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ScienceDirect

Acta Materialia 61 (2013) 7109–7120

Acta MATERIALIA

www.elsevier.com/locate/actamat

Phase transformations in Pu–Ga alloy: Synergy between simulations and experiments to elucidate direct and indirect reversion competition

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Received 22 May 2013; received in revised form 29 July 2013; accepted 29 July 2013
Available online 11 September 2013

Abstract

Reverse transformation in plutonium alloyed with a small amount of gallium (Pu–1 at.% Ga) was investigated in detail by coupling CALPHAD-based simulations with experiments. As observed previously, reverse transformation in a two-phase $\delta + \alpha'$ alloy exhibits the existence of competition between direct reversion ($\alpha'_{1at.\%} \rightarrow \delta_{1at.\%}$) and indirect reversion ($\alpha'_{1at.\%} \rightarrow \beta_{pure\ Pu}(+\delta_e) \rightarrow \gamma_{pure\ Pu}(+\delta_e) \rightarrow \delta_{1at.\%}$). The latter leads to Ga enrichment of the δ phase (δ_e) as well as the emergence of several phases of pure Pu. The present paper focuses on the thermodynamic and kinetic aspects of the competition between these two reversion modes, especially between direct reversion and the first step of indirect reversion, whenever competition occurs. Thermodynamic simulations indicated that both reversion modes were possible and that indirect reversion was more favorable. Specific isothermal experiments combined with simulations revealed the existence of two potential Ga diffusion paths during indirect reversion: (i) from the α′ phase to the δ phase and (ii) from a new transient β′ phase, preceding the appearance of β phase of pure Pu, to the δ phase. These newly discovered mechanisms have enabled the present authors to fully understand the competition between the reversion modes. Finally, the ratio of direct to indirect reversion was found to depend on three factors, namely heating rate, initial α′ phase fraction and Ga content. All simulations were confirmed experimentally and highlighted key aspects of reversion mechanisms.

Keywords: Phase transformation; Thermodynamics; Diffusion; CALPHAD; X-ray diffraction

1. Introduction

Plutonium metal (Pu) has six crystal structures with many different physical properties between room temperature and its melting point. For example, the volume difference between the simple monoclinic α phase (which has the lowest crystallographic symmetry, but the highest density) and the face-centered cubic δ phase (which has the highest crystallographic symmetry, but the lowest density) is ~20%. In view of its unusual properties, much research has been and is still carried out to characterize and understand the behavior of pure plutonium [1–3]. A summary of the various studies can be found in a review by Hecker [4]. The stability range of the manufacturing phase has been defined as being between 315 and 457 °C, which corresponds to the δ phase. This temperature range is quite narrow, but it has been proved that the δ-phase stability can be extended to room temperature by alloying Pu with "δ-phase stabilizing" elements such as aluminum (Al), americium (Am) or gallium (Ga) [5–8].

When Pu–Ga alloys with a Ga content <3 at.% are cooled to subambient temperatures, a partial transformation of the metastable δ phase into the hard and brittle α′ phase occurs. The $\delta \rightarrow \alpha'$ transformation corresponds to an isothermal martensitic process, whereby the α′ phase denotes the α phase of pure Pu with δ-phase stabilizing elements trapped inside it [9,10]. As a consequence, the α′

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http://dx.doi.org/10.1016/j.actamat.2013.07.060

crystal structure is similar to the simple monoclinic structure of the α phase of pure Pu, albeit with slightly different lattice parameters. In a previous study, Ravat et al. [11] showed that the $\delta \rightarrow \alpha'$ martensitic transformation occurring at low temperatures was direct and led to the formation of a two-phase $\delta + \alpha'$ alloy. The goal of the present paper is to detail the reversion mechanisms that occur in this two-phase $\delta + \alpha'$ alloy upon heating.

