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Section 3. Oxides and other materials

Mass spectrometric study of UO_2–ZrO_2 pseudo-binary system

M. Baïchi [a,*], C. Chatillon [b], C. Guèneau [c], S. Chatain [c]

[a] *DRN/DEC/SECI/LARA, CEA Grenoble, 17 rue des Martyrs, Grenoble F-38054, France*
[b] *Laboratoire de Thermodynamique et de Physico-Chimie Métallurgiques, (UMR 5614, CNRS-INPG/UJF) ENSEEG, BP75, Saint Martin d'Hères F-38402, France*
[c] *DCC/DPE/SPCP/LEPCA, CEA Saclay, Gif-sur-Yvette cedex F-91191, France*

Abstract

The thermodynamic activity of UO_2 in the UO_2–ZrO_2 pseudo-binary system, for fractional concentrations of ZrO_2 from 0 to 1 in the 2000–2400 K temperature range was investigated by partial pressure measurements of UO_2 (g) using the multiple Knudsen cell-mass spectrometric method. This system exhibits a positive deviation from the ideal behavior at 2200 K and becomes close to ideal near 2500 K. © 2001 Published by Elsevier Science B.V.

1. Introduction

During a severe nuclear accident, the temperature can rise to above 2500 K. In order to understand what happens at these temperatures, analytical experiments were performed [1]. Among the different possible scenarios [2], the fuel cladding may be totally oxidized to zirconium dioxide and interact with uranium dioxide [3]. Besides the existence of a phase diagram, only a few thermodynamic data concerning the pseudo-binary system UO_2–ZrO_2, at temperatures above 2000 K, are available in the literature.

In the UO_2–ZrO_2 system, the cubic phase (U, Zr)O_2 and the tetragonal phase (Zr, U)O_2 are in equilibrium for a broad two-phase region at 1973 K [4]. Activity data for some compositions of this system have already been determined [5,6] but large discrepancies exist [7,8]. In this study, the multiple Knudsen cell technique, developed 25 years ago [9–12] was chosen to obtain new activity determinations. The activity of the element i, a_{i}, is the ratio of ionic intensities of element i as measured over the mixture $U_{1-y}Zr_yO_2$ and the pure UO_2 as reference:

$$a_{UO_2} = I_{UO_2}^{\text{mixture}} / I_{UO_2}^{\text{reference}}.$$

2. Experimental technique

Samples for the experiments were obtained by grinding UO_2 and ZrO_2 powders in the appropriate compositions. The mixture was compacted and sintered at 1973 K for 96 h in a dry hydrogen atmosphere. These conditions were chosen because 1973 K is the minimum temperature for attaining equilibrium of this refractory oxide system in reasonable times [4,13]. This led to stoichiometric oxide mixtures with $O/(U+Zr) = 2.00060.005$. The masses of the samples rich in UO_2 and rich in ZrO_2 were 5 and 3 g, respectively. The samples were of cylindrical shape, with 6 mm height and 10 mm diameter.

The quadrupole mass spectrometer used has been described [14] and is shown in Fig. 1. Between experiments, the quadrupole mass spectrometer was automatically drawn out of its axis, and a valve allowed the vacuum conditions to be maintained around the mass spectrometer. It facilitated the restoring of ultra high vacuum conditions in the source housing, which was typically lower than 10^{-8} mbar. According to Younés [15,16], who analyzed the effect of ionization potential, we chose to work at 12 V to avoid any fragment ions contribution from UO_3, UO_2 and UO gaseous species to lower mass species.

The envelope of the four effusion cells was made of tantalum, and the four Knudsen cells (crucible and lid) were made of tungsten. The selection of tungsten material was a significant factor in performing the experiments [15,17]. The effusion orifices were of 2 mm

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[*] Corresponding author. Tel.: +33-4 76 88 39 69; fax: +33-4 76 88 51 51.
E-mail address: baichi@dtp.cea.fr (M. Baïchi).

