SAVANNAH RIVER LABORATORY MONTHLY REPORT

²³⁸Pu Fuel Form Processes

JULY 1973

E. I. du Pont de Nemours & Co.
Savannah River Laboratory
Aiken, S. C. 29801

MASTER

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SUMMARY

The extension to the Alpha Materials Facility is now operational using maximum quantities of 5 g ^{238}Pu . Work with larger quantities will begin on completion of the automatic fire suppression system and ventilation modifications.

(p 13)

Observation of grain boundary porosity caused by release of stored helium on heating to 1200 and 1600°C in dense $^{238}\text{PuO}_2$ shards about 11 mo after fabrication indicates that the size of grain boundary pores increases progressively with annealing temperature between 1000 and 1600°C.

(p 5)

BET surface area analyses of krypton adsorption on 9- μ direct-strike $^{238}\text{PuO}_2$ were reproducible on repetitive analyses with the same 300-mg samples, but gave significantly different results on different samples from the same powder lot.

(p 6)

Based on economic and design considerations and on thermodynamic analyses, the maximum nitrogen concentration in the recirculating argon atmosphere of the PuFF Facility will be set at 1000 ppm.

(p 9)

Operation of the chemical vapor deposition (CVD) system was evaluated further using 4% H_2 - 96% He. However, because of decreased funding, further development on PMC process development has been postponed until FY-75.

(p 11)

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INTRODUCTION

This report is one of a series to summarize progress in the Savannah River Laboratory (SRL) ^{238}Pu Fuel Form Program; this program is supported by the AEC Divisions of Space Nuclear Systems (SNS) and Military Applications (DMA).

Goals of the SRL program for SNS are: to provide technical support for the transfer for SNS ^{238}Pu fuel form fabrication operations from Mound Laboratory to a new facility to be built at the Savannah River Plant (SRP), to provide the technical basis for ^{238}Pu scrap recovery at SRP, and to assist in sustaining plant operations. This part of the program includes:

Demonstration of processes and techniques, currently in use at Los Alamos Scientific Laboratory (LASL) and Mound, for production at SRP, thereby providing design information and the data upon which technical standards and operating procedures will be based.

Technical Support to assist plant startup, and to assure continuation of safe and efficient production of high quality heat source fuel.

Process Development after startup to accommodate changes in product and product specifications, to assist user agencies in improving product performance, and to assist the plant in developing process steps that increase efficiency and product reliability.

The goal of the SRL program for DMA is to demonstrate the applicability and fabrication processes for SRP oxalate-based $^{238}\text{PuO}_2$ as fuel for the Milliwatt Radioisotope Thermoelectric Generator should production of this fuel to be transferred to SRP.

PROCESS DEVELOPMENT AND DEMONSTRATION

METALLOGRAPHY OF MOUND SHARDS

Observation of grain boundary porosity caused by release of stored helium on heating to 1200 and 1600°C in dense $^{238}\text{PuO}_2$ shards about 11 mo after fabrication indicates that the size of grain boundary pores increases progressively with annealing temperature between 1000 and 1600°C. Similar porosity was

observed after heating at 1400°C, but not at 1000°C (June report, p. 6).

The shards being examined were obtained from production operations at Mound Laboratory last September. Metallography is being done to develop metallographic techniques and to investigate the effect of decay helium release on microstructure to provide a basis for avoiding the introduction of detrimental porosity during production of similar shards made from oxalate-based $^{238}\text{PuO}_2$ in the ^{238}Pu Fuel Form Fabrication Facility (PuFF).

The shards, all from the same lot, were fired at 1600°C and aged for approximately 10½ to 11 mo at low temperatures and then heated for one hour at the indicated temperatures. The structures of shards heated to 1200 and 1600°C are shown in Figures 1 and 2. In both large and small grained shards, strings of very fine pores can be seen at the grain boundaries after heating at 1200°C, Figure 1. Similar but considerably larger pores are observed on heating to 1600°C, Figure 2. Heating to 1600°C has also caused noticeable grain separation and formation of elongated grain boundary porosity.

