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Thermodynamic investigation of the moderately dilute liquid Bi–Fe–Sb alloys

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Abstract

The molar enthalpies of formation of liquid ternary Bi–Fe–Sb alloys have been determined at 1065 K by direct reaction calorimetry using the drop method. Measurements were performed along two sections: $X_{\mathrm{Bi}}/X_{\mathrm{Sb}} = 1/9$ and 1/4. The experimental calorimetric data and estimated values with a Redlich-Kister formulation are compared.

Keywords: Liquid alloys; Direct reaction calorimetry; Enthalpy of mixing; Iron; Antimony; Bismuth

1. Introduction

The present calorimetric investigation concerns the ternary Bi–Fe–Sb system as a part of a more general research on ternary systems based on iron antimonides. Indeed, the transition metal antimonides exhibit in particular some interesting thermoelectric properties [1]. Only a few phase diagrams are available in the literature [2]. More, no thermodynamic functions of mixing has been published for these systems.

Knowledges of thermodynamic properties and phase diagram are nessary to predict the thermal behaviour and the microstructure evolution of alloys. As no literature data for the ternary system Bi–Fe–Sb is available, the main purpose of this thermodynamic study was the determination of the enthalpies of formation of ternary liquid alloys.

These calorimetric results will further be combined with new experimental phase diagram data and calorimetric data to evaluate more precisely the equilibrium phase fields of this ternary system by using an optimization procedure over the whole ternary diagram.

2. Bibliographic survey

2.1. The system Bi–Fe

Bi and Fe present very limited solubilities in the solid and liquid states. The critical point of the liquid miscibility gap is very high.

No direct measurement of the enthalpy of mixing of the liquid is available in the literature. Nevertheless, reliable data of the enthalpy of formation of liquid alloys were calculated indirectly by optimization of the system by using the available solubility data [3,4].

2.2. The system Bi–Sb

The Bi–Sb phase diagram exhibits a continuous solution as well in the liquid state as in the solid state.

The thermodynamic properties and the phase diagram of Bi–Sb system are well known. The system has been evaluated critically in 1992 by Feutelais et al. [5]. Both functional and diagramatic data were well represented by the optimized thermodynamic description. For the calorimetric study of ternary Bi–Fe–Sb, the data relative to the binary alloys provided by that evaluation will be retained.

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2.3. The system Fe–Sb

The Fe–Sb phase diagram shows two stable intermediate phases: ε-FeSb and $FeSb_2$: the hexagonal NiAs-type phase ε is characterized by a broad nonstoechiometric domain between about 40 and 47 at.% Sb and by a congruent melting point. The orthorhombic-type $FeSb_2$ phase is a stoichiometric compound and decomposes peritectically into ε-FeSb and an antimony rich liquid. Two solid solutions of antimony in pure iron are observed: one in the α-iron and the second in the γ-iron forming a γ-loop. In contrast, iron shows no obvious solubility in solid antimony.

Three invariant reactions are distinguished: two eutectic reactions at 1282 and 901 K and one peritectic reaction at 1023 K.

Despite several works devoted to the Fe–Sb system, there is still a serious lack of knowledge of the enthalpy of mixing in liquid Fe–Sb. No calorimetric data were so far published for the enthalpic function. Only data of Vecher et al. [6] obtained by the EMF method at 1125 K in the range $0 \leq X\mathrm{Fe} \leq 0.25$ are available.

Pei et al. [7] optimized the thermodynamic functions of the system and calculated the phase diagram.

In this work, the enthalpy of mixing of liquid Fe–Sb were determined at 1065 K.

3. Experimental procedure

The pure elements were purchased from Aldrich: Fe (4N), Bi (5N) and CERAC coating materials Sb (5N).

The determination of the enthalpies of formation were performed at 1065 K using a Tian-Calvet high-temperature microcalorimeter described elsewhere [8–10]. For the measurements in the binary Fe–Sb system, the final liquid mixtures were synthesized by successive additions to about 10 g of liquid antimony at the experimental temperature (T), of pieces of about 10–30 mg of pure solid iron maintained initially at room temperature (T_0). For the measurements in the Bi–Fe–Sb ternary system the initial liquids were Bi_xSb_{1-x} mixtures at the temperature T. The dissolutions are performed in graphite crucibles.

