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Reproducible phase transformation in a single Pu–1.9 at.% Ga specimen

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ABSTRACT

The partial martensitic $\delta \rightarrow \alpha'$ transformation in Pu–Ga alloys is sensitive to lattice strains, defects, and dislocations as well as a near–ambient–temperature conditioning treatment. Because the $\delta \rightarrow \alpha'$ transformation and reversion inherently induce strains, plastic deformation, and defects, remnants of a previous transformation of a Pu–1.9 at.% Ga alloy can inhibit the phase transformation upon subsequent cooling. On the other hand, a conditioning treatment with isothermal holds as short as 6 h at room temperature can dramatically increase the volumetric amount of transformation. These two factors can prohibit systematic study of the $\delta \rightarrow \alpha'$ transformation unless experiments can be performed on multiple identical samples or a single sample can be treated such that these effects are eliminated. The latter approach requires an understanding of the conditions necessary to remove the effects of previous transformation as well as conditioning as they relate to the inhibition or promotion of the $\delta \rightarrow \alpha'$ transformation. Herein, we identify and report a thermal procedure, specifically an anneal at 375 °C for 30 min or more, sufficient to remove the effects of conditioning and previous transformation in order to reliably return a sample to an initial state, from which reproducible amounts of $\delta \rightarrow \alpha'$ transformation can be achieved with consecutive cycling.

1. Introduction

In the Pu–Ga alloy system containing $\lesssim$3% Ga, an incomplete martensitic phase transformation can be induced at sub-ambient temperatures [1–3], where the metastable face–centered–cubic δ phase partially transforms to the metastable monoclinic α' phase. The 'prime' is conventionally used to indicate that the martensitic product traps solute during formation and exists in the crystal structure of unalloyed α-Pu, but with an expanded lattice parameter. While this partial transformation would be best described as

$$\delta \rightarrow (x)\alpha' + (1-x)\delta,$$

where x is the fractional amount of α' phase formed, the literature has historically used the shorthand $\delta \rightarrow \alpha'$ to represent the partial transformation. Like all martensitic transformations, the $\delta \rightarrow \alpha'$ transformation in Pu–Ga alloys is diffusionless, is composition-invariant, and produces a product phase (α') with a specific orientation relationship to the parent phase (δ) [4,5]. Furthermore, this $\delta \rightarrow \alpha'$ transformation belongs to the isothermal subset of martensitic transformations, where formation of the martensitic phase is a function of both time and temperature, as opposed to the athermal subset, which evinces no time dependence in forming the product phase [6]. The $\delta \rightarrow \alpha'$ transformation is observable when a sample is continuously cooled or isothermally held, where, in a Pu–1.9 at.% Ga alloy, the fractional amount of α' phase formed typically does not exceed 25%.

Isothermal transformations characteristically display a C-shaped curve on a time–temperature–transformation (TTT) diagram, where the amounts of transformation are represented by contours in the time–temperature plane. However, for the specific case of a Pu–1.9 at.% Ga alloy, the isothermal martensitic transformation proceeds with kinetics that anomalously appear as a double-C when plotted on a TTT diagram [7,8]. The origin of this double-C remains a mystery three decades after its discovery. In addition to the unconventional double-C behavior observed in Pu–1.9 at.% Ga alloys, the amount of martensitic transformation is sensitive to a 'conditioning' treatment – wherein a sample is isothermally held for several hours in the vicinity of room temperature following a high temperature anneal [9]. When a sample is conditioned at room temperature for as little as 6 h prior to cooling, the $\delta \rightarrow \alpha'$ martensitic transformation can yield an order of magnitude more α' product phase as compared to an unconditioned, but annealed, sample. The exact role that conditioning plays in the $\delta \rightarrow \alpha'$ transformation is not fully understood, but radiation damage and α-embryo formation have been postulated as candidate explanations for conditioning [9].

