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DIRECT FABRICATION OF $^{238}PuO_2$ FUEL FORMS

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James W. Congdon

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Savannah River Laboratory
Aiken, SC 29808

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Approval Date: July 1982

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ABSTRACT

The current process for the fabrication of $^{238}PuO_2$ heat sources includes precipitation of small particle plutonium oxalate crystals (4 to 6 μm diameter), calcination to PuO_2, ball milling, cold pressing, granulation (60 to 125 μm), and granule sintering prior to hot pressing the fuel pellet.

A new two-step direct-strike Pu(III) oxalate precipitation method which yields mainly large well-developed rosettes (50 to 100 μm diameter) has been demonstrated in the laboratory and in the plant. These large rosettes are formed by agglomeration of small (2 to 4 μm) crystals, and after calcining and sintering, were directly hot pressed into fuel forms, thus eliminating several of the powder conditioning steps.

Conditions for direct hot pressing of the large heat-treated rosettes were determined and a full-scale General Purpose Heat Source pellet was fabricated. The pellet had the desired granule-type microstructure to provide dimensional stability at high temperature.

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INTRODUCTION AND SUMMARY

The Plutonium Fuel Fabrication (PuFF) Facility is producing $^{238}PuO_2$ fuel pellets for use in radioisotope thermoelectric generators. The process used presently for fuel form fabrication is complex and includes precipitation of small Pu oxalate crystals, calcination to PuO_2, ball milling, granulation, and granule sintering of the $^{238}PuO_2$ prior to hot pressing the fuel pellet. A simplified process has been developed whereby large agglomerates of small crystals are precipitated rather than formed mechanically as in the GPHS process. This direct fabrication process eliminates several of the powder conditioning steps and the resulting process for producing $^{238}PuO_2$ fuel forms is safer, simpler, and more cost effective.

Several Pu(III) oxalate direct-strike precipitations in the Savannah River Plant (SRP) HB-Line have demonstrated that large agglomerates of small crystals (40 to 100 μm), similar to those precipitated in laboratory tests by this method, are produced. The Plant Pu(III) oxalate was calcined to PuO_2 and the PuO_2 was hot pressed to form a full-scale integral GPHS fuel pellet.

Although the entire direct fabrication process has been demonstrated successfully at full-scale, more development is necessary to establish process limit conditions, to perform impact verification tests, and to complete required documentation before direct fabrication is implemented as a production process.

BACKGROUND

The GPHS Fuel Fabrication process was developed at Los Alamos National Laboratory (LANL) and refined for production by the Savannah River Laboratory (SRL). The flowsheet is shown in Figure 1. The PuO_2 feed for this process is produced by calcining Pu(III) oxalate (4 to 6 μm) precipitated by reverse strike. The PuO_2 is ball milled to <1 μm which is easily airborne and is a potential hazard if containment is lost. The fine powder is cold-pressed into compacts and the compacts are broken and screened to <125 μm for hot pressing into fuel forms.[1] In order to simplify the fuel form fabrication process and make it safer, several precipitation methods were tested to produce PuO_2 with particle

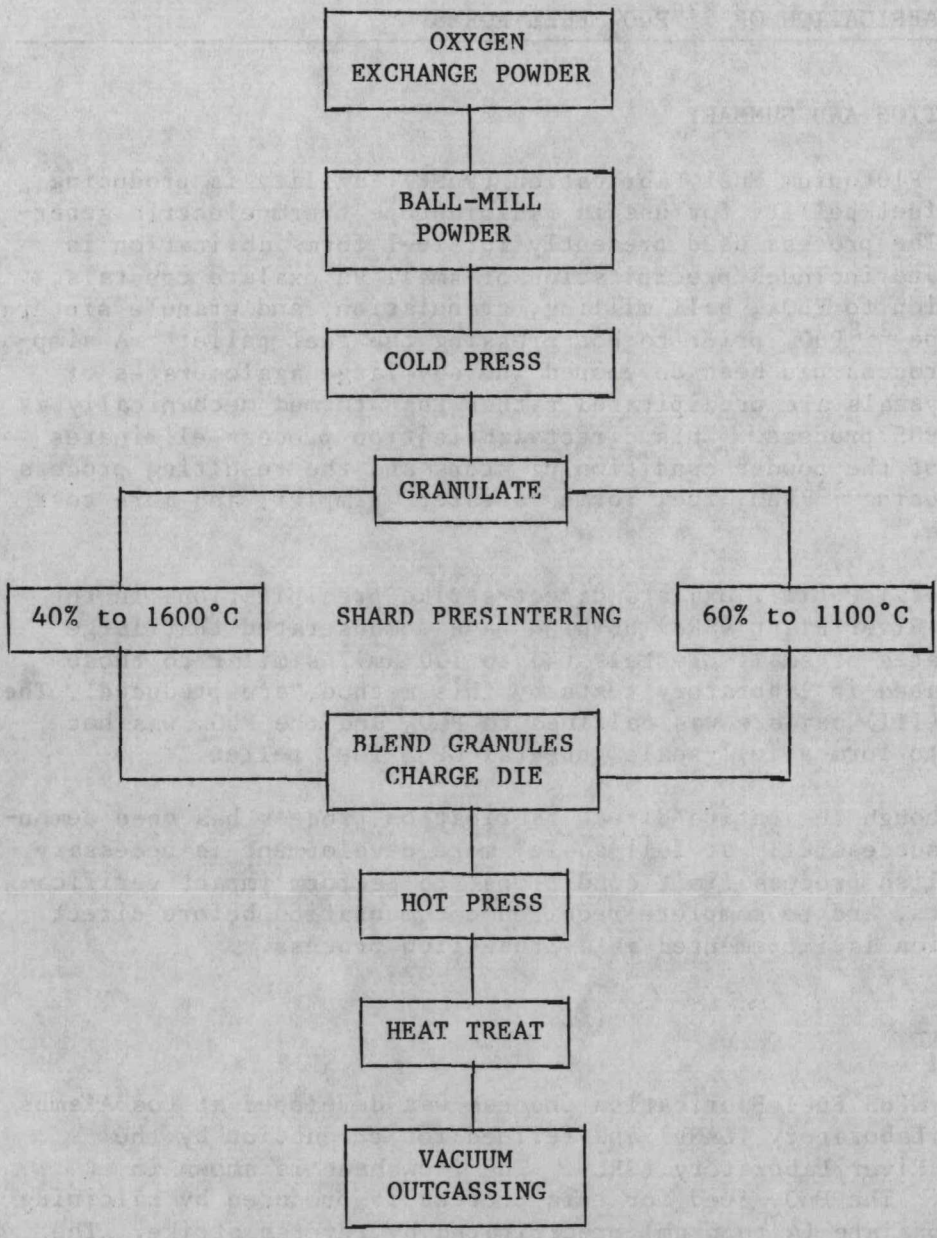


FIGURE 1. GPHS PROCESS FLOWSHEET

size and morphology that could be fabricated directly to the fuel form.[2] This approach eliminates the milling to very small particles of PuO_2 and results in improved safety and housekeeping. Also, elimination of powder conditioning steps decreases cycle time and cost and decreases metallic impurities in the fuel pellet.

The first approach for developing a direct fabrication process for $^{238}PuO_2$ fuel was based on calcining Pu(IV) oxalate precipitated by reverse strike. The PuO_2 particles are uniform 15 to 20 μm platelet-shaped crystals with tap density ~40% of theoretical crystal density (Figure 2a). The particle size and shape of the Pu(IV) oxalate precipitated in laboratory tests was generally quite insensitive to variations in precipitation conditions. Several 1 to 2 gram pellets with uniform microstructure and density were made by direct fabrication using 15 to 20 μm PuO_2 platelets (Figure 2c).

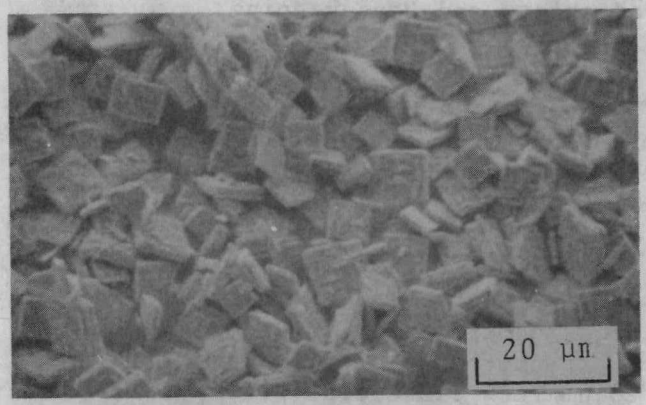
Several Pu(IV) reverse strike precipitations in plant facilities yielded much smaller particle sizes and different morphologies than Pu(IV) oxalate crystals which were produced in laboratory tests (Figure 2b). The PuO_2 from calcination was not useful for direct fabrication so another precipitation method was developed in the laboratory. A direct fabrication method based on Pu(III) oxalate precipitated by direct strike has been demonstrated in both SRL and SRP. This process is accomplished by precipitating large agglomerates (40 to 100 μm) of small crystals (2 to 3 μm) rather than forming large granules mechanically. The large agglomerates are calcined to PuO_2 and 40% are sintered in a reducing atmosphere to densify prior to hot pressing the fuel pellet (Figure 3). The results of this process development are discussed in this report.

EXPERIMENTAL PROCEDURES

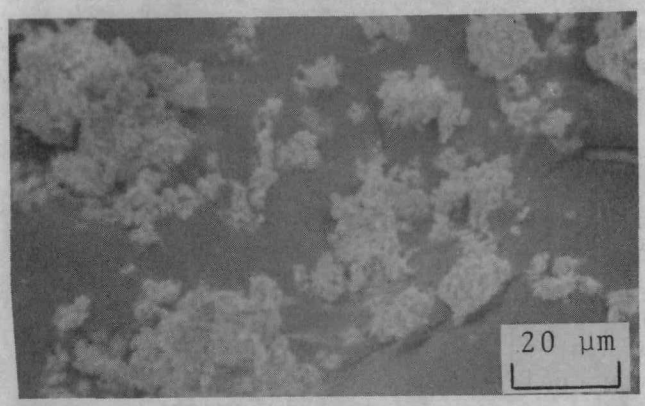
Precipitation Equipment

Two precipitators were used for laboratory tests. For 1 gram-scale precipitations, a jacketed glass vessel (3 in. ID and 4 in. high) with four baffles and a stirrer was used. The four 1/4 in. baffles were equally spaced on the vessel wall. The stirrer had two paddles with four blades each. Each paddle was 1/4 in. wide and the diameter across two blades was 1-1/4 in.

