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# Nucleation and growth of the alpha-prime martensitic phase in Pu-Ga alloys

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## Abstract

In a Pu-2.0 at% Ga alloy, it is observed experimentally that the amount of the martensitic alpha-prime product formed upon cooling the metastable delta phase below the martensite burst temperature ( $M_b$ ) is a function of the holding temperature and holding time of a prior conditioning (“annealing”) treatment. Before subjecting a sample to a cooling and heating cycle to form and revert the alpha-prime phase, it was first homogenized for 8 hours at 375°C to remove any microstructural memory of prior transformations. Subsequently, conditioning was carried out in a differential scanning calorimeter apparatus at temperatures in the range between -50°C and 370°C for periods of up to 70 hours to determine the holding time and temperature that produced the largest volume fraction of alpha-prime upon subsequent cooling. Using transformation peak areas (*i.e.*, the heats of transformation) as a measure of the amount of alpha-prime formed, the largest amount of alpha-prime was obtained following holding at 25°C for at least 6 hours. Additional time at 25°C, up to 70 hours, did not increase the amount of subsequent alpha-prime formation. At 25°C, the Pu-2.0 at% Ga alloy is below the eutectoid transformation temperature in the phase diagram and the expected equilibrium phases are  $\alpha$  and Pu<sub>3</sub>Ga, although a complete eutectoid decomposition of delta to these phases is expected to be extremely slow. It is proposed here that the influence of the conditioning treatment can be attributed to the activation of alpha-phase embryos in the matrix as a beginning step toward the eutectoid decomposition, and we discuss the effects of spontaneous self-irradiation accompanying the Pu

radioactive decay on the activation process. Subsequently, upon cooling, certain embryos appear to be active as sites for the burst growth of martensitic alpha-prime particles, and their amount, distribution, and potency appear to contribute to the total amount of martensitic product formed. A modeling approach based on classical nucleation theory is presented to describe the formation of alpha-phase embryos during conditioning. The reasons why the holding times during conditioning become eventually ineffective in promoting more alpha-prime formation on cooling are discussed in terms of the differences in the potency of the embryos created in the delta matrix during conditioning and in terms of growth-impeding volume strains in the matrix resulting from an increasing number of martensite particles, thus opposing further growth. It is suggested that the disparate amounts of the alpha-prime formation reported in the literature following various studies may be in part a consequence of the fact that conditioning times at ambient temperatures are inevitably involved in any handling of radioactive samples prior to testing.

## **Introduction**

The occurrence of a martensitic transformation below ambient temperatures during thermal cycling of Pu-rich Pu-Ga alloys is well documented in the literature [1-4]. Typically, a sample is initially homogenized at some relatively high temperature in the fcc  $\delta$  phase field and is then cooled at various rates to temperatures in the range of  $-160^{\circ}\text{C}$ . The martensitic transformation product, the monoclinic  $\alpha'$ , can be obtained in this way, with a maximum volume fraction of about 30% for a Pu-2.0 at% Ga alloy (on continuous cooling, the volume fraction is approximately 20%). On re-heating, the martensite can be made to revert gradually to the original  $\delta$ , provided that the temperature is raised to approximately  $32^{\circ}\text{C}$ , depending on the Ga content. A further heating to higher temperatures, approximately  $375^{\circ}\text{C}$ , is expected to remove all traces of the martensitic product and the accompanying elastic/plastic stress fields [5].

The progress and reversal of a martensitic transformation can be studied with repeated thermal cycling [5], or with isothermal holding. During the repeated cycling, it was found that the amount of  $\alpha'$  formed during each cycle typically became progressively smaller than that obtained during the preceding cycle [6, 7]. This was true even if after each run the sample was re-homogenized at 375°C for 8 hours. On the other hand, if the sample was thermally conditioned for a time period near the ambient temperature (25°C) *after* the anneal at 375°C, a reproducible amount of the martensitic product was always obtained during each subsequent cycle. However, while such additional conditioning times at the ambient temperature tended to increase the resulting amount of the transformation product, this occurred only up to a certain holding time limit. The documentation and discussion of these unusual observations are the subject of this paper.

The composition of the alloy used here, Pu-2.0 at% Ga, is shown by a vertical line on the modified equilibrium Pu-Ga phase diagram in Figure 1. This figure is based on the equilibrium Pu-Ga phase diagram initially proposed by Chebotarev, *et al.* [8] and later by Timofeeva [9] and Hecker and Timofeeva [10]. Here, the phase diagram has been extended to lower temperatures and lines indicating martensite burst ( $M_b$ ) and reversion start ( $R_s$ ) temperatures for the metastable  $\delta/\alpha'$  transformations have been added. Transformations between the metastable  $\delta$  and  $\alpha'$  phases proceed via a burst martensite mode (*i.e.*, once activated, each individual martensite unit grows nearly instantaneously) [5]. The nature of the transformation to  $\alpha'$  is often referred to as having isothermal features because it has been demonstrated that the nucleation stage of the transformation involves thermal activation, and hence the transformation can also proceed at a constant temperature [4, 5, 11].

During continuous cooling at rates between 0.3 and 20°C/min, the  $\delta \rightarrow \alpha'$  transformation begins at approximately  $-120^\circ\text{C}$  for the Pu-2.0 at% Ga alloy. Here, we have used differential scanning calorimetry (DSC) to study the  $\delta \rightarrow \alpha'$  martensitic transformation in this alloy, with particular attention to systematic conditioning (annealing) treatments to which the sample was subjected prior to each transformation cycle. By integrating the areas of DSC peaks corresponding to the  $\delta \rightarrow \alpha'$  forward transformation and the  $\alpha' \rightarrow \delta$  reversion, we estimated the relative amounts of  $\alpha'$  formed as a function of the temperature and time of the prior conditioning treatments.

## Experimental

A Pu-2.0 at% Ga alloy with an average grain size of approximately 25  $\mu\text{m}$  was used in all experiments. Samples were initially annealed at  $430^\circ\text{C}$  for 12 hours to produce a uniform, but not fully homogenized, distribution of single-phase  $\delta$  throughout the sample. Following this anneal, samples were cut to size with a diamond saw and the surface oxide was removed by mechanical polishing. Samples were then subjected to a second anneal at  $175^\circ\text{C}$  for 30 minutes to remove any  $\alpha'$  that may have formed on the surface during polishing.

All of the experiments were carried out while the sample was mounted in a differential scanning calorimeter (DSC). The sample was a 2.8-mm diameter cylinder with a mass of approximately 220 mg. One flat face of the cylinder was in contact with the sample pan to provide good thermal contact. The sample was contained in a gold-lined stainless steel pan sealed with a gold-plated copper gasket. The instrument used for the experiments was a Perkin-Elmer Diamond power-compensation DSC with liquid nitrogen cooling. The heat flow and temperature measurements were calibrated with adamantane (solid-solid transformation at

65.53°C,  $\Delta H = 24.78$  J/g [12], indium (solid to liquid transformation at 156.6°C,  $\Delta H = 28.45$  J/g), and zinc (solid to liquid transformation at 419.47°C,  $\Delta H = 108.37$  J/g). The purge gas was a mix of 90% Ne and 10% He [13].

A single Pu-Ga sample was used for all experiments to reduce the practical and safety-related issues associated with removing radioactive samples from the DSC. The sample was removed from the DSC only once to clean oxide off the surface. Because this single sample was scanned repeatedly, a control run was performed before each thermal cycle run. The purpose of these control runs was two-fold: first, the data from the control runs provided confirmation that the sample did not systematically change structurally over the course of many thermal cycles that followed, and second, the control runs allowed the sample to return to the same starting condition before each thermal cycle, thus providing a fair comparison of data obtained from many cycles. The control run involved an 8 hour anneal at 375°C, a 12 hour conditioning treatment at 25°C, a cooling to -160°C, followed by heating to 350°C, and a final cooling back to 25°C, all at 20°C/min.

Prior to each experimental run, the Pu-Ga sample was re-annealed at 375°C for 8 hours to revert any remaining  $\alpha'$  to the  $\delta$  matrix and to remove any plastic deformation that resulted from the large volume difference between the two phases. It was then subjected to various conditioning treatments lasting up to 70 hours at temperatures between -50°C and 370°C. During the subsequent runs, the sample was cooled from the conditioning temperature to -160°C, held for 1 minute, heated to 350°C, held for 1 minute, and then cooled to 25°C. The cooling and heating rates were 20°C/min.

