Phase Equilibria in the Uranium-Plutonium-Oxygen Ternary Phase Diagram at \((U_{0.55},Pu_{0.45})O_{2-x}\) and \((U_{0.45},Pu_{0.55})O_{2-x}\)

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Abstract

In the present experimental study, after studying the impact of phase separation on \((U_{1-y},Pu_y)O_{2-x}\) MOX fuel at \(y=0.45\) and 0.55 at room temperature, phase equilibria has been investigated at high temperature up to 1700K by High Temperature X-Ray Diffraction measurements. We provide new data on the phase separation temperature, demonstrating that phase equilibria are highly influenced by fuel composition. In addition, data on Linear Thermal Expansion Coefficient have been calculated for corresponding hypo-stoichiometric solid solution at high temperature and compared to literature. We believe these results might further assess the description of U-Pu-O phase diagram.

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Keywords: Uranium; Plutonium; Phase Diagram; Fuel; XRD; Phase Equilibria; O/M

1. Introduction

Due to their relevance in fast breeder reactors for the IV\textsuperscript{th} Generation, interest for plutonium rich mixed oxide MOX fuels is increasing, particularly on hypo-stoichiometric MOX for Sodium Fast neutron nuclear Reactors (SFR). However, heating and cooling during sintering as well as fission process can induce, according to plutonium content, phase separations in the material. Therefore fuel properties can be significantly affected such as thermal cracking, thermal expansion, thermal conductivity and gas release. Although \((U_{1-y},Pu_y)O_{2-x}\) are

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extensively investigated at stoichiometric state (x=0) on the wide range of Pu [1-3], hypo-stoichiometric domain of U-Pu-O phase diagram (x>0) is complex and still incomplete.

At room temperature, for relatively low plutonium content MOX (y<0.15), a solid solution is observed up to all plutonium cations are trivalent. At higher plutonium content, the reduction of plutonium cations is responsible for a phase separation of the cubic lattice. The hypo-stoichiometric U-Pu-O system exhibits different multiphasic equilibria according to plutonium and oxygen contents: while a miscibility gap of fluorite phase is observed up to almost y=0.40, a triphasic domain, composed of two fluorite phase plus a sesquioxyde α-Pu₂O₃ type phase, exists at higher contents [4].

Some studies on phase separation versus temperature were performed at different plutonium content by High Temperature X-Ray Diffraction (HT-XRD) measurements [3,5] or Differential Thermal Analysis (DTA) [6-10]. While the critical temperature, the highest phase separation temperature, is measured for PuO₂ near 1000K [11,12], addition of uranium leads to a decrease of this temperature and the phase separation temperature at y=0.20 is measured at 430K [7]. Equilibria are clearly depending on O/M ratio of samples. These experimental data are in relatively good agreement although some contradictions observed at very high plutonium content with modeling data calculated by a thermodynamical model [13]. In addition, all authors confirm the difficulty to accurately measure such solid-solid phase transition at low temperature.

A review of Martin and Carbajo et al. [14,15] of Linear Thermal Expansion Coefficient (LTEC) results established that no contribution of plutonium content is observed on the LTEC by comparing UO₂, PuO₂ and (U₁−y,PUy)O₂ data. However, a diminution of O/M ratio induces a real effect on the evolution of lattice parameter with a significant increase when the reduction of the MOX goes on. In the review of Martin [14], the LTEC recommendation for hypo-stoichiometric MOX has been assessed in the range of 1.94≤O/M≤2.00 at 293≤T≤1273K.

2. Experimental

2.1. Starting samples

Uranium-plutonium mixed oxides containing y=0.45 and 0.55 of plutonium were elaborated by a co-grinding process of UO₂ and PuO₂ powders, already described in [4]. Stoichiometric samples were first sintered to obtain the best homogeneous (U₁−y,PUy)O₂ solid solution. Sample at y=0.45 is slightly containing metallic inclusions present in starting PuO₂ powder (white spots in Figure 1). The homogeneity of plutonium distribution was already characterized in [4]. These samples were then reduced in situ in the high temperature chamber of the XRD.

Plutonium content of both samples was measured by chemical potentiometric titration [4]: y=0.4601(6) and y=0.538(1) for y=0.45 and 0.55, respectively. A good agreement is observed between measured and expected Pu contents.

The O/M ratio of our samples was determined by gravimetric method: a considerable care was taken to weight samples before and after a reducing thermal treatment in a heating furnace where Ar+5%H₂ was applied as a reducing atmosphere. The determined O/M ratios at room temperature were respectively equal to 1.912(3) and 1.896(3) for y=0.45 and 0.55.

2.2. In situ high temperature X-ray diffraction characterization

XRD measurements were performed at ambient pressure as a function of temperature with a Bragg–Brentano θ-θ BRUKER D8 Advance XRD using copper radiation from a conventional tube source (Kα₁+ Kα₂ radiation, λ=1.5406Å and 1.5444Å) used at 40kV and 40mA and a LynX’Eye fast counting PSD detector. The instrument is implemented in a glovebox dedicated to the handling of nuclear materials and filled with nitrogen.
After each setup adjustment, a temperature calibration was carried out in steps of 100K from room temperature up to 1700°C using tungsten powder (ALDRICH, 99.999%). Admitted lattice parameters as a function of temperature for tungsten were taken from literature. The analysis of the results allows the determination of a constant temperature uncertainty of ±10K regardless of temperature.

