Low-Temperature Martensitic and Pressure-Induced Delta to Alpha-Prime Phase Transformations in a Pu-Ga Alloy

A. J. Schwartz, M. A. Wall, D. L. Farber, K. T. Moore, K. J. M. Blobaum

March 18, 2008

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

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.
Low-Temperature Martensitic and Pressure-Induced δ to α′ Phase Transformations in a Pu-Ga Alloy

2008 Materials Research Society Spring Meeting
March 25, 2008
San Francisco, CA


Lawrence Livermore National Laboratory, P. O. Box 808, Livermore, CA 94551
This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344

LLNL-CONF-xxxxxx
Understanding the phase transformations remains as one of the significant Pu metallurgical challenges

- Equilibrium phase diagram
- 5 allotropic phase transformations
- Phase transformations and phase stability
  - The $\delta \rightarrow \alpha'$ isothermal martensitic transformation
  - The $\delta \rightarrow \alpha'$ transformation under pressure
    - Pu-Al
    - Pu-Ga
    - Amorphous phase?
    - Characterization of the recovered sample
For decades, the “West” accepted that the $\delta$ phase was thermodynamically stable at ambient conditions.

The $\delta$-phase retained to room temperature is metastable. Timofeeva (2003) estimated 10,000 years to decompose.
Plutonium undergoes five solid-solid allotropic phase transformations between the ground state and the liquid.

- **α (Low temperature - 126°C)**
  - Monoclinic (P2₁/m)
  - $\rho = 19.8 \text{ g/cm}^3$

- **β (126°C - 214°C)**
  - Base-centred monoclinic (C2/m)
  - $\rho = 17.8 \text{ g/cm}^3$

- **γ (214°C - 323°C)**
  - F.c. orthorhombic (Fdd)
  - $\rho = 17.1 \text{ g/cm}^3$

- **δ (323°C - 468°C)**
  - F.c. cubic (Fm$\bar{3}$m)
  - $\rho = 15.9 \text{ g/cm}^3$

- **δ' (468°C - 486°C)**
  - Base-centred tetragonal (I4/mmm)
  - $\rho = 16.0 \text{ g/cm}^3$

- **ε (486°C - 640°C)**
  - B.c. cubic (I$m\bar{3}$m)
  - $\rho = 16.5 \text{ g/cm}^3$

- **Liquid (640°C +)**
  - $\rho = 16.5 \text{ g/cm}^3$

Hecker, LA Science (2000)
Low-temperature $\delta \rightarrow \alpha'$ martensitic transformation

Upon cooling to sub-ambient temperatures, $\delta$ transforms to $\alpha'$ via an isothermal martensitic transformation

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

The martensite start temperature, $M_s$ is a function of Ga content

Like the $\delta$-phase at room temperature, $\alpha'$ is also metastable

Lawrence Livermore National Laboratory
The $\alpha'$ particles that form from the isothermal martensitic transformation appear as lathes in optical microscopy.

The $\delta \rightarrow \alpha'$ isothermal martensitic transformation goes to $\sim 25\%$ completion.
The crystallography and morphology of the $\delta \rightarrow \alpha'$ transformation have been characterized with TEM

- The orientation relationship between $\alpha'$ and $\delta$ is:
  
  $(111)_\delta \parallel (020)_{\alpha'}$
  
  $[-110]_\delta \parallel [100]_{\alpha'}$


- $\alpha'$ particles consist of 2 variants rotated 60° around $<020>_{\alpha'}$

- TEM shows $(205)_\alpha$ twinning as a lattice invariant deformation mode

- The $\alpha'$–$\delta$ interface is composed of a terrace and ledge structure that is faceted on $111_\delta$

- The dislocation density is ~ an order of magnitude greater in the vicinity of $\alpha'$ particles
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.
The $\delta \rightarrow \alpha'$ transformation and reversion characteristics are a strong function of composition

- Under pressure, Pu-Ga alloys transform directly to $\alpha'$ and undergo either a direct ($\alpha' \rightarrow \delta$) or indirect ($\alpha' \rightarrow \beta + \delta \rightarrow \gamma + \delta \rightarrow \delta$) reversion.
- Reversion characteristics are similar to those in thermally-induced transformations.

