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Transformation Crystallography and Plasticity of the $\delta \rightarrow \alpha'$ Transformation in Plutonium Alloys

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ABSTRACT

In delta phase Pu-Ga alloys, the transformation from the ductile face-centered cubic (fcc) δ phase that is retained at room temperature to the brittle low-temperature monoclinic α' phase is a thermally activated diffusionless transformation with double-c kinetics. Accurate modeling of the phase transformation requires detailed understanding of the role of plastic flow during the transformation and of the crystallographic transformation path. Using transmission electron microscopy (TEM), we find a significant increase in dislocation density in δ near the α' plates, which suggests that plastic deformation contributes to the accommodation of the 20% reduction in volume during the transformation. Analysis of a series of optical micrographs of partially transformed alloys suggests that the α' habit plane is usually nearly perpendicular to $\langle 111 \rangle \delta$. However, a small number of TEM observations support a habit plane near $\langle 112 \rangle$ or $\langle 123 \rangle$, in agreement with earlier work.

MOTIVATION

The δ to α' transformation in plutonium has many unusual characteristics [1]. It involves an extremely large volume change (20%) and thermal hysteresis ($> 150^\circ\text{C}$ in some alloys). The transformation is isothermal and does not proceed to completion (typically $< 30\%$ α' is formed). In addition the transformation has unusual “double-c” kinetics, such that there are two temperatures at which the transformation rate is maximized [2].

A model for the thermal hysteresis based on plastic dissipation induced by the large volume change was first developed by Wolfer [3]. This model implies that there will be significant dislocation movement and multiplication near the interface between δ and α' .

A reasonable hypothesis for the incomplete transformation to α' is based on the interaction between growing α' nuclei or plates with α' that was formed previously. Because α' growth requires both local and long-range elastic and plastic rearrangements and since an array of high strength α' plates will make these accommodations more difficult, growth of α' will also become more difficult as the volume fraction of α' increases.

To explore the effects of α' plate interactions numerically, Jin *et al.* [4] developed a phase-field model (see Wang and Khachatryan and by Jin *et al.* [5, 6] for more details) for the $\delta \rightarrow \alpha'$ transformation that was based on the transformation strain and habit plane (perpendicular to $\langle 123 \rangle$ type directions in δ) predicted by Adler *et al.* [7] and experimentally observed by Zocco *et al.* [8]. The result of a single crystal simulation is shown in figure 1. As expected, there are 24 variants predicted by the simulation. However, in most typical micrographs of a partially transformed Pu-Ga alloy (ex. figure 1) only 3-4 variants are seen in any given grain.

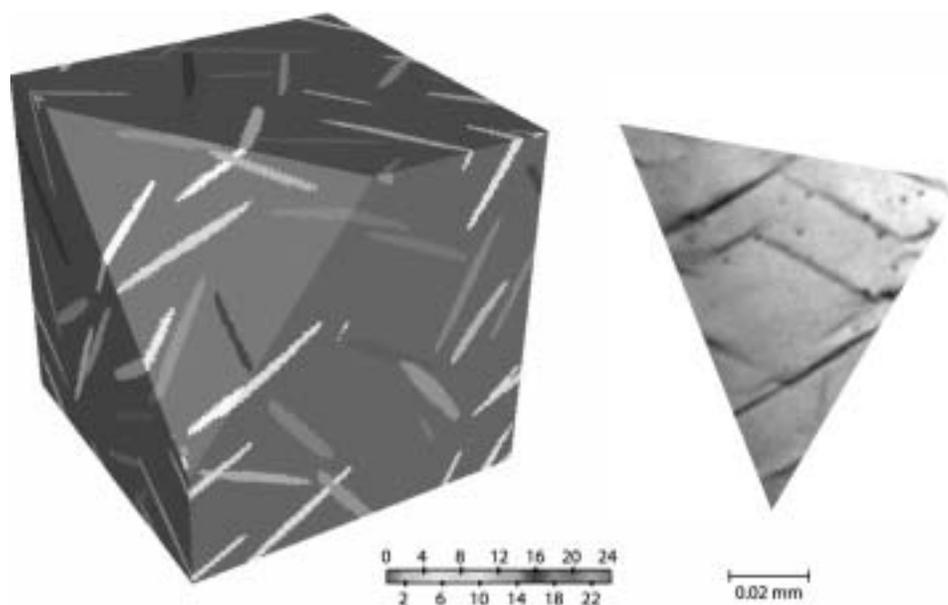


Figure 1. The cube on the left illustrates results of a three dimensional simulation of the δ to α' transformation in plutonium. The δ phase matrix is medium grey. Each of the 24 crystallographically distinct α' variants is shaded uniquely. The image on the right is an optical micrograph of a similar structure observed experimentally.

