

In-situ High Temperature X-ray Diffraction Study of the Am-O System

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ABSTRACT

In the frame of minor actinide recycling, (U,Am)O₂ are promising transmutation targets. To assess the thermodynamic properties of the U-Am-O system, it is essential to have a thorough knowledge of the binary phase diagrams, which is difficult due to the lack of thermodynamic data on the Am-O system. Nevertheless, an Am-O phase diagram modelling has been recently proposed by Gotcu. Here, we show a recent investigation of the Am-O system using *in-situ* High Temperature X-ray Diffraction under controlled atmosphere. By coupling our experimental results with the thermodynamic calculations based on the Gotcu model, we propose for the first time a relation between the lattice parameter and the departure from stoichiometry.

INTRODUCTION

Minor actinides (MA) like Am, Np and Cm significantly contribute to the long-term radiotoxicity of the spent nuclear fuel. One of the options envisaged for reducing the nuclear waste inventory is the transmutation of these elements in fast neutron reactors. The possibility of using advanced fuels containing MA has led to the necessity of investigate the structural and thermodynamic properties of these elements and their compounds. In this frame, the attention is mainly focused on U-Am mixed oxides [1], [2].

The assessment of the thermodynamic behavior of the U-Am-O ternary system is not possible without a thorough knowledge of the simpler binary systems. Unfortunately, the Am-O system is far from being well known: its phase diagram is still not defined, even if various representations have been proposed [3] [4]–[7].

In the O/Am ratio ranging from 1.5 to 2.0, one dioxide, two sesquioxides and one intermediate cubic phase (C-AmO_{1.62}) have been identified [8]–[10]. The FCC fluorite phase AmO_{2-x} has a large hypo-stoichiometric existence domain above 1300 K; for this phase, DTA measurements pointed out the existence of a miscibility gap [4]. The sesquioxide exists in two crystal structures: the hexagonal A-type *P-3m1* Am₂O₃ (s.g. (space group) 164, prototype La₂O₃) and the BCC C-type Am₂O₃ (*Ia-3* structure, s.g. 206, prototype Mn₂O₃) [9], [10]. Moreover, another C-type intermediate phase with an O/Am around 1.61 has been reported for temperature higher than 600 K [10]. However, the existence domains of these phases are not well defined. An attempt to give a coherent version of the Am-O phase diagram was made by Thiriet and Konings [6]. Recently, a thermodynamic model of the Am-O system with the Calphad method has been proposed by Gotcu *et al.*, [11]. However, because of the lack of thermodynamic data, some simplifications were necessary for the modelling: the intermediate C-type phase (AmO_{1.62}) was considered with a fixed stoichiometry and, for the sesquioxides, only the hexagonal form was considered. Here, the Calphad model of Gotcu was considered as a starting point for an *in-situ* High-Temperature X-ray Diffraction (HT-XRD) study of the Am-O system. The model predictions were used to choose the temperatures and atmospheres for the experiment, whose

main aim was investigating the AmO₂ lattice parameter variation induced by thermal expansion and hypo-stoichiometry.

EXPERIMENT

Thermodynamic computations

The Am-O Calphad model of Gotcu [11], which is currently available in the TAF-ID (Thermodynamic of Advanced Fuels- International Database) [12], was used to perform thermodynamic computations with the ThermoCalc software. Some of the results are represented in Figure 1: the dashed curves on the phase diagram represent the equilibrium points in the temperature range 750-1400 K under fixed Oxygen partial pressures (pO₂).

According to the Calphad model, the AmO₂ starts to be reduced under air at around 1200 K. The miscibility gap should be observed for oxygen pressures ranging from 10⁻⁶ atm to 10⁻⁵ atm. At 1400 K, the appearance of the hexagonal sesquioxide A-Am₂O₃ is expected for oxygen pressure lower than 10⁻⁶ atm. Finally, for 1000 K < T < 1200 K, the AmO_{2-x}-AmO_{1.62} two-phase region is expected for reducing atmospheres (pO₂ ≤ 10⁻⁷ atm).