The measured heat effects correspond to the reactions:

$$y\mathrm{Fe}(s, T_0) + (1-y)\mathrm{Bi}_x\mathrm{Sb}_{1-x}(1, T)$$
$$\rightarrow \mathrm{Fe}_y\mathrm{Bi}_{x(1-y)}\mathrm{Sb}_{(1-x)(1-y)}(1, T)$$

where the heat effects corresponding to the binary Fe–Sb are obtained for $x = 0$.

The heat capacities of the pure elements were those published by Hultgren et al. [11]. The reference states were solid pure iron and liquid pure elements for the solvents at experimental temperature.

During the experiments, high-purity argon were flowed through the calorimetric cell and some turnings of Ti–Zr alloy acting as oxygen getter (oxygen equilibrium partial pressure of about 10^{-40} atm), were placed just above the crucible in the hot zone of the calorimeter in order to prevent any oxidation. Indeed, no oxidation was apparently observed.

The vapour pressure (Table 1) of the pure elements was not high enough at 1065 K to hinder calorimetric measurements.

Table 1
Vapour pressure of pure elements at 1100 and 1200 K

Metals T (K)	Pressure (atm) [11] 1100	 1200
Bi	3.19×10^{-4}	1.73×10^{-3}
Fe	1.3×10^{-12}	5.0×10^{-11}
Sb	2.92×10^{-3}	8.39×10^{-3}

The calorimeter is calibrated by additions of certified α-alumina at the end of each experiment. The heat content values are taken from the reference table supplied by NIST [12].

The standard deviations of calibration experiments were about 3% and the uncertainties in the final values for the enthalpies of mixing were estimated to be ±8%.

4. Results

Taking into account the important vapour pressure of antimony and bismuth at higher temperatures, the experiments were carried out at 1065 K that restricts the area in composition of the study as well for the binary system as for the ternary system.

4.1. Fe–Sb system

For this system the experimental measurements have been performed at 1065 K in the $0 < X_{\mathrm{Fe}} < 0.30$ concentration range. The experimental values obtained are presented in Fig. 1 and summarized in Table 2. The plot of the enthalpy of mixing shows clearly two parts:

- for $0 < X_{\mathrm{Fe}} < 0.15$, the curved line corresponds to the formation of the homogeneous single liquid phase;
- for $X_{\mathrm{Fe}} > 0.15$, the straight line observed corresponds to the formation of a binary solid compound, that should be for instance the ε-FeSb phase, in equilibrium with the Fe–Sb liquid solution.

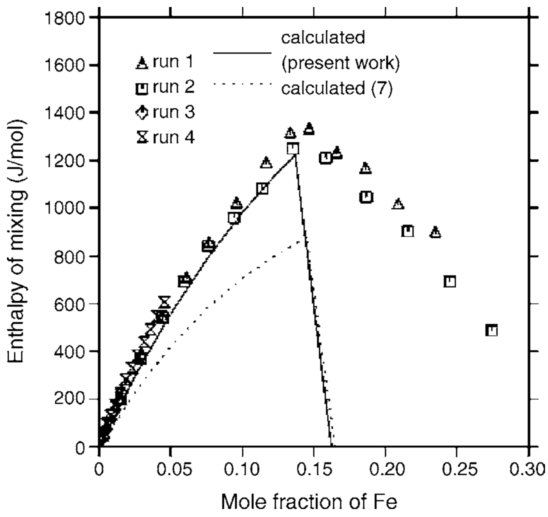

Fig. 1. Experimental and calculated integral mixing enthalpies of Fe-Sb alloys at 1065 K.

