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New insight into δ -Pu alloy oxidation kinetics highlighted by using *in-situ* X-ray diffraction coupled with an original Rietveld refinement method

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ABSTRACT

The reactivity of a δ -Pu alloy was studied under dry oxygen at different temperatures. Phase analysis has shown the presence of α - and β -Pu₂O₃, PuO₂, as well as the destabilisation of the δ -phase. The oxidation kinetics were studied using *in-situ* X-ray diffraction coupled with an original method of Rietveld refinement enabling an individual monitoring of the growth of each oxide. The results have evidenced a parabolic stage resulting from the thickening of the α -Pu₂O₃ layer, in which a compressive stress state develops. This stage is followed by the linear growth of a porous PuO₂ scale.

1. Introduction

Plutonium displays highly unusual behaviour that makes it one of the most complex elements in the periodic table. As a consequence, many studies are still being devoted today to the behaviour of pure plutonium [1–4]. Indeed, plutonium metal has six allotropic phases between room temperature and its low melting point (640 °C) at ambient pressure. For Pu alloys, the existence of these phase domains are particularly sensitive to temperature, time, stress and alloy chemical composition [5]. At room temperature, the stable phase is the brittle (simple monoclinic) α -phase. The high-temperature (face-centred cubic) δ -phase can also be held at room temperature and pressure by alloying plutonium with “ δ -phase stabiliser” elements, such as: Al, Am, Ce and Ga. However, this δ -phase remains thermodynamically metastable and exhibits martensitic transformation and reversion in temperature [6–11]. Furthermore, the δ -phase is the most ductile and oxidises at a lower rate in comparison with the other phases, especially the α -phase, therefore it is the most interesting phase for metallurgical applications. However, δ -Pu is still very sensitive to corrosion, which may be severe for long-term storage under an inadequately controlled atmosphere.

Although the corrosion of δ -Pu alloys has been studied for several decades [12–16], this subject is still under debate. Indeed, plutonium oxidation kinetics have been studied by *in-situ* ellipsometry [17,18] and more widely by mass gain monitoring [19–24]. These experiments are well suitable for monitoring kinetics and to collect general information about the growth of the oxide scale, but they cannot provide more

details about its inner composition. Therefore, these experiments needed to be completed by *ex-situ* analyses to characterise the nature of the oxide scale using either XPS [25–31] or XRD analyses [19,21,24,32–34]. Consequently, due to a lack of concomitant information about kinetics monitoring and oxide scale description, many questions remain about the nature and the arrangement of each phase forming the oxide scale, its individual growth and the mechanisms governing the oxidation process. The purpose of the present paper is to finally give answers to these interrogations.

Thus, in order to improve our knowledge of the oxidation mechanism of plutonium, we have focused our study on the reactivity of a δ -Pu alloy at the limit of metastability under a dry oxygen atmosphere at different temperatures. The originality of this work lies in a continuous *in-situ* X-ray diffraction (XRD) analysis performed during the oxidation process coupled with an original method of Rietveld refinement specifically adapted to a multilayered sample, since classical Rietveld analysis is efficient for homogeneous mixture of phases and irrelevant for a stacking-layer configuration. This approach enables a specific analysis of the individual growth kinetics of the different oxides present in the oxide scale, with the characterisation of their crystalline structure and the assessment of their thickness.

Details on material, specific equipment and methods are reported in Section 2. The original XRD data processing method is detailed in the calculation Section 3. The results regarding the phase analysis and the oxidation kinetics study are presented in Section 4, and the mechanisms involved during the oxidation process are discussed in Section 5.

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2. Experimental details

Our study was carried out on a δ -Pu alloy at a limit of δ -metastability (as described in [6]), fully homogenised through a high temperature treatment for 1000 hours at 470 °C under high vacuum conditions (2×10^{-7} mbar). After machining and microcutting, samples with dimensions of 15 mm diameter and 1.5 mm height were obtained. All of the samples were polished with SiC abrasive papers of different levels of coarseness and then electropolished as detailed in [35]. An annealing treatment at 360 °C was then performed for 30 min to restore the initial δ -phase crystalline structure by producing the 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.

Then, the sample oxidation was analysed using *in-situ* X-ray diffraction (XRD) during isothermal exposures at high temperature (150 °C and 200 °C) under 100 mbar of a dry oxygen atmosphere. More precisely, the experiments consisted in monitoring the oxidation using a classical θ/θ diffractometer (BRUKER AXS D8 ADVANCE[®]) in Bragg Brentano geometry, with a high-speed positive sensitive detector (BRUKER AXS VANTEC[®]). In order to perform XRD analyses at different temperatures under a controlled atmosphere, a temperature chamber (TTK 450 Anton Paar[®]) was mounted at the goniometer centre. The whole device was located inside a glove box, in order to meet all of the safety criteria relevant to the analysis of plutonium alloys. A molybdenum X-ray tube was used to improve the diffracting volume and to reduce the recording time. The calibration of this setup was verified before and after each series of experiments by using a lanthanum hexaboride powder standard (LaB₆ NIST SRM 660a[®]). Before starting the oxidation experiment, the sample was at room temperature in the reaction chamber which was pumped down to 10^{-3} mbar, and then filled with 100 mbar of dry oxygen (less than 1 ppm of H₂O). The sample was then heated to 150 °C or 200 °C. Once the dwell temperature reached (after about 5 min), XRD patterns started to be acquired. The recording times of the XRD diagrams lasted for 30 min (during the 2 first hours of exposure), then one hour (during the 22 following hours) and two hours (until the experiment was stopped) in order to accurately study the oxidation kinetics.

