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Spiked Alloy Production for Accelerated Aging of Plutonium

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The accelerated aging effects on weapons grade plutonium alloys are being studied using ^{238}Pu-enriched plutonium metal to increase the rate of formation of defect structures. Pyrochemical processing methods have been used to produce two ^{238}Pu-spiked plutonium alloys with nominal compositions of 7.5 wt% ^{238}Pu. Processes used in the preparation of the alloys include direct oxide reduction of PuO_2 with calcium and electrorefining. Rolled disks were prepared from the spiked alloys for sampling. Test specimens were cut out of the disks for physical property measurements.

Introduction

While metals in general have been studied for thousands of years, plutonium occupies a rather unique place amongst the metals as it has only been studied as a metal for less than a century. The pit of a nuclear weapon is subject to the constant self-irradiation from the radioactive plutonium that it contains. It is possible that this radiation could produce a significant amount of damage over the lifetime of the pit. The aging effects most of concern are thought to be helium bubble formation and void swelling. Since it is assumed that the damage produced should scale with the radiation dose received, replacing a portion of the ^{239}Pu with a much more radioactive isotope of plutonium would allow experiments to be conducted over a period of a few years that should reflect the aging behavior of plutonium in a weapon in excess of 50 years.

Spiked Alloy Production

The plutonium starting materials for the spiked alloy production were weapons grade (WG) plutonium, either as the oxide or the metal, and ^{238}Pu-enriched PuO_2. The ^{238}Pu-enriched oxide contains approximately 70 wt% $^{238}PuO_2$, 15 wt% WG PuO_2, 14 wt% $^{234}UO_2$ and 0.3 wt% $^{241}AmO_2$. The ^{238}Pu-enriched oxide will be referred to henceforth as $^{238}PuO_2$. Pyrochemical processing methods were used to produce ^{238}Pu-spiked alloys with 7.5 wt% ^{238}Pu and 1 wt% gallium nominal composition. The aging in a 7.5% ^{238}Pu-spiked plutonium alloy is about 16 times faster than in weapons grade plutonium.

All the plutonium used for the alloy had to be first reduced to the metal, for this a direct oxide reduction (DOR) [2] process was used in which calcium metal is used to

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reduce the $^{238}PuO_2$ and WG PuO_2 to ^{238}Pu-spiked metal. The reduction was carried out in a MgO crucible and dry $CaCl_2$ salt at ~900 ^{o}C. All of the reagents, plutonium, calcium and $CaCl_2$, are molten at this temperature. The reduction of plutonium oxides by calcium produces plutonium metal and CaO, which is soluble in the molten $CaCl_2$. The molten ^{238}Pu-spiked metal from the reduction is insoluble in the molten $CaCl_2$, and forms droplets in the salt. These droplets coalesce in the stirred salt and eventually settle to the bottom of the crucible, which is later recovered as an ingot (see Figure 1). Each DOR reaction produced approximately 1 kg of ^{238}Pu-spiked Pu metal.

Figure 1 DOR Button

Following the reduction, the metal must be purified by electrorefining [2]. Electrorefining is used to remove metallic impurities from the plutonium, such as iron, nickel, aluminum, gallium, americium and uranium. Electrorefining is a low yield process due to the fact that it retains a significant amount of plutonium in the electrolyte and impure plutonium containing all the impurities in the anode heel. About three DOR runs were needed to provide enough plutonium for one electrorefining run. The electrorefiner uses a cast plutonium ingot for the anode and dry $CaCl_2$ salt as the electrolyte. Either $PuCl_3$ or Cs_2PuCl_6 (dicesiumhexachloroplutonate, DCHP) is added to the salt to provide the initial plutonium ions in the electrolyte. The electrorefining is carried out at ~850 ^{o}C and 1-2 volts DC for about 6 days duration. See Figure 2 and Figure 3. The electrolytic reactions are:

$$\text{Anode: impure Pu}^{\circ} \rightarrow Pu^{+3} + 3e^{-} \quad (1)$$

$$\text{Cathode: } Pu^{+3} + 3e^{-} \rightarrow \text{purified Pu}^{\circ} \quad (2)$$

