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M3FT-15OR0202212: SUBMIT SUMMARY REPORT ON THERMODYNAMIC EXPERIMENT AND MODELING OF THE U-Y-O AND U-Pr-O SYSTEMS

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1. INTRODUCTION

Modeling the behavior of nuclear fuel with a physics-based approach uses thermodynamics for key inputs such as chemical potentials and thermal properties for phase transformation, microstructure evolution, and continuum transport simulations. Many of the lanthanide (Ln) elements and Y are high-yield fission products. The U-Y-O and U-Ln-O ternaries are therefore key subsystems of multi-component high-burnup fuel. These elements dissolve in the dominant urania fluorite phase affecting many of its properties. This work reports on an effort to assess the thermodynamics of the U-Pr-O and U-Y-O systems using the CALPHAD (CALculation of PHase Diagrams) method. The models developed within this framework are capable of being combined and extended to include additional actinides and fission products allowing calculation of the phase equilibria, thermochemical and material properties of multicomponent fuel with burnup.

2. LITERATURE REVIEW

The CALPHAD method relies on both thermochemical and phase equilibria data to refine the models. Therefore, a critical review of the studies reporting thermodynamic measurements is necessary to discover what data exist and select the most reliable subset when there are disagreements between authors. For the U-Pr-O system, the phase relations at 1250°C were determined by De Alleluia et al. [1]. However, with regard to equilibrium oxygen potentials (μ_{O_2}) only a study authored by Yamashita et al. [2] reports very limited results for the fluorite structure $U_{1-y}Pr_yO_{2\pm x}$ phase. Therefore, the μ_{O_2}-composition-temperature relationship for $U_{1-y}Pr_yO_{2\pm x}$ was determined from thermogravimetric analysis (TGA) measurements to accumulate sufficient thermochemical data to develop a compound energy formalism (CEF) model for $U_{1-y}Pr_yO_{2\pm x}$.

Conflicting phase relations in the U-Y-O ternary were determined experimentally by Bartram et al. [3] and Aitken and Joseph [4] with those of Bartram et al. [3] judged reliable [5]. Additionally, TGA determinations of μ_{O_2} vs O/M (oxygen to metal ratio) were made by Hagemark and Broli [6] and U, UO, and UO_2 equilibrium vapor pressures using Knudsen effusion mass spectrometry are reported by Nakajima et al. [7]. However, the UO vapor pressures over UO_{2+x} calculated using the well-accepted CEF model for pure $UO_{2\pm x}$ [8] are several orders of magnitude lower than the measurements reported by Nakajima et al. [7] at corresponding values of *x*; thus, the data reported in [7] was judged inconsistent and not used in the U-Y-O assessment.

3. EXPERIMENTAL

Urania powder (>99.85 mass % uranium oxide) from the Areva Company and Pr_6O_{11} from American Elements (>99.995 mass % Rare Earth oxide) were mechanically mixed, pressed into a disc (5mm in diameter and 1mm in height), and conditioned at 1350°C for 17 hrs in an oxygen atmosphere corresponding to $\log p_{O_2} = -13$ to both sinter and form a single phase solid solution with an approximate O/M = 2. A SPEX mill was then used to grind it back into powder for an additional mixing, pressing, and conditioning step followed by X-ray diffraction (XRD) analysis. As a representative example, the XRD pattern for $U_{0.90}Pr_{0.10}O_{2.00}$ shown in Fig. 1 confirms the formation of a single phase fluorite structure $U_{1-y}Pr_yO_2$ solution. The oxygen potential-temperature-composition relationship for $U_{1-y}Pr_yO_{2\pm x}$ was measured using a Netzsch STA 449 F1 Jupiter TGA for y = 0.10 and 0.20 from 1000 to 1500°C. The experimental procedure for the TGA technique used here is described in detail in [9-11]. The results are given in Table 1.