Table 2
Molar integral enthalpies of mixing of Fe–Sb liquid alloys at 1065 K refered to pure liquid Sb and pure solid Fe in the BCC-A2 structure

X_{Fe}	$\Delta_{mix}H_m$ (J/mol) run 1	X_{Fe}	$\Delta_{mix}H_m$ (J/mol) run 2	X_{Fe}	$\Delta_{mix}H_m$ (J/mol) run 3	X_{Fe}	$\Delta_{mix}H_m$ (J/mol) run 4
0	0	0.0148	200.28	0.0025	39.03	0.0023	48.90
0.0135	198.60	0.0290	371.42	0.0049	73.84	0.0055	97.40
0.0292	382.15	0.0442	546.06	0.0075	116.90	0.0080	132.49
0.0445	535.62	0.0591	691.75	0.0102	150.08	0.0114	178.82
0.0609	704.88	0.0762	841.55	0.0129	190.51	0.0144	223.90
0.0765	852.31	0.0942	960.12	0.0157	225.14	0.0187	282.10
0.0960	1017.06	0.1139	1081.93	0.0188	260.92	0.0232	330.46
0.1167	1184.69	0.1353	1250.49			0.0271	383.21
0.1336	1311.29	0.1584	1210.68			0.0316	439.12
0.1468	1328.44	0.1868	1045.69			0.0359	491.96
0.1660	1227.20	0.2159	902.41			0.0407	548.04
0.1862	1163.05	0.2450	691.83			0.0455	606.59
0.2089	1012.18	0.2744	487.32				
0.2351	893.85						

The intersection of the curved part of $\Delta_{mix}H_m$(Fe–Sb) = $f(X_{Fe})$ with the linear part determines the solubility limit at 1065 K which is also a characteristic point of the binary liquidus of the equilibrium phase diagram.

In order to verify the nature of the precipitate, the solvent after dissolution at $X > 0.15$ were examined by EPMA. The microstructures obtained around the iron nodules in the samples of both runs 1 and 2 are similar. This typical microstructure represented on Fig. 2 presents four phases, which have been chemically analysed. Obviously, the sample is not in equilibrium because the apparently slow dissolution process has been stopped by quenching. Along the decreasing iron potential the four phases are observed as: (a) pure iron, (b) a dark grey phase which surrounds the iron nodule, (d) a light grey phase which never presents points of contact with pure iron and (c) a large white phase which is the rich antimony solidified liquid. The (b) phase, which is always surrounded by the (d) phase seems to disappear far from the iron nodule where the proportion of the (d) phase becomes more and more important. The reproducible analysis of the (b) phase gives the average value of 67 at.% Fe. It does not correspond to any stable compound of the equilibrium phase diagram. The (d) phase is richer in Sb and the exact composition could not be surely determined because of the always simultaneous presence of the two phases. The expected stable phase ε-FeSb does not clearly appear and is perhaps represented by the (d) phase.

Obviously, the dissolution becomes very slow in the two-phases region due surely to the presence of the (b) phase, which acts as a diffusion barrier and so hinders the rate of formation of the ε phase. We have no explanation for the presence of such a Fe_2Sb type metastable compound. In the literature, only the $FeSb_3$ and $FeSb_4$ metastable phases have been already mentioned [15,16]. It can be yet mentioned that Me_2Sb type compounds are present in the Mn–Sb, Rb–Sb or Ni–Sb phase diagrams. The enthalpy of formation of the metastable Fe_2Sb phase is expected to be very close to those of the mechanical mixing of the αFe and ε phases.

This observation explains the great discrepancy between calculated and experimental data in the two-phases domain: the enthalpy of formation of the ε-FeSb phase obtained elsewhere by a dissolution method [13] is more negative than that which

