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The competition between InBi- and In_2Bi-like atomic distributions before solidification

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The enthalpy of mixing of binary In–Bi melts was measured by means of a calorimetric method at T = 1023, 875, 483 K. Its concentration dependence reveals a flat minimum in the region between the intermetallic phases InBi and In_2Bi. The shape of the curve of the integral enthalpy of mixing for liquid In-Bi alloys is in agreement with the assumption of a competition between InBi- and In_2Bi-like chemical ordering before solidification.

Enthalpy of mixing / In-Bi molten alloys / Intermetallic phase / Associate

Introduction

The structure of binary liquid alloys is in correlation with the equilibrium phase diagram. It has been shown early that the existence of chemical compounds or of eutectic points in the phase diagram is often linked to a deviation of the structure of the liquid from a random atomic distribution and that there is interrelation between the phase diagram and thermochemical data [1]. Particularly, alloys with eutectic points form preferably groups of atoms of the same kind, whereas binary systems with chemical compounds reveal the existence of associates whose structure is, in some aspects, similar to the atomic arrangement in the solid compounds. However, it should be noted that the stoichiometry of the solid compounds can also be different from the stoichiometry of the associates. Diffraction studies and measurements of different physical properties indicate deviations of the structure from an ideal one for various binary systems [2,3].

Unfortunately, there is no clear interpretation of such deviations, although chemical compound models have been used for a long time. According to the model of associates proposed by Sommer *et al.* [4], the interpretation of the thermodynamic properties of liquid In-Bi binary alloys considers the existence of In_2Bi associates, and their fraction is maximum for the stoichiometric concentration. We assume that another intermetallic phase, InBi, can also influence the atomic distribution in the concentration region close to these chemical compounds. Viscosity measurements and X-ray diffraction data revealed an anomalous behavior, which was attributed to a competition between In_2Bi- and InBi-like atomic distributions in the liquid state [5]. It seemed of interest to investigate if such an assumption agrees with thermodynamic data, and this was the reason for the measurements of the enthalpy of mixing of liquid In-Bi alloys.

Experimental details

The measurements were performed with a high-temperature Calvet-type microcalorimeter HT-1000 (Setaram, Lyon, France). A detailed description of the experimental technique was reported in [6]. The alloy samples for these measurements were prepared from pure Bi and In (both 99.999%). All experiments were performed under a gas flow of pure Ar (approx. 30 cm^3/min). Thermal equilibrium was reached after 30 to 50 min, which was a reasonable value for liquid alloys formed by the addition of a solid constituent to a liquid metal or alloy. The interval between individual drops increased with decreasing temperature, accordingly. For the determination of the calorimeter constant (calibration of the heat flow) drops of high purity Al_2O_3 (NIST, Gaithersburg, MD, USA) were used.

The measured enthalpy ΔH_{signal} (integrated heat flow at constant pressure) is given by

$$\Delta H_{signal}=n_i(H_{m,i(l),Texp}-H_{m,i(s),DT})+\Delta H_{reaction} \quad (1)$$

where n_i is the number of moles of the dropped metal i; $H_{m,i(l),Texp}$ is the molar enthalpy of the liquid metal i

at the experimental temperature T_{exp} in the calorimeter; $H_{m,i(s),DT}$ is the molar enthalpy of the solid metal *i* at the drop temperature (usually about 298 K). The values of $H_{m,i(l),Texp}$-$H_{m,i(s),DT}$ were calculated using Dinsdale polynomials for the thermodynamic data of pure elements [7]. For all temperatures (DT, T_{exp}) the average values for each drop of a run were taken because their scattering was low enough (±0.6 K) to keep the experimental error small. Because of the rather small masses that were added in each individual drop, the partial enthalpies h_i can be approximated by:

$$h_i \approx \Delta H_{reaction}/n_i \qquad (2)$$

Results and discussion

Experimental values of the heat of mixing obtained at T = 1023, 875, and 483 K are shown in Fig. 1; considering the rather small absolute values, the scatter of the data is very satisfactory. A least-square regression analysis of these data results in the following Redlich-Kister polynomial, as proposed by Ansara and Dupin [8]:

$$\Delta H_{mix}=x_i x_j \Sigma\, {}^{(v)}L_{i,j}(x_i-x_j)^v \qquad (3)$$

and the data fitted for 875 K yield the interaction parameters $L^{(0)}$ = -7557 J/mol and $L^{(1)}$ = -1553 J/mol (see Fig. 2).

