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Analysis of density changes in plutonium observed from accelerated aging using Pu-238 enrichment

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Abstract

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 length by 0.048–0.052% and now exhibit a near linear dimensional 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 cause by a constant helium in-growth rate as a result of α-particle decay.
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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 60 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 alloys [1]. In this paper, it will be shown that the decrease in density is associated with a transient expansion in Pu lattice, which saturates within approximately 3 years of natural aging, and continues due to build-up of helium in-growth. The current understanding of this phenomenon is supported by analysis of X-ray diffraction data from aged Pu.

2. Experimental

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 Fig. 1. Alloys are δ-phase Pu with nominal compositions of ∼2 at.% Ga. Details of experiments are presented elsewhere [1]. Two different lengths of ^{238}Pu-enriched alloy specimens (3 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 system reference material (Schott glass "Zerodure", "zero" expansion glass).

The immersion densities on the enriched and reference alloys were obtained shortly after the initial fabrication and then subsequently at least every 6 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 Fig. 2. Prior to each measurement, the system is calibrated

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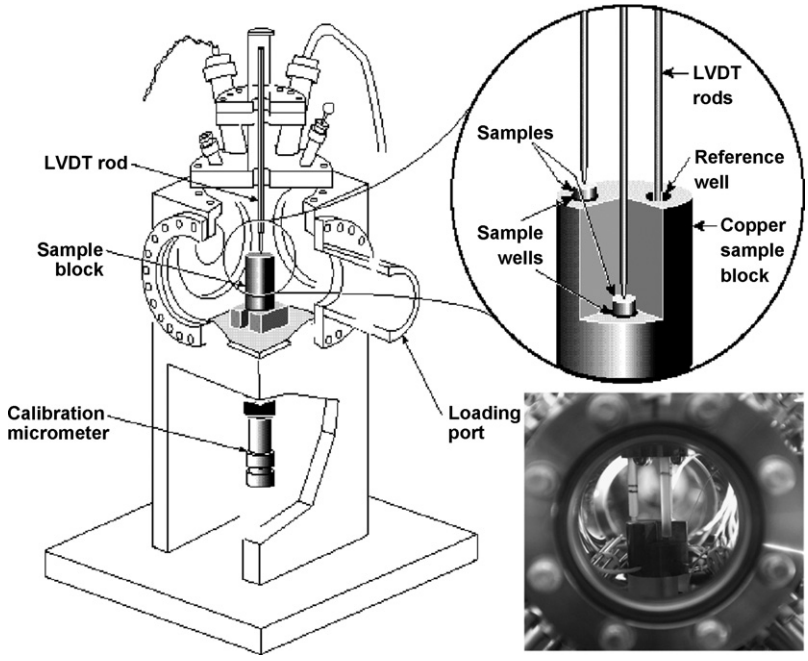

Fig. 1. The schematic of dilatometer system designed to monitor length change in Pu alloys. Actual photograph of Pu samples mounted inside a dilatometer is also shown.

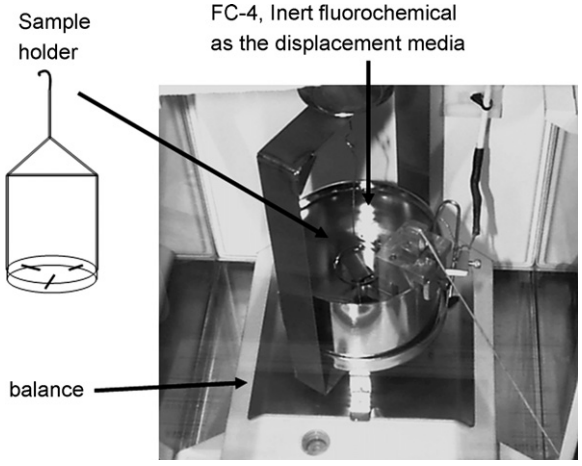

Fig. 2. A photograph of immersion density equipment closely matching design by Bowman et al. [2].

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 Kα source with a measurement accuracy of $\pm 5 \times 10^{-4}$ Å. Solid Pu samples are confined in a plastic film allowing a good transparency to X-rays, and are placed in a sample holder.

3. Results and discussion

The length change (ΔL) normalized with the initial length (L_o) of two spiked alloys at 35 °C is shown in Fig. 3 as dotted lines. The time (X-axis) is represented as an equivalent time (in years) obtained by multiplying the measurement time by the accelerating factor (e.g. an initial 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 (3 cm) and short (2 cm) 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

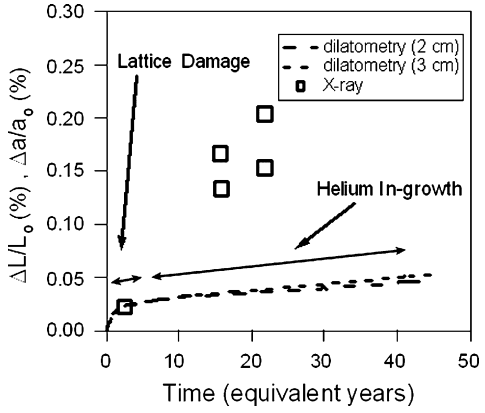

Fig. 3. Dilatometer and X-ray diffraction results show dimensional expansion with aging. The initial expansion is dominated by the lattice damage followed by the helium in-growth. Dilatometry specimen temperature is 35 °C.

