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# Determination of Solution Enthalpy of Zirconium in Liquid Aluminum

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## Abstract

The work presented in this paper is the continuation of our earlier publication (Barrachin et al. [1]) where the literature data on the calorimetric measurements of the zirconium dissolution in liquid aluminum at temperatures around 1000 K were carefully analyzed. In this previous study, we showed that these different data were erroneously interpreted by their authors in terms of dissolution enthalpies. In our interpretation, the measured thermal effects rather resulted from the initial complete transformation of Zr into Al<sub>3</sub>Zr, due to the quick diffusion of aluminum towards the zirconium sample core. In this scenario, the subsequent dissolution of the aluminide particle in the melt, which is very slow at this temperature, was likely to remain undetected in the calorimetric experiments. To overcome these difficulties, the partial drop-solution enthalpy of zirconium at infinite dilution is indirectly derived from Al<sub>3</sub>Zr dissolution in liquid aluminum at 1173 K. It is found to be  $\Delta_{ds}\overline{H}_{Zr,298K}^{\infty,1173K} = -130 \pm 9 \text{ kJ}\cdot\text{mol}^{-1}$ . The corresponding partial mixing enthalpy of Zr at the liquid state is  $\Delta_{mix}\overline{H}_{Zr}^{\infty,1173K} = -175 \pm 10 \text{ kJ}\cdot\text{mol}^{-1}$ . This value is consistent with the results obtained by various authors having performed calorimetric experiments at temperatures higher than 1700 K. It can hence be concluded that the zirconium partial mixing enthalpy at infinite dilution does not depend on temperature between 1173 K and 2045 K.

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## 1. Introduction

Molten aluminum was used as a solvent in many high temperature solution calorimetry studies around 1000 K in order to measure the standard enthalpy of formation of zirconium-based binary compounds, e.g. in the Cu-Zr [2, 3], Ni-Zr [3–5], Co-Zr [6, 7], U-Zr [8], and Ag-Zr [9] systems. In these studies, dissolution of zirconium, of the

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second metallic element (i.e. Cu, Ni, Co, U and Ag respectively) and of the compound of interest in liquid aluminum are conducted in three separate experiments. The partial drop solution enthalpies of the elements and of the compound are first extrapolated at infinite dilution and then combined in a thermodynamic cycle to yield the standard enthalpy of formation of the compound.

In a previous paper [1], we critically reviewed the different experimental data related to the partial drop solution enthalpy of zirconium in liquid aluminum at infinite dilution around 1000 K. We demonstrated that there is an incompatibility between the durations of the thermal effects reported by the different authors and the durations which can be estimated from a dissolution kinetic model. As a consequence, we concluded that, contrary to the authors expectations, the zirconium samples were likely to be not fully dissolved in these experiments.

The main reason is linked to the formation of an  $\text{Al}_3\text{Zr}$  layer,  $\text{Al}_3\text{Zr}$  being the richest Al stoichiometric compound in the Al-Zr phase diagram, at the liquid/solid metal interface at the beginning of the "dissolution" reaction. Once this layer created, the direct contact between the pure zirconium sample core and the aluminum liquid is prevented. The kinetics of the dissolution process then becomes essentially governed by two competing mechanisms, firstly, the aluminide layer dissolution by liquid aluminum and secondly, the growth of this layer towards the sample core. Kidson [10] showed that solid-state diffusion of aluminum across  $\text{Al}_3\text{Zr}$  at temperatures between 800 and 900 K is much faster than the one of zirconium. The Al (fcc) and  $\text{Al}_3\text{Zr}$  ( $\text{D0}_{23}$ ) structures presents similarities in terms of interatomic distances which makes the Al diffusion through the aluminide easier, leading to a quick growth of the  $\text{Al}_3\text{Zr}$  layer, to the exclusion of the growth of other Al-Zr compound. Extrapolating this experimental observation to the liquid aluminum/solid zirconium interaction during calorimetric experiments around 1000 K, a more or less a complete transformation of the zirconium sample into the aluminide is expected. Large  $\text{Al}_3\text{Zr}$  precipitates, having typical size of several 10  $\mu\text{m}$ , are effectively observed in our experiments [10]. They were probably not formed when the aluminum bath, after being extracted from the calorimeter, was cooled down to room temperature, but rather *in situ*, at the calorimeter temperature. Moreover, we put in evidence that the enthalpy values consistently measured in these different experiments including ours [2–9, 11, 12] could quantitatively match with our formation of  $\text{Al}_3\text{Zr}$  scenario.

At this stage, the measurement of the standard formation enthalpy of Zr-based compounds by high temperature solution calorimetry seemed to be compromised and required, in order to enhance the dissolution kinetics, either to change the solvent and/or to increase the measurement temperature, keeping in mind that our Tian-Calvet calorimeter is not designed to work above 1373 K<sup>1</sup>. An alternative possibility would be to use a stirring device to promote liquid aluminum convection during the experiment. Such a technique has been implemented by Maciag [14] and used to dissolve zirconium in liquid aluminum at 1073 K in the frame of calorimetric experiments aiming at determining the standard formation enthalpy of various Al-Zr compounds. His results

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<sup>1</sup>The zirconium dissolution at room temperature was shown to be feasible by Klein *et al.* [13] using an acid mixture containing hydrofluoric acid. This technique will be not discussed in this paper.

will be discussed in detail in this paper.

From our side, the possibility to dissolve zirconium in other metallic solvents was firstly investigated. In liquid tin, Zr partial mixing enthalpies values in the liquid at infinite dilution were reported by Bouhajib *et al.* [15] at 1173 K, and at higher temperatures by Valishev [16] at 1973 K and by Sudavtsova *et al.* [17] at 1889 K. These literature results suggested that, in spite of the large discrepancy between the different measurements, liquid tin could be a potential solvent for Zr. Our preliminary tests, at 996 K as well as at 1173 K, have shown such a large dispersion that deriving a reliable value of the partial mixing enthalpy of zirconium in liquid tin was impossible. The zirconium samples were suspected to be floating on the bath, due to the lower density of solid Zr compared to the liquid tin one, preventing an efficient dissolution process. To our best knowledge, no test was performed before in liquid indium. In our experiments at 996 K and at 1173 K, previous difficulties related to the unfavorable ratio between the densities of the solvent and the solute, were also identified. The dissolution process was similarly found to be erratic with the impossibility to derive an accurate value of the Zr partial mixing enthalpy. An additional reason could be the strongly reduced driving force for Zr dissolution because of the extremely low zirconium solubility in liquid indium at these temperatures [18].