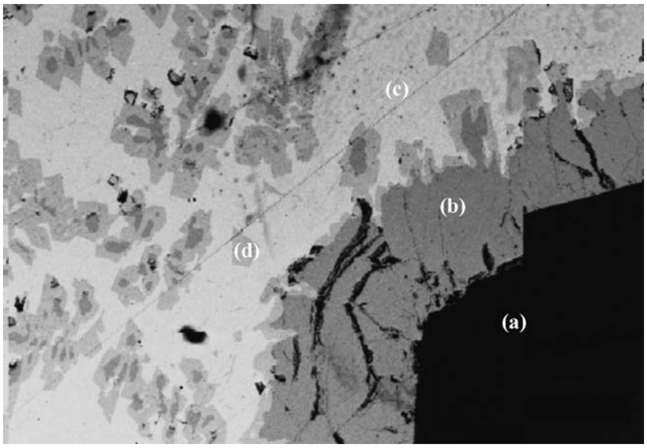

Fig. 2. Microstructure of the $Fe_{0.2744}Sb_{0.7256}$ alloy slowly cooled from 1065 K. EPMA absorption photograph: dark phase (a) Fe, dark grey phase (b) Fe_2Sb, white phase (c) Sb, light grey phase (d) FeSb.

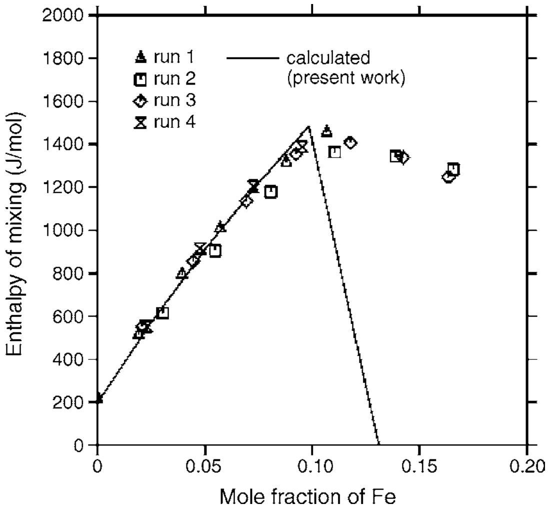

Fig. 3. Experimental and calculated integral enthalpies of mixing of Bi–Fe–Sb alloys at 1065 K, section $X_{Bi}/X_{Sb} = 1/9$.

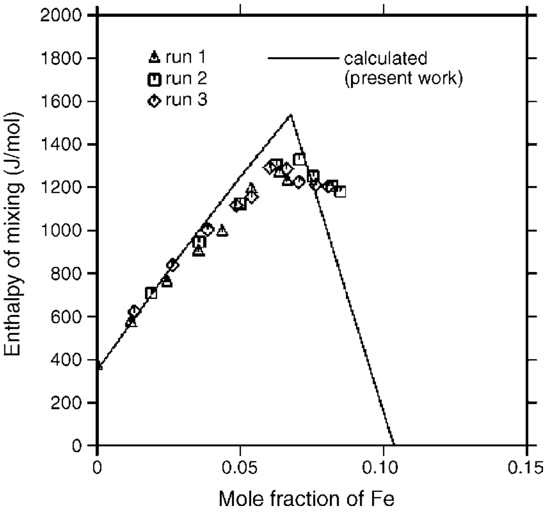

Fig. 4. Experimental and calculated integral enthalpies of mixing of Bi–Fe–Sb alloys at 1065 K, section: $X_{Bi}/X_{Sb} = 1/4$.

could be obtained in the present curve by extrapolation in the two-phases region.

4.2. Bi–Fe–Sb system

The enthalpies of formation of the ternary Bi–Fe–Sb alloys have been determined by measuring the heat evolved when solid iron is added to the liquid binary alloys defined by $X_{Bi}/X_{Sb} = 1/9$ and 1/4. The experiments are performed within the $0 < X_{Fe} < 0.20$ and $0 < X_{Fe} < 0.10$ ranges, respectively.

These two sections belong to the Sb-rich region. As shown in the Fe–Sb system the single-phase liquid domain is narrow. The $\Delta_{mix}H_m(\text{Bi–Fe–Sb}) = f(X_{Fe})$ curves present a breakdown at the liquidus branch. From that solubility limit a binary or ternary solid phase precipitates from the Bi–Fe–Sb liquid solution. As for the Fe–Sb system, these particular points belong to the ternary liquidus surface in the equilibrium phase diagram in the 1065 K section.

The results are shown in the Figs. 3 and 4 and are reported in Tables 3 and 4.

