New insight in the Am-O system by coupling experimental HT-XRD and CALPHAD modeling

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Context and Objectives

In the frame of **minor actinide recycling** in sodium cooled fast reactors, **(U, Am)O_2** mixed oxides 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[1]. Nevertheless, an **Am-O phase diagram** modeling has been recently proposed by Gotcu *et al.*[1] in which a fluorite-type dioxide, a sesquioxide and an intermediate phase are reported for an O/Am ratio ranging from 2 to 1.5. Here, we show an investigation of the Am-O system coupling thermodynamic modeling based on the **CALPHAD** method and ***in situ* high temperature X-Ray Diffraction (XRD)**.

Methods

Experimental Setup

Powder XRD was performed with a Bragg-Brentano θ-θ Bruker D8 Advance X-ray diffractometer using Copper radiation and a LynX'Eye fast-counting PSD detector. The **heating stage** is constituted by a Pt strip and a radiant heating element.

The **atmosphere is controlled** through a flowing gas whose partial oxygen pressure (**pO_2**) is measured and adjusted at the inlet of the chamber with a *Gen'Air* device (probe and pump oxygen) in order to have the desired **oxygen potential ΔGO_2**.

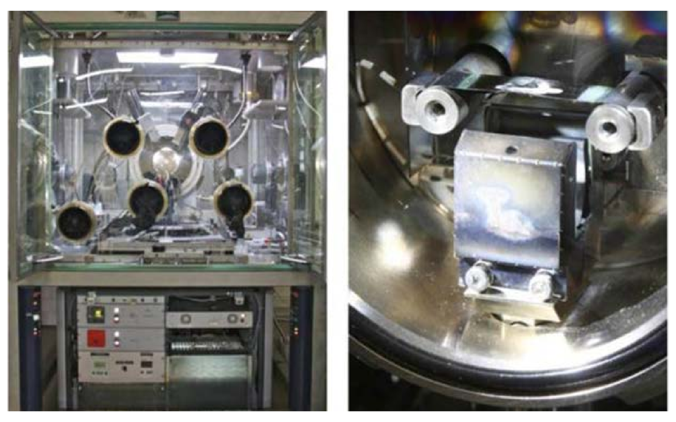


Fig. 1 The diffractometer glove box and the heating stage.

Thermodynamic Calculations

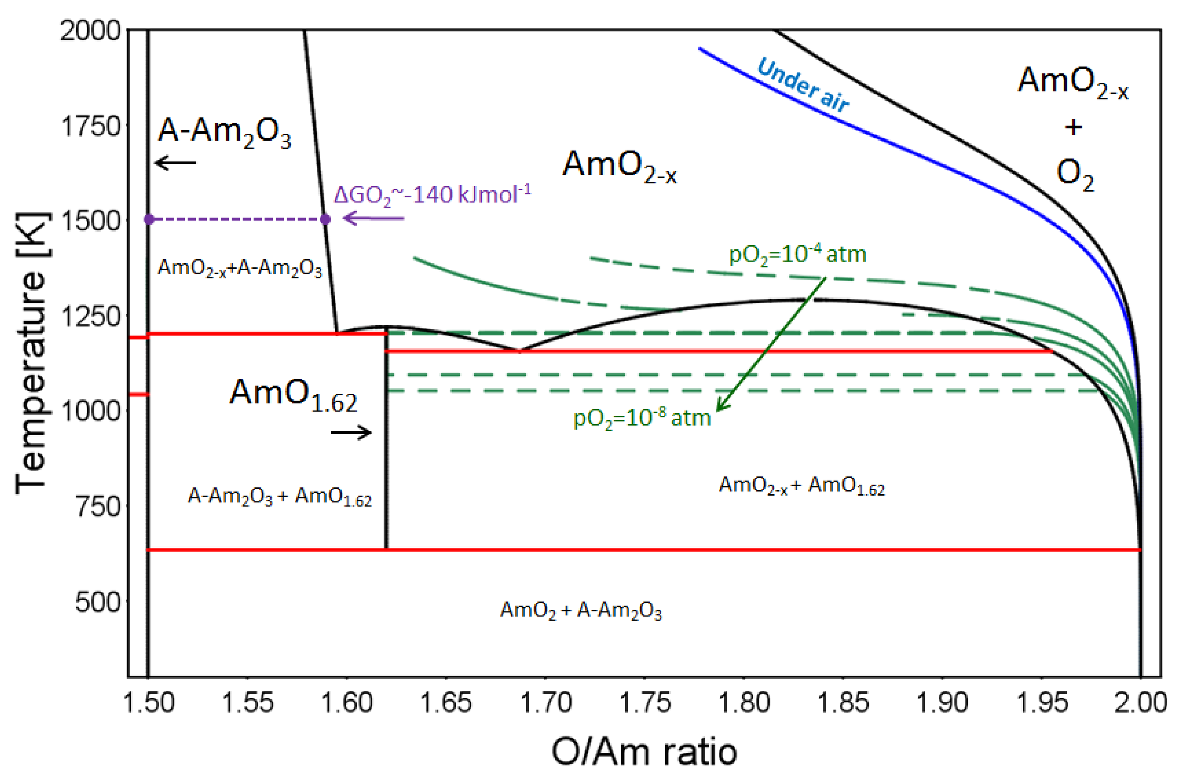
In order to set up the most interesting experimental conditions (temperature T and ΔGO_2), thermodynamic calculations based on the CALPHAD method were performed, using the **TAF-ID** (Thermodynamic of Advanced Fuels-International Database)[2] containing the model [1].

