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Enthalpies of mixing of liquid In–Sn and In–Sn–Zn alloys

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ABSTRACT

Partial and integral enthalpies of mixing of liquid ternary In–Sn–Zn alloys were determined at 500 °C along seven sections over a large composition range. Additionally, binary alloys of the constituent system In–Sn were investigated at the same temperature. The measurements were carried out using a Calvet-type microcalorimeter and a drop calorimetric technique. The binary data were evaluated by means of a standard Redlich–Kister polynomial fit whereas ternary data were fitted on the basis of an extended Redlich–Kister–Muggianu model for substitutional solutions.

1. Introduction

Interest in Sn–Zn based alloys has recently considerably increased again, mainly due to their possible application as high-temperature lead-free solders [1,2]. According to still valid exemptions to the RoHS Directive of the European Union [3], Pb–Sn alloys with Pb contents of up to 95% are still in use for high-temperature soldering, preventing a full transition to a lead-free technology. High-temperature solders are typically used for die attachment, flip-chip packages, optical packages and modules, heat resistant vehicle packages and other purposes, and the necessary requirements include the right melting interval as well as the right thermal and mechanical properties. One of the concerns about Sn–Zn solders had been that they can easily corrode in high humidity which would clearly be a drawback for the reliability of corresponding solder joints. Various ternary and quaternary additions have been discussed in the past to further improve the properties of binary Sn–Zn solders, among them also the element In. Already in 1994, McCormack and Jin [4,5] reported that the addition of In to Sn–Zn alloys can improve the wetting characteristics of the alloys and lower their melting temperature.

This was the reason that ternary In–Sn–Zn alloys had been included in the COST 531 Thermodynamic Database [6]. Unfortunately, there had been problems to model the available thermodynamic information for the liquid phase in a proper and consistent way (see below), and therefore it was decided to initiate a thorough reinvestigation of the enthalpies of mixing of liquid ternary In–Sn–Zn alloys over the entire composition range including the binary In–Sn system.

2. Literature survey

In this section an overview is given on the available literature information on the enthalpy of mixing of liquid alloys for the ternary In–Sn–Zn system as well as for the limiting binary systems.

2.1. The binary systems

Several calorimetric investigations of the enthalpy of mixing of liquid In–Sn alloys can be found in the literature. They cover the entire composition range and a temperature range from 248 to 900 °C. Kleppa [7] was the first to measure the integral enthalpy of mixing at 450 °C from 6 to 34 at.% In by means of direct-reaction calorimetry; he was followed by Wittig and Scheidt [8] who investigated the entire composition range at 371 °C using direct-reaction calorimetry. The same method was used by Yazawa et al. [9] at 450 °C from 19 to 90 at.% In and finally by Bros and Laffitte [10] at 248 °C over the entire composition range. Values for the integral enthalpy published prior to 1971 were collected by Hultgren et al. [11], and the agreement among these authors is generally quite good. All experimental data show small negative values for the enthalpy of mixing of liquid In–Sn alloys. Several thermodynamic assessments of the In–Sn system were presented based on these experimental data, i.e. by Lee et al. [12], by Korhonen and Kivilahti

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[13], and more recently by David et al. [14]. In all cases good agreement was obtained between calculated and experimental data. The most recent experimental investigation of the enthalpy of mixing, using direct-reaction calorimetry at 900 °C over the entire composition range, was by Luef et al. [15].

The enthalpy of mixing for liquid In–Zn alloys was determined calorimetrically by Oelsen and Zühlke [16] at 457 °C, by Kleppa [17] at 450 °C, and by Wittig and Müller [18] at 460 °C. Emf methods were applied to derive the corresponding values by Svirbely and Selis [19] at 427 °C, by Bohl and Hildebrandt [20] at 470 °C, and by Moser [21] between 441 and 532 °C, whereas Ferro et al. [22] used a torsion-effusion method at 427 °C. All experimental data show positive values for the enthalpy of mixing. Lee [23] presented a thermodynamic assessment based on the above-mentioned experimental data [16–22] for the enthalpy of mixing of liquid In–Zn alloys, and the calculated and experimental results were in good agreement.

For liquid Sn–Zn alloys, several calorimetric investigations of the enthalpy of mixing are also available in the literature, i.e. by Kleppa [24] at 430 and 525 °C, by Oelsen [25] between 422 and 546 °C, by Schürmann and Träger [26], by Moser et al. [27], and by Genot and Hagege [28]. Itagaki and Yazawa [29] used a quantitative thermal analysis method to derive enthalpy values, whereas Ptak [30], Sano et al. [31], Fiorani and Valenti [32], and Scheil and Müller [33] used emf methods for this purpose. All experimental data show positive values for the enthalpy of mixing of liquid Sn–Zn alloys. Several thermodynamic assessments of the enthalpy of mixing of liquid Sn–Zn alloys were reported, i.e. by Bourkba et al. [34] at 444 °C, by Lee [23] (based on the experimental data from Refs. [24–29,31–33]), and more recently by Ohtani et al. [35] at 477 °C.