Scoping dissolution tests of zirconium in liquid aluminum were also performed at 1173 K, i.e. more than 150 K higher than the temperature of our previous experiments [9]. Once again, the measured drop-solution heats were largely scattered preventing the determination of a reliable value at infinite dilution. Moreover, the inconsistency between the duration of the observed thermal effect and the dissolution time calculated with our kinetic model was an additional indication that the aluminide formation could not be excluded at this temperature. The driving force of the dissolution process is the zirconium concentration difference between the solid/liquid interface, which is equal to the zirconium solubility in liquid aluminum, and the bulk of the liquid. In this case, the increase of the calorimeter temperature was not sufficient to significantly increase this driving force.

In the above described scenario of the competition between aluminide formation and aluminide dissolution, the dissolution of the aluminide principally occurs after the complete conversion of zirconium into aluminide. This dissolution is expected to take place during the experiments but, unfortunately, detection of the associated thermal effect proved to be difficult, the main reason being that the dissolution kinetics is much slower than the heat release linked to the aluminide formation and can easily be hidden in baseline fluctuations of the calorimetric signal. After very deep inspection of some thermograms, an endothermic signature, likely associated to the aluminide dissolution, could be identified unambiguously (Figure 1) before a complete return of the signal to the baseline. However, in many thermograms, such identification remained unclear and the quantitative measurement of the heat associated to this process was not reliable. To overcome these difficulties, it was later tried to directly measure the partial drop-solution enthalpy of  $\text{Al}_3\text{Zr}$  samples in liquid aluminum. This value was then used to derive the partial drop-solution enthalpy of zirconium in liquid aluminum by a thermodynamic cycle.

## 2. Experimental

### 2.1. Instrumentation and experimental procedure

The instrumentation and the calorimetric method already described in detail in [9] for Zr is applied for Al<sub>3</sub>Zr drop-solution experiments.

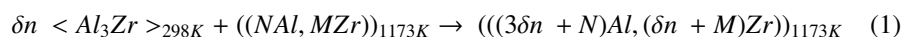
The calorimeter temperature was set to 1173 K. Aluminum (Alfa Aesar, Table 1) was used as solvent and calibration material. The protective atmosphere in the calorimeter was argon gas (Air Liquide, Table 1) with a pressure equal to 0.11MPa. For each run, a mass around 8.4-8.5 g of Al was loaded in a graphite crucible. At the beginning of the experiment, the calorimeter was calibrated by four Al drops. Then, small fragments of Al<sub>3</sub>Zr slugs (zirconium aluminide Al<sub>3</sub>Zr, CAS 12004-83-0, D0<sub>23</sub>, Alfa Aesar, Table 1) were successively dropped into the bath until a target final concentration was reached. The differential signal of the calorimeter was continuously monitored and recorded during the process. The next addition was triggered once the signal has returned to the baseline. The final concentration of the bath was chosen to ensure that the concentration in zirconium was not exceeding the solubility limit in liquid aluminum [19] at the calorimeter temperature.

The processing of the acquisition data file consists in computing the area of each peak by numerical integration after having subtracted the baseline from the calorimetric signal. The main source of error arises from the choice of the baseline which is made to compute the area of each individual peak. The worst case corresponds to a peak of small height and a fluctuating baseline for which different equally probable baseline selections may affect the computed area by several percent.

### 2.2. Al<sub>3</sub>Zr dissolution experiments in liquid aluminum at 1173 K

Three runs of Al<sub>3</sub>Zr dissolution in liquid aluminum measurements were performed at 1173 K.

Within one run, each drop of  $\delta n$  moles of aluminide in the bath containing  $N$  moles of Al and  $M$  moles of Zr corresponds to the following reaction:



The associated heat effects  $Q_1$  which have been measured, are reported under the heading  $\Delta_{ds}\overline{H}_{Al_3Zr,298K}^{1173K}(x_{Al_3Zr}) = Q_1/\delta n$  in Table 1.

The typical thermogram recorded during the drop of an Al<sub>3</sub>Zr fragment is portrayed in Figure 2. Two successive endothermic peaks are seen. The first sharp one is due to the fast heating of the fragment upon entering the aluminum bath while the second smeared peak results from its subsequent slower dissolution.

In the investigated composition range,  $\Delta_{ds}\overline{H}_{Al_3Zr,298K}^{1173K}(x_{Al_3Zr})$  was found to be independent on  $x_{Al_3Zr}$ . Hence, the partial drop-solution enthalpy of Al<sub>3</sub>Zr at infinite dilution in liquid aluminum,  $\Delta_{ds}\overline{H}_{Al_3Zr,298K}^{\infty,1173K}$ , was simply calculated by taking the average of the 10 measurements reported in Table 1.  $\Delta_{ds}\overline{H}_{Al_3Zr,298K}^{\infty,1173K}$  is equal to  $173 \pm 7$  kJ.mol<sup>-1</sup>.

The uncertainty reported here is an expanded uncertainty with a coverage factor of 2. It combines the standard uncertainty on the calorimeter calibration coefficient and the standard uncertainty on the Al<sub>3</sub>Zr dissolution heats. In assessing the uncertainty

of the calibration coefficient, it was further assumed that the uncertainty on the heat increment of pure aluminum calculated with the SGTE data [20] was 1% at 1173 K. From the standard enthalpy of formation of  $Al_3Zr$  reported by Meschel *et al.* [21], the drop-solution enthalpy of zirconium at infinite dilution in liquid aluminum at 1173 K can be calculated with the following expression:

$$\Delta_{ds}\overline{H}_{Zr,298K}^{\infty,1173K} = \Delta_f H_{Al_3Zr}^{298K} - 3\Delta H_{Al,298K}^{1173K} + \Delta_{ds}\overline{H}_{Al_3Zr,298K}^{\infty,1173K} \quad (2)$$

with  $\Delta_f H_{Al_3Zr}^{298K} = -193.6 \pm 5.2 \text{ kJ.mol}^{-1}$  [21], and  $\Delta H_{Al,298K}^{1173K} = 36.4 \text{ kJ.mol}^{-1}$  [20], the aluminum heat increment from 298 K to 1173 K.

The partial drop-solution enthalpy of zirconium,  $\Delta_{ds}\overline{H}_{Zr,298K}^{\infty,1173K}$ , at 1173 K in liquid aluminum calculated according to (2) is equal to  $-130 \pm 9 \text{ kJ.mol}^{-1}$  with the following reference states : solid zirconium at 298 K and liquid aluminum at 1173 K.

