LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

LLNL-PROC-402757

Ambient-temperature Conditioning as a Probe of Double-C Transformation Mechanisms in Pu-2.0 at. % Ga

Jason R. Jeffries, Kerri J. M. Blobaum, Mark A. Wall, Adam J. Schwartz

April 7, 2008

Materials Research Society Spring Meeting
San Francisco, CA, United States
March 24, 2008 through March 28, 2008

Disclaimer

Mater. Res. Soc. Symp. Proc. Vol. 1104 © 2008 Materials Research Society 1104-NN01-06

Ambient-temperature Conditioning as a Probe of Double-C Transformation Mechanisms in Pu-2.0 at. % Ga

Jason R. Jeffries[1], Kerri J. M. Blobaum[1], Mark A. Wall[1], and Adam J. Schwartz[2]
[1]Chemistry, Materials, Earth, and Life Sciences Directorate, Lawrence Livermore National Laboratory, Livermore, CA, 94550
[2]Physical Sciences Directorate, Lawrence Livermore National Laboratory, Livermore, CA, 94550

ABSTRACT

The gallium-stabilized Pu-2.0 at. % Ga alloy undergoes a partial or incomplete low-temperature martensitic transformation from the metastable δ phase to the gallium-containing, monoclinic α′ phase near -100 °C. This transformation has been shown to occur isothermally and it displays anomalous double-C kinetics in a time-temperature-transformation (TTT) diagram, where two nose temperatures anchoring an upper- and lower-C describe minima in the time for the initiation of transformation. The underlying mechanisms responsible for the double-C behavior are currently unresolved, although recent experiments suggest that a conditioning treatment—wherein, following an anneal at 375 °C, the sample is held at a sub-anneal temperature for a period of time—significantly influences the upper-C of the TTT diagram. As such, elucidating the effects of the conditioning treatment upon the δ→α′ transformation can provide valuable insights into the fundamental mechanisms governing the double-C kinetics of the transition. Following a high-temperature anneal, a differential scanning calorimeter (DSC) was used to establish an optimal conditioning curve that depicts the amount of α′ formed during the transformation as a function of conditioning temperature for a specified time. With the optimal conditioning curve as a baseline, the DSC was used to explore the circumstances under which the effects of the conditioning treatment were destroyed, resulting in little or no transformation.

INTRODUCTION

While the face-centered-cubic δ phase of a Pu-2.0 at.% Ga alloy is metastable at room temperature, owing to the kinetics associated with eutectoid decomposition, this alloy is also metastable at low temperature with respect to partial transformation to the monoclinic α′ structure, an expanded structure with Ga trapped in a lattice of the same crystalline symmetry as that of α-Pu. This δ→α′ transformation proceeds via an isothermal martensitic transformation near -100 °C with the amount of transformation product dependent upon both time and temperature, unlike classic athermal martensites (e.g., in Fe-C steels) where temperature alone defines the amount of transformation product. Due to the competition of two opposing forces such as the free energy difference between phases and diffusion, isothermal transformations typically exhibit a characteristic "C" shape with a maximum transformation rate when plotted on a time-temperature-transformation (TTT) diagram; however, an alloy of Pu-2.0 at.% Ga exhibits an anomalous "double-C" curve, showing two local maximal transformation rates defining an upper- and lower-C, when plotted on a TTT diagram [1, 2].

This exotic behavior in the Pu-Ga system has remained an unsolved mystery for over 30 years. The questions surrounding the double-C behavior of Pu-Ga alloys include details of morphology, mechanism, and driving force. Previously reported results suggest that the upper- and lower-C of the $\delta \rightarrow \alpha'$ transformation proceed via different mechanisms [3, 4]. In addition, a previous study revealed that the $\delta \rightarrow \alpha'$ transformation responded in a non-trivial manner to a conditioning procedure, in which a specimen is isothermally held in the vicinity of room temperature [5]. In this paper, we report differential scanning calorimetery (DSC) measurements designed to illuminate the role that conditioning plays in the $\delta \rightarrow \alpha'$ transformation of a Pu-2.0 at.% Ga alloy.

EXPERIMENTAL DETAILS

A Pu-2.0 at.% Ga alloy was annealed at 460 °C for 534 hours to ensure a single-phase δ-Pu material with a homogeneous gallium distribution [6, 7]. Subsequently, the sample, a 2.8 mm diameter cylinder with a mass of 177.92 mg, was cut from the annealed Pu-2.0 at.% Ga alloy. The sample was sealed in a gold-plated stainless steel pan with an atmosphere of dry nitrogen, and the pan was loaded into a previously calibrated Perkin-Elmer Diamond power-compensation differential scanning calorimeter (DSC).