Studying the double-C kinetics and the conditioning effect of the transformation requires observing the results of the $\delta \rightarrow \alpha'$ transformation or the $\alpha' \rightarrow \delta$ reversion under various experimental conditions. Acquiring sufficient data to form valid conclusions about the martensitic phase transformation is made difficult by

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its sensitive dependence on time and temperature histories of the sample, as well as sample purity, Ga homogenization, and grain size. To overcome the uncertainties of these sample-dependent factors, one could perform many individual experiments on multiple, identical samples or many experiments on a single specimen. There are practical issues – including, but not limited to, safety concerns, materials processing, and time involved in sample preparation – associated with obtaining multiple samples of sufficiently identical character; but a single sample circumvents many of these issues. Provided that a single sample is representative of the innate behavior of Pu–1.9 at.% Ga and that successive thermal cycling induces no enduring change (with respect to the $\delta \rightarrow \alpha'$ transformation) over the course of an experiment, using the single sample would greatly facilitate the systematic exploration of the $\delta \rightarrow \alpha'$ transformation. However, studying a single specimen requires that the specimen be reliably returned to a state that yields reproducible results (*i.e.*, an initial state from which each subsequent thermal cycle can begin).

Radiation damage and daughter products continually accumulate in any Pu-containing material, but on short time scales this radioactive decay does not affect significantly the composition of the material. The martensitic $\delta \rightarrow \alpha'$ transformation, on the other hand, has immediate consequences to the microscopic environment of the material, especially concerning subsequent transformation. The $\delta \rightarrow \alpha'$ transformation yields an α' phase that has a volume approximately 18% smaller than the δ phase ($V_{\alpha'} \approx 0.82V_{\delta}$) [1,10]. This volume difference causes significant elastic and plastic strains in the vicinity of the transforming α' particle [5], and these strains likely limit the volumetric amount of α' product phase to about 25%. Thus, after undergoing the partial $\delta \rightarrow \alpha'$ transformation and being returned to room temperature, a Pu–1.9 at.% Ga alloy is no longer single phase, and has additional interfacial and strain energies present in the remaining δ matrix. Heating above 100 °C completes the $\alpha' \rightarrow \delta$ reversion, which removes the α' phase and its interfacial energy, but potentially leaves elastic and plastic strains as well as defects or dislocations in the δ matrix [5]. The microstructural path resulting from a thermal cycle starting in the δ phase, cooling through the martensitic transformation (Eq. (1)), and then heating through the reversion (Eq. (2)) can be represented by

$$\delta \rightarrow (x)\alpha' + (1-x)\delta + \mathscr{S}, \tag{1}$$

$$(x)\alpha' + (1-x)\delta + \mathscr{S} \rightarrow \delta + \mathscr{S}, \tag{2}$$

where $\mathscr{S}$ represents the remnant strains and dislocations generated from the martensitic transformation. Even though the δ phase is recovered with this cycle, the microstructure of a sample immediately following reversion is not the same as that before the $\delta \rightarrow \alpha'$ transformation; the accumulated strains and defects can thus affect any subsequent transformation, obscuring comparisons between the results of consecutive thermal cycles. Previously published dilatometry measurements, wherein the sample was cycled several times through the $\delta \rightarrow \alpha'$ transformation and the $\alpha' \rightarrow \delta$ reversion, reveal that subsequent transformation is, in fact, inhibited by the remnants of transformation from previous cycles [2].

There are thus two effects that have dramatic consequences on the reproducible cycling of a single sample of Pu–1.9 at.% Ga: remnants of previous martensitic transformation, which inhibits subsequent transformation; and conditioning, which promotes transformation relative to direct cooling from high temperature. In this paper, we report differential scanning calorimetry measurements aimed at determining a thermal heating schedule that yields both the destruction of conditioning and the annealing of accumulated defects and strains from previous transformation in a minimum amount of time. Using such a heating schedule would establish an initial condition from which identical experiments on a single sample would exhibit reproducible results, thus facilitating the study of the anomalous behaviors associated with the partial $\delta \rightarrow \alpha'$ martensitic transformation in Pu–Ga alloys.