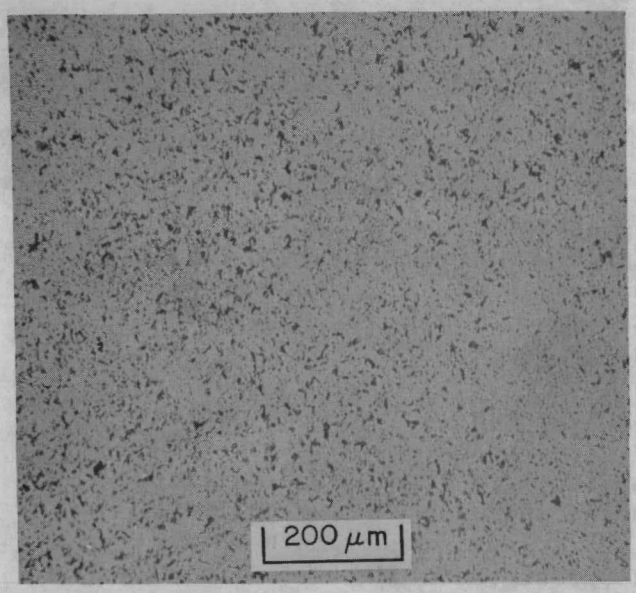
For 5 gram-scale precipitations, a scaled down model of the plant precipitator was used. The jacketed stainless steel vessel (5 in. ID and 7 in. high) was equipped with stirrer and baffles. The four 1/2 in. baffles were equally spaced on the vessel wall. The stirrer had two paddles with four blades each. Each paddle was 3/4 in. wide and the diameter across two blades was 3 in. The plant precipitator is similar in design to the 5 gram laboratory precipitator except the plant scale is ~100 grams.



a. PuO_2 From SRL Precipitation



b. PuO_2 From Plant Precipitation



c. Microstructure of Pellet From SRL PuO_2

FIGURE 2. PuO_2 From Pu(IV) Reverse-Strike

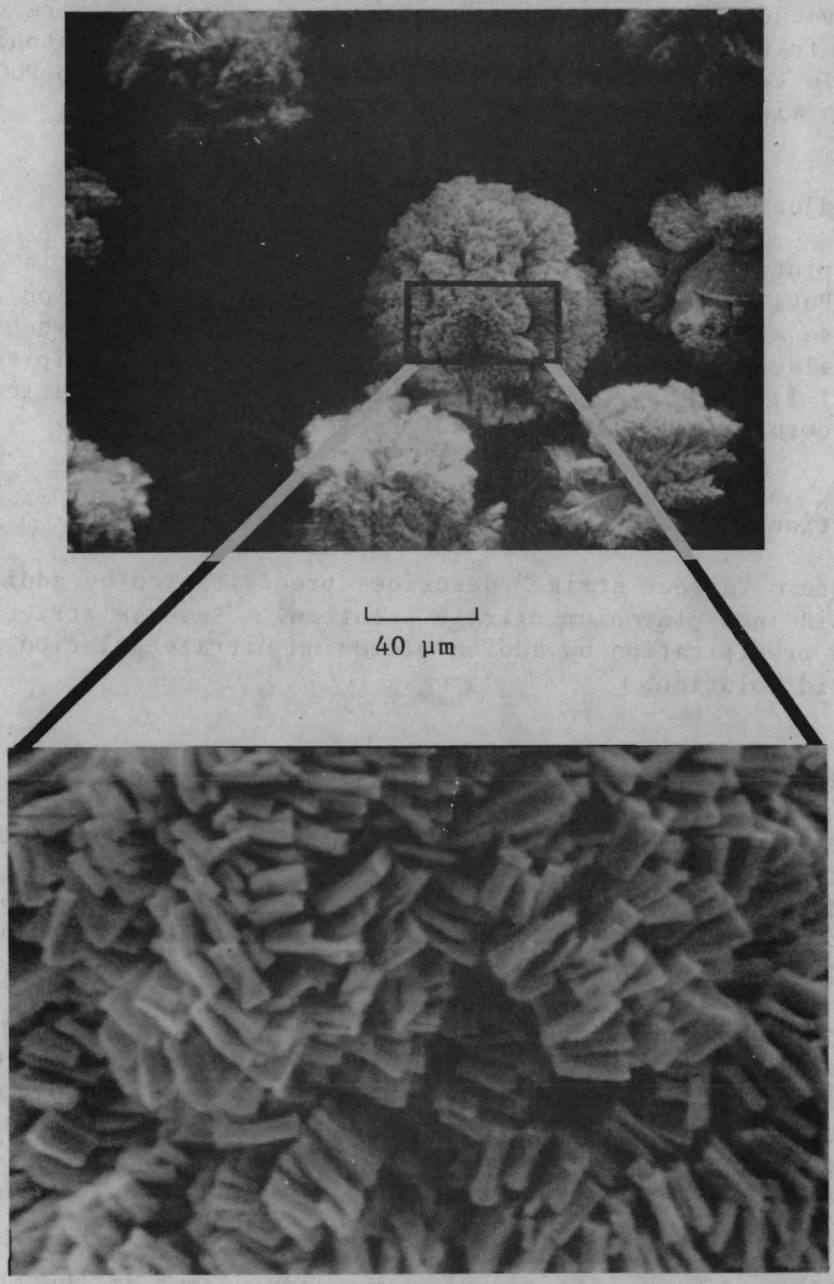


FIGURE 3. Pu(III) Direct-Strike Rosettes (Run 1)

The vacuum filtered plutonium oxalate precipitates were collected on fritted glass disks of medium porosity. The plutonium oxalate was transferred to a platinum boat and calcined to PuO_2 by heating in air at 650 to 700°C for two hours.

Valence Adjustment

The plutonium nitrate feed for oxalate precipitation is 5 to 8 g Pu(IV)/L in 1 to 2M nitric acid obtained by elution from strong base anion exchange resin. No adjustment is made when Pu(IV) oxalate is precipitated. For Pu(III) oxalate precipitation, the Pu(IV) is rapidly adjusted to Pu(III) with 0.05M hydrazine and 0.075M ascorbic acid just prior to precipitation.

Precipitation Procedure

The term "direct strike" describes precipitation by adding oxalic acid into plutonium nitrate solution. "Reverse strike" describes precipitation by adding plutonium nitrate solution into oxalic acid solution.

PuO_2 Powder Characterization

The particle size and morphology of the plutonium oxalate is dependent on the valence, the precipitation method and other variables. Both Pu(III) and Pu(IV) form insoluble oxalate compounds. The crystal form for Pu(III) oxalate is monoclinic and for Pu(IV) oxalate triclinic but nearly tetragonal.

Particle morphology from different precipitation methods was determined with a contained scanning electron microscope (SEM). A Coulter counter normally used for particle size distribution measurement was not useful for measuring the large size crystals precipitated for direct fabrication and the approximate size was determined by SEM analysis.

The small-scale fabrication and sintering tests and all of the metallographic characterization was carried out in the Alpha Materials Facility (AMF). A horizontal tube furnace was used for sintering and a resistance heated "mini-hot press" was used to form the small-scale pellets. A contained Leitz* MM5 metallograph with a remote controlled stage was used for metallographic analysis.

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* Leitz, Germany

The full-scale fabrication tests were carried out in the Plutonium Experimental Facility (PEF). A vertical tube furnace with a platinum rack was used for $^{16}O_2$ exchange simulation, a horizontal tube furnace was used for high temperature sintering, and a contained induction heated vacuum hot press* with a load capacity of 100,000 lbs. was used to form the pellets. Ceramic trays were used for high temperature sintering in a reducing atmosphere and platinum was used in oxidizing atmospheres.

LABORATORY RESULTS

Precipitation Methods

The original one-gram Pu(III) direct-strike oxalate precipitation at SRL (two-stage oxalic acid addition flowsheet in glass precipitator, Run 1, Table 1) yielded spherical, rosette-shaped aggregates 60 to 100 μ in diameter (Figure 3a). The surface of these rosettes was composed of small (2 to 3 μm) platelets which are densely packed (Figure 3b). The relatively high density of the as-calcined rosettes is shown in the polished cross-section (Figure 4a). When sintered at 1600°C for 6 hr the rosettes are densified to >95% theoretical density (TD) (Figure 4b) and appear similar to mechanically formed shards used for hot pressing in the present process.

Five 5-gram precipitations (Pu(III) direct-strike, two step oxalic acid addition) were made using the SRL miniprecipitator (a stainless steel scale model of the plant HB-line precipitator). Precipitation conditions for Run 2, Table 2 were the same as used in the original one-gram test. The powder had the same rosette morphology but was slightly smaller (50 to 60 μm, Figure 5). Additional 5 gram-scale Pu(III) direct-strike precipitations were made in the mini precipitator to identify process limits and produce PuO_2 for hot pressing. Temperature, addition rate, and procedure for addition were varied (Runs 3 to 6, Table 2). The morphology of the precipitate is dependent on each of the parameters tested (Table 2) so careful control of conditions is necessary to precipitate acceptable direct-fabrication feed material at 23°C.

Since the particles precipitated at 35°C (Table 2) were generally not spherical but rather lower density aggregates of large lathes (20 to 40 μm), several precipitations were made on the 1 gram-scale at 15°C (Table 3). Precipitation at 15°C instead of 23°C increased the range of other precipitation conditions that yield acceptable PuO_2 for direct fabrication (Tables 2 and 3 and Figures 6 to 14).

---

* Centorr, N.H.

TABLE 1

Flowsheet for Direct-Strike Pu(III) Oxalate Precipitation (Two-Step)

1. Feed Adjustment

   - 1.2 ±0.2M HNO_3
   - 5 ±2 g Pu/L
   - 0.05M $N_2H_5NO_3$
   - 0.05M Ascorbic Acid

2. Transfer Adjusted Feed to Precipitator

3. Oxalic Acid Addition to Precipitator

   23° ±3°C

   Oxalic Acid Adjustment No. 1 to $\frac{[H_2C_2O_4]}{[H+]^3} = 0.011 \pm 0.002$
   (Addition Time 10 Minutes)

   Digest for 20 Minutes with Mixing

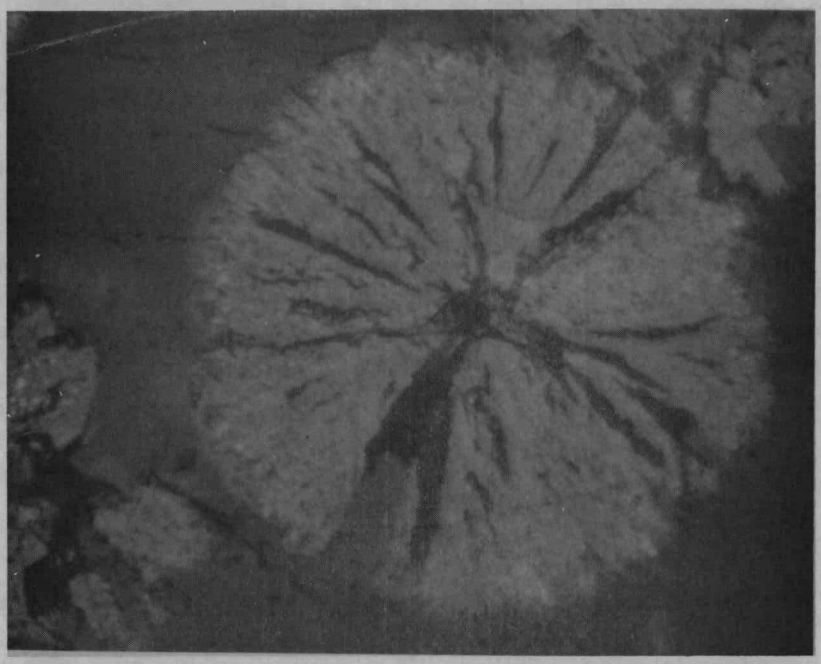
   Oxalic Acid Adjustment No. 2 to 0.22 ±0.02M Oxalate in Supernate (Addition Time 20 Minutes)

   Mix 5 minutes (After Oxalic Acid Addition Complete)

4. Filter

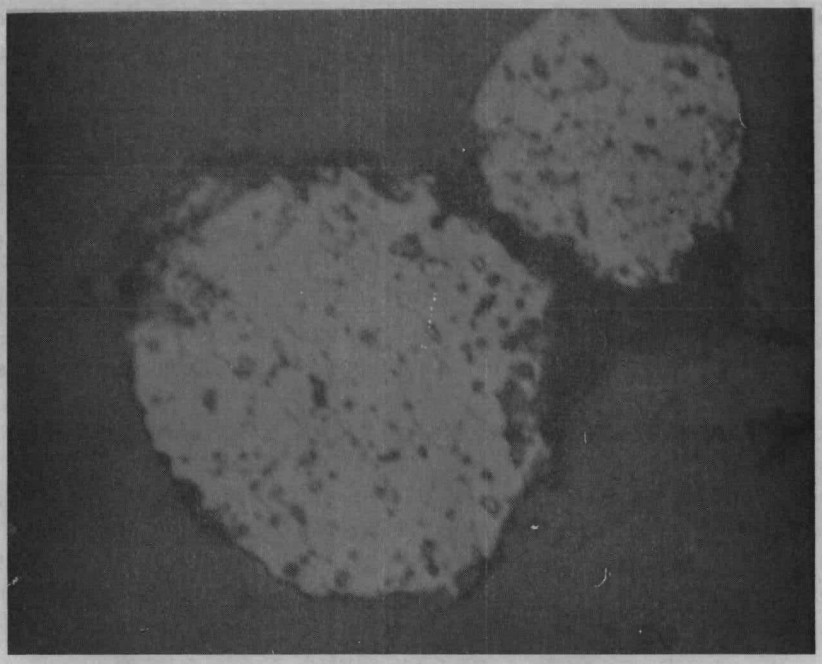
5. Wash the Pu oxalate with three cake volumes of 1.5M HNO_3 - 0.3M $H_2C_2O_4$ - 0.1M hydrazine - 0.1M ascorbic acid

