Journal of Nuclear Materials 385 (2009) 95–98

Contents lists available at ScienceDirect

Journal of Nuclear Materials

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

Unconventional δ-phase stabilization in Pu–Ga alloys

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A B S T R A C T

Face-centered cubic δ-phase Pu stabilized with less than 3 at.% Ga will partially transform martensitically to monoclinic α′-phase at cryogenic temperatures. Thermal cycling of young alloys in a dilatometer tends to stabilize δ Pu by shifting the transformation to lower temperatures and reducing the amount of transformation. Similar experiments using samples aged naturally or by doping with ^{238}Pu will stabilize δ Pu such that annealing at or above 150 °C is required before normal transformation behavior occurs. We discuss the role that radiation damage and recovery play in this unconventional stabilization of δ-phase Pu.

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1. Introduction

The first plutonium metallurgical studies during the Manhattan Project revealed that monoclinic α-phase Pu is hard and brittle and therefore difficult to machine. The addition of as little as 1 at.% Ga, Al, Ce, Am, Sc, or In was found to stabilize the softer, higher-temperature, face-centered cubic δ-phase down to room temperature (RT), thereby improving its manufacturing properties. Interestingly, this stabilization happens with the addition of elements with smaller (e.g., Ga) and larger (e.g., Ce) atomic radii than Pu's. Stabilization is thought to be due to the modification of plutonium's lattice spacing by these δ stabilizers, thus causing the 5*f* electrons to become more localized. Further details on the alloying behavior of plutonium and δ-phase stabilization are summarized in Hecker et al. [1].

At cryogenic temperatures and by applying pressure, Ga-stabilized δ-phase alloys can partially transform to the monoclinic α′-phase. We refer to the thermal variety as α'_t and the pressure-induced variety as α'_p. The general term α′ is used to distinguish pure α Pu from this Ga-saturated allotrope with a relatively expanded lattice. The $\delta \rightarrow \alpha'_t$ transformation is martensitic, has a >150 °C hysteresis loop, and rarely exceeds 25% completion. The volume difference between pure δ and α Pu is about 20%, so a complete $\delta \rightarrow \alpha'_t$ transformation is assumed to result in 20% volume contraction. The reverse transformation has proven to be a particularly rich area of investigation recently with the observation that it occurs in bursts [2,3]. During our investigations of the $\delta \rightarrow \alpha'_t$ transformation, we have found conditions of enhanced stabilization of the low-temperature δ-phase field. The two conditions we will discuss here are caused by (1) thermal cycling through the $\delta \leftrightarrow \alpha'_t$ forward and reverse transformations and (2) aging.

2. Experiments

Three types of Pu-2 at.% Ga materials were used in this study: an alloy that was several months up to 2 years old; a naturally-aged alloy that was 22-years old at the time of the experiments; and a ^{238}Pu-spiked alloy with an accelerated equivalent age of 90 years. Samples were cut using a low-speed saw and surfaces were ground parallel. Care was taken to minimize formation of α'_p caused by mechanical damage during sample preparation. The presence of α'_p is observed using dilatometry as it reverts to δ during heating above about 125 °C. Sample thicknesses ranged from 1 to 9 mm.

Dilatometry experiments were preformed on a Netzsch 402C dilatometer using a low-temperature furnace and silica sample tube and pushrod. Cooling and heating rates were 2–5 °C/min, and all measurements were performed in a dynamic He atmosphere with a gas flow rate of 30 ml/min. Two types of temperature profiles were commonly used: (1) thermal cycling from RT to between −150 and −165 °C and back up to 200–375 °C and (2) heating of the sample from room temperature to 120–200 °C before cooling to between −150 and −165 °C. The former profile was used to investigate thermal cycling effects on the $\delta \rightarrow \alpha'_t$ transformation, whereas the latter was used to study possible aging effects on the transformation. Some thermal cycling experiments incorporated a room temperature rest of 2 h between 200 °C and the following cycle. This resting was in conjunction with complementary and more exhaustive DSC experiments performed by K. Blobaum and colleagues at Lawrence Livermore National Laboratory [4].