2.2. The In–Sn–Zn ternary system

Enthalpies of mixing of liquid In–Sn–Zn alloys have already been measured by several authors. Studying the In–Pb–Sn–Zn quaternary system, Fiorani et al. [36] determined the partial and the integral enthalpies of mixing along three sections: $x_{\mathrm{In}}/x_{\mathrm{Sn}} = 1/1$ and $x_{\mathrm{Sn}}/x_{\mathrm{Zn}} = 1/1$ at 447 °C, and $x_{\mathrm{In}}/x_{\mathrm{Zn}} = 1/1$ at 483 °C. Later, Anres et al. [37] used direct-reaction calorimetry at 440 and 634 °C along the sections $x_{\mathrm{In}}/x_{\mathrm{Sn}} = 1/3$, 1/1, 3/1 and $x_{\mathrm{Zn}}/x_{\mathrm{In}} = 1/3$, 1/1. Cui et al. [38] applied a CALPHAD-type approach to calculate the partial enthalpies of mixing of In, Sn and Zn, but the comparison with the experimental data by Fiorani et al. [36] was not fully satisfactory. Xie et al. [39] used a similar approach for a thermodynamic assessment of the In–Sn–Zn ternary system based on a rather limited number of literature data and observed good agreement with the literature. Recently, Moelans et al. [40], also used the CALPHAD method in a thermodynamic assessment of the quaternary Bi–In–Sn–Zn system; for this purpose they calculated the enthalpy of mixing of liquid In–Sn–Zn alloys at 441 and 634 °C for the section $x_{\mathrm{In}}/x_{\mathrm{Sn}} = 1/3$ in comparison with experimental data from Anres et al. [37]. They found that it was not possible to model the temperature dependence of the mixing enthalpy in a correct way. In some composition ranges, the calculated temperature dependence was found even opposite to that determined experimentally [37].

3. Experimental procedure

The calorimetric measurements were carried out in a Calvet-type microcalorimeter (SETARAM, Lyon, France; thermopile with more than 200 thermocouples, wire wound resistance furnace, automatic drop device for up to 30 drops, control and data evaluation with LabView HiQ as described by Flandorfer et al. [41]). To prevent oxidation of the samples, all measurements were performed under a flow of pure Ar (approximately 30 mL/min). At the end of each series the calorimeter was calibrated by four or five drops (between 30 and 50 mg each) of NIST standard α-Al_2O_3 (National Institute of Standards and Technology, Gaithersburg, MD).

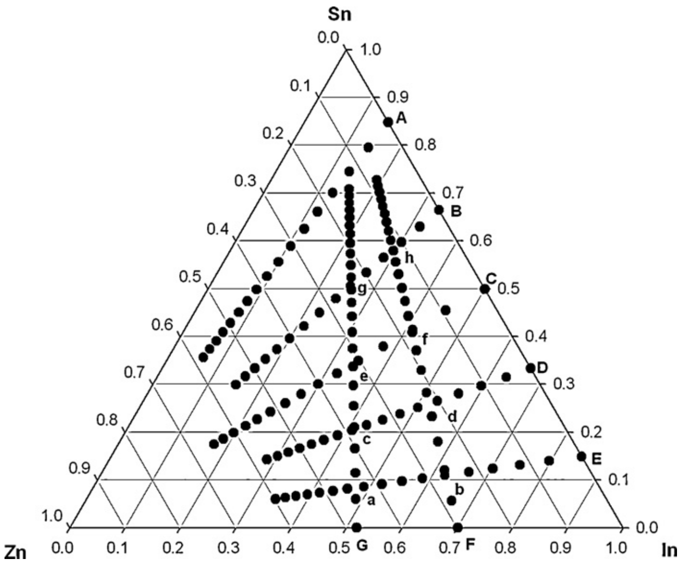

Fig. 1. Investigated sections and alloy compositions in the ternary In–Sn–Zn system at 500 °C (intersections a–h indicated, see Table 3).

The samples were prepared from In rods (99.999%, ASARCO, South Plainfield, NJ), and Sn rods (99.998%, Alfa Johnson Matthey, Karlsruhe, Germany), and Zn (99.999%, ASARCO, South Plainfield, NJ). The three metals were used without further purification.

In a first step, the enthalpies of mixing of the In–Sn system were determined at 500 °C. For this purpose, small pieces (18–52 mg) of pure Sn were dropped into a bath of liquid alloy, beginning with pure In (about 158 mg). In addition to this, pieces of pure In were also dropped into a molten bath starting from pure Sn.

In the ternary In–Sn–Zn system, the enthalpies of mixing of about 120 molten samples were determined along seven sections at 500 °C (Fig. 1). Pieces of pure Zn (18–40 mg) were dropped into about 300–600 mg of molten $\mathrm{In}_x\mathrm{Sn}_{1-x}$ along five sections ($x = 0.15$; 0.34; 0.50; 0.67 and 0.85). To cross-check the enthalpies of mixing at several intersections, pieces of pure Sn were also dropped into molten $\mathrm{In}_x\mathrm{Zn}_{1-x}$ along two sections ($x = 0.52$ and 0.70).

