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FABRICATION OF PLUTONIUM-242 METAL DISKS

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William V. Conner, Stephen G. Proctor, and Donald L. Baaso

Abstract. The preparation of three ^{242}Pu metal target disks is described. The disks were 1.00 ± 0.010 inch in diameter and 0.010-, 0.040-, and 0.180-inch thick. The disks were prepared using casting techniques. The variation in the thickness for each disk was within 3% of the disk's average thickness. The conversion of the $^{242}\text{PuO}_2$ to metal and the recovery of the metal reduction and casting residues are also described.

INTRODUCTION

The Rocky Flats plant has for several years been involved in the preparation of small quantities of actinide metals for other AEC Laboratories.^{1,2} This metal is often fabricated into targets for neutron cross-section and other measurements. Recently, a request was received from the Los Alamos Scientific Laboratory (LASL) for the fabrication of three plutonium-242 metal disks. Since there was a limited amount of material available for this project, the disk fabrication had to be accomplished with a minimum loss of material.

The fabrication of actinide metal targets usually involves rolling of metal buttons to the required thickness and cutting or machining the resulting rolled sheet or foil into the desired shape.³ However, the rolling and forming operations will usually generate large amounts of scrap. The scrap generation can be reduced if the metal button is cast into a rolling ingot, but even with this method the amount of scrap generated is still fairly large. The problems associated with rolling can be eliminated if the buttons are cast directly into the desired shape.

Techniques have been developed at Rocky Flats for casting small actinide metal disks, ingots, and foils.⁴ These casting techniques were used to prepare the three plutonium-242 metal disks for LASL. The disks were to be 1.00 ± 0.010 inch in diameter and 0.010-, 0.040-, and 0.180-inch thick. The actual thickness of each disk was not critical, but the variation in the thickness of each disk was not to exceed 3% of the disk's average thickness. A tilt-pour casting technique was used for the 0.180-inch-thick disk whereas the 0.040- and 0.010-inch-thick disks were prepared using an injection casting technique.

The plutonium-242 (98% ^{242}Pu) for this project was supplied as PuO_2 by the Lawrence Livermore Laboratory (LLL). In return for the use of this material, LLL specified that all the residues generated during this project had to be collected and processed back to a pure oxide. These residues were processed using anion exchange and precipitation techniques.

EQUIPMENT

The plutonium-242 used for this project was isotopically enriched (98% ^{242}Pu) and, therefore, could not be contaminated with other plutonium isotopes. Before this project was started, the glovebox was cleaned by sweeping up all loose dust and then wiping the inside surfaces of the box with damp paper towels. The fluorination, reduction, and casting equipment was also cleaned. The equipment in intimate contact with the ^{242}Pu , such as the fluorination boat, reduction crucible, melting crucible, and molds, was new.

Conversion to Metal

The fluorination system is shown in Figure 1. The fluorination reactor was fabricated from Monel metal. The reactor

Figure 1. Fluorination System Used to Convert $^{242}\text{PuO}_2$ to PuF_4 .

body consisted of a 4¼-inch-long piece of Schedule 40 pipe (4½-inch o.d. by 4-inch i.d.) with a ¼-inch-thick bottom plate and a ⅝-inch-thick top flange. The lid was fabricated from ½-inch Monel plate and contained a thermocouple well which extended to the top of the fluorination boat. The fluorination boat, 3¾ inches in diameter by 2¼ inches in height, was fabricated from porous alumina by the Coors Porcelain Company. A stainless steel O-ring was used to seal the reactor. Flexible lines of Teflon® tubing covered with stainless steel braid were used to connect the reactor to the F₂ supply and exhaust lines. The F₂ was exhausted into Monel disposal traps which were filled with charcoal. The reactor was heated with a hot plate.

The reduction vessel (Figure 2) consisted of a MgO crucible and crucible lid, and a stainless steel pressure vessel and vessel lid. The crucible was placed in the pressure vessel and the annulus between the crucible and pressure vessel was filled with MgO sand. A copper gasket was used to obtain a seal between the pressure vessel and the vessel lid.

Figure 2. Fifty-Gram-Scale Reduction Vessel.

