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On the present state of investigation of thermodynamic properties of solid and liquid UO_{2+x} ☆

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1. Introduction

The U–O system has been investigated for almost fifty years, and, in particular, the $UO_{2\pm x}$ solid-solution phase boundary was considered as established since the beginning of the 1980s. Nevertheless, the results of thermodynamic measurements at temperatures above 2500 K performed with traditional techniques are probably affected by large errors. These are mostly due to reactions of the sample with the containment and to poor control of the equilibrium vapour pressure, with consequent composition instabilities.

In order to overcome intrinsic limits of the previous measurements, new experiments have been carried out in our laboratories based on container-less laser heating in conjunction with fast spectral pyrometry. In particular, uranium dioxide melting and thermodynamic properties of the liquid have been extensively investigated. Some of the new measurements were not in full agreement with the previous ones; others provided novel details that are indispensable to a better understanding of the thermodynamic properties of UO_2.

Now, in a recent issue of the Journal of Nuclear Materials two review articles by Baichi et al. [1,2] were published dealing with the thermodynamic properties of uranium dioxide at high temperatures. These authors ignored or discarded part of this new experimental evidence questioning the adequacy of the modern measurement techniques. Actually, the arguments they provide are insufficient, as their fundamental tenet is that new measurements are only valid if they reproduce data obtained with ‘conventional’ techniques; what is incongruous since the new methods have been indeed developed to explore conditions where these latter fail to be sufficiently accurate.

It is not our purpose to discuss of the whole content of these two papers; however, a few words are in order here regarding three subjects treated, namely the heat capacity of solid UO_2 at high temperatures, the solidus/liquidus boundaries of UO_{2+x}, and the heat capacity of liquid UO_2.

2. The heat capacity of solid UO_2 at high temperatures

The high temperature behaviour of $C_p(T)$ in solid UO_2 is mostly controlled by lattice defect

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☆ Comments to the papers: M. Baichi, C. Chatillon, G. Ducros, K. Froment, Thermodynamics of the O–U system. IV – Critical assessment of chemical potentials in the $U–UO_{2.01}$ composition range, J. Nucl. Mater. 349 (2006) 17 and M. Baichi, C. Chatillon, G. Ducros, K. Froment, Thermodynamics of the O–U system: III – Critical assessment of phase diagram data in the $U–UO_{2+x}$ composition range, J. Nucl. Mater. 349 (2006) 57.

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formation – mainly oxygen Frenkel pairs (FP) – supported by disproportioning of the cation valence. An observed pre-melting λ-transition leads to a steep increase of the anion defect concentration at a temperature of approximately 2670 K. At higher temperatures, though saturation of the FP concentration is expected, a further increase in C_p with temperature is still observed, whereby, due to the occurrence of the λ-transition, direct calorimetric measurements above 2700 K are less precise [3–5].

In their first paper [1], Baichi et al. propose a constant C_p value (167.04 J K^{-1} mol^{-1}) for solid UO_2 at temperatures above 2673 K. This corresponds to a previous estimate derived from enthalpy data, and later rejected in the review of Fink [6], who gives significant weight to the high-temperature data of Ronchi et al. [3]. These data were obtained by *direct* measurements of C_p under quasi-stationary conditions, *i.e.*, *not* from cooling rate measurements. The technique used is an extension of the laser-flash method for simultaneous measurement of thermal diffusivity and heat capacity, and was successfully tested with graphite and zirconia at very high temperatures [4] showing a good agreement with drop calorimetry results. Experimental results [3] indicate that C_p in solid UO_2 monotonically increases at temperatures higher than 2670 K. This provides a selection criterion for a proper fitting function of the enthalpy *vs.* temperature data. In this perspective, using a linear fitting for $H = H(T)$ entails an unjustified shortcoming. The analysis of the drop calorimetry data made by Fink [6] correctly accounts for the independent measurements of H and C_p, reproducing both data with a high accuracy.

Finally, there are physical reasons from which an increase of C_p up to the melting point is expected, and these predictions are confirmed by the experiment in a number of solids similar to UO_2 [7].

3. The liquidus/solidus of UO_{2+x}

In their second paper [2], Baichi et al. analyse the experimental measurements of the liquidus/solidus points in $UO_{2\pm x}$. Two sets of data are examined in the hyperstoichiometric range: those of Latta and Fryxell [8] published in 1970 and the recent ones by Manara et al. [9]. The results of the two experiments are substantially different (Fig. 1).