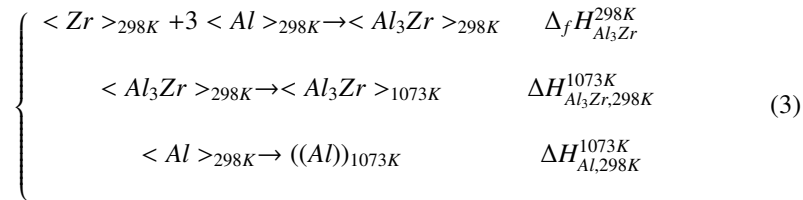
Using the heat increment of Zr between the solid state at 298 K and the supercooled liquid state at 1173 K,  $\Delta H_{Zr,298K}^{1173K} = 44.7 \text{ kJ.mol}^{-1}$  calculated with the SGTE data [20], it is then possible to derive the partial mixing solution of zirconium at infinite dilution in aluminum at 1173 K,  $\Delta_{mix}\overline{H}_{Zr}^{\infty,1173K}$  which is equal to  $-175 \pm 10 \text{ kJ.mol}^{-1}$  with the following reference states : liquid zirconium and aluminum at 1173 K. It is worth noting that the uncertainty on this value is very difficult to assess because it depends on the standard uncertainty of the heat increment of liquid Zr, 955 K below its melting point. This standard uncertainty which is unknown has been assumed to be 10% of its SGTE value in the present work.

### 3. Discussion

#### 3.1. Partial drop-solution enthalpy of zirconium in liquid aluminum

The partial drop-solution enthalpy of zirconium in liquid aluminum at infinite dilution at 1073 K has been very recently reported by Maciag [14]. The value,  $-244.5 \pm 5.4 \text{ kJ.mol}^{-1}$ , is rather consistent with the previous measurements [2–9, 11, 12] at similar temperatures (Table 3) even if it can be underlined that this value is the most negative of the data set. This value is in strong disagreement with the value determined in this paper,  $-130 \pm 9 \text{ kJ.mol}^{-1}$ .

In the past experiments, as mentioned in the introduction, it was suspected that the thermal effects were erroneously interpreted in terms of Zr dissolution. It was shown that they more likely corresponded to the zirconium transformation into  $Al_3Zr$ . If we assume that such a process occurs in Maciag's experiments, the associated heat,  $\Delta\overline{H}_2$ , can be estimated from the heats involved in the following reactions:



The heat involved ,  $\overline{\Delta H_2}$ , can be written:

$$\overline{\Delta H_2} = \Delta_f H_{Al_3Zr}^{298K} + \Delta H_{Al_3Zr,298K}^{1073K} - 3\Delta H_{Al,298K}^{1073K} \quad (4)$$

with, for the Maciag's experimental conditions,  $\Delta_f H_{Al_3Zr}^{298K} = -193.6 \pm 5.2 \text{ kJ.mol}^{-1}$  [21],  $\Delta H_{Al,298K}^{1073K} = 33.3 \text{ kJ.mol}^{-1}$  [20], and  $\Delta H_{Al_3Zr,298K}^{1073K} = 79.7 \pm 0.4 \text{ kJ.mol}^{-1}$  [1].

The calculated value,  $\overline{\Delta H_2}$ , equal to  $-213.8 \pm 5.3 \text{ kJ.mol}^{-1}$ , is not far from the Maciag's value (Table 3) in such a way that the hypothesis of aluminide formation in the calorimeter cannot be fully excluded.

In our previous article [1], a dissolution kinetic model was developed in order to estimate the duration of the thermal effect expected in a dissolution process driven by diffusion and natural convection induced by the density difference between zirconium and aluminum. The dissolution process of a solid sample in liquid aluminum is described by the Nernst-Shchukarev equation (commonly used, see e.g. [22, 23]) :

$$\frac{dC(t)}{dt} = K \frac{S}{V} [C_s - C(t)] \quad (5)$$

where  $C(t)$  is the concentration of the dissolved metal in the liquid bulk at time  $t$ ,  $C_s$ , the metal concentration in the liquid at saturation as given by the Al-Zr phase diagram,  $t(s)$  the dissolution time,  $S (m^2)$  the sample surface area,  $V (m^3)$  the melt volume, and  $K (m.s^{-1})$ , the mass transfer coefficient.

Equation (5) of the evolution of the zirconium concentration in the liquid is expressed under the following form :

$$\frac{dC(t)}{dt} = \frac{S}{V} B_0 [C_s - C(t)] + \frac{S}{V} B_1 [C_s - C(t)]^{5/4} \quad (6)$$

with the following definitions for  $B_0$ , and  $B_1$  :

$$\begin{cases} B_0 = \frac{3.47D_0}{S^{1/2}} \\ B_1 = 0.51 \frac{D_0}{S^{1/2}} \left( \frac{A_1 g S^{3/2}}{D_0 \nu} \right)^{1/4} \end{cases} \quad (7)$$

where :

$$A_1 = \frac{\rho_{l,Zr} - \rho_{l,Al}}{\rho_{l,Al} C_s + \rho_{l,Zr} (1 - C_s)} \quad (8)$$

with  $g (m.s^{-2})$  is acceleration due to gravity,  $d (m)$  the diameter of the sphere,  $\rho_{l,i} (kg.m^{-3})$  the density of  $i$  at the liquid state,  $\nu (m^2.s^{-1})$ , the kinematic viscosity,  $D_0 (m^2.s^{-1})$  the diffusion coefficient of solute in liquid, and  $S$  the sample surface. The numerical values of these different parameters can be found in [1].

Under our experimental conditions at 1173 K, we have firstly simulated (Figure 3) the dissolution of the first dropped aluminide sample of Run 3 (whose thermogram can be seen in Figure 2). The calculation shows that the sample should be dissolved in  $\approx 2000 \text{ s}$ . This value is consistent with the duration of the thermal effect which can be estimated from the thermogram.

To make our model consistent with the stirring mechanism adopted in the Maciag’s experiments, the mass transfer coefficient,  $K$ , should be modified to take into account the forced convection. Nevertheless it can be underlined that the masses of the zirconium dropped samples in his experiments are about 0.36 g [24] for an initial aluminum bath of 50 g, i.e. a zirconium content about 0.2 at.%. After the first drop, the zirconium concentration in the bath is very close to the solubility limit at 1073 K [19]. In these conditions, the dissolution kinetics becomes extremely reduced, even in case of forced convection, due to the very small difference between the zirconium concentration in the bath and the solubility limit. These conditions are favorable to the transformation of the zirconium sample into aluminide.

The large negative values of the standard enthalpies of formation of Al-Zr compounds determined by Maciag can be explained by his large negative value of  $\Delta_{ds}\overline{H}_{Zr,298K}^{\infty,1073K}$ . It is the case for  $\text{Al}_3\text{Zr}$  and  $\text{Al}_2\text{Zr}$ , with values which are respectively 13  $\text{kJ}\cdot\text{mol}^{-1}$  and 15  $\text{kJ}\cdot\text{mol}^{-1}$  more negative than other experimental determinations by Meschel [21] using high temperature direct synthesis calorimetry for  $\text{Al}_3\text{Zr}$  and by Klein *et al.* [13] using acid solution calorimetry for  $\text{Al}_2\text{Zr}$ .