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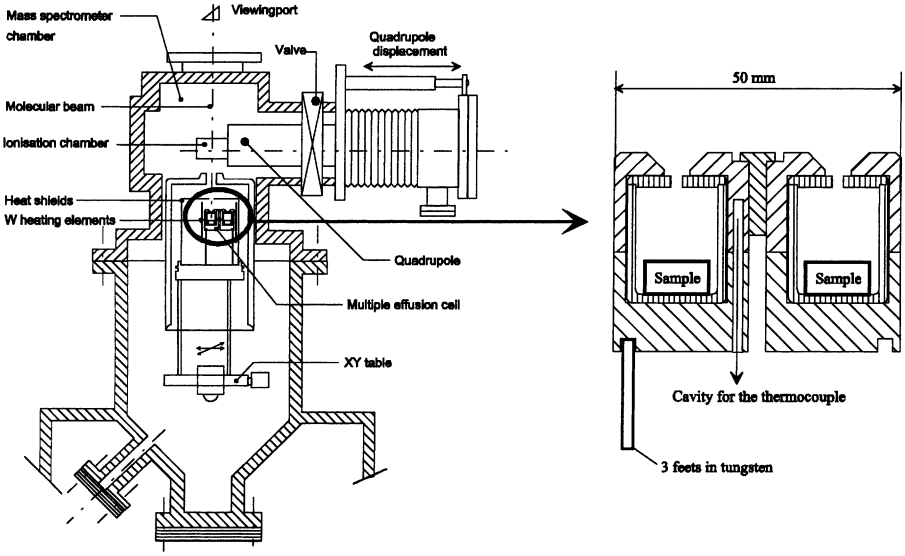
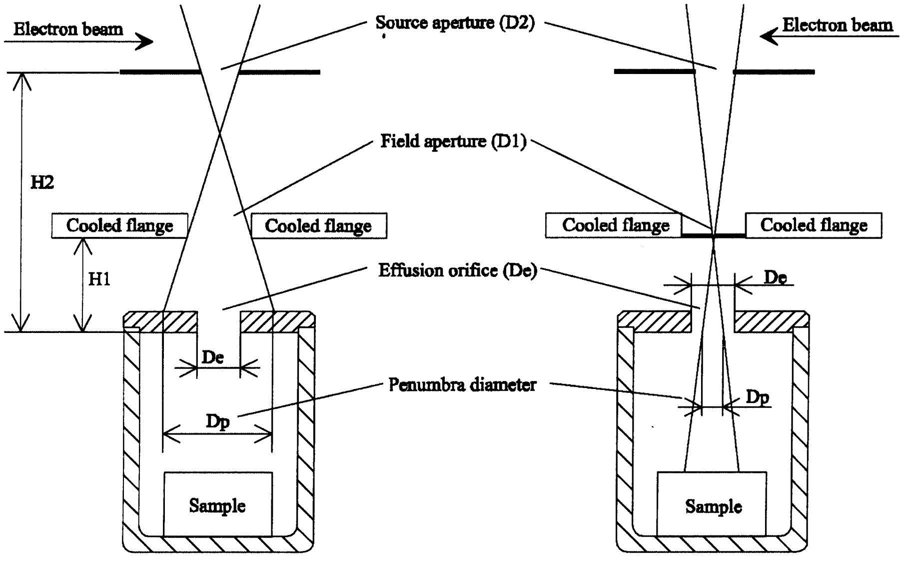


Fig. 1. Multiple Knudsen cell mass spectrometric apparatus.

diameter and 2 mm length. The ratio $(sC)/S$, where s is the orifice cross-section, C the Clausing coefficient and S the cell cross-section, was equal to 9.5×10^{-3}. The mass loss of each cell (crucible + lid + sample) was measured in order to check for any evolution of the composition. The increase in the U/Zr ratio was about 2% for the samples rich in UO_2 and less than 0.1% for samples rich in ZrO_2.

A restricted collimation was used [18] to discard the detection of the parasitic surface re-vaporization [9]. The difference between conventional sampling and the restricted collimation sampling by the ionization chamber is shown in Fig. 2. In order to let the ionization chamber receive molecules coming only from the interior of the effusion cell, we used an optimized restricted collimation. The geometrical constraints are $H1 = 18.1$ mm,



Conventional sampling

Restricted collimation

Fig. 2. Conventional and restricted collimation of molecular effused beams.

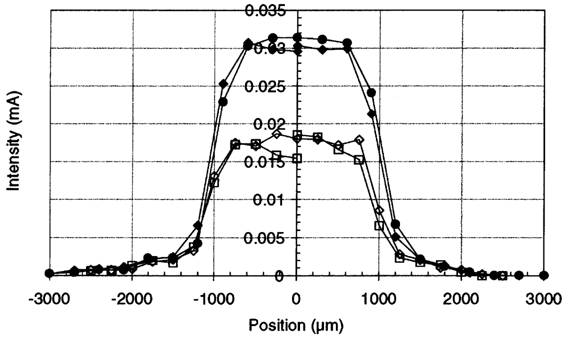


Fig. 3. Ionic intensity of UO_2^+ (●; ◆) and UO^+ (□; ◇) monitored as a function of the cell positioning forward and backward for one effusion orifice.

$H2 = 73.8$ mm, $De = 2$ mm and $Dp = 1.8$ mm as defined in Fig. 2. The choice of the two apertures D1 and D2 corresponds to the maximum solid angle for molecular transmission as already explained in [18] for a given effusion orifice.