Previous studies have shown that the investigation of reverse transformation is particularly complex, and the mechanisms involved are still the subject of much debate. In 1998, Deloffre et al. [12] reported that, in Pu–1.2 at.% Ga, reverse transformation is partly indirect and mainly direct. However, Deloffre did not make any mention of a possible mechanism for explaining the dilatometry results supporting these findings. Later, Mitchell et al. [13] studied phase stability and phase transformations in Pu–Ga alloys by carrying out dilatometry and differential scanning calorimetry (DSC) measurements. The authors described the direct $\alpha' \rightarrow \delta$ reverse transformation in Pu–Ga alloy (1.2–2 at.% Ga) as a martensitic transformation, characterized by a series of bursts and dependent on bulk composition, grain size and Ga distribution. Similarly, Blobaum et al. [14] reported the presence of transformation bursts during thermal cycling of Pu–2 at.% Ga. Direct reversion appeared to be the result of an interplay between the autocatalytically driven reversion of a cascade of individual martensite units and self-quenching (caused by small changes in temperature or stress) that accompanied each individual transformation burst. In spite of the extensive DSC and dilatometry analysis performed during thermal cycling of Pu–Ga alloys, indirect reverse transformation that occurs upon heating remains poorly understood because of the lack of sufficient experimental data. However, previous work [11] revealed that reverse transformation in a fully homogenized Pu–1 at.% Ga results from competition between a direct mechanism

$$\alpha'_{1\text{at.}\%} + \delta_{1\text{at.}\%} \rightarrow \delta_{1\text{at.}\%}$$

which can be reduced to

$$\alpha'_{1\text{at.}\%} \rightarrow \delta_{1\text{at.}\%}$$

and an indirect mechanism

$$\alpha'_{1\text{at.}\%} + \delta_{1\text{at.}\%} \rightarrow \beta_{\text{pure Pu}} + \delta_e \rightarrow \gamma_{\text{pure Pu}} + \delta_e \rightarrow \delta_{1\text{at.}\%}$$

which can be rewritten as

$$\alpha'_{1\text{at.}\%} \rightarrow \beta_{\text{pure Pu}}(+\delta_e) \rightarrow \gamma_{\text{pure Pu}}(+\delta_e) \rightarrow \delta_{1\text{at.}\%}$$

So, the emergence of several phases of pure Pu and a Ga-enriched δ phase (δ_e) has been reported. It should be noted that this competition can be reduced to that between direct reversion and the first step of indirect reversion (emergence of the pure-Pu β phase, which then reverts like pure Pu). These results are in closer agreement with those of Deloffre, who observed indirect reversion in Pu–1.2 at.% Ga in specific conditions, than with the results obtained for Pu–Ga (1.7–2 at.% Ga), for which only the direct reversion mode was characterized [12–14]. In the first study [11], Ga diffusion, which is a key feature of indirect transformation, was clearly identified (enrichment of the δ phase and emergence of pure-Pu phases) and established as contributing to the competition between the two reversion modes for Pu–1 at.% Ga. However, Ga diffusion paths must be studied in detail in order to define and understand the mechanisms involved during indirect reversion. This would enable us to establish a list of key aspects pertaining to reversion and explain certain discrepancies observed in the literature. For example, it will help to shed light on why competition between direct and indirect reverse transformation is observed for Pu–1 at.% Ga but not for Pu–Ga (1.7–2 at.% Ga).

In the present work, reverse transformation in a fully homogenized Pu–1 at.% Ga alloy was investigated using both modeling and experimental methods (until the $\beta_{\text{pure Pu}}(+\delta_e)$ phase region, where competition between reversion modes ceases). Thermodynamic and kinetic calculations were performed with Thermo-Calc and DICTRA software packages (based on the CALPHAD method) combined with Pu–Ga databases. In addition, X-ray diffraction (XRD) measurements were used to thoroughly describe mechanisms involved during reversion. Coupling modeling and experimental results enabled us to elucidate the complex phenomena associated with reverse competition. Both computational and experimental details are given in Section 2. The results and accompanying discussions are presented in Sections 3 and 4, respectively.

2. Computational and experimental details

2.1. Computational details

The CALPHAD (CALculation of PHAse Diagrams) method is clearly described in textbooks [15–17]. The Thermo-Calc® and DICTRA[1] (DIffusion Controlled TRAnsformation) software packages used in the present study are based on this method, and a brief overview of the general philosophy of the modeling approaches is given below [18,19].

2.1.1. Thermodynamic modeling

The aim of the CALPHAD method is to express the Gibbs energy functions of phases in terms of composition, temperature and pressure. In practice, CALPHAD is an iterative method that adjusts the parameters describing the Gibbs energies of various phases in a system in order to construct a phase diagram that best fits the available experimental and calculated thermodynamic and phase diagram data for the system [20]. The Thermo-Calc software uses thermodynamic databases that contain such functions for reproducing phase diagrams, enthalpies of

[1] Thermo-Calc and DICTRA software packages are products of Thermo-Calc AB.