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

Sample	$\Delta L/L_o$ at 45 years (%)	A (10^{-4})	B (year^{-1})	C (10^{-5} year^{-1})	He/vacancy ratio
2 cm	0.048	2.5	0.9	0.48	2.8
3 cm	0.052	2.2	1.2	0.65	2.1

alternate sites for the capture of self-interstitial plutonium atoms. As the density of these alternate sites increases, the rate of swelling is 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 (atomic parts per million) 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

$$\frac{\Delta L}{L_o} \cong A\,[1 - \exp(-Bt)] + Ct$$

where A, B, and C are the 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 $\Delta L/L_o$ 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. At this ratio, it is estimated that the pressure inside the helium bubble is almost off-set by the surface tension of the bubble formed in plutonium [1]. It is therefore important to examine void swelling mechanisms for any significant future dimensional changes.

The $\Delta a/a_o$ of the sample measured by X-ray diffraction technique is also shown in Fig. 3, where $\Delta a/a_o$ represents the measured lattice constant change (Δa) normalized with the initial lattice constant (a_o). The lattice constants of as-fabricated (a_o) and aged samples were measured from chemically identical Pu–Ga alloys of various ages. Then the Δa is the difference in the lattice constant of each alloy sample from the as-fabricated alloy. As shown the self-irradiation damage correlates with expansion of plutonium lattice. At 3 years of aging, the $\Delta a/a_o$ 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, the 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 Fig. 4. The immersion density measurement on the reference (weapons-grade Pu) and three ^{238}Pu-spiked alloys showed initial densities of 15.795 and 15.78 g/cm^3, respectively. Large error bars in density data originates primarily from the effects of convection currents (heating) in the immersion fluid generated by the alpha decay of plutonium [1]. The initial density value for the dilatometry data is set to 15.795 g/cm^3 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 3 years of aging. Chebotarev and Utkina also observed this initial transient stage using X-ray diffraction on plutonium alloys stored for 2–3 years [6]. Following the initial transient, the change is mainly caused by continued build-up of helium in-growth. Although the X-ray diffraction technique

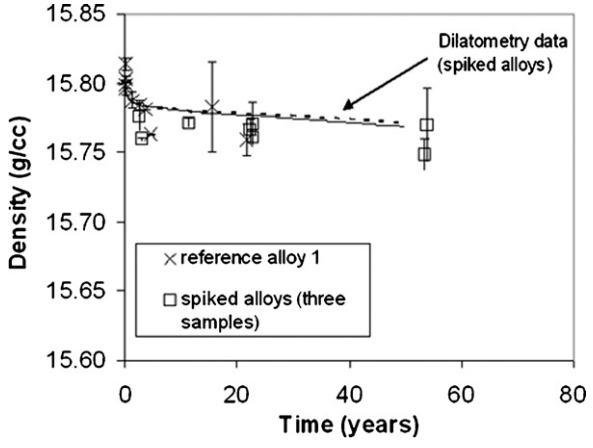

Fig. 4. Immersion densities of reference and three enriched (spiked) alloys. Dilatometry data is converted to density for comparison. Data to 25 years are presented elsewhere [1].

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 behaviors between enriched and reference alloys from combined dilatometry and immersion density measurements. Based on X-ray diffraction, the initial volume increase is due primarily to an increase in lattice parameter cause by Frenkel defects. This initial stage is observed in the current work up to about 3 equivalent years of aging for samples at 35 °C where the volume expansion becomes reduced. After the initial transient stage, the dilatometry work shows almost linear volume expansion primarily caused by the helium in-growth. By modeling the volume swelling measured by the in situ dilatometry, the average He-to-vacancy ratio from tested specimens is estimated to be around 2.5 indicating that the helium bubble pressure is approximately in equilibrium with the surface tension of the bubble formed in plutonium alloy. The discrepancy between the lattice constant and bulk changes requires further investigation to resolve. Potential future work includes investigation into the role of gallium distribution, nature of lattice damage by Frenkel-type defects and helium in-growth, and volume change by helium bubbles.

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References

[1] B.W. Chung, S.R. Thompson, C.H. Woods, D.J. Hopkins, W.H. Gourdin, B.B. Ebbinghaus, J. Nucl. Mater. 355 (2006) 142.
[2] H.A. Bowman, R.M. Schoonover, M.W. Jones, J. Res. Nat. Bur. Stand. 71C (1967) 179.
[3] W.J. Weber, J.W. Wald, Hj. Matzke, J. Nucl. Mater. 138 (1986) 196.
[4] W.J. Weber, F.P. Roberts, Nucl. Technol. 60 (1983) 178.
[5] A.J. Schwartz, M.A. Wall, T.G. Zocco, W.G. Wolfer, Philos. Mag. 85 (2005) 479.
[6] N.T. Chebotarev, O.N. Utkina, in: H. Blank, R. Lindner (Eds.), Plutonium, Other Actinides, 1975, North-Holland Publishing Company, Amsterdam, 1976, p. 559.