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Journal of Nuclear Materials 274 (1999) 315–319

journal of nuclear materials

www.elsevier.nl/locate/jnucmat

In situ purification, alloying and casting methodology for metallic plutonium

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Received 11 November 1998; accepted 22 February 1999

Abstract

Plutonium metal that has been double ER (electrorefined/electrorefining) was further purified via zone refining, using a floating molten zone to minimize the introduction of impurities. The temperature of the molten zone was 750°C, and the atmosphere was 10^{-5} Pa. A total of ten zone refining passes were made at a travel rate of 1.5 cm/h. There were 19 elements reduced to quantities below the minimum detectable limits (MDL) by zone refining, while P, K, and W were significantly reduced. The zone-refined metal was then used in an in situ distillation, alloying, and casting step to prepare tapered specimens for single-crystal growth experiments. Specifically, ^{241}Am was distilled from Pu metal by levitating Pu metal with 1 wt% Ga in the melt in a Crystallox vertical electromagnetic levitation crucible at 10^{-5} Pa. The Pu is alloyed with Ga to stabilize the δ phase (fcc symmetry) upon solidification. The Pu was chill-cast directly from the electromagnetic levitation field into 1- cm tapered specimens. A water-cooled ceramic mold was used, and the Pu metal was cooled at a rate of 100°C/min. A microstructure examination of the specimen showed 10×25 μm acicular grains with a density of 15.938 g/cm^3 (±0.002 g/cm^3).

1. Introduction

The purification of plutonium metal is a complex and time-intensive procedure. Just as no one purification technique is applicable to all the actinide elements, it is equally the case that no one purification method alone will remove all the different impurity species in plutonium. Plutonium metal processing at Los Alamos includes a molten salt extraction (MSE) step, followed by one or two ER runs. In these two processes, Pu metal shows a strong affinity for crucible materials and anode/cathode materials. For example, it has been reported that two of the principals metallic impurities present in Pu produced by the ER process are W and Fe, which are caused by the interaction between Pu and the container material [1,2]. Similarly, it has been shown that Al, Cr, and Ni are usually reduced to low levels by the ER process, but they seem to be affected by the impurity content of the anode material or by the electrolysis condition [3].

The daughter products that grow into Pu over time are always present as impurities, and they add a new degree of complexity to purification. The principal daughter products of Pu are isotopes of uranium and americium. The ^{235}U nuclei grows into Pu from the α-decay of the ^{239}Pu nuclei, and ^{241}Am is present from the β-decay of the ^{241}Pu nuclei [4]. Typically, the ^{235}U nuclei grows into Pu at 30 ppm per year, and ^{241}Am grows in at 120 ppm per year depending on the initial ^{241}Pu composition. Therefore the initial Pu isotopic composition and the time interval between sample preparation and analysis are important factors that can affect the analytical results.

Understanding the effects of Pu trace impurities on the intrinsic properties and on grain growth has been a primary goal of our research. Since the discovery of plutonium in 1941, the measured intrinsic properties of the metal have shown an extreme sensitivity to alloying and to the presence of trace elemental impurities [5]. For example the negative coefficient of thermal expansion has been a hallmark of δ-plutonium. However, the thermal expansion becomes less negative and finally becomes positive with increasing alloying additions of

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0022-3115/99/$ – see front matter
PII: S0022-3115(99)00074-4

aluminum, gallium, zinc, zirconium, indium, and cerium [6,7]. Conversely, the lower-temperature phases of unalloyed plutonium all exhibit positive coefficients of thermal expansion [8].

The large effects that small impurity concentrations exert on the thermal expansion behavior and on the δ stability field highlight the importance of a thorough characterization of trace elemental impurities. Historically, the total impurity numbers reported in Pu metal have been reported on a relatively small set, usually 20–40 impurity elements. Our efforts are directed at revisiting fundamental property measurements and grain growth with high-purity plutonium metal. The trace impurities reported here are measured by inductively coupled plasma mass spectrometry (ICP-MS) and atomic emission spectroscopy (ICP-AES). These methods detect a suite of 75 trace impurities, and the total impurity levels are quantified to the 100-ppm [1] level, which corresponds to 99.99 wt% metal.