2. Experimental details

A single polycrystalline sample of Pu–1.9 at.% Ga, originally cast in 2001, was machined into a 177 mg, 3 mm diameter disc. The sample was subjected to a homogenization treatment in which the sample was held at 460 °C for 534 h. This treatment ensured a single phase δ-Pu alloy with a very homogeneous Ga distribution [1,11,12]. The sample was sealed in a commercial, gold-plated stainless steel pan with a gold-plated copper gasket. The pan was placed in a Perkin–Elmer Pyris Diamond differential scanning calorimeter (DSC), capable of controlling temperature in the range from −160 °C to 450 °C. Continuous cooling DSC traces were taken at 20 °C/min, and a smooth baseline was subtracted to reveal the $\delta \rightarrow \alpha'$ and $\alpha' \rightarrow \delta$ transformations upon cooling and heating, respectively. Measured heats of transformation were obtained by numerically integrating the continuous heating trace of the $\alpha' \rightarrow \delta$ reversion. While the measured heat was proportional to the volumetric amount of transformation, the precise heat of transformation (ΔH) for the $\alpha' \rightarrow \delta$ reversion has not been well-established in the literature. As such, extracting an absolute value for the amount of transformation was impossible, and instead the measured heats have been plotted in lieu of fractional transformation.

Three specific isothermal holds were used in this study: (1) *annealing*, where the sample was held at 375 °C for greater than 30 min; (2) *conditioning* – which always followed annealing in this study – where the sample was held at 25 °C for 8 or 12 h; and (3) *post-conditioning* – which always followed conditioning in this study – where the sample was held for a period of 1 or 4 h at various temperatures between 25 °C and 375 °C. The purpose of the post-conditioning treatment was to investigate a thermal procedure to destroy the effects of conditioning. These isothermal holds were all performed *in situ* in the DSC. The first set of experiments was carried out to determine what anneal time at 375 °C was sufficient to remove the effects of previous transformation (Section 3.1), while the second set of experiments was performed to determine what post-conditioning time and temperature was sufficient to destroy the effects of conditioning (Section 3.2).

3. Results and discussion

3.1. Annealing after previous transformation

To investigate the effects of high temperature annealing time on the subsequent low temperature martensitic $\delta \rightarrow \alpha'$ transformation, the sample, which had previously been transformed at low temperatures, was annealed at 375 °C for a variable time (between 30 min and 8 h) and then conditioned for an extended period of time (8 or 12 h) to ensure maximal transformation upon cooling to −160 °C [9]. After undergoing the $\delta \rightarrow \alpha'$ transformation, the sample was heated to 375 °C at 20 °C/min and the heat flow associated with the $\alpha' \rightarrow \delta$ reversion peak was measured. The subtracted heat flow of the reversion is shown in the inset of Fig. 1. Peaks characteristic of the burst nature of the martensitic transformation are evident as intermittent spikes in the subtracted heat flow that appear overlaid on the main peak of the reversion [13–15].

The areas under the reversion peaks from DSC scans are plotted as the measured heats in Fig. 1. The fluctuations in the baseline of the subtracted heat flow were the predominant contribution to errors in the measured heat. The numerical integration was

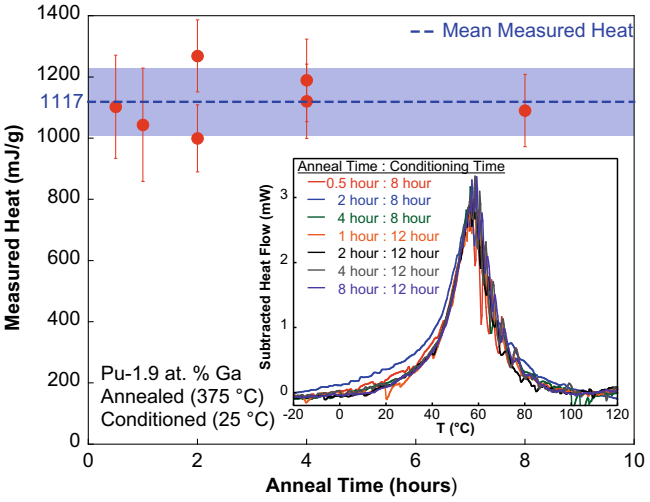

Fig. 1. Measured heat (area under the reversion peaks of inset) as a function of anneal time. The error bars correspond to fluctuations in the baseline heat flow. Anneal times between 30 min and 8 h produce comparable measured heats with an average value of 1117 mJ/g. The standard deviation of the annealing data is represented by the blue, shaded region. Inset: DSC traces showing the subtracted heat flow as a function of temperature for the $\alpha' \rightarrow \delta$ reversion for various combinations of annealing and conditioning treatments. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

