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## **BURST MARTENSITIC TRANSFORMATIONS IN A STEEL AND IN A PU-GA ALLOY**

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### **Abstract**

Upon cooling a Pu-2.0 at% Ga alloy from the ambient temperature, the metastable delta phase partially transforms martensitically to the alpha-prime phase. Because this transformation involves a 25% volume contraction, plastic accommodation by the delta matrix must occur. When the material is isochronally heated or isothermally annealed above ambient temperatures, the reversion of alpha-prime to delta is likely to occur by the alpha-prime/delta interface moving to consume the alpha-prime particles. This reversion exhibits a burst martensitic mode and is observed as sharp spikes in differential scanning calorimetry data and as steps in resistometry data. These large bursts appear to be the result of an interplay between the autocatalytically driven transformation of individual alpha-prime particles and self-quenching caused by small changes in temperature and/or stress accompanying each burst. The behavior of this Pu-Ga alloy is compared to that of a steel referred to as a “burst martensite” in the literature, which also exhibits bursts during both thermal cycling and isothermal holds.

### **Introduction**

Pure plutonium exhibits at least 6 phases below the melting temperature. At ambient conditions, the brittle monoclinic  $\delta$  phase is the equilibrium phase. By alloying Pu with a few atomic percent of an element such as gallium or aluminum, however, the ductile fcc  $\delta$ -phase can be retained almost indefinitely in a metastable state at room temperature. Upon cooling the metastable  $\delta$ -phase to subambient temperatures, a partial transformation to the  $\delta'$ -phase occurs (the  $\delta'$ -phase is monoclinic and has nearly the same lattice parameters as the  $\delta$ -phase, but it has Ga supersaturated in the lattice). The  $\delta \rightarrow \delta'$  phase transformation and the reversion have unique attributes. For example, the forward transformation involves an unusually large volume contraction of ~25%, and when heated, the  $\delta'$ -phase reverts completely to the  $\delta$ -phase with a transformation hysteresis of approximately 150°C. The  $\delta \rightarrow \delta'$  transformation is reported to be martensitic [1, 2], and its kinetics result in 2 “noses” in a time-temperature-transformation (TTT) diagram (this is also referred to as “double-C behavior”) [3].

Using differential scanning calorimetry (DSC) and resistometry, we are studying the thermodynamics and kinetics of the  $\delta \rightarrow \delta'$  phase transformation and reversion in a Pu-2.0 at% Ga alloy. Here, we report on recent work that suggests a burst martensite mode for the  $\delta/\delta'$  phase transformations. Specifically, unusual sharp spikes are observed during the  $\delta' \rightarrow \delta$  reversion in continuous heating scans in the DSC. We compare results from the Pu-Ga alloy to data from a steel burst martensite reported in the literature [4].

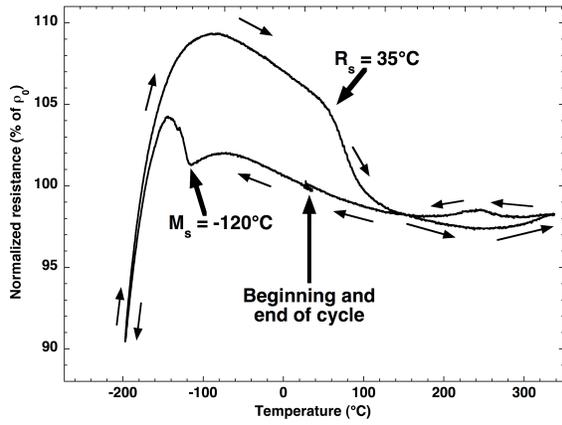


Figure 1. Resistometry data from a thermal cycle of Pu-2.0 at% Ga showing the  $M_s$  (martensite start, beginning of  $\square \rightarrow \square'$  transformation) and  $R_s$  (reversion start, beginning of  $\square' \rightarrow \square$  reversion) temperatures.