Endothermic enthalpies of the single liquid phase are measured for the ternary system at 1065 K. In Table 3, the ternary mixing enthalpy for $X_{Fe} = 0$ (217.24 J/mol) corresponds to the enthalpy in the Bi–Sb binary system for $X_{Sb} = 0.9$. This value is in good agreement with the data of Hultgren et al. [14].

5. Discussion

The results are analytically first described by using the Redlich-Kister equation [17] where the excess Gibbs energy G^{xs} of a binary solution is expressed by

$$G^{xs} = x_i x_j \sum_{\nu} {}^{\nu}L_{i,j}(x_i - x_j)^{\nu} \tag{1}$$

Table 3
Molar integral enthalpies of mixing of ternary Bi–Fe–Sb liquid alloys at 1065 K where $X_{Bi}/X_{Sb} = 1/9$, refered to pure liquid Sb, pure liquid Bi and pure solid Fe in the BCC-A2 structure

X_{Fe}	$\Delta_{mix}H_m$ (J/mol) run 1	X_{Fe}	$\Delta_{mix}H_m$ (J/mol) run 2	X_{Fe}	$\Delta_{mix}H_m$ (J/mol) run 3	X_{Fe}	$\Delta_{mix}H_m$ (J/mol) run 4
$X_{Bi}/X_{Sb} = 1/9$							
0	217.24	0.0304	613.97	0.0208	553.89	0.0231	551.70
0.0193	515.72	0.0548	904.62	0.0445	855.12	0.0478	913.93
0.0394	796.09	0.0808	1178.76	0.0694	1134.65	0.0725	1203.44
0.0572	1009.22	0.1106	1363.48	0.0925	1353.87	0.0955	1388.10
0.0880	1315.54	0.1390	1343.38	0.1178	1407.45		
0.1068	1455.59	0.1658	1282.62	0.1423	1338.35		
				0.1636	1246.47		

Table 4
Molar integral enthalpies of mixing of ternary Bi–Fe–Sb liquid alloys at 1065 K where $X_{Bi}/X_{Sb} = 1/4$, refered to pure liquid Sb, pure liquid Bi and pure solid Fe in the BCC-A2 structure

X_{Fe}	$\Delta_{mix}H_m$ (J/mol) run 1	X_{Fe}	$\Delta_{mix}H_m$ (J/mol) run 2	X_{Fe}	$\Delta_{mix}H_m$ (J/mol) run 3
$X_{Bi}/X_{Sb} = 1/4$					
0	368.19[a]	0.0189	710.18	0.0130	623.69
0.0118	573.60	0.0357	945.18	0.0263	838.52
0.0245	758.78	0.0500	1123.31	0.0387	1002.90
0.0353	900.51	0.0627	1303.84	0.0487	1115.44
0.0437	993.91	0.0707	1328.87	0.0540	1154.46
0.0539	1190.13	0.0754	1250.52	0.0603	1292.24
0.0637	1267.51	0.0821	1205.48	0.0662	1284.84
0.0664	1227.41	0.0850	1180.77	0.0706	1223.77
				0.0763	1211.83
				0.0807	1204.17

[a] Hultgren et al. [14].

Table 5
Values of the parameters describing the excess Gibbs energy of liquid phase (in J mol^{-1})

System	Parameter	Reference
Bi–Fe	$^0L_{\mathrm{Bi,Fe}} = 62327.74 - 4.3931T$, $^1L_{\mathrm{Bi,Fe}} = -3362.48$	Present work
Bi–Sb	$^0L_{\mathrm{Bi,Sb}} = 2176.50 - 0.65972T$, $^1L_{\mathrm{Bi,Sb}} = -25.50$	[5]
Fe–Sb	$^0L_{\mathrm{Fe,Sb}} = -20094.45 + 16.4818T$, $^1L_{\mathrm{Fe,Sb}} = -17411.15 + 11.5984T$	Present work
Bi–Fe–Sb	$^0L_{\mathrm{Bi,Fe,Sb}} = -18210.96$, $^1L_{\mathrm{Bi,Fe,Sb}} = -18210.96$, $^2L_{\mathrm{Bi,Fe,Sb}} = -18210.96$	Present work

