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Electromagnetic levitation and its application in high temperature calorimetry[1]

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Abstract

The electromagnetic levitation technique is presented. It is a useful method to measure the thermophysical properties of high melting metals. The levitation alloying calorimetry (LAC) is described. Using the associate model and the TAP series, the excess heat capacities of the systems Fe–V and Fe–Ti are calculated on the basis of the concentration and temperature dependent descriptions of their mixing enthalpies. The relation between the levitation alloying and drop calorimetry is discussed. Using the temperature dependent description of the mixing enthalpy given by the associate model, the enthalpy of the intermetallic compound Fe_2Zr is calculated. The calculated and measured enthalpies were in perfect accordance.

Keywords: Electromagnetic levitation; Enthalpy; Mixing enthalpy; Excess heat capacity; Binary metallic melts

1. Introduction

In their historical review about levitation calorimetry, Bonnell et al. [1] described that the first successful application in determining the enthalpy of high melting metals was performed by Margrave and Bonnell in 1968 [2]. Meanwhile the electromagnetic levitation-drop calorimetry was introduced in several laboratories. Besides the possibility of reaching very high experimental temperatures (about 4000 K), levitation enables us to work without crucibles, so that reactions with these materials can be avoided. Further this

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experimental technique is destined to reach high supercooling of the sample. Today the levitation technique is applied in many different measurements:

- enthalpy by levitation drop calorimetry,
- mixing enthalpy by levitation alloying calorimetry,
- heat capacity by frequency modulation technique,
- surface tension by oscillating drop technique,
- viscosity by oscillating drop technique and
- growing velocity of dendrites and crystals by trigger technique.

The summary demonstrates how broad the field of levitation technique is today. In the following, levitation alloying calorimetry is presented and its correlation with drop calorimetry is worked out.

2. Levitation alloying calorimetry

At the Institute of General Metallurgy of the Technical University Berlin levitation melting was started at the end of the 1960s [3]. The first measurements dealt with the solubility of gases and material transport. Later, calorimetric applications were taken up working with an isoperibolic calorimeter, in particular concerning the determination of the enthalpy of 5b and 6b refractory metals [4–6]. At the same time, the first steps in levitation alloying calorimetry were done, measuring the mixing enthalpies of these metals with silicon and iron with copper [7–10]. Different alloying techniques were used in order to combine a levitated basic sample with a secondary sample. These techniques are shown in Fig. 1:

- the addition of a formerly levitated liquid secondary sample to the basic sample,

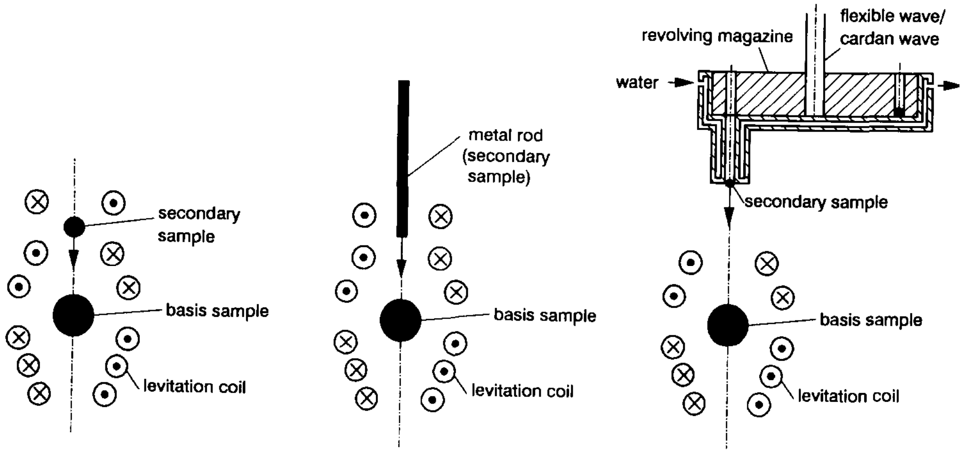

Fig. 1. Different alloying techniques to combine a levitated basis sample with a secondary sample.

