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*Martensitic Nature of  $\delta \rightarrow \gamma$  Allotropic  
Transformation in Plutonium*

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# MARTENSITIC NATURE OF $\delta \rightarrow \gamma$ ALLOTROPIC TRANSFORMATION IN PLUTONIUM

by

P. C. Lopez, J. R. Cost, and K. M. Axler

## ABSTRACT

Isothermal and isoplethal studies using differential scanning calorimetry have been conducted to characterize the allotropic transformations of plutonium. The  $\delta \rightarrow \gamma$  transformation (upon cooling) was observed to have a classic martensitic nature. The work described herein is the first quantitative study of this phenomena in plutonium.

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## INTRODUCTION

Differential scanning calorimetry (DSC) has recently been shown to have several advantages over traditional methods for studying solid-state phase transformations in metals.<sup>1-3</sup> The main advantage is that during a single temperature scan it directly measures the rate of heat flow and, thus, the actual reaction rate during a transformation. From this, the transformation kinetics can be correctly determined. This is in contrast to indirect techniques which measure some physical property, such as resistivity or length change, and infer the reaction kinetics by assuming that the fraction transformed is proportional to the fractional change in the measured property.

During DSC studies of solid-state phase transformations in plutonium, we have found new evidence for the martensitic nature of the phase transformation  $\delta \rightarrow \gamma$  which occurs during cooling. We observe this reaction to occur martensitically over the relatively large temperature range, 230°C to 150°C. This transformation was previously observed qualitatively using differential thermal analysis<sup>4-6</sup>; however, our experiments are the first to quantitatively investigate the martensite behavior of the  $\delta \rightarrow \gamma$  reaction.

The face-centered orthorhombic  $\gamma$  phase of plutonium is stable from 215°C to 320°C. Above 320°C, plutonium forms the face-centered cubic  $\delta$  phase which is stable up to 463°C. There is a 6.9% increase in volume for the  $\gamma \rightarrow \delta$  transformation upon heating.<sup>7</sup>

On cooling the reverse reaction,  $\delta \rightarrow \gamma$ , occurs. The transformation was initially reported to be martensitic by Pascard<sup>5</sup> in 1960 based upon dilatometric measurements. In support of the martensite interpretation, he also observed a sequence of abrupt breaks and small peaks in his differential thermal analysis measurements over the range 220°C to 150°C.<sup>4,5</sup> Similar thermal results in substantive agreement with this were reported by Spriet.<sup>6</sup> Further evidence that the transformation was martensitic came from dilatometric measurements by Abramson<sup>8</sup>, Hill<sup>9</sup>, and Hocheid et al.<sup>10</sup> which showed martensite-like abrupt discontinuous contractions during cooling below 250°C. Other than an internal friction study in 1969<sup>11</sup>, there have been no more recent investigations of this transformation.

## EXPERIMENTAL

In these experiments, the DSC was enclosed in an argon atmosphere glovebox, as previously described.<sup>1</sup> As before, the DSC was calibrated for both temperature and heat output using reference materials. The sample was a single piece of electrorefined plutonium weighing 92.06 mg. The chemical analysis was provided in an earlier report.<sup>1</sup> The plutonium metal was preserved under an argon atmosphere in a hermetically sealed aluminum encapsulation chamber. This method has been shown to give reproducible DSC scans for plutonium cycled through multiple solid-state transformations.

## RESULTS AND DISCUSSION

Figures 1(a) and 1(b) show the rate of heat flow versus temperature for heating and cooling scans at 1.0°C/min, respectively. For the heating scan in Figure 1(a), there are peaks for three allotropic phase transformations:  $\alpha \rightarrow \beta$ ,  $\beta \rightarrow \gamma$ , and  $\gamma \rightarrow \delta$ . The endothermic character of the reactions in Figure 1(a) is indicated by the downward orientation of the thermal arrests upon heating (negative heat flow). The reaction enthalpies, as obtained from the peak areas, agree with literature values<sup>7</sup> and reveal a classic nucleation and growth mechanism.