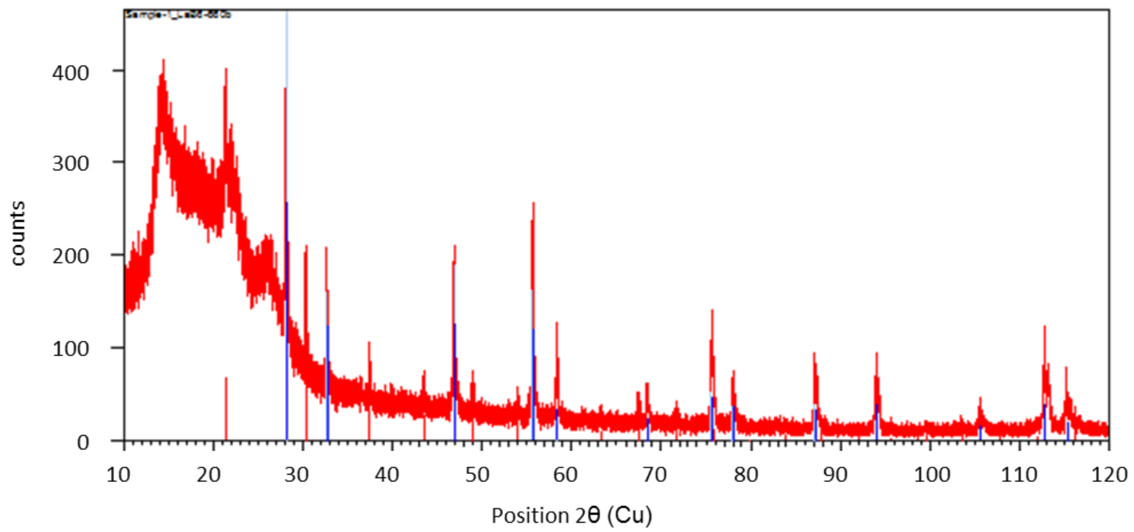

Fig. 1. XRD pattern for $U_{0.90}Pr_{0.10}O_{2.00}$ showing the presence of only a single phase fluorite structure solution.

Table 1. Equilibrium oxygen pressures versus O/M measruments for $U_{1-y}Pr_yO_{2\pm x}$ from thermogravimetry.

y	Temperature (°C)	O/M	Error in O/M	$\log p_{O_2}$	Error in $\log p_{O_2}$
0.1	1000	1.999	0.0010	-18.0	0.079
0.1	1000	2.000	0.0010	-16.0	0.079
0.1	1000	2.000	0.0010	-14.0	0.128
0.1	1000	2.227	0.0028	-4.0	0.767
0.1	1300	2.000	0.0030	-14.0	0.055
0.1	1300	2.002	0.0030	-12.0	0.055
0.1	1300	2.003	0.0030	-10.0	0.057
0.1	1300	2.112	0.0033	-4.0	0.226
0.1	1300	2.192	0.0039	-3.0	0.059
0.1	1500	1.998	0.0020	-12.0	0.041
0.1	1500	2.000	0.0020	-10.0	0.041
0.1	1500	2.002	0.0020	-8.0	0.041
0.1	1500	2.010	0.0020	-6.0	0.135
0.1	1500	2.218	0.0035	-2.0	0.041
0.2	1000	1.997	0.0034	-18.0	0.079
0.2	1000	2.000	0.0034	-14.4	0.079
0.2	1000	1.999	0.0034	-16.0	0.079
0.2	1000	2.000	0.0034	-14.0	0.128
0.2	1000	2.216	0.0038	-4.0	0.767
0.2	1285	1.995	0.0060	-14.2	0.055
0.2	1285	1.998	0.0060	-12.2	0.055
0.2	1285	2.001	0.0060	-10.2	0.057
0.2	1285	2.105	0.0061	-4.0	0.226
0.2	1285	2.175	0.0062	-3.0	0.059
0.2	1500	1.995[a]	0.0050	-12.0	0.041
0.2	1500	1.999	0.0050	-10.0	0.041

0.2	1500	2.001	0.0050	-8.0	0.041
0.2	1500	2.003	0.0050	-6.0	0.135
0.2	1500	2.026	0.0050	-4.0	0.223
0.2	1500	2.167	0.0052	-2.0	0.041

[a] Mass loss rate was outside of the uncertainty due to balance drift.