Table 1
Partial and integral molar enthalpies of mixing of liquid In–Sn alloys at 500 °C; standard states: pure liquid components.

Drop	Drop enthalpy	Partial enthalpy		Integral enthalpy[a]	
n(i) (mmol)	ΔH_{drop} (J)	x(Sn)[b]	$\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Sn}}$ (J/mol)	x(Sn)	$\Delta_{\mathrm{mix}}H$ (J/mol)
Starting amount: n(In) = 1.3731 mmol					
i = Sn					
0.1525	2879	0.0500	−1834	0.1000	−183
0.1834	3440	0.1483	−1956	0.1966	−374
0.2471	4902	0.2473	−873	0.2981	−437
0.3479	7177	0.3511	−83	0.4041	−383
0.4430	9150	0.4521	−58	0.5002	−331
Starting amount: n(Sn) = 1.4274 mmol					
i = In					
0.1631	2582	0.9488	−850	0.8975	−87
0.2184	3482	0.8433	−735	0.7891	−165
0.2597	4133	0.7396	−764	0.6901	−241
0.3311	5298	0.6673	−679	0.5949	−301
0.4526	7370	0.5839	−398	0.5005	−316

[a] Per mole of binary mixture.
[b] Average of x(Sn) before and after the drop.

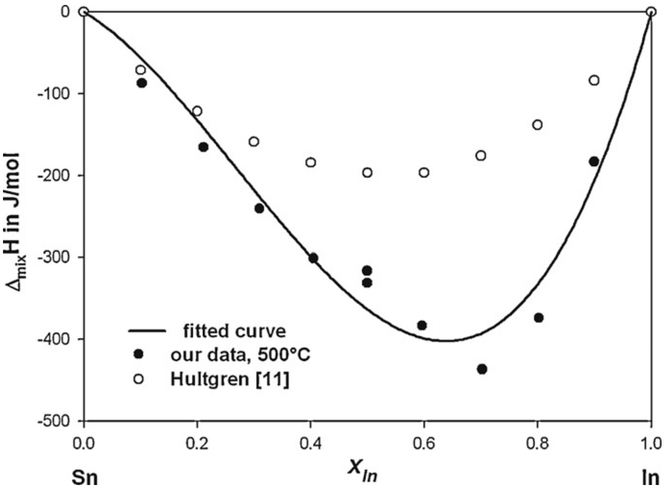

Fig. 2. Integral molar enthalpies of mixing of liquid In–Sn alloys at 500 °C and comparison with literature data from Hultgren et al. [11]; standard states: pure liquid metals.

The time interval between individual drops was usually 40 min and the effective heat flow acquisition interval was about 0.73 s. The obtained signals were recorded and integrated. The measured drop enthalpy (integrated heat flow at constant pressure) is:

$$\Delta H_{\mathrm{drop}} = n_{\mathrm{i}}[\boldsymbol{H}_{\mathrm{i(l)},T_{\mathrm{exp}}} - \boldsymbol{H}_{\mathrm{i(s)},\mathrm{D}T}] + \Delta H_{\mathrm{reaction}} \tag{1}$$

where n_{i} is the number of moles of the dropped element i, $\boldsymbol{H}_{\mathrm{i(l)},T_{\mathrm{exp}}}$ is the molar enthalpy of the liquid element i at the experimental temperature T_{exp} (in K) and $\boldsymbol{H}_{\mathrm{i(s)},\mathrm{D}T}$ the molar enthalpy of the solid element i at the drop temperature. The difference $[\boldsymbol{H}_{\mathrm{i(l)},T_{\mathrm{exp}}} - \boldsymbol{H}_{\mathrm{i(s)},\mathrm{D}T}]$ was calculated using the SGTE data for pure elements [42]. For the respective temperatures DT and T_{exp} the average of the values for each drop of a run were taken because their scatter was low enough in order not to influence the experimental error. Because of the rather small masses added, the partial enthalpies can be directly obtained as:

$$\Delta_{\mathrm{mix}}\bar{H} \approx \frac{\Delta H_{\mathrm{reaction}}}{\mathrm{n_i}}. \tag{2}$$

The accuracy of the temperature measurements using a Pt/Pt–10Rh thermocouple is estimated to be ±2 K, that of the enthalpy measurement ±300 J/mol.

4. Results and discussion

4.1. Experimental results

Measurements of the partial and integral molar enthalpies of mixing in the liquid In–Sn and In–Sn–Zn alloys were performed at 500 °C. The corresponding results are collected in Tables 1, 2a and 2b . These tables contain information on starting molar amounts, added amounts, measured heat effects and the obtained partial and integral enthalpy values versus concentration..