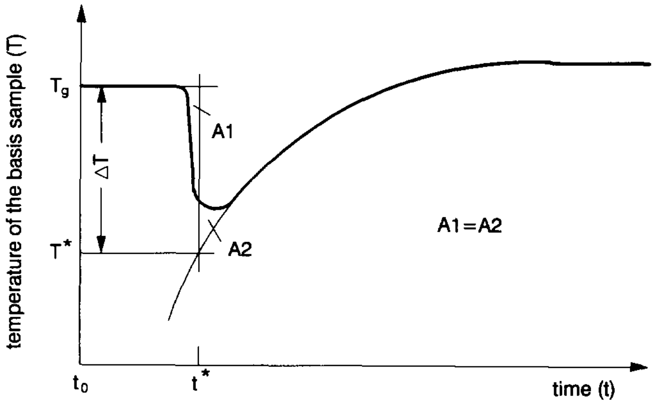

Fig. 2. Schematic temperature curve of an alloying process.

- the addition of a secondary sample which melts down from an inductively heated metal rod,
- the addition of secondary samples from a revolving magazine.

The last technique was successfully applied by us [11–15]. As several samples can be added consecutively, large concentration ranges can be determined in a single experiment. The alloying of the liquid basis sample with a solid secondary one induces a temperature effect which is continuously recorded by a quotient pyrometer. This effect is shown in Fig. 2. The mixing enthalpy is determined with the aid of an energy balance of this alloying process:

$$0 = \Delta H_{\mathrm{ap}} + \Delta H_{\mathrm{m}} + \Delta H(T_{\mathrm{exp}}) \tag{1}$$

The energy balance comprises the heat effect of the alloying process, ΔH_{ap} the heat amount necessary to increase the temperature of the secondary sample from room temperature to experimental temperature, $\Delta H(\mathrm{T}_{\mathrm{exp}})$, and the mixing enthalpy, ΔH_{m}. In accordance with other calorimetric evaluations, a time lag free heat exchange is presumed.

The determination of mixing enthalpies of binary systems of early with late transition metals is of great interest because of their special technological properties. Due to the great differences in the melting and evaporation temperatures of these metals, it is not possible to measure the whole concentration region at one uniform temperature. Fig. 3a,b shows the measurements of the mixing enthalpies Fe–V [11] and Fe–Ti [14] together with the literature data [16–21]. In the Fe–V system the measurements in the iron rich range were performed at a mean temperature of $T = 1990$ K, in the vanadium rich range at $T = 2320$ K. For the Fe–Ti system these values yield $T = 1950$ K and $T = 2112$ K. As these systems show a distinct temperature dependency of the mixing enthalpy it is difficult to give a description of the total system in dependence of concentration and temperature. Applying the associate model we found a good possibility to describe such measurements [22]:

$$\Delta H_{\mathrm{m}} = \frac{n_{\mathrm{A_f}} \cdot n_{\mathrm{B_f}}}{n} C1 + \frac{n_{\mathrm{A_f}} \cdot n_{\mathrm{AB}}}{n} C2 + \frac{n_{\mathrm{B_f}} \cdot n_{\mathrm{AB}}}{n} C3 + n_{\mathrm{AB}} \cdot \Delta H_{\mathrm{AB}} \tag{2}$$

