Journal of Nuclear Materials 385 (2009) 91–94

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Evolving density and static mechanical properties in plutonium from self-irradiation

B.W. Chung *, S.R. Thompson, K.E. Lema, D.S. Hiromoto, B.B. Ebbinghaus

Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, CA 94551, USA

ARTICLE INFO

PACS:
61.80.−x
6182.Bg

ABSTRACT

Plutonium, because of its self-irradiation by alpha decay, ages by means of lattice damage and helium in-growth. These integrated aging effects result in microstructural and physical property changes. Because these effects would normally require decades to measure, studies are underway to assess the effects of extended aging on the physical properties of plutonium alloys by incorporating roughly 7.5 wt% of highly specific activity isotope ^{238}Pu into the ^{239}Pu metal to accelerate the aging process. This paper presents updated results of self-irradiation effects on ^{238}Pu-enriched alloys measured by immersion density, dilatometry, and tensile tests. After nearly 90 equivalent years of aging, both the immersion density and dilatometry show that the enriched alloys continue to decreased in density by ~0.002% per year, without void swelling. Quasi-static tensile measurements show that the aging process increases the strength of plutonium alloys.

1. Introduction

The assessment of aging effects in plutonium lies at the heart of science-based stockpile stewardship [1,2]. Plutonium metal in stockpile ages with time because the plutonium undergoes alpha decay, which leads to self-irradiation induced structural damage and chemical changes in the material. The primary aging effects are believed to be lattice damage, helium bubble in-growth, and potential void swelling. The corresponding consequences to plutonium metal include potential reduction in density, dimensional swelling, hardening, and embrittlement [1,2].

Radiation damage from alpha decay in plutonium occurs at a rate of ~0.1 dpa (displacement per atom) per year. Because the effects of interest occur over decades, our approach is to accelerate the effects of radiation damage in plutonium metal by incorporating 7.5 wt% of the higher specific activity isotope ^{238}Pu into the ^{239}Pu lattice. The objective of this work is to assess the impact of extended aging on the quasi-static properties of plutonium alloys. Changes in quasi-static density and mechanical properties at ambient temperature and pressure are expected due to the aging process. Past results have shown gradual decrease in density, increase in strength, and expansion in volume of plutonium alloys due to aging [3–7]. In this paper we update changes in both density and mechanical properties of plutonium alloys due to aging.

2. Experimental

Details of sample preparation and operation of the dilatometer system and immersion density techniques are presented elsewhere [5], so only a brief description is provided here. Specifically designed dilatometers were set up inside a nitrogen atmosphere glovebox to monitor long-term growth resulting from the lattice damage and helium in-growth in ^{238}Pu-enriched alloys. Each dilatometer unit consists of a sample vacuum chamber fitted with linear variable differential transducers (LVDTs). An LVDT measures minute changes, 0.1 micron or less, in the position of a push-rod by monitoring changes in the inductance of a detector coil. In the current design, the detector coil is placed outside of the sample chamber. Two different lengths (2 and 3 cm) of alloy specimens are used to differentiate between surface oxidation and volumetric swelling in the materials. These alloys have nominal gallium concentration of 0.6 wt%. These specimens are placed in the copper well located inside the dilatometer system at 35 °C storage temperatures. A reference low thermal expansion glass (Zerodur) is also placed in the copper well to monitor the stability of the dilatometry system.

The immersion density equipment closely matches a design used by Bowman et al. [8] and uses about 200 ml of Fluorinert Electronic Liquid FC-43 as the immersion fluid. Prior to use, the system is calibrated using NIST glass (SRM 1827A). Because the ^{238}Pu-enriched alloys generate heat, a test sample is left overnight in the immersion bath to allow the temperature of the bath to stabilize and the measurements to be reproducible. A correction needs to be applied to the measured density to compensate for the heat generated by the ^{238}Pu-enriched sample. Details of density correction are described elsewhere [5].

* Corresponding author. Tel.: +1 925 4233896; fax: +1 925 4242491.
E-mail address: chung7@llnl.gov (B.W. Chung).

