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Experimental oxygen potentials for $U_{1-y}Pr_yO_{2\pm x}$ and thermodynamic assessment of the U-Pr-O system[☆]

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ABSTRACT

Thermogravimetric analysis (TGA) was used to determine the oxygen potentials of fluorite urania-praseodymia ($U_{1-y}Pr_yO_{2\pm x}$) solid solutions for $y = 0.10$ and 0.20 between 1000 and 1500 °C. A thermodynamic assessment of U-Pr-O system was performed using the CALPHAD (CALculation of PHAse Diagrams) method. The models well reproduce the TGA measurements and the computed phase relations are in good agreement with those proposed from an X-ray diffraction investigation.

1. Introduction

In recent years, increases in computing power have facilitated advances in multi-physics based fuel performance simulations. Key components of this approach, such as the modeling of transport phenomena and phase transformations, rely on thermodynamics for inputs. Since the Ln (lanthanide) elements and Y are high yield fission products that dissolve extensively in fluorite urania, they affect many of the properties of nuclear fuel. Therefore, many experimental studies are devoted to the U-Ln-O ternaries. Particular emphasis is placed on heat capacity measurements and determining the oxygen potential (μ_{O_2}) of the fluorite $U_{1-y}Ln_yO_{2\pm x}$ solid solution as well as understanding the phase relations in the integral system. Further, there is an international effort to model the phases in U-Ln-O ternaries using the CALPHAD (CALculation of PHAse Diagrams) method whereby the individual subsystems can be used to develop a global multicomponent description, e.g. to represent nuclear fuel with burn-up. Thermodynamic assessments that can be used within this framework for U-Pu-O [1], U–Ce–O [2], U–La–O [3], U–Y–O [4], and U-Nd-O [5] already exist. However, Pr is also a high yield fission product (FP) but CALPHAD models for the phases in the U-Pr-O system have yet to be developed. Therefore, this work aims to perform a thermodynamic assessment of U-Pr-O system using the CALPHAD approach.

The CALPHAD method uses both thermochemical and phase equilibria data for model development. Unfortunately, experimental investigations reporting both types of this information for U-Pr-O are scarce compared to some of the other U-Ln-O systems. A literature survey revealed only one study authored by Yamashita et al. [6] reporting limited equilibrium oxygen potentials (μ_{O_2}) at 1350 °C in air, He, and under vacuum. Therefore, the μ_{O_2}-composition-temperature relationship for $U_{1-y}Pr_yO_{2\pm x}$ was measured by thermogravimetric analysis (TGA) to accumulate sufficient thermochemical data necessary to develop a

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compound energy formalism (CEF) representation for the fluorite $U_{1-y}Pr_yO_{2\pm x}$ solution. These TGA results and the phase relations shown in Fig. 1, taken from Ref. [7] and based on the work of De Alleluia et al. [8], were used to perform the integral U-Pr-O assessment.

2. Experimental

2.1. Sample preparation

Areva UO_{2+x} powder (>99.85 mass % uranium oxide) and Pr_6O_{11} from American Elements (>99.995 mass % Rare Earth oxide) were mechanically mixed in ratios corresponding to 1/10 and 1/5 Pr to U. These compositions were pressed into a disc (5 mm in diameter and 1 mm in height) that was then conditioned at 1350 °C for 17 h in an oxygen atmosphere corresponding to log $p_{O2} = -13$ to both sinter and form a single phase solid solution with an approximate O/M = 2. A SPEX mill was then used to reform the powder for an additional mixing, pressing, and conditioning step as described above. An X-ray diffraction (XRD) analysis revealed only the presence of a single phase solution corresponding to the fluorite crystal structure. As can be seen in Fig. 2, the lattice parameters obey Vegard's law and are well represented by the relation given by Ohmichi et al. [9] for $U_{1-y}Ln_yO_2$ where Ln is a fixed trivalent cation.

2.2. Thermogravimetric technique

The oxygen potential-temperature-composition relationship for $U_{1-y}Pr_yO_{2\pm x}$ was determined by TGA using a Netzsch STA 449 F1 Jupiter for y = 0.10 and 0.20 from 1000 to 1500 °C. Feed gases were procured from Air Liquide S.A. and oxygen potentials were fixed by mixing Ar-3% H_2 and Ar-2%O_2 in appropriate ratios determined from thermodynamic calculations.