We report here novel methods of δ-Pu alloy synthesis for specimens that will be used in subsequent grain growth experiments. In the first of a three-step process, double ER Pu is vacuum-cast into rods. The Pu rods are further purified by floating zone refining, then by levitation distillation at reduced pressure. The floating zone refining method targets metals and metalloids, then the levitation distillation method targets ^{241}Am. In the third step, Pu metal is cast directly from the electromagnetic field into tapered specimens. Tapered castings serve three purposes: first, specimens can be alloyed in a electromagnetic field thereby minimizing the introduction of impurities, and second, chill casting directly from the electromagnetic field produces a fine grain size thereby reducing the concentration gradients of Ga, and lastly, the specimens are cast into the correct geometry for subsequent grain growth experiments, thereby eliminating the need for machining.

The zone refining approach was largely based on previous zone refining experiments done at Los Alamos [9]. It was shown in this previous work that the zone melting process promoted a reduction of impurity elements within a Pu rod. Specifically, the impurity elements Al, Co, Cr, Fe, Mn, Ni, and Si were found to move in the directions predicted from their respective binary phase diagrams. It was anticipated that using a combination of a floating molten zone with the ability to measure 75 trace elements would prove beneficial. It was also anticipated that a fine grain size would eliminate or significantly reduce the coring of Ga. It has been reported that Ga coring and the presence of insoluble impurities at the grain boundaries are two factors that exert detrimental effects on grain growth [10,11].

[1] ppm is defined as (μg/g).

2. Experimental procedure

All work is carried out in a glove box under an argon or vacuum atmosphere. Starting material for the initial series of runs was double-ER Pu that is cast into rods having a total impurity level of 590 ppm (see Table 1, first column). The ER process used a feed of recycled Pu alloys, and all specimens had a density <19 g/cm^3. The double-ER rods were further purified by passing a 10 mm-wide molten floating zone ten times through a cast rod at a travel rate of 1.5 cm/h at 10^{-5} Pa. Zone refining was done at reduced pressures with a floating molten zone to take advantage of volatile impurities. The temperature of the molten zone was 750°C, which was measured using an infrared thermometer.

The floating molten zone was induction melted using a radio-frequency-power-induced electric current. The crucible acts as a transformer inducing a current in the Pu sample in a direction opposite to the current in the crucible. Magnetic fields in the crucible and the plutonium are opposed, causing repulsion and levitation of the plutonium a small distance from the crucible walls. The induction parameters used for the zone refiner was a 50-kHz frequency at 20 kW of power. After each pass the thin oxide layer was removed with a stainless steel wire brush. Core samples were removed for analysis using a cobalt drill bit powered with a variable speed drill motor under an atmosphere of argon. The final trace element analysis of zone-refined rods is shown (Table 1, second column).

The zone-refined rod, weighing approximately 240 g, was placed in a water-chilled copper crucible along with sufficient gallium to make a 1 wt% alloy. The Crystallox levitation crucible was in a vertical position. The bottom of the crucible was fitted with a 1-cm tapered Mycor ceramic mold (Fig. 1). The vertical crucible operates in the same manner as the zone refining crucible described above with the exception of the induction parameters. Specifically the parameters used for the levitation distillation were a variable frequency 2–3 kHz operated at 40 kW, and the Pu and Ga were induction melted at 800°C. The Pu and Ga mixture was levitated in the melt for 30 min to ensure thorough mixing by the induction currents. Gallium was purchased in ingot form (99.9999%) from Alpha Aesar and was used without further purification. The Ga was added in excess to correct for volatilized Ga. A water-cooled copper condenser was located above the crucible to trap the volatile ^{241}Am. Next, the alloy is chill-cast directly from the magnetic field into a ceramic mold at the bottom of the crucible by reducing the furnace power. The cooling rates of the Pu castings are measured using an infrared thermometer.

