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Phase transformations in PuGa 1 at.% alloy: Study of whole reversion process following martensitic transformation

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ABSTRACT

The purpose of this work was to study PuGa 1 at.% alloy behavior from martensitic transformation to the whole reversion process. The relevant phase transformations were investigated as a function of temperature via *in situ* X-ray diffraction and dilatometry analyses carried out at low and high temperatures. The results show that the δ-to-α′ martensitic transformation occurring at low temperatures is direct and does not involve any intermediate γ′ phase. They also reveal that the reverse transformation of the two-phase δ + α′ alloy during heating involves two competing modes, namely direct and indirect reversion. The latter is associated with a Ga diffusion process that governs the ratio between these reversion modes. More precisely, our study demonstrates that the indirect reversion process consists of a Ga-enrichment of the remaining δ phase as well as the emergence of the β and γ phases of pure plutonium. Every stage of indirect reversion has been discussed in relation to the equilibrium phase diagram of the Pu–Ga binary system.

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1. Introduction

At ambient pressure, plutonium metal has six different phases between room temperature and its (relatively low) melting point (640 °C). At room temperature, the thermodynamically stable phase of pure plutonium is the brittle α phase (simple monoclinic structure). However, the high-temperature δ phase (face-centered cubic structure), which has the highest crystallographic symmetry but the lowest density and is stable from 315 to 457 °C, can be retained at room temperature by alloying plutonium with a few atomic percent of so-called “δ-phase stabilizing” elements such as Al, Am, Ce and Ga. Recently, US and Russian scientists concurred with each other in the view that the δ phase is metastable under ambient conditions, and that in Pu–Ga systems, this phase goes through an extremely slow eutectoid decomposition into α Pu and the intermetallic compound Pu_3Ga when cooled to temperatures below 100 °C; this process takes place over an estimated period of more than 10,000 years [1,2].

Furthermore, when the metastable δ phase of PuGa alloys with Ga contents lower than 3 at.% is cooled to subambient temperatures, a partial transformation into the martensitic α′ phase occurs. The crystal structure of the α′ phase is similar to that of the simple monoclinic α phase, consisting in a slightly expanded unit cell as a result of Ga atoms being trapped in the lattice (the prime here is used to indicate the presence of Ga atoms in the crystalline structure). The crystallographic aspects of the δ-to-α′ martensitic transformation in PuGa alloys such as the α′–δ orientation relationship, habit planes and twin relationships have been thoroughly investigated and described [3–9]. A consequence of this martensitic transformation on the parent δ phase is an increase in the anisotropic lattice microstrain induced by the occurrence of microstresses resulting from a volume difference of approximately 20% between the α′ and δ phases [10–12]. The time–temperature–transformation (TTT) diagram for the δ-to-α′ transformation also exhibits most unusual kinetics in the form of a double-C curve [13], the origin of which is still under discussion. According to Orme et al. [14], it may be the result of a martensitic transformation (displacive transformation) or a massive transformation. Deloffre et al. [15], on the other hand, attribute it to the existence of both a direct and an indirect δ-to-α′ transformation, whereby the indirect mode involves an intermediate γ′ phase (face-centered orthorhombic structure). From density functional theory calculations, Sadigh et al. [16] suggest that the double-C kinetics are related to the random distribution of Ga atoms or their special position in the simple monoclinic α′ structure (induced by a short-range diffusion mechanism), whereas from transmission electron microscopy analyses Moore et al. [3] have singled out the existence of different habit planes as the reason for this behavior. The isothermal martensitic transformation in the Pu–Ga system is still being studied in terms of its kinetics, the nucleation processes involved and the associated growth and activation energies [17–23].

