UO₂ particles used in the alumina-coating work ranged from 44 to 350 μ. However, in individual coating runs, particles of a narrow size range were used, most of the experience having been with 105 to 149-μ material.

Figures 1 and 2 show the coating equipment. The fluidized-bed reactor consisted of a 30-mm Vycor tube with a conical bottom attached to a 2-mm-capillary tube through which the fluidizing gas and the aluminum chloride were introduced into the reactor. A Vycor tube, extending axially down from the top of the reactor and terminating just below the top of the static bed, permitted introduction of the water vapor into the reactor separately and thus prevented premature hydrolysis.

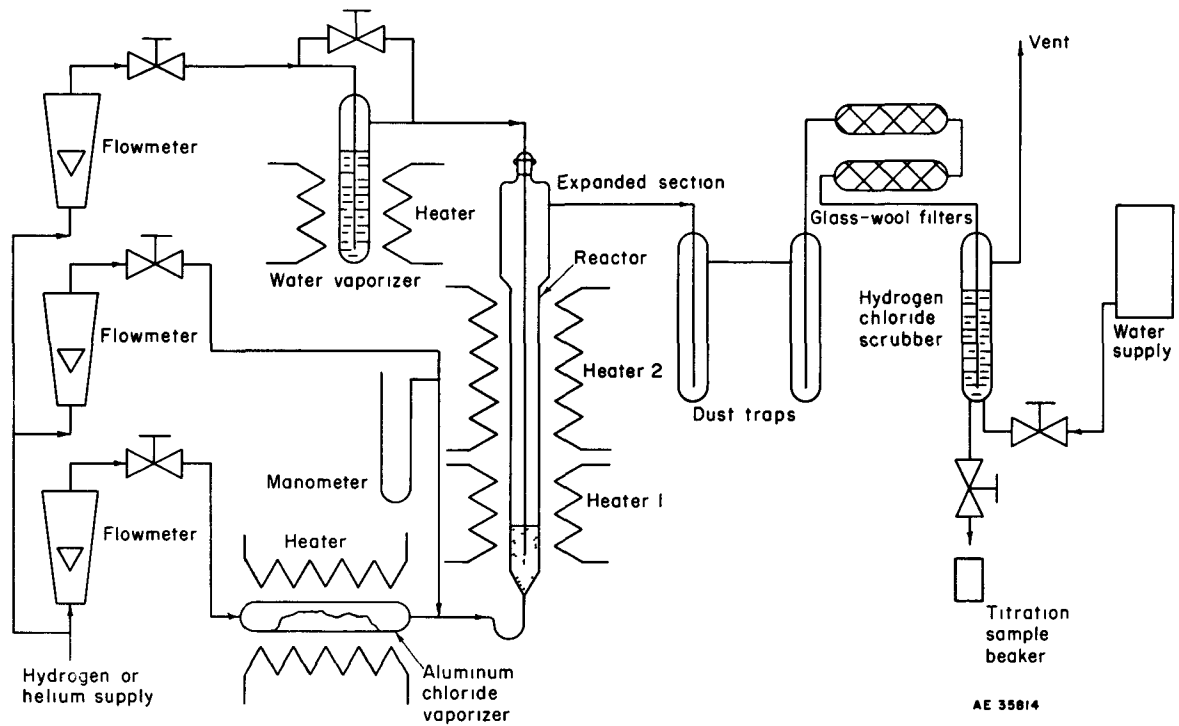
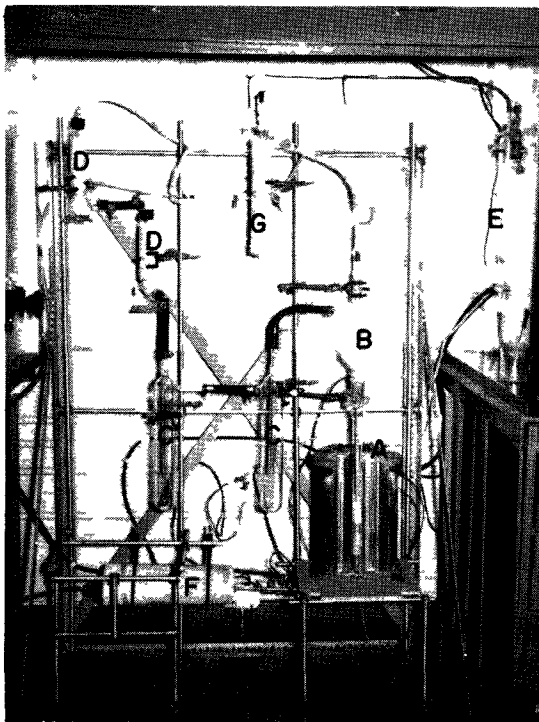