3. Results

3.1. Thermal cycling of young material

During a typical thermal cycling dilatometer experiment on young material, the first martensitic transformation occurs at a

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0022-3115/$ - see front matter Published by Elsevier B.V.
doi:10.1016/j.jnucmat.2008.10.022

higher-temperature than the subsequent transformations, and the amount of transformation decreases or saturates as a function of thermal cycling [1,2]. An example of this behavior is represented in Fig. 1(a), which shows the hysteresis loop for a sample that has been thermally cycled three times. In addition to a lower M_s (martensite start temperature) and less α'_t ingrowth, the second and third cycles have fewer prominent steps, or bursts in the dL/dt curve, during the reversion that are so obvious in the first cycle (Fig. 1(b)). The origin of bursting during the reversion is attributed to repeated autocatalysis followed by self quenching [3] (Fig. 2).

The results of four separate thermal cycling experiments are compiled in Table 1. These experiments include the following temperature profiles: (1) thermal cycling three times between cryogenic and 200 °C; (2) profile 1 with a 2 h RT rest between cycles 2 and 3; (3) profile 1 with a 375 °C anneal between cycles 2 and 3; and (4) profile 1 with 300 °C anneals and a 2 h RT isothermal between cycles 2 and 3. All of these experiments use the same Pu–Ga alloy starting material from which the samples were extracted, although 07Pu0901 had been homogenized for 200 h vs. 50 h for the other samples. Also note that experiment 03Pu1402 is the same sample as that used for 03Pu1401, and that the 03Pu1402 occurred 18 h after 03Pu1401. Observations from these experiments include the following:

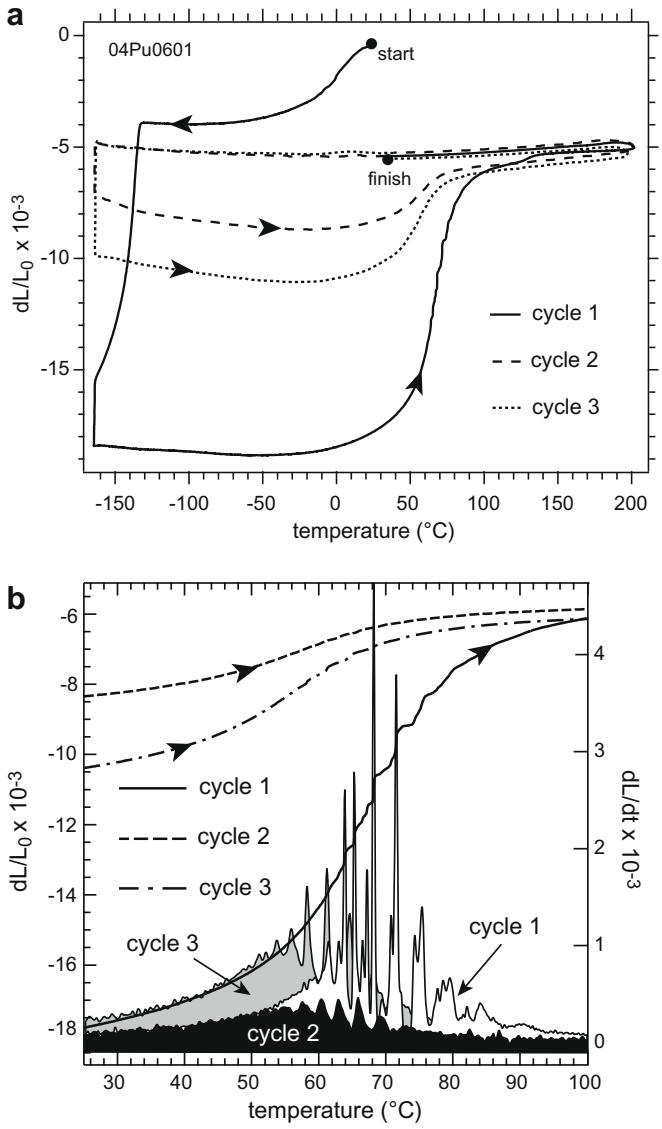

Fig. 1. (a) Dilatometry of a 1-year old sample during three thermal cycles between −165 and 200 °C. Note the decrease in % α' and lower M_s as a function of thermal cycling. The contraction during the first cooling segment before transformation was caused by a temporary cooling irregularity. (b) Detail of the dL/dt curve through the reverse transformation of the experiment shown in Fig. 1b.