The surface morphology was characterised at room temperature after the oxidation treatment. Imaging was performed with a SEM LEO Stereoscan 440, equipped with LaB₆ emitter, placed in a glove box. Secondary electron images were obtained with an accelerating voltage of 20 kV, a probe current of 200 pA and a working distance of around 20 mm.

3. Rietveld refinement method for the XRD diagram analysis of a multilayered specimen

Classical Rietveld analysis on X-ray diagrams recorded in Bragg-Brentano geometry is adapted to the analysis of homogeneous mixtures of phases. It enables the calculated diffraction pattern to be matched to an experimental one by adjusting positions and intensities of the Bragg peaks. This is carried out by taking into account structure factors of the phases present in the sample and by refining the structural parameters, crystallite size and microstrain of these phases. Furthermore, in a specimen composed of phase mixture, the phase amounts can also be assessed by considering a mean X-ray absorption coefficient corresponding to a homogeneous mixture of phases. This method cannot be applied directly for the study of the oxidation of a bulk metallic material, since it can be readily assumed that the oxidation products do not constitute a homogeneous mixture but rather a layer stacking. Thus, in this part, the way in which common Rietveld analysis was modified to be able to refine the thickness instead of the phase amount for a multilayered sample is presented. Notice that this approach is relatively similar to the method described in Scardi et al. and Lutterotti et al. papers [36,37].

3.1. General aspect of the diffracted intensity

The absolute diffracted intensity of an infinitely-thick single-phase specimen is expressed by the following Eq. (1):

$$I^{diff} = \frac{K}{2\mu_m^2} P(\theta) L(\theta) m_{hkl} |F_{hkl}|^2 A_{beam} \quad (1)$$

where $L(\theta)$ is the Lorentz term (geometry of the diffraction analysis), $P(\theta)$ is the polarisation term of the X-ray beam, μ is the linear absorption coefficient, F_{hkl} is the structure factor of the phase, V_c is the volume of the unit cell, m_{hkl} is the multiplicity of the crystallographic planes $\{hkl\}$, and A is the incident beam section. All of these terms are either calculated or refined. K is an intrinsic factor of the device including specific diffractometer settings, notably the nature of the optics mounted on the goniometer and the detection system. Thus, this factor is related to the photon emission rate of the X-ray source and the efficiency of the detector. This parameter is experimentally determined from the analysis of a well-crystallised and homogeneous sample and is defined for the set of XRD experimental conditions used. Since the δ -Pu alloy substrate is fully crystallised, it was used as external standard.

3.2. Intensity diffracted by layer stacking

As previously mentioned, the corrosion scales formed on oxidised samples are assumed to be composed of successive layers of plutonium oxides. This excludes the direct use of the Rietveld classical approach as defined in Eq. (1). The development of a new data processing method is needed to take into account the specific structure. The values of the parameters connected to the diffraction device features remain unchanged and are not influenced by the nature of the stacking. However, the intensity diffracted by one layer depends on its location in the stacking, the absorption coefficients of the phases present and the finite-thickness character of all of the layers that compose the sample.

All of these characteristics are gathered in Eqs. (2) and (3), which give the intensity correction functions to be applied to Eq. (1). They permit the diffracted signal coming from the layer i surmounted by ($i-1$) layers Eq. (2) and from the substrate Eq. (3) to be described.

$$C_{Abs}^{Li}(\theta) = \prod_{j=1}^{i-1} \exp\left(-2\frac{\mu_{Lj} t_{Lj}}{\sin \theta}\right) \left[1 - \exp\left(-2\frac{\mu_{Li} t_{Li}}{\sin \theta}\right)\right] \quad (2)$$

$$C_{Abs}^{Sub}(\theta) = \prod_{j=1}^n \exp\left(-2\frac{\mu_{Lj} t_{Lj}}{\sin \theta}\right) \quad (3)$$

where μ_{Lj} are the linear absorption coefficients, t_{Lj} are the thicknesses of the layers j surmounting the diffracting layer i and n is the number of layers on the substrate.

More precisely, linear absorption coefficients μ_{Lj} were determined taking into account the chemical composition and density of the phases present as well as the energy of the X-ray beam. The finite-thickness character of the diffracting layer has been taken into account by the second term of Eq. (2). It describes the fact that a part of the incident beam may go through the layer without interacting with it. Let us note also that this second term disappears for the substrate, since it is considered to have an infinite thickness against X-ray penetration. Furthermore, the correction corresponding to the absorption of the incident and diffracted beam during its path into the surrounding layers is also taken into account through the first term in Eq. (2) (this is the only intensity correction term for the substrate). This correction depends on the incidence angle θ and the thickness of the outer layers traversed by the X-ray. It is important to note that since voids and porosity are not detected by X-ray diffraction, the thickness assessed from this approach corresponds to the thickness of a dense material. Consequently this thickness is directly related to the real amount of formed oxide. Thus, this assessed thickness may be slightly lower than a thickness deduced from a cross-section image in which voids and porosity are included.

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