FIGURE 1. SCHEMATIC DIAGRAM OF APPARATUS FOR APPLYING COATINGS OF ALUMINA ON FUEL PARTICLES



- A. Reactor
- B. Expanded section
- C. Dust traps
- D. Glass-wool filters
- E. Hydrogen chloride scrubber
- F. Aluminum chloride vaporizer
- G. Water vaporizer

FIGURE 2. COATING APPARATUS SET UP IN LABORATORY

An expanded disentrainment section was used at the top of the reactor above the heated zone to minimize the loss of urania particles from the bed. Downstream of the reactor were solids traps and glass-wool filters to remove urania and alumina dust, and a scrubber to dissolve the by-product HCl. The HCl content of the exit gas was monitored to determine the rate of alumina formation.

The equipment upstream of the reactor consisted of a system for metering hydrogen and helium independently to the aluminum chloride vaporizer, to the water vaporizer, and to the fluidized-bed reactor, the latter being the main fluidizing-gas stream. A manometer for determining pressure drop through the reactor and exit portion of the system was included as an aid to operation. The lines from the aluminum chloride vaporizer and the water vaporizer to the reactor were maintained above the dew points of the respective reactants.

The two vaporizers were electrically heated and their temperatures controlled by reference to thermocouples. The electrically heated fluidized-bed reactor furnace had a split heater which permitted independent control of the top and bottom sections of the reactor. Temperature measurements were made by thermocouples attached to the reactor walls. Depending upon the depth of bed, particle size, and gas flow, the error involved in measuring the temperature in this manner may amount to between 10 and 100 F. (2) In the present small-scale work, it was thought adequate to monitor the temperature by means of the external thermocouple rather than introduce the complication of another re-entrant tube within the bed. Thus, the actual bed temperatures involved in the present work were lower than the recorded temperatures by a varied but small amount.

The equipment was assembled as described above after weighing the aluminum chloride vaporizer, water vaporizer, and urania bed. Initially, and during the preliminary heatup period, the bed was fluidized with helium. As operating temperatures were approached, hydrogen was substituted for helium as the fluidizing gas. Hydrogen was used to prevent oxidation of the urania during the initial phase of coating formation. Both the vaporizers and the fluidized bed were heated to operating temperature concurrently with no gas flow through the aluminum chloride vaporizer and with the carrier gas bypassing the water vaporizer. When the fluidized-bed reactor had reached operating temperature, controlled flow of carrier gas through the reactant vaporizers was initiated. The feed rate of each reactant was controlled by adjusting the vaporizer temperature and carrier-gas flow. The reaction rate was determined at 15-min intervals by titrating the hydrogen chloride content of 100 to 200-cm³ increments of scrubber water. When the coating operation was to be terminated, the startup procedure was essentially reversed. The gas flow and power to the reactant vaporizers were cut off while the fluidizing-gas stream was maintained. Fifteen minutes later, the reactor-furnace power was cut off, and the furnace was opened to permit rapid cooling. Helium was substituted for the hydrogen as a safety precaution. When cool, the equipment was dismantled, and changes in weight of the urania bed, aluminum chloride vaporizer, and water vaporizer were determined.

