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Determination of oxygen stoichiometry of oxide fuel during high temperature vapour pressure measurement

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ABSTRACT

This study presents an original approach of oxygen stoichiometry determination during high temperature (>2000 K) measurements of vapour pressure using the Knudsen effusion mass spectrometry technique. The method has been developed taking into account the vapour pressure measurements of series of $(U_{1-x}, Pu_x)O_{2-\delta}$ samples with $x(Pu) = 0.25, 0.5, 0.75$ together with pure $UO_{2-\delta}$ and $PuO_{2-\delta}$ end-members coupled with equilibrium calculations based on thermodynamic assessment of the U–Pu–O system. The presented method consists of two steps; in the first step the oxygen potential of the oxide phase is determined based on the measured partial vapour pressures of UO(g), UO_2(g), PuO(g) and PuO_2(g) gaseous species and during the second step the thus determined oxygen potential is linked with the matching oxygen stoichiometry of the sample. From the obtained results it has been demonstrated that it is possible to accurately estimate the oxygen stoichiometry of the mixed oxide fuel samples knowing the description of the oxygen potential of the corresponding end-members only.

1. Introduction

Actinide oxides are nuclear materials used in most commercial power plants worldwide. Among them the most common fuel is based on a UO_2 matrix while some reactors utilize plutonium in the form of $(U_{1-x}, Pu_x)O_{2-\delta}$ solid solution, referred as mixed oxide fuel (MOX). For the safety assessment of a nuclear reactor it is important to know the high temperature properties of the fuel. These are affected not only by the actual concentration of various actinides in the fuel, but also, and very significantly, by the oxygen stoichiometry. It is therefore very important to know the exact oxygen stoichiometry of the analyzed sample during high temperature measurements.

This is especially the case of high temperature vapour pressure measurements by Knudsen effusion Mass Spectrometry (KEMS) that are in most of the cases performed in ultra vacuum conditions, under which the actinide oxide tends to reduce, thus decreasing oxygen stoichiometry. The vapour pressure signature of a sample is important for two main reasons: (i) it tells us the volatility of the sample, and (ii) by measuring the vapour pressure one can determine the activity coefficients of various components in the solid solution, thus obtaining a measure of stability of the system. Since the vapour pressure belongs to the group of properties that are significantly influenced by the O/M ratio of the oxide fuel, the exact determination of the oxygen stoichiometry is mandatory for complementary interpretation of the data.

In this study we propose a method to determine the O/M ratio during vapour pressure measurement by KEMS and we demonstrate this technique on measurements of a series of (U,Pu)O_2 samples. This system has been selected as an ideal candidate as full thermodynamic description of the complete U–Pu–O ternary system is available [1] and was needed to correlate with the obtained experimental results.

2. Method

During the high temperature investigation of oxide fuel the oxygen stoichiometry changes, much depending on the external partial pressure of oxygen. If the measurement is performed in conditions with no control of the oxygen pressure, e.g. in ultra high vacuum, it is very challenging to determine the actual O/M ratio of the analyzed sample. In our recent efforts, several methods have been proposed based on the post-analysis by thermogravimetry, X-ray diffraction or chemical analysis, however the accuracy of these methods was never very reliable. Moreover, all post-analysis methods can only provide information about the sample state after completion of the measurement and not during the performed experiment.

More recently [2], it has been proposed to heat the sample for several hours until reaching the congruent vapourization point which is a state at which the composition of the vapour is the same

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as the one of the sample. Thus, in ideal case it would be possible to precisely determine the O/M ratio summing the partial vapour pressures of all gaseous species in equilibrium. Unfortunately, this method leads to doubtful results as it is not always possible to detect all species, particularly the O_2 and O species due to relatively high background at the low mass range of the mass spectrometer.

In this study we propose a technique that leads to a reliable estimation of O/M ratio of the sample during the measurement. The method is based on the determination of oxygen potential coupling the experimentally obtained partial vapour pressures of actinide oxide gaseous species with thermodynamic calculations. The easiest way would be measuring the O_2 partial vapour pressure, but for the reasons mentioned above this is technically not possible. Since the actinide oxide species are easily identified by mass spectrometry, not interfering with others, it is possible to use e.g. the following equilibrium reaction for identification of the vapour pressure of O_2:

$$\mathrm{AnO(g)} + 0.5\mathrm{O_2(g)} \rightarrow \mathrm{AnO_2(g)}. \tag{1}$$

Note, that the choice of reaction in the gas phase is based on the experimentally determined vapour pressures of An-bearing species and it is advised to select the one which is based on the species with highest partial vapour pressure, as that provides the most accurate results. In the present case, in which we demonstrate the technique on the mixed oxide solution of uranium and plutonium the major detected species were UO(g), UO_2(g), PuO(g) and PuO_2(g) (see Section 4).

As mentioned above, for the determination of oxygen potential reliable thermodynamic data (Gibbs energies) of oxygen and all relevant actinide oxide species are needed. The data on uranium and plutonium bearing species were taken from a recent critical review of thermodynamic data of actinide oxides [3], while the data for oxygen were taken from CODATA [4].