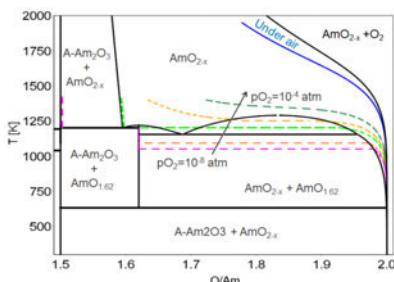


Figure 1. Calculated phase diagram after Gotcu *et al.*, [11] and the results of thermodynamic computations. Solid line: equilibrium points under air; dashed lines: equilibrium points with pO₂ ranging from 10⁻⁸ atm to 10⁻⁴ atm with steps of one decade.

Experimental settings

The experiment was carried out in the LEFCA facility at CEA/Cadarache, using an entire nuclearized HT-XRD set-up, which was described in previous works [3], [13]. The heating stage was a Pt metal strip. The atmosphere was controlled through a flowing gas whose pO₂ is measured and adjusted at the inlet of the chamber with an oxygen pump in order to have the desired Oxygen potential. In order to achieve the pO₂ range chosen with the thermodynamic computations (10⁻⁸-0.25 atm), the flowing gas used in the measurements were air and He/O₂(500ppm).

The diffraction pattern refinement and the lattice parameter calculation were performed using Pawley method on the DIFFRACplus TOPAS V4 software.

The AmO_{2-x} powder used in this experiment was obtained by an oxalic route in the CEA Marcoule Atalante facility [14]. ICP-AES analysis showed several percent of impurities, especially Ce (1.7(5) wt%). Moreover, calculations predicted 0.30 wt% of ²³⁷Np from ²⁴¹Am α

decay. Further characteristics of this AmO_{2-x} powder were reported in a previous work [3]. Only few mg(15-20 mg) of powder were available for this study.

DISCUSSION

Measurements under air

The lattice parameter thermal expansion of americium dioxide was measured between Room Temperature (RT) and 1900 K under air. First, the sample was heated at 1900 K for five hours in order to recover the effects of the self-irradiation. During cooling, diffraction patterns were acquired with steps of 100 K. In Figure 2, we show the lattice parameters resulting from these measurements (squares) and we compare them to the Fahey's data [15] (circles), which are limited to 1100 K.

The slope change of the thermal expansion at around 1200 K probably indicates the onset of the AmO_2 reduction, in fact the lattice parameter increases when the O/Am decreases. This is consistent with the Gotcu model [11], as shown by the triangles in Figure 2, which represent the computed O/Am ratios at different temperatures under air: the departure from stoichiometry (O/Am=2) is expected at $T \approx 1180$ K.

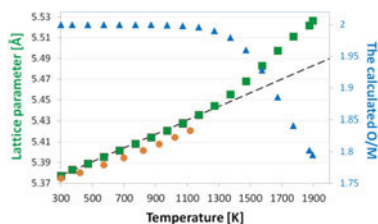


Figure 2. Lattice parameters of AmO_{2-x} (primary axis) and O/Am (secondary axis) as a function of T. ■: this work (under air). ●: Fahey data [15]. ▲: computed O/Am.

Measurements under reducing conditions

Measurements were performed under reducing atmospheres (10^{-8} atm $<$ $p\text{O}_2 <$ 10^{-5} atm) in the temperature range 1200-1500 K in order to investigate the phase boundary between AmO_{2-x} and the A- $\text{Am}_2\text{O}_3 + \text{AmO}_{2-x}$ two-phase region.

First, we tried to observe the hexagonal sesquioxide at $T = 1500$ K. According to the thermodynamic computations, the phase transition should occur at this temperature under $p\text{O}_2 \approx 2 \cdot 10^{-5}$ atm. The experiment was performed in two steps: the desired oxygen pressure was initially stabilized at RT and then the sample was heated up to 1500 K. The sequences of the measure are shown in Figure 3(a), in which a portion of the acquired diffraction patterns is reported. The result of this experiment is consistent with the model predictions: the AmO_2 was rapidly reduced and the characteristic peaks of the A- Am_2O_3 phase ($P-3m1$ structure) appeared in few minutes.