with

$$n = n_{\mathrm{A_f}} + n_{\mathrm{B_f}} + n_{\mathrm{AB}} \tag{3}$$

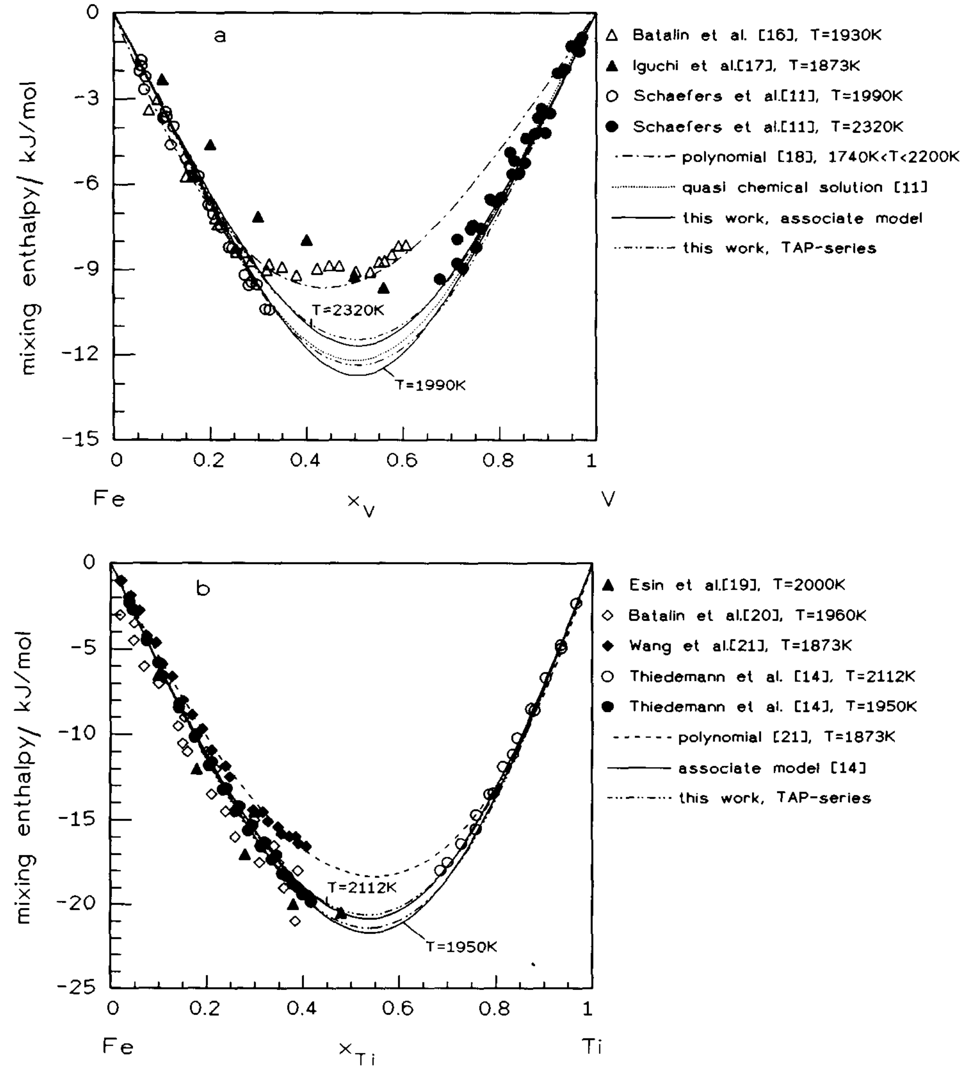

Fig. 3. Measured and calculated mixing enthalpies of the Fe–V (a, left side) and Fe–Ti (b, right side) systems.

This model treats the binary melt as a solution of the reactants: free atoms of the pure metal A, A_f, free atoms of the pure metal B, B_f, and associate, AB; n_{A_f}, n_{B_f} and n_{AB} are their mole numbers, respectively. The parameters $C1$, $C2$ and $C3$, respectively, describe the interactions between $A_f \leftrightarrow B_f$, $A_f \leftrightarrow AB$ and $B_f \leftrightarrow AB$. The equilibrium and its equilibrium constant is

$$A_f + B_f = AB \tag{4}$$

$$K = \frac{a_{AB}}{a_{A_f} \cdot a_{B_f}} = \exp\left(- \frac{\Delta H_{AB} - T \cdot \Delta S_{AB}}{RT} \right) \tag{5}$$

