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**Analysis of Density Changes in Plutonium Observed from Accelerated Aging using
Pu-238 Enrichment**

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We present dimensional and density changes in an aging plutonium alloy enriched with 7.3 at. % of ^{238}Pu and reference alloys of various ages. After 45 equivalent years of aging, the enriched alloys at 35°C have swelled in volume by 0.14 to 0.16 % and now exhibit a near linear volume increase, without void swelling. Based on X-ray diffraction measurements, the lattice expansion by self-irradiation appears to be the primary cause for dimensional changes during the initial 2-3 years of aging. Following the initial transient, the density change is primarily caused by a constant helium in-growth rate as a result of α -particle decay.

KEYWORDS: δ -Pu(Ga), ^{238}Pu -spiked alloys, Plutonium Aging, Dilatometry

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1. Introduction

Plutonium, because of its radioactive nature, relentlessly undergoes self-irradiation damage through out its volume. Plutonium decays to uranium by α -particle emission. The α -particle takes away most of the energy and eventually comes to rest as a helium atom. Together, both particles produce displacement damage in the form of Frenkel-type defects, but most of the damage results from the uranium recoil nucleus. While most of the initial damage is annealed out at room temperature, the residual lattice damage and helium in-growth drive microstructural and physical property changes. Because these self-irradiation effects would normally require decades to measure, one approach to better characterize the kinetics of dimensional and density changes is to accelerate the effects of self-irradiation damage in plutonium by doping with a small amount of more active isotope ^{238}Pu into the ^{239}Pu lattice. By adding 7.3 at. % of ^{238}Pu , the rate of aging process accelerates significantly. Using this method, the radiation damage in plutonium equivalent to sixty years of natural aging can be simulated in only a few years.

Previously, we reported the observation of density and volume changes due to self-irradiation in enriched alloys¹. In this paper, it will shown that the decrease in density is a result of the expansion in Pu lattice, which saturates within approximately three years of natural aging, and the continued build-up of helium in-growth. This analysis is founded upon the analysis of X-ray diffraction results.

2. Experimental

The length change is primarily determined by dilatometry measurements. The dilatometry result is supported by immersion density and X-ray diffraction measurements.

Dilatometers have been set up to monitor long-term growth resulting from the lattice damage and helium in-growth in (~ 7.3 at. %) ^{238}Pu -enriched alloys as shown in Figure 1. Alloys are δ -phase Pu with nominal compositions of ~ 2 at. % Ga. Details of experiments are presented elsewhere¹. Two different lengths of ^{238}Pu -enriched alloy specimens (3 cm and 2 cm) are used to differentiate between surface oxidation and volumetric swelling in the materials. The dilatometer chamber atmosphere is helium backfilled after evacuation with an oil-less vacuum pump. Each dilatometer has three wells: one for a 3 cm long specimen, one for a 2 cm long specimen, and one for a zero-dur reference material.

The immersion densities on the enriched and reference alloys were obtained shortly after the initial fabrication and then subsequently at least every six months. Between measurements, the samples were stored in a helium-filled incubator at 50°C . The equipment closely matches a design used by Bowman *et al.*² and uses about 200 ml of Fluorinert Electronic Liquid FC-43 as the immersion fluid as shown in Figure 2. Prior to each measurement, the system is calibrated using NIST glass (SRM 1827A) and a tantalum specimen as standards. This is generally followed by a measurement on the plutonium reference alloy and the ^{238}Pu -enriched alloy. To obtain stable measurements and ensure that all surface oxide is removed, multiple measurements are performed.

X-ray diffraction methods are used to measure the lattice parameters of chemically identical Pu-Ga alloys of various ages. The measurements are made with Rigaku Geigerflex X-ray diffractometer fitted with a Cu K α source.