Fig. 2 shows the experimental data of the integral molar enthalpy of mixing for the In–Sn system at 500 °C. This experimental temperature was high enough to obtain fully liquid alloys over the complete concentration range. All measured enthalpies of mixing are slightly exothermic. A comparison with the assessed values by Hultgren et al. [11] shows that the present experimental values are more exothermic, and the difference at the minimum is approximately 200 J/mol. This is hardly significant considering an accuracy of ±150 J/mol. The more recent data by Luef et al. [15] show better agreement with our results. The present experimental values were fitted using standard Redlich–Kister polynomials (see Section 4.2).

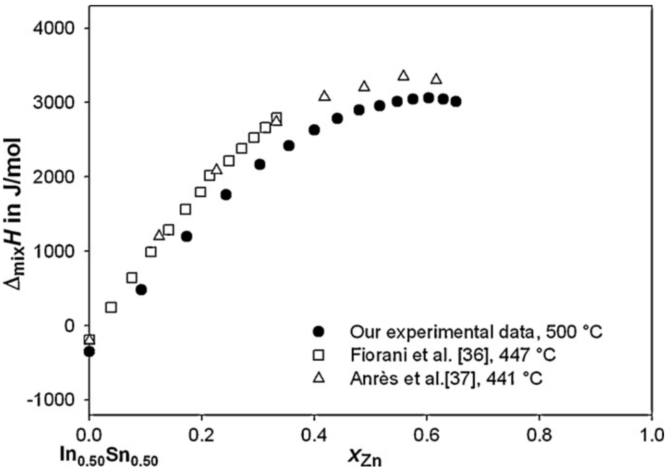

Fig. 3. Integral molar enthalpies of mixing of liquid In–Sn–Zn alloys, pure Zn dropped into molten $In_{0.5}Sn_{0.5}$ (section C) at 500 °C in comparison with previous experimental data [36,37]; standard states: pure liquid metals.

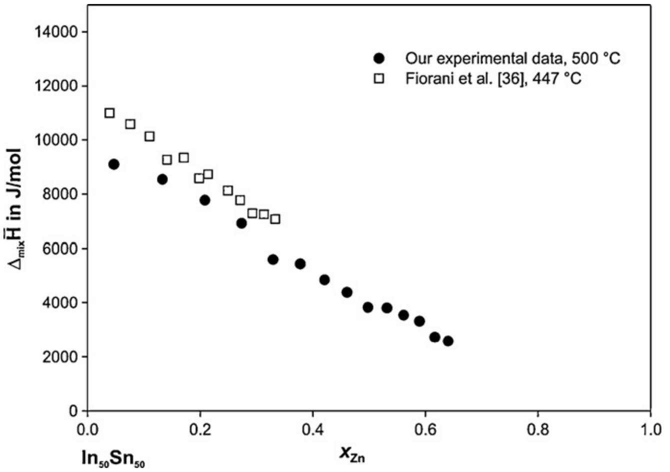

Fig. 4. Partial molar enthalpies of mixing of liquid In–Sn–Zn alloys, pure Zn dropped into molten $In_{0.5}Sn_{0.5}$ (section C) at 500 °C in comparison with previous experimental data [36]; standard states: pure liquid metals.

The fitted curve in Fig. 2 shows a minimum of −410 J/mol at 60 at.% In.

Partial and integral molar enthalpies of mixing in liquid ternary In–Sn–Zn alloys were investigated along seven isopleths: dropping Zn to liquid In_xSn_{1-x} with x_{In}/x_{Sn} = 0.152/0.848 (section A), 0.336/0.664 (B), 0.501/0.499 (C), 0.667/0.333 (D), 0.851/0.149 (E) and dropping Sn to liquid In_xZn_{1-x} with x_{In}/x_{Zn} = 0.702/0.298 (F), 0.519/0.481 (G); see also Fig. 1. Figs. 3 and 4 show, as an example, the integral and the partial molar enthalpies of mixing along section C. All measured enthalpies of mixing are endothermic with a maximum of about 3000 J/mol around 60 at.% Zn. The present experimental values are compared with previous data reported by Fiorani et al. [36] and Anres et al. [37] along approximately the same section (Figs. 3 and 4) and good agreement is observed, both for the integral as well as the partial enthalpies of mixing.

Figs. 5 and 6 show the integral and the partial molar enthalpies of mixing along section G where pure Sn was dropped into liquid $In_{0.519}Zn_{0.481}$. The obtained integral enthalpy of mixing is also endothermic over the entire experimental concentration range (up to about 70 at.% Sn). Along this section, the integral enthalpy of mixing decreases nearly linearly with increasing Sn content (Fig. 5) while the partial molar enthalpy of tin remains close to zero for the whole section (Fig. 6). A similar effect was observed for section F.

Table 2a
Partial and integral molar enthalpies of mixing of liquid In–Sn–Zn alloys at 500 °C: Zn-drops; standard states: pure liquid components.