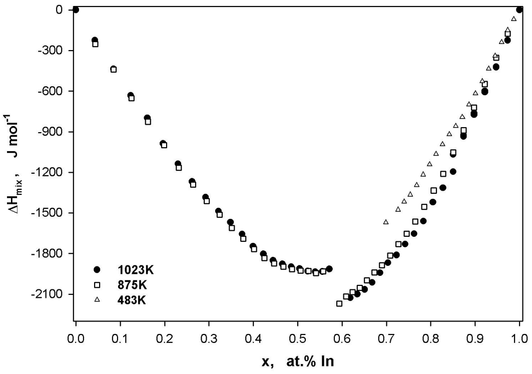

Fig. 1 Integral enthalpy of mixing as a function of composition for liquid In-Bi alloys at three different temperatures: 1023 K, 875 K and 474 K.

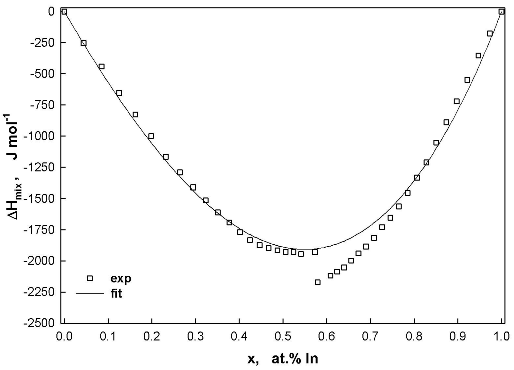

Fig. 2 Integral enthalpy of mixing as a function of composition and least square fit using Redlich-Kister polynomials (full line) for liquid In-Bi alloys at 875 K.

The obtained curve shows a minimum that is shifted to the indium-rich side of the 1:1 composition, to somewhere around 55 at.% In. This composition corresponds neither to InBi nor to In$_2$Bi, although an analysis of the enthalpy of mixing for metallic binaries with compound formation shows that minima of ΔH_{mix} are very often in accordance with the stoichiometric concentrations more exactly when the interaction between unlike atoms is stronger.

In the case of the In–Bi binary system, the intermetallic phases In$_2$Bi and InBi have melting temperatures that are below the corresponding melting points of the two components. Therefore, most of the experimental enthalpy of mixing data was obtained at temperatures significantly higher than the melting points. Consequently, it is to be expected that any associates in the liquid are already partly dissociated.

In this work we attempt to interpret the measured concentration dependence of the enthalpy of mixing based on a competition between two kinds of chemically ordered associate, i.e. InBi- and In$_2$Bi-like ones. This assumption is supported by the anomalous behavior of the temperature dependence of the viscosity and the structure parameters [5]; in addition, we take also into account the conclusions of [9] where the authors supposed the existence of associates in In-Bi binary melts within a temperature range up to about 750 K. We observed an increase of the viscosity with heating within a narrow temperature region, as well as an increase of the height of the principal peak in the structure factors [5].

The present experimental data on the concentration dependence of the enthalpy of mixing are in general agreement with available literature data (Fig. 3).

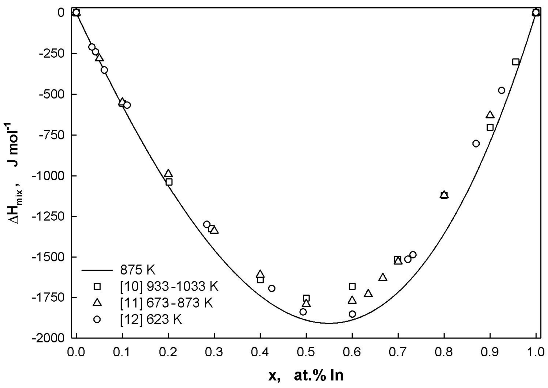

Fig. 3 Integral enthalpy of mixing as a function of composition for liquid In-Bi alloys compared with literature data from [10-12]. The full line shows the least square fit using Redlich-Kister polynomials in this work at 875 K.