6. Calcine the Pu oxalate at 650°C ±50° for two hours in air



a. As Calcined, Polished

10μm



10μm

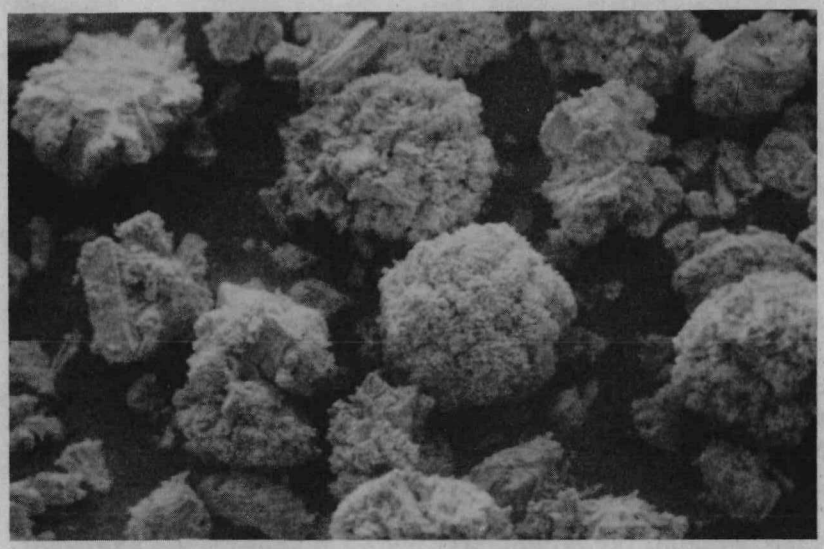
b. Heat Treated (1600°C, 6 hr)
Polished With Grain-Boundary Etch

FIGURE 4. Cross Sections of Pu(III) Direct-Strike Rosettes (Run 1)

TABLE 2

Pu(III) Direct-Strike Parametric Precipitation Test (23°C Centerline)

Run	Run Conditions	PuO_2 Characteristics
1	1 gram-scale, glass precipitator, 23°C. Oxalic acid added in two increments with intermediate digestion of 20 min. First increment of oxalic was stoichiometric amount for precipitation plus enough to adjust the solution so $\frac{H_2C_2O_4}{[H^+]^3} = 0.011$ The second addition adjusted the supernate to 0.22M oxalate. Five minute mixing after completion of oxalic acid addition.	Spherical aggregates 60 to 100 μm formed from small (2 to 3 μm) platelets (Figure 3)
2	5 gram-scale, mini-precipitator. All other conditions (except for possible variation in mixing) the same as Run 1.	Same as Run 1 except 50 to 60 μm aggregates (Figure 5).
3	Same as Run 2, except 35°C.	Lower density aggregates of large lathes (20 to 40 μm) with aggregate at end of each bundle made up of smaller platelets. Generally not spherical (Figure 6).
4	Same as Run 2, except all addition and digestion times reduced one-half.	Aggregates 20 to 40 μm. Platelets larger than Run 1 (Figure 7).
5	Same as Run 2 except first increment of oxalic acid increased by 50%.	Similar to #3 but only 10 to 20 μm (Figure 8)
6	Same as Run 2 except all addition and digestion times were doubled.	Quite similar to Run 5 (Figure 9)



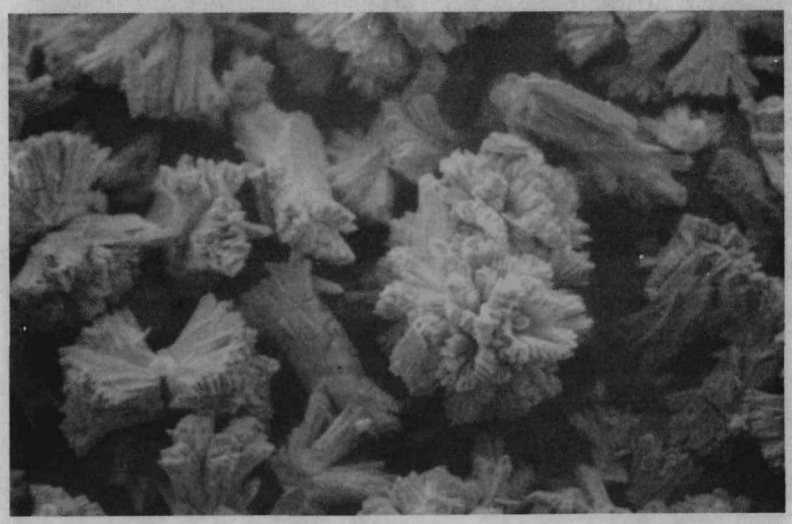
40 µm

FIGURE 5. Pu(III) Direct-Strike Rosettes Precipitated in Miniprecipitator (Run 2)

TABLE 3

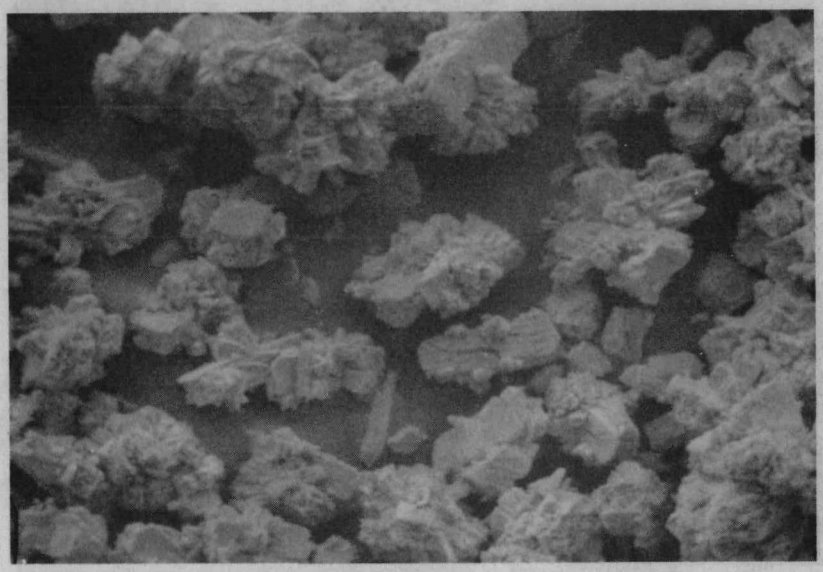
Pu(III) Direct-Strike Parametric Precipitation Test (15°C Centerline)

Run	Run Conditions	PuO_2 Characteristics
1	1 gram-scale, glass precipitator, 15°C. Oxalic acid added in two increments with intermediate digestion of 20 min. First increment was stoichiometric amount for precipitation plus enough to adjust the solution so $\frac{H_2C_2O_4}{[H^+]^3} = 0.011$ The second addition adjusted the supernate to 0.22M oxalate. Five minute mixing after completion of oxalic acid addition.	Spherical aggregates 50 to 70 μm formed from small (2 to 5 μm) platelets. Most aggregates (Figure 10).
2	Same as Run 1, except precipitation temperature 5°C.	Spherical aggregates 40 to 60 μm formed from small (1 to 3 μm) platelets. Mostly aggregates (Figure 11).
3	Same as Run 1, except all addition and digestion times reduced one-half.	Spherical aggregates 40 to 60 μm formed from small (2 to 5 μm) platelets. More smaller pieces of lathes than in Run 1 (Figure 12).
4	Same as Run 1, except first increment of oxalic acid increased by 50%.	Spherical aggregates 40 to 60 μm formed from small (2 to 5 μm) platelets. Quite similar to Run 1.
5	Same as Run 1, except addition and digestion times were doubled.	Spherical aggregates 50 to 70 μm formed from small (2 to 5 μm) platelets. There may be more individual platelets than Run 1 (Figure 13).
6	Same as Run 1, except intermediate digestion time doubled and second addition time halved.	Spherical aggregates 40 to 60 μm formed from small (2 to 5 μm) platelets. There are more individual platelets than Run 1 (Figure 14).



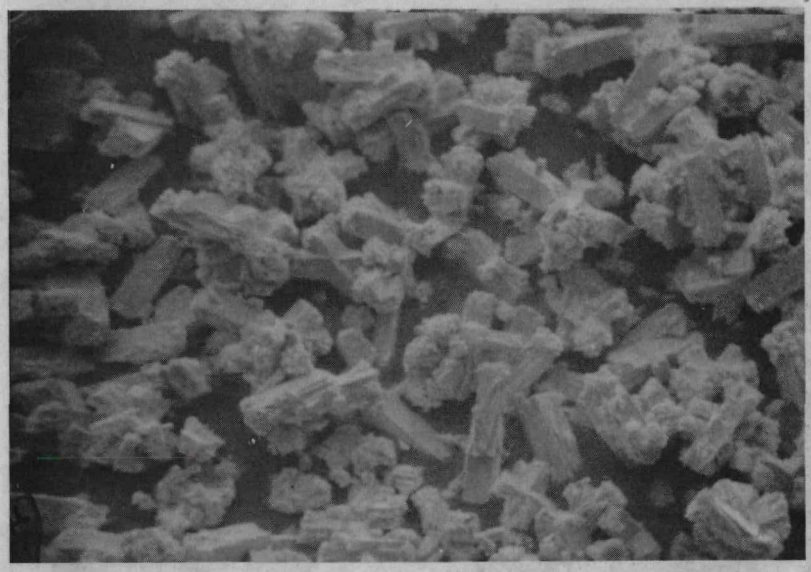
40 μm

FIGURE 6. Pu(III) Direct-Strike (at 35°C) Rosettes (Run 3)



40 μm

FIGURE 7. Pu(III) Direct-Strike Rosettes. Addition and Digestion Times Reduced by Half (Run 4)

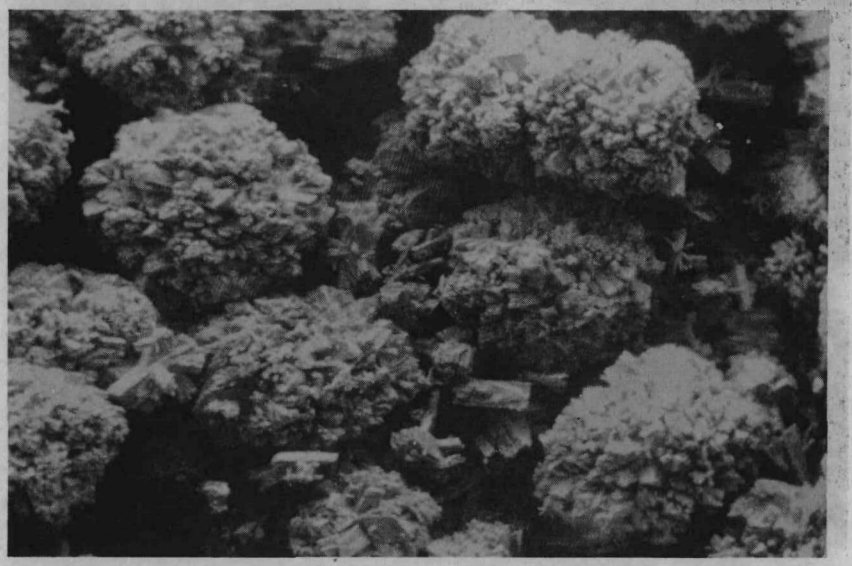


40 µm

FIGURE 8. Pu(III) Direct-Strike Rosettes. First Increment of Oxalic Acid Increased 50% (Run 5)