Thermo-Calc Software

A new improved thermodynamic assessment of the Am-O system was also performed. Both computations and modeling were performed using the *Thermo-Calc software*.

CALPHAD

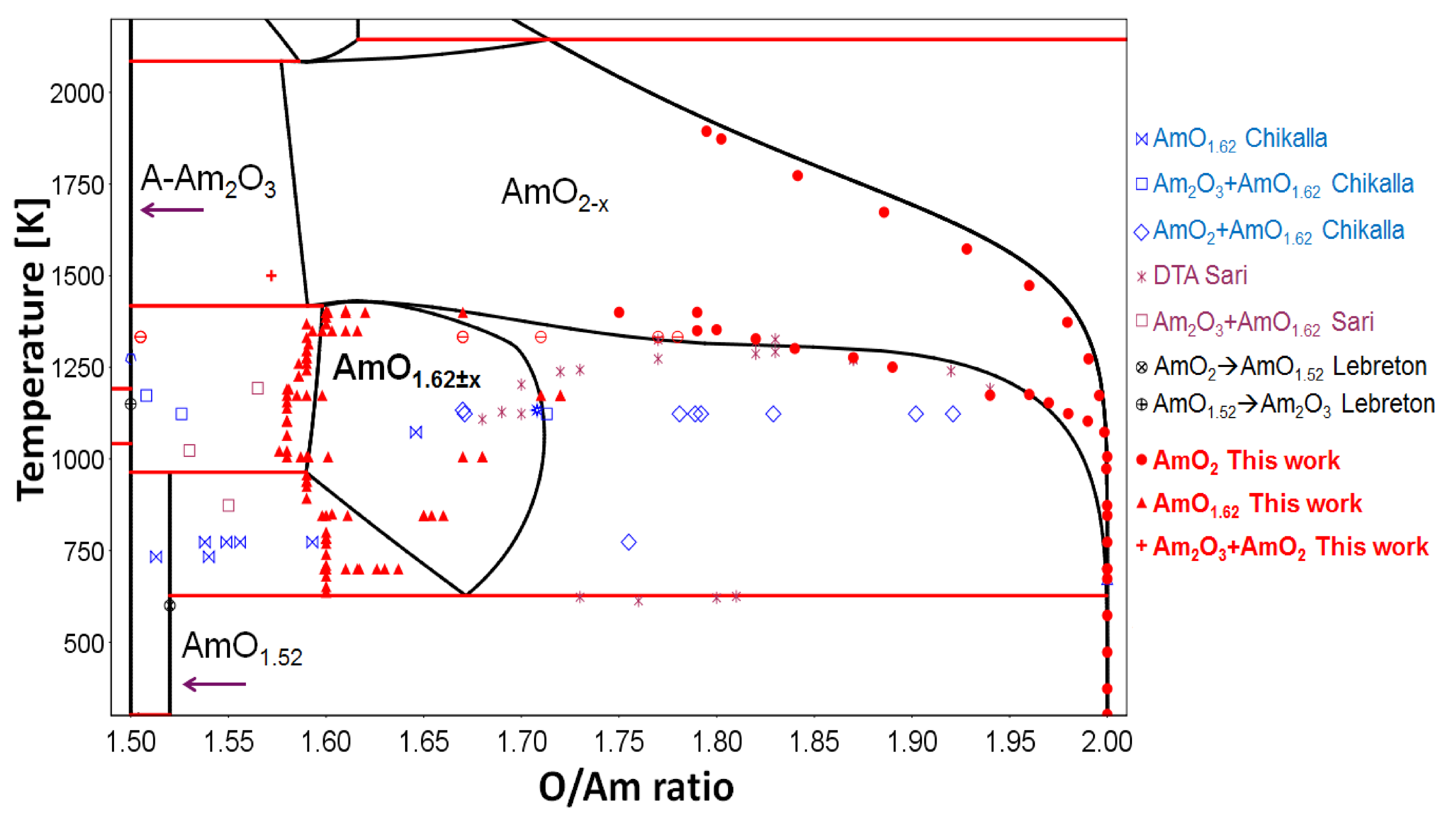
Calculations based on the literature model[1]