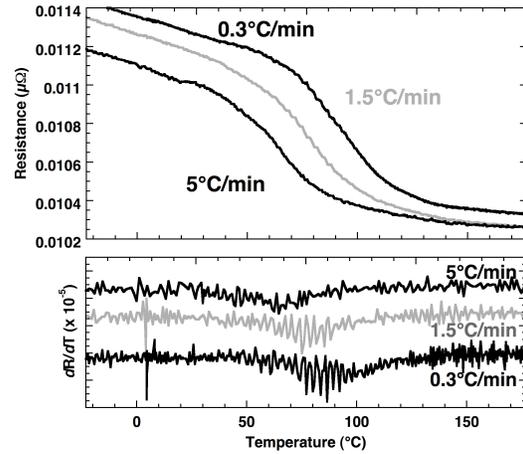


Figure 2. Enlargement of the  $\square' \rightarrow \square$  reversion section of resistance data from a thermal cycle of Pu-2.0 at% Ga showing steps that correspond to the reversion (top). Resistance data differentiated with respect to temperature showing distinct peaks that correspond to the reversion (bottom).

## Results

### Pu-Ga Alloy Results

A 17 mg, 150  $\mu\text{m}$  thick Pu-2.0 at% Ga disc was thermally cycled at 1.5°C/min in a vacuum chamber ( $10^{-3}$  torr) while the resistance was continuously monitored with a four-point probe. A plot of the normalized resistance vs. temperature is shown in Figure 1. Because the  $\square'$  resistivity is approximately 45% higher than the resistivity of the  $\square$ -phase, the martensite start ( $M_s$ ) temperature is indicated by a rise in the resistance at -120°C. (Note that the resistivities of both the  $\square'$  and  $\square$  phases drop off significantly at low temperatures [5, 6].) The  $\square' \rightarrow \square$  reversion is indicated by a drop in resistance at 35°C (reversion start,  $R_s$ ). Close examination of the resistance data during the reversion reveals that the resistance does not decrease smoothly, but, rather, it decreases in discrete steps. When the resistance is differentiated with respect to temperature ( $dR/dT$ ), sharp peaks are clearly distinguishable from the random, noise spikes at temperatures below and above the reversion. The reversion portions of resistometry scans at 0.3, 1.5, and 5°C/min are shown in the upper plot in Figure 2. The differentiated data is shown in the lower plot in Figure 2.

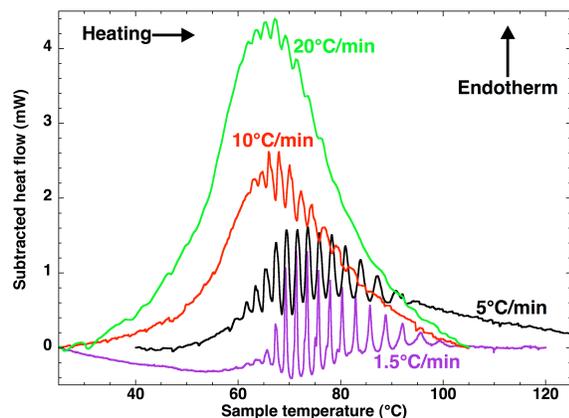


Figure 3. DSC data showing sharp peaks that correspond to the  $\square' \rightarrow \square$  reversion.

A 230 mg sample of the same Pu-Ga alloy was encapsulated in a DSC pan designed for high pressure work. These gold-plated stainless steel pans seal when a threaded lid screws onto the base and compresses a gold-plated copper gasket. Heat flow vs. temperature data for the reversion (heating) portions of scans at 1.5, 5, 10, and 20°C/min are shown in Figure 3. Sharp peaks with an endothermic envelope are observed at all heating rates, although they are most pronounced in the 1.5°C/min scan. Interestingly, these peaks are nearly periodic

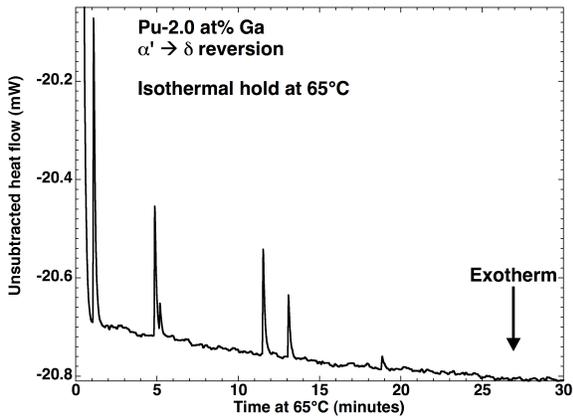


Figure 4. Isothermal hold of a Pu-2.0 at% Ga alloy at 65°C. The randomly spaced peaks correspond to the  $\alpha' \rightarrow \alpha$  reversion.

with respect to temperature, regardless of heating rate, and the period correlates with the period of the spikes observed in the differentiated resistometry data.