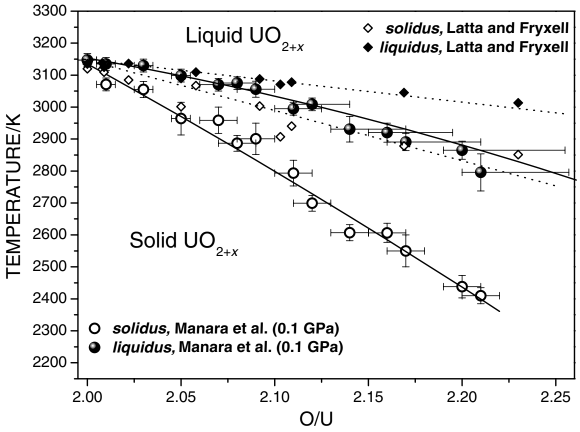

Fig. 1. Experimental UO_{2+x} solidus and liquidus points measured by Latta and Fryxell [8] (diamonds and dotted lines) and by Manara et al. [9] (circles and solid lines). Circles and diamonds are the experimental data points, the lines serve only as a guide for the eye.

Latta and Fryxell used an induction furnace with samples sealed in tungsten or rhenium capsules. These measurements had been already criticised [10] not only because of the considerable solubility of the crucible metal in the sample,[1] but also because of the large losses of excess oxygen occurring on melting. On the other hand, Manara et al. [9] used a container-less laser heating technique to investigate the solidus/liquidus transition in the composition range $UO_{2.00}$–$UO_{2.21}$. In these experiments the temperature was measured with a high precision, fast two-channel pyrometer, whereby the spectral emissivity was simultaneously measured with a multi-channel spectrometer. Liquidus points were detected from thermal arrest during the temperature pulse. In addition, changes induced in the sample angular reflectivity by formation of liquid were monitored with a probe-laser during sample heat-up, allowing to detect the solidus. The experiments were carried out under inert gas pressures up to 250 MPa with pulse times of a few tens of milliseconds. The advantages of this method are evident: absence of contamination, suppression of non-congruent evaporation, prevention of phase segregation and preservation of the *local* thermodynamic equilibrium. Data on pressure dependence of the melting point of stoichiometric UO_2 were obtained up to 2.5 kbar [11]. The melting-line slope of 9.29 K/kbar found [9,11] is in excellent agreement

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[1] Baichi et al. corrected the results according to Raoult's law to take into account the sample contamination with the crucible material (W or Re), but omitted correction of the temperature from IPTS-48 (used in the 1970s) to ITS-90.

with the value calculated from the Clausius–Clapeyron equation (9.38 ± 3.75 K/kbar).

Baichi et al. elaborated the results presented in [9,11] correcting the compositions by a 0.011 shift in the O/U (according to Ref. [12]) and the temperatures by 9 K, i.e. the difference between the measured $UO_{2.00}$ congruent melting point (3147 K) in [9] and their selected value (3138 K). One can easily see that these corrections are almost negligible in the investigated temperature range, and anyway hardly relevant compared to the data uncertainty obtained by Manara et al. [9] through a detailed error analysis, error analysis which is on the other hand largely missing in Latta and Fryxell's paper.

Since even after 'correction' solidus and liquidus data by Manara et al. obviously remained systematically lower than those measured by Latta and Fryxell, these latter were finally preferred by Baichi et al. [2], who give personal explanations of the disagreement between the two datasets, namely (*litteratim*):

1. '*we can postulate (sic!) that Manara observed the disappearance of the liquid phase due to a change of the refraction index or total emissivity (liquid to solid)... assuming the observation of the solidus*';
2. '*large quenching speed*' resulting in '*a metastable phase diagram due to problems in the growth of the solid phase*';
3. '*possibility of time-limited composition segregation*'.

All these arguments are fully inconsistent for the following reasons:

- The solidus temperatures were determined by Manara et al. by analysing the reflected light signal during the *heating* stage of the pulse and *not* on *cooling*, as Baichi et al. suggest. The solidus was determined by detecting the temperature of first appearance of the liquid phase on the sample surface, as the sample was laser-heated. This was realised in two independent ways: by analysing the 'reflected light signal' (Fig. 5 of [9]) to detect the change in the surface angular dependence of reflectivity due to the liquid formation and by visual inspection of the specimen (Fig. 7 of [9]). Both methods ensure the observation of the solidus independently of any effect linked to temperature, quenching speed and composition segregation. Ceramographs of samples heated just above the detected solidus temperature confirm that the observed change in the optical parameters of the sample surface did correspond to the appearance of liquid, *i.e.* the solidus transition.
- Occasional formation of metastable structures, formed by too fast quenching, were revealed in the thermograms by undercooling pits of a few tens of K, which were, however, promptly recovered with re-calescence effects within a few milliseconds. The suitability of the adopted quenching conditions to detect phase transition was checked in a number of compounds, finding good agreement with the reference data [15,16].
- The problem of oxygen segregation was solved by measuring the solidus from the 'bottom' and the liquidus from the 'top' for each composition. The remaining uncertainty was taken into account in the reported O/U error, and does not significantly affect our results.