A more general tendency can be obtained by comparing the standard enthalpies of formation obtained by Maciag for  $\text{Al}_3\text{Zr}$ ,  $\text{Al}_2\text{Zr}$ ,  $\text{Al}_3\text{Zr}_2$ ,  $\text{AlZr}$ ,  $\text{Al}_2\text{Zr}_3$ ,  $\text{AlZr}_2$ , and  $\text{AlZr}_3$  with the consistent set of DFT standard enthalpies of formation from Duan *et al.* [25] and selected by Fischer *et al.* [26] in their Calphad assessment of the Al-Zr phase diagram. Table 4 shows that the discrepancy between the two sets of values tends to increase from  $\text{Al}_3\text{Zr}$  to  $\text{AlZr}_3$ . It also indirectly validates the assumption that Maciag’s value of the drop-solution enthalpy of zirconium is too negative.

Assuming only an incorrect value for the drop-solution enthalpy of zirconium in the Maciag’s study and a reliable set of DFT values from [25], a linear variation of the discrepancy between the Maciag’s and Duan’s compound standard enthalpies of formation with the zirconium content,  $x$  of the compound written under the form  $\text{AlZr}_x$ , should be expected. The observed variation deviates from this tendency (Figure 4). It could take its origin in the measured heats of dissolution of the compounds themselves. For  $\text{Al}_3\text{Zr}$ , a direct comparison with our measurement is possible. From the values of  $\Delta_f H_{\text{Al}_3\text{Zr}}^{298K} = -206.4 \pm 9.2 \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta_{ds}\overline{H}_{Zr,298K}^{\infty,1073K} = -244.5 \pm 5.4 \text{ kJ}\cdot\text{mol}^{-1}$  reported by Maciag,  $\Delta_{ds}\overline{H}_{\text{Al}_3\text{Zr},298K}^{\infty,1073K}$  measured in his experiments and not reported in his article can be inferred<sup>2</sup>, 61.8  $\text{kJ}\cdot\text{mol}^{-1}$ . It is in strong disagreement with our value, even if both values were obtained at two temperatures 100 K apart. Using the heat increment of  $\text{Al}_3\text{Zr}$  from 298 to the calorimeter temperature 1073 K, 79.7  $\text{kJ}\cdot\text{mol}^{-1}$  [1] and the melting enthalpy of  $\text{Al}_3\text{Zr}$  ( $\approx 88 \text{ kJ}\cdot\text{mol}^{-1}$  [27]), it is deduced that the partial mixing enthalpy of  $\text{Al}_3\text{Zr}$  (liquid state) at infinite dilution in liquid aluminum at 1073 K is a strongly exothermic process ( $\approx -106 \text{ kJ}\cdot\text{mol}^{-1}$ ) according to Maciag’s data. By contrast, we put in evidence a slightly exothermic process<sup>3</sup>, about  $\approx -6.2 \text{ kJ}\cdot\text{mol}^{-1}$ . Such discrepancy cannot be accounted for by the difference of the calorimeter temperatures in both datasets. As in zirconium drop-solution experiments, Maciag [24] used rather

<sup>2</sup>The heat increment of Al from 298 to 1073 K is taken from [20] and is 33.3  $\text{kJ}\cdot\text{mol}^{-1}$ .

<sup>3</sup>The heat increment of  $\text{Al}_3\text{Zr}$  from 298 to calorimeter temperature 1173 K is 91.2  $\text{kJ}\cdot\text{mol}^{-1}$  [1].



large masses of  $\text{Al}_3\text{Zr}$  ( $\approx 0.4$  g). Under these experimental conditions, the dissolution process could have been drastically slowed after the first drop.

Plotting the convex hull at 298 K from Maciag's results in Figure 4, it can be seen in the region of compositions lower than 50%Zr that  $\text{Al}_2\text{Zr}$  and  $\text{Al}_3\text{Zr}_2$  should be less stable than mechanical mixtures of  $\text{Al}_3\text{Zr}$  and  $\text{AlZr}$ . This conclusion contradicts the state of the art of the Al-Zr phase diagram [28] and the DFT calculations from [25].

### 3.2. Partial zirconium mixing enthalpy at liquid state

We have reported in Table 3 and on Figure 6, the existing data related to the partial mixing enthalpies of zirconium at infinite dilution in liquid aluminum.

They can be divided into two groups, the low temperature data, obtained between 984 K and 1073 K, are between  $-243$  and  $-285$   $\text{kJ}\cdot\text{mol}^{-1}$  while the high temperature data, obtained between 1693 K and 2045 K, give much less exothermic values in the range  $-139$  to  $-177$   $\text{kJ}\cdot\text{mol}^{-1}$ .

The partial zirconium mixing enthalpy in liquid aluminum at 1173 K obtained in this paper,  $-175 \pm 10$   $\text{kJ}\cdot\text{mol}^{-1}$ , correlates well with the high temperature measurements of Witusiewicz *et al.* [29], Esin *et al.* [30] and Sudavtsova *et al.* [31]. This good correlation would suggest that Zr partial mixing enthalpy at infinite dilution in liquid Al does not depend on temperature in the range 1173-2045 K.

Comparing now our partial zirconium mixing enthalpy with the low temperature data, a variation between 67 and 109  $\text{kJ}\cdot\text{mol}^{-1}$ , depending on the considered value in the data set [2-9, 11, 12, 14], can be calculated over a temperature interval less than 200 K. Variation of this magnitude over such a narrow temperature interval would be very surprising, even more if we consider that most of these data have been obtained under rather similar experimental conditions.

This unexpected enthalpy variation can be discussed in terms of excess heat capacity of Al-Zr liquid. In the recent assessment of the Al-Zr phase diagram [26], Fischer *et al.* choose a composition dependency Redlich-Kister polynomial of second degree to model the Gibbs energy of the liquid phase in the Al-Zr system. The analysis of the experimental data relative to the mixing enthalpy of the liquid phase (Figure 3 of [26]) shows that the regular solution model can be considered as a rather good approximation to describe the mixing enthalpy. Within this framework, the excess mixing enthalpy can be written as:

$$\Delta_{mix}H^{liq,xs}(x_{Zr}, T) = \zeta(T)x_{Zr}(1 - x_{Zr}) \quad (9)$$

where  $\zeta(T)$ , the interaction parameter.

The zirconium partial mixing enthalpy in liquid aluminum takes the following expression :

$$\Delta_{mix}\bar{H}_{Zr}^T = \zeta(T)(1 - x_{Zr})^2 \quad (10)$$

where  $\zeta(T)$ , appears to be the zirconium partial mixing enthalpy at infinite dilution.