Using the selected thermodynamic data the equilibrium constant, *K*, of reaction (1), in which An = U or Pu is calculated according to:

$$\begin{aligned}\triangle G_r^0 &= -RT\ln K \\ &= \triangle G^0(\mathrm{AnO_2(g)}) - \triangle G^0(\mathrm{AnO(g)}) - 0.5 \triangle G^0(\mathrm{O_2(g)}),\end{aligned} \tag{2}$$

in which $\triangle G_r^0, \triangle G^0(\mathrm{AnO_2(g)}), \triangle G^0(\mathrm{AnO(g)})$ and $\triangle G^0(\mathrm{O_2(g)})$ are the standard Gibbs energy of Reaction (1) and the standard Gibbs energy temperature functions of AnO_2, AnO and O_2 gaseous species respectively. The equilibrium constant is further defined as:

$$K = \frac{p(\mathrm{AnO_2(g)})}{p(\mathrm{AnO(g)}) \cdot p^{0.5}(\mathrm{O_2(g)})}, \tag{3}$$

in which $p(\mathrm{AnO_2(g)}), p(\mathrm{AnO(g)})$ and $p(\mathrm{O_2(g)})$ are the partial pressures of corresponding species (in *bar* units), the former two experimentally determined from the Knudsen measurement, while the partial pressure of oxygen calculated.

The last step of this analysis is supported by the full thermodynamic description of the U–Pu–O system which has been assessed by Guéneau et al. [1,5,6] based on several experimental data, including the measured oxygen potentials of $UO_{2-\delta}$ [7,8], $PuO_{2-\delta}$ [9–13] and $(U_{1-x},Pu_x)O_{2-\delta}$ phases [12,14–16]. It is mandatory to have a thermodynamic description that well reproduces the measured oxygen potentials, because only with such fulfilled condition it is possible to perform good correlation between the model and the calculated partial pressure of oxygen from Eq. (3) in order to assign the right O/M ratio to the sample.

With such performed correlation we first analyzed the oxygen stoichiometry of the $UO_{2-\delta}$ and $PuO_{2-\delta}$ end-members and based only on these results we proposed and tested a method to estimate the O/M values in the intermediate range. The method is based on the assumption that if the initial sample is stoichiometric or slightly hyperstoichiometric (possible case of $UO_{2\pm\delta}$) and if the first heating ramp is performed with relatively rapid speed we could use a linear interpolation of the obtained O/M ratios of the end-members to estimate the values in the mixed oxide solutions. The idea is supported by the assumption that upon the first heating the change of the composition is relatively fast, driven by loss of oxygen (under imposed vacuum conditions), thus one can expect the same driving force of the composition change as given by the end-members. Due to the kinetic nature of the redox change plus taking into account that rather big samples were used for the measurement, not a significant change of the Pu/U ratio was expected during the first heating cycle. The calculated ratio of the total vapour pressure of all U-bearing species versus the total vapour pressure of all Pu-bearing species gives almost constant value for the first heating period for all measured intermediate compositions, justifying our assumption. This assumption can be further explained by the relatively low volatility of actinide bearing species in the temperature range of the initial heating. We must stress here that for the mentioned arguments only the results from the first heating ramp can be used for the proposed method. Further heating of the sample at constant temperature for several hours, e.g. the one presented in our previous paper [2], would eventually lead to the congruent vapourization point and the O/M ratio of this point can no longer be estimated based on the proposed linear approximation. This is confirmed by the thermodynamic model of Guéneau et al. [1] which indicates a minimum on the curve of the congruent O/M composition plotted versus the Pu concentration.

3. Experiment

3.1. KEMS analysis

The vapour pressure measurements of $UO_{2-\delta}$, $PuO_{2-\delta}$ and $(U_{1-x},Pu_x)O_{2-\delta}$ with x(Pu) = 0.25, 0.5 and 0.75 were performed with the Knudsen effusion cell coupled with mass spectrometer (KEMS) installed within the alpha tight and gamma shielded glove box allowing handling of highly radioactive materials. During the experiment the sample is placed into the Knudsen cell made of tungsten metal with very small orifice on the top which is placed in the high temperature furnace made of tungsten coil and surrounded by series of thermal shield. Upon heating, the sample evaporates and the escaping gaseous species are driven through a cross beam electron bombardment where they are ionized and successively analyzed in the quadrupole mass spectrometer. For more details about the KEMS device used in this study we refer to our recent paper [17].

The vapour pressure of the molecular species, p_i, is determined from the obtained intensity of the detected signal according to general equation:

$$p_i = I_i^+ \cdot T_i \cdot K, \tag{4}$$

in which I_i^+ refers to the measured intensity of the corresponding cation of a species i, T is the absolute temperature and the K term is obtained by multiplying the calibration factor, K_{Ag}, with a species dependent correction factor K_i:

$$K = K_{\mathrm{Ag}} \cdot K_i. \tag{5}$$

K_{Ag} is defined in analogous way as Eq. (4), thus:

$$K_{\mathrm{Ag}} = \frac{p_{\mathrm{Ag}}}{I_{\mathrm{Ag}}^+ \cdot T_{\mathrm{Ag}}}, \tag{6}$$

and is fitted to a constant value based on the measurement of silver that has been used as a calibration material. Hence, in Eq. (6), p_{Ag} is