Thus the conclusion of Baichi et al. that the liquidus found by Manara et al. would correspond to solidus by Latta and Fryxell makes no sense. The disagreement between the two data sets (increasing with the O/U ratio) is more likely due to the O/U ratio of the samples of Latta and Fryxell that likely decreased during the experiments.[2]

After analysing the chemical compatibility of UO_2 with different containers Baichi et al.came to the conclusion that tungsten capsules are appropriate. This is true for hypostoichiometric samples. In fact, Edwards et al. [13] showed that oxygen vapour over $UO_{2.000\pm0.0004}$ at 2427 K does not permeate through the containment. However, the same conclusion cannot be extended to hyperstoichiometric oxides at temperatures close to 3000 K, where the equilibrium vapour pressure over UO_{2+x} dramatically increases[3] by several orders of magnitude [14].

Furthermore, Latta and Fryxell's thermograms indicate deviations from the ideal conditions. For, instance, both solidus and liquidus transitions do not result in clear inflection points (Fig. 2 and 6 of

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[2] Due to the fast oxygen diffusion in UO_{2+x}, the chemical analysis made after the experiments (in Table 2 of [8]) is only roughly indicative of the state of the samples during the melting/freezing; most probably they were strongly depleted in excess oxygen during the prolonged exposure to high temperature (several tens of minutes above 2500 K).

[3] Above 2500 K, the equilibrium partial pressures of O_2 and UO_3 over $UO_{2.1}$ exceed 10^4 Pa.

[8]) and the melting/freezing thermal arrest is not very clear even for the effectively stoichiometric sample #190. One may suppose that the inflection points for highly non-stoichiometric samples, whose thermograms are not reported, are much blurrier.

On the other hand, in the paper of Manara et al. [9] the evolution of the shape of the thermograms for different U/O ratios is reported, showing essential differences in stoichiometric and non-stoichiometric samples.

4. The heat capacity of liquid UO_2

Finally, Baichi et al. [1] question the analysis of Fink [6] concerning the C_p data of liquid UO_2, on the peculiar ground that this author 'introduced results from the laser pulse technique into the analyses of the earlier conventional calorimetric measurements' [1].

The 'earlier' enthalpy *vs.* T data above the melting point between 3150 K and 3500 K [17,18] are no doubt insufficient to deduce a trend for $C_p(T)$. Actually, non-linear fitting on these few data, obtained in a very narrow temperature interval (*ca.* 80 K above the melting point in [17] and 400 K in [18]), is hardly possible. A linear fitting of $H = H(T)$ gives a slope corresponding to $C_p(\text{liq}) = 131\ \text{J K}^{-1}\ \text{mol}^{-1}$. Yet, a conclusive evaluation of the uncertainty of this estimate cannot be obtained from the available data. In addition, it is difficult to imagine physical mechanisms capable to maintain the heat capacity of liquid UO_2 at a level so near to that of the solid near melting ($\sim 170\ \text{J K}^{-1}\ \text{mol}^{-1}$), where the lattice defect behaviour largely controls the enthalpy and entropy variation with temperature.

The recent analysis of Fink included the C_p measurements by Ronchi et al. [4,5]. In this work the heat capacity of liquid UO_2 was measured up to 8000 K from the analysis of the cooling curve of small spherical samples heated, under high hydrostatic pressure conditions, by four similar, tetrahedrally-oriented laser beams. The heat capacity of liquid $UO_{2.0}$ was found to decrease with temperature down to approximately $90\ \text{J K}^{-1}\ \text{mol}^{-1}$ at $\sim$4000 K, and then to grow, reaching at 8000 K the value of $110\ \text{J K}^{-1}\ \text{mol}^{-1}$.

Due to problems related to the respective equilibrium composition in the liquid and gaseous state, dramatically diverging at very high temperatures, the interpretation of the experimental results required an adequate thermodynamic model for the equation of state up to the critical point.[4] A theoretical study addressing this aspect [19] gave predictions that are in agreement with the observed behaviour of $C_p(T)$.

5. Conclusions

We have discussed three important features of the high-temperature thermodynamic properties of UO_2 for which the 'critical assessment' by Baichi et al. is erroneous or faulty.

- Contrary to the personal opinion of these authors, the laser-flash method used to determine the high temperature heat capacity of solid UO_2 gives results that are consistent with conventional drop calorimetric techniques if both techniques are applied under the same conditions. The heat capacity above the λ-transition at 2670 K further increases with temperature up to the melting point.
- Rejecting the solidus/liquidus data for UO_{2+x} obtained by a laser heating technique is fully unfounded.
- It was demonstrated that laser experiments can give unique information on the dependence on temperature of the heat capacity of liquid UO_2 in temperature ranges inaccessible to conventional techniques. The constant value assessed of Baichi et al. corresponds to a zeroth approximation estimate.

Finally, we would like to stress out that progress in the field of high-temperature thermodynamics is presently relying on development of new experimental methods. Conservative, if not regressive argumentations as those produced by Baichi et al. in the two mentioned review papers prevent a sound scientific discussions on questions whose definitive answer is till being pursued.

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