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Phase transformation in Pu–Ga alloys at low temperature and under pressure: limit stability of the δ phase

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Abstract

The mechanisms and morphologies obtained during partial transformation δ-(PuGa)$\rightarrow\alpha'$ at low temperature and under uniaxial or isostatic pressure have been determined. Depending on the conditions of treatment, one can observe two different phenomena: i) diffusion and martensitic transformations occur simultaneously and α' phase morphology is plate shaped, ii) only martensitic transformation occurs and α' phase morphology is lenticular. © 1998 Published by Elsevier Science S.A.

Keywords: Martensitic transformation; PuGa alloys; Phase morphology

1. Introduction

The cubic face centred δ phase, stable in unalloyed plutonium between 310°C and 450°C, is retained down to room temperature through the addition of small amounts of stabilizing elements such as gallium. But in the very low-solute regions, solid solution δ-(PuGa) is metastable and may partially transform into monoclinic-α' phase by cooling below room temperature and under uniaxial or isostatic pressure (25°C<100°C) with an accompanying volume decrease of ≈20%. Despite the unusually large volume change, most of studies conclude that the $\delta\rightarrow\alpha'$ transition proceeds via a martensitic mechanism. However, J.T. Orme et al. [1] indicate that the $\delta\rightarrow\alpha'$ transformation may occur by a massive transformation under certain conditions and a martensitic transformation under other conditions. Thus, our study has been undertaken to better understand the $\delta\rightarrow\alpha'$ transformation in PuGa alloys. First we have examined the influence of the low temperature treatments and gallium content on α' formation mechanisms and morphologies. Moreover, α' formation mechanisms and morphologies under uniaxial or isostatic pressure at room temperature are also given. For this study, the following techniques have been used: densitometry, metallography, X-ray diffraction, electron probe microanalyser, dilatometry and microcalorimetry.

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2. Material and experimental methods

2.1. Material

Alloys were cast into an arc furnace under argon. Samples were machined and subsequently annealed for 200 hours at 440°C. This treatment was realized to homogenize the Ga distribution in the δ phase and remove the α phase. For experimental tests at low temperature, two PuGa alloys with 1.2 and 1.9 at.% Ga were elaborated. For those under pressure, a wide range of gallium compositions from 1 to 3 at.% has been used. The average grain size was 60 μm and each alloy contained less than 500 ppm weight total impurities.

2.2. Experimental methods

The samples were cooled below room temperature in a dewar flask. The sample support was movable with regard to the flask so that the test temperature could be variable and reached very quickly. The compression experiments were carried out on a hand-operated isostatic or uniaxial press. Density measurements were realized in a monobromobenzene bath in order to estimate the amount of α or α' phase. Micrography and X-ray examinations required mechanical polishing and electropolishing in order to reveal the microstructure and to remove the strain-hardening layer. X-ray data were collected with a Bragg–Brentano goniometer with CuKα radiation. The $\alpha'\rightarrow\delta$ reverse

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transformations have been studied in an Adamel direct dilatometer between 25°C and 400°C under vacuum (heating and cooling rates were 50°C·h^{-1}) and in a calorimeter.

3. Experimental results

3.1. Low temperature treatments

This study aimed at expressing $\delta \rightarrow \alpha'$ transformation mechanisms and α' phase morphologies as a function of treatment temperatures and gallium contents. The two compositions of Pu–Ga alloys have been chosen on both sides of the TMS slope-change which occurs for a gallium content of about 1.5 at.% [2]. Several thermal treatments have been realized in each nose of the double C curve [1] (Fig. 1). The experimental conditions are shown in the following table.

Composition	Transformation nose	Temperature (°C)	Holding time (min)	Cooling rate (°C·min^{-1})
Pu–Ga 1.2 at.%	first nose	−50	30	≈1970
	second nose	−180	30	≈1970
Pu–Ga 1.9 at.%	first nose	−110	30	≈1970
	second nose	−180	30	≈1970

After quench, the samples have been quickly reheated at room temperature. Some metallographical examinations of the resulting structure are shown in Figs. 2 and 3. The dilatometry results about the $\alpha' \rightarrow \delta$ reverse transformation are given in Figs. 4 and 5.