Drop	Drop enthalpy	Partial enthalpy		Integral enthalpy[a]		
n(Zn) (mmol)	ΔH_{drop} (J)	x(Zn)[b]	$\Delta_{mix}\bar{H}_{Zn}$ (J/mol)	x(Sn)	x(Zn)	$\Delta_{mix}H$ (J/mol)
Section A; starting amount: n(In) = 0.6364 mmol; n(Sn) = 3.5447 mmol						
–	–	–	–	0.8478	0.0000	−122
0.2763	8290	0.0310	9360	0.7952	0.0620	465
0.3028	8768	0.0918	8310	0.7446	0.1217	964
0.3034	8658	0.1480	7893	0.7000	0.1743	1380
0.3049	8520	0.1977	7303	0.6603	0.2212	1716
0.3091	8570	0.2424	7079	0.6243	0.2636	2008
0.3431	9235	0.2846	6273	0.5887	0.3056	2251
0.3564	9578	0.3250	6234	0.5558	0.3444	2474
0.3658	9719	0.3622	5926	0.5257	0.3799	2661
0.3720	9642	0.3961	5281	0.4982	0.4124	2798
0.3750	9663	0.4271	5125	0.4733	0.4418	2914
0.3868	9771	0.4555	4618	0.4500	0.4692	2998
0.3999	10053	0.4820	4496	0.4283	0.4948	3070
0.4009	9982	0.5065	4254	0.4085	0.5182	3125
0.4026	9897	0.5289	3942	0.3904	0.5395	3161
0.4176	10201	0.5497	3786	0.3732	0.5598	3189
0.4493	10807	0.5697	3415	0.3563	0.5797	3199
Section B; starting amount: n(In) = 1.7389 mmol; n(Sn) = 3.4398 mmol						
–	–	–	–	0.6642	0.0000	−251
0.2842	8626	0.0260	9709	0.6297	0.0520	267
0.3000	8938	0.0767	9152	0.5969	0.1014	729
0.3307	9556	0.1258	8254	0.5645	0.1501	1138
0.3528	10082	0.1734	7937	0.5336	0.1967	1510
0.3603	10152	0.2179	7532	0.5054	0.2392	1829
0.3782	10422	0.2592	6914	0.4788	0.2792	2096
0.4686	12565	0.3013	6171	0.4494	0.3234	2346
0.5088	13410	0.3444	5715	0.4214	0.3655	2556
0.5288	13787	0.3848	5433	0.3958	0.4041	2731
0.5318	13814	0.4213	5335	0.3730	0.4385	2881
0.5349	13692	0.4539	4954	0.3525	0.4693	2995
0.5492	13850	0.4834	4577	0.3337	0.4976	3079
0.5682	14229	0.5107	4403	0.3163	0.5238	3148
0.6304	15587	0.5369	4087	0.2990	0.5499	3200
Section C; starting amount: n(In) = 1.3709 mmol; n(Sn) = 1.3739 mmol						
–	–	–	–	0.5006	0.0000	−354
0.2805	8342	0.0464	9103	0.4541	0.0927	483
0.2932	8557	0.1328	8539	0.4140	0.1729	1195
0.3102	8815	0.2082	7774	0.3786	0.2436	1758
0.3120	8598	0.2735	6916	0.3486	0.3035	2166
0.3142	8243	0.3292	5596	0.3229	0.3549	2419
0.3219	8390	0.3776	5428	0.3002	0.4003	2631
0.3358	8558	0.4208	4845	0.2797	0.4413	2782
0.3631	9088	0.4605	4390	0.2604	0.4797	2893
0.3923	9596	0.4977	3819	0.2424	0.5157	2957
0.3924	9592	0.5314	3801	0.2267	0.5471	3012
0.3988	9643	0.5611	3537	0.2127	0.5751	3044
0.4664	11172	0.5894	3311	0.1984	0.6037	3062
0.4734	11062	0.6164	2726	0.1857	0.6290	3041
0.4783	11106	0.6403	2579	0.1744	0.6516	3013
Section D; starting amount: n(In) = 3.3187 mmol; n(Sn) = 1.6527 mmol						
–	–	–	–	0.3324	0.0000	−406
0.2796	8604	0.0266	10132	0.3147	0.0532	155
0.3178	9657	0.0803	9744	0.2968	0.1073	702
0.3258	9660	0.1320	9006	0.2804	0.1566	1161
0.3400	9740	0.1796	8005	0.2651	0.2026	1534
0.3483	9860	0.2237	7671	0.2511	0.2448	1859
0.3566	9883	0.2642	7073	0.2382	0.2836	2127
0.3826	10370	0.3023	6463	0.2257	0.3210	2353
0.3927	10417	0.3383	5889	0.2142	0.3556	2533
0.4060	10658	0.3717	5611	0.2035	0.3878	2687
0.4364	11286	0.4034	5220	0.1931	0.4190	2816
0.4552	11544	0.4337	4721	0.1834	0.4484	2913
0.4650	11572	0.4619	4246	0.1744	0.4754	2978
0.4772	11675	0.4880	3824	0.1660	0.5006	3019
0.5259	12839	0.5131	3773	0.1577	0.5256	3056
0.5347	12950	0.5372	3579	0.1500	0.5487	3082
0.5857	13967	0.5601	3206	0.1425	0.5715	3088