4. MODELING

In the CALPHAD method, Gibbs energy models are developed based on the physical and chemical properties of the phases they represent along with as much of the available thermodynamic data as possible [12]. The major advantage to this approach is extrapolations outside of the range of experimental validation can be expected to be more reliable. The aim is self-consistent robust models that predict properties, thermochemistry, and phase equilibria and that can be combined and extended for multicomponent database development.

The dominant phase in reactor fuel is the fluorite urania solution with minor actinides and fission products; it is therefore critical to correctly model its behavior for accurate performance predictions. The CEF has been shown to well represent the thermodynamics of $(U,Pu)O_{2\pm x}$ [8, 13] and $U_{1-y}Ln_yO_{2\pm x}$ [14-18] and is therefore used in this work for $U_{1-y}Y_yO_{2\pm x}$ and $U_{1-y}Pr_yO_{2\pm x}$. However, to accurately describe $U_{1-y}Ln_yO_{2\pm x}$, the other phases in the integral U-Ln-O ternary must also be properly represented. The two-sublattice ionic liquid model (TSML) and appropriate CEF variations are used for the melt and ternary solid solution phases [5, 11]. Pure elements and compounds are taken from [19, 20].

An iteration scheme within the Optisage module of FactSage [21] software was used to simultaneously optimize all adjustable parameters of the CALPHAD models in order to achieve a self-consistent set of values that gave a best fit to the available data judged reliable. The resulting thermodynamic functions for the U-Y-O and U-Pr-O systems are reported in [5] and [11] respectively.

5. NUCLEAR FUEL DATABASE DEVELOPMENT

Multi-component thermodynamic descriptions can be constructed from binary and ternary fundamental subsystems assuming only two and three body interactions. There are many studies devoted to phase relations and thermochemistry of urania with a fission product (FP), in particular the Ln elements since these are high yield FPs. The relatively low concentrations of FPs, even at high burnup, mean FP-FP interactions can be neglected, to a first approximation, since the magnitude of the effect scales with composition. Therefore, the approach is to assess the U-O, Ln-O, U-Ln, and U-Ln-O subsystems and then combined them for a thermodynamic representation of multi-component high-burnup nuclear fuel. So far a database including U-Pu-Ce-La-Nd-Y-Pr-

Gd-Th-O-C-N has been developed based on experimental data provided for the binaries and ternaries.

6. RESULTS AND DISCUSSION

The equilibrium oxygen pressures measured by TGA for $U_{1-y}Pr_yO_{2\pm x}$ compare very well to the CEF derived values as can be seen in Fig 2. The calculated ternary phase diagram (Fig. 3) is in very good agreement with the one based on the experimental work of Alleluia et al. [1]. In Fig. 4, the computed oxygen pressures over $U_{y-1}Y_yO_{2\pm x}$ agree well with the values reported by Hagemark and Broli [6]. Figure 5 compares experimental phase relations from [3] to those predicted by the models developed for the U-Y-O system.