40 µm

FIGURE 9. Pu(III) Direct-Strike Rosettes. Addition and Digestion Times Doubled (Run 6)

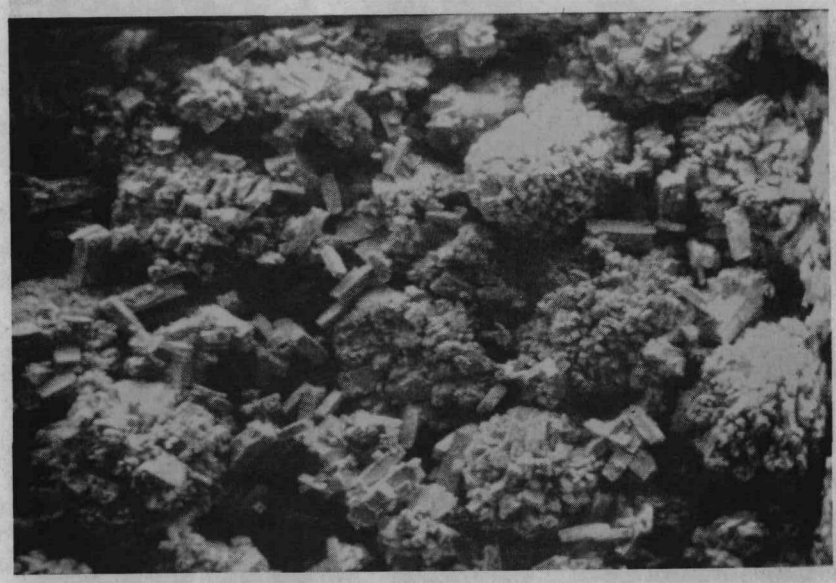


40 μm

FIGURE 10. Pu(III) Direct-Strike Rosettes (15°C)

40 μm

FIGURE 11. Pu(III) Direct Strike Rosettes (5°C)



40 µm

FIGURE 12. Pu(III) Direct-Strike Rosettes (15°C) (All Addition and Digestion Times Reduced One-Half)

40 µm

FIGURE 13. Pu(III) Direct-Strike Rosettes (15°C) (Addition and Digestion Times Doubled)

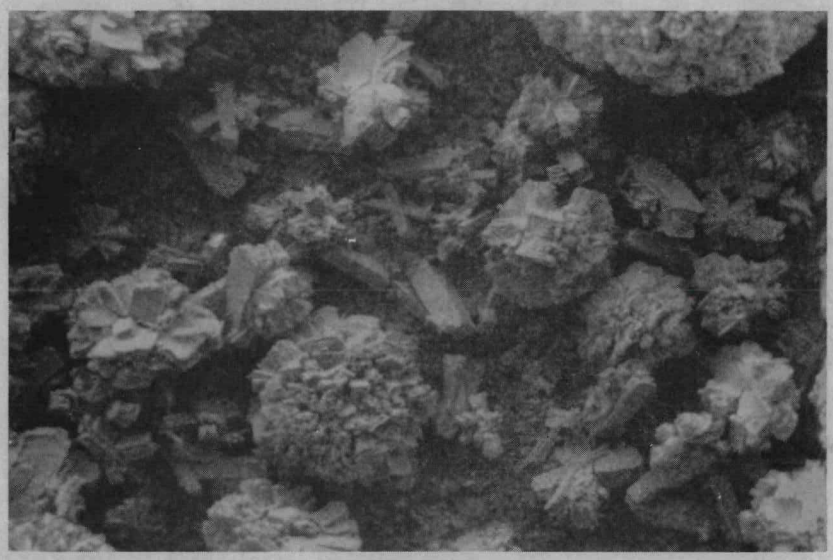


FIGURE 14. Pu(III) Direct-Strike Rosettes (15°C) (Intermediate Digestion Time Doubled and Second Addition Time Halved)

A second simplified Pu(III) direct-strike procedure was also demonstrated in the laboratory to produce large spherical aggregates of small platelets. The temperature was 23°C and the oxalic acid was added continuously at about one-third the rate used for the two step addition method. The flowsheet is given in Table 4.

TABLE 4

Flowsheet for Direct-Strike Pu(III) Oxalate Precipitation (One-Step, Slow-Addition Rate)

1. Feed Adjustment
   - 1.2 ±0.2M HNO_3
   - 5 ±2g Pu/ℓ
   - 0.05M $N_2H_5NO_3$
   - 0.05M Ascorbic Acid
2. Transfer Adjusted Feed to Precipitator
3. Add Oxalic Acid Continuously to Precipitator to 0.22 ±0.02M Oxalate in Supernate
   - Temperature <25°C
   - Addition Time 50 to 60 Minutes
   - Mix 5 Minutes (After Oxalic Acid Addition Complete)
4. Filter
5. Wash the Pu oxalate with three cake volumes of 1.5M HNO_3 - 0.3M $H_2C_2O_4$ - 0.1M hydrazine - 0.1M ascorbic acid
6. Calcine the Pu oxalate at 650 ±50° for two hours in air

Pellet Fabrication

The PuO_2 powder obtained from the 5-gram precipitation test (Run 2, Table 2) was 50 to 60 μm (Figure 5). A 2-gram pellet was successfully fabricated with this feed material using a grog mixture of 40% rosettes sintered at 1600°C and 60% as-calcined rosettes. Metallographic characterization of the pellet showed uniform microstructure with density ~82% TD and no cracks (Figure 15a). As shown in Figure 15b, the identity of the rosettes was retained in the hot pressed pellet resulting in large pores which help to stabilize the microstructure at high temperature. The average grain size exceeds 10 μm, which should be sufficiently large to minimize the generation of fines if the iridium shell ruptures on impact.

FULL-SCALE PELLET FABRICATION USING "$^{240}PuO_2$" SIMULANT

A "$^{240}PuO_2$" simulant* material was used initially to demonstrate full-scale pellet fabrication from a rosette-shaped material because sufficient quantities of $^{238}PuO_2$ rosettes were not immediately available.

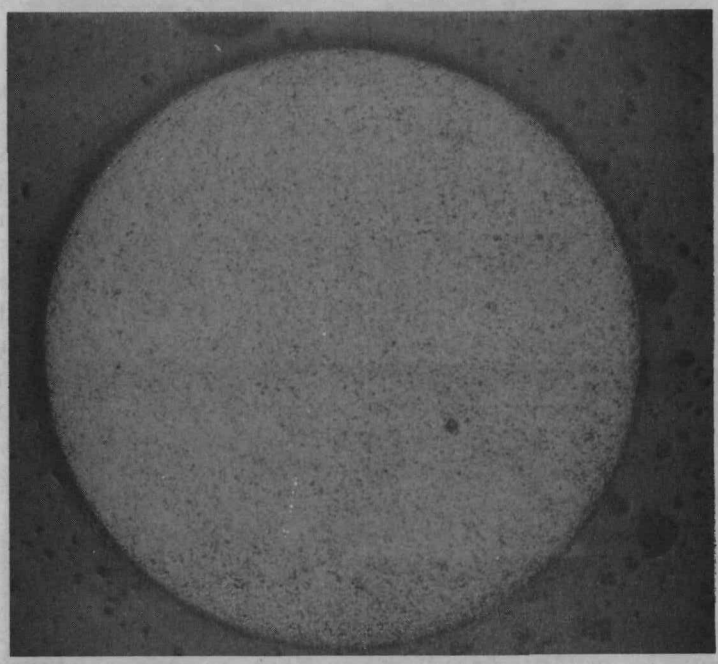
SEM characterization of the "$^{240}PuO_2$" rosettes indicated that this material was an adequate simulant for $^{238}PuO_2$ direct-strike rosettes. As shown in Figure 16, the "$^{240}PuO_2$" consisted of spherical aggregates, up to 120 μm in diameter but with a large volume of fines. Metallographic characterization showed that "$^{240}PuO_2$" rosettes sintered in dry argon at 1600°C for 6 hr had a density of only about 85% TD (Figure 17a) while "$^{240}PuO_2$" rosettes sintered 6 hr at 1600°C in He/4% H_2 had a density >95% TD (Figure 17b).

Direct Fabrication (DF) Pellet 1

A full-scale GPHS pellet (Direct Fabrication (DF) Pellet 1) was fabricated using the "$^{240}PuO_2$" feed. The fabrication conditions and physical properties of DF Pellet 1 are reported in Tables 5 and 6. It was desirable to densify the granules prior to hot pressing to increase the pour density and to better duplicate the "grog" feed material presently being used in the GPHS process. Therefore, 50% of the granules were sintered at 1100°C in argon, and 50% of the granules were sintered at 1600°C in argon.

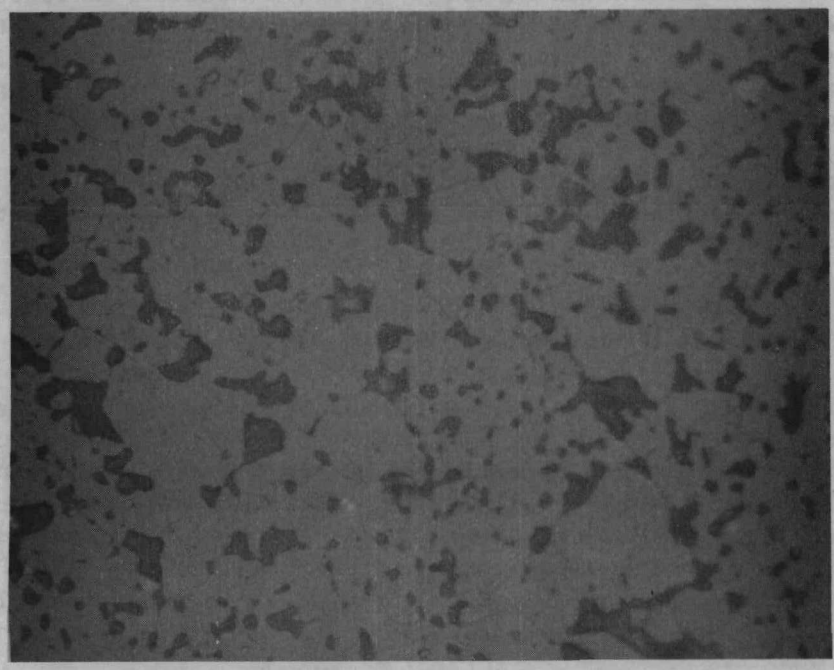
---

* Pu isotopic composition ~20% $^{240}PuO_2$ + ~80% $^{239}PuO_2$. This material was originally precipitated in JB-Line as feed for the SRP program for fabrication of reactor fuel tubes to be used to produce ^{242}Pu.