The positioning of the effusion orifices on the ionization source axis was done with a mechanical clearance less than 0.05 mm in order to use optimized restricted collimation for sampling the molecular beam. Fig. 3 shows a profile of the ionic intensity of UO_2^+ and UO^+ as a function of the distance of the cell position in front of the collimation device. A flat portion near the center of the effusion orifice shows that we are detecting molecules effusing out of the Knudsen cell through the effusion orifice. The profiles were obtained with the UO_2^+ and UO^+ signals. At approximately 1200–1400 μm from the center, we could observe the effect of outside surface vaporizations. These profiles were done at the beginning of each experiment to position the orifice on the field aperture axis, which is at the center of the flat portion. Thus, the different orifices were automatically positioned during the experiment.

3. Experimental results

For each temperature plateau and for each cell, 10 data measurements were made. The highest and lowest ones were eliminated and the mean average of the remainder calculated. As an example the ionic intensity ratios or activities obtained for each composition are shown in the Fig. 4 as a function of temperature for the cubic phase. From the least square fits, the activity of UO_2 in the UO_2–ZrO_2 system versus the molecular composition of ZrO_2 for two temperatures, 2205 and 2498 K, are shown in Figs. 5 and 6, respectively. Our values are reported with the S.D. of our fits on the figures. Figs 5 and 6 also show the literature data for comparison.

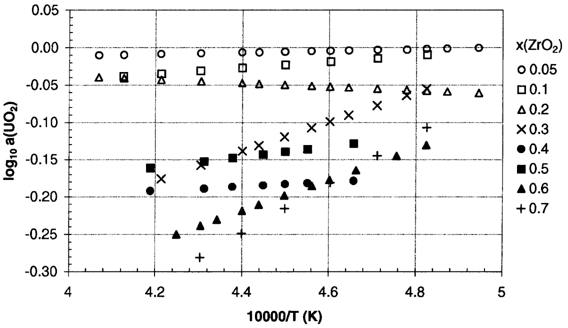


Fig. 4. Decimal logarithm of activity measurements versus $10000/T$ for 8 values of x, the fraction of ZrO_2 in the system.

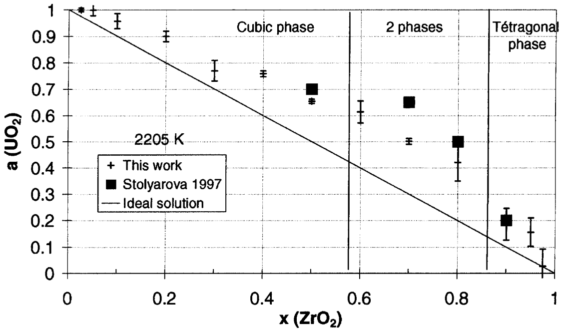


Fig. 5. Activity of UO_2 versus molar fraction of ZrO_2 at 2205 K.

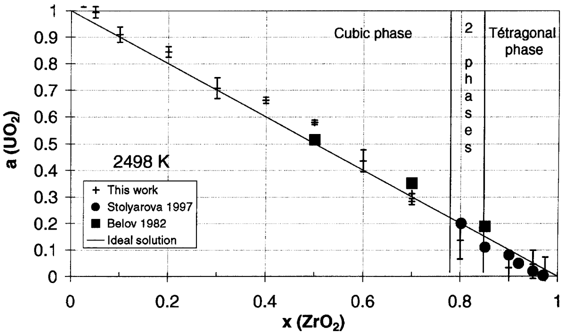


Fig. 6. Activity of UO_2 versus molar fraction of ZrO_2 at 2498 K.

4. Discussion

At 2205 K, the activity of UO_2 in UO_2–ZrO_2 showed a positive deviation from the ideality, and agrees with the other data obtained using the same mass spectrometric technique [5]. This indicates a strong tendency towards immiscibility for the cubic phase.

This deviation from ideality decreases when temperature rises. At 2498 K, the system showed a slightly positive deviation from ideality, which agrees with Belov [6] who used the same technique for this system. The slightly negative deviation from ideality for the tetragonal phase agrees with the results of Stolyarova [5]. At 2700 K, Alexander et al. [7] found a positive deviation with a transpiration technique. Gross et al. [8] found a negative deviation from ideality at 2700 K by Knudsen collection.

This work confirms preceding mass spectrometric determinations. Our method has the advantage of measuring more compositions (13) between UO_2 and ZrO_2 and our results exhibit a regular trend in agreement with other mass spectrometric data [5,6]. The clear advantage of mass spectrometry is its analytic capability for the direct measurement of activity through the lone UO_2 (g) species. The data obtained here will be used in a computational optimization of U–O–Zr system [19].

Acknowledgements

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