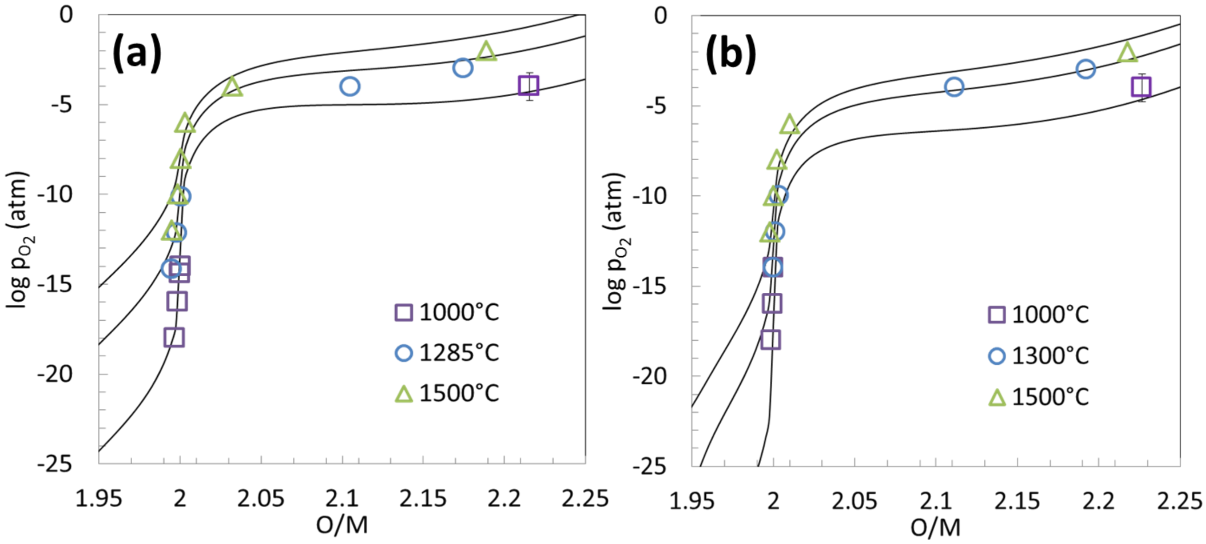

Fig. 2. Computed (lines) and experimental (symbols) equilibrium oxygen pressures over $U_{0.9}Pr_{0.10}O_{2\pm x}$ (a) and $U_{0.80}Pr_{0.20}O_{2\pm x}$ (b) [11].

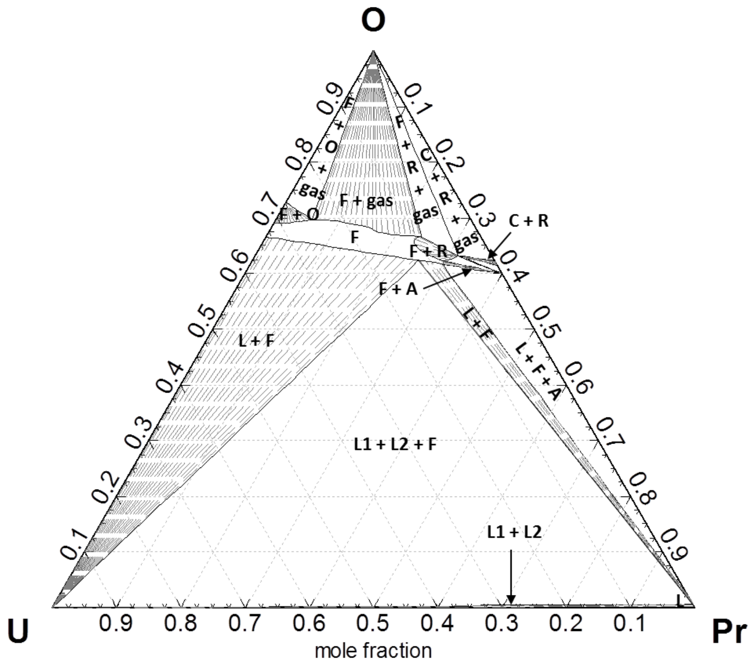

Fig. 3. Computed U-Pr-O ternary isotherm at 1250°C [11].