BET* SURFACE AREA ANALYSES

BET surface area analyses of krypton adsorption on 9-μ direct-strike $^{238}\text{PuO}_2$ were reproducible on repetitive analyses with the same 300-mg samples, but gave significantly different results on different samples from the same powder lot. These additional measurements (June report, p. 5) are part of a continuing effort to correlate particle size with surface area of self-heating $^{238}\text{PuO}_2$ powder. Data taken on 300-mg samples are listed in Table I. Sample-to-sample variations are probably due to temperature variations caused by differences in powder configuration in the sample flask. An analysis for errors in surface area determinations due to uncompensated temperature differences shows that variations of only a few degrees could give errors of the order of 100%. These data on direct-strike $^{238}\text{PuO}_2$ will be compared with results from 300-mg samples of reverse-strike $^{238}\text{PuO}_2$ powder, which should have a much higher surface area.

*Brunauer-Emmett-Teller

(a) Small Grain Shard, Etched

40 μ

(b) Large Grain Shard, Etched

40 μ

FIGURE 1. HIGH DENSITY SHARDS AGED APPROXIMATELY 11 MONTHS AT LOW TEMPERATURE THEN HEATED TO 1200°C FOR ONE HOUR.

Helium released damage barely resolvable at grain boundaries.

(a) Small Grain Shard, Etched and Repolished 40 μ

(b) Large Grain Shard, Etched and Repolished 40 μ

FIGURE 2. HIGH DENSITY SHARDS AGED APPROXIMATELY 11 MONTHS AT LOW TEMPERATURE THEN HEATED TO 1600°C FOR ONE HOUR.

Helium release damage present as distinct grain boundary porosity.

TABLE I

APPARENT SPECIFIC SURFACE AREAS OF 9- μ
DIRECT-STRIKE $^{238}\text{PuO}_2$ CALCINED AT 700°C

<u>Sample</u>	<u>wt.,g</u>	<u>Area, m²/g</u>
1	0.313	0.73 (June report, p. 5)
2	0.311	1.26
	0.311	0.92
	0.311	0.89
	0.311	1.22
	0.311	<u>1.22</u>
		1.10 avg
3	0.313	1.63
	0.313	1.81
	0.313	1.79
	0.313	1.74
	0.313	<u>1.66</u>
		1.73 avg

NITROGEN CONTENT IN CELL ATMOSPHERES

Based on economic considerations, nitrogen in the argon atmosphere of process cells in the PUFF Facility will be controlled to less than 1000 ppm. Thermodynamic analysis, as well as a literature survey, indicate that higher nitrogen levels, even to pure nitrogen might be acceptable; however, no demonstrated experience exists for $^{238}\text{PuO}_2$ fuel fabrication.

A 1000-cfm recirculating argon system, from which water and oxygen are continuously removed, will supply protective inert gas to the process cells. The nitrogen concentration will build up from air inleakage if nitrogen is not removed. The nitrogen content can be controlled by purging with a sidestream of pure

argon, scrubbing with Ti-Zr getter beds, or by preventing inleakage. The simplest and most economical of these alternatives is the use of a sidestream purge. The cost of argon consumed is estimated to range conservatively from 0.3 million dollars per year to maintain 100 ppm N_2 to about one-tenth of this to maintain 1000 ppm.

The required nitrogen level is not presently specified at Mound Laboratory; however, the nitrogen level in the once-through argon system is estimated to be about 50 ppm during production of pure plutonium oxide (PPO) spheres. Satisfactory results were also obtained during fabrication development at Mound at an estimated nitrogen level of 200 ppm. Because the large operating cost in maintaining <500 ppm in the PuFF Facility, the possible problems caused by higher nitrogen impurity levels were examined to define any deleterious interactions in the process.