A baseline scan with empty pans conventionally done in DSC experiments could not be performed after each scan because the same sample was repeatedly scanned and was not

removed from the DSC after each cycle. To compensate for this, a straight line was subtracted from the raw data to correct the slope and facilitate comparisons among the runs. Although this method does not achieve absolute accuracy in the estimation of the heats of transformation ( $\Delta H_t$ ), or heat capacities, it provides a consistent method for comparing all data. For the purpose of ascertaining the amount of  $\alpha'$  formed, this relative comparison is as quantitative as would be the comparison of the actual amounts of  $\alpha'$  formed. Comparison of the raw and analyzed data, seen in Figures 2 and 3, confirms that this method does not significantly alter the peak shapes, although the apparent onset temperature can be shifted by this data manipulation. Therefore, we determine onset temperatures and peak areas from the raw data. The amount of transformation is directly proportional to the peak area, and the relative peak areas are sufficient to compare the amounts of transformation resulting from the different conditioning treatments. The reason why the area of the  $\delta \rightarrow \alpha'$  transformation peak is smaller than the area of the  $\alpha' \rightarrow \delta$  reversion peak is that some additional transformation occurs while holding briefly at  $-160^\circ\text{C}$  and during the heating. This transformation is not separately detected by the DSC, and is therefore not accounted for in the  $\delta \rightarrow \alpha'$  peak area.

## Results

### Effect of Conditioning Time:

The first set of experiments was designed to measure the amount of transformation as a function of *conditioning time* at  $25^\circ\text{C}$ . The cooling portions of the thermal cycles corresponding to the  $\delta \rightarrow \alpha'$  transformation are plotted in Figure 2. The transformation begins at approximately  $-110^\circ\text{C}$ , as evidenced by a broad exothermic peak. In the raw data (Figure 2a), it is clear that the peaks do not return to the baseline, indicating that the reaction is incomplete (*i.e.*, the



transformation is continuing even at  $-160^{\circ}\text{C}$ , as expected from the TTT diagrams of Orme, Faiers, and Ward [11]). The heating portions of the thermal cycles corresponding to the  $\alpha' \rightarrow \delta$  reversion are shown in Figure 3. The reversion begins at  $32^{\circ}\text{C}$  and is evidenced by a Gaussian-shaped endothermic peak. In each figure, the control runs are shown in gray. Peak areas for 14 different runs are tabulated in Table 1 and plotted as a function of conditioning times at  $25^{\circ}\text{C}$  in Figure 4.

Table 1: DSC peak areas for  $\delta \rightarrow \alpha'$  transformation and  $\alpha' \rightarrow \delta$  reversion for thermal cycles following conditioning treatments at  $25^{\circ}\text{C}$ . Peak areas were measured on unsubtracted (raw) DSC data and the integration endpoints were the same for all runs. Negative signs indicate exothermic peaks. The absolute value is important for comparing the relative amounts of transformation.

Conditioning time at $25^{\circ}\text{C}$ (hr)	$\delta \rightarrow \alpha'$ transformation Peak area (mJ/g)	$\alpha' \rightarrow \delta$ reversion Peak area (mJ/g)
0	-26	2080
0.5	-32	1990
1	-52	2350
2	-135	2950
3	-338	3430
4	-462	3380
6	-794	3610
12	-750	3380
12	-767	3670
12	-765	3590
12	-636	3440
12	-617	3440
12.25	-817	3490
70	-685	3490

There are several notable features in these data. First, a conditioning treatment at  $25^{\circ}\text{C}$  is effective in increasing the amount of transformation to  $\alpha'$  upon subsequent cooling, compared to the amount of  $\alpha'$  formed when a conditioning treatment is not employed. Second, the general trend is for the amount of transformation to increase with conditioning time, but the amount saturates after about 6 hours of conditioning. Even treatments as long as 70 hours generate

essentially no additional transformation compared with the 6 and 12-hour treatments. A small amount of transformation occurs even if no conditioning treatment is employed. Third, the peak temperature of the  $\alpha' \rightarrow \delta$  reversion shifts to lower temperatures (*i.e.*, reversion becomes easier) as the conditioning time decreases. In the forward  $\delta \rightarrow \alpha'$  transformation peaks, the onset temperatures and maximum peak positions also shift to lower temperatures (*i.e.*, forward transformation becomes more difficult) as the conditioning time decreases. This suggests that the last  $\alpha'$  particles to form upon cooling are the first to revert upon heating.

Note that the peak areas calculated for the transformation and reversion in the control runs (12 hours of conditioning at 25°C) are approximately the same in each run. The areas do not systematically increase or decrease as the sample is subjected to repeated thermal cycling, suggesting that the annealing and conditioning process (8 hours at 375°C, followed by 12 hours at 25°C) can successfully return the sample to a similar starting condition before each run.

#### Effect of Conditioning Temperature:

A second set of experiments was designed to investigate the effect of the *conditioning temperature* on the amount of subsequent transformation. Conditioning treatments were carried out at -50°C, 25°C, 100°C, 150°C, 200°C, and 370°C. Interspersed with these runs, three control runs, preceded by 25°C/12 hour conditioning treatments, offered confirmation that the sample was not systematically changing through the course of these experiments. The sample was removed from the DSC between the 25°C conditioning experiments (Table 1) and the new set of experiments with conditioning treatments at different temperatures. When the sample was removed, it was re-polished and re-annealed, which may account for the difference between the peak areas in Tables 1 and 2.

The cooling and heating portions of the DSC scans for the conditioning temperature experiments are shown in Figures 5 and 6, respectively. Integrated peak areas are tabulated in Table 2 and plotted as a function of temperature in Figure 7.

Table 2: DSC peak areas for  $\delta \rightarrow \alpha'$  transformation and  $\alpha' \rightarrow \delta$  reversion for thermal cycles following conditioning above and below 25°C. Peak areas were measured on unsubtracted (raw) DSC data and the endpoints were consistent for all runs. (The conditioning treatments at -50°C were actually performed on a separate sample, but the data was normalized to data from the first sample to facilitate a fair comparison.)

<b>Conditioning temperature (°C)</b>	<b>Conditioning time (hr)</b>	<b><math>\delta \rightarrow \alpha'</math> transformation Peak area (mJ/g)</b>	<b><math>\alpha' \rightarrow \delta</math> reversion Peak area (mJ/g)</b>
no conditioning	0	-91	746
no conditioning	0	-88	511
-50	3	-78	488
-50	12	-114	442
25	12	-767	1820
25	12	-730	1870
25	12	-790	1880
25	12	-783	1990
100	13	-187	1470
100	13	-399	1570
150	13	-143	1170
150	13	-188	1220
150	6	-146	1050
150	13	-220	1430
150	3	-66	757
150	13	-234	1240
150	13	-258	1430
200	13	-124	517
200	24	-172	947
370	16	-61	395

The largest amount of transformation occurs after conditioning at 25°C for 12 hours. Note that runs with no prior conditioning treatment and runs following conditioning treatments at -50°C and 370° had nearly the same amount of  $\alpha'$  transformation. As the conditioning temperature was increased from 100°C to 370°C, the amount of transformation decreased. In both the heating and cooling data, a shift in the peak temperature correlates with the amount of transformation; as the peak temperature shifts to lower temperatures, amount of transformation

decreases. This trend is also observed in the first set of experiments where only the conditioning time at 25°C was the variable.

## Discussion

As already mentioned in the Introduction and shown in Figure 1, the martensitic  $\delta \rightarrow \alpha'$  transformation occurs in the phase diagram region where the projected equilibrium constitution involves two phases below the eutectoid temperature,  $\alpha + \text{Pu}_3\text{Ga}$ . Hence, both the transforming  $\delta$  matrix and the  $\alpha'$  product are metastable.

During a martensitic transformation, particles of the new phase ( $\alpha'$ , in this case) nucleate and grow. Both of these processes contribute to the total amount of the  $\alpha'$  product obtained, but the accumulating strain in the remaining untransformed  $\delta$  matrix is likely to oppose both nucleation and growth. Since the  $\delta \rightarrow \alpha'$  transformation has isothermal features (*i.e.*, thermal activation is involved in the nucleation and thermally-activated growth is possible when growth occurs isothermally), the question of what constitutes an initial nucleus of the martensite, how it originates in the matrix, and how it grows, is of considerable interest. The terminology used in the literature for describing nucleation, particularly a heterogeneous nucleation, introduces concepts of *intrinsic sites*, *embryos*, *nucleation sites*, *critical nuclei*, etc., but the physical (atomistic) picture of each such feature is not clear. Intrinsic sites are assumed to be various pre-existing imperfections, stacking faults, He bubbles, dislocation tangles, grain boundaries, etc. that can facilitate agglomeration of atoms. If a diffusion-assisted process, as in a eutectoid decomposition, is in some way involved in activating the martensitic transformation during the conditioning treatment, it may require initial formation of  $\alpha$  embryos that eventually develop into viable  $\alpha'$  nuclei. These embryos of the  $\alpha$  phase may be dynamic fluctuations or static

distortions that may already have, at this stage, distinct structural and crystallographic characteristics and habits of martensite within the  $\delta$  matrix because of the large lattice strain considerations in the  $\delta \rightarrow \alpha$  transformation. Even though they are activated thermally as an initial stage of the eutectoid reaction during conditioning, such embryos would be ready to “burst” into full-fledged  $\alpha'$  crystals of martensite on cooling below  $M_b$ . Indeed, diffusional precipitation reactions involving a martensitic-like habit along strain-invariant planes of the matrix have been discussed in the literature [14].