In order to investigate the $\delta \rightarrow \alpha'$ transformation, the sample underwent a transformation cycle—in which the specimen was cooled from 25 °C to -160 °C, heated to 350 °C, and finally cooled back to 25 °C. This transformation cycle revealed the low-temperature $\delta \rightarrow \alpha'$ transformation as well as the $\alpha' \rightarrow \delta$ reversion that occurred above room temperature. Before any conditioning treatments or transformation cycles were performed, the sample was annealed *in situ* in the DSC at 375 °C for 2 hours to remove any α' phase resulting from the previous cutting procedure or prior transformation cycles. Following this anneal process, the sample was conditioned, post-conditioned, or cycled depending on the goals of the particular experiment, which will be discussed in the following section.

RESULTS

Optimal Conditioning

The first experiments performed were designed to quantify the effects of conditioning temperature on the amount of α' formation. To achieve this, the specimen was conditioned (after the anneal procedure) at various temperatures below the anneal temperature of 375 °C for 8 hours, a time previously determined to be sufficient to elicit maximum transformation upon cooling [5]. Following the conditioning treatments, the sample underwent a transformation cycle. The conditioning temperature was varied and the transformations analyzed to determine the amount of transformation as a function of conditioning temperature and the optimal conditioning temperature.

Figure 1 displays the results of the transformation cycles for various conditioning temperatures, T_{COND}. The baseline data has been subtracted to yield the displayed data for Pu-2.0 at.% Ga, which detail the $\delta \rightarrow \alpha'$ transformation (Figure 1a) and the $\alpha' \rightarrow \delta$ reversion (Figure 1b). It can be readily seen from the data that varying T_{COND} dramatically affects the resulting transformations.

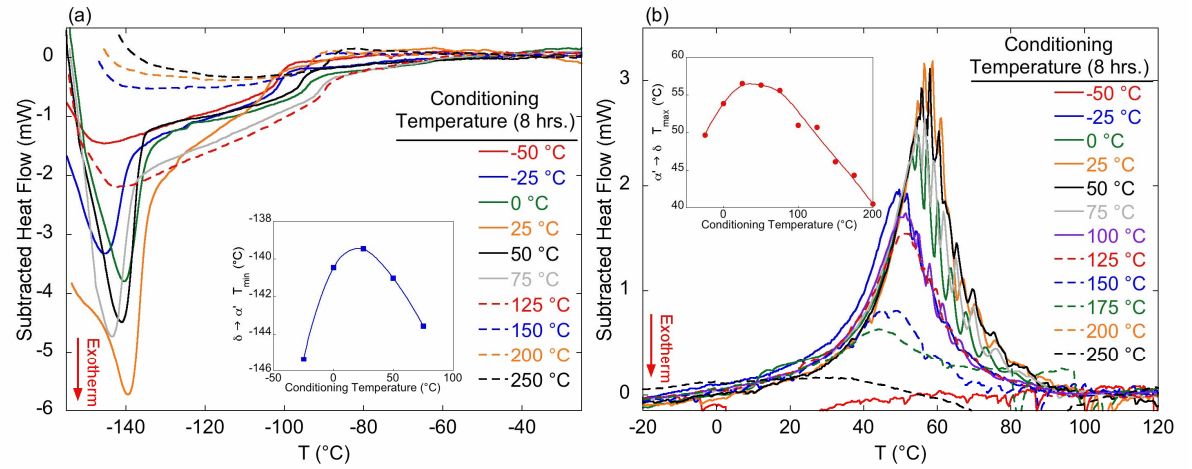

Figure 1: (color online) Differential scanning calorimetry data as a function of temperature T for the δ→α′ (a) and α′→δ (b) transformations after the specimen was conditioned for 8 hours at various temperatures. The insets of (a) and (b) display the evolution of the positions of the minimum (δ→α′ transformation) and maximum (α′→δ reversion) with conditioning temperature, respectively.

In Figure 1a, several of the experimental curves do not return to zero, which is likely a consequence of the δ→α′ transformation proceeding below the minimum temperature achievable in the DSC of -160 °C. Nonetheless, the data reveal the development of a large exothermic peak near -140 °C as T_{COND} is increased above -50 °C. At T_{COND} = 25 °C, this exothermic peak reaches its minimum value (maximum deviation from the baseline), after which the magnitude of the exothermic peak decreases with increasing T_{COND}. The inset of Figure 1a shows the evolution of the peak position of the exothermic peak as a function of T_{COND}. The peak position, T_{min}, exhibits a maximum at T_{COND} = 25 °C; above and below this temperature, T_{min} decreases slightly as the peak becomes ill-defined from the data in Figure 1a.