A thermodynamic analysis was performed, based on possible chemical reactions of nitrogen with the $^{238}\text{PuO}_2$ fuel components and equipment to be used at elevated temperatures. Free energy changes for the formation of nitrides were calculated for fuel components at estimated ambient temperatures and for various furnace element materials at different operating temperatures for atmospheres containing 50 ppm oxygen with nitrogen levels up to 5000 ppm. Published values of standard free energies of formation for the various compounds were used, although extrapolation of the data to lower temperatures was necessary for the PuO_2 calculations.

Results of the calculations for 1000 ppm nitrogen and 50 ppm oxygen are shown in Table II. Large positive free energy changes are shown for the formation of PuN from PuO_2 at a PPO sphere temperature of 600°C . The formation of molybdenum oxides in the plutonia-molybdenum cermet (PMC) fuel at 327°C is greatly favored over nitride formation. As a result, PuN formation in either fuel is highly unlikely and surface oxidation will most likely preclude significant nitriding of the molybdenum in PMC. The high positive free energy changes associated with nitriding the various furnace elements indicate no potential problems.

The indications of the thermodynamic study that nitriding of PuO_2 and molybdenum will not occur to any significant extent at higher nitrogen levels in the fabrication cells are substantiated by several experimental studies. Houston¹ sintered PuO_2 at 1600°C in N_2 -6% H_2 and oxygen atmospheres and found the density of pellets sintered in the reducing atmosphere to be less than those sintered in oxygen. X-ray diffraction studies showed significant amounts of $\alpha\text{-Pu}_2\text{O}_3$ in the N_2 -6% H_2 sintered bodies and the presence of PuN was not reported. PuO_2 has a theoretical density of 11.46 g/cc; that of $\alpha\text{-Pu}_2\text{O}_3$ has been calculated

to be 10.20 g/cc. PuN has a calculated density of 14.22 g/cc, higher than that for PuO₂. Consequently, Houston concluded that the lower densities of pieces sintered in N₂-6% H₂ were primarily caused by the presence of the substoichiometric oxide.

Work by Henderson and Galletly² and Lakhtin and Kogan³ has shown that effective surface nitriding of molybdenum metal will only occur at temperatures greater than 850°C. Furthermore, nitriding had to be done in atmospheres containing hydrogen along with the nitrogen to prevent the formation of molybdenum oxides.

TABLE II

FREE ENERGY CHANGES FOR REACTIONS WITH CELL ATMOSPHERE
AT 1000 ppm N₂ AND 50 ppm O₂

COMPONENT	REACTION	TEMP, °K	ΔG, K-cal
PPO sphere	$\text{PuO}_2 + 0.5 \text{ N}_2 = \text{PuN} + \text{O}_2$	873°	151.5
Mo in PMC	$2 \text{ Mo} + 0.5 \text{ N}_2 = \text{Mo}_2\text{N}$	600°	-3.3
	$\text{Mo} + 1.5 \text{ O}_2 = \text{MoO}_3$	600°	-126.1
	$\text{Mo} + \text{O}_2 = \text{MoO}_2$	600°	-97.1
	No nitrides		
Ir shell	$3 \text{ SiO}_2 + 2 \text{ N}_2 = \text{Si}_3\text{N}_4 + 3 \text{ O}_2$	1900°	287.9
	$3 \text{ SiO}_2 + 2 \text{ N}_2 = \text{Si}_3\text{N}_4 + 3 \text{ O}_2$	1300°	331.7
MoSi ₂ furnace element with SiO ₂ coating	$3 \text{ SiO}_2 + 2 \text{ N}_2 = \text{Si}_3\text{N}_4 + 3 \text{ O}_2$	1900°	80.1
	$3 \text{ SiO}_2 + 2 \text{ N}_2 = \text{Si}_3\text{N}_4 + 3 \text{ O}_2$	1300°	19.3
SiC furnace element	$3 \text{ SiC} + 2 \text{ N}_2 = \text{Si}_3\text{N}_4 + 3 \text{ C}$	1900°	80.1
	$3 \text{ SiC} + 2 \text{ N}_2 = \text{Si}_3\text{N}_4 + 3 \text{ C}$	1300°	19.3
Pt-Rh furnace element	No nitrides		
Nichrome, Chromel, Kanthal furnace elements with Cr ₂ O ₃ and/or Al ₂ O ₃ coatings	$2 \text{ Cr}_2\text{O}_3 + 2 \text{ N}_2 = 4 \text{ CrN} + 3 \text{ O}_2$	1300°	300.8
	$2 \text{ Al}_2\text{O}_3 + 2 \text{ N}_2 = 4 \text{ AlN} + 3 \text{ O}_2$	1300°	441.7