0022-3115/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2008.09.031

Each tensile test specimen was dimensionally inspected for the gage diameter and its length (GL), and loaded into a specially designed fixture for the tensile test. With a 0.24 inch GL extensiometer for the strain measurement, all testing was performed at crosshead speed of 1.27 mm/min, so that the ultimate strain rate was about 3.5×10^{-3}/s. Aluminum specimens of known tensile strength were tested to verify the equipment integrity before and after each test specimen. The load and displacement data was recorded on a computer using the Instron Series IX software package in conjunction with an Instron Model 4444 test machine. Data was recorded from preloading until failure. Plutonium specimens for the tensile test have nominal gallium concentration of 0.6 wt%.

3. Results and discussion

3.1. Dilatometry and immersion density

The volume change (ΔV) normalized with the initial volume (V_o) of enriched alloys is shown in Fig. 1. The time is represented as an equivalent time (in year) obtained by multiplying the measurement time by the accelerating factor (e.g. an average factor of 17). To calculate this factor, the α-decay activities of the ^{238}Pu-enriched alloy and the reference alloy are determined using the concentration of isotopes in each alloy. Then the activity of the enriched alloy is normalized to that of the reference alloy to obtain the factor. This accelerating factor will decrease as the material ages due primarily to decreasing concentration of ^{238}Pu in the specimen. Since the volume expansion due to self-irradiation damage is assumed isotropic in the bulk of material and is small compared to the total volume, the $\Delta V/V_o$ of the specimen can be obtained with the approximate relation $\Delta V/V_o \cong 3\ \Delta L/L_o$ where $\Delta L/L_o$ represents the measured specimen length change (ΔL) normalized with the initial length (L_o). As plotted in Fig. 1, the enriched alloys have increased in volume significantly. During the early stage of measurement, samples expanded in volume as a result of self-irradiation damage and follow the inverse exponential-type of expansion on dose or time during the initial stage of aging. This macroscopic swelling has been attributed mostly to the lattice damage, remnants of the displacement cascades that the uranium recoils produce. After 2–3 years of equivalent years of aging, the swelling rate is reduced and the volume expansion is nearly linear. This behavior has been interpreted as one of several effects of radiation damage in materials [9,10]. 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 is thereby reduced. After the initial expansion, the volume change exhibits a significantly lower rate of increase and a near linear expansion behavior attributed to a constant helium in-growth rate of ~41 appm (atomic parts per million) per year.

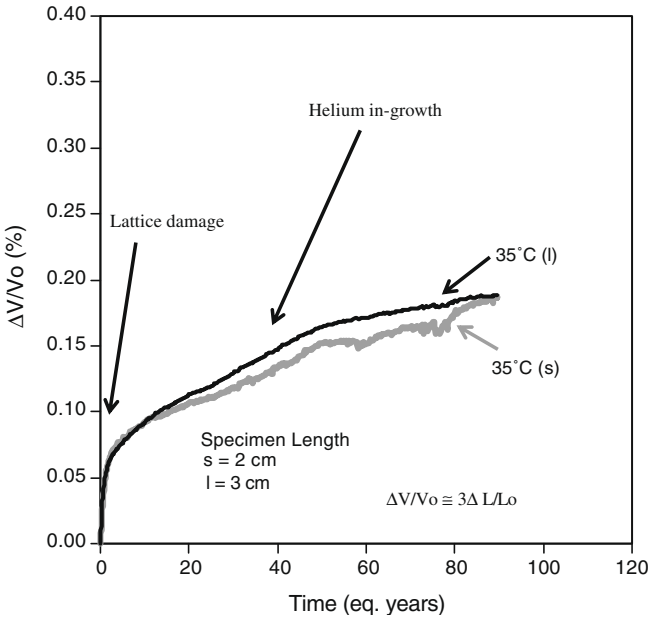

Fig. 1. The normalized volume changes for ^{238}Pu-enriched alloys measured using dilatometry under helium atmosphere at 35°C. A pair of 2 and 3 cm length specimens was tested. The time is represented as an equivalent aging time calculated by taking the measurement time and multiplying by the accelerating factor.