Metallographic studies of the  $\alpha'$  crystals in the  $\delta$  matrix indicate a needle-like or plate-like morphology [4]. We will assume here that each embryo bursting into an  $\alpha'$  particle may be considered to be associated with a certain average quantity of transformation. It follows that the larger the number of initial embryos, the larger will be the volume fraction of the observed martensitic  $\alpha'$  phase, at least at the early stages of conditioning. We shall utilize this concept to connect the quantity and potency of viable  $\alpha$  embryos arising from the eutectoid reaction with the resulting quantity of the  $\alpha'$  martensite obtained subsequently. This approach makes it possible to model the expected quantity of nucleating embryos as a function of the conditioning temperature, utilizing the classical nucleation theory [15].

The picture during the reversal on heating is substantially different. Here, the  $\alpha'$  grains merely revert into existing portions of the untransformed  $\delta$  matrix without the need for nucleation, and the process then involves large avalanches of multiple reversal bursts giving rise to characteristic spikes, as observed in dilatometric, resistometric, and DSC studies [5].

In order to interpret the presently observed transformation trends, we will consider first how the conditioning treatments at different temperatures may be generating a quantity of viable  $\alpha$  embryos, or other sources of  $\alpha'$  nucleation during each treatment. Subsequently, we will

consider the effect of changing the duration times of the conditioning on the generation of viable  $\alpha$  embryos. Both the formation of the initial embryos and their effectiveness in  $\alpha'$  nucleation are likely to be significantly affected by the ongoing self-irradiation effects in a Pu alloy.

### *1. The possible role of plutonium self-irradiation*

The dominant plutonium isotope in our samples, Pu-239, continuously undergoes a radioactive decay at a constant rate, regardless of temperature or thermal history. When a Pu atom decays into a uranium atom and a helium nucleus (a.k.a. an alpha particle), the recoil generates approximately 2500 Frenkel pairs in the lattice, and, over time, the accumulation of He results in the formation of He bubbles [16, 17]. At temperatures of approximately 37°C and above, the majority of these defects rapidly anneal out. At lower temperatures, however, the damage can remain and can accumulate in the lattice [18]. If radiation damage accumulates during a conditioning treatment, it may generate additional potential nucleation sites for  $\alpha'$ , supplementing the intrinsic sites already present. However, based on our experimental data, we do not believe that damage sites caused by self-irradiation are the primary cause of the  $\alpha'$  enhancement, as discussed below. It is more likely that self-irradiation facilitates the formation of the  $\alpha$  phase embryos expected from the eutectoid reaction, and assists in diffusional composition changes of the embryos and in the surrounding matrix as time goes on. It has been well documented in the literature that irradiation can profoundly affect diffusion rates [19-22].

Regarding the direct enhancement of  $\alpha'$  nucleation through damage accumulation accompanying the Pu self-irradiation, if this were the main cause of subsequent martensitic formation, we would expect to observe as much, or more  $\alpha'$  formation following the conditioning treatments at -50°C than following the treatments at 25°C because more decay damage can be retained at the lower temperature. Our data, however, show that a 12 hour conditioning

treatment at  $-50^{\circ}\text{C}$  results in substantially less  $\alpha'$  formation than following a similar treatment at  $25^{\circ}\text{C}$  (see Figure 7). According to Fluss, *et al.*, who mapped out the various stages of defect annealing in Pu-Ga alloys with isochronal annealing and resistivity measurements, Stage V (vacancy cluster dissolution) occurs between  $-23^{\circ}\text{C}$  and  $37^{\circ}\text{C}$  [18]. At temperatures below  $-23^{\circ}\text{C}$ , individual vacancies are mobile, but vacancy clusters are sessile. At this point, we can state that either vacancy cluster migration is a key component of  $\alpha$  embryo formation, or that damage accumulation from Pu self-irradiation cannot be the primary cause of enhanced  $\alpha'$ -phase formation.

## 2. *The role of the $\delta \rightarrow \alpha + \text{Pu}_3\text{Ga}$ eutectoid decomposition in $\alpha'$ phase formation*

If the eutectoid form of the equilibrium diagram is accepted, the thermodynamically dictated stable phases in a Pu-2.0 at% Ga alloy at  $25^{\circ}\text{C}$  are  $\alpha$  and  $\text{Pu}_3\text{Ga}$  [8-10]. Upon cooling this alloy from the  $\delta$  phase field, however, only the martensitic  $\alpha'$  phase is typically detected at low temperatures. It has been estimated that a complete eutectoid decomposition to  $\alpha + \text{Pu}_3\text{Ga}$  may require times of the order of 10,000 years [10]. Nevertheless, the present study and interpretation suggest that even on the time scales subtended by the present experiments (several hours at  $25^{\circ}\text{C}$ ) some quantities of  $\alpha$ , or  $\text{Pu}_3\text{Ga}$ , embryos may be forming, statically or dynamically, particularly because of the assistance from self-irradiation. The most potent of these embryos can then serve as nuclei of  $\alpha'$  upon subsequent cooling. Many binary eutectoid decompositions, such as divorced eutectoid transformations, are initially dominated by the formation of only one of the two expected phases [23, 24]. In the case of Pu-Ga, it is likely that  $\alpha$  embryos will form more readily than  $\text{Pu}_3\text{Ga}$  because their equilibrium composition is closer to that of the  $\delta$  matrix, and may initially be the same as  $\delta$ , making them ideal nucleation sites for  $\alpha'$

martensites which will form by a composition-invariant transformation. We shall refer to such embryos as  $\alpha_m$ .

The proposed hypothesis involving the formation of the  $\alpha_m$  embryos could, in principle, be tested by conditioning the sample above the eutectoid temperature (97°C) [6]. Unfortunately, at temperatures above the eutectoid, other phases could also begin to nucleate as well as the  $\alpha$  phase ( $\alpha$  between 97°C and 125°C,  $\beta$  between 125°C and 251°C, and  $\gamma$  between 215°C and ~305°C). Therefore, it would be necessary to condition the sample in the single-phase  $\delta$  region (~305°C to ~460°C). After conditioning above the eutectoid at 370°C for 16 hours, as seen in Figures 5 - 7 and in Table 2, the amount of  $\alpha'$  formed (and reverted) is less than the amount formed after conditioning for 12 hours at 25°C. This reaffirms the interpretation that  $\alpha_m$  (and/or  $\text{Pu}_3\text{Ga}$ ) embryos form during the conditioning treatments at 25°C and are the primary cause of the large volume fraction of the  $\alpha'$  phase observed on subsequent cooling. This is most likely because of the structural similarity between  $\alpha_m$  and  $\alpha'$ .

The proposition advanced here about the diffusional activation of the  $\alpha_m$  embryos below the eutectoid temperature as the main facilitator of martensite formation indirectly confirms the Russian Pu-Ga phase diagram, which introduced the eutectoid concept [8-10].

### *3. Relative potencies of various $\alpha'$ nucleation sites*

Since more  $\alpha'$  martensite results from conditioning treatments in the  $\beta + \delta$  phase field, compared with lack of any conditioning, or with conditioning at temperatures where a second phase is not expected (370°C), it is plausible that  $\beta$  embryos do indeed begin to form and provide some nucleation sites for  $\alpha'$ . On the other hand, the amount of  $\alpha'$  formed following conditioning treatments in the  $\beta + \delta$  phase field is less than amount formed following the 25°C treatments.