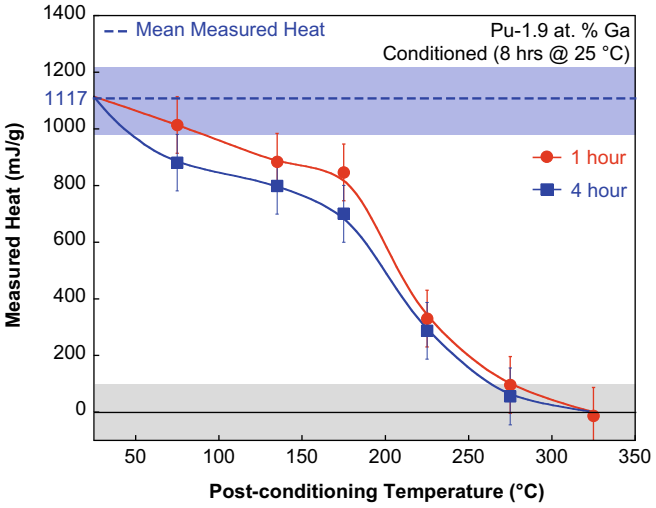

Fig. 2. Measured heat as a function of post-conditioning temperature (1 h holds – red circles, 4 h holds – blue squares) following an 8 h conditioning treatment at 25 °C. The solid lines are guides to the eye. The gray swath at the bottom of the figure represents the region of measured heat associated with transformation of an unconditioned sample (see text). The blue, dashed line and the blue, shaded region are identical to those of Fig. 1. The transformation-promoting effects of conditioning are reduced with increasing post-conditioning temperature; destroying the effects of conditioning is fully realized for $T > 275$ °C. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

performed from the maximum and minimum of these fluctuations, which yielded the extreme values (end points of error bars) of the measured heat. The red circles in Fig. 1 represent the average of the two extreme values determined for each anneal treatment. The mean of the measured heats for all anneal times was calculated as 1117 mJ/g with a standard deviation of approximately 90 mJ/g; these value are displayed as a blue, dashed line and a shaded blue region, respectively, in Fig. 1. Within error, the sample undergoes a comparable amount of $\delta \rightarrow \alpha'$ transformation for all anneal times investigated. From the data displayed in Fig. 1, it can be concluded that anneal times as short as 30 min at 375 °C are sufficient to remove the defects, dislocations, and elastic/plastic strains associated with any previous $\delta \rightarrow \alpha'$ transformation or $\alpha' \rightarrow \delta$ reversion.

3.2. Destroying the effects of conditioning

To determine the thermal treatment necessary to destroy the effects of ambient-temperature conditioning, a sample was first conditioned (following an anneal at 375 °C) for 8 h at 25 °C. This combination of conditioning temperature and time was previously found to elicit a maximal amount of $\delta \rightarrow \alpha'$ transformation and reversion [9]. Following the conditioning treatment, the sample was post-conditioned for 1 or 4 h at elevated temperature and then cooled to −160 °C to permit the $\delta \rightarrow \alpha'$ transformation. The sample was then heated and, as employed in the previous section, the reversion peak was used to quantify the amount of transformation.

Without conditioning, the sample showed only a modest amount of transformation on cooling, which is consistent with a previous optical metallography study [16]. Heating the unconditioned specimen resulted in no experimental signature of the reversion in the DSC, although it is reasonable to assume that the reversion occurred; the lack of an experimental signature is a consequence of instrument noise, which is of order 100 mJ/g for this particular sample mass. Multiple measurements on this sample show similar results, and these results are indicated in Fig. 2 as a gray swath, which represents the region of measured heat associated with uncertainty in the reversion of an unconditioned sample.