3.2. Treatments under uniaxial and isostatic pressure at room temperature

The treatments under uniaxial and isostatic pressure have been realized in the plastic deformation area. The Pu–Ga 1.2 at.% alloy has been studied under uniaxial pressure. A wide range of compositions from 1 to 3 at.% has been used for experiments under isostatic pressure. One metallographical examination of resulting microstructure is shown in Fig. 6.

4. Discussion

4.1. At low temperature two phenomena have been observed

Above ≈−100°C, the $\delta \rightarrow \alpha'$ martensitic transformation is athermal [1] and the isothermal growth of the α' phase proceeds by short range diffusion. The mechanism of this

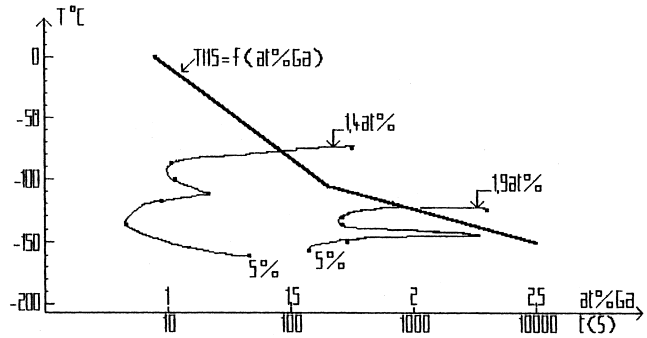

Fig. 1. Superposition of PuGa 1.4 and 1.9 at.% alloys TTT curves [1] and TMS=f(at.%Ga) [2].

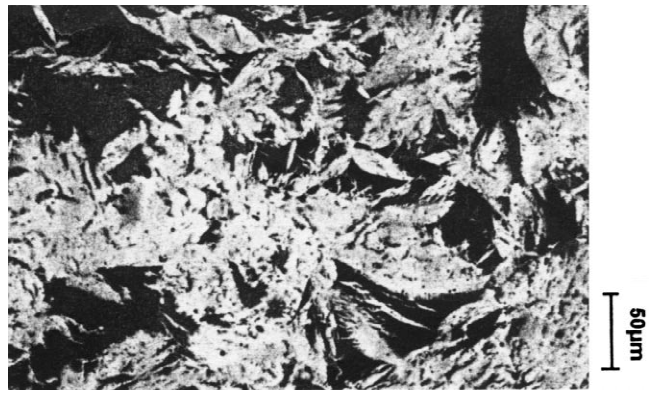

Fig. 2. Pu–Ga 1.2 at.% treated at −50°C for 30 min. The micrograph shows α' plate shaped (white) in a δ matrix (black).

previous transformation is $\delta \rightarrow \gamma' \rightarrow \alpha'$ and it is allowed by an isothermal atomic reorganization of the α' [3] phase or a stress relaxation in the habit plane [4]. The morphology of α' phase is plate shaped (Fig. 2). This kind of transformation appears in the case of gallium content below 1.5 at.% and at a temperature lower than TMS (first transformation nose of the TTT curve). In this case the reverse transformation $\alpha' \rightarrow \delta$ is partly indirect (Fig. 4) and

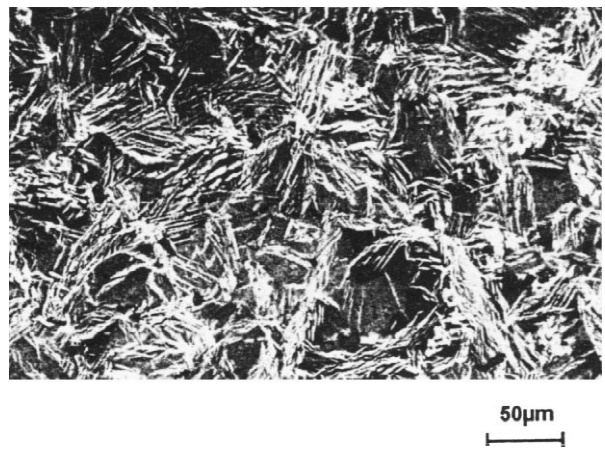

Fig. 3. Pu–Ga 1.2 at.% treated at −180°C for 30 min. The micrograph shows α' lenticular (white) in a δ matrix (black).