Casting

The casting furnace, (Figure 3), was a System VII General Purpose Metallurgical Facility manufactured by Vacuum Industries. This furnace consisted of a tilt-pouring, 4-inch diameter by 6-inch-high water-cooled induction coil enclosed in a water-cooled vacuum chamber. The coil contained a quartz insulator sleeve and a ¼-inch-thick sleeve of WDF graphite felt insulation manufactured by Union Carbide.

The power for the coil was supplied by an Inductotherm 15-kW motor-generator unit. A 3-kW ceramic mold heater

Figure 3. Interior of Casting Furnace.

was added to the vacuum chamber when a separate mold heater was required. The mold heater was a resistance-type unit fabricated by the Rocky Flats Research and Development Ceramics Laboratory. Temperature measurements were obtained with either Chromel-Alumel or platinum-rhodium thermocouples. The vacuum system consisted of a 4-inch diffusion pump with a mechanical roughing pump.

A split mold design was used for this project (see Figure 4). The upper portion of the mold contained a melting section that opened into the disk cavity. The molds were vented from the top of the disk cavity. The molds were fabricated from stack pole graphite and were coated with calcium fluoride before being used. The same mold design was used for both the tilt-pour casting of the 0.180-inch-thick disk and the injection casting of the 0.040- and 0.010-inch-thick disks.

A melting crucible was required for the tilt-pour casting. A tantalum crucible (Figure 5) was used for this project. The crucible was heated to 500°C in air for 20 minutes to form a protective oxide coating on the surface of the tantalum before the crucible was used.

A separate melting crucible was not required for the injection castings because the metal was melted in the mold. A tantalum metal rod was used to force the molten metal from the melting section into the disk cavity of the mold.

Figure 4. Cross-section Showing the Two Halves of the Split Mold Used for Casting ^{242}Pu Disks.

Figure 5. Tantalum Melting Crucible and Graphite Susceptor Used for Tilt-pour Casting.

The end of the rod in contact with the molten metal was coated with CaF_2 before the rod was used.

EXPERIMENTAL PROCEDURE

Conversion to Metal

The $^{242}\text{PuO}_2$ was calcined at 600°C for 6 hours to remove any volatiles and to ensure a reactive oxide. The calcined oxide was placed in an alumina boat which was subsequently weighed and placed in the reactor. The reactor was heated to 100°C and F_2 was introduced at 200-cc per minute. During the fluorination, the pressure in the F_2 supply line was maintained at 6 psig and the disposal traps were vented to the glovebox atmosphere. The F_2 flow rate was increased to 400-cc per minute after 10 minutes and held for an additional 50 minutes. The F_2 flow was then turned off and the system allowed to cool. The boat was removed from the reactor and reweighed to determine the weight gained during fluorination.

The PuF_4 was reduced in two batches containing 50 g of plutonium each. A 0.5-g piece of high purity aluminum wire was added to each reduction charge to stabilize the plutonium metal in the delta phase. The reduction charges were prepared using a 30% excess of Ca, 0.25 moles of I_2 per mole of plutonium, and 0.2 moles of CaCl_2 per mole of plutonium.

The charges were loaded by first placing 10 wt% of the I_2 and Ca in the bottom of the crucible. The PuF_4 was mixed with the rest of the Ca and I_2 and added to the crucible. The aluminum wire was placed in the middle of the charge and the $CaCl_2$ was placed on top of the charge. The lid was bolted on the vessel and the assembled vessel was checked for leaks and purged with argon. The prepared reaction vessel was placed in a vertical crucible furnace which had been preheated to $950^\circ C$. The furnace was turned off after 30 minutes and the vessel was allowed to cool. The resulting metal buttons were pickled in distilled water and buffed to remove any adhering calcium metal and slag.

Casting

The 0.180-inch-thick disk was cast using a tilt-pour casting procedure. The two metal buttons were placed in a tantalum melting crucible and the crucible was placed in a graphite susceptor in the induction coil. The mold was placed in the mold heater and the chamber was sealed and evacuated to 10^{-5} torr. The metal was heated to $950^\circ C$ and the mold was heated to $700^\circ C$. The molten metal was then poured into the heated mold and allowed to cool under vacuum.