The curves for dilatometry to 50 equivalent years of age in Fig. 1 are quite accurately represented by the combination of exponential and linear growth equations of the form [5,10]

$$\Delta V/V_o \cong A[1 - \exp(-Bt)] + Ct, \quad (1)$$

where A, B, and C are constants and t is the time in years [5,7]. The He-to-vacancy association ratio can be approximated using the slope (C) [1,5,7]

$$C = (\Delta V/V_o)_{He}/t \cong [\mathrm{He}]/(R), \quad (2)$$

where $(\Delta V/V_o)_{\mathrm{He}}$ is the helium-induced volume expansion, R represents the He-to-vacancy ratio, and the helium concentration [He] is given in atomic parts per million per year. The average ratio extracted from the curve fit is ~2.5. This ratio represents the average number of helium atom filling the volume of a vacancy and the volume expansion induced by the formation of these helium bubbles in Pu metal [5,7]. Both positron annihilation and transmission electron microscope (TEM) data corroborate presence of significant number of helium-filled vacancies in aged plutonium metal [11–13]. TEM also revealed that these helium bubble size appears to increase in the early years of aging then remaining constant at ~1.4 nm while the number of density continues to increase [12,13].

The curves for dilatometry show slight change in their slopes starting around 50 equivalent years of age, deviating from their earlier linear trend described by Eq. (1). Helium generated in the alpha decay of plutonium accumulates in the form of nanometer-size bubble. Since the helium content increases at a constant rate of ~41 appm per year, the volume swelling is assumed to also increase linearly with time. However, this simple analysis does not account for a number of other contributions to the volume swelling. We still have work to do to better understand the contribution from the continued in-growth of the actinide daughter products americium, uranium and neptunium [14]. Additionally, we do not have complete understanding into the mechanism of the interaction between the helium bubble formation and radiation damage. For instance, the observed increase in the number of helium bubble density with age could cause less probability for the interstitial-vacancy recombination with age, leading to increase in Pu interstitial concentration. In such a picture, the contribution of Pu interstitials to the volume swelling needs to be included in Eq. (1). These combined contributions and integrated effects with helium in-growth and defect clusters (or precipitate Pu_3Ga [14]) need further investigation.

Fig. 2 shows results of immersion density measurements on the reference (identical composition to enriched alloys with the exception of the ^{238}Pu) and ^{238}Pu-enriched alloys. Included in the plot are the dilatometry data from Fig. 1 converted to density for comparison with the initial density set to 15.78 g/cm^3. The ages of reference samples for the immersion density range from 0.2 to 21 years. Large error bars in density data originates primarily from

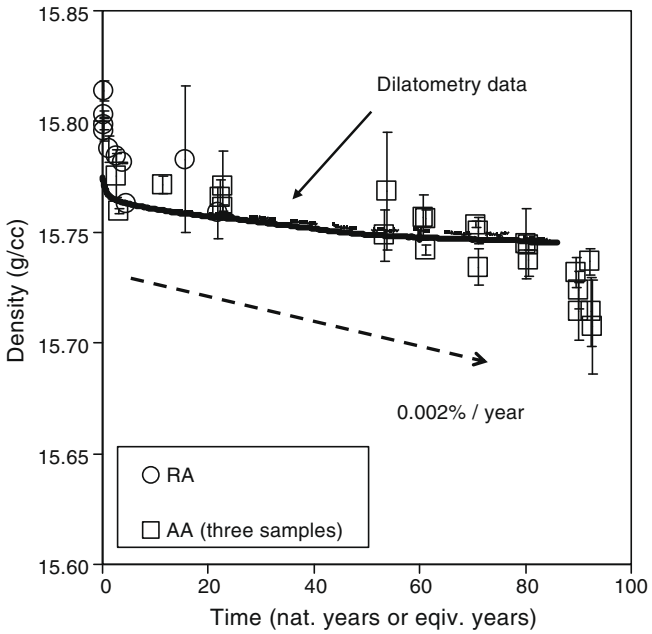

Fig. 2. Immersion densities of both enriched and reference alloys showing the decrease in density is less than 0.002% per year. Circles are reference alloys (RA) and squares are enriched alloys (AA). Dilatometry data from Fig. 1 is converted to a relative change in density for comparison.