Why do Pu-Al alloys transform through $\beta'$ whereas Pu-Ga alloys transform directly to $\alpha'$?
Pressure-induced $\delta \rightarrow \alpha'$ martensitic transformation

Diamond anvil cell experiments on a Pu - 2 at.% Ga alloy reveal $\delta \rightarrow \gamma' \rightarrow \alpha'$ transformation sequence

In the DAC, Pu - 2 at. Ga transforms through the sequence $\delta \rightarrow \gamma' \rightarrow \alpha'$


Sadigh and Wolfer, PRB (2005)
Pressure-induced $\delta \rightarrow \alpha'$ martensitic transformation

Upon cooling, Harbur reported that a 0.68 at.% Ga alloy has a density intermediate between $\delta$ and $\alpha$ phases

Harbur proposes that the $\delta$ phase transforms to $\alpha' +$ amorphous phase
- on cooling low solute alloys
- under pressure

<table>
<thead>
<tr>
<th>Alloy</th>
<th>% $\alpha'$</th>
<th>% $\delta$</th>
<th>% amorphous</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 at.% Ga</td>
<td>87</td>
<td>0</td>
<td>13</td>
</tr>
<tr>
<td>1.7 at.% Ga</td>
<td>66</td>
<td>0</td>
<td>34</td>
</tr>
<tr>
<td>2.5 at.% Ga</td>
<td>68</td>
<td>12</td>
<td>20</td>
</tr>
</tbody>
</table>

Harbur, JALCOM (2007)
Pressure-induced $\delta \rightarrow \alpha'$ martensitic transformation

**We are coupling low pressure recovery experiments with TEM to elucidate the mechanism and morphology**

2.3 mm diameter specimens are slowly compressed to 1 GPa in the large volume moissanite anvil cell
Pressure-induced $\delta \rightarrow \alpha'$ martensitic transformation

Optical microscopy and x-ray diffraction of the compressed specimen reveals $\alpha'$ and $\delta$ phase

Optical microscopy does not have the resolution to differentiate between phases

Our X-ray diffraction does not indicate the presence of an amorphous phase
Pressure-induced $\delta \rightarrow \alpha'$ martensitic transformation

Preliminary TEM reveals fine-grained $\alpha'$ and small amounts of $\delta$ – no evidence of an amorphous phase

Pressure-induced $\delta \rightarrow \alpha'$ transformation
  Average $\alpha'$ grain size $\sim 100s$ nm
  Implies nucleation dominated mechanism

Low-temperature-induced $\delta \rightarrow \alpha'$ isothermal martensitic transformation
  Average $\alpha'$ particle size $\sim 1000s \times 10,000s$ nm
  Implies nucleation limited mechanism (strain)
Pressure-induced $\delta \rightarrow \alpha'$ martensitic transformation

**Preliminary TEM reveals fine-grained $\alpha'$ and small amounts of $\delta$ – no evidence of an amorphous phase**

$\delta$ phase is observed dispersed between the $\alpha'$ grains
High dislocation density
No apparent orientation relationship (yet)
Summary

- Low temperature isothermal $\delta \rightarrow \alpha'$ transformation
  - Nucleation limited
  - Lath-shaped particles
  - Intermediate phases possible
- Pressure-induced $\delta \rightarrow \alpha'$ transformation
  - Nucleation dominated
  - Very fine grain size
  - No evidence of the amorphous phase
  - Intermediate phases likely

Intermediate phases:
- $\beta'$-phase (C2/m)
- $\gamma'$-phase (Fmmm)

$\delta$-phase (Fm3m)