where a_{A_f}, a_{B_f} and a_{AB} are the activities of the reactants and ΔH_{AB} and ΔS_{AB} are the formation enthalpy and formation entropy of the associate, respectively. The descriptions by means of the associate model were performed assuming associates of the stoichiometric composition 1:1 for both systems. This choice was made because of the compositions of the minima of the mixing enthalpies. To fit the parameter presented in Table 1, we used an iterative regression, developed by us [23]. Using polynomial series, it is hardly possible to evaluate measurements at different concentration ranges and simultaneously differing temperatures. Polynomials, however, have the advantage that they are easier to handle. Polynomials can be fitted with the calculated graphs of the associate model. We have decided to choose the TAP-series, which is especially advantageous when the degree of the polynomial is smaller than 8 [24]. Concerning the Fe–V system, a TAP-series of third degree, and for the Fe–Ti system a series of fourth degree, was applied. The polynomials are presented in Table 2. The calculated mixing enthalpy curves by means of the associate model and the TAP-series are drawn in Fig. 3ab.

3. Calculation of the excess heat capacity

The mixing enthalpy is a thermodynamic excess quantity. Its partial derivation to the temperature is the excess heat capacity, C_p (xs):

Table 1

Parameter of the associate model for the binary Fe–V and Fe–Ti systems

Parameter	System (A–B)	
	Fe–V	Fe–Ti
$C1$/kJ mol^{-1}	–31.52	–58.84
$C2$/kJ mol^{-1}	+14.64	–7.82
$C3$/kJ mol^{-1}	+11.97	–26.7
ΔH_{AB}/kJ mol^{-1}	–47.86	–72.23
ΔS_{AB}/J mol^{-1}·K	–13.84	–22.37

Table 2

Polynomials of the mixing enthalpies for the binary systems Fe–V and Fe–Ti, calculated by means of the TAP-series, in kJ mol^{-1}

$$\Delta H_{\mathrm{m}}(\mathrm{FeV}) = (1 - x_{\mathrm{Fe}})\left[\left(-35.47 + \frac{5113.47}{T}\right)x_{\mathrm{Fe}} + \left(44.56 - \frac{225806}{T}\right)x_{\mathrm{Fe}}^{2} + \left(-44.94 + \frac{232464.5}{T}\right)x_{\mathrm{Fe}}^{2}\right]$$

$$\Delta H_{\mathrm{m}}(\mathrm{FeTi}) = (1 - x_{\mathrm{Fe}})\left[\left(-55.17 - \frac{37991}{T}\right)x_{\mathrm{Fe}} + \left(72.46 - \frac{318224}{T}\right)x_{\mathrm{Fe}}^{2} + \left(-142.19 + \frac{621408}{T}\right)x_{\mathrm{Fe}}^{3} + \left(64.85 - \frac{268400}{T}\right)x_{\mathrm{Fe}}^{4}\right]$$

$$C_{\mathrm{p}}(\mathrm{xs}) = \frac{\partial \Delta H_{\mathrm{m}}}{\partial T} \tag{6}$$

This value added to the heat capacity calculated from the pure components by Neumann-Kopp, $C_{\mathrm{p}}(\mathrm{NK})$, yields the real heat capacity, C_{p}

$$C_{\mathrm{p}} = C_{\mathrm{p}}(\mathrm{NK}) + C_{\mathrm{p}}(\mathrm{xs}) \tag{7}$$

By means of the temperature and concentration dependent description of the mixing enthalpy, the excess heat capacity can be calculated in the system; from this the real heat capacity can be determined.