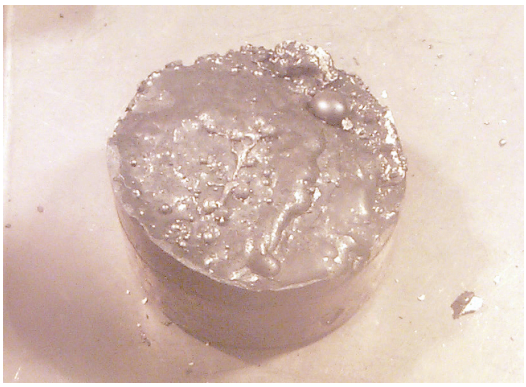

Figure 2 Cast anode for electrorefining feed

Figure 3 Electrorefined ring

The electrorefined plutonium (see Figure 3) is next cast into cookies. Cookies are solid cylinders 1.5" in diameter by 3/8" high (see Figure 4). Gallium and a small amount of iron are added at this point. After pouring into the molds the castings are annealed at ~450 ^{o}C to stabilize the plutonium δ-phase. The cookie castings are then cooled and removed from the molds and the cookies are machined to obtain clean surfaces and flat parallel top and bottom faces (see Figure 5). After machining, the cookies are rolled into 1/8" thick stock in the shape of disks (see Figure 6). The disks are annealed at ~450 ^{o}C to remove cold work and test specimens are machined out of the disks. Test specimens are machined into special shapes for measurement and testing (see Figure 7).

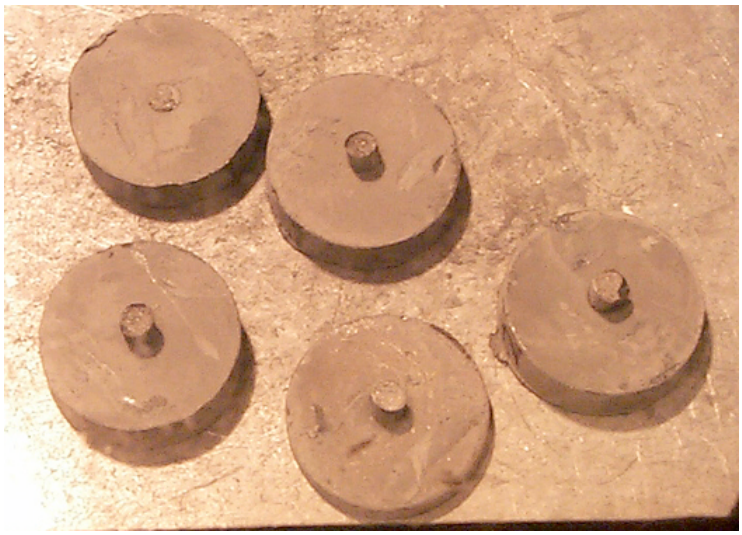

Figure 4 Cast Cookies

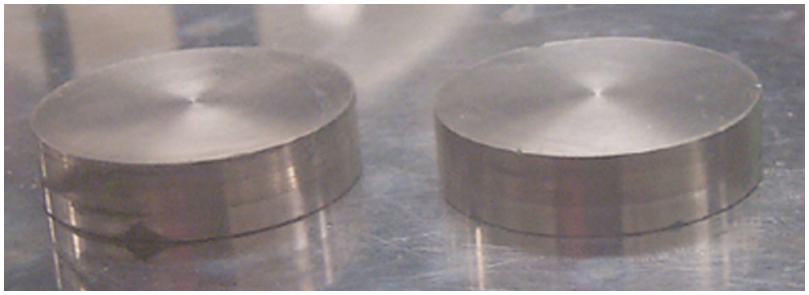

Figure 5 Machined Cookies

Figure 6 Rolled and Annealed Disk

Figure 7 Specimens are rough cut from the disk

Unspiked WG Pu material with a similar composition to the spiked alloy was also produced, and test specimens were machined for physical property measurements. This material is referred to as reference alloy.

Isotopic and elemental analyses were carried out by Induction Coupled Mass Spectrometry on the spiked materials and compared with the reference alloy. The analyses on the individual disks showed very small variations from the values.