The excess heat capacity can be written as:

$$C_p^{liq,xs}(x_{Zr}, T) = x_{Zr}(1 - x_{Zr})\frac{d\zeta(T)}{dT} \quad (11)$$

Using our measured values at 996 K from [9] and 1173 K from this work, the mean

excess heat capacity of Al-Zr liquid in the temperature range [996 K–1173 K] can be roughly estimated by the following expression:

$$C_p^{liq,xs}(x_{Zr}, 1084.5K) \approx x_{Zr}(1 - x_{Zr}) \frac{\zeta(1173) - \zeta(996)}{1173 - 996} \quad (12)$$

or:

$$C_p^{liq,xs}(x_{Zr}, 1084.5K) \approx 474 x_{Zr}(1 - x_{Zr}) J.mol^{-1}.K^{-1} \quad (13)$$

The previous expression of  $C_p^{liq,xs}$  yields  $118.5 J.mol^{-1}.K^{-1}$  at the average temperature of 1084.5 K and at the equimolar composition. At the same composition and temperature, the ideal heat capacity of liquid,  $C_p^{liq,id}$ , according to the Neumann-Kopp rule<sup>4</sup>, is equal to  $32.7 J.mol^{-1}.K^{-1}$ . Considering that the excess heat capacity in most cases contribute only little to the heat capacity of a metallic liquid, the excess heat capacity derived from the measurements at 996 K can be considered as unrealistic.

Fischer and Colinet [26] underscored that the Calphad modelling of the Al-Zr system is very constrained by the standard enthalpies of formation of the numerous intermetallic compounds in order to guarantee their stability at 298 K. In this context, Fischer and Colinet gave more weight to Witusiewicz *et al.* liquid enthalpy data [29] in their optimization process and obtained a good fit of the phase diagram in the aluminum-rich region.

In their modelling, the mixing enthalpy of the liquid phase,  $\Delta_{mix}H$ , is not temperature dependent. The partial enthalpy of mixing of zirconium at infinite dilution can be derived from the assessed interaction parameters of the liquid using the following equation:

$$\Delta_{mix}\overline{H}_{Zr}^{\infty} = \lim_{x_{Zr} \rightarrow 0} \left[ \Delta_{mix}H - x_{Al} \left( \frac{\partial \Delta_{mix}H}{\partial x_{Al}} \right)_{T,p} \right] = -156.7 kJ.mol^{-1} \quad (14)$$

Our experimental value,  $-175 \pm 10 kJ.mol^{-1}$  is in the  $[-120; -180 kJ.mol^{-1}]$  range of the values of the Zr partial enthalpy of mixing at infinite dilution in liquid Al measured by calorimetry at the highest temperatures [29–33]. Moreover, our value is also in reasonable agreement with the value calculated from the parameters assessed by Fischer *et al.* [26], the magnitude of the difference, roughly  $20 kJ.mol^{-1}$ , being comparable to the experimental scattering affecting Witusiewicz's data, as shown in Fig 4 of [26]. Being aware of the ability of the Calphad approach to test the compatibility between phase diagram data and thermodynamic functions of individual phases, this agreement can be considered as an additional indirect validation of our measurement.

#### 4. Conclusion

In the past, several consistent values for the partial drop-solution enthalpy of zirconium in liquid aluminum around 1000 K were reported. In a previous study, we showed

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<sup>4</sup>  $C_p^{liq,id} = x_{Al}C_p^{liq,Al} + x_{Zr}C_p^{liq,Zr}$ , with the heat capacities of Al and Zr taken from [20].

that these different data have to be rather interpreted in terms of transformation of Zr into  $\text{Al}_3\text{Zr}$ .

To overcome these difficulties, in this work, the zirconium partial drop-solution enthalpy at infinite dilution is indirectly derived from  $\text{Al}_3\text{Zr}$  drop-solution experiments in liquid aluminum at 1173 K. It is found to be  $\Delta_{ds}\overline{H}_{\text{Zr},298\text{K}}^{\infty,1173\text{K}} = -130 \pm 9 \text{ kJ}\cdot\text{mol}^{-1}$ . The corresponding zirconium partial mixing enthalpy at infinite dilution in liquid aluminum is  $\Delta_{mix}\overline{H}_{\text{Zr}}^{\infty,1173\text{K}} = -175 \pm 10 \text{ kJ}\cdot\text{mol}^{-1}$ . This value is consistent with literature data obtained by calorimetric experiments performed at temperatures higher than 1700 K and likely indicates that the partial mixing enthalpy of Zr at infinite dilution in liquid Al does not depend on temperature between 1173 K and 2045 K.

Table 1: Element purities

Chemical name	Source	Commercial grade	Initial purity	Purification method
Al	Alfa Aesar	-	0.9999 (mass)	None
Al <sub>3</sub> Zr	Alfa Aesar	-	0.99 (mass)	None
Ar	Air Liquide	Alphagaz 1	0.99999 (mole) <sup>1</sup>	None

<sup>1</sup> H<sub>2</sub>O < 3 ppm mole, O<sub>2</sub> < 2 ppm mole, C<sub>n</sub>H<sub>m</sub> < 0.5 ppm mole according to Air Liquide data.

Table 2: Partial drop-solution enthalpy ( $\text{kJ}\cdot\text{mol}^{-1}$ ),  $\Delta_{ds}\overline{H}_{Al_3Zr,298K}^{1173K}(x_{Al_3Zr})$ , of  $Al_3Zr$  in liquid aluminum at  $T = 1173\text{ K}$  - The experimental pressure is  $p = 0.11\text{ MPa}$ . The reference states are solid  $Al_3Zr$  at  $T = 298\text{ K}$  and liquid aluminum at  $T = 1173\text{ K}$ .  $M_{Al}^{init}$  and  $\delta m_{Al_3Zr}$  in g,  $\delta n_{Al_3Zr}$  in mmol.  $M_{Al}^{init}$  is the sum of the bath mass plus the masses of the 4 aluminum calibration samples.  $x_{Al_3Zr}^1$  is the molar fraction of  $Al_3Zr$ . The uncertainties are indicated below the Table<sup>2</sup>.