1000 µm

a. Polished Cross Section



20 µm

b. Microstructure of Section Polished with Grain-Boundary Etch

FIGURE 15. Two-Gram Pellet Made From Direct-Strike-Precipitated Pu(III) Oxalate

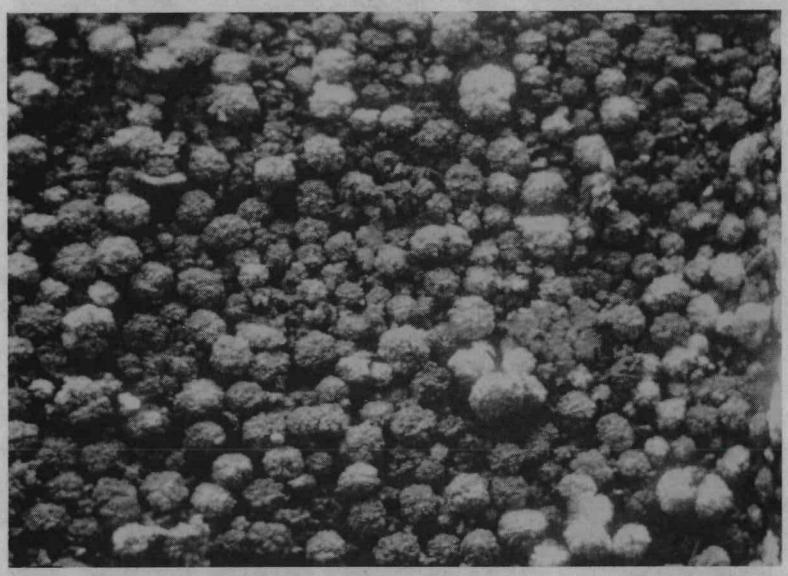
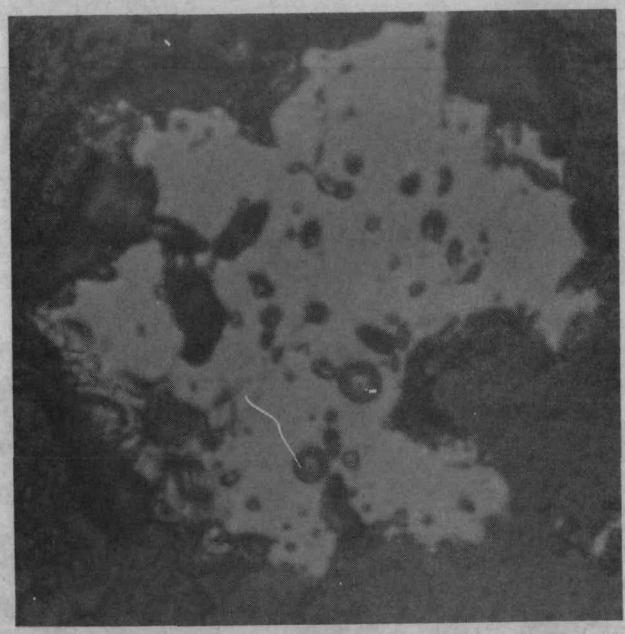
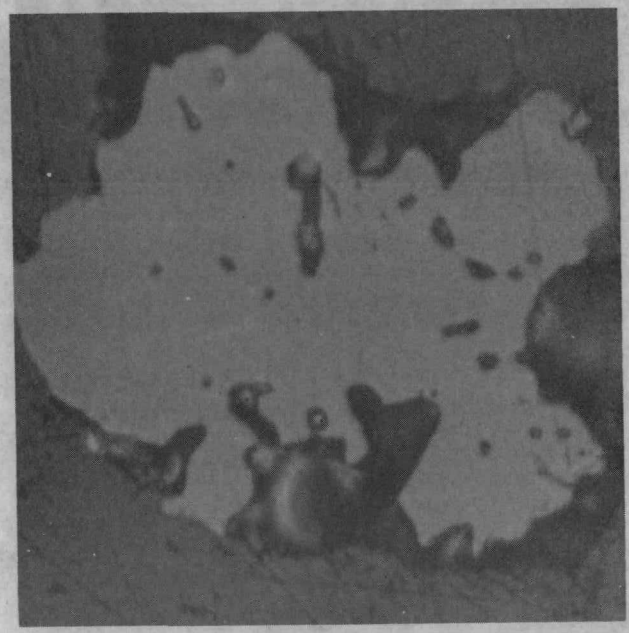


FIGURE 16. "$^{240}PuO_2$ Simulant" Rosettes, as Received



10 μm

a. Granule Sintered 1600°C, 6 hr, Ar



10 μm

b. Granule Sintered 1600°C, 6 hr, He/4% H_2

FIGURE 17. Polished Sections of Sintered "$^{240}PuO_2$ Simulant" Granules

TABLE 5

Process Conditions for Direct Fabrication Pellets

DF Pellet No.	Feed Material	Granules		Die Material	Hot Press Conditions		Heat Treatment (HT)
		Low-Fired	High-Fired		Pressure, psi	Temp., °C	
1	$^{240}PuO_2$	50% at 1100°C, 6 hr, Ar	50% at 1600°C, 6 hr, Ar	W-2% ThO_2	10,700	1615	1425°C, 6 hr, O_2
2	$^{240}PuO_2$	48% at 800°C, 6 hr, Ar	52% at 1600°C, 6 hr, He-4% H_2	Graphite	9300	1570	1525°C, 6 hr, O_2

TABLE 6

Physical Properties of Direct Fabrication Pellets

DF Pellet No.	Weight, g	Diameter, in.	Length	Density, % TD	Microstructure	Degree of Fracture
1						
As Pressed	62.937*	-	-	-	High-density shell (2 mm wide)	Pellet broken during ejection from die liner, additional surface cracking after HT
HT	62.900*	-	-	-		
% Dif.	-0.06%	-	-	-		
2						Small, hairline cracks after HT
As Pressed	148.706	1.0830	1.0810	84.5	Uniform density	
HT	149.420	1.0814	1.0836	85.0		
% Dif.	+0.48%	-0.15%	+0.24%	+0.5		

* Section of pellet

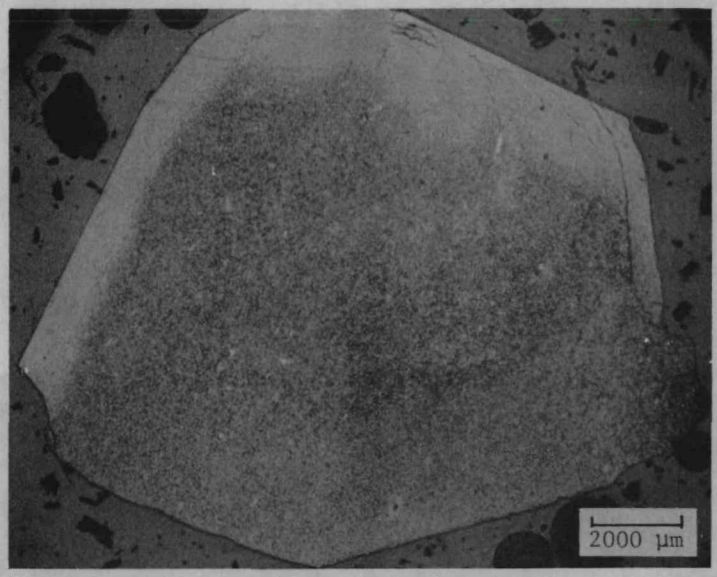
As discussed earlier, the "$^{240}PuO_2$" rosettes had a density of only 85% TD after sintering 6 hr at 1600°C in argon. High-fired shards in the GPHS grog feed normally have a density of ~95% TD. The low-fired granules are very difficult to characterize, but the density and/or sinterability of the low-fired "$^{240}PuO_2$" granules may not have been the same as that of the low-fired shards in the GPHS grog feed.

These differences in the granule feed material were the likely causes for the relatively high temperature (1615°C versus a GPHS centerline temperature of 1525°C) and pressure (10,700 psi vs. a GPHS centerline condition of about 2700 psi) required to hot press DF Pellet 1. It should also be noted that DF Pellet 1 was hot pressed in a W-2% ThO_2 die and that this test apparently exceeded the physical limitations of the die. DF Pellet 1 was broken when the die liner fractured during pellet extraction. Additional surface cracks formed in the piece which was heat treated. As shown in Figure 18, the metallographic examination of a section from DF Pellet 1 revealed a clearly defined, high-density (~98% TD) outer shell which was ~2 mm wide. The density of the remainder of the pellet was ~83 to 85% TD and fairly uniform. The high-density shell may have been related to the characteristics of the granules and/or the hot pressing parameters.

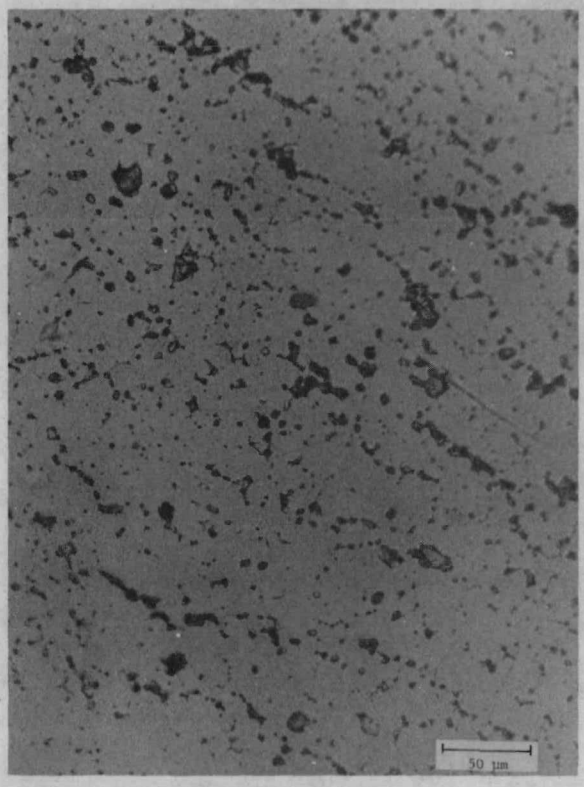
DF Pellet 2

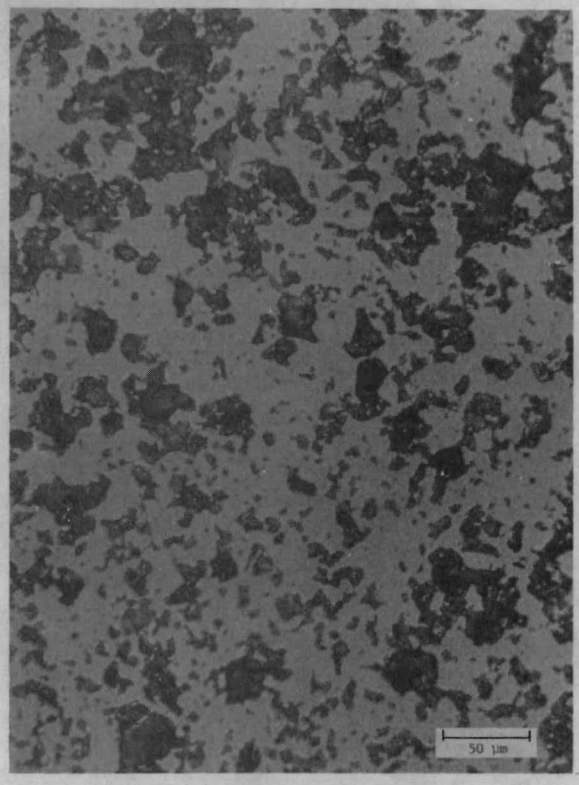
The conditions used to sinter the granules for DF Pellet 2 were adjusted (Table 5) to produce denser, high-fired granules and more-sinterable, low-fired granules. These changes in granule sintering conditions helped reduce the pressure and temperature required to hot press the pellet. The pellet had no visible surface cracks following heat treatment (Figure 19). On the basis of microstructural analysis (Figure 20), the change in process conditions apparently helped to alleviate density gradients. There was no evidence of a high-density shell in DF Pellet 2 although a slightly higher density was observed near the side of the pellet than at the ends or center of the pellet. Some cracking was also observed in a section of the pellet cut from near the side of the pellet.

A graphite die, rather than W-2% ThO_2, was used to hot press DF Pellet 2. This may have contributed to some of the processing and microstructural differences, but there was no evidence to substantiate this possibility.