Table 2a (Continued)

Drop	Drop enthalpy	Partial enthalpy		Integral enthalpy[a]		
n(Zn) (mmol)	ΔH_{drop} (J)	x(Zn)[b]	$\Delta_{\text{mix}}\bar{H}_{\text{Zn}}$ (J/mol)	x(Sn)	x(Zn)	$\Delta_{\text{mix}}H$ (J/mol)
Section E; starting amount: n(In) = 3.4884 mmol; n(Sn) = 0.6118 mmol						
–	–	–	–	0.1492	0.0000	−303
0.2777	8646	0.0317	10493	0.1398	0.0634	381
0.2867	8599	0.0922	9349	0.1312	0.1210	933
0.2944	8576	0.1471	8484	0.1234	0.1732	1381
0.2959	8406	0.1965	7767	0.1164	0.2197	1741
0.3389	9455	0.2434	7255	0.1094	0.2670	2075
0.3534	9748	0.2888	6939	0.1029	0.3106	2364
0.3659	9846	0.3306	6270	0.0969	0.3505	2590
0.4091	10674	0.3703	5448	0.0910	0.3901	2764
0.4093	10493	0.4076	4996	0.0858	0.4251	2892
0.4174	10600	0.4410	4757	0.0810	0.4569	2995
0.4192	10406	0.4711	4180	0.0768	0.4854	3058
0.4248	10413	0.4985	3871	0.0729	0.5115	3099
0.4287	10452	0.5233	3739	0.0694	0.5352	3130
0.4459	10790	0.5464	3558	0.0660	0.5576	3151
0.4499	10727	0.5678	3203	0.0630	0.5781	3153
0.4670	11022	0.5877	2962	0.0601	0.5974	3144

[a] Per mole of ternary mixture.

[b] Average of x(Zn) before and after the drop.

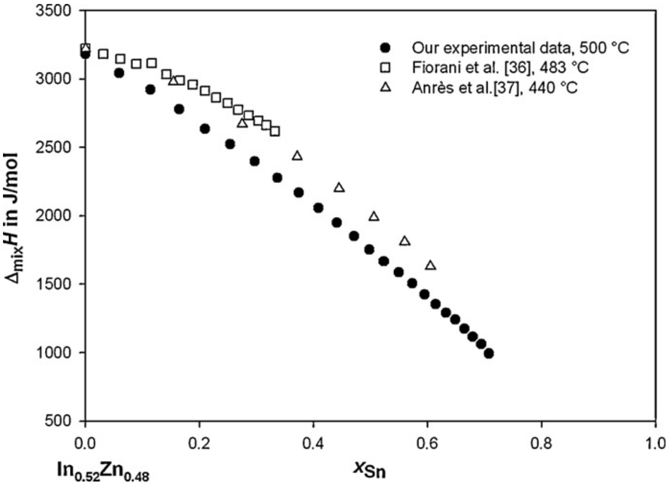

Fig. 5. Integral molar enthalpies of mixing of liquid In–Sn–Zn alloys, pure Sn dropped into molten $In_{0.52}Zn_{0.48}$ (section G) at 500 °C in comparison with previous experimental data [36,37]; standard states: pure liquid metals.

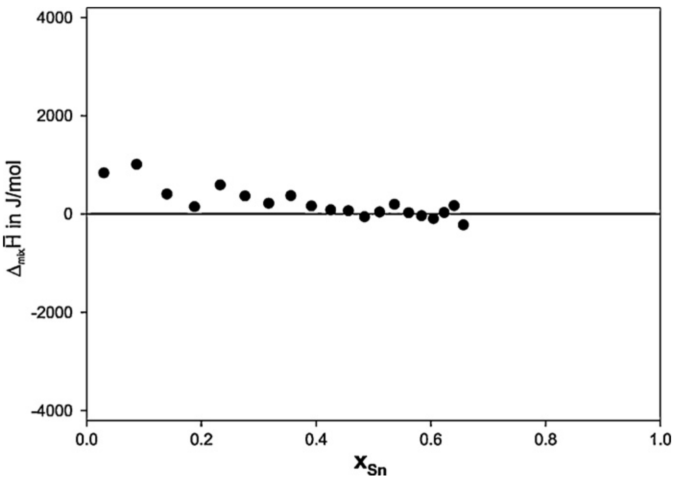

Fig. 6. Partial molar enthalpies of mixing of liquid In–Sn–Zn alloys, pure Sn dropped into molten $In_{0.52}Zn_{0.48}$ (section G) at 500 °C; standard states: pure liquid metals.

This indicates an almost ideal mixing behavior for additions of Sn to the binary In–Zn alloys.