	$M_{Al}^{init}$	$\delta m_{Al_3Zr}$	$\delta n_{Al_3Zr}$	$x_{Al_3Zr}$	$\Delta_{ds}\overline{H}_{Al_3Zr,298K}^{1173K}(x_{Al_3Zr})$
Run 1	8.45740	0.01317	0.076495	0.00012201	168
		0.01501	0.087182	0.00038296	184
		0.02496	0.144974	0.00075286	173
Run 2	8.56149	0.01060	0.061568	0.00009701	184
		0.01143	0.066388	0.00029855	173
		0.01432	0.083174	0.00053403	166
		0.01600	0.092932	0.00081116	175
Run 3	8.50833	0.00952	0.055295	0.00008767	164
		0.01009	0.058605	0.00026820	179
		0.01096	0.063659	0.00046192	(147) <sup>3</sup>
		0.01150	0.066795	0.00066853	160

<sup>1</sup> For the  $i^{th}$  drop of  $n_i$  moles of  $Al_3Zr$  in the aluminum bath containing initially  $n_{Al}$  moles of pure Al, the molar fraction of  $Al_3Zr$ ,  $x_i$ , corresponding to the measured partial enthalpy, is calculated according to :

$$x_i = \frac{\sum_{j=1}^{i-1} n_j + \frac{n_i}{2}}{\sum_{j=1}^{i-1} n_j + \frac{n_i}{2} + n_{Al}} \quad (15)$$

<sup>2</sup> Uncertainties :  $u(T)=1\text{ K}$ ,  $u(p)=10\text{ kPa}$ ,  $u_c(M_{Al}^{init})=0.000045\text{ g}$ ,  $u_c(\delta m_{Al_3Zr})=0.00002\text{ g}$ ,  $u_c(\delta n_{Al_3Zr})=0.00012\text{ mmol}$ ,  $u_c(x_{Al_3Zr})=0.000001$ .  $U_c(\Delta_{ds}\overline{H}_{Al_3Zr,298K}^{\infty,1173K})=7\text{ kJ}\cdot\text{mol}^{-1}$ , combined expanded uncertainty on the average of 10 measurements with a coverage factor of 2. The subscript c denotes a combined uncertainty according the nomenclature in [34].

<sup>3</sup> Indicative value, not considered as reliable, due to difficulty of the baseline choice. Not taken into account in the average for the calculation of  $\Delta_{ds}\overline{H}_{Al_3Zr,298K}^{\infty,1173K}$ .

Table 3: Partial drop-solution and mixing enthalpies, of zirconium in liquid aluminum at infinite dilution,  $\Delta_{ds}\overline{H}_{Zr,298K}^{\infty,T_{cal}}$ , and  $\Delta_{mix}\overline{H}_{Zr}^{\infty,T_{cal}}$ , respectively in  $\text{kJ}\cdot\text{mol}^{-1}$ . The references states are solid zirconium at 298 K and liquid aluminum at the calorimeter temperature ( $T_{cal}$ ) for  $\Delta_{ds}\overline{H}_{Zr,298K}^{\infty,T_{cal}}$ . The references states are liquid zirconium and liquid aluminum at the calorimeter temperature for  $\Delta_{mix}\overline{H}_{Zr}^{\infty,T_{cal}}$ .  $x_{Zr}$  is the maximum zirconium molar fraction reached in the different experiments. (\*) The more recent values of Turchanin *et al.*, according to the authors [3], are considered to be a refinement of the previously published ones.(\*\*) n.r. : not reported.

Authors	$T_{cal}$ (K)	$x_{Zr}$	$\Delta_{ds}\overline{H}_{Zr,298K}^{\infty,T_{cal}}$	$\Delta_{mix}\overline{H}_{Zr}^{\infty,T_{cal}}$
Ansara <i>et al.</i> [4]	984	$\leq 0.0014$	-212.4	-250.8
Nagarajan <i>et al.</i> [8]	991	$\leq 0.0267$	$-220.3\pm 9.5$	$-258.9\pm 9.5$
Decreton <i>et al.</i> [9]	996	$\leq 0.0022$	$-221.5\pm 5.8$	$-260.3\pm 5.8$
Turchanin <i>et al.</i> [2, 3]	1022	$\leq 0.0055$	$-235.0\pm 4.3^*$	$-274.7\pm 4.3$
Turchanin <i>et al.</i> [5, 11, 12]	1026	$\leq 0.0044$	$-217.4\pm 8.5$	$-257.2\pm 8.5$
Gomozov <i>et al.</i> [6, 7]	1030	$\leq 0.0006$	$-203.3\pm 4.9$	$-243.2\pm 4.9$
Maciag [14]	1073	n.r.**	$-244.5\pm 5.4$	$-285.9\pm 5.4$
Sudavtsova <i>et al.</i> [32]	1693	n.r.**	-76.2	-140.0
Batalin <i>et al.</i> [33]	1773	$\leq 0.09$	$-52.6\pm 1.3$	$-119.5\pm 1.3$
Sudavtsova <i>et al.</i> [31]	1790	$\leq 0.18$	$-102.4\pm 20.0$	$-170\pm 20.0$
Esin <i>et al.</i> [30]	1970	$\leq 0.60$	-91.7	-166.5
Witusiewicz <i>et al.</i> [29]	2045	$\leq 0.54$	$-99.4\pm 10.1$	$-177.3\pm 10.1$
This work	1173	$\leq 0.001$	$-130\pm 9$	$-175\pm 10$

Table 4: Standard enthalpies ( $\text{kJ}\cdot\text{mol}^{-1}$ ) of formation measured by drop-solution calorimetry [14] and calculated by DFT [25]

	$\text{AlZr}_{1/3}$	$\text{AlZr}_{1/2}$	$\text{AlZr}_{2/3}$	$\text{AlZr}$	$\text{AlZr}_{3/2}$	$\text{AlZr}_2$	$\text{AlZr}_3$
Maciag [14] (1)	$-68.8\pm 1.6$	$-84.5\pm 3.3$	$-99.3\pm 4.0$	$-142.6\pm 8.8$	$-122.5\pm 7.8$	$-168.3\pm 9.3$	$-174.4\pm 9.2$
Duan <i>et al.</i> [25] (2)	-62.4	-77.4	-83.1	-89.8	-95.7	-102.7	-116.0
$\Delta(1-2)$	-6.4	-7.1	-16.2	-52.8	-26.8	-65.6	-58.4