Spiked Alloy Characterization and Physical Property Measurements

Metallographic images are shown in Figure 8 of the reference and spiked alloy. The microstructures appear to be similar. The average grain size between the alloys show good agreement in grain size. TEM was carried out on the reference and spiked alloys. A few bubbles are found in the spiked alloy, but none are seen in the reference alloy. The reference alloy was also characterized by X-ray diffraction, which verified that the material is delta phase plutonium.

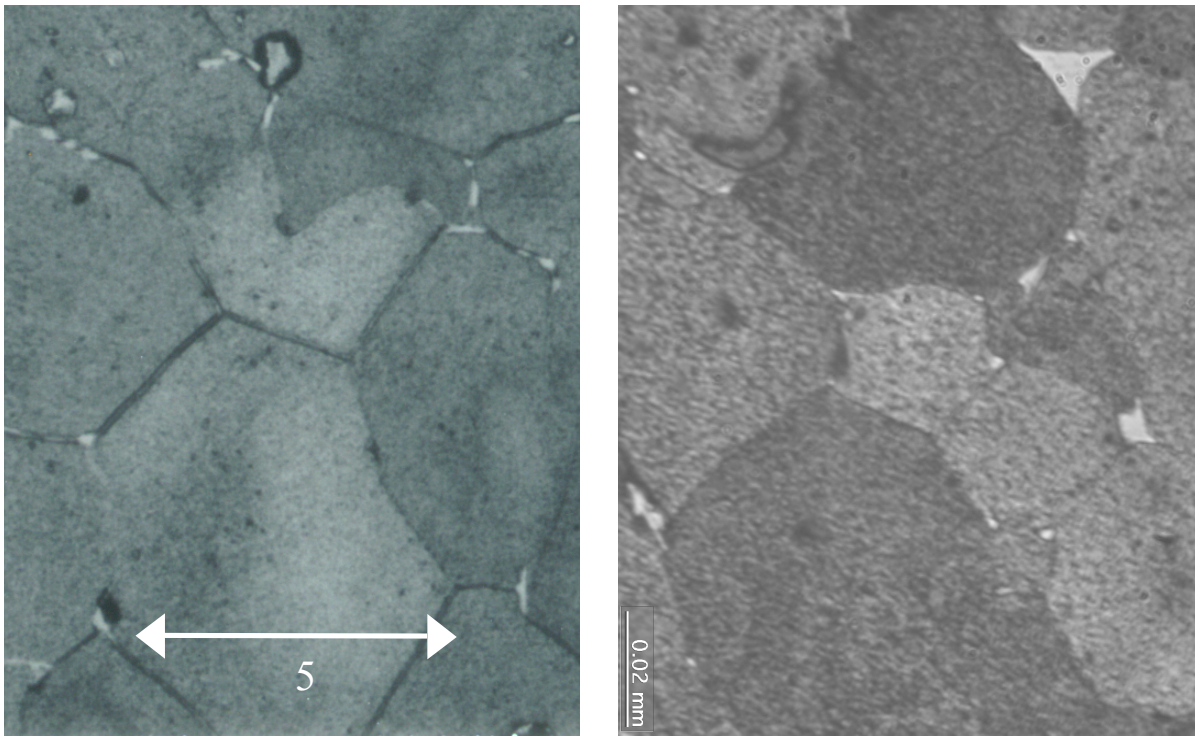

Figure 8. Metallographic images are shown at ~700X of reference alloy and spiked alloy.

Conclusions

The ^{238}Pu-spiked alloys were successfully prepared by pyrochemical processing. Comparison of chemical analyses on the spiked alloys with that of the reference alloy showed similar impurity levels. The ^{238}Pu contents, 7.38 wt % and 7.16 wt %, were found to be somewhat lower than the goal of 7.5 wt %, but were sufficiently close as to allow aging determinations to be made within a reasonable time.

Characterization by metallography, grain size, Vickers hardness and TEM of the spiked alloy showed excellent consistency with the reference alloy. Tensile testing generally showed good consistency between the spiked alloy and the reference alloy.

Acknowledgements

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References

[1] K. E. Dodson, "Pyrochemical Treatment of Salts," *in Separation Techniques in Nuclear Waste Management,* eds. T. E. Carlson, N. A. Chipman, C. M. Wai, (CRC Press, 1996).