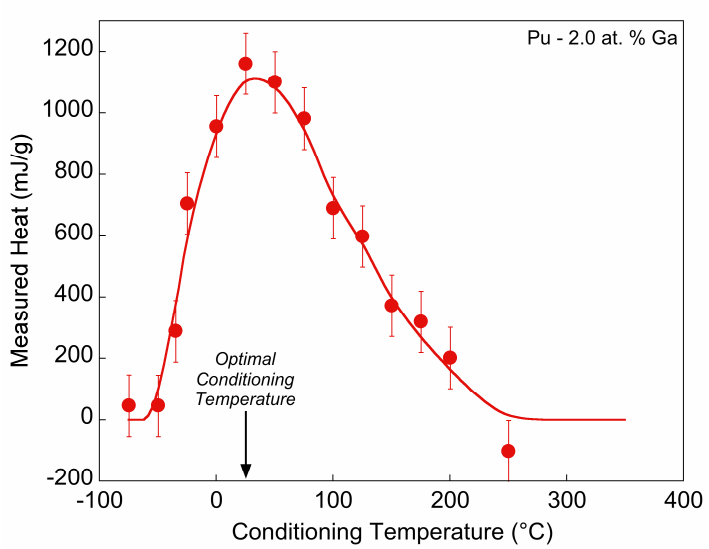

Figure 2: (color online) Measured heat as a function of conditioning temperature in Pu-2.0 at.% Ga. The solid line is a guide to the eye. Optimal conditioning is realized for T_{COND} = 25 °C, above and below which the amount of α′ transformation is reduced.

Figure 1b shows the DSC data as a function of temperature and for various conditioning temperatures for the α′→δ reversion. As in the low-temperature δ→α′ transformation of Figure 1a, the data taken for T_{COND} = 25 °C exhibit the largest heat

flow, decreasing in either direction away from 25 °C. Similarly, the inset of Figure 1b shows that the position of the endothermic peak reaches a maximum for T_{COND} = 25 °C. Also evident in several of the DSC curves are spikes, which have previously been attributed to transformation bursts [8].

The inability to observe an untruncated $\delta \rightarrow \alpha'$ transformation at low temperature prohibits determination of the heat of transformation, $\Delta H^{\delta \rightarrow \alpha'}$, from the data in Figure 1a; however, the $\alpha' \rightarrow \delta$ reversion, shown in Figure 1b, occurs entirely within the range of the DSC instrument, permitting the determination of the measured heat. By integrating the endothermic peak of the DSC curves shown in Figure 1b to yield the area under each curve, the measured heat as a function of conditioning temperature can be obtained as plotted in Figure 2; the error bars are estimated to be ±100 mJ/g from the noise in the data and uncertainty in the subtracted baseline. The martensitic $\delta \rightarrow \alpha'$ transformation in Pu-2.0 at.% Ga is strain limited, resulting in an incomplete transformation yielding a maximum transformation of approximately 25% [9]. As such, the measured heat is proportional to both the thermodynamic heat of transformation ($\Delta H^{\alpha' \rightarrow \delta}$) and the amount of α' transformed and thus subsequently reverted. Since the reversion always involves the same initial (α') and final states (δ), then $\Delta H^{\alpha' \rightarrow \delta}$ is constant, and the change in the measured heat with varying T_{COND} signifies a change in the amount of α' formed during the low-temperature phase transformation. From Figure 2, it can be seen that conditioning temperatures between -25 °C and 200 °C increase the amount of α' transformation—with the maximum transformation, corresponding to approximately 1160 mJ/g, occurring at the optimal conditioning temperature of 25 °C.

Destroying Optimal Conditioning and Stable Phase Regions

To understand the role of conditioning on the $\delta \rightarrow \alpha'$ transformation, it was useful to determine the circumstances required to destroy the positive effects of conditioning. The data described in the preceding section provided a baseline for understanding the conditioning treatment and also determined the optimal temperature, 25 °C, for an 8-hour conditioning treatment. The sample was optimally conditioned at 25 °C for 8 hours and then held at various temperatures above 25 °C for 1 and 4 hours. The latter isothermal holds were defined as post-conditioning. Following post-conditioning, the sample was subjected to a transformation cycle to quantify the amount of transformation in the same manner as previously described.