Furthermore, conditioning treatments at 150°C and 200°C led to subsequent  $\alpha'$  formation at lower temperatures on cooling than following conditioning treatments at 25°C. Thus, either  $\beta$  embryos provide less potent nucleation sites for  $\alpha'$  than  $\alpha_m$  embryos, or the formation of  $\beta$  embryos involves slower kinetics than the formation of  $\alpha_m$  embryos. The  $\beta$  phase is C-centered monoclinic (C2/m) with 34 atoms per unit cell, while the  $\alpha$  and  $\alpha'$  phases are both simple monoclinic (space group P2<sub>1</sub>/m) with 16 atoms per unit cell. It then follows that the  $\beta$  embryos that form would require more undercooling to activate these sites into  $\alpha'$  martensite compared with the  $\alpha_m$  embryo sites, presumably due to the difference between the crystal structures in each case. Since, in the absence of conditioning, any pre-existing intrinsic sites seem to require the most undercooling to generate  $\alpha'$ , we conclude that intrinsic sites are even less potent than both  $\alpha_m$  and  $\beta$  embryos. These intrinsic sites will be limited in number, but they are likely to provide nucleation sites for some  $\alpha'$  particles, regardless of the conditioning treatments employed. Indeed, a small amount of  $\alpha'$  forms on cooling even if the conditioning step is omitted. Conversely, our data show that the peak temperature for the reversion of the  $\alpha'$  formed primarily on intrinsic sites is at a lower temperature than the  $\alpha'$  formed primarily from  $\alpha_m$  embryos. Thus, the  $\alpha'$  nucleated on intrinsic sites forms last and reverts first during the cooling and heating cycle. The potency of nucleation sites is therefore as follows:  $\alpha_m$  embryos >  $\beta$  embryos > intrinsic sites. However, even if the generation of  $\alpha_m$  embryos is assisted by Pu self-irradiation, not all decay events appear to be able to generate embryos having the same effective potency.

#### *4. The most effective conditioning temperature and modeling of $\alpha_m$ embryo nucleation*

Of all the conditioning temperatures and times investigated here, the treatments exceeding 6 hours at 25°C resulted in the largest amount of  $\alpha'$  formation upon subsequent cooling. Assuming that the primary role of these conditioning treatments is to facilitate the formation of  $\alpha_m$  embryos, which subsequently develop into  $\alpha'$  nuclei, we now consider the conditions under which the highest rate of  $\alpha_m$  embryo formation can occur. In this approach, we envision an interchangeability of identity between  $\alpha_m$  embryos and  $\alpha'$  martensitic particles resulting from them.

Theoretical approaches to nucleation based on the classical nucleation theory involving diffusion [15] indicate that conditioning at a temperature significantly below the eutectoid temperature should provide the necessary driving force for  $\alpha_m$  embryo formation, but lack of sufficient diffusion making this possible will be the opposing factor at these low temperatures. Conversely, conditioning at a higher temperature in the  $\alpha + \text{Pu}_3\text{Ga}$  phase field, where diffusion is faster, will involve a reduced driving force. Hence, the nucleation rate of the  $\alpha_m$  embryos may be expected to become largest at some moderate amount of undercooling below the eutectoid, resulting in a reverse C-shaped curve [25].

The heterogeneous nucleation rate equation takes the competing effects of driving force (undercooling) and atomic mobility (diffusion) into account. The heterogeneous nucleation rate,  $N_{het}$ , is given by (1) [25]:

$$N_{het} = \omega C_1 \exp\left(-\frac{\Delta G_m}{RT}\right) \cdot \exp\left(-\frac{\Delta G^*}{RT}\right) \quad (1)$$

where  $\omega$  is a factor that includes the atomic vibrational frequency and the surface area of a critical nucleus,  $C_1$  is the concentration of heterogeneous nucleation sites per unit volume of the material,  $\Delta G_m$  is the activation energy for atomic migration,  $\Delta G^*$  is the activation energy barrier,

$R$  is the gas constant, and  $T$  is absolute temperature. The term  $\exp(-\Delta G_m/RT)$  expresses the atomic mobility and the term  $\exp(-\Delta G^*/RT)$  essentially represents the concentration of viable nuclei.  $\Delta G_m$  can be regarded as a constant for a spherical nucleus [25], and the term  $\Delta G^*$  is given by (2) [25]:

$$\Delta G^* = \frac{16\pi\gamma^3}{3(\Delta G_v - \Delta G_s)^2} \quad (2)$$

where  $\gamma$  is the interface energy,  $\Delta G_v$  is the volume free energy change driving the nucleation of  $\alpha_m$ , and  $\Delta G_s$  is the misfit strain energy per unit volume.  $\Delta G_v$  may be expressed as in (3):

$$\Delta G_v = -\Delta T \Delta S = -\Delta T \frac{Q}{T_0} \quad (3)$$

where, for the present situation,  $\Delta T$  is the difference between  $T_0$  and the conditioning temp ( $\Delta T = T_0 - T$ ; *i.e.*, it represents the undercooling),  $Q$  represents the heat of nucleation, and  $\Delta S$  is the entropy of the transformation taking place ( $\Delta S = Q/T_0$ ). We assume that initially the  $\alpha_m$  embryos, like the martensite  $\alpha'$ , will have an average composition the same as that of the  $\delta$  matrix, and  $T_0$ , in this case, is the temperature at which the free energies of the two phases involved ( $\delta$  and  $\alpha_m$ ) are equal. Assuming further that the metastable  $\alpha_m$  embryos represent the initial stage of martensitic formation, and utilizing the measured trends of  $M_b$  and  $R_s$  as a guide to  $T_0$  (see Figure 1), then for the Pu-2.0 at% Ga alloy, we have  $T_0$  as approximately 30°C.

The terms  $\exp(-\Delta G_m/RT)$  and  $\exp(-\Delta G^*/RT)$ , along with the resulting nucleation rate ( $N/\omega C_I$ ), are plotted in Figure 8.<sup>◇</sup> *At small undercoolings, the low driving force mainly controls the process of the transformation, resulting in a low nucleation rate; at large undercoolings, diminished thermal activation becomes the major factor.*

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<sup>◇</sup>A plot of the term  $\exp[-\Delta G_m/(RT)]$  results in 2 branches, only one of which is applicable to the nucleation rate equation. Similarly, a corresponding plot of the nucleation rate,  $N$ , is expected to have branches, only one of which is useful for the present discussion.

Based on the present experiments, 25°C is near the temperature at which the nucleation rate of potent  $\alpha_m$  embryos is largest. One of the main factors opposing the nucleation of  $\alpha_m$  embryos is likely to be the strain in the matrix characterized by  $\Delta G_s$  because of the large volume change. Using the approach outlined above, we can derive a value of this parameter as follows. From earlier work we have the heat for the  $\delta \rightarrow \alpha'$  transformation,  $Q = 4.13$  kJ/mole [5], and we will assume that this is also a reasonable estimate of the heat for the composition-invariant  $\delta \rightarrow \alpha_m$  reaction as an initial step to the eutectoid decomposition in the Pu-Ga alloy. From equation (3),  $\Delta S = +13.6$  J/mole•K. The interface energy,  $\gamma$ , is reported to be between 40 and 120 mJ/m<sup>2</sup> [26], which converts to 0.6 to 1.8 J/mole (optical microscopy indicates that the interfacial area of an  $\alpha'$  particle is approximately 10  $\mu\text{m} \times 10 \mu\text{m}$ ); here, we used the average value, 1.2 J/mole. For Pu atoms diffusing in the  $\delta$ -phase,  $\Delta G_m = -106$  kJ/mole [9]. Using these values and equations (1) and (2), requiring that the largest nucleation rate occurs at 25°C, and requiring that the transformation cannot begin at a temperature above  $T_\theta$  (30°C), we obtain  $\Delta G_s = 0.05$  J/mole.

The application of the classical nucleation and growth model [15, 25] to embryo formation prior to the Pu-Ga martensitic transformation demonstrates that the magnitude of  $\Delta G_s$  is close to the magnitude of  $\Delta G_v$  at  $T_p$  (at 25°C, when  $\gamma = 1.2$ ,  $\Delta G_v = -0.22$  J/mole and  $\Delta G_s = 0.05$  J/mole). Because the volume change between  $\delta$ -Pu and  $\alpha$ -Pu is approximately 25%, strain energy is expected to play a large role in the transformation. Indeed, the shape of the  $N/(\omega C_I)$  plot,  $T_p$ , and the onset temperature for nucleation are sensitive to  $\Delta G_s$ . We can conclude that even at the initial stage of  $\alpha_m$  embryo formation in the  $\delta$  matrix, the associated matrix strain already plays a significant role in controlling the process. An additional similar effect may be expected in the subsequent growth of the  $\alpha'$  particles into  $\delta$ , when more strain is generated.

As might be expected, modeling with the classical nucleation theory of the initial stages of the  $\delta \rightarrow \alpha'$  martensitic transformation does not accurately reproduce the temperature dependence of the nucleation rate (as represented by the amount of  $\alpha'$  formed on subsequent cooling). However, it does appear to reproduce the generally expected features, such as a rapid decline of the nucleation rate on the low temperature side of the nucleation bulge (Figure 8) and a more gradual decline of the nucleation rate on the high temperature side of the bulge. This shape can also be seen in the data shown in Figure 7.