We suppose that within the composition region between the compounds InBi and In$_2$Bi the structure of the liquid is characterized by hetero-coordinated atomic arrangements, which “remember” the In$_2$Bi-like chemical ordering. The In_2Bi-like structural units are supposed to show significant fluctuations of their size and concentration. In order to confirm the suggestion about the competition between InBi- and In_2Bi-like atomic arrangements in the liquid state we decided to calculate the mole fractions of the corresponding associates.

We assume that a binary liquid In-Bi alloy consists of a pseudo quaternary mixture of n_{A_1} and n_{B_1} moles of In and Bi atoms, and of $n_{A_iB_j}$ and $n_{A_lB_k}$ moles of the two types of chemical complexes InBi and In_2Bi, respectively. The total number of moles, *n*, is given by

$$\begin{gathered} n = n_{A_1} + n_{B_1} + n_{A_iB_j} + n_{A_lB_k} \\ n_A = n_{A_1} + i n_{A_iB_j} + l n_{A_lB_k} \\ n_B = n_{B_1} + j n_{A_iB_j} + k n_{A_lB_k} \end{gathered} \tag{4}$$

The absolute concentrations are obtained as

$$x_A = \frac{n_A}{N} \quad \text{and} \quad x_B = \frac{n_B}{N}$$

for 1 mole of a binary alloy (*N*=1). Similarly, the following expressions can be written for the particle concentrations in the liquid:

$$\begin{aligned} x_{A_1} &= \frac{n_{A_1}}{n_{A_1} + n_{B_1} + n_{A_iB_j} + n_{A_lB_k}} \\ x_{B_1} &= \frac{n_{B_1}}{n_{A_1} + n_{B_1} + n_{A_iB_j} + n_{A_lB_k}} \\ x_{A_iB_j} &= \frac{n_{A_iB_j}}{n_{A_1} + n_{B_1} + n_{A_iB_j} + n_{A_lB_k}} \\ x_{A_lB_k} &= \frac{n_{A_lB_k}}{n_{A_1} + n_{B_1} + n_{A_iB_j} + n_{A_lB_k}} \end{aligned} \tag{5}$$

Using the regular solution model, ΔH^{reg} is determined as

$$\Delta H^{reg} = zN_0 x_A x_B \left[\varepsilon_{AB} - \frac{(\varepsilon_{AA} + \varepsilon_{BB})}{2} \right] \tag{6}$$

where ε_{AB}, ε_{AA}, ε_{BB} are the energies for A-B, A-A and B-B pairs of atoms respectively, N_0 is the Avogadro constant, and z the coordination number. For the system In-Bi, a value for the term in square brackets in Eq. (6) (the interchange energy) was obtained from [13], and this was used to calculate ΔH^{reg}.

The deviation of the experimental data for the enthalpy of mixing from the curve obtained by the regular solution model is shown in Fig. 4. The difference between the two curves will be called 'excess part enthalpy of mixing' (ΔH^{exs}).

The chemical potentials μ_v of the assumed species *v* (*v*=A_1, B_1, A_iB_j, A_lB_k) (for a review see reference [14]) are

$$\begin{aligned} \mu_{A_1} &= \mu^0_{A_1} + RT\ln x_{A_1} = \mu^0_A + RT\ln x_A \gamma_A \\ \mu_{B_1} &= \mu^0_{B_1} + RT\ln x_{B_1} = \mu^0_B + RT\ln x_B \gamma_B \end{aligned} \tag{7}$$

where *R* is the gas constant, *T* the absolute temperature and γ the corresponding activity coefficient. From this one can calculate

$$\begin{aligned} \gamma_A &= \frac{x_{A_1}}{x_A} \exp\left(\frac{\mu^0_{A_1} - \mu_{A_1}}{RT} \right) \\ \gamma_B &= \frac{x_{B_1}}{x_B} \exp\left(\frac{\mu^0_{B_1} - \mu_{B_1}}{RT} \right) \end{aligned} \tag{8}$$