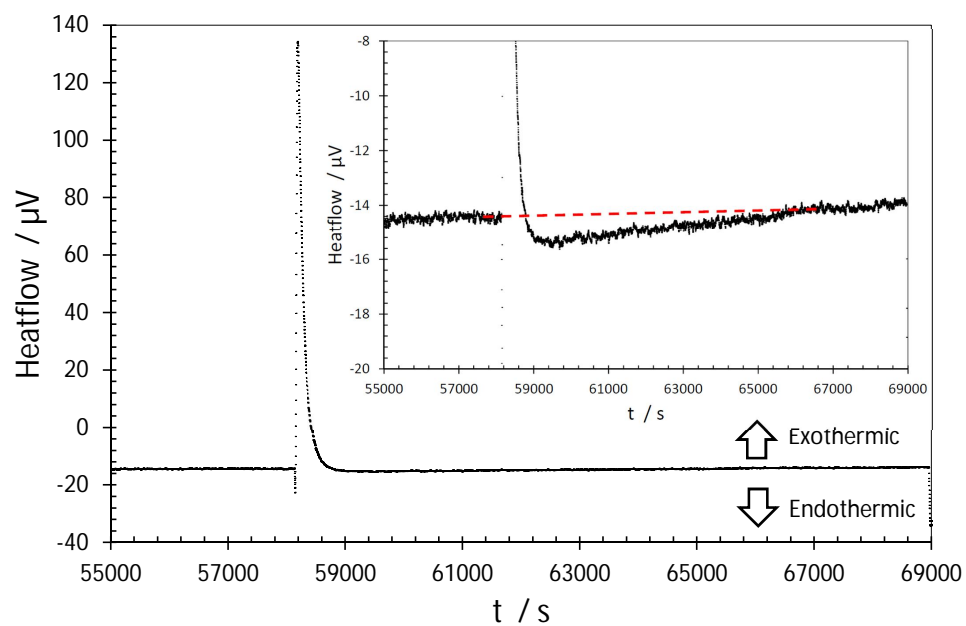


Figure 1: Representative thermogram of the "dissolution" of a Zr sample in liquid aluminum at 1173 K. The differential signal of the calorimeter is plotted vs. time. The mass of the dropped Zr fragment is 12.23 mg. Interpretation of this complex thermal event is as follows. The very first small endothermic deviation corresponds to the heating of the fragment which is quickly counterbalanced by a large exothermic deviation due to the  $\text{Al}_3\text{Zr}$  formation reaction. Subsequent  $\text{Al}_3\text{Zr}$  endothermic dissolution is only seen at greater magnification in the figure inlay, in which the linearly interpolated baseline is plotted as a red dashed line.

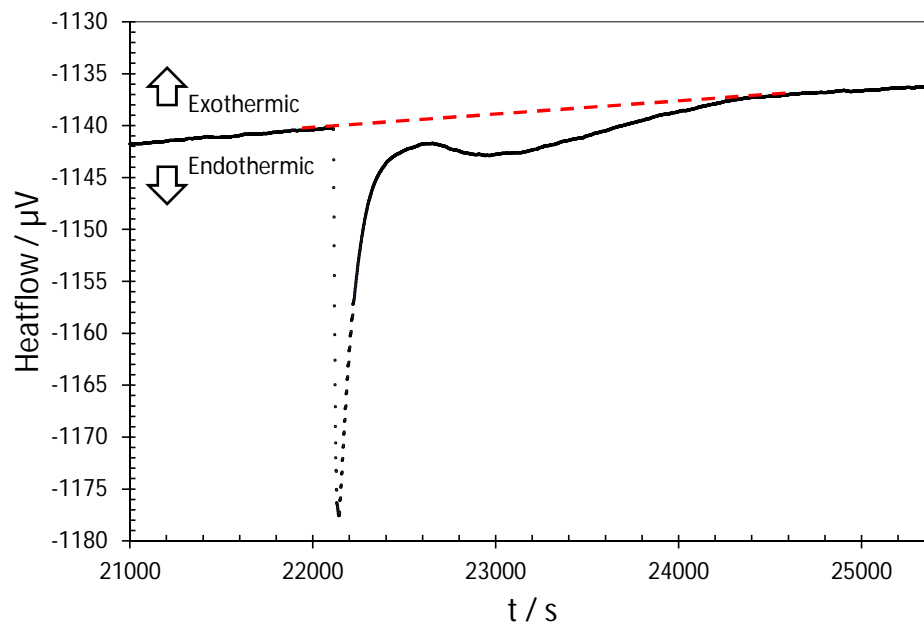


Figure 2: Representative thermogram of the dissolution of an  $\text{Al}_3\text{Zr}$  sample in liquid aluminum at 1173 K. The differential signal of the calorimeter is plotted vs. time. The mass of the dropped  $\text{Al}_3\text{Zr}$  fragment is 9.52 mg. Interpretation of the thermal event is as follows. The first sharp endothermic deviation corresponds to the heating of the fragment and is followed by its slower dissolution which is also endothermic, before the signal final return to the baseline. The linearly interpolated baseline is plotted as a red dashed line.



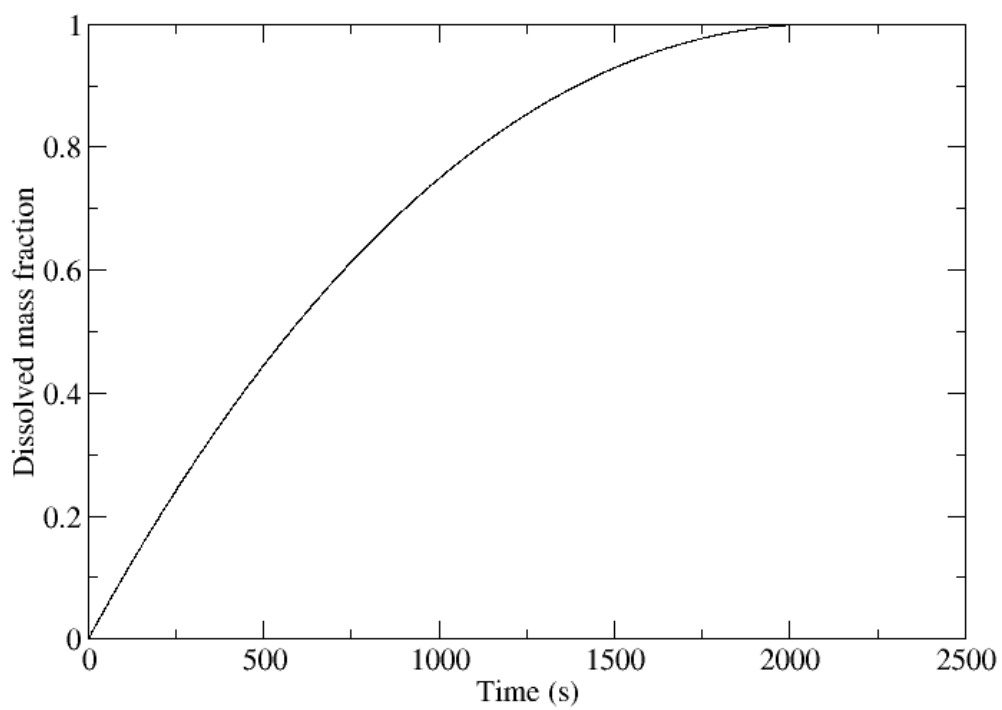


Figure 3: Calculated evolution of the dissolved mass fraction of  $\text{Al}_3\text{Zr}$  for Run 3 conditions, first dropped sample.