The results of the post-conditioning treatment are summarized in Fig. 2, where the average measured heat of the $\alpha' \rightarrow \delta$ reversion determined in Section 3.1 is displayed as a blue, dashed line. Deviations from this mean measured heat indicate the destruction of the conditioning effect. With increasing temperature, both the 1 h and 4 h post-conditioning treatments reduce the effects of conditioning. It is necessary to post-condition at temperatures in excess of 275 °C to completely destroy the effects of conditioning (*i.e.*, to reduce the measured heat to that of an unconditioned sample) on a 1–4 h timescale. For temperatures up to approximately

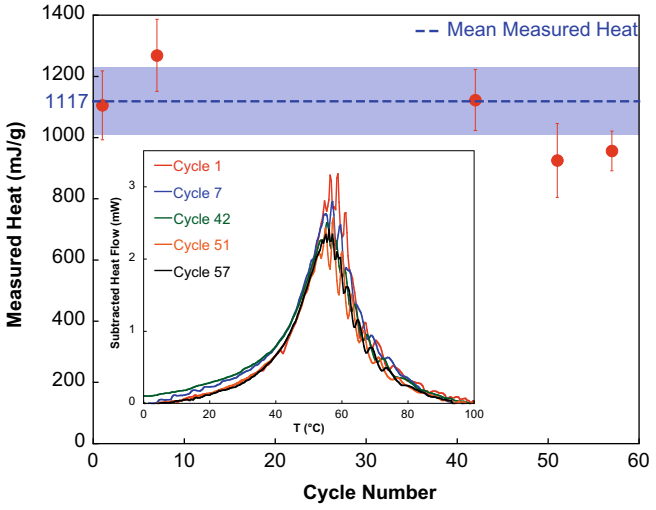

Fig. 3. Measured heats as a function of consecutive thermal cycles as determined from the DSC traces represented in the inset. The blue, dashed line and the blue, shaded region are identical to those of Fig. 1. The amount of transformation is reproducible, within error, over the course of nearly 60 consecutive thermal cycles. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

250 °C, the transformation-promoting effects of conditioning were previously found to induce an increase in the amount of α' phase formed at low temperature [9,17]. Therefore, in order to remove the effects of conditioning, it is not surprising that post-conditioning must be performed at temperatures above 250 °C, outside the nominal temperature range in which conditioning occurs. A smooth interpolation (solid lines in Fig. 2) suggests that removing the effects of conditioning is more thoroughly accomplished for post-conditioning temperatures $\gtrsim 325$ °C.

4. Conclusions

After thermal cycling of a Pu–1.9 at.% G a alloy such that the incomplete $\delta \rightarrow \alpha'$ transformation occurred, it is necessary to anneal the sample at 375 °C for times as short as 30 min to remove the transformation-induced factors – such as defects, dislocations, plastic strains, and elastic strains – that would inhibit further transformation on subsequent cooling. If such an anneal is performed prior to conditioning or cooling the sample, a reproducible amount of transformation at low temperature is expected for consecutive thermal cycles. Destroying the effects of conditioning, which saturate at room temperature in as little as 6 h, can be achieved by holding the sample at temperatures above 325 °C for 1 h. Therefore, one can be reasonably assured that a sample annealed at 375 °C for 1 h has few remnants of either conditioning or previous transformation.

This 1 h anneal at 375 °C can be used to establish an initial state for experiments, providing a starting point with a 'clean' δ phase. If experiments employing identical thermal procedures begin from this initial state, then the results of those experiments should be reproducible, permitting a systematic study of the fundamental nature of conditioning and the kinetics of the $\delta \rightarrow \alpha'$ transformation. Example DSC traces of the $\alpha' \rightarrow \delta$ reversion for various thermal cycles, which all employed the anneal schedule identified herein as well as an 8 h conditioning treatment, are given in the inset of Fig. 3. These traces appear similar, and, when analyzed, yield the data points of Fig. 3, which shows the measured heat as a function of the number of thermal cycles to which the sample was subjected. Over the course of nearly 60 consecutive thermal cycles from 375 °C to −160 °C, the $\alpha' \rightarrow \delta$ reversion yields comparable amounts of transformation that fall within the bounds determined from the annealing experiment of Section 3.1. It should be noted that the leftmost data point of Fig. 3 corresponds to the first $\delta \rightarrow \alpha'$ transformation experienced by the sample, suggesting that the mechanisms at work in the initial and subsequent transformations are identical. While these results from DSC measurements do not indicate any significant changes in the Pu–Ga sample with thermal cycling, future measurements, potentially encompassing more thermal cycles and using other techniques (*e.g.,* dilatometry, X-ray diffraction, TEM, etc.), would be helpful in corroborating these findings.

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