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Effect of cooling rate on achieving thermodynamic equilibrium in uranium–plutonium mixed oxides

Romain Vauchy [a, b, *], Renaud C. Belin [b], Anne-Charlotte Robisson [b], Fiqiri Hodaj [c, d]

[a] CEA, DEN, DTEC, Marcoule, 30207, Bagnols-sur-Cèze, France
[b] CEA, DEN, DEC, Cadarache, 13108, Saint-Paul-lez-Durance, France
[c] Univ. Grenoble Alpes, SIMAP, F-38000, Grenoble, France
[d] CNRS, Grenoble INP, SIMAP, F-38000, Grenoble, France

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ABSTRACT

In situ X-ray diffraction was used to study the structural changes occurring in uranium–plutonium mixed oxides $U_{1-y}Pu_yO_{2-x}$ with y = 0.15; 0.28 and 0.45 during cooling from 1773 K to room-temperature under He + 5% H_2 atmosphere. We compare the fastest and slowest cooling rates allowed by our apparatus *i.e.* 2 K s^{-1} and 0.005 K s^{-1}, respectively. The promptly cooled samples evidenced a phase separation whereas samples cooled slowly did not due to their complete oxidation in contact with the atmosphere during cooling. Besides the composition of the annealing gas mixture, the cooling rate plays a major role on the control of the Oxygen/Metal ratio (O/M) and then on the crystallographic properties of the $U_{1-y}Pu_yO_{2-x}$ uranium–plutonium mixed oxides.

1. Introduction

Uranium–plutonium mixed oxides $U_{1-y}Pu_yO_{2-x}$ with high amounts of plutonium are envisaged as fuel for future Sodium-cooled Fast Reactors (SFRs) [1]. Although the exact nature of SFRs' nuclear fuels is still under consideration, general trends are already defined. The fuel will be oxygen-hypostoichiometric uranium–-plutonium mixed oxides (O/(U + Pu) = O/M ratio < 2.0) with a plutonium content ranging between $0.20 \leq y \leq 0.30$. Furthermore, depending upon the fabrication route and raw materials used for nuclear fuel processing, *i.e.* upon cation distribution homogeneity, local high and low Pu content zones might be present within the fuel. These local variations in the plutonium content (y) might go up to ~0.45 or down to ~0.15 in the case of co-converted powders [2]. In the UO_2–PuO_2–Pu_2O_3 sub-system, corresponding to the domain of interest for nuclear fuel for future SFRs, $U_{1-y}Pu_yO_{2-x}$ mixed oxides with high plutonium content (y > 0.20) are multi-phasic at room temperature [2–16].

In this system, a miscibility gap exists and is composed of two fluorite face-centered cubic *fcc* phases for the lower Pu contents ($0.20 \leq y \leq 0.45$) and of an *fcc* phase in equilibrium with an α-Pu_2O_3-type body centred cubic *bcc* phase in the higher plutonium content range [5–9]. The two phases constituting the hypo-stoichiometric mixed oxides exhibit different oxygen content and are so called “high-oxygen” and “low-oxygen” phases, respectively [13–16].

The effect of fast cooling rate on phase equilibria, O/M ratio and microstructure of $U_{1-y}Pu_yO_{2-x}$ was presented in previous studies

* Corresponding author. CEA, DEN, DTEC, Marcoule, 30207, Bagnols-sur-Cèze, France.
E-mail address: romain.vauchy@cea.fr (R. Vauchy).

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[13,14]. However, to our knowledge, very slow cooling rates as those used in this work (0.005 K s^{-1}), have never been studied by high-temperature X-ray diffraction (HT-XRD). Therefore, the aim of the present work was to investigate the variations in O/M ratio and structural changes of uranium–plutonium mixed oxides $U_{1-y}Pu_yO_{2-x}$ with y = 0.15; 0.28 and 0.45 when subjected to very slow cooling rates under the same thermodynamic conditions as in previous studies within the scope of comparing the associated results [13,14]. Furthermore, lattice contraction of the three considered uranium–plutonium mixed oxides was also investigated during cooling.

2. Materials and methods

2.1. Materials

The uranium dioxide powder was produced by a wet fabrication route based on the formation of ammonium diuranate (ADU) from uranyl nitrate precipitated with ammonia. The obtained particles were then atomized, dried and calcinated, leading to spherical-shaped agglomerates of around 20 μm. Plutonium dioxide powder was produced by precipitation of a plutonium nitrate solution with oxalic acid to form plutonium oxalate. The particles were heated in air at 923 K and parallelepiped-shaped PuO_2 particles were obtained with an average size of 15 μm.