Thermodynamic calculations were performed in order to foresee the explored regions of the phase diagram:

Fig. 2: The phase diagram computed with the available model

Improved CALPHAD assessment



- The **$AmO_{1.62}$** composition domain was described
- The **$AmO_{1.52}$** phase was added
- The miscibility gap was not included in this model

Fig. 7: The phase diagram computed with the new model

EXPERIMENTAL RESULTS

Results in agreement with the literature model

The $AmO_{2-\delta}$ behavior at HT under air

- The slope change of the thermal expansion at **T≈1200K** indicates the starting of the AmO_2 **reduction under air**, in agreement with the model previsions

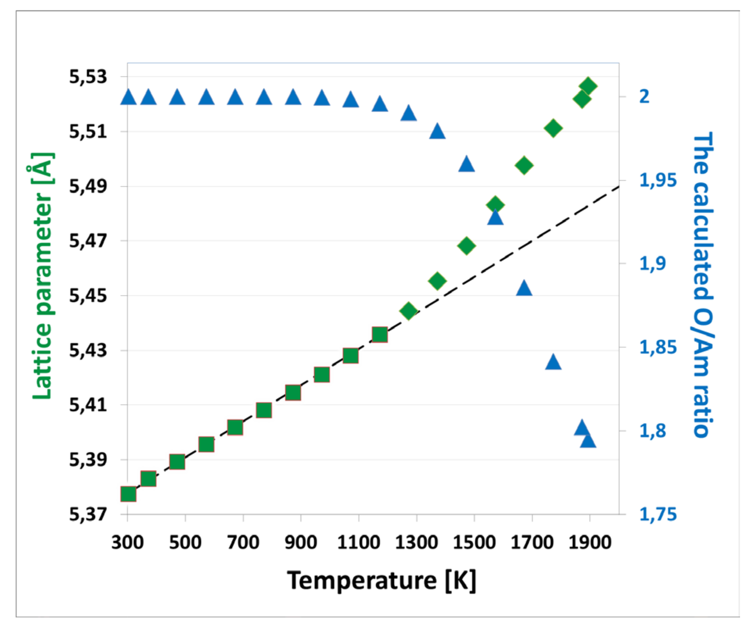


Fig. 3: Green points: measured lattice parameters during cooling from 1900K to RT under air; Blue points: the O/Am ratio calculated with Thermocalc.

The $AmO_{2-\delta}$/A-Am_2O_3 two-phase region

- At **T=1500K**, the hexagonal **A-Am_2O_3** phase was observed by imposing the **ΔGO_2** expected by the model (≈-140 kJ/mol)

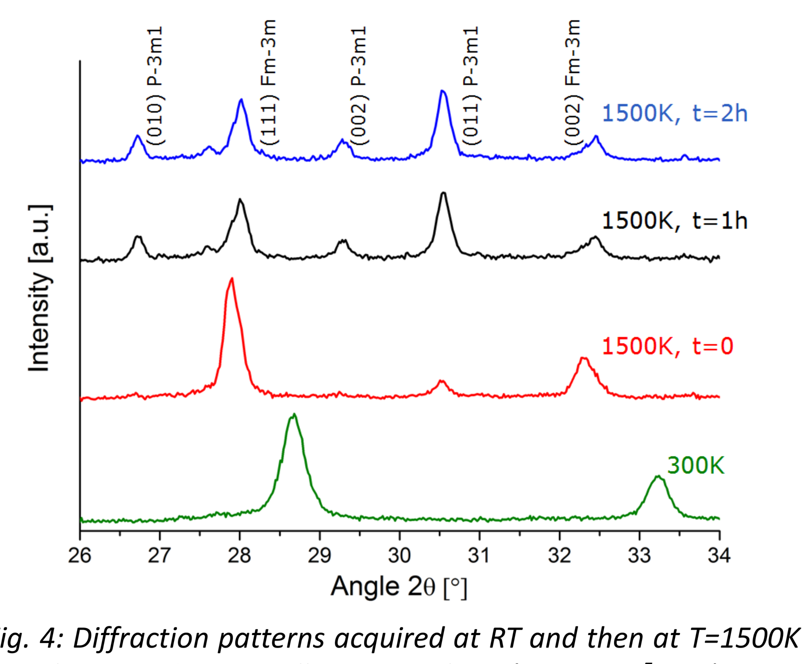


Fig. 4: Diffraction patterns acquired at RT and then at T=1500K for 2 hours under controlled atmosphere (pO_2≈2 10^{-5} atm).

