In Situ X-Ray Diffraction of the Delta to Alpha-Prime Transformation in Pu-Ga Alloys


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In situ x-ray diffraction of the $\delta \rightarrow \alpha'$ transformation in Pu-Ga alloys

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The mechanisms and kinetics of the $\delta \rightarrow \alpha'$ transformation in Pu-Ga alloys remain unresolved.

**Unalloyed Pu**
- 5 allotropic solid-solid transformations
- 20% volume change between FCC $\delta$ phase and monoclinic $\alpha$

**Equilibrium Thermodynamics**
- FCC $\delta$ phase in Pu-1.9 at.% Ga is metastable at ambient temperature
- At low $T$, $\delta$ transforms to metastable $\alpha'$ phase


Schwartz et al., *Prog Mat Sci.* (2009)
Upon cooling to sub-ambient temperatures, $\delta$ transforms to $\alpha'$ via an isothermal martensitic transformation.

Time-Temperature-Transformation diagram exhibits double-C curve kinetics.

The $\delta \rightarrow \alpha'$ isothermal martensitic transformation can be induced with continuous cooling experiments.

TTT diagrams of Pu-1.4 & 1.9 at.% Ga alloys show two separate knees.

This observation implies two distinct, thermally activated mechanisms must exist for this transformation.

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The amount of the $\delta \rightarrow \alpha'$ transformation is dependent on details of the thermal cycling and “conditioning”

The amount of transformation in Pu – 1.8 at.% Ga alloys decreases with each thermal cycle

Conditioning times of ~ 6 hours are required for reproducible amounts of transformation


A time-dependent process enhances $\delta \rightarrow \alpha'$ transformation at -120 °C and enables the transformation at -155 °C
Nucleation of low Ga equilibrium phases may be the underlying mechanism of conditioning.

Free energy – composition diagrams

- Free energy as a function of conditioning temperature

$A^\alpha = 3.5 \times 10^7$

$B^\alpha = -2.7$

$A^\beta = 5.0 \times 10^7$

$B^\beta = -9.2$

Normalized amount of transformation as a function of conditioning temperature

Jeffries et al. PRB (2009)
The $\delta \rightarrow \alpha'$ transformation can also be induced by pressure.

Pu - 2 at.% Al alloys transform first to $\beta'$ then to $\alpha'$ under pressure.
Diamond anvil cell experiments on Pu-Ga alloys reveal $\delta \rightarrow \gamma' \rightarrow \alpha'$ transformation sequence

The pressure-induced transformation proceeds $\delta \rightarrow \gamma' \rightarrow \alpha'$; how about the isothermal martensitic transformation?
The isothermal $\delta \rightarrow \alpha'$ transformation was monitored \textit{in situ} with XRD to probe for a $\gamma'$ intermediate phase

- Advanced Photon Source at Argonne National Lab
- 90 $\mu$m x 90 $\mu$m spot size, rastered
- 15°C/min cooling rate + isothermal hold (-120°C, -155°C)
- 8 second collection time for XRD patterns
- Transmission geometry
- Well-homogenized sample, $\sim$30 $\mu$m grain size
- Pu-1.9 at.% Ga alloy, 30 – 80 $\mu$m thick
$\delta \rightarrow \alpha'$ transformation was observed at both C-curve temperatures, even in a 30 $\mu$m thick sample.
The majority of the $\alpha'$ phase forms quickly, and it continues to grow in for several hours.

The onset of $\alpha'$ formation and transformation rate correlate well with data in the literature.
The δ lattice parameter increases to accommodate formation of the α’ phase

- Density of α’ is 24% higher than δ
- Formation of α’ causes significant elastic and plastic deformation in the δ lattice
- Expansion is greater at -155°C than at -120°C
- -120°C: 0.2% expansion after 90 minutes
- -155°C: 0.35% expansion after 80 minutes

The onset of α’ formation is evidenced by a shift in the δ (111) peak position
After $\alpha'$ forms, the $\delta$ lattice parameter does not return to its pre-transformation value at 25°C.

Both XRD patterns collected at 25°C.

- Before cooling to -155°C
- After cooling to -155°C

Normalized intensity (a.u.)

2 theta

Peaks:
- $\delta (111)$
- $\alpha (113)$
- $\delta (020), \alpha (211)$
- $\delta (200)$
At -155°C, a shoulder grows on the δ (111) peak

- A shoulder is evident after ~15 minutes
- Becomes a distinct peak after ~43 minutes
- This secondary peak disappears when the sample is reheated to 25°C
- Origin of this peak is unknown
- Tetragonal distortion of the δ lattice?
At -155°C, a shoulder grows on the δ (111) peak

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At -155°C, a shoulder grows on the $\delta$ (111) peak

- A shoulder is evident after $\sim$15 minutes
- Becomes a distinct peak after $\sim$43 minutes
- This secondary peak disappears when the sample is reheated to 25°C
- Origin of this peak is unknown
- Tetragonal distortion of the $\delta$ lattice?
Conclusions

- $\gamma'$ is not observed as an intermediate in the $\delta \rightarrow \alpha'$ transformation (Pu-1.9 at. % Ga alloy)
- The double-C curve kinetics are not the result of intermediate phase formation
- The $\delta$ lattice parameter expands to accommodate the $\alpha'$ phase
- Formation of a secondary peak on the $\delta(111)$ peak at -155°C was identified
  - Origin of this peak remains unknown
- XRD experiments will be repeated with a lower-Ga alloy in the future

Isothermal: –155°C/4 hours
Pressure-induced: 1 GPa