Plutonium castings are prepared for metallographic examination by cutting on a slow-speed diamond saw using a PF-5060 (freon substitute) lubricant under an

Table 1
Table of Pu impurities[a]

Impurity element	Double electrorefined concentration (ppm)	Zone refined concentration (ppm)	Minimum detection limit (MDL) (ppm)
Lithium	2.70	<0.40	0.40
Beryllium	0.80	<0.18	0.18
Sodium	115.00	<8.80	8.80
Phosphorus	95.00	7.00	5.60
Potassium	95.00	40.00	14.00
Calcium	3.70	<0.50	0.50
Chromium	3.10	4.20	0.13
Manganese	1.00	<0.07	0.07
Iron	61.00	<60.00	60.00
Cobalt	1.00	<0.10	0.10
Nickel	2.10	<0.40	0.40
Copper	1.90	0.80	0.13
Germanium	5.00	<0.32	0.32
Rubidium	1.00	<0.11	0.11
Niobium	1.00	<0.40	0.40
Silver	1.00	<0.13	0.13
Palladium	1.00	<0.07	0.07
Cadmium	1.00	0.05	0.04
Indium	1.00	<0.06	0.06
Tin	1.00	<0.03	0.30
Cesium	1.00	<0.09	0.09
Cerium	1.00	<0.04	0.04
Hafnium	1.00	0.18	0.05
Tantalum	16.00	<2.20	2.20
Tungsten	61.00	10.00	2.20
Rhenium	1.00	0.20	0.14
Gold	1.00	<0.36	0.36
Lead	2.40	1.70	0.08
Uranium	121.00	110.00	0.07
Total	590 (± 88)	174 (± 26)	

[a]Trace elemental impurities present in double-electrorefined plutonium. Analysis was performed by ICP-MS for 75 elements. Elements that do not appear are below their respective (MDL), and hence they cannot be quantified. The relative standard deviation of the analysis by the ICP method was ± 15%. The elements below the MDL in both electrorefined and zone refined are: B, Mg, Al, Si, S, Sc, Ti, V, Zn, As, Se, Sr, Y, Zr, Mo, Tc, Ru, Sb, Te, Ba, La, Os, Ir, Pt, Hg, Tl, Bi, Po, Fr, Ra, Ac, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th, and Pa. In the as-cast specimen the ^{241}Am concentration was 1.50 ppm (±0.30 ppm) as measured by γ-ray spectroscopy.
The impurity results of ER metal reported in the first column differ from impurity results reported in ER Pu metal done in the 1960 era. Although the ER process has not changed significantly in the past 30–40 yr, the analytical chemistry methods have. For example, the ER metal results reported here are based on 75 elements with lower detection limits for most elements. Earlier ER metal results are based on a total 20–35. Another source of difference is the original Pu metal used for feed in the current ER process consisted of recycled alloys that are old relative to the feed material used in the 1960 era. The feed metal used in the 1960 era had not aged significantly between reactor production and processing. Uranium is the primary impurity reported in the first column and is a direct result of using older recycled material as an ER feed.

argon atmosphere. Samples are mounted in Epon 815 epoxy, and the epoxy is allowed to dry for 12 h. Samples are then mechanically polished on polishing wheels starting at 230-grit paper and ending up with a 0.25-μm diamond paste. Final polishing is done in an electrochemical cell in a 10% solution of nitric acid in 90% dimethyl formamide. The samples are electrochemically etched in the same solution to relieve the grain structure. The samples are then photographed at various magnifications. The standard ASTM line-intercept method was used to determine average grain size. Density was measured by the density immersion method at room temperature in an immersion bath of bromobenzene.

3. Experimental results

The trace elemental impurities in double electrorefined plutonium metal determined by ICP-MS and ICP-AES are listed in Table 1, first column. The major