The results of the 1-hour and 4-hour post-conditioning treatments are summarized in Figure 3, in which the post-conditioning results (green diamonds and black squares) are plotted with the conditioning treatment results of Figure 2 (red circles). Overlaid on Figure 3 are the stable phase fields of a Pu-2.0 at.% Ga alloy including the eutectoid decomposition of α-Pu + Pu_3Ga (blue), α-Pu + δ-Pu (orange), β-Pu + δ-Pu (green), γ-Pu + δ-Pu (red), and single-phase δ-Pu (white). The black, vertical dashed lines demarcate the approximate phase boundaries, while the red, horizontal dashed line indicates the measured heat from optimal conditioning. Error bars are determined as in the previous section.

It can be seen from Figure 3 that the amount of transformation was enhanced (compared to no conditioning) with conditioning temperatures within the α-Pu + Pu_3Ga, α-Pu + δ-Pu, and β-Pu + δ-Pu regions. Conditioning in the γ-Pu + δ-Pu or single-phase δ-Pu regions yielded no net increase in transformation product. The position of the optimal conditioning curve with respect to the stable phase regions suggests that the formation of α or β embryos or nuclei may play a

significant role in augmenting the δ→α′ transformation. How these posited embryos or nuclei promote a greater amount of low-temperature transformation is currently not understood.

Post-conditioning at elevated temperatures above 25 °C had the effect of decreasing the amount of transformation gradually up to 175 °C, after which the reduction in transformation due to post-conditioning fell precipitously towards the complete destruction of the positive effects of conditioning at 325 °C, within the single-phase δ phase field of this Pu-Ga alloy. The 1-hour and 4-hour post-conditioning treatments yielded very similar results, suggesting a weak time dependence for post-conditioning isothermal holds greater than 1 hour. At this time, the temperature dependences of the post-conditioning curves are not fully understood, but the data in Figure 3 suggest an intimate connection between the destruction of conditioning and accessing the high-temperature phase regions.