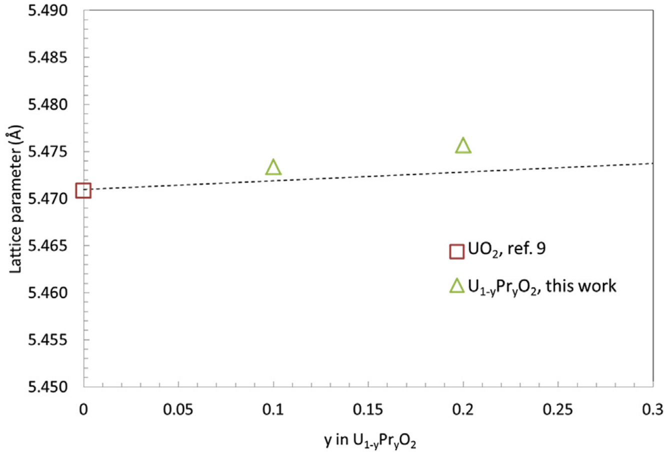

Fig. 2. Lattice parameters for fluorite structure $U_{1-y}Pr_yO_2$ as a function of Pr content. The experimental values (symbols) are compared to those computed (dashed line) using the relation proposed by Ohmichi et al. [9].

The details of the particular experimental technique used here are described in in Refs. [10,11]. In brief, a $U_{1-y}Pr_yO_{2\pm x}$ sample of approximately 1 g was conditioned to an O/M of 2. A change in oxygen potential results in a weight gain (or loss) that can be correlated to a new O/M using the relation:

$$O/M = 2 + \frac{mw_s \times \Delta m}{16\frac{g}{mol} \times mass_s} \tag{1}$$

where mw_s is the molecular weight of $U_{1-y}Pr_yO_{2.00}$, Δm is the change in mass due to uptake or release of oxygen and $mass_s$ is the sample mass at room temperature. A precise value of $mass_s$ for $U_{1-y}Pr_yO_{2\pm x}$ at the operating temperature of the measurement cannot be known since cooling from the conditioning step in Ar-3% H_2 likely causes the sample to become hypo-stoichiometric. Changes in the microbalance signal due to gas buoyancy are well documented in TGA. Therefore, the $mass_s$ during conditioning cannot be directly compared to the $mass_s$ reading at room

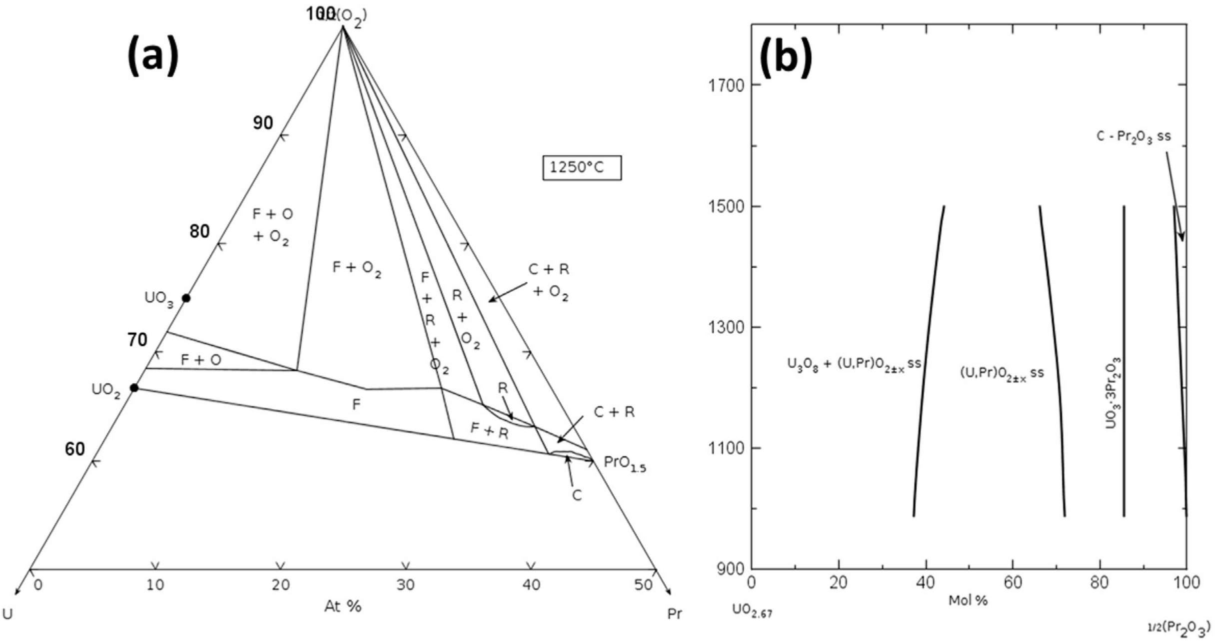

Fig. 1. Experimentally determined phase relations from De Alleluia et al. [8] for (a) the U-Pr-O ternary at 1250 °C and (b) at 1 atm O_2 pressure. Reprinted with permission of The American Ceramic Society (www.ceramics.org).