Table 3 lists the experimental values of the integral enthalpy of mixing at the intersection points of sections with Zn additions and with Sn additions, labeled “a” through “h” in Fig. 1. The comparison of these values is used as a criterion for the reliability and reproducibility of the calorimetric results. Taking into account the experimental accuracy and the small absolute values of the thermal effect of mixing, the agreement is considered to be very good.

4.2. Binary and ternary modeling

In a first step, the experimental data for binary liquid In–Sn alloys at 500 °C were treated by a least squares fit using the following Redlich–Kister polynomial as proposed by Ansara and Dupin

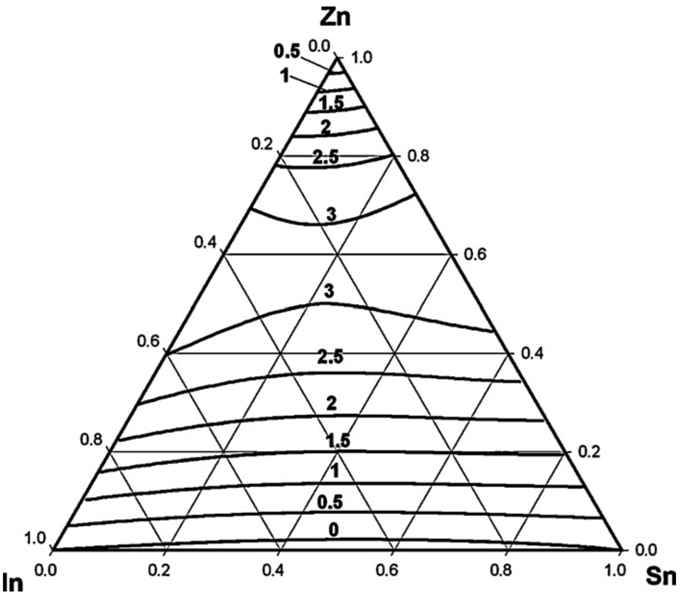

Fig. 7. Isoenthalpy plot of the integral enthalpy of mixing in In–Sn–Zn at 500 °C; values in kJ/mol.

Table 2b
Partial and integral molar enthalpies of mixing of liquid In–Sn–Zn alloys at 500 °C: Sn-drops; standard states: pure liquid components.

Drop	Drop enthalpy	Partial enthalpy		Integral enthalpy[a]		
n(Sn) (mmol)	ΔH_{drop} (J)	x(Sn)[b]	$\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Sn}}$ (J/mol)	x(In)	x(Sn)	$\Delta_{\mathrm{mix}}H$ (J/mol)
Section F; starting amount: n(In) = 1.7914 mmol; n(Zn) = 0.7599 mmol						
–	–	–	–	0.7021	0.0000	2519
0.1512	3046	0.0280	−560	0.6629	0.0559	2346
0.1965	4110	0.0879	209	0.6179	0.1199	2202
0.2114	4270	0.1498	−506	0.5760	0.1797	2018
0.2143	4385	0.2062	−251	0.5388	0.2326	1871
0.2307	4722	0.2575	−243	0.5039	0.2824	1734
0.2472	5175	0.3057	227	0.4711	0.3290	1636
0.2513	4957	0.3498	−985	0.4419	0.3706	1474
0.2620	5326	0.3897	−386	0.4151	0.4088	1361
0.2631	5359	0.4258	−345	0.3912	0.4428	1263
0.2660	5419	0.4581	−341	0.3698	0.4734	1175
0.2722	5704	0.4874	246	0.3501	0.5014	1125
0.3107	6318	0.5157	−379	0.3300	0.5300	1039
0.3149	6503	0.5428	−63	0.3119	0.5557	979
0.3155	6383	0.5673	−481	0.2957	0.5789	903
0.3285	6753	0.5897	−156	0.2805	0.6005	848
0.3349	6898	0.6105	−113	0.2665	0.6204	800
0.3477	7113	0.6298	−250	0.2534	0.6391	749
0.3531	7341	0.6477	77	0.2414	0.6563	717
0.3589	7509	0.6642	212	0.2302	0.6721	694
0.3717	7650	0.6796	−131	0.2197	0.6871	656
0.3897	7988	0.6942	−215	0.2097	0.7013	616
0.3954	8162	0.7079	−67	0.2004	0.7146	586
0.4185	8641	0.7209	−62	0.1915	0.7273	557
Section G; starting amount: n(In) = 1.3105 mmol; n(Zn) = 1.2157 mmol						
–	–	–	–	0.5188	0.0000	3181
0,1597	3440	0.0297	838	0.4879	0.0594	3042
0,1665	3616	0.0869	1012	0.4595	0.1143	2923
0,1734	3662	0.1397	407	0.4331	0.1651	2779
0,1740	3629	0.1878	147	0.4096	0.2105	2636
0,1893	4032	0.2325	592	0.3867	0.2546	2522
0,2049	4318	0.2758	368	0.3647	0.2971	2399
0,2173	4548	0.3171	219	0.3439	0.3371	2275
0,2278	4803	0.3558	375	0.3245	0.3745	2167
0,2349	4903	0.3917	164	0.3066	0.4089	2057
0,2494	5186	0.4252	84	0.2897	0.4415	1949
0,2500	5195	0.4561	66	0.2746	0.4707	1850
0,2574	5317	0.4843	−58	0.2605	0.4978	1752
0,2683	5567	0.5105	41	0.2473	0.5233	1666
0,3060	6398	0.5363	197	0.2338	0.5493	1586
0,3110	6449	0.5611	27	0.2215	0.5730	1504
0,3145	6503	0.5838	−36	0.2103	0.5945	1426
0,3173	6542	0.6044	−93	0.2002	0.6142	1352
0,3193	6623	0.6232	31	0.1908	0.6321	1291
0,3281	6852	0.6405	170	0.1821	0.6489	1240
0,3330	6821	0.6567	−224	0.1741	0.6644	1175
0,3501	7208	0.6719	−125	0.1663	0.6793	1117
0,3823	7883	0.6868	−95	0.1586	0.6942	1061
0,3902	7897	0.7011	−472	0.1515	0.7080	992