In further experiments, we attempted to explore the same two-phase region at lower temperature ($1200 \text{ K} < T < 1400 \text{ K}$). Measurements were performed under two reducing atmospheres: 10^{-7} and 10^{-8} atm. In both cases, the A- Am_2O_3 phase was not observed, but the obtained lattice parameters

Figure 3(b) are rather large: this indicates a very low O/Am ratio. Moreover, the values of the lattice parameters seem linearly related to that one measured for the AmO_{2-x} in the two-phase point at 1500 K: for this reason, we think that the sample composition was very near the phase boundary.

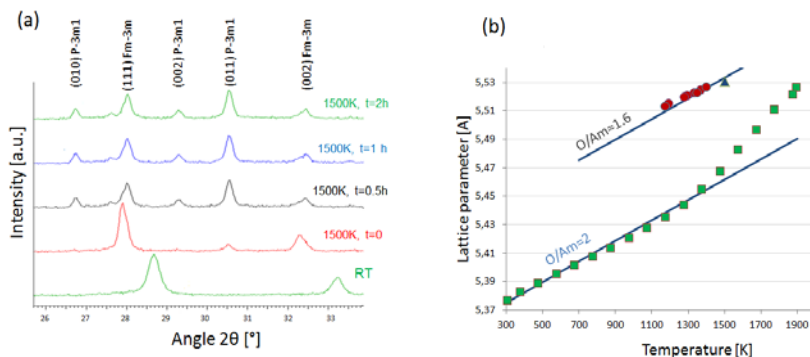


Figure 3. Experiments in reducing conditions. **(a)** Diffraction patterns of AmO_2 at RT and of $\text{AmO}_{2-x}+\text{Am}_2\text{O}_3$ at 1500 K and different times. **(b)** Lattice parameters of AmO_{2-x} . \blacksquare : measures under air; \blacktriangle : point in the $\text{AmO}_{2-x}+\text{Am}_2\text{O}_3$ region at 1500 K; \bullet : measures under 10^{-8} atm and 10^{-7} atm, between 1200-1400 K.

Relation between lattice parameter and composition

One of the problems in the interpretation of XRD experiments on AmO_{2-x} is the lack of data concerning the variation of the lattice parameter as a function of the O/Am ratio. For the first time, we propose a relation between the lattice parameter, the O/Am and the temperature based on a coupling of our experimental data and the thermodynamic computations. As we have seen, the measurements described in the previous sections seem consistent with the model, which justifies the use of the thermodynamic calculations to assess the sample composition during the experiment. Therefore, the computed O/Am ratios have been assigned to the experimental temperature-lattice parameter points of Figure (b). From the comparison with similar systems as UO_{2+x} and PuO_{2-x} [16], a linear relation between the quantities was supposed:

$$a(T, \text{O/Am}) = C_0 + C_1 \cdot T - C_2 \cdot \text{O/Am}$$

The C_0 , C_1 and C_2 constants were found by fitting the data with the least square minimization method; the resulting values are $C_0 \approx 5.7101$ [Å], $C_1 \approx 7.222 \cdot 10^{-5}$ [Å K⁻¹] and $C_2 \approx 0.1783$ [Å].

CONCLUSIONS

HT-XRD measurements were performed on AmO_2 powder both under air and under reducing atmospheres.

The lattice parameter thermal expansion of the AmO_2 was measured up to 1900 K under air, whereas data in literature were limited to lower temperature (1100 K). This experiment also showed that the onset of the americium dioxide reduction appears at around 1200 K.

The variation of the lattice parameter induced by hypo-stoichiometry was studied by exploring the phase boundary between AmO_{2-x} and $\text{AmO}_{2-x} + \text{A-Am}_2\text{O}_3$. The general consistency between these measurements and the thermodynamic computations based on the Calphad model of Gotcu [11] allowed the assessment of the O/Am for the observed experimental points. Thanks to the coupling of experimental data and computations, for the first time we proposed a relation between the AmO_{2-x} lattice parameter, the departure from stoichiometry and the temperature. This relation will be very useful for future investigations on the americium dioxide, allowing estimating the O/Am from the lattice parameter measurement.

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