CHEMICAL VAPOR DEPOSITION OF MOLYBDENUM

Operation of the chemical vapor deposition (CVD) system was evaluated further using 4% H₂ - 96% He. Use of 100% hydrogen was delayed pending completion of equipment modifications to assure safe operation.

A third 200-g batch of 180-300- μ ThO₂ shards was coated with 13.8 wt % molybdenum in a run of several days that revealed the need for improvements in the CVD system. Normal operation of the system was hindered mainly by pluggage of the inlet (January report, p. 15) caused by condensation of MoCl₅ vapor in the small annulus between the bayonet heater and central tube. Several leaks developed during operation of the system that prevented accurate monitoring of the HCl being generated in the coating process. Transport of liquid from the scrubbers as mist in the gas stream interfered with monitoring of HCl and the total gas flow. Several changes in equipment design are required to improve performance of the CVD system.

The system was operated with the fluid bed at 800°C and 4% H₂-96% He flowing at 15 cfh to investigate monitoring the process with an electrolytic conductivity cell on a water scrubber and controlling the process by varying the MoCl₅ vaporizer temperature and flow of argon carrier gas. The vaporizer was charged with 144 g of MoCl₅, which is sufficient to produce a coating of 17 wt % molybdenum (at 80% coating efficiency) and 4.65 wt % HCl in the 2 l water scrubber. When the run was terminated, 232 g of molybdenum-coated ThO₂ shards were retrieved. The water scrubber contained 1.4 l of 2.78 wt % HCl. The 26 g of MoCl₅ remaining in the vaporizer indicated that up to 41.4 g of molybdenum metal could have been produced. The 32 g of metal apparently deposited on the shards thus corresponds to a coating efficiency of 77.3%. A sample of the shards has been submitted for chemical analysis of molybdenum content.

Operation of the system was interrupted five times: three times when MoCl₅ vapor condensed and plugged the inlet at the junction of the transfer line and central tube, and twice when a bayonet heater was inserted in the central tube. Pluggage was indicated by a pressure increase in the vaporizer and a decreased flow of argon carrier gas. In each case, the inlet was removed from the coater, the pluggage washed out, and the system reassembled and restarted. A low temperature at the small annular opening in the inlet apparently caused the pluggages. An improved inlet system with larger openings and more uniform heating is required.

Leaks developed during operation of the CVD system because of deterioration of silastic seals on the liquid scrubbers, accidental melting of a plastic line to a manometer, and attack of the silver-soldered joints in the inlet by the hot MoCl₅ vapor. These leaks were indicated by the decrease in gas flow measured by a flowmeter in the scrubber exhaust. Loss of HCl through these leaks prevented accurate monitoring of the process. These defects have been corrected.

Liquid loss as a mist from the scrubbers reduced the accuracy of HCl monitoring and interfered with operation of the exhaust flow meter. Replacement of the NaOH back-up scrubber with an "Ascarite"/"Drierite"*** scrubber allowed normal flowmeter operation. An improved scrubber exhaust is needed to reduce the amount of mist produced. However, mist losses will not be as significant in the much shorter runs when 100% hydrogen is used.

Because of decreased funding, further development on PMC process development has been postponed until FY-1975.

DOCUMENTATION

No documents were issued this month.

EQUIPMENT AND FACILITIES

ALPHA MATERIALS FACILITY (AMF)

The five glove boxes comprising an extension that doubles the area of the AMF are now operational at a level of 5 g of ^{238}Pu . Operation at the full 50-g ^{238}Pu level will require completion of the automatic fire suppression system and installation of additional HEPA filters and constant air monitors.