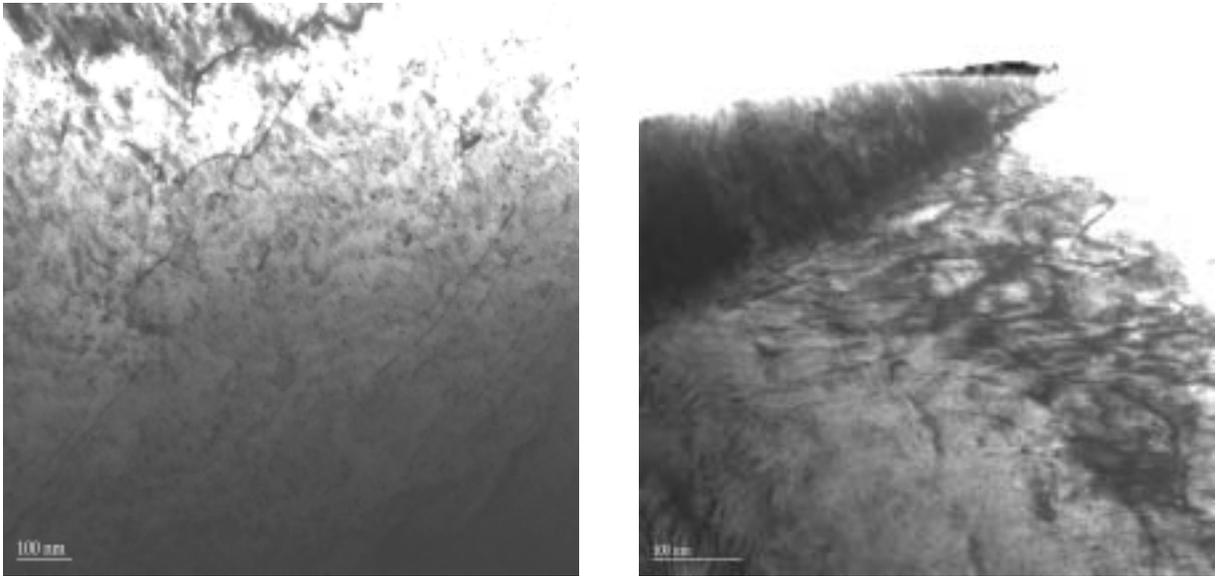
The goal of the work presented here was two-fold. First, we aimed to determine whether there was any evidence of local plastic flow associated with the δ to α' transformation in order to validate the modeling work by Wolfer. Second, we wanted to understand the discrepancy between the modeled and observed microstructures in Fig. 1.

EXPERIMENTAL DETAILS

We investigated a Pu-0.6 wt% Ga alloy using optical microscopy and transmission electron microscopy (TEM). The alloy was prepared by induction heating and was approximately two years old. After casting, the material was usually annealed for at 425-440°C to homogenize the Ga distribution. α' was formed by quenching to either -120°C or -155°C, which were in the upper and lower “c-curves” respectively. Optical specimens were mechanically polished and then lightly etched chemically. Samples were prepared for TEM by electropolishing 3mm diameter discs, 150 μ m thick, to electron transparency using a Fischione Instruments electropolishing system. The thinning process was performed in an inert atmosphere glove box and the samples were transferred under vacuum to the TEM using a vacuum transfer specimen holder. The TEM work was performed on a FEI CM300FEG operating at 300 KeV with a double tilt specimen holder. Additional details of the TEM specimen preparation and the electron microscope have been described by Wall *et al.* [9].

OBSERVATIONS OF PLASTICITY

In an as received Pu-Ga specimen quenched to -120°C for 10 hours, dislocation density measurements were made with a line-intercept technique at 18 locations in the foil: 16 near α' plates and 2 in regions of δ well removed from α' plates. The average density near the α' plates was 1.6×10^{11} dislocations/cc. In isolated δ the density was 2.5×10^{10} dislocations/cc, a factor of 6 lower. Figure 2 shows two typical micrographs that were used for this analysis. The difference in



(a)

(b)

Figure 2. a) Transmission electron micrograph showing background dislocation density in regions of δ well removed from α' plates. b) Micrograph illustrating increase of dislocation density near the tip of an α' plate (in the upper left corner).

dislocation density is apparent. In addition, figure 2b shows the dislocation density near the dislocation tip is apparently higher than the density on the flank.