Typical operating conditions were as follows:

Bed weight	100 g
UO ₂ particle size	105-149 μ
Reactor-wall temperature	1830 F

Aluminum chloride-vaporizer temperature	300 to 320 F
Water-vaporizer temperature	Controlled at an oven temperature roughly indicative of water temperature; water feed determined on basis of previous calibration
Gas flow through aluminum chloride vaporizer	0.75 liter per min STP
Gas flow through water vaporizer	0.75 liter per min STP
Main fluidizing-gas flow	2 liters per min STP
Reactant composition	
Hydrogen	96.5 mole per cent
Al ₂ O ₃	1.3 mole per cent
Water	2.2 mole per cent
Coating rate	3 g per hr
Fraction of alumina as coating	50 w/o
Fraction of alumina as entrained dust	50 w/o
Al ₂ Cl ₆ conversion efficiency	95 per cent
Coating time	50 hr
Coating thickness	40 μ

The above conditions are typical of the coating runs which have been made and are not to be construed as optimum. The coating temperature has been increased to 2012 and 2550 F in several recent runs in a Mullite reactor, and, by increasing the concentration of reactants, the coating rate has been increased to 12 g per hr with only minor problems.

In the more recent coating experiments, the fraction of alumina formed as coating on the particles has been increased to approximately 75 per cent by an increase in bed depth and decrease in flow rate of the fluidizing gas.

To prevent continued contamination of the coating by feedback of elutriated UO₂ dust from the walls of the reactor, the coatings were generally applied stepwise. That is, after application of 3 to 6 μ of Al₂O₃, the bed was removed, washed in 1:1 HNO₃, rinsed, dried, and returned to a clean reactor for continued processing.

EVALUATION OF COATED PARTICLES

The coated particles were evaluated in several laboratory tests to determine the relative continuity and porosity of the coating and the resistance of the coated powder to thermal cycling. The following evaluation procedures were used:

- (1) Metallography
- (2) Petrographic analysis of the coating material after crushing of the particles and dissolution of the UO_2
- (3) Acid leach of the as-produced particles
- (4) Air oxidation at elevated temperatures
- (5) Measurement of alpha emission from a thin layer of the particles
- (6) Repetition of one or more of the above after thermal cycling
- (7) Elevated-temperature fission-gas release after neutron activation.

The color of an alumina-coated urania particle can range from the dark color of the urania to any shade of gray-white, depending on the coating thickness and the porosity. Samples have been obtained with 12- μ coatings which were sufficiently transparent to appear uncoated. When the as-prepared particles are examined microscopically, the coating appears to be free of cracks, and is dense and uniform in color.

Figure 3 shows photomicrographs and an electron micrograph of typical alumina-coated urania particles. As can be noted from these micrographs, the coatings, prepared at 1830 F, were uniform in thickness, dense, and relatively free of voids. Petrographic and X-ray diffraction analyses revealed that the alumina formed at 1830 F was the alpha modification having a grain size of less than 5 μ .

As can be seen from the data in Table 1, deposition of Al_2O_3 at 1290 F gives a porous coating (determined by petrographic examination to be gamma and kappa Al_2O_3) even in a thickness of 8 μ . In contrast, a 5- μ alpha alumina coating deposited at 1830 F is sufficiently nonporous to partially protect the urania from nitric acid. However, a 10- μ coating of alpha alumina is needed to give essentially complete protection. This conclusion is confirmed by the results of the 1830 F oxidation test. The samples of coated particles exposed to air at 1200 F were essentially not affected. The results of the thermal-cycling test indicated that the alumina-coated particles are generally resistant to thermal cycling between 600 and 2500 F.