After annealing the Pu-2.0 at% DSC Ga sample [7], it was cooled at 20°C/min to -160°C to form some  $\alpha'$ . The sample was then heated to 65°C and held isothermally for 70 minutes. The isothermal data is shown in Figure 4. Initially, a large peak is observed and then several successively smaller peaks follow at random intervals in time. After the small peak at approximately 19 minutes, no additional peaks are apparent.

### Burst Martensite Steel Results

Brook and Entwisle reported burst martensitic transformation in a high-nickel steel [4]. A sample of the same composition (75.329% Fe, 23.96% Ni, 0.51% C, 0.11% Mn, 0.03% Si, 0.03% Cr, 0.016% S, 0.01% Mo, 0.005% P) was fabricated at the Materials Preparation Center at the Ames Laboratory (Ames, Iowa, USA). In Brook and Entwisle's paper [4], dilatometry data corresponding to the burst martensitic transformation in this steel showed that the transformation occurred in discrete steps, similar to those we observed in the resistometry data corresponding to the  $\alpha' \rightarrow \alpha$  reversion in Pu-Ga. Here, small steel samples (60 – 95 mg) were cut and sealed in the same DSC pans used for the Pu-Ga experiments. Upon cooling, the steel began to transform at approximately -42°C and -67°C at cooling rates of 1.5°C/min and 20°C/min, respectively (Figure 5). In both cases, a large exothermic peak was followed by many randomly spaced additional peaks. In the scan at 1.5°C/min, the additional peaks are more sharp and numerous than the additional peaks in the 20°C/min scan. The heat of transformation is -15 J/g at 20°C/min.

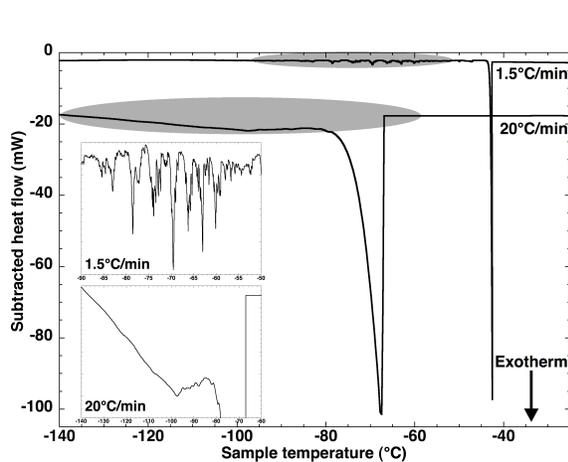


Figure 5. DSC scans of a burst martensite steel. The shaded regions are enlarged in the insets.

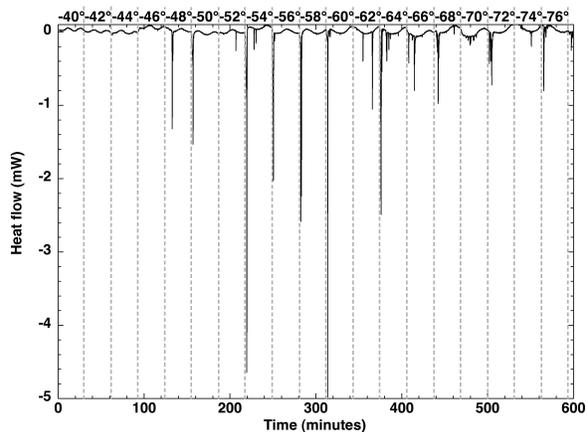


Figure 6. DSC data from a burst martensite steel held isothermally at 2°C increments from -40°C to -78°C. The large sharp exothermic peaks correspond to burst martensite transformations. The smooth wave pattern near the top is caused by small furnace adjustments during the isothermal holds

A separate sample of the burst martensite steel was cooled at 1.5°C/min to -40°C and held isothermally for 30 minutes. The temperature was lowered by 2 degree increments, with a 30 minute hold at each temperature. At -48°C, a sharp peak was observed after holding for approximately 8.5 minutes. Similarly, additional sharp peaks were observed at the other temperature intervals, with some intervals hosting several randomly spaced peaks. Data from these isothermal holds are shown in Figure 6.