The *reliable* data were fitted using the least square minimization in order to find a linear relation between **the Lattice Parameter a**, the **O/Am ratio** and **Temperature**.

This relation allowed a **coherent interpretation** of all the experimental data and lead to the **re-definition of the phase boundaries** of the phase diagram.

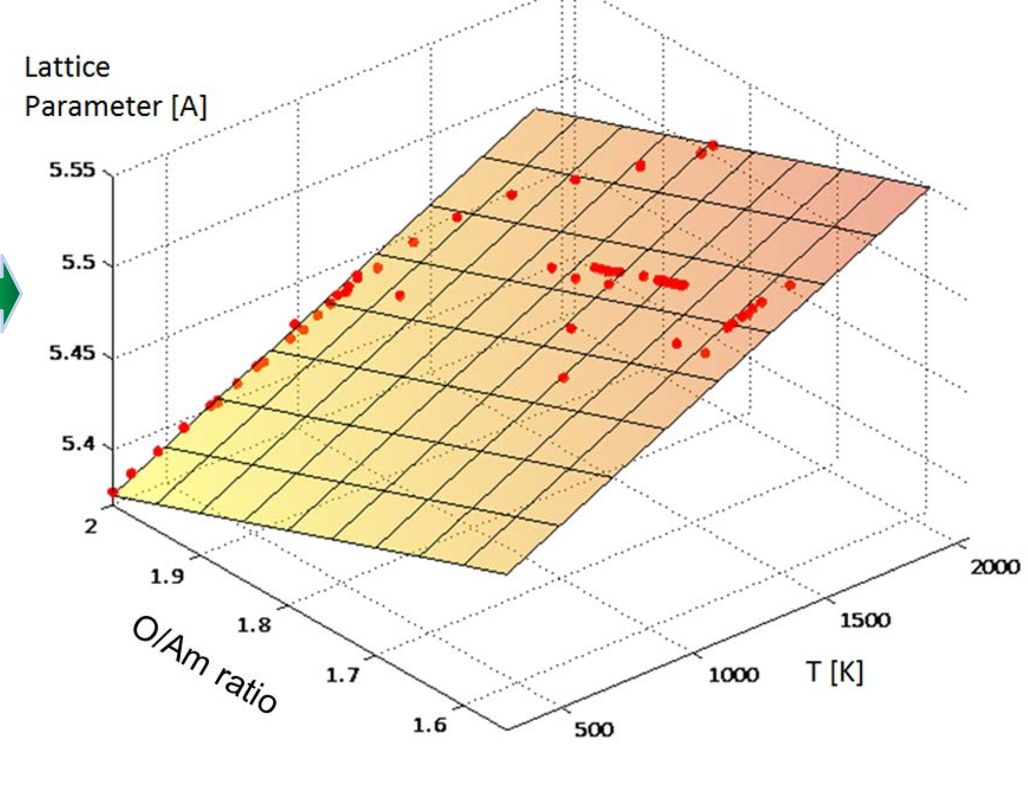


*Fig. 5: Fit of the "reliable" data: **a** as a function of **T** and **O/Am***

$$a\left(T,{}^{O}/_{Am}\right)=\ C_1\ +C_2T-C_3O/Am$$

New insight

Contrary to the Pu-O system, Iso-T measurements at 1280 K and 1210 K have not shown the presence of a **miscibility gap**. The AmO_{2-x} → $AmO_{1.62±x}$ phase transition was observed. **BCC $AmO_{1.62±x}$** was found to have a wide **composition domain.**