##### *5. Limitations to the completion of the $\delta \rightarrow \alpha'$ transformation (the influence of matrix strain)*

Keeping in mind the strain effects accompanying the martensitic reaction, with 25% volume change, we now consider why the amount of  $\alpha'$  formed upon cooling strongly relates to the conditioning time at ambient temperatures during the initial hours of conditioning, but the amount is not increased after further conditioning (up to 70 hours). This behavior is evident in Figure 4. Previous work [5] indicates that the maximum amount of transformation during continuous cooling in a Pu-2.0 at% Ga alloy is approximately 20%.

It is to be expected that work hardening and transformation hardening may arrest the progress of the  $\delta \rightarrow \alpha'$  transformation before it is complete. Since the volume of  $\alpha'$  is 25% smaller than that of the  $\delta$ -phase, the  $\delta$  matrix must undergo significant plastic deformation to accommodate the phase transformation [5]. As the matrix deforms, it is likely to work harden, making further transformation more difficult. At some point, the activation barrier to further transformation cannot be surmounted, and the transformation stops. A similar effect is observed in TRIP steels (TRIP is an acronym for TRansformation Induced Plasticity) [27]. In these materials, strain-induced martensite forms and causes plastic deformation in the matrix. This can induce

additional transformation, and the rate of matrix hardening increases. In the present case, the two phase  $\delta + \alpha'$  structure is actually a composite, with a significantly higher yield strength than the  $\delta$  phase alone. Both effects make transformation more difficult.

Thus, a certain amount of conditioning is a requirement for maximizing the amount of  $\alpha'$  formed upon subsequent continuous cooling. Ultimately, however, the amount of  $\alpha'$  formed is limited by stress in the  $\delta$  matrix, and no amount of conditioning can increase this amount.

#### *6. The role of the holding times*

We have established that conditioning at 25°C, which is some 70°C below the eutectoid temperature in the phase diagram, generates the largest amount of  $\alpha'$  (approximately 20%) during subsequent cooling. Why does the influence of the holding time decrease (become saturated) after some 6 hours at 25°C? If we assume that during the initial stages of the eutectoid reaction embryos of  $\alpha_m$  form first and that they have nearly identical composition to the subsequently forming  $\alpha'$ , we may assume that after some 6 hours at 25°C  $\alpha_m$  embryos no longer form, or that they become in some way ineffective in triggering  $\alpha'$  later, or both. Regarding the first possibility, we recognize that the initial appearance of  $\alpha_m$  utilizes some intrinsic imperfection sites in the matrix and these sites can be expected to be exhausted with time leading to a saturation of the time conditioning effect. Regarding the second possibility, we recognize also that in order to be effective as a triggering embryo for  $\alpha'$ , each  $\alpha_m$  should retain its composition close to that of  $\alpha'$ . However, with time and the continued self-irradiation,  $\alpha_m$  will tend to reject Ga into the  $\delta$  matrix moving their composition toward 0 at% Ga, as dictated by the eutectoid reaction. During the hundreds of picoseconds after a uranium recoil disrupts the lattice, the annealing of the defects and the thermodynamic drive of the eutectoid reaction could

create fluctuations in the damage cascade that resemble  $\alpha_m$  embryos. It is perhaps for this reason that the eutectoid reaction, which is projected to require very long times to complete, can nevertheless produce the  $\alpha_m$  embryos in the  $\delta$  matrix. Self-irradiation will also facilitate the Ga-enrichment surrounding the original  $\alpha_m$  embryos, which would further reduce their subsequent effectiveness.

At this point, we cannot distinguish whether it is strain surrounding  $\alpha_m$  embryos, or composition variations that lead to saturation of the conditioning effect after about 6 hours. The number of alpha decays in Pu atoms, however, is more than adequate to generate sufficient potent  $\alpha_m$  embryos for  $\alpha'$  formation. A 25- $\mu\text{m}$  diameter spherical grain of the  $\delta$  matrix contains approximately  $3.3 \times 10^{14}$  atoms. Using an alpha decay rate of 41ppm/year [16] yields  $\sim 1.4 \times 10^{10}$  decays/year/grain or  $\sim 1.5 \times 10^6$  decays/hour/grain. Optical microscopy of samples held isothermally at  $-120^\circ\text{C}$  has revealed on the order of hundreds of  $\alpha'$  particles per grain [28]. Thus, there are some 10,000 times more alpha decays per grain than the observed number of  $\alpha'$  particles formed in it. So, only a few spontaneous decay events result in embryo formation, or the strain and/or composition effects accompanying the transformation eventually arrest the progress of the reaction even if potential embryos are still there.

## Conclusions

1. Conditioning treatments at different temperatures and times are a factor in the subsequently obtained quantity (percent) of the martensitic  $\alpha'$  phase product during a cooling and heating cycle. This conditioning has been introduced deliberately in the present study, but it probably occurs inadvertently in all studies involving the handling of self-irradiating Pu-based alloys.

2. The eutectoid nature of the phase diagram in the region of the metastable  $\delta$  phase is responsible for the generation of  $\alpha_m$  embryos during conditioning treatments. Self-irradiation effects in Pu assist this process. The presence of  $\alpha_m$  embryos can subsequently trigger the martensitic transformation to  $\alpha'$  on cooling.
3. The quantity of  $\alpha_m$  embryos resulting from short conditioning times (up to 6 hours at 25°C) largely determines the subsequent quantity of the  $\alpha'$  martensite obtained on cooling. The general trend of  $\alpha_m$  embryo nucleation can be modeled using the classical nucleation theory [15]. This modeling also confirms that strain in the lattice is a major factor in controlling the process of martensite formation.
4. The potencies of the  $\alpha_m$  embryos for triggering  $\alpha'$  are not all the same, and they depend on how they have originated in the  $\delta$  matrix and on how they change with time due to self-irradiation. The progress of the martensitic transformation on cooling is related to the activation of the  $\alpha_m$  embryos of different potencies generated at different conditioning temperatures.
5. Other nucleation sites that are already present in a given sample (*i.e.*, intrinsic sites), as well as sites that can be generated during treatments within two-phase fields above the eutectoid temperature (*i.e.*, the  $\beta + \delta$  phase field), appear to be less potent in formation of the  $\alpha'$  than are the  $\alpha_m$  embryos. In general, their potency decreases in the order the  $\alpha_m > \beta > \text{intrinsic}$ , although the ranges of these potencies may overlap.
6. The effect of holding times on the quantity of the  $\alpha'$  obtained on cooling is related to the generation of  $\alpha_m$  embryos of different potencies. Initially, over time, the number of  $\alpha_m$  embryos of sufficient potency increases with time, and their composition is close to that of the  $\delta$  matrix. Any additional  $\alpha_m$  nucleation after 6 hours does not lead to additional  $\alpha'$  on cooling mostly



because of strain interactions resulting from the increasing number of the  $\alpha'$  particles in the  $\delta$  matrix which hinder further martensite formation.