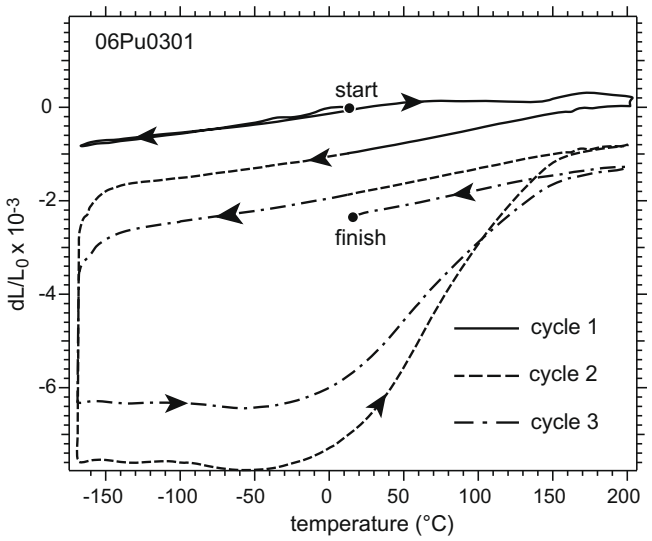

Fig. 2. Dilatometry of a 22-year old sample during thermal cycling between −165 and 200 °C. Note the lack of transformation in cycle 1 compared to subsequent cycles.

1. For samples that have not been thermally cycled previously, the M_s for cycle 1 is higher than subsequent cycles.
2. For samples that have not been thermally cycled previously, the amount of α'_t is less in cycle 2 than cycle 1 and less than or equal to the cycle 2 amount during cycle 3.
3. Room temperature resting between cycles might allow for the reduction in α'_t ingrowth to saturate, but it does not restore normal transformation behavior after heating to 200 °C even after 18 h.
4. Annealing at or above 300 °C following cycle 1 allows the amount of α'_t transformation to increase, but not to the amount seen in cycle 1.
5. Thermal cycling shifts R_s (reversion start temperature) down by 10–20 °C and R_f (reversion finish temperature) down by 5–10 °C. This results in a contraction of the $\delta + \alpha'_t$ metastability field for these experimental conditions. Heating at or above 300 °C allows R_s and R_f to drift back up towards cycle 1 values.
6. The increased homogenization of 07Pu0901 resulted in a higher R_s, lower R_f, and a smaller temperature range during which the reverse transformation takes place.

3.2. Thermal cycling of old material

Table 2 summarizes a series of experiments performed on naturally- and accelerated-aged plutonium samples. We were surprised to find that during the cycling experiments both types of aged material do not transform during cooling to below −155 °C (Fig. 3). Only after heating up to 200 °C or greater and cooling down during cycle 2 is the transformation observed. Normal thermal cycling-assisted stabilization follows the second thermal cycle, although the M_s is slightly higher on the third cool down for naturally-aged material and slightly lower for the accelerated-aged material in Fig. 3. As with the experiments summarized in Table 1, thermal cycling lowers R_s and R_f and contracts the $\delta + \alpha'_t$ metastability field. When compared to the young material, the aged samples show much less α' ingrowth, lower R_s and R_f, a much larger

Table 1
Transformation and reversion characteristics of young material.

Experiment	Cycle	Maximum T before M_s (°C)	M_s (°C)[a]	α_t' (vol. %)	R_s (°C)	α_t' + δ field (°C)[b]	R_f (°C)	$\alpha_t' \rightarrow \delta$ T range (°C)
04Pu0601[c]	1	RT	−133.6	17.8	48.5	203.5	80.4	31.9
	2	200	−164 (37.6 min)	2.3	25.2	180.2	71.6	46.4
	3	200	−163.2 (33.1 min)	5.7	23.0	178.0	74.9	51.9
07Pu0901	1	RT	−129.8	12.5	47.6	202.6	80.8	33.2
	2	200	−167.3	9.1	38.2	193.2	72.9	34.7
	3	200	−167.4 (5.6 min)	9.3	37.3	192.3	70.6	33.3
03Pu1401	1	RT	−124.7	13.5	39.9	194.9	90.5	50.6
	2	200	−155 (14.5 min)	8.3	27.2	182.2	82.5	55.3
		2 h RT rest						
	3	200	−155 (13.2 min)	8.3	28.1	183.1	82.2	54.1
03Pu1402[d]	1	200	−155 (12.3 min)	9.3	28.0	183.0	83.9	55.9
	2	200	−155 (35.7 min)	2.7	6.1	161.1	80.1	74
	3	375	−142.5	8.3	19.3	174.3	80.3	61
03Pu1501	1	RT	−124.7	12.7	33.4	188.4	90.3	56.9
	2	300	−155.8 (3.7 min)	6.8	23.8	178.8	79.8	56
		2 h RT rest						
	3	300	−155 (0.6 min)	9.5	28.3	183.3	83.3	55