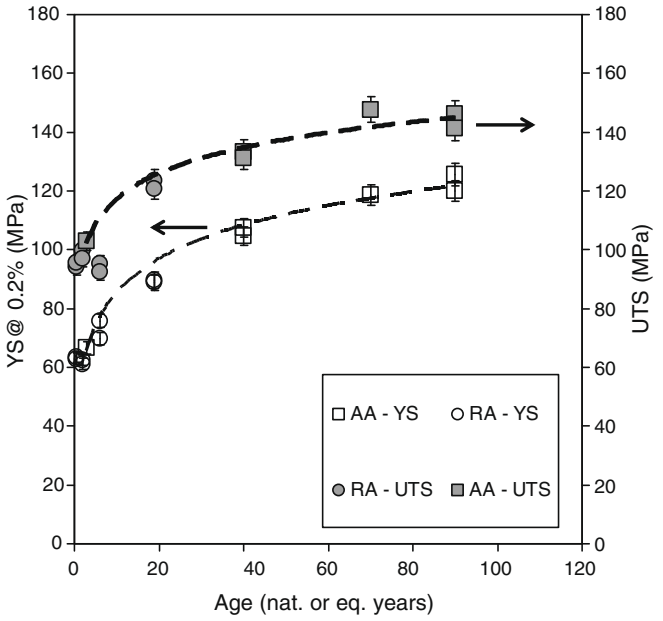

Fig. 4. Evolution of both yield strength (YS) and ultimate tensile strength (UTS) for plutonium alloys from aging. Circles are reference alloys and squares are enriched alloys.

the effects of convection currents (heating) in the immersion fluid generated by the alpha decay of plutonium. Following the initial state, the rate of density reduction becomes reduced, similar to the reduced volume expansion rate from the dilatometry. The rate decrease in the immersion density due to the helium in-growth is ~0.002% per year which corresponds well with the measured volumetric swelling rate from the dilatometry. Because of the large error bars in the density data, we do not see the change in the rate of density decrease after 50 equivalent years of age as in the dilatometry. Both dilatometry and immersion density measurements show dimensional and density changes in enriched Pu alloys induced by the self-irradiation damage but no evidence of void swelling.

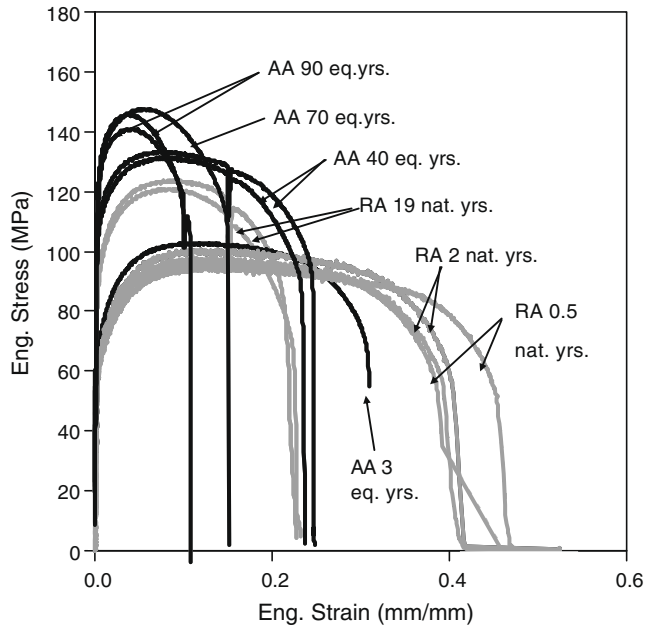

Fig. 3. Tensile tests at room temperature show increase in the strength and decrease in the ductility as plutonium alloys are aged. RA is reference alloy and AA is enriched alloy.