The 0.040- and 0.010-inch-thick disks were cast using an injection casting technique. The mold was placed in the induction coil and the metal to be cast was placed in the melting section of the mold (see Figure 4). The induction coil and mold were tilted at a 45° angle and a tantalum metal rod was placed in the upper portion of the melting section of the mold. The vacuum chamber was sealed and evacuated and the mold was heated to $850^\circ C$. The induction coil and mold were then moved to a vertical position, allowing the tantalum metal rod to drop onto the molten metal and force it into the disk cavity of the mold. The mold was then allowed to cool under vacuum.

Residue Recovery

The residues from the conversion to metal and casting operations were processed using anion exchange and precipitation techniques. The residues from the conversion-to-metal operation consisted of the MgO crucibles and sand, and the CaF_2 - CaI_2 slags. The casting residues consisted of impure skull oxides and the excess metal which contained the aluminum added to stabilize the plutonium in the delta phase. The process used for the casting residues will be described first.

The casting residues were first contacted with $6M$ HCl to dissolve the metal and then concentrated HNO_3 - $0.1M$ HF

was added to dissolve the oxide. The solution was filtered and the resulting heel was contacted twice more with concentrated HNO_3 - $0.1M$ HF at $100^\circ C$. The solutions were combined and made $1M$ in $NaOH$ to precipitate the plutonium and leave the aluminum in solution. The plutonium hydroxide precipitate was digested for 20 hours, filtered, and washed with a $0.1M$ $NaOH$ solution. This precipitate was dissolved in concentrated HNO_3 and the resulting solution was prepared for an oxalate precipitation to separate the plutonium from the remaining impurities. The acidity was adjusted to $0.8M$ H^+ with water, and the solution was heated to $50^\circ C$. Ascorbic acid (1 g of ascorbic acid per g of plutonium) was added to reduce the plutonium to $Pu(III)$. Sufficient oxalic acid was added to precipitate the plutonium and leave the solution $0.1M$ in oxalic acid. The precipitate was digested for 20 hours, filtered, washed with water, and calcined at $650^\circ C$ for 3 hours.

The reduction residues plus the 1 g of heel from the casting residue processing were dissolved in concentrated HNO_3 . Following dissolution, aluminum nitrate was added to complex the fluoride ion from the CaF_2 slag.

The solution acidity was then adjusted to $7.5M$ H^+ . The adjusted solution was passed through a bed of Dowex 1-X4, nitrate form, anion exchange resin. The resin was washed with 7 column volumes of $7.5M$ HNO_3 to remove the impurities. The plutonium was then eluted with $0.35M$ HNO_3 - $0.02M$ ascorbic acid and prepared for an oxalate precipitation. The acidity of the solution was adjusted to $0.8M$ H^+ with water and the solution was heated to $50^\circ C$. The plutonium was adjusted to $Pu(III)$ with ascorbic acid and sufficient oxalic acid was added to precipitate the plutonium and leave the solution $0.1M$ in oxalic acid. The precipitate was digested for 20 hours, filtered, water-washed, and calcined at $650^\circ C$ for 3 hours. The combined PuO_2 products were sampled and analyzed for plutonium assay, plutonium isotopic distribution, and impurity content.

RESULTS

The conversion of the $^{242}PuO_2$ to metal produced a 98.8% metal yield. The fluorination step produced a 100% conversion to plutonium tetrafluoride, while the reduction step produced metal yields of 99.6 and 98.0 percent. The fluorination and reduction data are given in Table 1.

The cast disks satisfied all the specifications. The disk diameters were 1.00 ± 0.010 inch and the variation in thickness of the three disks ranged from 0.4 to 2%. The thickness of the 0.010-inch-thick disk varied from 0.0096 to 0.0098 inch, which was a variation of only 0.0002 inch. The weights and dimensions of the disks are given in Table 2.

Table 1. Fluorination and Reduction Data.