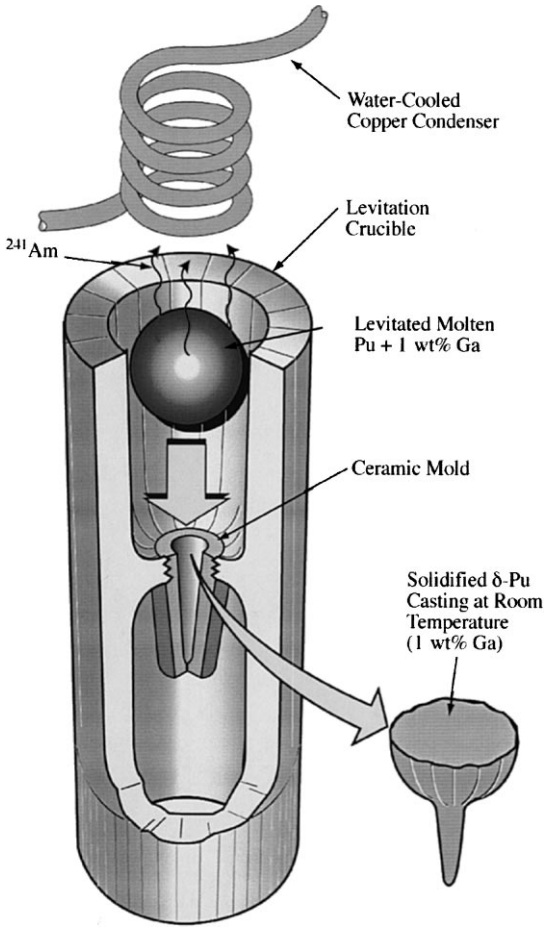

Fig. 1. In situ americium distillation, alloying, and chill-casting step. A mixture of α-Pu and Ga are added in a levitation crucible. The mixture is heated to the melt while suspended in a magnetic levitation field. As the Ga mixes with the Pu in the melt, it will stabilize the δ phase upon solidification. While in the melt, ^{241}Am distilled from the Pu, is collected onto a water-cooled condenser. Next, the furnace power is reduced and Pu is cast directly from the electromagnetic field into a ceramic mold.

impurities present in the ER material were Na, K, Fe, Ta, W, and U. High concentrations of Na and K are a result of salts that become trapped during the ER process. The presence of Fe, Ta and W is caused by the interactions of Pu with the anode/cathode used in the current ER process. High uranium concentrations are a result of using older Pu for the initial ER feed.

The trace impurity levels after zone refining are given in Table 1, second column. Results from zone refining have shown the reduction of impurities in double-electrorefined and vacuum-cast unalloyed plutonium from a total of 590 ppm (±88 ppm) impurities to 174-ppm (±26 ppm) through floating zone refining. A total of 19 elements were reduced to quantities below the minimum detectable limits by zone refining, while levels of P, K, and W were significantly reduced. The elements that were removed by the zone refining process were Li, Be, Na, Ca, Mn, Fe, Co, Ni, Ge, Rb, Nb, Pd, Ag, In, Sn, Cs, Ta, Au and Ce. Uranium accounts for 110 ppm of the measured 174 ppm in the zone refined Pu. Presumably, this is a result of a very small slope in the low uranium concentration portion of the liquid–solid curve in the plutonium–uranium phase diagram [12].

The castings show fine acicular grains with an average grain size of 10 × 25 μm (Fig. 2) with an average density of 15.938 g/cm^3 (±0.002). The standard density of a fully homogenized δ-Pu (1 wt% Ga alloy) specimen is 15.70 g/cm^3 [13]. Presumably, our density is slightly higher because of a small amount of the higher density α phase that has been retained. This was confirmed by optical metallography. In particular the lighter areas around the grain boundaries in Fig. 2 are small pockets of the low-temperature α phase of plutonium. Darker areas show the δ phase and are rich in gallium. Structures of this type are desirable for grain growth studies because homogenization time is minimized as a result of a small grain size.

4. Conclusions

The combination of floating zone refining with an in situ distillation, alloying, and casting technique has produced good specimens used for subsequent grain growth experiments. Based on the experimental data presented above, the following conclusion may be summarized:

1. ER metal containing 590 ppm can be further purified by floating zone refining to a total impurity level of 174 ppm.
2. Chill-cast specimens are obtained in the correct geometry for subsequent grain growth experiments thereby eliminating the need to perform additional machining steps.
3. Rapid solidification rates of 100°C/min minimize Ga coring, and produce a small grain structure with a density of 15.938 g/cm^3.
4. Molten plutonium does not react with containment vessels, and compared to current metal processing methods, electromagnetic levitation minimizes waste generation.
5. This density of the castings, very close to that of fully homogenized δ-Pu, indicates that a small amount of α-Pu has formed, which was confirmed by optical metallography.
6. In the context of plutonium's unusual properties, the combination of electromagnetic levitation and casting directly from the electromagnetic levitation field has been a robust method to enhance the current MSE and ER processes for the preparation of high-purity research samples.