For $x_A \to 1$, the effective mole fraction of the monomer molecules x_{A_1} tends to a limit $x^0_{A_1}$, the mole fraction of monomers in the pure liquid, and so

$$x^0_{A_1} = \exp\left(-\frac{\mu^0_{A_1} - \mu_{A_1}}{RT} \right) \tag{9}$$

$$\gamma_A = \frac{1}{x^0_{A_1}} \frac{x_{A_1}}{x_A}$$

in a similar way we obtain

$$\gamma_B = \frac{1}{x^0_{B_1}} \frac{x_{B_1}}{x_B} \tag{10}$$

Since the pure components are usually non-associated in liquid metals, and since it does not seem reasonable to take into account more than two types of associate [15] we obtain $x^0_{A_1} = 1$ and $x^0_{B_1} = 1$. With this the equations for the activity coefficients can be rewritten:

$$\begin{aligned} \gamma_A &= \frac{x_{A_1}}{x_A} \\ \gamma_B &= \frac{x_{B_1}}{x_B} \end{aligned} \tag{11}$$

This leads to

$$\begin{aligned} \gamma_A &= \frac{x_{A_1}}{x_A} = \\ &= \left(1 + (i+j-1)x_{A_iB_j} + (l+k-1)x_{A_lB_k}\right) - \frac{\left(i x_{A_iB_j} + l x_{A_lB_k}\right)}{x_A} \\ \gamma_B &= \frac{x_{B_1}}{x_B} = \\ &= \left(1 + (i+j-1)x_{A_iB_j} + (l+k-1)x_{A_lB_k}\right) - \frac{\left(j x_{A_iB_j} + k x_{A_lB_k}\right)}{x_B} \end{aligned} \tag{12}$$

To calculate the mole fractions of the associates, data for $\gamma_A = \gamma_{In}$ and $\gamma_B = \gamma_{Bi}$ were taken from Hultgren *et al.* [16], and the result is given in Fig. 5.

A comparison of Fig. 4 and Fig. 5 suggests that both InBi and In_2Bi associates have an influence on ΔH^{exs}. However, because of the rather small values of the 'excess part enthalpy of mixing' only a rough analysis is possible. But taking into account the position of the minimum in the experimental data of the enthalpy of mixing, we suggest that both chemical compounds are effectively influencing the structure of the molten alloys. Most probably it is this competition that is responsible for the shape of the enthalpy of mixing curve with a minimum in the concentration range between InBi and In_2Bi.

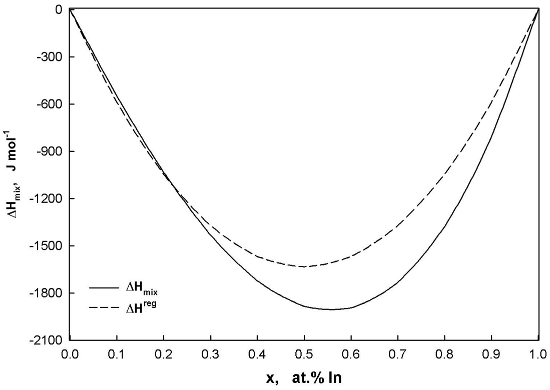

Fig. 4 Comparison of experimental data with regular solution enthalpy of mixing for liquid In–Bi alloys at 900 K.

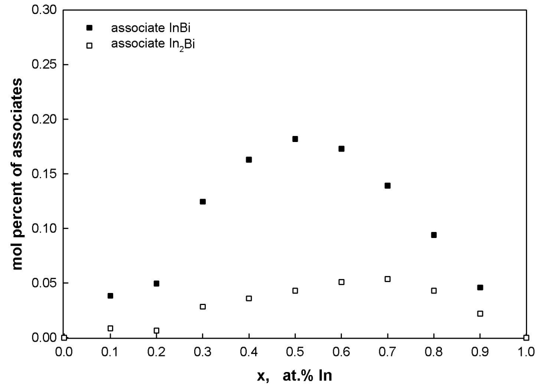

Fig. 5 Mole fraction of InBi and In_2Bi associates in liquid In–Bi alloys at 900 K.

Conclusions

The concentration dependence of the integral enthalpy of mixing for In–Bi molten alloys reveals an asymmetric behavior with a flat minimum. This feature is suggested to be attributed to a competition between InBi and In_2Bi-like chemical ordering on the structure and to a corresponding interatomic interaction in the melts with concentrations between the InBi and In_2Bi stoichiometric points.

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