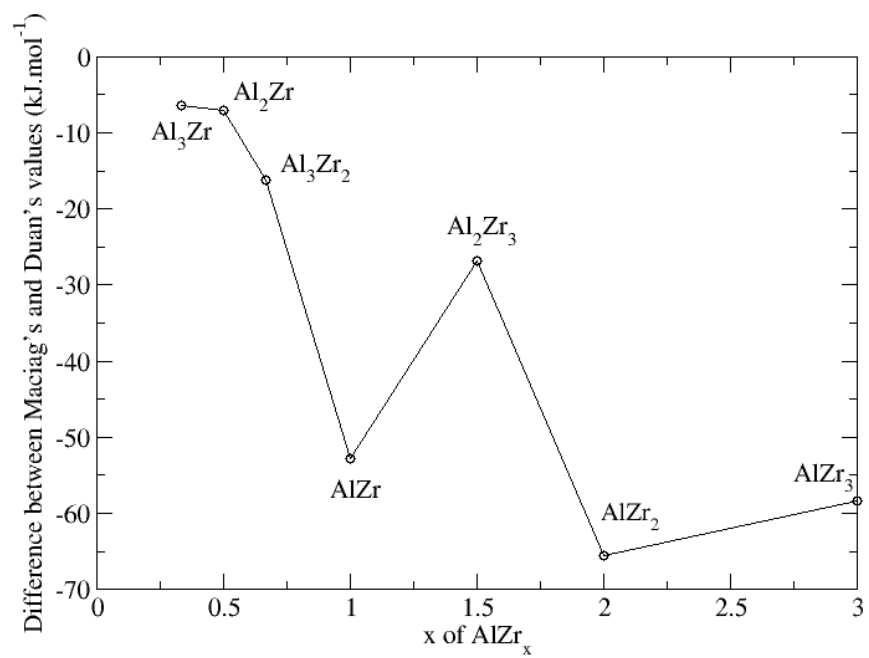


Figure 4: Difference between the standard enthalpies of formation of the different Al-Zr binary compounds measured by Maciag [14] and calculated by Duan [25] as function of  $x$ , zirconium composition of the compound of formula AlZr <sub>$x$</sub>  (see Table4)

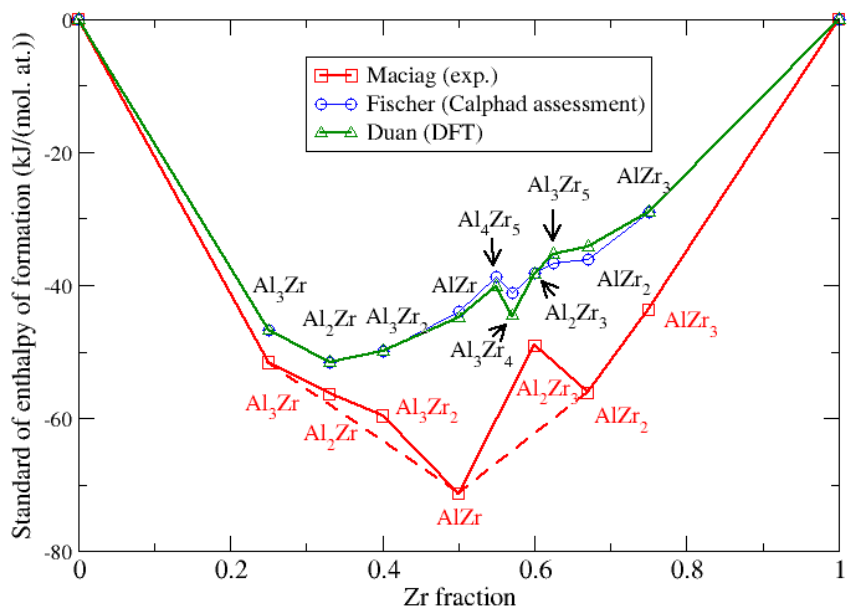


Figure 5: Standard enthalpies of formation of the different Al-Zr binary compounds as measured by Maciag [14], as calculated by Duan [25] and as assessed by Fischer and Colinet [26]. In dashed red line, the convex hull at 298 K from Maciag's results shows that, according to his values,  $\text{Al}_2\text{Zr}$  and  $\text{Al}_3\text{Zr}_2$  should be less stable than mechanical mixtures of  $\text{Al}_3\text{Zr}$  and  $\text{AlZr}$ .

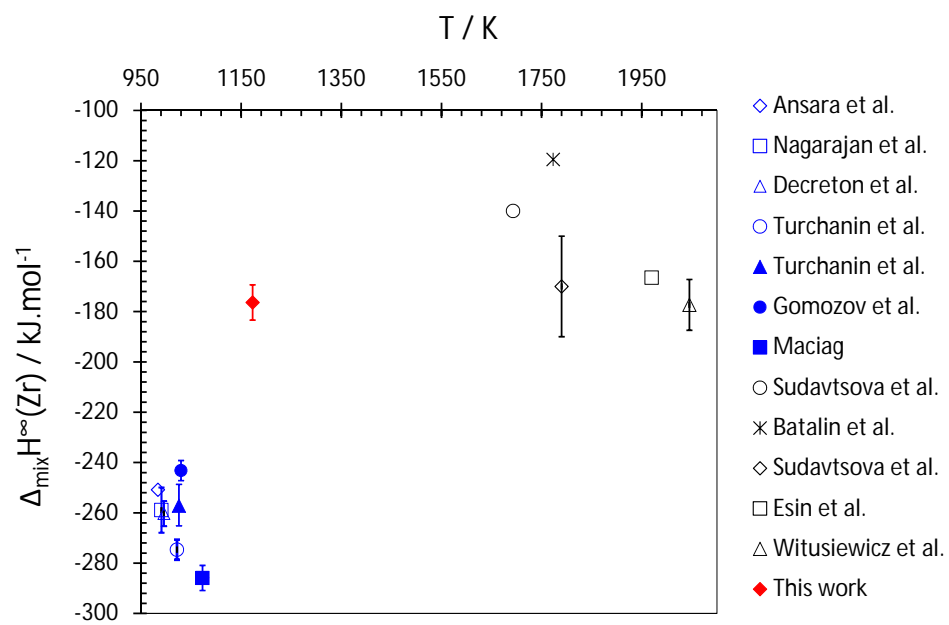


Figure 6: Partial mixing enthalpy of zirconium at infinite dilution in liquid aluminum vs. temperature according to different authors (see values in Table 3, 5<sup>th</sup> column). The references states are liquid zirconium and liquid aluminum at the calorimeter temperature.

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