Fluorination								
<u>PuO₂ Wt (g)</u>	<u>PuF₄ Wt (g)</u>	<u>Conversion to PuF₄ (%)</u>	<u>Starting Temp. (°C)</u>	<u>Max. Temp. Reached (°C)</u>	<u>Length of Fluorination (minutes)</u>			
116.1	132.6	100	100	175	60			
Reduction								
<u>Batch No.</u>	<u>PuF₄ Wt (g)</u>	<u>Pu Wt (g)</u>	<u>Al Wt (g)</u>	<u>Ca Excess (%)</u>	<u>$\frac{\text{mol I}_2}{\text{mol Pu}}$</u>	<u>CaCl₂ Wt (g)</u>	<u>Button Wt (g)</u>	<u>Metal Yield (%)</u>
1	66.3	50	0.5	30	0.25	4.65	50.3	99.6
2	66.3	50	0.5	30	0.25	4.65	49.5	98.0

Table 2. Weights and Dimensions of ²⁴²Pu Disks.

Disk No.	Disk Wt (g)	Diameter (inch)		Thickness (inch)		Variation in Thickness (%)
		Minimum	Maximum	Minimum	Maximum	
1	34.83	0.9977	1.0038	0.1765	0.1772	0.4
2	7.90	0.9940	1.0037	0.0405	0.0409	1.0
3	1.80	0.9905	1.0005	0.0096	0.0098	2.0

Samples of the sprue from the 0.010-inch-disk casting were submitted for isotopic and impurity analyses. The isotopic analyses obtained from samples of the ²⁴²PuO₂ feed and the metal are given in Table 3. As the data in Table 3 show, the isotopic analysis obtained from the metal sample was (within the limits of the analytical technique used) the same as the analysis obtained from the ²⁴²PuO₂. This verifies that no contamination of the ²⁴²Pu had occurred. The results obtained from the impurity analysis of the metal are given in Table 4. This analysis indicated 1363 ppm of total impurities with 1106 ppm of non-actinide impurities. The major impurity was oxygen at 450 ppm. Analysis of the metal for aluminum by atomic absorption showed an aluminum content of 0.9772 wt%.

Table 3. Isotopic Analysis of ²⁴²PuO₂ Feed and ²⁴²Pu Metal Disks.

Pu Isotope	Analysis (wt%)	
	PuO ₂ Feed	Metal Disks
238	0.195	0.188
239	0.174	0.178
240	1.369	1.352
241	0.166	0.146
242	97.897	97.941
244	0.199	0.195
	100.000	100.000

Residue Recovery

The residues from the conversion to metal and casting operations contained 54.5 g of plutonium. Fifty-four grams of this plutonium were recovered as purified oxide, which gave a 99% plutonium recovery. The isotopic analysis of the plutonium feed and the purified product are given in Table 5. As the data in this table show, the isotopic integrity was maintained throughout the project. The purified oxide contained 422 ppm of detectable impurities as determined by optical emission spectroscopy. The aluminum content was reduced from 10,000 to 43 ppm. These data are given in Table 6.

DISCUSSION

Plutonium-242 with the isotopic enrichment required for this project (98% ²⁴²Pu) was in very limited supply, and only 100 g of plutonium-242 as PuO₂ were available. The total required weight of the three finished disks was 45 g which left only a 55 g excess of plutonium. Each casting charge required a certain amount of excess metal to fill the sprue and the conical metal basin at the bottom of the melting section of the mold. Also, a certain amount of metal was lost as skull in each casting, as the data in Table 7 show. If fresh metal had been used for each casting, a total of 175 g of plutonium would have been required.

Table 4. Spark Source Mass Spectrographic Analysis of ^{242}Pu Metal Disks.

Element	Concentration (ppm)*
Ag	5
B	0.9
C	229
Ca	90
Cl	20
Co	0.4
Cr	7
Cu	7
F	97
Fe	50
Ga	1
I	2
K	1
Mg	2
Mn	6
N	5
Na	3
Ni	29
Np	220
O	450
P	0.8
Pb	2
Sc	0.1
Sn	34
Tb	12
Ti	2
U	24
Y	0.07
Zn	63

*Impurities are expressed as micrograms impurity per gram Pu — only detectable impurities are listed.
Total detectable impurities = 1363 ppm.

Table 5. Isotopic Analysis of $^{242}\text{PuO}_2$ Feed and Purified $^{242}\text{PuO}_2$ From Residues.