Uranium–plutonium mixed oxide samples $U_{1-y}Pu_yO_2$ were obtained by mixing UO_2 (respectively 1−y = 0.85, 0.72 and 0.55) with PuO_2 (respectively y = 0.15, 0.28 and 0.45). Each of these three mixtures was then micronized by co-milling in order to improve the U–Pu distribution in the final material. Then, each of the powders was pressed into ~2 g pellets at ~400 MPa, sintered at 2023 K for 24 h under Ar + 5% H_2 + ~1500 volume per million (vpm) H_2O and slowly cooled at ~0.01 K s^{-1}. These conditions were determined according to the thermodynamic model proposed by Guéneau et al. [17] to obtain stoichiometric compounds (Oxygen/Metal = 2.000) at room temperature. The obtained pellets were free from defects (cracks, exacerbated pores …) with a high density (>95% of the theoretical density). The average grain size was determined by observing the microstructure of polished dense pellets after chemical etching and was equal to 30–40 μm regardless of the Pu content (Fig. 1). The detailed fabrication process is described elsewhere [18].

2.2. High-temperature X-ray diffraction

XRD measurements were performed at ambient pressure and various temperatures with a Bragg–Brentano θ–θ BRUKER D8 Advance X-ray diffractometer using copper radiation from a conventional tube source ($K\alpha_1$ + $K\alpha_2$ radiation: λ = 1.5406 and 1.5444 Å) at 40 kV and 40 mA, and a LynX'Eye fast-counting PSD detector with an opening angle of 3° 2θ. The entire apparatus resides in its own custom-built nitrogen-filled glove-box dedicated to handling of nuclear materials at the LEFCA facility (CEA Cadarache, France). The diffractometer is equipped with heating stage from MRI PhysikalischeGerate GmbH TC-Radiation of volume 0.5 L, allowing heating of the sample up to 2273 K. Under reducing atmosphere, it uses both a molybdenum strip as a direct heater and a tantalum radiant heater. After each setup adjustment, a temperature calibration was carried out in steps of 100 K from room-temperature to 1973 K, using tungsten powder (ALDRICH, 99.999%). Tungsten lattice parameters as a function of temperature were taken from Refs. [19,20]. Temperature calibration was repeated several times. Calibration results were then compared, giving a constant temperature uncertainty of 15 K across the temperature range used. Rocking curve and displacement corrections were systematically applied to take into account the angular position and displacement of the strip. Full powder diffraction patterns were obtained by scanning from 22° to 145° 2θ in isothermal conditions at each temperature. A counting time of 0.3 s per step and step-intervals of 0.02° 2θ were chosen.

2.3. HT-XRD data refinements

Contrary to some of our previous studies [13,14], the angular range of the full powder diffraction patterns made it possible to determine lattice parameters and phase fractions as a function of time and temperature. Powder patterns were refined according to the Pawley [21] or the Rietveld [22] methods, based on the fundamental parameter approach [23] available in the DIFFRACplus TOPAS V4 software package [24]. The line profile shapes are described by convoluting the wavelength distribution of the emission profile, considering the instrument geometry and aberrations and physical properties of the sample. The microstructural contributions were simulated with a physical broadening function added to the refinement. As the fundamental parameter approach adequately fits the instrumental contributions to the observed peak profiles (geometry, tube type and slit system), a standard refinement of sample effects such as crystallite size can be performed. The background was approximated by a Chebyshev polynomial function with three terms. The refinement procedure first considers the zero detector and background parameters, then lattice parameter and crystallite size. The uncertainty on the lattice parameter is estimated less than 0.001 Å at any temperature.

2.4. Atmosphere control

The oxygen partial pressure pO_2 of the gas used here (He + 5% H_2 + z vpm H_2O), controlled *via* its moisture content z, was generated by a SETNAG yttria stabilized zirconia oxygen pump operating at 1073 K. Furthermore, pO_2 was also monitored using a similar device operating at 948 K. The moisture content z of the gas was also measured and recorded using a VAISALA DM70 capacitive

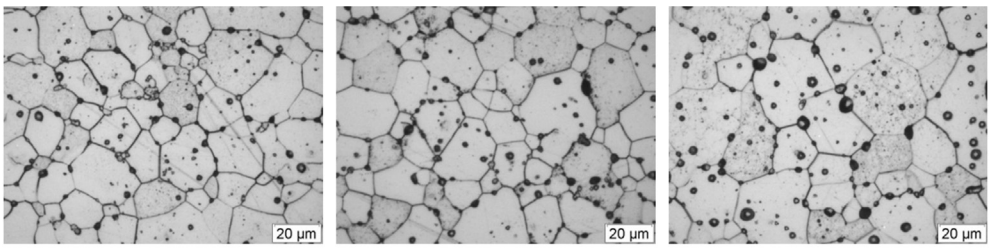

Fig. 1. Microstructures of $U_{1-y}Pu_yO_2$ mixed oxides after chemical etching.