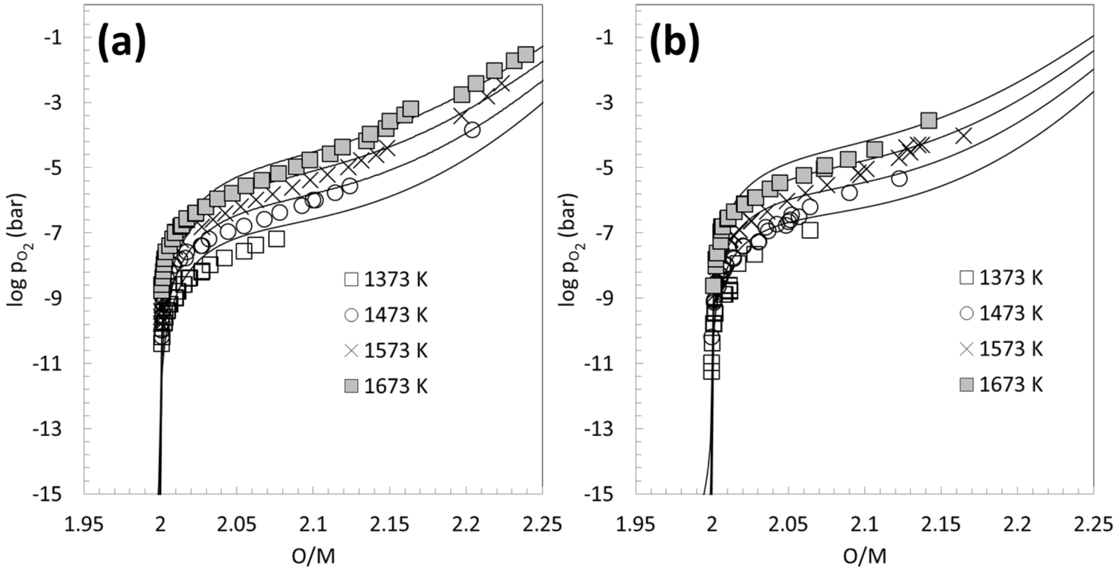

Fig. 4 Oxygen pressures for (a) y= 0.025 and (b) y = 0.05 in $U_{1-y}Y_yO_{2+x}$ from Hagemark and Broli [6] (symbols) and computed values (lines) [5].

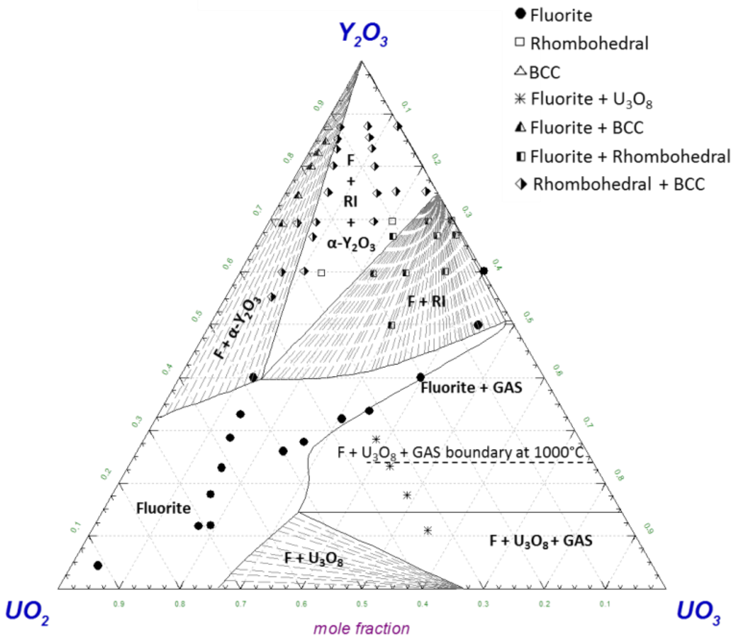

Fig. 5. Computed phase diagram [5] for Y_2O_3-UO_2-UO_3 pseudo-ternary at 1500°C with data from Bartram et al. [3] shown as symbols where F and RI refer to the fluorite and rhombohedral phases, respectively. The dashed line represents the model predictions for the F + U_3O_8 + GAS three phase boundary at 1000°C corresponding to the temperatures used in [3].

7. SUMMARY

A critical assessment of the available thermodynamic studies reported in the literature resulted in the selection of a consistent and reliable data set for the U-Y-O and U-Pr-O systems. It was determined that more thermochemical measurements were needed to develop a reliable CEF for $U_{1-y}Pr_yO_{2\pm x}$. Therefore, TGA was used to characterize the μ_{O_2} -composition-temperature relationship. These measurements were combined with those from the literature to perform assessments of the U-Y-O and U-Pr-O systems. The calculated results show a good fit to the experimentally determined thermodynamic data judged to be reliable. The solution phases were represented by CALPHAD models to facilitate more reliable extrapolations and multicomponent database development to support physics based performance simulations and fabrication of conventional and advanced nuclear fuel forms.

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