Flow limiting orifices are being installed in the "Halon"*** suppression system to prevent pressurization of the glove boxes on delivery of the "Halon". The actual performance of these orifices was tested with an alcohol fire in the largest glove box, under flow rates of air through the HEPA filters representing new and partially plugged filters. The "rate-of-rise" fire detectors responded automatically about 20 sec after the fire was started to discharge "Halon" simultaneously through two orifices. The fire was extinguished in about 20 sec more. The pressure in the box increased initially from -0.8 in. of water to nearly room pressure from the heat of the fire, but did not pressurize the gloves. The pressure dropped to -0.6 in. of water from the cooling effect of the "Halon" as the fire was quenched and slowly increased to a maximum of about -0.15 in. of water until the "Halon" was exhausted. The "Halon" addition from the 18 lb cylinder lasted about 20 min, and the fire could not be reignited until 45 min after the initial "Halon" addition. Apparently decomposition of the "Halon" gas

*Trademark of Authur H. Thomas Co.

**Trademark of W. A. Hammond Drierite Co.

***Trademark of ICI America, Inc.

caused a deposit on all steel surfaces that had to be removed chemically and abrasively. This test confirmed that the "Halon" system will perform effectively and not aggravate a possible release of $^{238}\text{PuO}_2$ powder by pressurization of the box either during a fire or as a result of an accidental "Halon" discharge.

Design has been completed for the installation of a third stage of HEPA filtration on the exhaust plenum from the glove boxes and for a second stage of HEPA filtration for the hoods exhausting room air from the AMF. Design is also complete for low ($<10^5$ α d/m) specific activity continuous air monitors to sample the glove box exhaust between the three stages of HEPA filtration. Provisions will also be made for collecting samples from other selected points in the exhaust train.

Specifications have been written and bids have been requested for the metallograph to replace the existing metallograph in the AMF so as to interface with the IMANCO* image analysis equipment. A mockup of the glove box arrangement has been completed.

The IMANCO image analyzer and Hewlett Packard mini-computer and plotter have been received.

The improved particle-size analyzer, a Model TA Coulter Counter and Population Accessory, was ordered. Delivery is scheduled for late September.

HOT PRESS FACILITY (HPF)

Design and construction of the production hot press is continuing on a schedule for delivery in February 1974. A design review meeting was held with the prime contractor, Centorr Associates. Materials of construction and component parts have been ordered. A full-scale model of the hot press is being built and will be available in September. This model will be used to select the position of the glove ports, the position and number of the sight ports, and will ensure that the necessary reach and sight are available to operate and maintain the hot press.

*Image Analysing Computers, Inc.

SCANNING ELECTRON MICROSCOPE (SEM)

Specifications for the SEM were completed and bids have been requested of three manufacturers. Specifications for purchasing the vacuum-coater unit are being prepared. Final drawings were made for electrical services, liquid detection, fire alarm and fire suppression systems. Specifications were written for the alarm panel to be used with these systems.

Full-size mockups of the top halves of the SEM and vacuum-coater glove boxes were constructed. Models were made of the SEM column and vacuum-coating chamber. Work is continuing to determine the optimum arrangement of glove ports, bag ports, instrumentation and services.

SCRAP RECOVERY

There was no ^{238}Pu recovered during the month.

REFERENCES

1. Houston, M. D., NUMEC-2389-6, Nuclear Materials and Equipment Corp., Apollo, Pennsylvania, (1965).
2. Henderson, G. G. and Galletly, J. C., *Journal of the Society of Chemical Industry*, 27, 387 (1908).
3. Lakhtin, Yu. M. and Kogan, Ya. D., *Metal Science and Heat Treatment*, 1, 24 (1968).

MEETINGS AND VISITS

L. D. Smith, J. P. Shoup, and M. K. Parsons of SLA visited July 23, 1973, for discussions on the Milliwatt RTG.

R. T. Huntoon, J. L. Womack, and A. A. Kishbaugh attended an ALO meeting on the Milliwatt RTG program at SLA July 31.