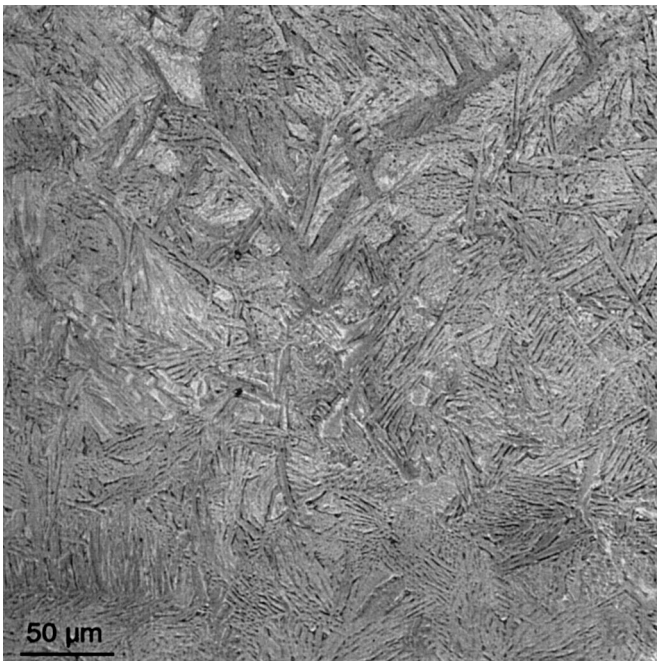

Fig. 2. Chill-cast Pu Microstructure. A microstructure of the chill-cast plutonium sample reveals small acicular grains 10×25 μm in size. The darker areas represent gallium-rich regions. Similarly, the light areas (around the grain boundaries) are areas that are deficient in gallium and represent the higher density α-Pu phase.

Acknowledgements

We are grateful to Roger Moment, Jim Smith, Siegfried Hecker, Galen Straub, John Wills, Dave Olivas, Jeff Terry, Dave Embury and Micheal Stevens for helpful suggestions. We thank Tom Yoshida, Debbie Figg, John Quagliano and Amy Wong for the trace elemental analysis. The authors are indebted to Michael Stout, Jerry Easdon, George Matlack and Tom Zocco for making useful suggestions on the manuscript. We thank Jack Kennison for measuring the density of the Pu samples. We also thank Ann Mauzy and Dennis Olive of the communications group. We also thank Larry Vaughn for induction support, and Fred Hampel and Kenny Vigil for laboratory assistance. This work was performed under the auspices of the Department of Energy.

References

[1] J.A. Leary, L.J. Mullins, LA-3356-MS, Los Alamos Scientific Laboratory, 1965.
[2] L.J. Mullins, J.A. Leary, I&EC Process Des. and Dev. 4 (4) (1965) 394.
[3] B. Blumenthal, M.B. Brodsky, The preparation of high purity plutonium, in: Plutonium 1960, Cleaver-Hume, London.
[4] G.T. Seaborg, W.D. Loveland, The Elements Beyond Uranium, Wiley, New York, 1990.
[5] J.E. Selle, B.B. Lawton, RFP-4327, EG&G Rocky Flats Report, 1991.
[6] E.A. Kmetko, The band structure, specific heat, magnetic susceptibility, and anomalous thermal expansion of δ-plutonium, in: Proceedings of the Third International Conference on Plutonium, Cleaver-Hume, London, 1965.
[7] F.W. Schonfeld, R.E. Tate, LA-13034-MS, Los Alamos National Laboratory, 1996.
[8] R.O. Elliot, K.A. Gschneidner, C.P. Kempter, Thermal expansion of some delta plutonium solid solution alloys, in: Plutonium 1960, Cleaver-Hume, London.
[9] R.E. Tate, R.W. Anderson, in: L.A. Wilkinson (Ed.), Some Experiments in Zone Refining Plutonium in Extractive and Physical Metallurgy of Plutonium and its Alloys, Interscience, New York, 1960.
[10] R.L. Moment, J. Cryst. Growth 2 (1968) 15.
[11] H.M. Ledbetter, R.L. Moment, Acta Metall. 24 (1976) 891.
[12] F.W. Schonfeld, E.M. Cramer, W.N. Miner, F.H. Ellinger, A.S. Coffinberry, Plutonium constitutional diagrams, in: Prog. in Nucl. Energy, Series V, vol. 2, Metallurgy and Fuels, Pergamon, New York, 1959, p. 579.
[13] R.L. Moment, Annealing and deformation twinning in delta-stabilized plutonium-gallium alloys, in: Plutonium 1970, The Metallurgical Society of the American Institute of Mining, Metallurgical, and Petroleum Engineers, New York.