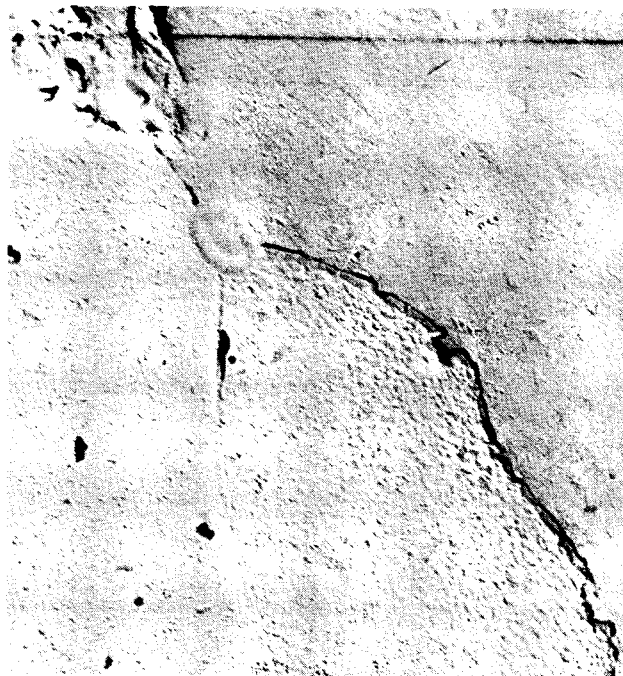
Alpha emission and the postirradiation release of fission gas after neutron activation were studied. Alpha particles emitted from the coated particles were measured by counting a monolayer of the material in an internal-sample proportional counter. The range of alpha particles in alumina is about 10 μ . Fission-gas release was measured by heat treating a neutron-activated sample in flowing helium, collecting the liberated xenon-133 in a refrigerated charcoal trap, and assaying the xenon-133 radioactivity with a well-type scintillation crystal. Small samples were irradiated to 1×10^{15} nvt for the latter study.



100X

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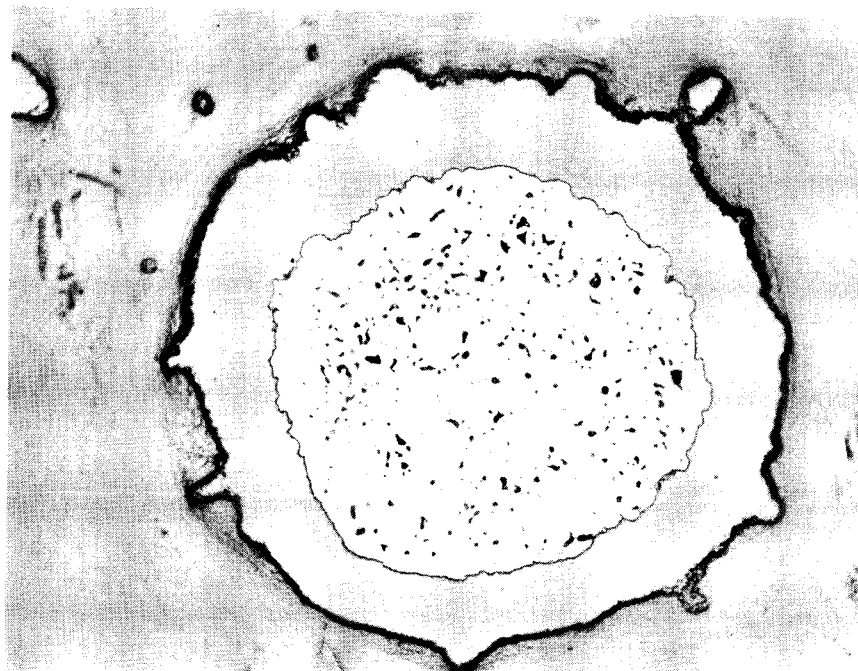
a. As-Polished Material From Lot 16587-6-1B



17, 200X

J422

b. Electron Micrograph of Material From Lot 16587-14-4E



500X

N65247

c. As-Polished Particle From Lot 16587-6-1B

FIGURE 3. STRUCTURES OF TYPICAL 20- μ ALUMINUM COATINGS ON 105 TO 149- μ UO_2 PARTICLES

The granular structure visible in the electron micrograph is the UO_2 .