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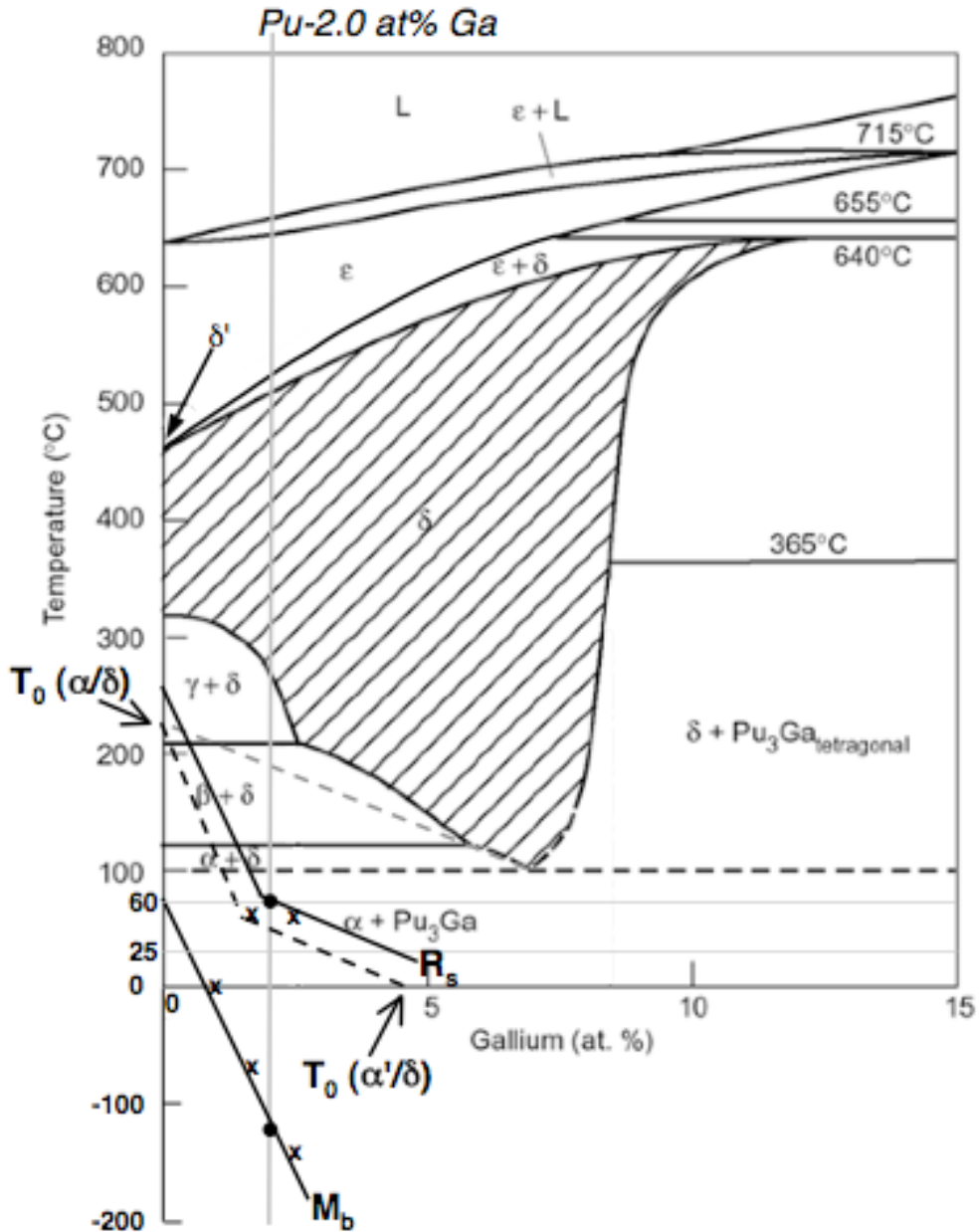


Figure 1: A Pu-Ga equilibrium phase diagram [8 – 10] that has been extended to lower temperatures. Lines corresponding to the martensite burst ( $M_b$ ) and reversion start ( $R_s$ ) temperature for the  $\delta$  to  $\alpha'$  transformation are superimposed on the diagram. The dark dashed line corresponds to the estimated  $T_0$  temperature, which is the temperature where the free energies of the  $\delta$  and  $\alpha'$  (or  $\alpha$ , for pure Pu) phases are equal.  $T_0$  is likely to be closer to the  $R_s$  temperature than the  $M_b$  temperature because the forward transformation ( $M_b$ ) requires nucleation, whereas the reversion ( $R_s$ ) only involves movement of the  $\delta/\alpha'$  interface [5]. The vertical gray line shows the composition of the samples used in the experiments described here, Pu-2.0 at% Ga. The **x**s are data points from reference 6 and the **•**s are data points from ref 5.

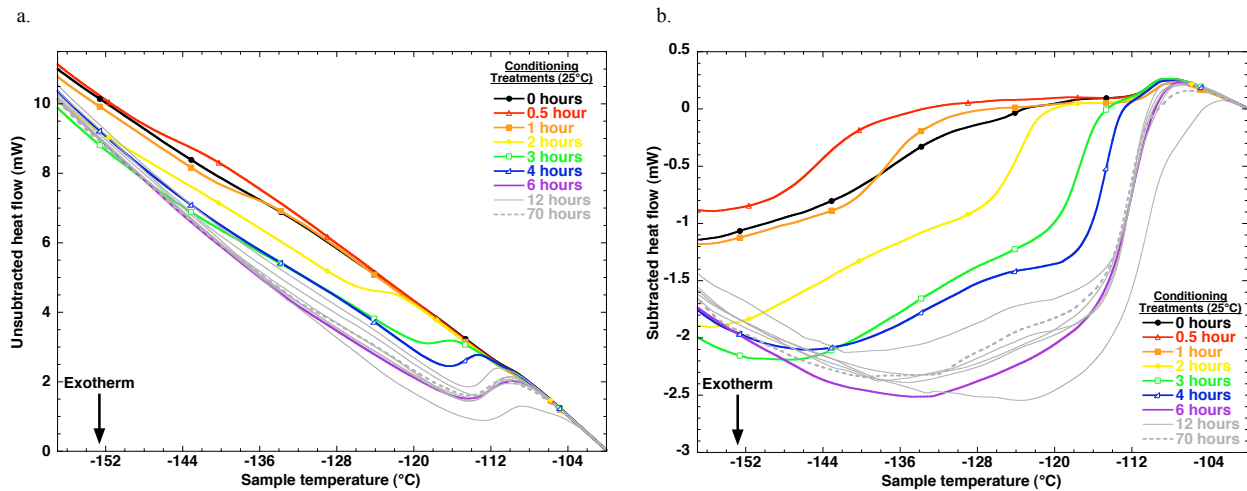


Figure 2: DSC thermograms corresponding to the  $\delta \rightarrow \alpha'$  transformation upon cooling after conditioning the sample at 25°C for various times between 0 and 70 hours. Control runs with a 12 hour conditioning time were performed after each run, and the data from these runs are shown in gray. This transformation is exothermic and begins at approximately -110°C, depending on the length of the conditioning treatment. (a). Unsubtracted (raw) data (b). Slope-corrected data

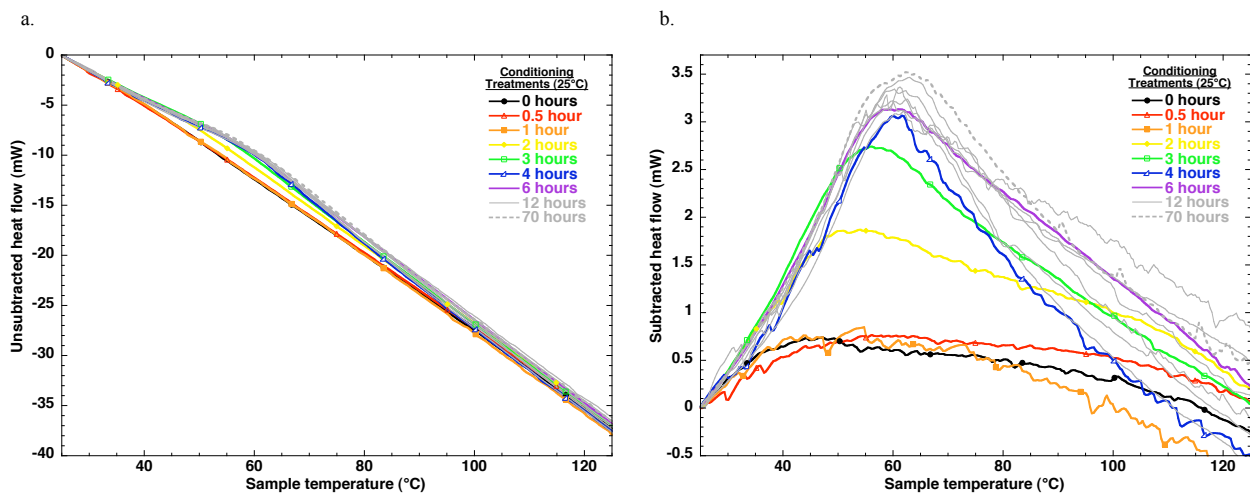


Figure 3: DSC thermograms corresponding to the  $\alpha' \rightarrow \delta$  reversion upon heating. Prior to this heating, the sample was conditioned at 25°C for various times between 0 and 70 hours and then cooled to -160°C at 20°C/min. Control runs with a 12 hour conditioning time were performed after each run, and the data from these runs are shown in gray. This transformation is endothermic and begins at approximately 35°C, regardless of conditioning treatment. (a). Unsubtracted (raw) data (b). Slope-corrected data