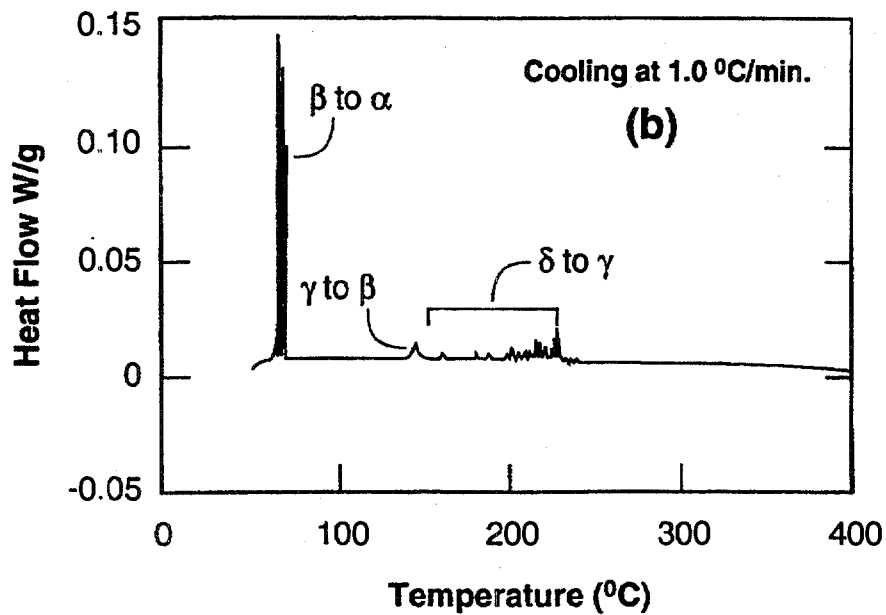
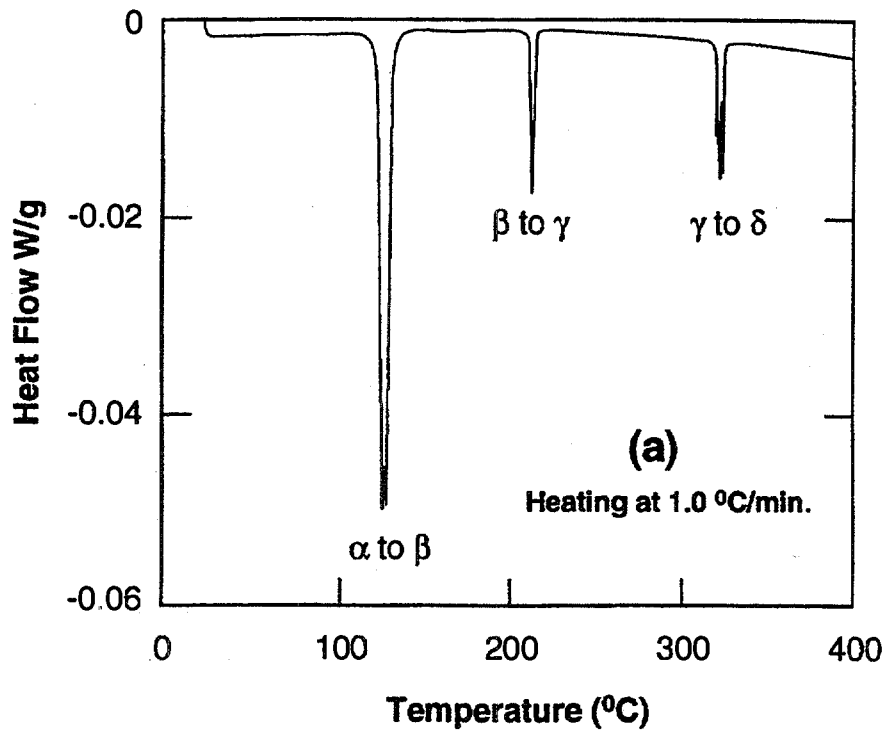


Figure 1. (a) DSC scan for heating at 1.0°C/min showing the endothermic peaks for the allotropic transformations  $\alpha \rightarrow \beta$ ,  $\beta \rightarrow \gamma$ , and  $\gamma \rightarrow \delta$ . (b) DSC scan for cooling at 1.0°C/min showing the martensitic nature of the heat release for the  $\delta \rightarrow \gamma$  transformation.