3. Results and Discussion

The length change (ΔL) normalized with the initial length (L_0) of each spiked alloys at 35°C is shown in Figure 3. The time (X-axis) is represented as an equivalent time (in years) obtained by multiplying the measurement time by the initial accelerating factor of 18. This accelerating factor will decrease as the material ages due primarily to decreasing concentration of ^{238}Pu in the specimen. Each dilatometer contains a pair of long (3cm) and short (2cm) length specimens. Both enriched samples have increased in length significantly. During the initial stage of aging, the length change follows approximately the inverse exponential-type of expansion. After 2-3 years of equivalent years of aging, the swelling rate is reduced and the length expansion is nearly linear. This behavior has been interpreted as one of the effect of radiation damage in materials [3, 4]. The amount of swelling is related to the number of Frenkel pairs that survive the radiation damage and subsequent annealing processes. The progressive accumulation of survivor vacancies provides an increasing number of alternate sites for the capture of self-interstitial plutonium atoms. As the density of these alternate sites increases, the rate of swelling thereby reduced. After the initial transient stage, the dilatometry work shows almost linear volume expansion primarily induced by a constant helium in-growth rate of ~ 41 appm per year. The helium that accumulates in plutonium immediately finds unfilled vacancies and forms bubbles inside the crystalline matrix and along grain boundaries [5].

The curves for dilatometry are quite accurately represented by the combination of exponential and linear growth equations of the form

$$\Delta L/L_0 \cong A [1-\exp(-Bt)] + Ct$$

where A , B , and C are constants and t is the time in years. A curve fit based on an exponential dependence was applied to time scale less than 3 year where $\Delta L/L_0$ curves for two specimens are similar. A second fit based on a linear relation was performed at the saturation (or linear) region to obtain the slope C . The values for constants are given in Table 1, along with the He/vacancy association ratios calculated using the slope (C). This ratio describes the volume expansion induced by the formation of the helium bubbles in plutonium.

The $\Delta a/a_0$ of the sample measured by X-ray diffraction technique is also shown in Figure 3, where $\Delta a/a_0$ represents the measured lattice constant change (Δa) normalized with the initial lattice constant (a_0). As shown the self-irradiation damage causes expansion of plutonium lattice. The initial change in $\Delta a/a_0$ is similar to that measured by dilatometry. This result indicates that the accumulation of vacancy and self-interstitial lattice defects from the initial cascade damage lead to expansion in volume of plutonium alloys. Such a formation of Frenkel-defects results in a decrease of the compactness of the atom packing and correspondingly in an expansion of the δ -Pu volume. Following the initial stage, however, X-ray diffraction measurement shows significantly larger changes compared to dilatometry. This disagreement is caused by the differences in the measurement techniques. The dilatometry technique measures the changes in the bulk of the material. Thus, it is sensitive to volume (length) changes caused by both the lattice damage and the helium accumulation. Although the X-ray diffraction technique can

measure the lattice parameter changes caused by the lattice damage, it is insensitive to the total bulk swelling caused by the helium accumulation. Thus, further work is required to understand the contribution of helium in-growth to the changes in lattice parameter and potential redistribution of gallium atoms in Pu lattice.

Comparison of density change observed in aged reference alloys to the 35°C dilatometry data is shown in Figure 4. The immersion density measurement on the reference (weapons-grade Pu) and ^{238}Pu -spiked alloys showed initial densities of 15.795 and 15.78 g/cc, respectively. The initial density value for the dilatometry data is set to 15.795 g/cc to compare to the reference alloys. The trend in the density change converted from the dilatometry corresponds well to the immersion density during the initial (exponential) transient stage predominately caused by the lattice damage from the radioactive decay. Following the initial stage, the rate of density reduction becomes reduced as observed from the dilatometry. Both dilatometry and immersion density measurements show dimensional and density changes in enriched Pu alloys induced by the self-irradiation damage. However, no evidence of void swelling is yet observed.

Based on dilatometry, density, and X-ray diffraction characterizations, the initial changes in the volume and density are primarily caused by the change in lattice parameters, which saturates within three years of aging. Following the initial transient, the change is mainly caused by continued build-up of helium in-growth. Although the X-ray diffraction technique can measure the lattice parameter changes caused by the lattice damage, it appears to be insensitive to the bulk swelling caused by the helium accumulation. The significantly larger change in lattice constants after the initial transient stage indicates larger expansion in plutonium bonds by helium bubbles while

total bulk changes are smaller. The change in Pu lattice by radiation damage requires further investigation.