Polished Section



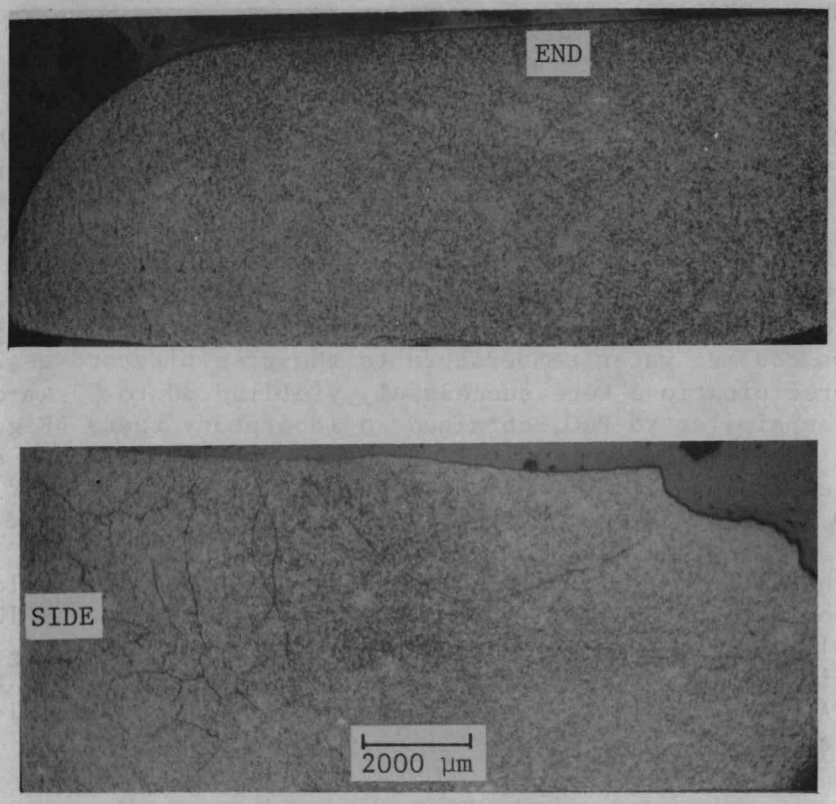


High-Density Shell

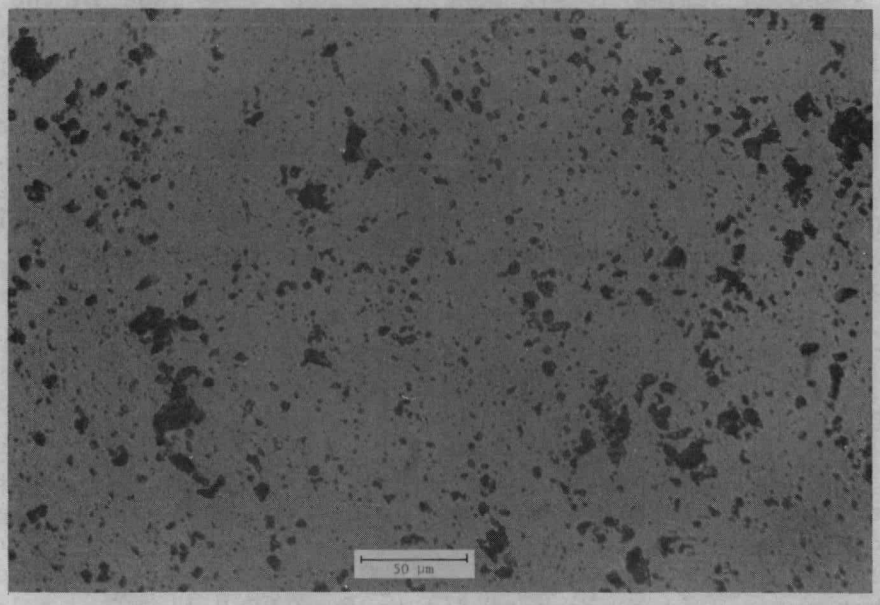
Low-Density Interior

FIGURE 18. Microstructural Analysis of DF Pellet 1

FIGURE 19. DF Pellet 2 After Final Heat Treatment



Polished Sections



Typical Microstructure

FIGURE 20. Microstructural Analysis of DF Pellet 2

HB-LINE Pu OXALATE PRECIPITATION

Plant Test I

Four batches, ~100 grams each, were precipitated in the first plant test. Two precipitation procedures, both of which yielded large spherical agglomerates of small crystals in laboratory precipitations, were tested.

The direct strike Pu(III) oxalate method (two-step oxalic acid addition, Table 1) was used for Runs 101-HA-217 and 101-HA-218. The process cooling water temperature to the precipitator was 21.5°C. Both precipitations were successful, yielding 30 to 50 μm-diameter rosettes similar to PuO_2 obtained in laboratory tests (Figure 21). (These particles were too large for quantitative particle size measurements using the Coulter Counter instrument used for standard $^{238}PuO_2$). This $^{238}PuO_2$ was used to fabricate DF Pellet-3.

The direct strike Pu(III) oxalate method (one-step slow-addition rate of oxalic acid, Table 4) was used for runs 101-HA-219 and 101-HA-220. This method did not yield acceptable PuO_2. One test yielded very small particles (101-HA-219); the other test (101-HA-220) yielded some rosette-shaped aggregates but also a large amount of relatively small particles (Figure 22).

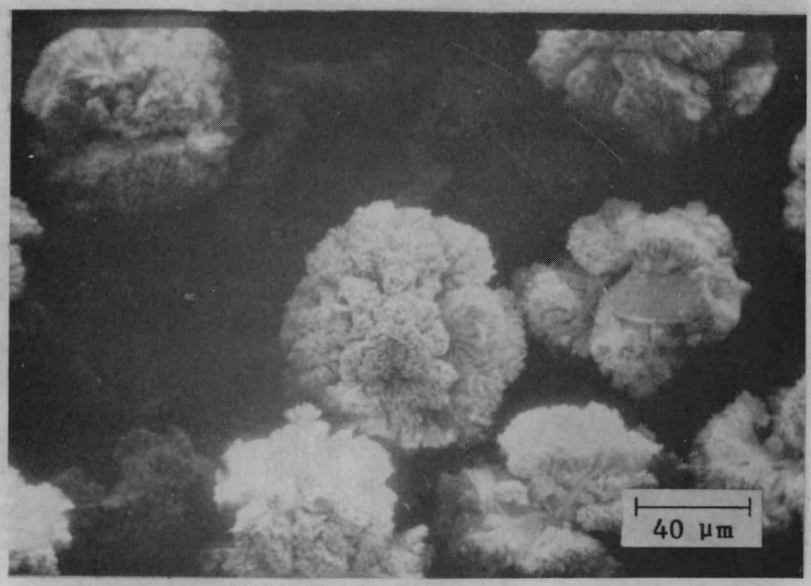
Plant Test II

A second series of six precipitations were made in the HB-Line using the two-step Pu(III) oxalate direct strike procedure. Each precipitation was ~100 gram-scale and the cooling water temperature was ~20°C. Two precipitation batches were combined for calcination and sampling so there were three batches for characterization (103 HA-248, 103 HA 249, and 103 HA 250). SEM analyses showed that large spherical agglomerates of small platelets were obtained from all precipitations (Figure 23). The PuO_2 from Plant Precipitation Test II was used to fabricate pellets DF-4 through DF-8.

FULL-SCALE PELLET FABRICATION WITH $^{238}PuO_2$

DF Pellet 3

$^{238}PuO_2$ from the two 100-gram two-step, plant precipitations (Runs 101 HA 217 and 101 HA 218) was used to demonstrate the direct fabrication process in the PEF. A blend of 40 wt % rosettes sintered for 6 hr at 1600°C in He/H_2O and 60% as-calcined rosettes was hot pressed in a graphite die to form DF Pellet 3. A load of 7000 lb (compared to 2600 lb for the GPHS process) was applied



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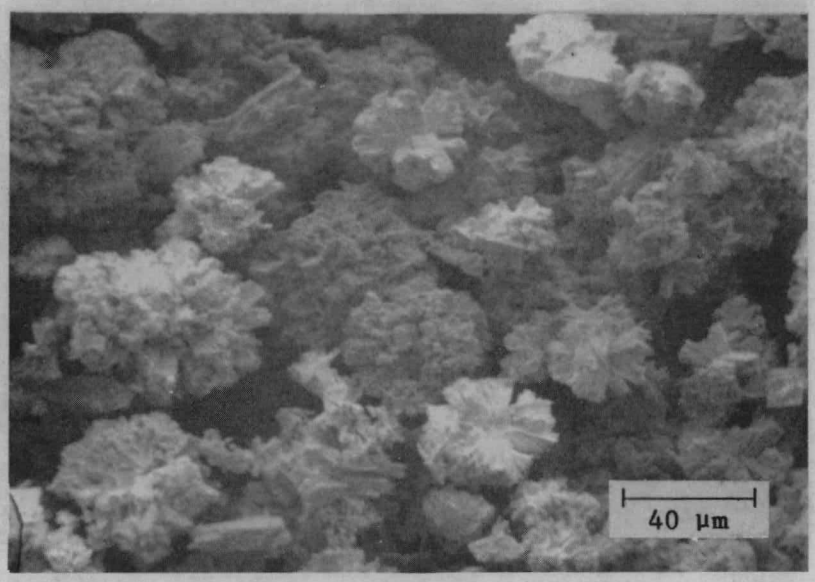
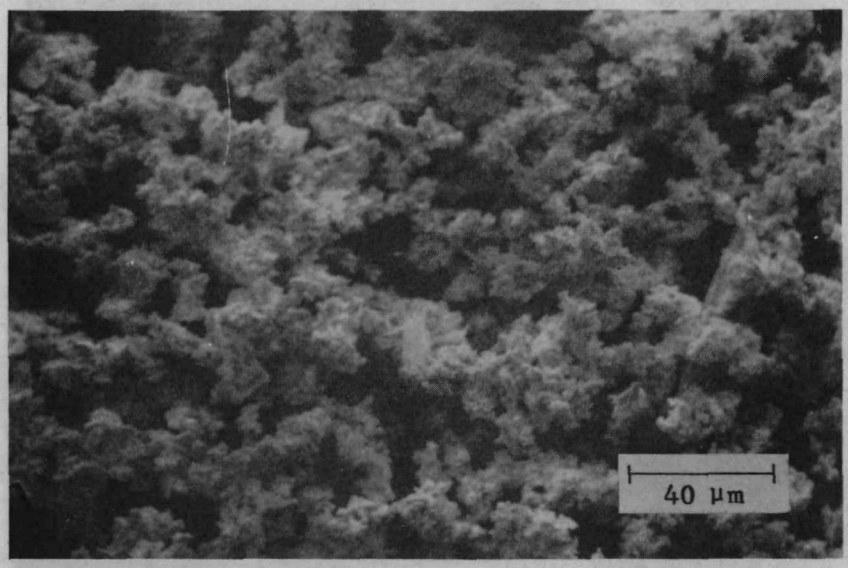
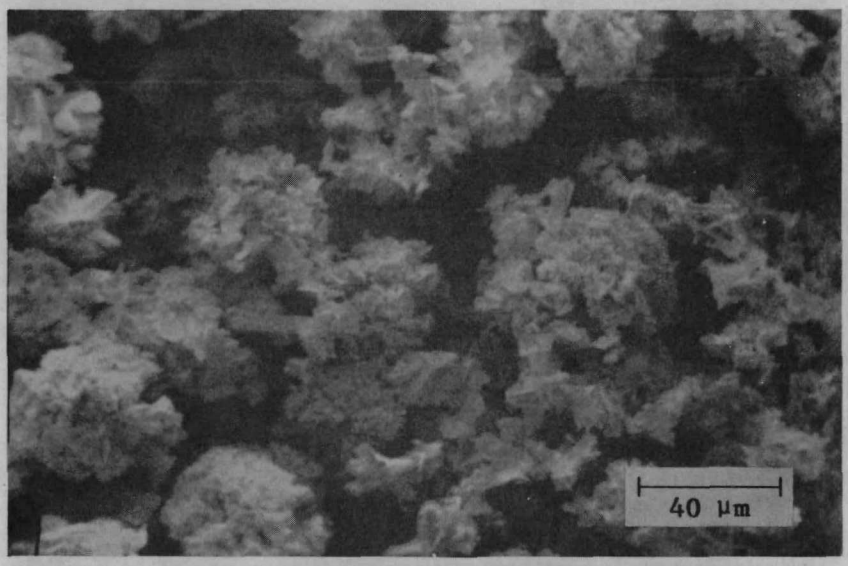