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The reverse α'-to-δ transformation that is observed upon heating is particularly multifaceted in nature. Indeed, this process depends on the Ga content. In PuGa alloys with Ga contents greater than 1.7 at.%, the reverse transformation is direct [24]. Moreover, as shown by dilatometry and differential scanning calorimetry investigations conducted by Mitchell et al. [25] and Blobaum et al. [26], this direct α'-to-δ reversion occurs via a burst martensitic mode characterized by a series of endothermic spikes that correspond to a cascade of α' particles reverting to the δ phase. In PuGa alloys with Ga contents close to 1 at.%, the reverse transformation has been found to be indirect before complete reversion to the δ phase, with the appearance of phases exhibiting body-centered monoclinic and face-centered orthorhombic crystalline structures that correspond respectively to the so-called β and γ structures of Pu [24]. However, the physics underpinning the behavior of Ga during this indirect reversion process remain unresolved. Indeed, based on an analysis of reverse transformation in cold rolled samples, Ekbom and Bogegård have suggested that the α' phase reversion is a non-diffusion transformation leading to the formation of a β' phase [27]. In addition, Spicer and White [28] have found that Ga acts as a β-phase stabilizer by enabling the β phase to be maintained all the way down to room temperature. Subsequently, based on dilatometry measurements, Deloffre et al. reported that the reverse transformation is part direct and part indirect, with the emergence of the β or β' and γ or γ' phases; this dilatometry analysis does not, however, enable a discussion of the behavior of Ga atoms [15]. More recently, Hecker et al. suggested that at reversion temperatures above 120 °C, Ga atoms may be sufficiently mobile to enable the emergence of the β and γ phases of pure Pu [24]. In summary, whether or not the indirect α'-to-δ reversion process involves Ga diffusion remains poorly understood and is still under much debate because of the lack of convincing experimental data for PuGa alloys with low Ga contents.

The purpose of this paper is to present new relevant experimental results that will contribute to a better understanding of PuGa 1 at.% alloy behavior from the martensitic transformation to the complete reversion process. Phase transformations were investigated *in situ* at low and high temperatures by means of X-ray diffraction and dilatometry. This enabled us to characterize the crystal structures and study the crystalline phase amounts as a function of temperature and heating rate. Details on the experimental equipment and the data collection methods are reported in Section 2. The results are presented in Section 3, then discussed in Section 4.

2. Materials and experimental methods

2.1. Sample description

Our study was carried out on a PuGa alloy with a gallium content of 1 at.%. Its density measured thanks to immersion density equipment is 15.83 ± 0.023 g cm^{-3}. The precise Ga concentration in this alloy is 0.967 at.% and the principal impurities which were characterized by chemical analyses are the following: Al (0.136 at.%), Am (0.104 at.%), Ta (0.077 at.%), U (0.059 at.%), Mg (0.024 at.%), Fe (0.023 at.%), Ni (0.010 at.%) and Cu (0.009 at.%). The alloy was heat treated for 1000 h at 470 °C under high vacuum conditions (2×10^{-7} mbar) to produce a single-phase δ alloy with a thoroughly homogeneous Ga distribution in all the grains. It was machined and microcut to obtain the following sample dimensions: a diameter of 15 mm and a height of 1.5 mm for X-ray diffraction and optical microscopy, and a diameter of 10 mm and a height of 4 mm for dilatometry. This was followed by a 3-h annealing treatment at 360 °C to restore the initial δ-phase crystalline structure by bringing about reversion of the α' phase generated by sample preparation. This heat treatment also enabled the annealing of δ-phase structural defects induced by self-irradiation resulting from the α decay of plutonium [29]. In addition, samples of pure plutonium metal were prepared for analysis. All the samples were electropolished to remove surface oxides.