[a] Time required to transform during isothermal segment shown in parentheses.
[b] Defined here as the temperature range between the warmest isothermal in the dataset (−155 °C) and the R_s.
[c] Heating rates through the transformation were 2.5, 5, and 7.5 °C/min for cycles 1, 2, and 3, respectively.
[d] Same sample as 03Pu1401 but run 18 h after prior experiment.

Table 2
Transformation and reversion characteristics of naturally- and accelerated-aged (AAP02KL29) material.

Experiment	Cycle	Maximum T before M_s (°C)	M_s (°C)[a]	α' (vol.%)	R_s (°C)	α' + δ field (°C)	R_f (°C)	$\alpha' \rightarrow \delta$ T range (°C)
06Pu0301	1	RT	–	–	–	–	–	–
	2	200	−150.1	7.4	4.8	159.8	133.5	128.7
	3	200	−147.4	4.6	−3	152	130.1	133.1
AAP02KL29	1	45[a]	–	–	–	–	–	–
	2	375	−127.9	5.3	30.9	185.9	96.5	65.6
	3	375	−133.3	0.40	–	–	–	–
06Pu0402[b]	–	120	–	0.84	−17.7	137.3	105.5	123.2
06Pu0501[b]	–	140	–	1.4	5.4	160.4	–	–
06Pu0601	–	160	−146.8	6.9	8.2	163.2	108.3	100.1
06Pu0701	–	180	−144.6	7.2	4.8	159.8	138.8	134
06Pu0201	–	200	−140.1	8.2	32	187	96.6	64.6

[a] Storage temperature for ^{238}Pu-spiked alloys.
[b] Transformation is minimal and difficult to quantify.

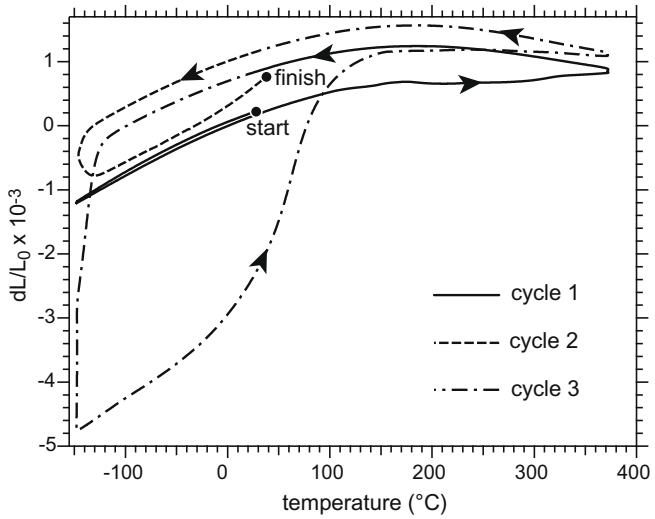

Fig. 3. Dilatometry of a ^{238}Pu-spiked Pu–Ga alloy (sample AAP02KL29) during thermal cycling between −150 and 200 °C. Note the lack of transformation in cycle 1 compared to subsequent cycles and the large decrease in α′ between cycles 2 and 3.

reverse transformation temperature range, and a smaller δ + α_t' metastability field. In general, the aged samples are more δ-phase stable than the newer alloys.