TABLE 1. SUMMARY OF TYPICAL RESULTS OF EVALUATION

Lot	UO ₂		Coating Thickness, μ	Coating Temperature, F	Treatment	Effect of Thermal Cycling From 600 F to 2500 F ^(a)
	Enrichment	Size, μ				
15638-7-5	Natural	149-250	8	1830	Leached in 1:1 HNO ₃ for 18 hr at room temperature	--
15638-10-8A	Natural	105-149	8 Porous	1290	Leached in 1:1 HNO ₃ for 18 hr at room temperature	--
15638-21-13A	Natural	44-53	9.5	1830	16 hr at 1830 F in air	--
15638-29-14C	Natural	44-53	15	1830	23 hr at 900 F in air 240 hr at 1832 F in air	--
16997-35-A2	Natural	105-149	2-3	1830	As prepared 8 hr at 1830 F in air 16 hr at 1830 F in air	-- -- --
16997-34-A1	Natural	105-149	4-5	1830	As prepared 8 hr at 1830 F in air 16 hr at 1830 F in air	-- -- --
16997-34-A1a	Natural	105-149	9-10	1830	As prepared 8 hr at 1830 F in air 16 hr at 1830 F in air 30 hr at 1830 F in air	-- -- -- --
16587-6-1B	Natural	105-149	20	1830	As prepared	--
16587-9-2	Natural	105-149	35-40	1830	5 hr at 1200 F in air As prepared 5 hr at 1200 F in air	-- No effect --
16587-12-3C	Natural	105-149	46-50	2010	Thermal cycling followed by 5 hr at 1200 F in air As prepared 5 hr at 1200 F in air Thermal cycled Thermal cycle followed by 5 hr at 1832 F in air	-- -- No effect -- -- --
16587-14-4E	Fully enriched	105-149	42	1830	As prepared 5 hr at 1200 F in air	-- --
16587-58-6H	Fully enriched	105-149	40-56	1830	As prepared 5 hr at 1200 F in air	No effect --
16587-84-7J	Natural	105-149	40	1830	As prepared Thermal cycled Thermal cycled and leached 5 hr at 1200 F in air	No effect -- -- --
17061-13-8G	Natural	297-350	20 porous + 130 dense	1290 1830	As prepared 5 hr at 1200 F in air Thermal cycled	No effect -- --

Footnotes appear on the following page.

TESTS ON ALUMINA-COATED URANIA PARTICLES

Results of Alpha Count		Results of Porosity Tests			Results of Neutron-Activation Experiment		
Net Alpha Activity Per G of Clad Particles ^(b) , cpm	Equivalent Uranium Per G of Clad Particles ^(c) , mg	UO ₂ Oxidized After Heating in Air ^(d) , per cent	UO ₂ Removed in HNO ₃ Leach Test ^(e) , per cent		Postirradiation Heat Treatment		Xenon-133 Release, per cent
			In 1 Hr	In 7 Hr	Temperature, F	Time, min	
--	--	--	0.319 (18 hr)		--	--	--
--	--	--	6.52 (18 hr)		--	--	--
--	--	0.09	--	--	--	--	--
--	--	0.56 to 1.26 ^(f)	--	--	--	--	--
--	--	--	10.78	17.21	--	--	--
--	--	6.40	--	--	--	--	--
--	--	5.91	--	--	--	--	--
--	--	--	2.48	1.28	--	--	--
--	--	20.15	--	--	--	--	--
--	--	5.83	--	--	--	--	--
--	--	--	0.002	<0.001	--	--	--
--	--	0.0	--	--	--	--	--
--	--	0.12	--	--	--	--	--
--	--	1.66	--	--	--	--	--
7.3 ± 1.3	0.019	--	--	--	1850	100	<1.7 × 10 ⁻²
--	--	--	--	--	2250	75	1.7 × 10 ⁻²
--	--	--	--	--	2400	135	1.6 × 10 ⁻²
--	--	<0.01	--	--	--	--	--
1.4 ± 1.0	0.0038	--	<0.001	<0.001	--	--	--
--	--	<0.01	--	--	1550	144	1.3 × 10 ⁻⁴
--	--	--	--	--	1500	60	<3.7 × 10 ⁻³
--	--	--	--	--	2000	50	3.7 × 10 ⁻³
--	--	<0.01	--	--	--	--	--
0.8 ± 0.8	0.0022	--	<0.001	0.217	--	--	--
0.8 ± 0.8	0.0022	<0.01	--	--	--	--	--
2.0 ± 1.0	0.0054	--	--	--	--	--	--
--	--	<0.01	--	--	--	--	--
--	--	--	<0.001	<0.001	--	--	--
20.7 ± 2.5	0.017	<0.01	--	--	1950	240	7.7 × 10 ⁻⁴
--	--	--	--	--	--	--	--
0.4 ± 1.2	0.00022	<0.01	--	--	--	--	--
0.5 ± 1.0	0.0014	--	0.29	0.016	--	--	--
0.4 ± 0.8	0.001	--	--	--	--	--	--
0.4 ± 0.6	0.003	--	--	--	--	--	--
--	--	<0.01	--	--	--	--	--
1.0 ± 0.6	0.0026	--	--	--	--	--	--
2.4 ± 0.9	0.0064	<0.01	--	--	--	--	--
3.4 ± 1.2	0.0092	--	--	--	--	--	--