2.2. In situ X-ray diffraction analysis as a function of temperature

In order to carry out an *in situ* X-ray diffraction (XRD) analysis as a function of temperature, a temperature chamber (TTK 450 Anton Paar®) was installed in a θ/θ diffractometer (BRUKER AXS D8 Advance®) and placed inside a glove box in order to meet all the safety criteria relevant to the analysis of plutonium alloys. The temperature range of this setup is between −193 and 450 °C, which is enabled by a heating/cooling block located within the chamber. This block is equipped with a circulating liquid nitrogen system (for cooling) and a resistive heater (for heating). The temperature was monitored with the help of a thermocouple inserted into the front surface of the sample holder. The diffractometer was equipped with a Mo Kα tube that was set to 50 kV and 40 mA, with K$_{\alpha1}$ and K$_{\alpha2}$ X-ray beam energies of 17.48 and 17.37 keV, respectively. To improve the count time, a high-speed positive sensitive detector (BRUKER AXS VANTEC®) capable of integrating over an angular range of 6° was used in conjunction with a 12-μm-thick zirconium foil for removing K$_\beta$ radiation. The divergence of the primary radiation beam was restricted using a 0.2-mm-width slit.

2.3. XRD data collection and analysis

Diffraction diagrams were recorded with a step size of 0.015° within a 2θ angle range of 12.5–56° for 2-h isothermal holds separated by steps of 10 °C. Between each step of temperature the cooling and heating rate was 30 °C min^{-1}. This is equivalent to a low cooling and heating rate of 5 °C h^{-1} on average. The calibration of the experimental device was verified before and after each set of measurements by using a lanthanum hexaboride powder standard (LaB$_6$ NIST SRM 660a). The recorded diffraction diagrams were analyzed with the full-pattern Rietveld refinement method by using the Fullprof program [30]. Of the different crystal structures of plutonium published by Zachariasen and Ellinger [31–33], the following were used in the Rietveld structural refinement: the simple monoclinic α phase (s.g. P2$_1$/m) containing 16 atoms per unit cell, the body-centered monoclinic β phase (s.g. I2/m) containing 34 atoms per unit cell, the face-centered orthorhombic γ phase (s.g. Fddd) containing eight atoms per unit cell, and the face-centered cubic structure δ phase (s.g. Fm3 m) containing four atoms per unit cell. During the Rietveld refinement process, the Pu atom positions were set according to the atomic positions defined by Zachariasen in the α, β, γ and δ phases. Diffraction peaks were fitted using a pseudo-Voigt function, and parameters of the refined diffraction diagram included line-broadening, diffuse-background, sample-displacement and cell parameters, as well as scale factors and the Debye–Waller factors.

2.4. Dilatometry

Dilatometry measurements were performed in a glove box by using a Netzsch 402C® dilatometer with a low-temperature furnace having a temperature range of −160 to 500 °C. The sample holders and pushrods in this device are made of quartz glass. The typical pushrod load on a sample was 5 cN. Before each test, a vacuum of less than 10^{-3} mbar was created, then filled by a high-purity inert gas (He).

2.5. Optical metallography

The samples were mounted in an epoxy resin and polished with SiC abrasive papers of different levels of coarseness. Microstructures were revealed by electrochemical etching, and metallographic observations were performed with an Olympus GX51® microscope. All these operations were carried out in a glove box.

3. Results

3.1. Macroscopic behavior and phase changes as a function of temperature

During the dilatometry measurements, the PuGa 1 at.% alloy sample was cooled from room temperature to −150 °C at a cooling rate of 0.5 °C min^{-1}. As Fig. 1 shows, the δ phase shrank slightly with decreasing temperature as a result of thermal contraction. Then, at −20 °C, which corresponds to the martensite start temperature (M_s), an abrupt fall in the dilatometry curve is observed. This sharp contraction resulted from a δ-to-α' transformation, during which a significant change in length was induced by the large atomic volume difference between the two phases, as indicated in Table 1. Meanwhile, many XRD experiments were carried out below the M_s temperature. Rietveld refinements of the diffraction diagrams consistently indicate the presence of a $\delta + \alpha'$ mixture, proving that the martensitic transformation that occurred in the PuGa 1 at.% alloy was a direct δ-to-α' transformation. A typical Rietveld structural refinement performed on an XRD diagram recorded at a subambient temperature is given in Fig. 2a, from which we may observe that the calculated and experimental XRD diagrams match perfectly when the face-centered cubic and simple monoclinic structures are used as structural models.

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