



Critical evaluation of experimental data of solution enthalpy of zirconium in liquid aluminum



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ABSTRACT

The aim of the present paper is to propose a new interpretation of the zirconium dissolution in liquid aluminum calorimetry experiments performed in the past in order to reconcile some apparently contradictory results and observations. It is supported by the development of a dissolution kinetics model. We show that probably most of the experiments interpreted in terms of dissolution must be considered in terms of (partial or total) transformation of zirconium into zirconium aluminide (Al_3Zr). In addition, on the basis of the developed model, we propose some recommendations in terms of experimental conditions to improve the dissolution process. These recommendations are consistent with some empirical rules derived in the past. It also puts in question past standard enthalpy measurements of some compounds in the Cu-Zr, Ni-Zr, Co-Zr and U-Zr systems.

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1. Introduction

In high temperature solution calorimetry, the standard enthalpy of formation of a compound A_xB_β , is determined from the separate experimental determinations of the solution enthalpies of the compound (A_xB_β) and its components A and B in a same solvent bath at the same temperature, according to the equation:

$$\Delta_f H^0(A_xB_\beta) = \alpha \Delta_{sol} H^\infty(A) + \beta \Delta_{sol} H^\infty(B) - \Delta_{sol} H^\infty(A_xB_\beta) \quad (1)$$

where:

- α and β are the stoichiometric coefficients of the A_xB_β compound,
- $\Delta_f H^0(A_xB_\beta)$, the standard enthalpy of formation of the A_xB_β compound,
- $\Delta_{sol} H^\infty(X)$, the solution enthalpy of $X = A$ (or B or A_xB_β) at infinite dilution in the solvent.

The solution enthalpy of X is determined by successive drops of X (initially at the standard temperature, 298.15 K) in the solvent and by measuring the associated heat effects which are, once

divided by the number of added moles of X, extrapolated at infinite dilution in order to obtain $\Delta_{sol} H^\infty(X)$.

For most transition metals and in particular for Group IV elements such as titanium, hafnium or zirconium, the choice of the solvent is a crucial problem since their dissolution in many ones classically used in high temperature calorimetry is a slow process. Such slow kinetics requires to guarantee the thermal stability of the calorimeter over large times and this is a difficult task at high temperature. However some refractory transition elements were successfully dissolved in metallic solvents, Ti and Hf in liquid tin [1] or in liquid germanium [2]. For zirconium, Yassin et al. [1] reported two very different values for solution enthalpies in liquid tin at infinite dilution from Sudavtsova et al. [3] and from Bouhajib et al. [4] whereas in liquid germanium, no data was available up to now. Preliminary experiments of zirconium dissolution in liquid germanium at 1273 K were performed in our laboratory to check the possibility of using this solvent. The measured solution enthalpies showed a large dispersion ($\pm 20 \text{ kJ}\cdot\text{mol}^{-1}$). Moreover there was apparently a non-linear variation of solution enthalpies with zirconium concentration, preventing any reliable extrapolation at infinite dilution.

Molten aluminum was also extensively used by different groups as reported in a review by Colinet [5]. Numerous experimental determinations of solution enthalpies of zirconium in liquid aluminum were performed at temperatures around $\approx 1000 \text{ K}$ [6–14]

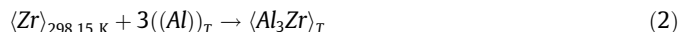
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and at higher temperatures, above 1673 K up to 2045 K [15–19]. In the framework of a recent study of the Ag–Zr phase diagram [20] devoted to the determination of the standard enthalpies of formation of AgZr and AgZr_2 compounds, new values of zirconium solution enthalpy in liquid aluminum at 996 K have been obtained by our group. The comparison between our value and the previous ones highlights a rather good agreement (Table 1) even if one can consider the values somewhat dispersed. Regarding these results, to use liquid aluminum for zirconium dissolution at temperatures around ≈ 1000 K seemed to be a promising way.

Colinet [5] mentioned that attempts to dissolve zirconium in liquid aluminum at temperatures around 1000 K usually failed, but without giving any explanation. In fact, the reason is linked to the formation of the intermetallic compound (Al_3Zr) at the liquid/metal interface in the very beginning of the dissolution process. Once a thin layer of zirconium aluminide forms by chemical reaction between zirconium and aluminum, the direct contact between the sample core and liquid is prevented. The kinetics of incorporation of zirconium atoms in the bath is then controlled by the competition between the dissolution of the outer layer of Al_3Zr by the liquid phase and the growth of this intermetallic layer towards the sample core. Solid-state diffusion experiments between 826 and 913 K by Kidson et al. [21] showed that the diffusion of aluminum in Al_3Zr was much higher than the one of zirconium. It was explained in [21] by the similarity of the Al (fcc) and Al_3Zr (D0_{23}) structures where the interatomic distances between aluminum atoms is 2.86 Å in the first one, whereas it is 2.80 Å and 2.85 Å in the second one. It leads to a rapid growth of a Al_3Zr layer (to the apparent exclusion of all other Al–Zr intermetallic compounds) which acts as a barrier for zirconium atoms. In the dissolution calorimetry experiments, such a phenomenon could lead to a complete transformation of the zirconium solid sample into aluminide before its sluggish dissolution.