Thermal treatment was specially set up to observe in situ phase separation after a reducing treatment of monophasic stoichiometric samples in a chamber (vol. 0.5L) to using both a molybdenum strip as a direct heater and a tantalum radiant heater. Samples were first heated at a very fast rate (300K.min⁻¹) to avoid a phase separation. The thermal treatment took place at 1750K during 5h and measurements of the (311) peak of cubic structure, in angular domain of 54° to 56°, were performed to follow the progress of reduction. Then, samples were similarly studied during cooling and a subsequent heating at slow kinetic rate of 3K·min⁻¹ according to measurement step at each 50K. Powder diffraction patterns were obtained by scanning a broad angular range from 25° to 145° 2θ in isothermal conditions. At the end, each investigation is achieved at an entire time of 30h approximately and more than one hundred diffractometers are refined according to the Pawley [16] and Rietveld [17] methods.

3. Results and discussion

At room temperature, comparison of optical micrographies of stoichiometric versus hypo-stoichiometric samples reveals severe effects of the phase separation on MOX pellets. While the microstructure of stoichiometric sample is dense and monophasic, a radically different microstructure is observed for biphasic samples (Figure 1). The phase separation induces damages with many fractures increasing with the plutonium content. Such a result is of main interest regarding the fuel design, as well as fuel modeling in reactor.

![Figure 1: Microstructure (U₁₋ₐ,Puₐ)O₂₋ₓ MOX for y=0.45 and 0.55 without chemical etching x20; (a) at stoichiometric state; (b) at hypo-stoichiometric state with original microstructure (clear grey) and second new microstructure (dark grey)](attachment)

Evolution of the (311) peak of cubic structure versus time during the reduction plateau is given in Figure 2. As expected, a shift of the peak to lower angles is observed, corresponding to an increase of the lattice parameter confirming the reduction process. The reducing rate is significant during the first hour of the treatment and is
then moderate. At the end of the thermal treatment, evolution of angular displacement is very small. Consequently we consider that the reducing treatment is satisfying considering element diffusion rates in the materials for a reasonable measurement time.

![Figure 2: Evolution during reducing treatment of the (311) peak of cubic phase for MOX at y=0.45 (left) and 0.55 (right); peak intensities being proportional to the grey levels](image)

Then complete powder diffraction patterns were measured by scanning from 25° to 145° 20 in isothermal conditions during cooling. As an example, the evolution of the (311) diffraction peak provides interesting information (Figure 3). A contraction of the cubic structure is first observed with the decrease of temperature. Then, a phase separation is detected in both samples in the 700<T<900K range with the emergence of a second (311) peak at lower angles corresponding to a more reduced cubic phase. At y=0.55, the deviation angle between both cubic phases is higher, which means that the gap in O/M ratio is much more important at this plutonium content.

![Figure 3: Evolution of the (311) peak of cubic phase during cooling for y=0.45 (left) and 0.55 (right); peak intensities are proportional to the grey levels](image)

The corresponding phase separation temperatures are accurately established from lattice parameter values and phase quantification obtained from the Rietveld method (see
Figure 4) at 790±10K and 850±10K for y=0.45 and 0.55, respectively. Each phase separation temperature is very close to the critical temperature. In agreement with previous studies [3,6,10], we demonstrate here that the phase separation temperature increases with the plutonium content. Following cooling, the same measurements were performed on heating and identical phase separation temperatures are determined. In addition, a departure of the lattice parameter from a linear thermal variation is found from temperature higher than 1200K for both investigations. This deviation could result from a decrease in O/M ratio at very high temperature inducing an increase in the lattice parameter due to additional oxygen defect in the structure. In such a case, the O/M ratio between phase separation and 1200K could be constant on this temperature range.

In this complete refinement study from room temperature to the phase separation, two cubic fluorite phases are observed. No sesquioxide α-Pu₂O₃ type phase was detected on the basis of a previous investigation at room temperature [4]. This could be explained by a modification of the HT-XRD using a molybdenum strip as a direct heater allowing high temperature measurements, contrary to a rotating sample-holder in our previous work, enhancing the resolution of data. Considering the very slight amount of sesquioxyde phase at room temperature, observation is difficult at high temperature considering the increase in the background noise of resulting diffractogrammes due to thermal agitation in the structure.

Then, our results at y=0.45 are compared with HT-XRD data at y=0.42 of Markin and Street [3] performed in the wide 1.789≤O/M≤2.000 range (Figure 5). Agreement between all experimental data is excellent and demonstrates the veracity of our investigation. Consequently O/M of our sample at the phase separation temperature can be estimated at O/M=1.91 considering Markin and Street thermogravimetric measurements. This
value is very close to that measured at room temperature within uncertainties, meaning that evolution of O/M ratio is insignificant in this temperature domain.