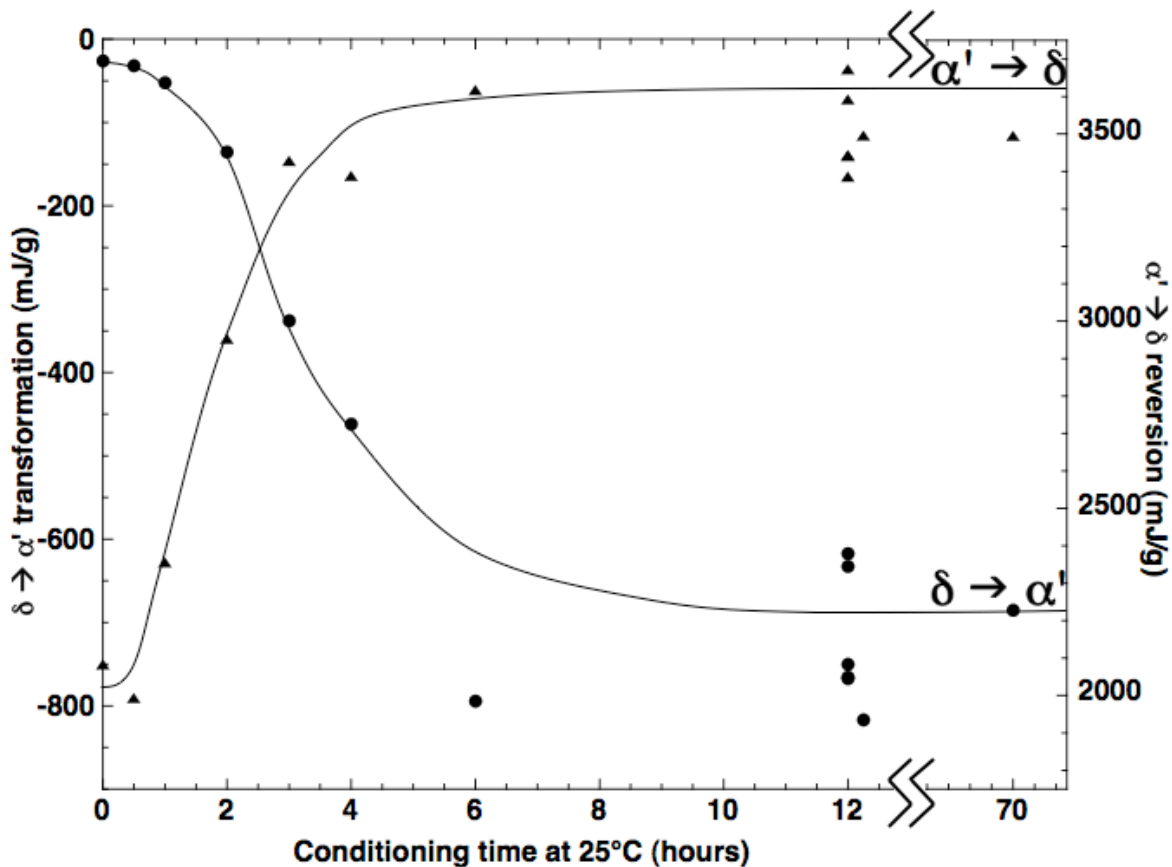


Figure 4: Peak areas for the  $\delta \rightarrow \alpha'$  transformation and  $\alpha' \rightarrow \delta$  reversion as a function of conditioning time at 25°C. Lines between the data points are drawn only to guide the eye. Note that the forward transformation is exothermic and peak areas are negative (triangles, left y-axis). In this case, the greatest amount of transformation corresponds to the area with the largest absolute value. The  $\alpha' \rightarrow \delta$  reversion is endothermic and peak areas are positive (circles, right y-axis); the greatest amount of transformation corresponds to the largest area. The amount of  $\alpha'$  formed (and subsequently reverted) increases with increasing conditioning time up to approximately 6 hours. Conditioning treatments greater than or equal to 6 hours result in nearly the same amount of  $\alpha'$  formed (and reverted).

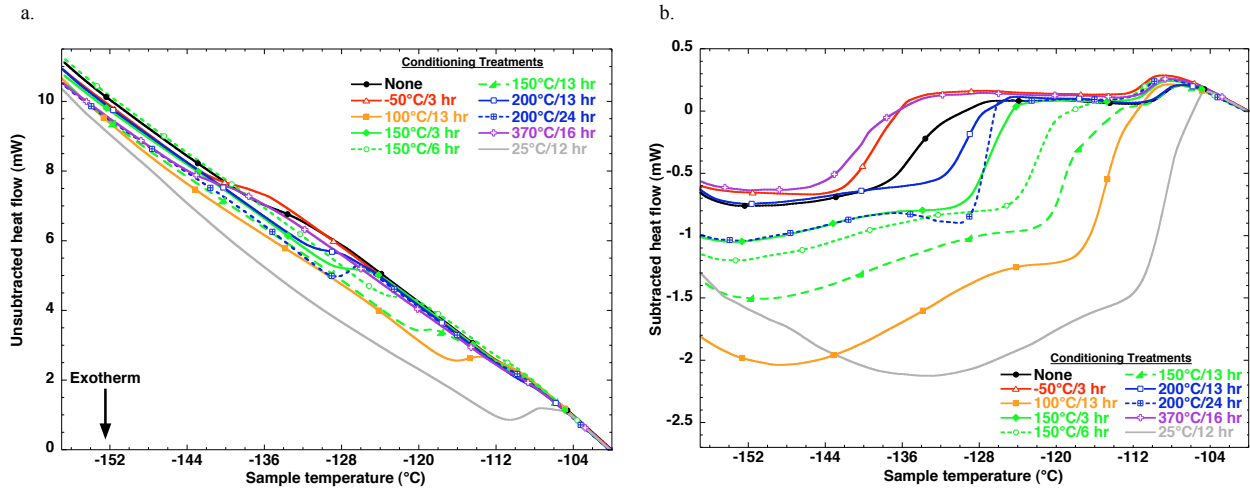


Figure 5: DSC thermograms corresponding to the  $\delta \rightarrow \alpha'$  transformation upon cooling after conditioning the sample at various temperatures between  $-50^{\circ}\text{C}$  and  $370^{\circ}\text{C}$  for 0 to 24 hours. This transformation is exothermic and begins at approximately  $-110^{\circ}\text{C}$ , depending on the temperature and length of the conditioning treatment. The largest amount of transformation occurs after the sample is conditioned at  $25^{\circ}\text{C}$  for 12 hours. (a). Unsubtracted (raw) data (b). Slope-corrected data

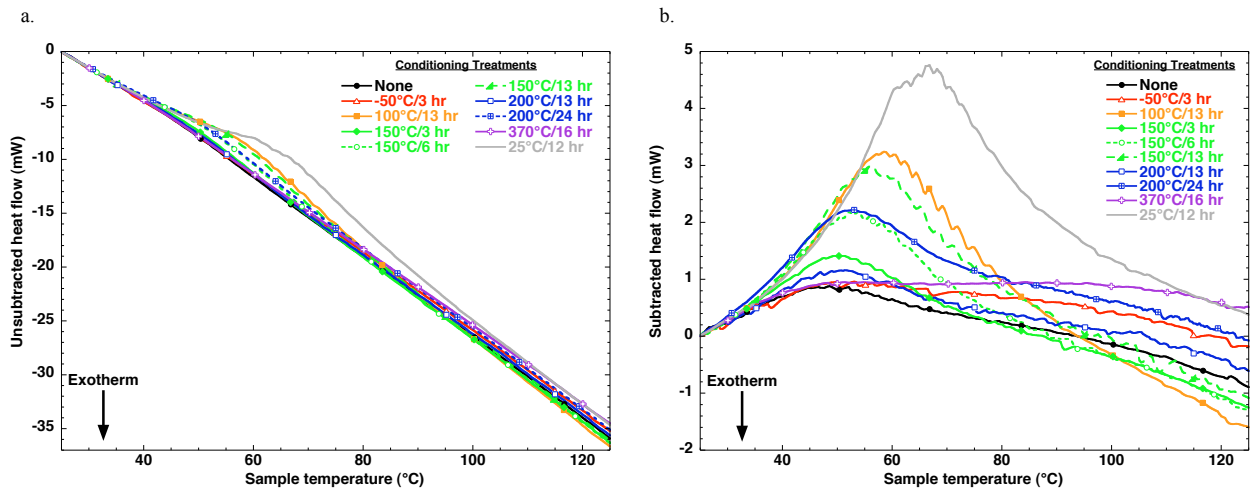


Figure 6: DSC thermograms corresponding to the  $\alpha' \rightarrow \delta$  reversion upon heating after conditioning the sample at various temperatures between  $-50^{\circ}\text{C}$  and  $370^{\circ}\text{C}$  for 0 to 24 hours. This transformation is endothermic and begins at approximately  $35^{\circ}\text{C}$ , regardless of conditioning treatment. (a). Unsubtracted (raw) data (b). Slope-corrected data