4. Conclusions

We found reasonable agreement in the density change behaviour between enriched and reference alloys from combined dilatometry and immersion density measurements. Based on X-ray diffraction, the decrease in plutonium alloy density is a result of the dimensional expansion from the accumulation of residual lattice damage and helium ingrowth.

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References

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Table 1. Values of constants from curve fit to dilatometry curves in Figure 3.

Sample	A (10^{-4})	B (year^{-1})	C ($10^{-5} \text{ year}^{-1}$)	He/ vacancy ratio
2 cm	2.5	0.9	0.48	2.8
3 cm	2.2	1.2	0.65	2.1

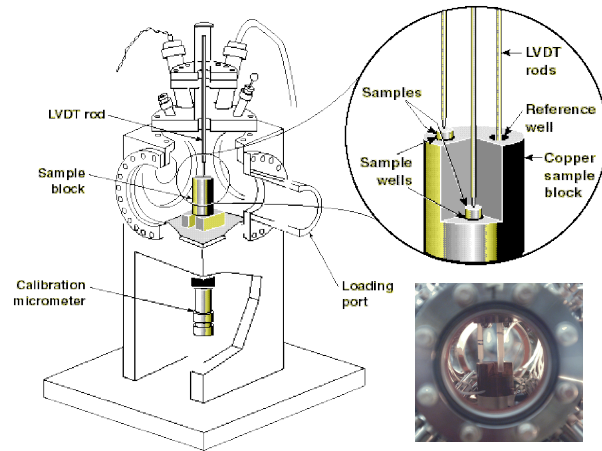


Figure 1. The schematic of dilatometer system designed to monitor length change in Pu alloys. Actual photograph of Pu samples mounted inside a dilatometer is also shown.

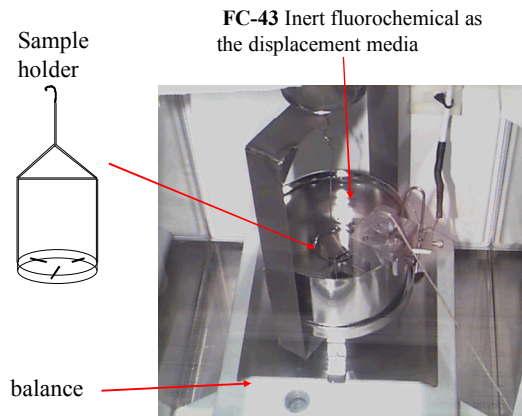


Figure 2. A photograph of immersion density equipment closely matching design by Bowman *et. al.*²

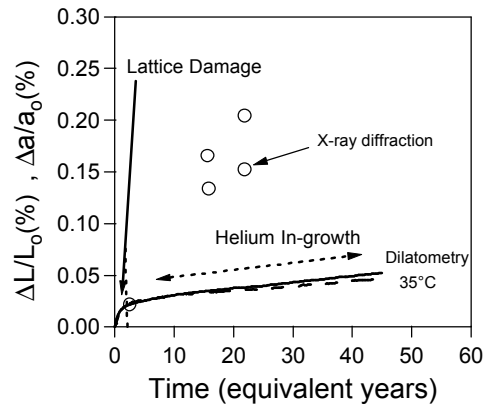


Figure 3. Dilatometer and X-ray diffraction results show dimensional expansion with aging. Dilatometry data to 25 years are presented elsewhere¹.

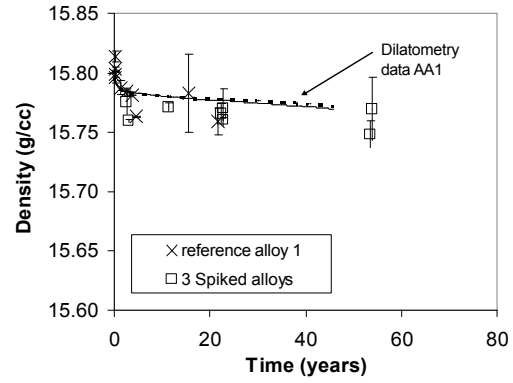


Figure 4. Immersion densities of enriched (spiked) and reference alloys. Dilatometry data is converted to density for comparison. Data to 25 years are presented elsewhere¹.