Figure 5: Comparison between our high temperature XRD results with those of Markin and Street [3]

Figure 6: The effect of O/M ratio on the linear thermal expansion at 298≤T(K)≤1200 of hypo-stoichiometric MOX

To go further, we compared the Linear Thermal Expansion Coefficient (LTEC) for y=0.45 and 0.55 with that recommended by Martin [14] as a function of O/M ratio according to data from literature [18-21]. While Martin recommendation was established in the 293≤T(K)≤1273 range from almost as dilatometry experiments, our results and those of Roth and al. [18] are the first obtained from lattice parameters for hypo-stoichiometric MOX. Values of LTEC at temperature T are calculated with the equation [13]:

\[ \text{LTEC} = \text{constant} \times (O/M - \text{ratio}) \]
LTEC (T) = \left(\frac{1}{a_{298}}\right) x \left(\frac{\partial a_T}{\partial T}\right),

where \(a_T\) is the lattice parameter at temperature T and \(a_{298}\) is the lattice parameter at the reference temperature at 298K. LTEC are determined at temperatures higher than the phase separation up to 1200K and \(a_{298}\) value is extrapolated from the linear regression of the lattice parameter as a function of temperature. Calculated LTEC are compared to Martin's recommendation (Figure 6). Our results are the first in a so reduced domain, highlighting the effect of O/M ratio on the LTEC. Within uncertainties on O/M ratio measurements, a correct agreement is observed with Roth et al. data considering their evolution with O/M ratio. However, the equation of Martin is not matching well with our results. This might suggest a reassessment of his recommendation. Further research is ongoing with similar HT-XRD investigations at different plutonium content.

4. Conclusions

Our investigation provides important new data regarding plutonium-rich MOX fuels as a function of temperature. These results might further assess the description of U-Pu-O phase diagram and contribute to bring further insight into the properties of next generation nuclear fuel.

References

[1]: F. Thuemmler, R. Theisen, E. Patrussi, Technical Report KFK-543, Kernforschungszentrum, Karlsruhe, Germany, p.44.
[2]: N.H. Brett, A.C. Fox, J. Inorg. Nucl. Chem. 28 (1966) 1191-1203.
[3]: T.L. Markin, R.S. Street, J. Inorg. Nucl. Chem. 29 (1967) 2265–2280.
[4]: T. Truphémus, R.C. Belin, J.C. Richaud, M. Reynaud, M.A. Martinez, I. Félines, A. Arredondo, A. Miard, T. Dubois, F. Adenot, J. Rogez, Accepted manuscript in J. Nucl. Mater.
[5]: G. Dean, J.C. Boivineau, P. Chereau, J.P. Marcon, in: Plutonium 1970, ed. W.N. Miner, New York, 1970, p.753.
[6]: C. Sari, U. Benedict, H. Blank, J. Nucl. Mater. 35 (1970) 267–77.
[7]: M. Koizumi, Y. Nakamura, Am. Ceram. Soc. Bull. 48(4) (1969) 476.
[8]: Y. Sagayama, Proc. Global 2005, Tsukuba, Japan, October 9-13, 2005, p.380.
[9]: M. Kato, K. Morimoto, A. Komeno, S. Nakamichi, M. Kashimura, Proc. Actinide and Fission Product Partitioning and Transmutation, Tenth Information Exchange Meeting OECD/NEA, Mito, Japan, 6-10 October, 2008, p.201.
[10]: A. Komeno, M. Kato, H. Uno, K. Takeuchi, K. Morimoto, M. Kashimura, Actinides 2009, in: IOP Conf. Series: Materials Science and Engineering, vol. 9, 2010, p.012016.
[11]: T.D. Chikalla, C.E. McNeilly, R.E. Skavdahl, J. Nucl. Mater. 12 (2) (1964) 131.
[12]: C.R. Gardner, T.L. Markin, R.S. Street, AERE Report 4602 (1964).
[13]: C. Guéneau, N. Dupin, B. Sundman, C. Martial, J.-C. Dumas, S. Gossé, S. Chatain, F.D. Bruycker, D. Manara, R.J.M. Konings, J. Nucl. Mater. 419 (2011) 145-167.
[14]: D. Martin, J. Nucl. Mater. 152 (1988) 94–101.
[15]: J.J. Carbajo, G.L. Yoder, S.G. Popov, V.K. Ivanov, J. Nucl. Mater. 299 (2001) 181–198.
[16]: G.S. Pawley, J. Appl. Cryst. 14 (1981) 357-361.
[17]: H.M. Rietveld, J. Appl. Cryst. 2 (1969) 65-71.
[18]: J. Roth, M.E. Hubert, J.R. Chery and C.S. Caldwell, Trans. Am. Nucl. Soc. 10 (1967) 457.
[19]: R. Lorenzelli, M. El Sayed Ali, J. Nucl. Mater. 68 (1977) 100-103.
[20]: J.M. Leblanc and H. Andriessen, EURATOM/USA Rep. EURAEC-434 (1962).
[21]: R.L. Gibby, Hanford Quarterly Technical Rep., July-Sep. 1974, Ed. E.A. Evans, HEDL-TME 74-3, Vol. 1, P. A-8.