Applying the associate model this procedure has been demonstrated for a number of systems where experimental measurements of the mixing enthalpy and the excess heat capacity were available [23]. It should be mentioned once again that the conversion of the associate model into the TAP-series is of great advantage in the case of deviations of other thermodynamic quantities from the mixing enthalpies. Fig. 4ab show the excess heat capacity of the Fe–V and Fe–Ti systems. In Fig. 3a,b the associate model produced a sharper minimum compared to the TAP-series. This behaviour is in accordance with the description of the excess heat capacity. The maximum of the excess heat capacity is not necessarily identical with the concentration resulting from the stoichiometry of the associate. For the Fe–V system the maximum of the excess heat capacity identifies the concentration range at $x_{\mathrm{V}} = 0.5$ as that of maximal interaction. For the Fe–Ti system the minimum of the mixing enthalpies was slightly above $x_{\mathrm{Ti}} = 0.5$, which is in accordance with the curves of the excess heat capacity.

4. Relation between levitation alloying and drop calorimetry

The mixing enthalpy is for the case of a compound tending towards a reduction of the

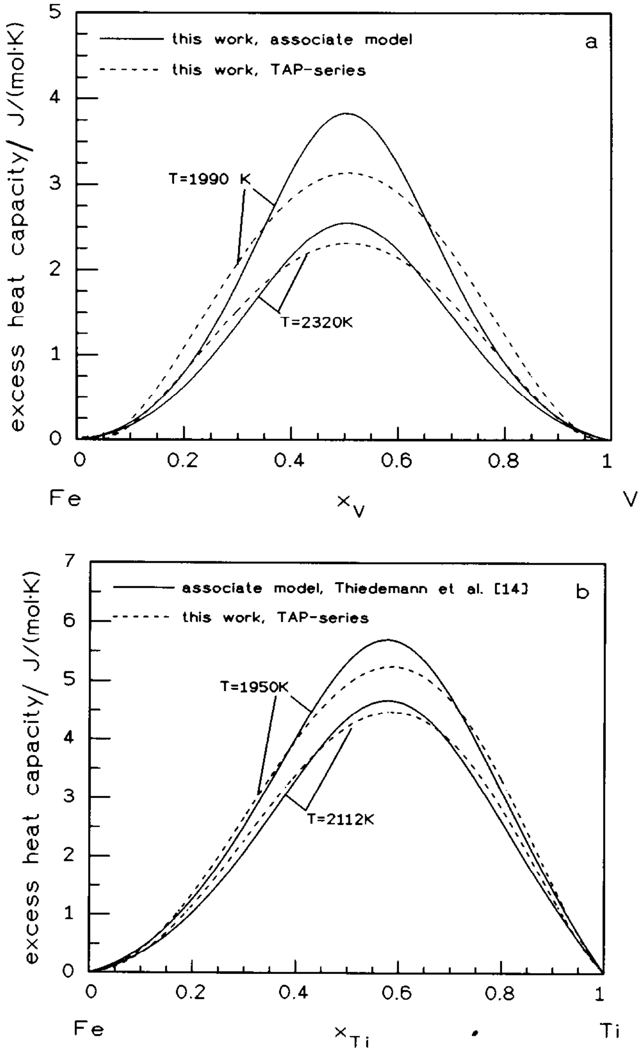

Fig. 4. Calculated excess heat capacities of the Fe–V (a, left side) and Fe–Ti (b, right side) systems.

energy of the liquid mixture compared to the ideal solution. The last value is determined by the application of Neumann-Kopp's rule, ΔH(NK). For this the enthalpies of the pure components are needed, so that the standard state of the enthalpy of the ideal solution is the pure components. In the solid state, the energy reduction is called formation enthalpy and for the case $T = 298$ K, standard formation enthalpy, $\Delta H(298)$. For the determination of the enthalpy, the reference temperature of the drop calorimeter normally corresponds to the standard temperature $T = 298$ K. The drop calorimetric experiment therefore gives the heat content of the sample, $\Delta H(T)$, referred to this temperature. Therefore, to com-