To better understand the lack of transformation during the first cycle in naturally-aged materials, we performed a series of experiments to identify the minimum annealing temperature which unlocks normal transformation behavior. These experiments began with a heating phase of 120–200 °C, followed by cooling to −165 °C to observe the δ → α_t' transformation. Experiments that started with an anneal at 120 or 140 °C showed very slight indication of the transformation (Table 2; Fig. 4). Analysis of the dL/dt during the reverse transformation temperature range and comparing these results to the thermal cycled samples suggests that 0.8 and 1.4 vol.%, respectively, transformed in these two experiments. The samples heated above 140 °C showed much more transformation, an increase from 6.9 to 8.2% during the temperature range 160–200 °C. As shown in Fig. 4, the largest increase is seen between the 140 and 160 °C annealing experiments.

4. Discussion

In addition to more conventional solute stabilization of δ-phase, thermal cycling and aging can act to enhance δ over a limited temperature range. In the case of thermal cycling, δ ↔ α_t' causes plastic deformation in δ and results in a high dislocation density. Transmission electron microscopy of similar thermally cycled material has shown that the dislocation density of samples heated at 300 °C for 4 h is reduced 86 times in the highly damaged regions near the α_t' plates [5]. Previous experiments on samples

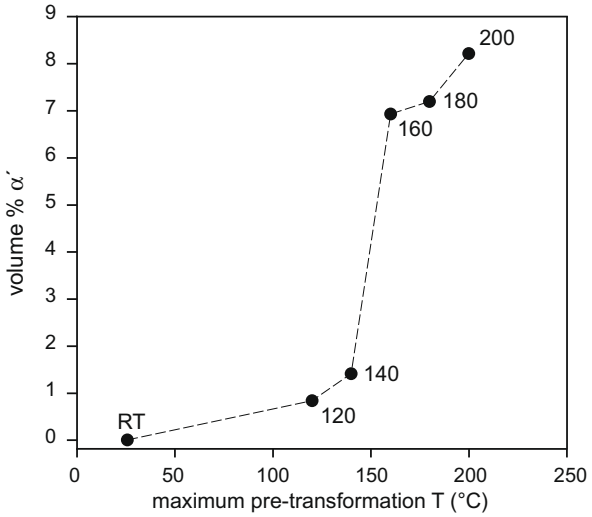

Fig. 4. Compilation of α' ingrowth measurements in 22-year old samples. Samples were annealed at progressively higher-temperatures (x-axis) and cooled to −165 °C to allow for the transformation to occur.

transformed using isostatic pressure showed that annealing at 440 °C for 200 h was needed before the thermally-induced transformation would occur, suggesting that significant Ga diffusion is required to fully reset the microstructure to the pre-transformation condition [1,6].

Our results on aged alloys suggest that Ga-stabilized δ-phase is further stabilized by the presence of lattice defects accumulated over many years of self-irradiation. These defects anneal out somewhere between RT and 200 °C, with our DSC and dilatometry work suggesting a narrower range of 140–150 °C. Specimens heated to 200 °C, and therefore free of these defects, undergo significant transformation to α'_t when cooled. Subsequent cycles with a maximum temperature of 200 °C result in less transformation to α'_t, due to the formation of new δ-stabilizing defects by the transformation–reversion process. Heating the material to 375 °C removes most of these defects, and specimens heated to this temperature again show large amounts of α' formation when cooled.

Based on their DSC experiments, Blobaum et al. [4] proposed that room temperature conditioning allows for incipient eutectoid decomposition of Ga-stabilized δ-phase Pu to $\alpha' + Pu_3Ga$. This effect saturates after 6 h, and the resulting α' embryos provide nuclei for α'_t during subsequent cooling. However, we believe that there is no dilatometry evidence from the data presented here that room temperature conditioning between cycles allows for the return of normal and reproducible transformation behavior, even after as much as 18 h of resting between cycles. In fact, what we consider to be normal transformation behavior does not return until a sample has been heated close to 400 °C. It is important to consider that the temperature profiles of our measurements do not exactly match those for the prior DSC experiments, so direct comparison between this study and that of Blobaum et al. [4] is limited. However, the discrepancy between these results may reflect differences in samples or the measurement technique (i.e., heat release vs. length change). Additionally, samples in this study, unless indicated otherwise, were used once, whereas those in the DSC experiments were used in dozens of separate measurements [4].

Acknowledgement

This work was funded by the United States Department of Energy under Contract W-7405-ENG-36.

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