The cooling scan for 400°C is shown in Figure 1(b). Note that there is no single exothermic peak below 320°C for the reverse transformation  $\delta \rightarrow \gamma$ ; however, there are such peaks for both the  $\gamma \rightarrow \beta$  and the  $\beta \rightarrow \alpha$  transformations. Instead of the usual single peak, the  $\delta \rightarrow \gamma$  reaction shows up as a series of multiple exothermic arrests over the temperature range 230°C to 150°C. The discontinuities within these thermal arrests are clearly presented in Figure 2. The reaction starts abruptly with the largest spikes at 230°C. It continues with diminishing amplitude to 150°C. As cooling continues below 150°C, the arrests are obscured by the onset of the  $\gamma \rightarrow \beta$  transformation. This temperature range, 230°C to 150°C, is roughly the same range in which the reaction was observed by Pascard<sup>4,5</sup> and Spriet.<sup>6</sup> Note that a peak due to the  $\beta \rightarrow \alpha$  transformation at 70°C was relatively large and was not shown in Figure 2 because of the scale selected.

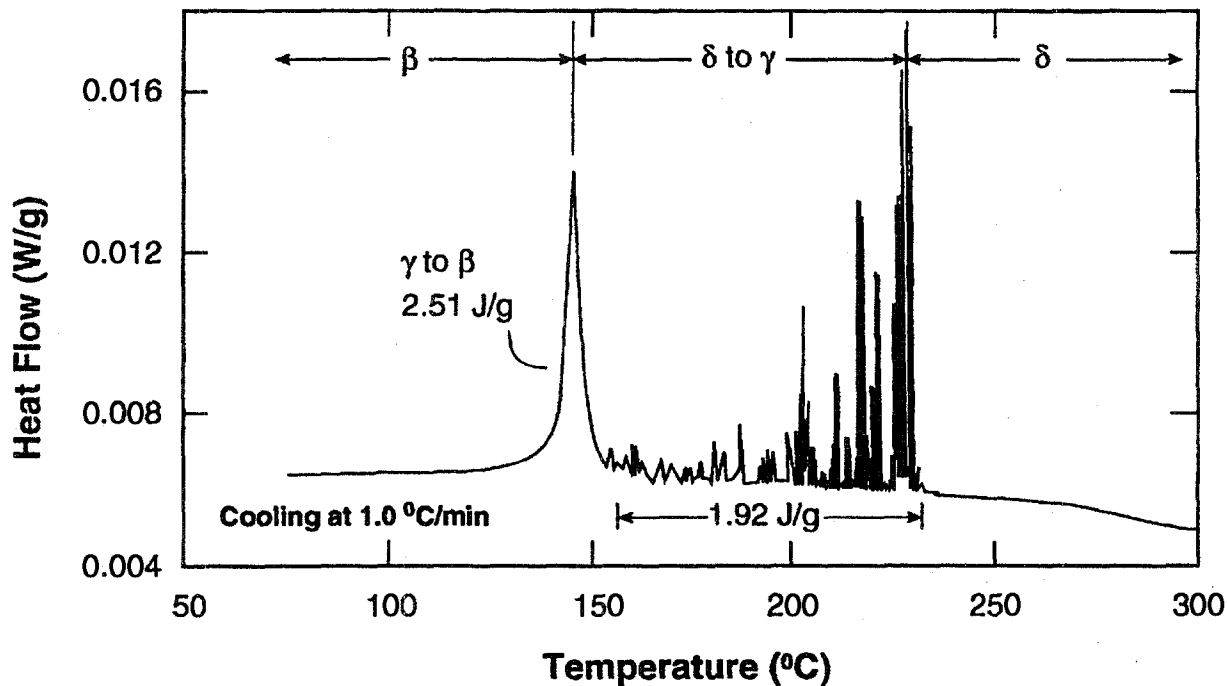


Figure 2. Magnification of Figure 1(b) showing sharp heat release spikes for the  $\delta \rightarrow \gamma$  transformation from 230°C to 150°C.