## Discussion

### The Burst Martensite Mode

Martensitic transformations can occur via two different modes: thermoelastic and burst [8]. Thermoelastic modes occur in systems where the parent and martensite phases have similar volumes and thus, the deformation can be accommodated elastically. In this case, the transformation can proceed smoothly with changes of temperature or stress. Burst modes occur when the parent and martensite phases have significantly different volumes. The transformation causes large matrix strains that require plastic deformation. In the burst mode, individual particles transform instantly at the speed of sound and the transformation proceeds in a step-wise fashion. In some cases, an autocatalytic sequence may occur where transformation of one (or more) particles may trigger the nearly-instantaneous transformation of a cascade of additional particles. Thus, a cascade of transformation occurs cooperatively.

Because  $\beta'$  martensitic transformations in the Pu-Ga system involve a 25% volume change, they most likely occur via the burst mode. The spikes and sharp peaks observed in resistometry and DSC data corresponding to the  $\beta' \rightarrow \beta$  reversion offer evidence of this mode. The number of spikes or steps observed is much smaller than the number of  $\beta'$  particles that revert, which indicates that the reversion must occur cooperatively, with cascades of  $\beta'$  particles reverting to  $\beta$  in an autocatalytic cascade. Finite-element modeling (FEM) lends support to this hypothesis. FEM indicates that plasticity during the  $\beta' \rightarrow \beta$  reversion results in stress fields surrounding the region of a reverted  $\beta'$  particle; along the length of the particles, additional reversion is decelerated, but at the particle tips, additional reversion is accelerated (Figure 7). Thus, stress may play a role in instigating a reversion cascade.

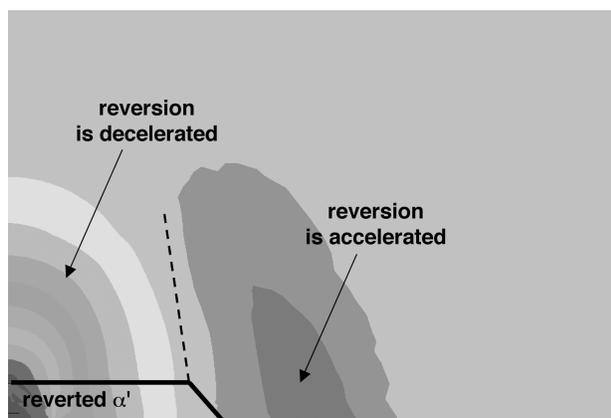


Figure 7. Finite-element map of the stresses surrounding an  $\beta'$  particle that has reverted to the  $\beta$ -phase. Along the length of the particle, additional reversion is hindered, while at the particle tips, additional reversion can occur more readily.

The cascades may be stopped by a combination of stress and temperature excursions. During the endothermic  $\beta' \rightarrow \beta$  reversion, the reversion itself may lower the temperature in the transformation regions, thus quenching further reversion. During continuous heating experiments, however, the instrument's heater rapidly re-heats the sample and another cascade can be initiated. This cycle results in the characteristic sharp peaks observed in DSC data. Similarly, the vertical "risers" on the steps observed in the resistometry data correspond to rapid decreases in resistivity when a cascade of  $\beta'$  particles reverts to the  $\beta$ -phase and the horizontal "treads" of the steps correspond to times during which the sample is being heated to initiate another cascade. A comparison of the observed burst transformations in the Pu-

Ga alloy and the steel supports this model. In the Pu-Ga alloy, the observed autocatalytic bursts occur during heating and the transformation is endothermic, which could cause the local temperature to decrease; in the steel, the observed bursts occur during cooling and the transformation is exothermic, which could cause the local temperature to increase. In both cases, the local temperature changes caused by the transformation are in the direction opposed to further transformation. This suggests that local temperature fluctuations caused by the transformations may cause the autocatalytic burst cascades to stop.