In the Al–Zr phase diagram, at ≈ 1000 K, the limit of the (Liquid + Al_3Zr) biphasic domain is reached for a zirconium atomic fraction of 0.0008, according to the recent experimental data of Dezellus et al. [22]. Almost all the groups (Table 1) investigated a range of zirconium atomic fractions exceeding the zirconium solubility in liquid aluminum. They surprisingly did not mention any composition dependence of the solution enthalpy of zirconium in liquid aluminum. In our experiments [20], the measured heat flows effectively showed slight or no difference below and above the solubility whereas different thermal effects are expected corresponding to a dissolution process below the solubility and a precipitation of a solid phase (i.e. Al_3Zr) above the solubility. From these observations, it can be assumed that the transformation that occurs in the calorimeter below and above the solubility could correspond to the same chemical process, i.e.:



Whereas they obtained a similar value that ours, Gomozov et al. [10,11], claimed that the examination of their bath after the

Table 1

Solution enthalpies ($\text{kJ}\cdot\text{mol}^{-1}$) of zirconium in liquid aluminum at infinite dilution near 1000 K. The references states are solid zirconium at 298.15 K and liquid aluminum at temperature. * The more recent values of Turchanin et al., according to the authors [14], are considered to be a refinement of the previously published ones.

Authors	Temperature (K)	x_{Zr}	$\Delta_{\text{sol}}H^\infty(\text{Zr})$
Ansara et al. [6]	984	≤ 0.0014	–212.4
Nagarajan et al. [7]	991	≤ 0.0267	-220.3 ± 9.5
Turchanin et al. [8,9,13]	1026	≤ 0.0044	-217.4 ± 8.5
Gomozov et al. [10,11]	1030	≤ 0.0006	-203.3 ± 4.9
Turchanin et al. [12,14]	1022	≤ 0.0055	$-235.0 \pm 4.3^*$
Decreton et al. [20]	996	≤ 0.0022	-221.5 ± 5.8

experiments showed an uniform distribution of zirconium in aluminum without aluminide precipitation. On the contrary Eremenko et al. [23] previously showed that, for dissolution tests of a zirconium disc specimen immersed in liquid aluminum at 973 K, zirconium was completely transformed into Al_3Zr .

The occurrence of Reaction (2) likely depends on the experimental conditions. On the basis of experimental observations on different chemical metallic aluminum-based systems, Eremenko et al. [24] derived some empirical rules required to prevent the growth of the aluminide layer, i.e. a bath temperature above 1050 K, a sample area-to-volume ratio of 10 m^{-1} and a concentration of dissolved metal below 0.4–0.6 times the solubility limit at the bath temperature.

The aim of the present paper is to propose a new interpretation of the zirconium dissolution in liquid aluminum calorimetry experiments performed in the past in order to reconcile some apparently contradictory results and observations. It is supported by the development of a dissolution kinetics model described in Section 3. As the thermal signal of the calorimeter is continuously recorded during the dissolution process, the return of the signal to the baseline after each zirconium drop provides an estimate of the duration of this process. The model predictions allow to evaluate the reliability of the published values of enthalpy of solution zirconium in aluminum bath around 1000 K.

2. Experimental observations in our tests

The experimental procedure and conditions of our tests are detailed in [20]. Some information are summarised here. The measurements were performed under argon gas at a pressure slightly over 1 bar in a Tian-Calvet high temperature calorimeter. The temperatures of the reference and the sample cells were measured by a Pt10%Rh–Pt thermocouple inserted between the cells in the isothermal alumina block. 9.1 g of aluminum was put in a graphite crucible. The crucible was inserted in a vitreous silica tube. As the silica tube was slowly lowered into the calorimeter maintained at the experiment temperature, the metallic load melted and after a transient thermal regime, the whole assembly reached thermal equilibrium and a stable baseline was obtained. Small fragments of zirconium about few mg were then dropped successively until a target final composition was reached. Masses were weighed on a balance of $\pm 10^{-5}$ g accuracy. The differential signal of the calorimeter was continuously recorded during the process. After each drop, a thermal effect was registered before the signal has returned to the baseline.

The duration of the dissolution process can be estimated as the time interval between the sample drop and the return to the baseline. This return can be in some cases difficult to assess. It is considered that our measurements of thermal effects are accurate within $\pm 5\%$. According to the fact that the thermal effect is proportional to the sample mass, approximately 95% of the sample is dissolved during the dissolution process duration. After the final zirconium addition, the atomic fraction of Zr in the bath was about 0.000667 (i.e. about 89% of the solubility limit at 996 K, i.e. 0.00075 [22]). The silica tube assembly containing the sample was then extracted from the calorimeter and the sample cooled down to room temperature under inert atmosphere for further analyses which are discussed in Part 4.

3. Description of the model

3.1. Introduction

As explained in detail by Yatsenko et al. [25], when there is no formation of intermetallic layer, the dissolution of zirconium in

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