HABIT PLANE DETERMINATION

Optical microscopy

Many tens of optical micrographs of dual phase δ plus α' have been examined, and in the vast majority of cases, only three or four unique trace directions were observed. Figure 3 shows a typical optical micrograph of a specimen annealed at 425°C for 7 days then quenched to -120°C

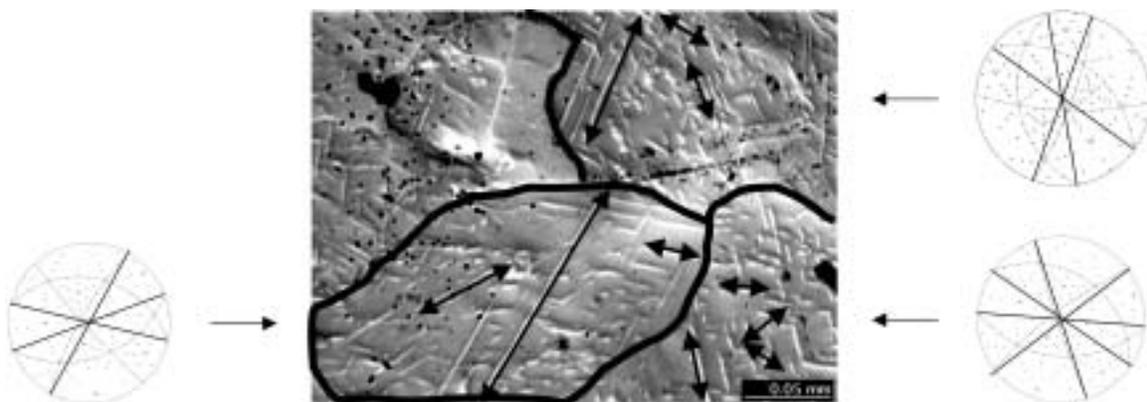


Figure 3. Optical micrograph of a partially transformed Pu-Ga alloy. The δ appears dark grey and the α light grey. Grain boundaries and habit plane traces have been highlighted with black. Stereographic projections of inverse trace analyses are at the left and right. In these projections, the traces perpendicular to $\langle 111 \rangle$ directions are shown with bold lines.

for 6 hours. Three grains were analyzed in detail. In two of the grains, three unique traces are seen. In the third grain, four unique traces are seen. Because these traces are generated by the intersection of the α' plates with the plane of the surface, it is not possible to determine the habit plane directly. However, with inverse trace analysis, it is possible to test whether the observed habit plane traces are consistent with any given habit plane orientation. Results of inverse trace analysis for three grains are shown in figure 3 to the left and to the right of the micrograph. In all three cases, it was possible to choose a trial orientation in which the observed traces were all perpendicular to a $\langle 111 \rangle$ direction.

Transmission electron microscopy (TEM)

In addition to providing high-resolution images of the morphology of α' , (TEM) also directly provides lattice orientation information. Because of the thinness of the specimen foils, the imaged α' plates are actually projections of thin, needle-like cross sections of larger plates, and it is difficult to directly determine the habit plane from a single image. As in the optical micrography results, the vast majority of δ grains contained α' with only three or four unique trace directions. Figure 4 shows an image of a specimen annealed at 440°C for 8 hours then quenched to -155°C for 10 hours. In this image, as in many others, the α' traces were perpendicular to $\langle 111 \rangle$ directions as determined by electron diffraction.

Although it is not possible to determine the orientation of an α' needle from a single TEM micrograph, two images taken along different crystallographic directions are sufficient, as long as the axis of rotation between the directions is not particularly close to the orientation of the needle. For redundancy, and to provide an estimate of experimental error, images along three different crystallographic orientations were used to determine the orientations of three α' needles in two different grains. The orientations of these needles with respect to the fcc δ matrix are