Isothermal measurement at 1210 K

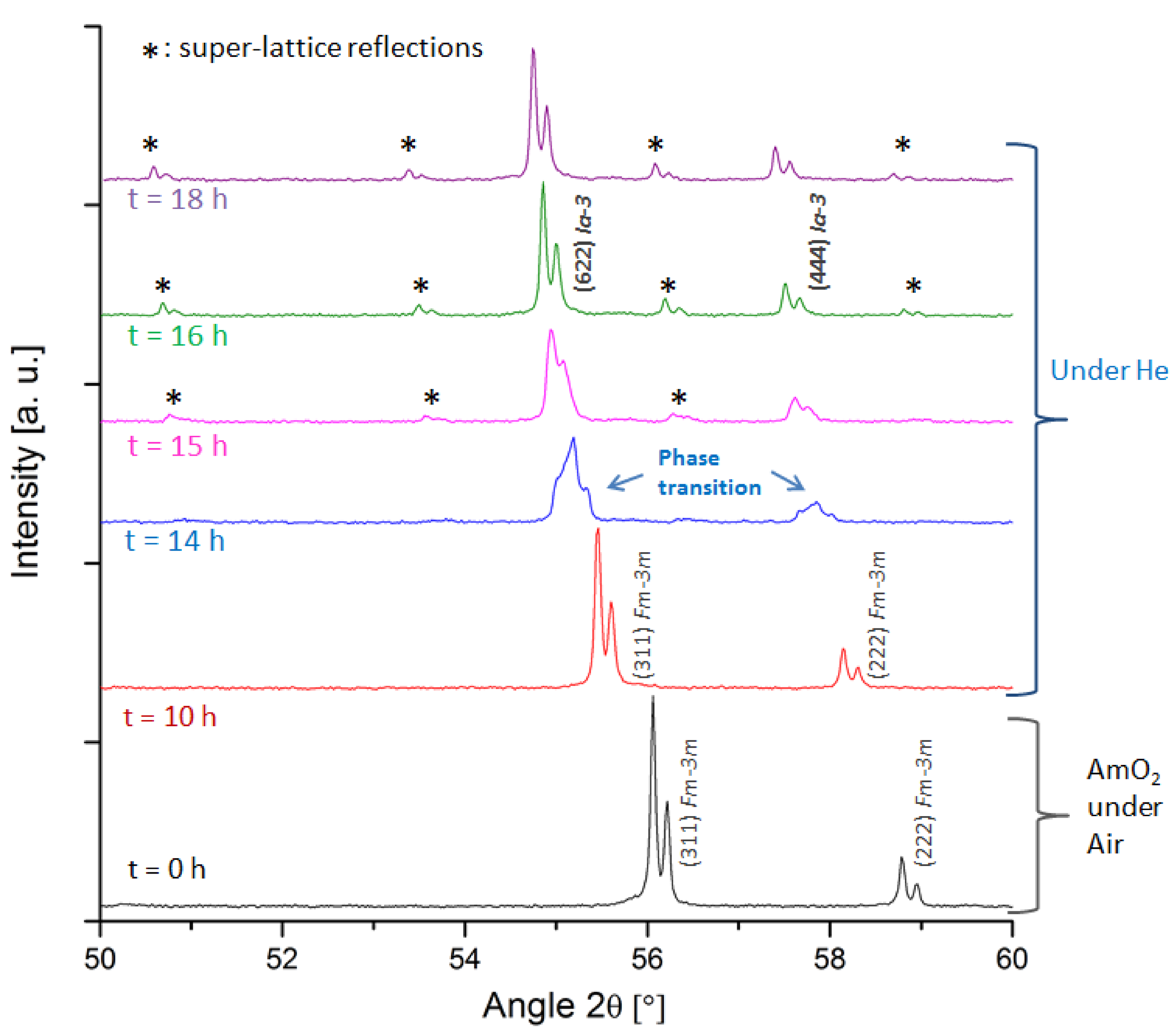


*Fig. 6: Diffraction patterns from an iso-T measurement at **1210 K** under He. After 14 h, the AmO_{2-x} → $AmO_{1.62±x}$ phase transition occurred. Then, the reduction of the $AmO_{1.62±x}$ was observed (shift of the peaks to lower angles), proving the existence of a composition domain*

Conclusions

In this work, an investigation of the Am-O system by HT-XRD was presented. The experimental conditions (T, ΔGO_2) were chosen according to thermodynamic computations based on the Gotcu Calphad model [1], with the aim of verify its accuracy. A good agreement between experimental results and calculations was found for the AmO_2 in the slightly hypo-stoichiometric region (experiments under air). The model has also proven to be able to predict the appearance of the A-Am_2O_3 phase at HT (1500K), but the agreement between results and calculation was lost at lower temperature. Using the least square minimization method, a **lattice parameter - O/Am - T** relation was found, which allowed a coherent interpretation of all the data and the definition of the phase boundaries of a *new* BCC phase. Finally, thanks to the new data acquired, an improved **Calphad assessment** was performed and a **new phase diagram representation** was proposed.

1. P. Gotcu-Freis, J.-Y. Colle, C. Guéneau, N. Dupin, B. Sundman, R. J. M. Konings, J. Nucl. Mater. 414 (2011) 408-421.
2. www.oecd-nea/science/taf-id.com
3. H. Lukas, S. G. Fries, Bo Sundma, *Computational Thermodynamic: The Calphad Method*, 2007.