SRP HB-Line

FIGURE 21. Pu(III) Direct-Strike Feed. Rosettes Produced by Two-Step Precipitation Method

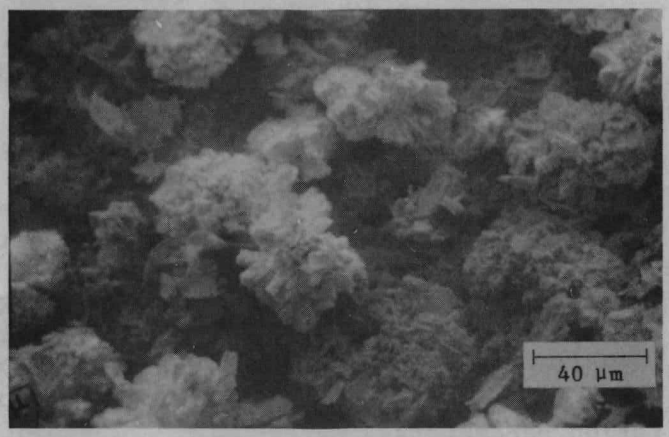


Run No. 101-HA-219

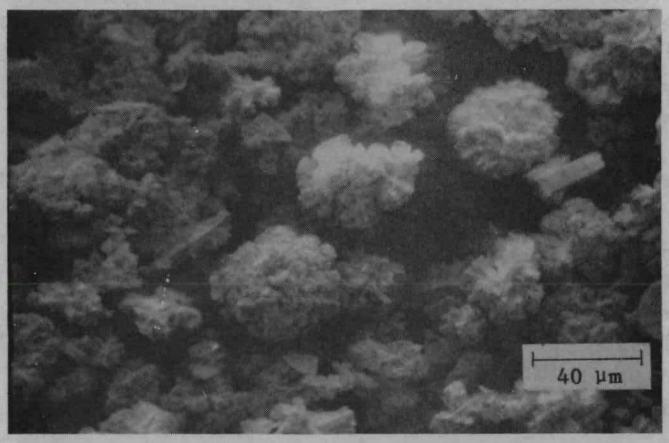


Run No. 101-HA-220

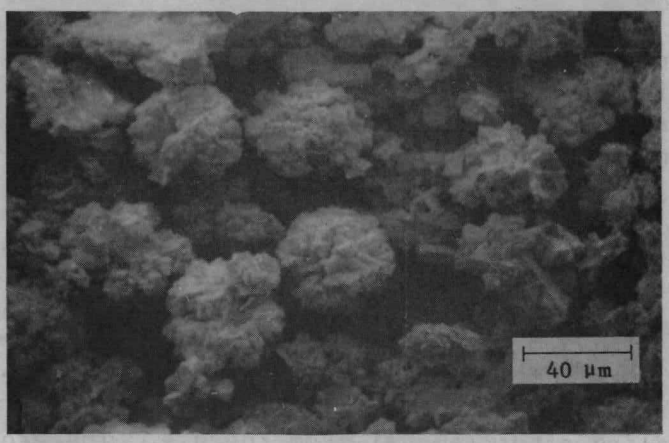
FIGURE 22. Pu(III) Direct-Strike Feed Produced in HB-Line by One-Step Precipitation Method



Run No. 103-HA-248



Run No. 103-HA-249



Run No. 203-HA-250

FIGURE 23. Pu(III) Direct-Strike Feed Produced in HB-Line by Two-Step Precipitation Method

using a slow preload followed by a six-minute parabolic load ramp. Die closure was completed two minutes after the maximum load was applied and at a temperature of 1540°C.

DF Pellet 3 was easily ejected from the die and was uncracked as-pressed. After heat treatment in oxygen the pellet had minor hairline cracks in both ends (Figure 24) similar to the cracks observed in most GPHS pellets fabricated in the PEF. DF Pellet 3 had a final density of 85.7% TD and a linear shrinkage of 0.6% during heat treatment. This shrinkage is only slightly greater than that typically observed in GPHS pellets and may be reduced if the percent fines in the feed can be reduced by controlling the precipitation parameters.

The pellet was sectioned with an Isomet* diamond saw for metallographic examination. After sectioning, the piece of pellet held by the clamp cleaved along a plane perpendicular to the pressing direction, (Figure 24b) probably along a pressing lamination. Further development work was able to reduce the load required for closure, thereby reducing the likelihood of pressing laminations.

Microstructural analysis of three sections of DF Pellet 3 indicated that the pellet had the desired granular-type microstructure with many pores in the 10 to 15 μm range (Figure 25). These relatively large pores in a matrix of grains with an average size of <10 μm give the pellet some microstructural and dimensional stability at high temperatures. Two of the sections were uncracked and the third section was cracked during sample preparation.

DF Pellet 4

In an effort to determine the optimum center line conditions for the direct fabrication of GPHS pellets and to obtain a better understanding of the compaction and sintering characteristics of Pu(III) direct-strike feed, DF Pellets 4, 5, and 6 were hot pressed from feed which had been presintered over a wide range of conditions.

DF Pellet 4 was hot pressed from as-calcined (800°C, 4 hr and 1000°C, 1 hr in O_2) Pu(III) direct-strike feed. The charged die had to be cold pressed because of the low packing density of the feed. Although it appeared that die closure was achieved at 4500 lb, a total of 10,000 lb was applied. DF Pellet 4 was very loose in the die and was easily removed. The pellet cracked during handling after removal from the die. The grog-type feed used for DF Pellet 3 appears to produce a more rugged pellet than

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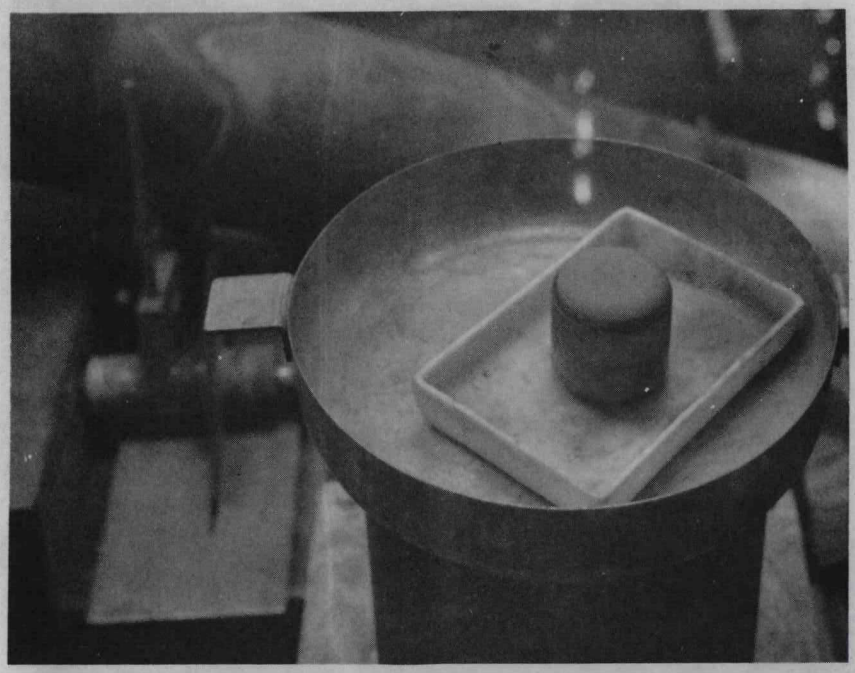
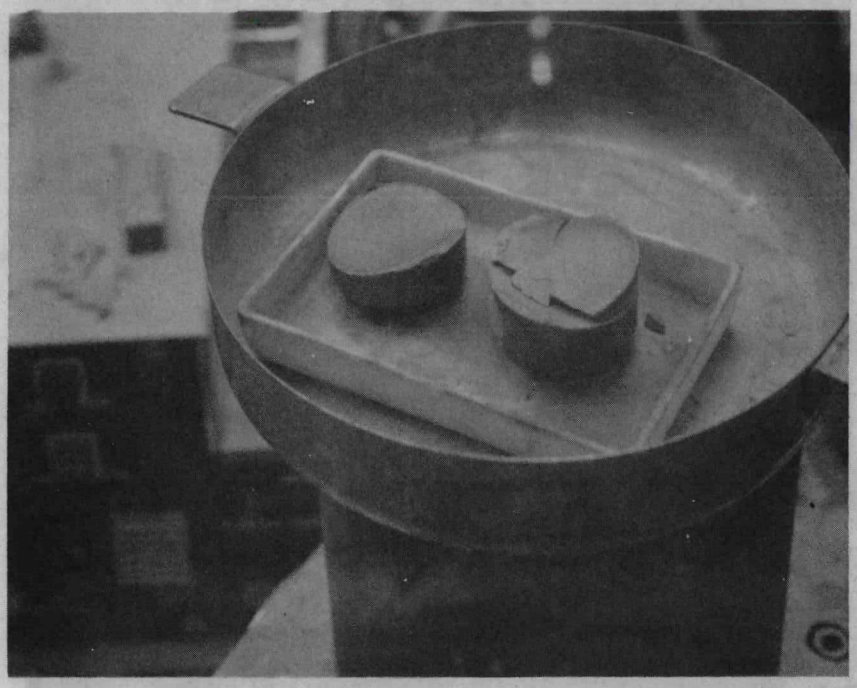
* Beuhler Ltd., 2120 Greenwood St., Evanston, Il 60204

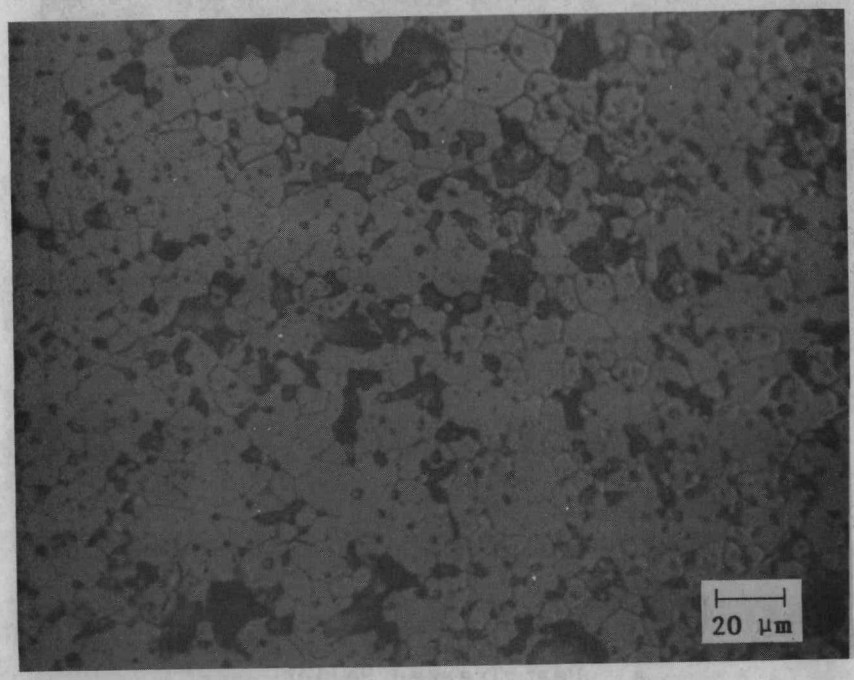


a. Heat-Treated Pellet

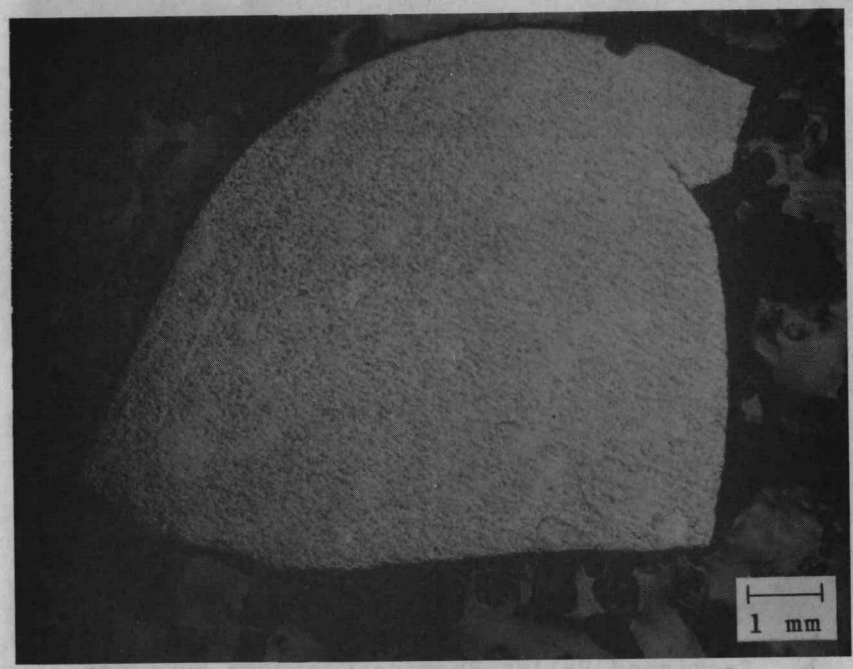


b. Sectioned Pellet Showing Cleavage Surfaces

FIGURE 24. Microstructure of DF Pellet 3



Microstructure (Grain-Boundary Etch)



Cross Section

FIGURE 25. Microstructure of DF Pellet 3

as-calcined feed. The as-calcined feed had a very low packing density and the high sinterability of the feed increased the shrinkage of the pellet.