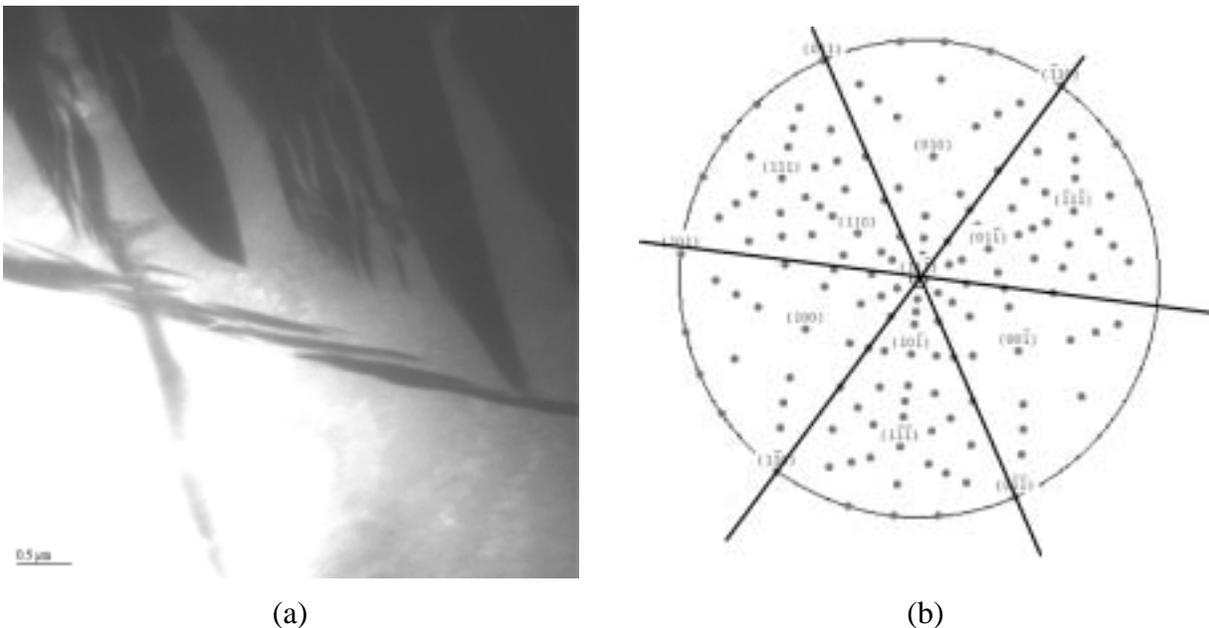


Figure 4. a) Transmission electron micrograph of α' plates imaged along a $\langle 111 \rangle$ direction in δ . b) Stereographic projection of the fcc δ lattice as determined from the indexed diffraction pattern. In this projection, the traces perpendicular to $\langle 111 \rangle$ directions are shown in with bold lines.

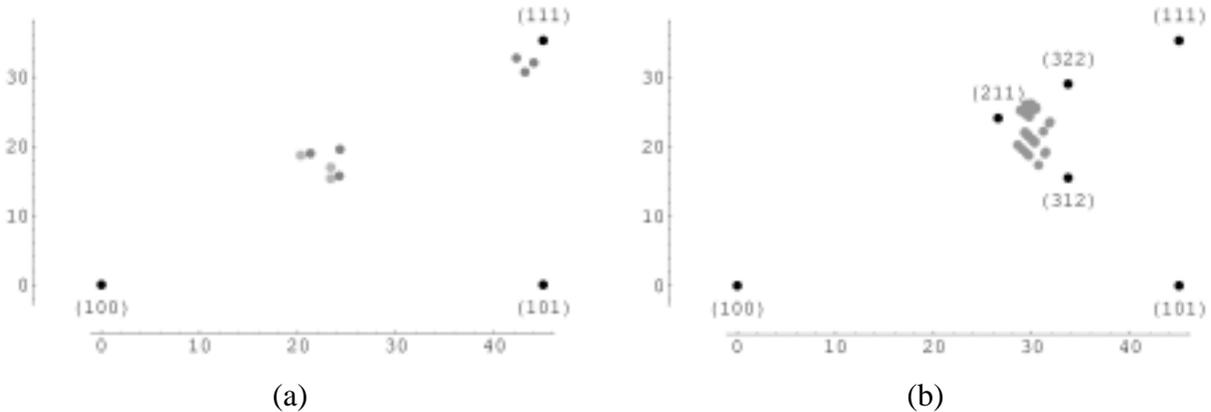


Figure 5. a) Orientations (in grey) of three α' needles determined from TEM trace analysis and plotted in the cubic unit crystallographic triangle of the fcc δ matrix. b) Estimation of the habit plane of the needles (also in grey), assuming that they all share a common habit plane orientation.

shown in figure 5a. In the cubic unit triangle, the orientations of the two needles from a single grain are very close to each other, which implies that they share a common habit plane. The experimental error is $\sim 5^\circ$.

If all the α' needles observed are assumed to share a common habit plane it is possible to determine solutions for this plane analytically, and the results of this analysis are shown in figure 5b, which shows solutions clustered near the $\{112\}$ and $\{123\}$ orientations in δ . This is consistent with the predictions of Adler *et al.* [10] and the observations of Zocco *et al.* [8]. At the same time it is puzzling because symmetry suggests that growth of α' on any of the 12 crystallographically unique $\{112\}$ planes or 24 distinct $\{123\}$ planes should be equally probable. However, in reality, we rarely see evidence of α' growth on more than three or four unique planes in a given grain.

One possible explanation for this discrepancy is that the growth of α' may proceed in a highly cooperative manner, and that once a single plate of α forms in a given grain, it will bias the growth of future plates, such that only 3-4 variants are allowed. However, it would be unwise to make this conclusion based on the observations of three α' needles, so further TEM analysis is planned.

SUMMARY

We have used transmission and optical microscopy to improve our understanding of the δ to α' transformation in Pu-Ga alloys. We have shown evidence of significant plastic deformation associated with the transformation. Although a small number of TEM measurements suggests that the habit plane of α' is near $\{112\}$ or $\{123\}$, we still have no definitive explanation for the small (~ 4) number of variants that are typically observed.

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