$^{\nu}L_{\mathrm{i,j}}$ ($\nu = 0,1,2,\ldots$) are the interaction parameters between the elements i and j. $^{\nu}L_{\mathrm{i,j}}$ can be temperature dependent as:

$$^{\nu}L_{\mathrm{i,j}} = {}^{\nu}A_{\mathrm{i,j}} + {}^{\nu}B_{\mathrm{i,j}}T + \cdots \quad (2)$$

x_{i} is the molar fraction of the element i.The excess Gibbs energy of the ternary Bi–Fe–Sb system is expressed as:

$$\begin{aligned} G^{\mathrm{xs}} &= x_{\mathrm{Bi}}x_{\mathrm{Fe}}\sum_{\nu} {}^{\nu}L_{\mathrm{Bi,Fe}}(x_{\mathrm{Bi}} - x_{\mathrm{Fe}})^{\nu} \\ &\quad + x_{\mathrm{Bi}}x_{\mathrm{Sb}}\sum_{\nu} {}^{\nu}L_{\mathrm{Bi,Sb}}(x_{\mathrm{Bi}} - x_{\mathrm{Sb}})^{\nu} \\ &\quad + x_{\mathrm{Fe}}x_{\mathrm{Sb}}\sum_{\nu} {}^{\nu}L_{\mathrm{Fe,Sb}}(x_{\mathrm{Fe}} - x_{\mathrm{Sb}})^{\nu} \quad (3) \end{aligned}$$

In a ternary system, when experimental informations for ternary thermodynamic properties of mixing are available, an extra term $L_{\mathrm{i,j,k}}$, expressing the ternary interactions can be added to Eq. (3). In the present work, this term is expressed as follow:

$$L_{\mathrm{Bi,Fe,Sb}} = x_{\mathrm{Bi}}^{0}L_{\mathrm{Bi,Fe,Sb}} + x_{\mathrm{Fe}}^{1}L_{\mathrm{Bi,Fe,Sb}} + x_{\mathrm{Sb}}^{2}L_{\mathrm{Bi,Fe,Sb}} \quad (4)$$

The $^{\mathrm{i}}L_{\mathrm{Bi,Fe,Sb}}$ terms can also vary with the temperature according to Eq. (2).

The thermodynamic description of the binary and ternary liquid phases was derived from an optimization procedure using the module PARROT developed by Jansson [18] included in the Thermo-Calc software [19]. The temperature dependance of Gibbs energy for the pure elements was taken from Dinsdale [20]. The optimized thermodynamic parameters of the liquid phase are listed in the Table 5.

This preliminary fit will be improved through new measurements in course and a consistent set of thermodynamic parameters will be then published with the other new measurements in a following paper.

The comparison between the experimental results and calculated values are shown in Fig. 1 for the Fe–Sb system and Figs. 3 and 4 for the Bi–Fe–Sb ternary system. The calculated and experimental enthalpies of mixing of the binary and ternary liquid alloys are in good agreement. However, Fig. 1 shows a discrepancy between our experimental data and the assessment of the FeSb system from Pei et al. [7]. Additional ternary interaction paramaters are needed to adequately describe the enthalpies of the ternary liquid Bi–Fe–Sb.

No measurements could merely be performed above 1100 K owing to the higher vapour pressure of antimony and bismuth.

6. Conclusion

The integral enthalpy of mixing of Fe–Sb and Bi–Fe–Sb liquid alloys have been determined at 1065 K. To represent these binary and ternary results, an analytical description of the Redlich-Kister equation was used. There is a very satisfactory agreement between calculated and experimental data.

The experimental study of phase equilibria occurring in the Bi–Fe–Sb system by differential scanning calorimetry and differential thermal analysis is already undertaken to complete this thermodynamic study.

The whole of our experimental results will be used for a thermodynamic evaluation of the Bi–Fe–Sb system that will be soon submitted for publication.

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