DF Pellet 5

DF Pellet 5 was hot pressed from Pu(III) direct-strike feed which had been heated at 1300°C for 6 hr in Ar/4% H_2. A load of 5500 lb was required to achieve die closure. The pellet was uncracked as-pressed but was cracked after heat treatment at 1520°C for 6 hr in Ar/5% O_2. The pellet broke into 5 pieces when it was dropped 1/2 in. during handling.

DF Pellet 6

In an attempt to determine if an oxidizing atmosphere could be used for granule presintering, DF Pellet 6 was hot pressed from Pu(III) direct strike feed (60% calcined 4 hr at 300°C, 1 hr at 1000°C, and 40% heated 6 hr 1600°C, in He/5% O_2). Die closure was achieved with only 4500 lb load (vs. 7000 lb for DF-3). The pellet was easily removed from the die and was uncracked as-pressed; however, the pellet was dropped and broken during gaging. One piece was sectioned, as-pressed for metallography and the remainder of the pieces were heat treated and sectioned for metallography. There were no visible cracks in the pellet piece after heat treatment.

DF Pellet 7

Since the DF-6 Pellet fabrication test was inconclusive, the test conditions were repeated for DF Pellet 7. DF Pellet 7 was uncracked as-pressed and dimensionally stable during heat treatment. However, after being placed in a graphite storage container and transferred to another glove box, the pellet split longitudinally. The oxidizing atmosphere used for granule presintering is known to cause a reduced sintering rate, compared to the reducing atmosphere used for DF Pellet 3 granules, and, apparently, the lower granule density affects the integrity of the pellet.

DF Pellet 8

The process conditions used for DF Pellet 8 were nearly a duplication of the DF-3 test. DF Pellet 8 was hot pressed from Pu(III) direct-strike feed (40% 1600°C, 6 hr, He/H_2O and 60% as-calcined) using a maximum load of 4500 lb (~4900 psi) at 1525°C.

After heat treatment, the pellet had a hairline crack in each end, typical of many GPHS pellets made in the PEF, but it was integral and suitable for encapsulation.

RECOMMENDED FLOWSHEET

A detailed flowsheet for a direct fabrication process is presented in Figure 26. This flowsheet represents the optimum process conditions which have been determined to date, however, the "optimum" centerline conditions will probably be adjusted based on the process limit test results. The conditions in Figure 26 successfully produced an integral pellet (DF-8) in the PEF. The hot pressing conditions used for DF-8 (which are also the suggested centerline hot pressing parameters) are presented in Figure 27.

FUTURE WORK

Test results obtained so far were very encouraging but a significant amount of work remains before a direct-fabrication production process could be implemented at SRP. A number of process parameters must be optimized to determine the centerline precipitation and pellet fabrication conditions. A series of pellet fabrication tests with microstructural analysis will be required to define the process limit conditions. These tests are necessary to provide a basis for the Technical Standards, although the GPHS process limit tests may provide a satisfactory basis for limits on some of the process parameters. The most important process parameters to be considered on the direct fabrication process will include particle size distribution, temperature and atmosphere used to sinter the high fired granules, and the hot pressing load and temperature. As with the GPHS process development, the load, temperature, and time at temperature should be minimized to lessen the likelihood of pressing laminations and to minimize reduction.

Modifications are required in HB-Line before any additional direct-strike precipitations are made. These modifications include rerouting of chilled water to the precipitator so that precipitations can be done at 15°C and improving control of oxalic acid addition during the precipitations. At least 2 kg of PuO_2 feed will be required to complete process limit tests and to provide centerline pellets for impact verification tests at LANL. Design verification impact tests and other evaluations must be made to verify the acceptability of direct-fabrication pellets for flight use.

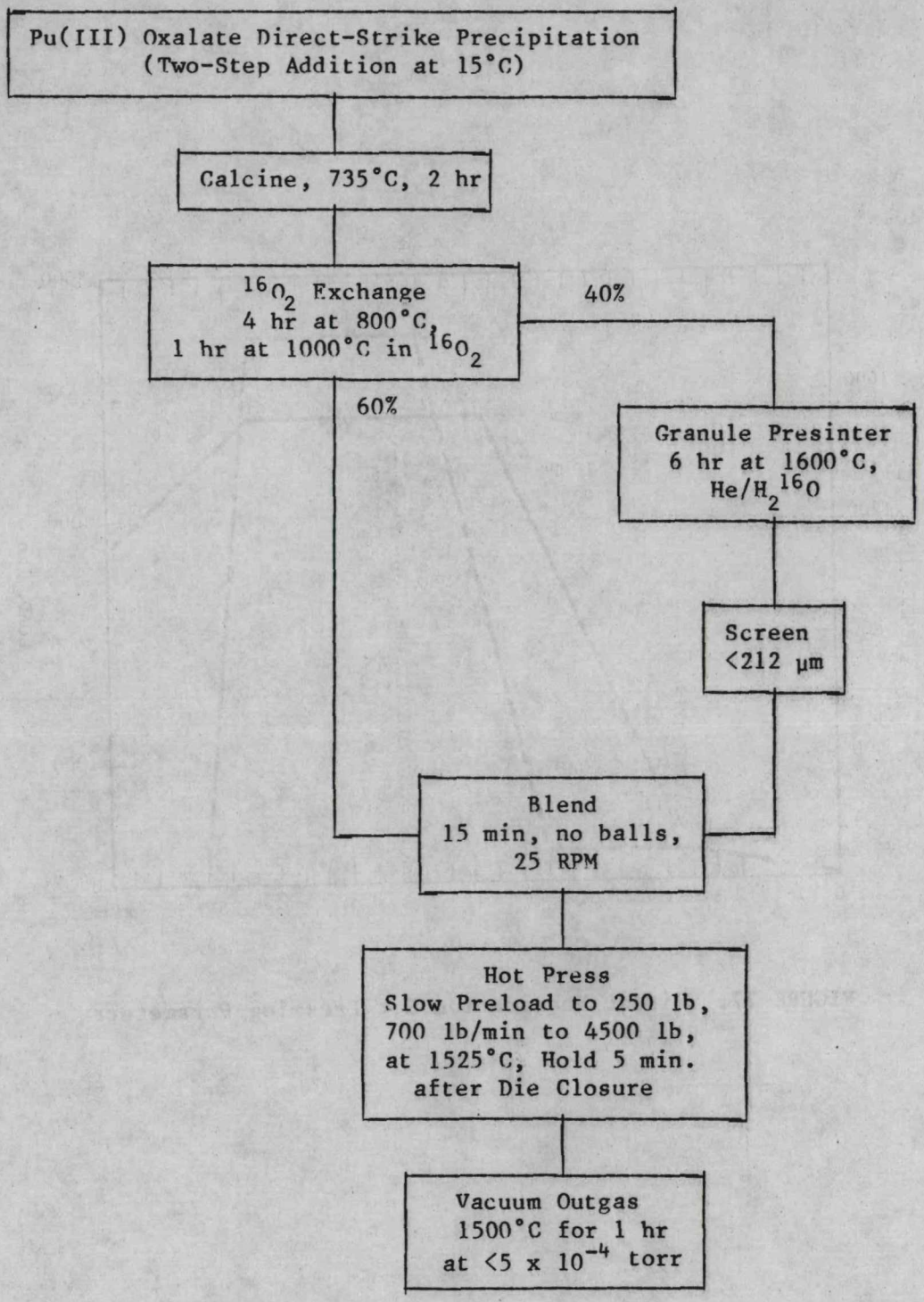


FIGURE 26. Direct Fabrication Flowsheet

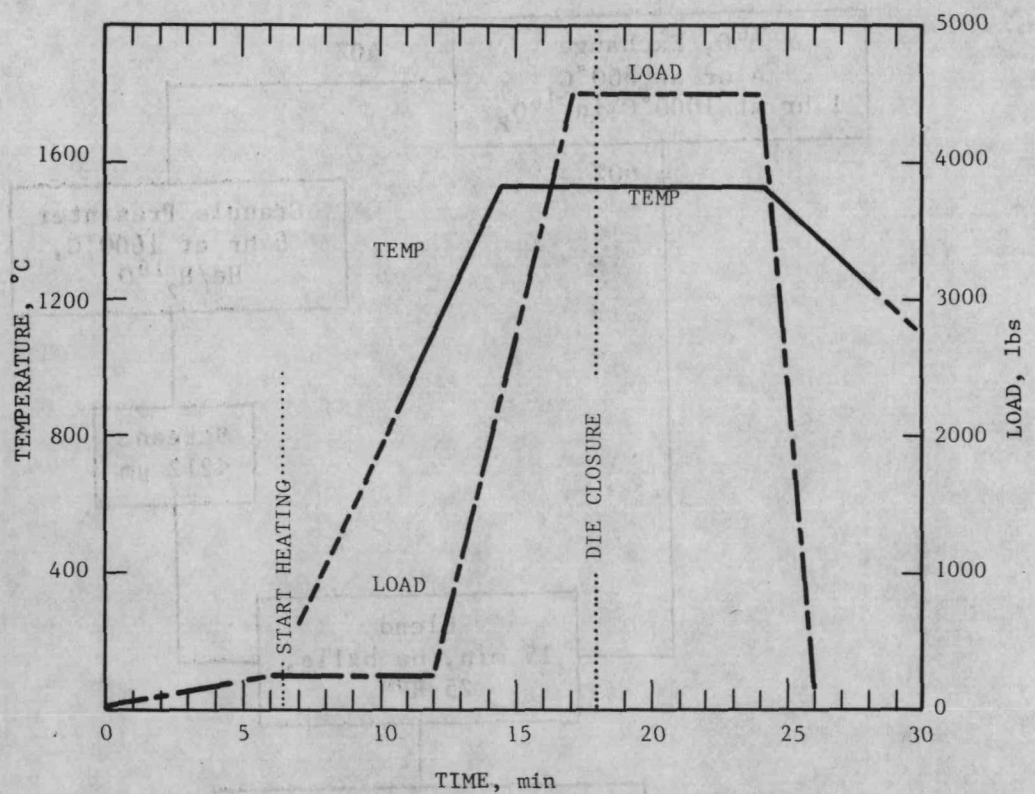


FIGURE 27. Direct Fabrication Hot Pressing Parameters

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2. D. F. Bickford, D. T. Rankin, and P. K. Smith. "Preparation, Microstructures, and Properties of PuO_2." Proceedings of 6th Int. Materials Symposium, February 1977.