Pu Isotope	Analysis (wt%)	
	PuO_2 Feed	Purified PuO_2
238	0.195	0.186
239	0.174	0.227
240	1.369	1.348
241	0.166	0.144
242	97.897	97.897
244	0.199	0.198
	100.000	100.000

Table 6. Emission Spectrographic Impurity Analysis of Recovered $^{242}\text{PuO}_2$.

Element	Concentration (ppm)*
Al	43
Ba	3
Bi	5
Cr	25
Cu	5
Fe	143
K	10
Mg	25
Ni	76
Pb	40
Si	43
Ti	4
Total detectable impurities	422

*Concentrations are expressed as micrograms impurity per gram of plutonium — only detectable impurities are listed.

Table 7. Charge and Product Weights for ^{242}Pu Disk Castings.

Casting No.	Disk Thickness (inch)	Charge Weight (g)	Weight of Disk and Sprue (g)	Weight of Excess Metal (g)	Skull Weight (g)
1	0.180	99.4	36.5	43.7	19.2
2	0.040	43.7	8.3	32.6	2.8
3	0.010	33.6	2.0	30.6	1.0

Therefore, it was necessary to conserve the available plutonium and to obtain as high a metal yield as possible from the conversion to metal process.

The PuO_2 was calcined prior to fluorination to remove any volatiles present and to ensure a reactive oxide. The reduction charges were prepared with 0.2 moles CaCl_2 /mole Pu to improve the metal yield. The addition of CaCl_2 to reduction charges has been found to have a beneficial effect on metal yields.⁵

To conserve the ^{242}Pu metal, the excess of metal from one casting was used for the next casting. The 0.180-inch disk was cast using the two metal buttons. The 0.040-inch disk was cast using the excess of metal from the 0.180-inch-disk casting and the 0.010-inch disk was cast using the excess of metal from the 0.040-inch-disk casting.

The 0.180-inch-disk casting was made using a tilt-pour casting technique so the metal buttons could be heated to a high enough temperature to drive off calcium and magnesium picked up from the metal reduction step, and any

other volatile impurities. An injection casting technique was used for the 0.040- and 0.010-inch disks, because this technique requires less metal than the tilt-pour technique. Also, the tilt-pour technique is not very effective for thin castings because the metal will not flow of its own accord into the thin cavities. The three disks are shown in Figure 6 prior to packaging for shipment to LASL.

Figure 6. Plutonium-242 Target Disks. (One inch in diameter.)

The reduction charges were prepared with sufficient aluminum metal to produce metal buttons containing 1 wt% aluminum. The aluminum was added to stabilize the plutonium metal in the delta phase to retard oxidation, and to facilitate removal of the sprue from the disks.

Residue Recovery

When the Lawrence Livermore Laboratory provided the $^{242}\text{PuO}_2$ for this project, they specified that all the residues had to be collected and processed to remove the aluminum and any impurities added during the project. Care was taken throughout the project to collect all of the residues for eventual recovery and purification. Care was also

taken throughout the recovery operation to keep the processing losses to a minimum. The material balance given in Table 8 shows that accountability was made for 100% of the plutonium.

Table 8. Material Balance for ^{242}Pu Disk Fabrication Project.

Starting Pu wt	100 g	
Wt of Pu in disks		44.1 g
Wt of Pu in recovered oxide		53.6 g
Wt of Pu in lab samples		1.8 g
Wt of Pu discarded in solid and liquid waste		0.5 g
Totals	100 g	100 g

The bulk of the plutonium was contained in the residues from the casting operation. The major impurity in this material was the 1 wt% aluminum which had been added to stabilize the metal in the delta phase. This plutonium was first precipitated with NaOH to separate the plutonium from the bulk of the aluminum. Plutonium is very insoluble in basic media, whereas aluminum forms a soluble complex. Further decontamination from aluminum was achieved by precipitating the plutonium with oxalic acid. The oxalate precipitation step also removed the other cationic impurities which form soluble oxalate complexes. This procedure was chosen because it required less time and generated less waste than the alternate anion exchange procedure. The plutonium in the reduction residues and the heel from the dissolution of the casting residues amounted to only 2 g and was recovered using anion exchange techniques. The gross amounts of impurities present in these residues would have made precipitation methods impractical.

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