[a] Per mole of ternary mixture.
[b] Average of x(Sn) before and after the drop.

[43] for substitutional solutions.

$$\Delta_{\mathrm{mix}}H = \sum_{i}\sum_{j>i}\left[x_i x_j \sum_{\nu} {}^{(\nu)}L_{i,j}(x_i - x_j)^{\nu}\right] \tag{3}$$

with i and j equal to 1 and 2 for the two elements in alphabetical order (In and Sn). ${}^{(\nu)}L_{i,j}$ ($\nu = 0, 1, 2, \ldots, n$) are the interaction parameters of the constituent binaries (see Table 4). As the In–Sn system shows a nearly regular course of the enthalpy of mixing curve with just one extreme (see Fig. 2), it was sufficient to use only ${}^{(0)}L$ and ${}^{(1)}L$ for a perfect fit. The interaction parameters for the two binary systems (In–Zn and Sn–Zn) were calculated according to the assessed values by Hultgren et al. [11].

In a second step, experimental data for ternary In–Sn–Zn alloys were treated by a least squares fit using the following Redlich–Kister–Muggianu polynomial [44] which takes also into

Table 3
Values of the enthalpy of mixing at the eight intersection points (see Fig. 1).

Intersection point	Molar fraction of alloy		$\Delta_{\mathrm{mix}}H$ (J/mol)	
	x_{Zn}	x_{Sn}	Zn addition	Sn addition
a	0.45	0.08	2958	2998
b	0.27	0.11	2107	2217
c	0.38	0.21	2654	2652
d	0.22	0.27	1676	1784
e	0.32	0,34	2273	2266
f	0.18	0.41	1295	1369
g	0.24	0.50	1827	1753
h	0.13	0.58	977	917

Table 4
Binary and ternary interaction parameters in the In–Sn–Zn system.

Interaction parameter	T (°C)	ν, α	J/mol	Reference
${}^{(\nu)}L_{\text{In,Sn}}$	500	0	−1488	This work
		1	−1041	
${}^{(\nu)}L_{\text{In,Zn}}$	427	0	13095	[11]
		1	−2682	
${}^{(\nu)}L_{\text{Sn,Zn}}$	477	0	12728	[11]
		1	−5074	
		2		
${}^{(\alpha)}M_{\text{In,Sn,Zn}}$	500	0	−12675	This work
		1	−2241	
		2	−19195	

account additional ternary interactions:

$$\Delta_{\text{mix}}H = \sum_{i}\sum_{j>i}\left[x_i x_j \sum_{\nu} {}^{(\nu)}L_{i,j}(x_i - x_j)^{\nu}\right] + x_A x_B x_C\left({}^{(0)}M_{A,B,C}x_A + {}^{(1)}M_{A,B,C}x_B + {}^{(2)}M_{A,B,C}x_C\right) \qquad (4)$$

with i and j equal to 1, 2, 3 for the elements In, Sn and Zn, respectively. ${}^{(\nu)}L_{i,j}$ ($\nu = 0, 1, 2$) are the interaction parameters of the constituent binaries which were taken from Table 4. The last term represents the additional mixing enthalpy due to ternary interactions where ${}^{(\alpha)}M_{A,B,C}$ ($\alpha = 0, 1, 2$) are the excess ternary interaction parameters which are also listed in Table 4.

Based on the refinements described above it was possible to calculate the integral enthalpy of mixing for any point of the In–Sn–Zn ternary system. The result is presented as an isoenthalpy plot shown in Fig. 7. Except for the region very close to the In–Sn binary, the entire ternary system shows weakly positive integral enthalpy of mixing with a maximum of 3340 J/mol at approximately 45 at.% In in the binary In–Zn system.

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