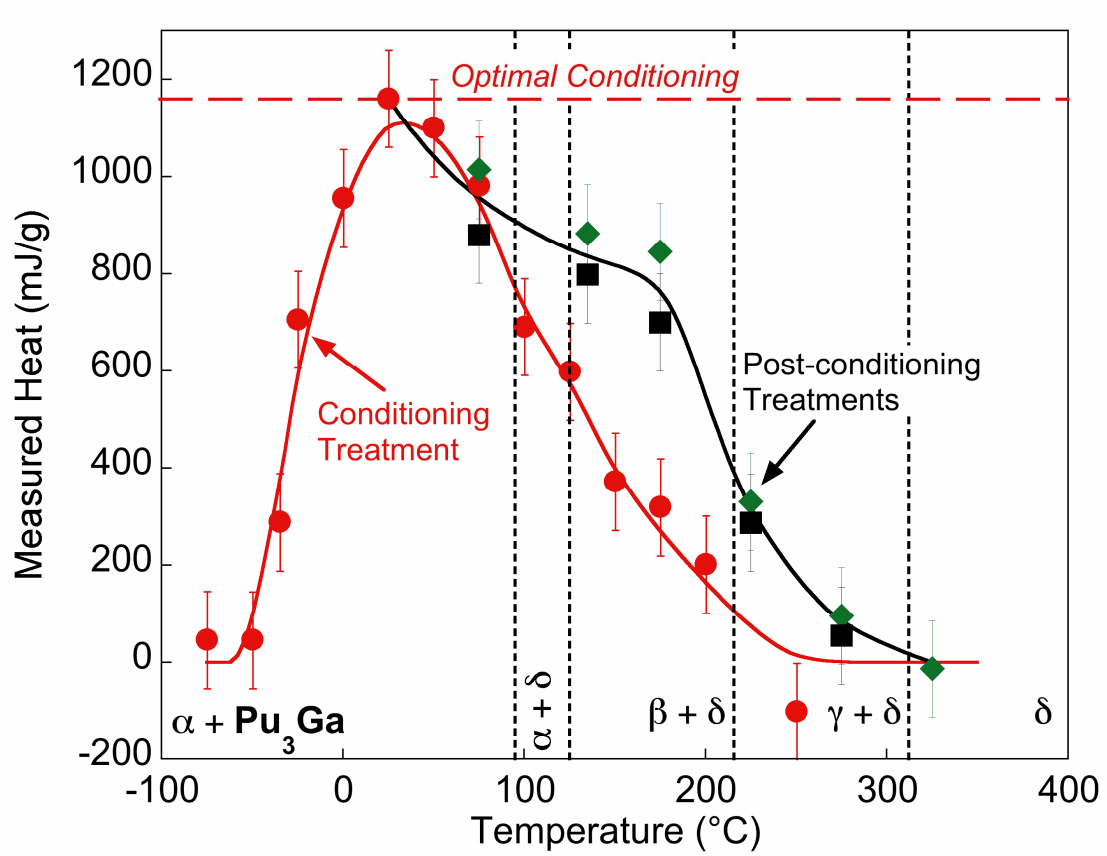

Figure 3: (color online) Measured heat as a function of conditioning temperature and post-conditioning temperature. The red circles reproduce the measured heat, proportional to the amount of transformation, for the conditioning treatment of Figure 2. The green diamonds and black squares indicate the measured heat as a function of post-conditioning temperature for 1-hour and 4-hour isothermal holds, respectively. The solid lines are guides to the eye. The stable phase fields of a Pu-2.0 at.% Ga alloy are represented by the different shaded regions, with the vertical dashed lines representing estimates of the phase boundaries. The red, horizontal dashed line indicates the measured heat obtained for optimal conditioning.

CONCLUSIONS

Differential scanning calorimetry measurements have revealed an enhancement of the $\delta \rightarrow \alpha'$ phase transformation with conditioning, wherein a specimen is isothermally held at temperatures below the annealing temperature but well above the martensite start temperature. This was realized through quantitative measurements of the measured heat of the $\alpha' \rightarrow \delta$ reversion, which is proportional to the total amount of transformation product. Varying the conditioning temperature indicated an optimal conditioning temperature of 25 °C as well as a correlation between the stable phase fields of a Pu-2.0 at.% Ga alloy and the amount of transformation product, suggestive of the formation of α or β embryos or nuclei during the conditioning process. It is possible that these embryos or nuclei serve as influential nucleation sites in excess of intrinsic sites for the martensitic phase transformation, thus increasing the amount of transformation.

After optimally conditioning a specimen, a second isothermal hold was implemented to investigate the circumstances necessary to destroy the positive effects of conditioning. This post-conditioning treatment was found to completely remove the effects of conditioning for temperatures within the δ phase field. Post-conditioning temperatures below the $\beta + \delta/\gamma + \delta$ phase boundary yielded a small reduction in the transformation product relative to optimal conditioning, whereas post-conditioning temperatures above the $\beta + \delta/\gamma + \delta$ phase boundary caused a rapid suppression in the amount of transformation. The exact nature governing the destruction of optimal conditioning is not currently understood.

ACKNOWLEDGMENTS

Lawrence Livermore National Laboratory is operated by Lawrence Livermore National Security, LLC, for the U.S. Department of Energy, National Nuclear Security Administration under Contract DE-AC52-07NA27344.

REFERENCES

1. J. T. Orme, M. E. Faiers, and B. J. Ward, in Plutonium 1975 and Other Actinides, edited by H. Blank and R. Lindner, North Holland Publishing Company, Amsterdam, 1975, pp. 761-773.
2. B. Oudot, K. J. M. Blobaum, M. A. Wall, and A. J. Schwartz, J. Alloy Compd. **444-445**, 230-235 (2007).
3. P. Deloffre, J. L. Truffier, and A. Falanga, J. Alloy Compd. **271-273**, 370-373 (1998).
4. P. Deloffre, Ph.D. Thesis, Université Paris XI Orsay, 1997.
5. K. J. M. Blobaum, C. R. Krenn, M. A. Wall, T. B. Massalski, and A. J. Schwartz, Acta Mater. **54**, 4001-4011 (2006).
6. S. S. Hecker, Los Alamos Sci. **26**, 291-335 (2000).
7. J. N. Mitchell, F. E. Gibbs, T. G. Zocco, and R. A. Pereyra, Metall. Mater. Trans. A **32A**, 649-659 (2001).
8. K. J. M. Blobaum, C. R. Krenn, J. N. Mitchell, J. J. Haslam, M. A. Wall, T. B. Massalski, and A. J. Schwartz, Metall. Mater. Trans. A **37A**, 567-577 (2006).
9. K. T. Moore, C. R. Krenn, M. A. Wall, and A. J. Scwhartz, Metall. Mater. Trans. A. **38A**, 212-222 (2007).