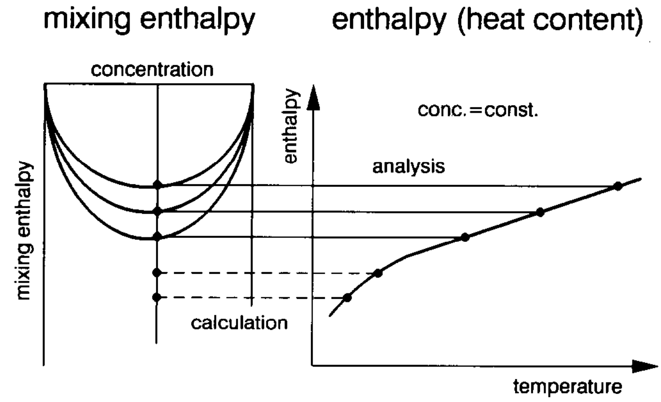

Fig. 5. Relation of the mixing enthalpy and the enthalpy with respect to the standard formation enthalpy (see Eq. (9)).

pare enthalpy values of pure metals and alloys, the experimentally determined enthalpy values of the alloys have to be corrected by the standard formation enthalpy. If enthalpy values and mixing enthalpy values are known for the same system, the standard formation enthalpy can be calculated:

$$\Delta H(298) = \Delta H(NK) + \Delta H_{\mathrm{m}} - \Delta H(T) \tag{8}$$

On the other hand, with respect to the standard formation enthalpy, the enthalpy of an alloy is represented as a section at constant concentration in a ΔH(M)–T–x diagram:

$$\Delta H(T) = \Delta H(NK) + \Delta H_{\mathrm{m}} - \Delta H(298) \tag{9}$$

The relation between the enthalpy and the mixing enthalpy is schematically shown in Fig. 5.

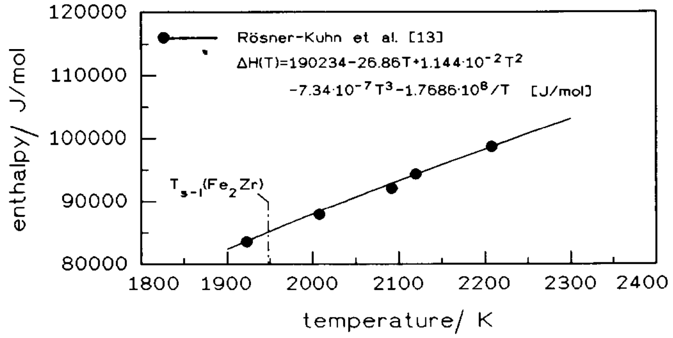

Fig. 6. Measured and calculated enthalpy of the intermetallic compound Fe_2Zr.

In the Fe–Zr system, Rösner-Kuhn et al. have measured the mixing enthalpy in the zirconium rich range at $T = 2180$ K and $T = 2280$ K [13]. Together with the experimental values of Wang, Lück and Predel in the iron rich range at $T = 1923$ K [25], a temperature and concentration dependent description of the mixing enthalpy was possible. Further, some values of the intermetallic compound Fe_2Zr were determined by us. In Fig. 6, these experimentally determined values of the enthalpy are compared with the curve calculated via the associate model from the mixing enthalpy. The agreement is perfect. To describe the enthalpy of the compound analytically in an easier form, a regression analysis was performed.

5. Conclusions

Electromagnetic levitation is the basis for several experimental calorimetric techniques. Levitation drop calorimetry is well known [26]. In order to measure the mixing enthalpies of high and highest melting alloys, levitation alloying calorimetry was developed and proved by us. Many systems have now been successfully determined.

As these measurements normally do not cover the whole concentration range of a system and, additionally, are not performed at the same temperature, the evaluation of the experimental values should be done by suitable thermodynamic models. Here the associate model has proved a valuable theoretical tool. This model is also able to calculate other thermodynamic properties, so that a complete thermodynamic analysis of a binary liquid system is possible. Two applications are presented here: the calculation of the excess heat capacity and the enthalpy. These thermodynamic properties can normally only be determined with great experimental effort.

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