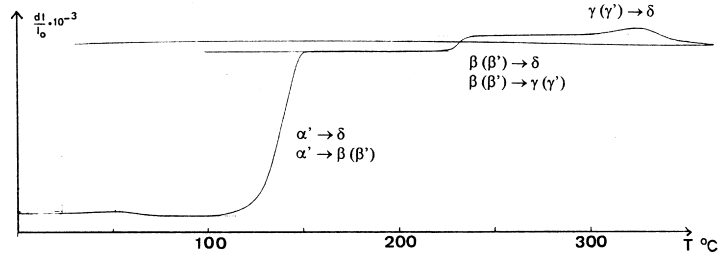

Fig. 4. Dilatometry thermal analysis of the reverse transformation α' plate shaped→δ for Pu–Ga 1.2 at.%.

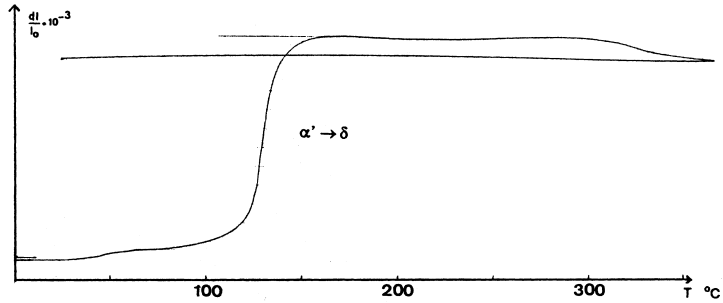

Fig. 5. Dilatometry thermal analysis of the reverse transformation α' lenticular→δ for Pu–Ga 1.2 at.%.

it is produced by both diffusion (indirect transformation) and displacive (direct transformation) transformations.

Under ≈ -100°C the martensitic transformation is isothermal [5] and the α' phase morphology is lenticular. This transformation occurs in alloys with gallium contents above 1.5 at.% or below if the temperature is very low (second transformation nose of the TTT curve). Depending on the gallium contents (which influence mechanical properties) and on the treatment temperatures, the martensitic needles slightly grow by a displacive transformation [6]. Growth appears in the first nose in alloys in which gallium content is higher than 1.5 at.% and in the second nose if it is lower than 1.5 at.%. The $\alpha'\rightarrow\delta$ reverse transformation on heating is direct and produced by a displacive transformation.

In both cases, the nucleation is heterogeneous [1,2,5]. Moreover the martensitic phase obtained is nonthermoelastic and leads to a plastic strain of the former phase [3].

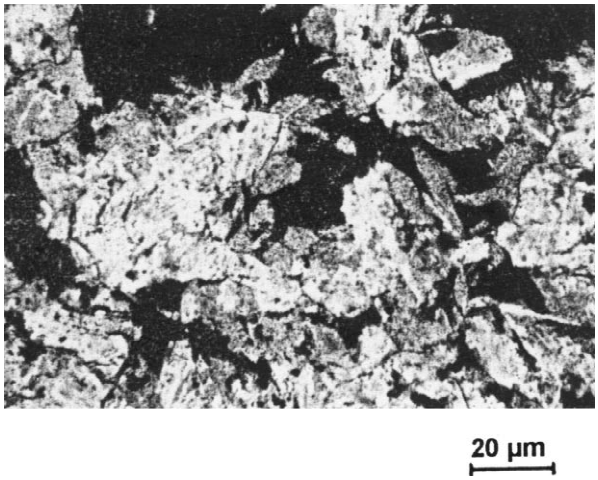

Fig. 6. Pu–Ga 1.2 at.% treated under uniaxial pressure. The micrograph ($\perp$ pressure) shows α' plate shaped (white) in a δ matrix (black).

4.2. Under any uniaxial or isostatic pressure

The morphology of the α' phase is always plate shaped whatever the gallium content is between 1 and 3 at.% (Fig. 6). The nucleation is athermal, heterogeneous and the defects contained in the δ phase lead to preferential nucleation sites [7,8]. Only a pressure increase allows the transformation to continue inside the grain. As for low temperature treatments leading to plate shaped α', a fast diffusion transformation is added to the martensitic transformation. The reverse $\alpha'\rightarrow\delta$ transformation is partly indirect [2,9] and displays both diffusion and displacive transformations. Besides the direct transformation percentage (by displacive transformation) increases with gallium content.

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