3.2. Quasi-static tensile

Fig. 3 shows the stress–strain curves of enriched alloys (AA) and reference alloys (RA) at different ages. The yield and ultimate tensile strength at different ages from Fig. 3 are plotted in Fig. 4. As can be seen from the data, both mechanical properties are about the same between the reference and enriched alloys at the early stage of aging. Data is also consistent with the values expected for alloys with ~0.6 wt% gallium [15]. While there is a difference in the total elongation between two alloys, both alloys show increase in strength and reduction in ductility from the aging process. Data also shows that both the yield and the ultimate tensile strength do not change after 70 equivalent years of aging, potentially the result of the saturation of aging effects. The Young's modulus is very consistent at near 40 GPa for tested samples irrespective of age.

4. Summary and conclusion

The immersion density, dilatometry, mechanical tests are underway on plutonium alloys enriched with 7.5 wt% of ^{238}Pu and reference plutonium alloys. Our measurements on aging plutonium alloys continue to show gradual expansion in dimension, decrease in density, increase in strength, and decrease in ductility due to the accumulation of residual lattice damage and helium in-growth. Dilatometry shows change in the linear volume swelling behavior after aging 50 equivalent years. Tensile properties show a possible saturation effect after 70 equivalent years. Results from both the dilatometry and tensile tests suggest a different contribution of defects depending on the time scale. This work reveals that it remains necessary to better understand an integrated contribution from several self-irradiation induced defects to plutonium alloys.

Acknowledgment

This work performed under the auspices of the US Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

References

[1] W.G. Wolfer, Los Alamos Sci. 26 (2000) 274.
[2] S.S. Hecker, J.C. Martz, Los Alamos Sci. 26 (2000) 238.
[3] B.W. Chung, S.R. Thompson, C.H. Conrad, D.J. Hopkins, W.H. Gourdin, B.B. Ebbinghaus, in: L. Soderholm, J.J. Joyce, M.F. Nicol, D.K. Shuh, J.G. Tobin (Eds.), Actinides-Basic Science, Applications, and Technology, Mater. Res. Soc. Proc., vol. 802, Pittsburgh, PA, 2003, p. 39.
[4] B.W. Chung, B. Choi, C. Saw, S.R Thompson, C.H. Conrad, D.J. Hopkins, B.B. Ebbinghaus, in: K.J.M. Blobaum, E.A. Chandler, L. Havela, M.B. Maple, M.P. Neu (Eds.), Actinides 2006-Basic Science, Applications, and Technology, Mater. Res. Soc. Proc., vol. 986, Pittsburgh, PA, 2006, p. 143.
[5] B.W. Chung, S.R. Thompson, C.H. Woods, D.J. Hopkins, W.H. Gourdin, B.B. Ebbinghaus, J. Nucl. Mater. 355 (2006) 142.
[6] N. Baclet, B. Oudot, R. Rynszpan, L. Jolly, B. Ravat, P. Faure, L. Berlu, G. Jomard, J. Alloys Compd. 444&445 (2007) 305.
[7] B.W. Chung, C.K. Saw, S.R. Thompson, T.M. Quick, C.H. Woods, D.J. Hopkins, B.B. Ebbinghaus, J. Alloys Compd. 444&445 (2007) 329.
[8] H.A. Bowman et al., J. Res. Nat. Bur. Stand. 71C (3) (1967) 179.
[9] W.J. Weber, J.W. Wald, Hj. Matzke, J. Nucl. Mater. 138 (1986) 196.
[10] W.J. Weber, F.P. Roberts, Nucl. Tech. 60 (1983) 178.
[11] P.A. Sterne, J. van Ek, R.H. Howell, Comput. Mater. Sci. 10 (1998) 306.
[12] A.J. Schwartz, J. Alloys Compd. 444&445 (2007) 4.
[13] A.J. Schwartz, M.A. Wall, T.G. Zocco, W.G. Wolfer, Phil. Mag. 85 (2005) 479.
[14] W.G. Wolfer, A. Kubota, P. Soderlind, A.I. Landa, B. Oudot, B. Sadigh, J.B. Sturgeon, M.P. Surh, J. Alloys Compd. 444&445 (2007) 72.
[15] H.R. Gardner, Mechanical properties, in: O.J. Wick (Ed.), Plutonium Handbook, The American Nuclear Society, IL, 1980, p. 59.