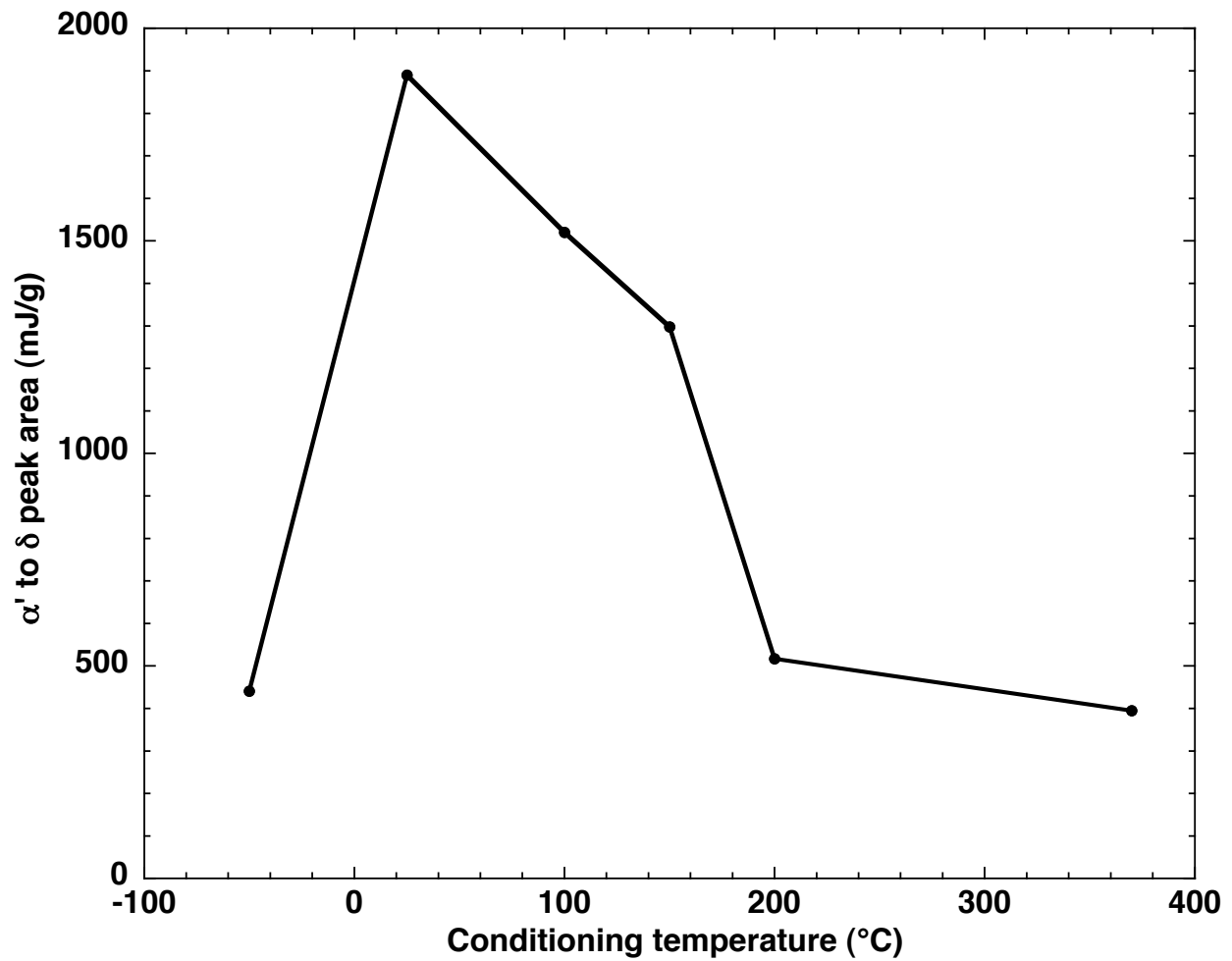


Figure 7: The  $\alpha' \rightarrow \delta$  reversion peak area plotted as a function of the conditioning temperature. Conditioning treatments were 12 hours, except for the one at 370°C, which was 16 hours. The plot shows that the maximum amount of  $\alpha'$  is formed after 12 hour conditioning treatments at 25°C. Conditioning treatments at temperatures lower and higher than 25°C result in less  $\alpha'$  formation (and thus less  $\alpha'$  reversion).

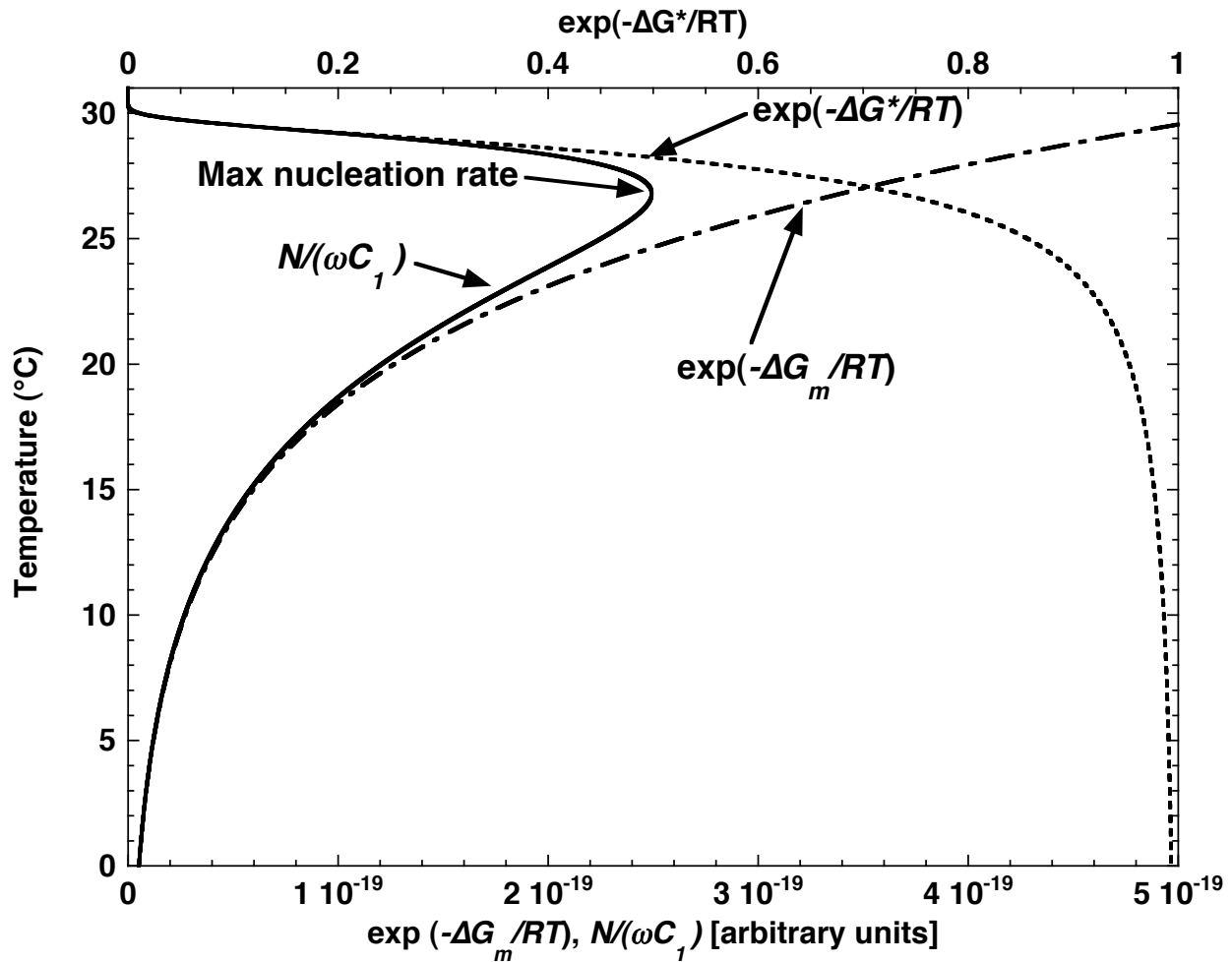


Figure 8: Plot of nucleation rate ( $N/(\omega C_1)$ ) as a function of temperature, showing the competing effects of driving force [ $\exp(-\Delta G^*/RT)$ ] and diffusion [ $\exp(-\Delta G_m/RT)$ ]. The maximum nucleation rate occurs at a temperature that balances the effects of fast diffusion at high temperatures and high driving force at low temperatures. In this case,  $\Delta G_s$  was chosen to maximize the nucleation rate at 25°C.