The reaction enthalpies obtained by integrating the peak areas are also shown in Figure 2. A heat release of 1.92 J/g was obtained for the  $\delta \rightarrow \gamma$  cooling reaction over the range 230°C to 150°C. The reaction heat measured in Figure 1(a) for the reverse transformation,  $\gamma \rightarrow \delta$ , upon heating was 2.21 J/g. Presumably, the heat for the cooling reaction is less than that for heating

because some of the heat release upon cooling was veiled by the  $\gamma \rightarrow \beta$  peak which starts to form at 150°C. The heat measured for this latter peak was 2.51 J/g, which must include some of the  $\delta \rightarrow \gamma$  heat (roughly 0.3 J/g) because an average value for the heat absorbed in the  $\beta \rightarrow \gamma$  reaction upon heating was 2.16 J/g.

Additional experiments were conducted to confirm that the sharp thermal arrests observed upon cooling were due to the martensitic  $\delta \rightarrow \gamma$  transformation. Sequential isoplethal runs were performed at 1.0°C/min to 505°C, 465°C, 355°C, and 280°C. These runs were all cooled at a rate of 1.0°C/min to 50°C. The transformations were thus observed in both temperature directions. For all the cycles that were heated above 315°C, invoking the  $\delta$  phase, the martensitic profiles ( $\delta \rightarrow \gamma$  reaction) were observed upon cooling. Upon cooling from the cycle heated to only 280°C, below the  $\delta$  phase range, no martensitic-type heat releases were observed. This indicates that the discontinuous arrests indicating a martensitic reaction were associated with the  $\delta \rightarrow \gamma$  transformation. The thermal arrests for the  $\delta \rightarrow \gamma$  transformation were reproducible in numerous subsequent DSC cycles.

For the above heat treatments, it was found that the  $M_s$  temperature for the  $\delta \rightarrow \gamma$  transformation varied between 234°C and 210°C, increasing slightly with increasing maximum temperature of the cycle. None of the cooling scans showed any indication of heat release above the  $M_s$  temperature. Thus, we conclude that the  $\delta \rightarrow \gamma$  reaction does not occur just below the phase equilibrium temperature of 320°C as reported by Pascard<sup>5</sup> and Hocheid et al.<sup>10</sup> It would appear that the isothermal changes in length at 300°C which was interpreted in those studies were due to some other cause such as stress relaxation of the sample. Using the DSC method in this work, the reaction under investigation is directly distinguished by the observation of concomitant heat flow.

## CONCLUSIONS

The martensitic nature of the  $\delta \rightarrow \gamma$  transformation in plutonium is as follows:

1. The heat release is discontinuous as shown by the many separate exothermic arrests upon cooling through the transformation range. This is completely different from a single continuous peak typical of transformations occurring by nucleation and growth.
2. The reaction rate as indicated by the height and density of the spikes is highest just below the  $M_s$  temperature. With decreasing temperature, the spike height decreases and the spacing increases. This is classical martensitic behavior: just below the  $M_s$ , the first shear

reactions occur most easily and involve larger volumes. Subsequent transforming volumes are smaller and require more thermal driving force because they are constrained by the larger regions which transformed at higher temperatures.

3. The transformation occurs over the relatively large temperature range of 80°C.
4. The transformation is 100% martensitic, which is in agreement with the indications reported by Pascard<sup>5</sup> and Selle and Focke.<sup>11</sup>

This is the first reported observation of a martensitic transformation by DSC. It is interesting that the DSC is able to resolve individual heat release events of the reaction. Such an event is probably a cascade of separately localized shear transformations triggered by a single shear incident at an initiating location. It may be that resolution of a packet of transformation events as reported here is not possible for all martensitic transformations, especially those involving less strain energy and, thus, occur over a more narrow temperature range. For the  $\gamma \rightarrow \delta$  transformation in plutonium, the large strain energy due to the 6.9% volume change is expected to require a large thermal driving force. This causes the reaction to occur over the relatively large temperature range of more than 80°C.

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