Footnotes for Table 1:

- (a) Microscopic examination. Thermal cycled nine times between 600 F and 2500 F in processing gas (nitrogen-10 volume per cent hydrogen) allowing 15 min at each temperature on each cycle.
- (b) Alpha count measured in an internal-sample proportional counter.
- (c) Distribution of urania assumed to be uniform throughout the outer 10 μ of coating.
- (d) Sample heated in static air. When more than one value is reported, they are additive.
- (e) Sample leached 1 hr and an additional 7 hr in 1:1 HNO₃ at approximately 200 F unless otherwise specified.
- (f) An uncertainty in this value results from uncertainty in the assignment of an apparent change in the weight of the crucible.

Results of the alpha assays are reported as milligrams of uranium per gram of coated particles. It is important to recognize that the alpha assay does not distinguish among core uranium exposed by a crack in the coating, uranium on the outside surface of the coating, or uranium in the top 10 μ of the coating. For this reason, the weight of uranium equivalent to a measured counting rate cannot be estimated with good precision. In this report, it is assumed that all uranium detected by alpha counting is in a 10- μ layer and that the distribution in this layer is uniform. In general, the alpha assays show that a very small fraction, $\sim 10^{-6}$, of the total uranium in the coated particles is "in" the coatings. For comparison, a UO_2 particle 120 μ in diameter and coated with 40 μ of alumina contains 40 w/o uranium.

Fission-gas retention of the coated particles, as determined by neutron activation, was good. In a 2-hr heat treatment at 2400 F, one lot (16587-6-1B) of material having a 20- μ coating released 1.6×10^{-2} per cent of the total xenon-133 present in the particles at the beginning of the heat treatment. Another lot (16587-9-2) with 35 to 40- μ coatings released 3.7×10^{-3} per cent in 50 min at 2000 F.

Lot 16587-14-4E showed a postirradiation release of 7.7×10^{-4} per cent in 240 min at 1950 F. In the light of its demonstrated fission-gas retention, this lot of coated powder has been selected for an in-pile capsule experiment.

CONCLUSIONS

- (1) Uniform, void-free coatings of dense alumina up to 150 μ in thickness have been deposited on fine uranium shot in a fluidized-bed reactor by the hydrolysis of aluminum chloride vapor.
- (2) The alumina-coated uranium exhibited excellent air-oxidation resistance and good fission-gas retention at temperatures up to 2400 F after low irradiation exposures.
- (3) Alumina coatings have been made which are sufficiently strong to withstand thermal cycling, even above the deposition temperature, where the greater expansion of the uranium core results in tensile stress in the coating.
- (4) The coating process has not been optimized, but it appears from a consideration of the preliminary work that, with additional development, commercial feasibility of the process can be demonstrated.

ACKNOWLEDGMENT

The authors acknowledge the contributions of several Battelle staff members, particularly those of J. H. Oxley, who provided technical consultation, A. K. Smalley, who performed the air-oxidation tests, and H. S. Rosenberg, who performed the alpha assays and fission-gas-release measurements.

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