Steps and sharp peaks are not observed in resistometry and DSC data, respectively, during the  $\alpha \rightarrow \alpha'$  forward transformation. Unlike the  $\alpha' \rightarrow \alpha$  reversion where the existing  $\alpha$  matrix simply consumes the  $\alpha'$  particles, nucleation of the new phase ( $\alpha'$ ) is required in the forward transformation. Because nucleation of each  $\alpha'$  particle is a difficult stochastic process with a high activation energy, each  $\alpha'$  particle nucleates and grows independently as local thermal fluctuations occur. Therefore, we do not expect autocatalytic cascades of transformation to occur. Individual  $\alpha'$  particles still form via the burst mode, but the techniques used are not sufficiently sensitive to detect these individual events. The observed signal is then the sum total of many  $\alpha'$  particles forming individually (but spaced closely in time), and thus a smooth signal is recorded. Nucleation is also required for martensitic growth in steels, but apparently the activation barrier is smaller, and it can be overcome autocatalytically.

It is interesting to note that the burst cascades observed in the Pu-Ga are periodic with respect to temperature and the period is not a function of heating rate, while the burst cascades observed during the transformation in the steel consist of one large peak followed by many smaller, randomly spaced peaks. In both cases, the peaks are more distinct at slower heating rates. The cause of the periodicity in the Pu-Ga alloy is under investigation.

### Isothermal Kinetics in a Burst Martensite Mode

The kinetics of some martensitic transformations can be described as isothermal. In this case, the amount of martensite formed is a function of the isothermal holding time at a particular temperature. The individual particles (or cascades) may still transform via a burst mode, but the overall amount of martensite formed has a time-dependent component. The kinetics of the  $\alpha \rightarrow \alpha'$  transformation in Pu-Ga alloys have been described as isothermal [1, 2], and Orme and Faires showed that there are two temperatures at which the transformation rate reaches a maximum [3]. The designation “isothermal martensite” usually implies that the transformation only occurs during an isothermal hold. Here, however, we have shown that the  $\alpha \rightarrow \alpha'$  transformation can occur during either isothermal holds (Figure 4) *or* continuous cooling (Figures 1 and 3). Similarly, the high-nickel steel investigated here can also transform under both of these conditions.

Additional work currently underway to investigate the isothermal nature of martensitic transformations in Pu-Ga alloys. Isothermal holds at sub-ambient temperatures are expected to clarify the reported double-C behavior in the TTT diagram [3]. At super-ambient temperatures, isothermal holds are expected to provide kinetic data about this unusual burst transformation.

### **Conclusions**

Using resistometry and differential scanning calorimetry, the martensitic  $\alpha \rightarrow \alpha'$  transformation and reversion were studied in a Pu-2.0 at% Ga alloy. Because the volume of the  $\alpha'$  phase is ~25% smaller than that of the  $\alpha$  phase and the deformation requires plastic accommodation, the transformations are likely to occur by the burst martensite mode. During continuous heating

experiments, the  $\delta' \rightarrow \delta$  reversion is observed as discrete steps in resistometry data and as sharp peaks that are periodic with respect to temperature in DSC data. These discrete increments suggest that the progress of the reversion occurs by autocatalytic cascades of  $\delta'$  particles reverting at nearly the same time. Finite-element modeling indicates that the cascades may be initiated by stress fields that surround the reverted  $\delta'$  particles. Because the  $\delta' \rightarrow \delta$  reversion is endothermic, it may lower the local temperature enough to quench a cascade. Additionally, stress may play a role in quenching the cascades. The  $\delta' \rightarrow \delta$  reversion can also occur isothermally. In this case, sharp DSC peaks were observed to occur randomly in time. With increasing hold time, these peaks decreased in intensity and area.

The DSC data from the Pu-2.0 at% Ga alloy and a high-nickel burst martensitic steel reported in the literature [4] were compared. In both materials, DSC data showed evidence of autocatalytic burst martensitic cascades during both continuous heating/cooling scans and isothermal holds. These cascades were observed as unusually sharp peaks in the DSC data.

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