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Thermodynamic Properties and Melting Behavior of Bi–Sn–Zn Alloys

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Summary. The partial and integral enthalpies of mixing of liquid Bi–Sn–Zn alloys were determined at 500°C by a drop calorimetric technique using a *Calvet*-type microcalorimeter. The ternary interaction parameters in the Bi–Sn–Zn system were fitted using the *Redlich-Kister-Muggianu* model for substitutional solutions, and isoenthalpy curves of the integral molar enthalpy of mixing at 500°C were constructed. Furthermore, a DSC technique was used to determine the liquidus temperatures in three sections (3, 5, and 7 at.% Zn) as well as the invariant reaction temperature of the ternary eutectic $L \rightleftarrows (Bi) + (Sn) + (Zn)$. The ternary eutectic reaction was found at 135°C.

Keywords. Alloys; Calorimetry; Thermochemistry; Enthalpy of mixing; Liquidus temperatures.

Introduction

Lead and lead-containing materials are notorious for posing a considerable threat to human life and environment [1, 2]. Concern about the use of tin–lead solders in the electronics industry stems from occupational exposure, lead waste derived from the manufacturing process, and the disposal of electronic assemblies. Although it is now widely agreed that there is no drop-in replacement for the standard tin–lead solders that are currently used worldwide, a range of possible alternatives has been investigated. Sn–Zn–Bi alloys are now commercially used for reflow soldering in Japan and South East Asia, the most popular composition beeing Sn–8Zn–3Bi [3, 4]. Major advantages of this alloy are the moderate melting point only slightly

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higher than the eutectic Sn-37Pb, and the low material cost as compared to Sn–Ag–Cu lead-free solders.

Our investigations are considered a contribution to the COST 531 Action of the European Union which is mainly aiming at generating and systematizing information on thermochemistry, phase relationships, and chemical and physical properties of alloy systems relevant to lead-free solder materials as well as on reliability issues. A lead-free solder database will be created forming the basis for a systematic alloy design which is desired to avoid complex and time consuming trial and error developing methods. Information on thermochemical properties such as mixing enthalpies and experimental information on reaction and liquidus temperatures are indispensable for the thermodynamic optimization of phase diagrams and the estimation of several physical properties, *e.g.* surface tension and wettability.

Literature Review

From the literature, a considerable amount of data is available on the enthalpy of mixing of liquid Bi–Sn alloys. The binary interaction parameters of Bi–Sn (see Table 1) were established by *Flandorfer et al.* [5] based on very recent emf measurements by *Asryan* and *Mikula* [6] at 450°C. These data are in very good agreement with earlier calorimetric measurements by *Wittig* and *Huber* [7] at 470°C, *Yazawa et al.* [8] at 417°C, and finally by *Sharkey* and *Pool* [9] at 452°C as well as with emf data reported by *Seltz* and *Dunkerley* [10] for 335°C. The enthalpy of mixing was found to be independent of temperature within the experimental errors.

The enthalpy of mixing of liquid Bi–Zn alloys was first determined by *Kawakami* [11] at 450°C and later by *Wittig et al.* [12] at 470 and 570°C. *Malakhov* [13] presented an assessment of the thermodynamic data based on the measurements by *Wittig et al.* [12] and concluded that the enthalpy of mixing was temperature independent. However, he used a model with seven interaction parameters to describe the liquid phase.

The experimental data on the enthalpy of mixing of liquid Sn–Zn alloys in the literature are quite numerous. The $\Delta_{\mathrm{mix}}H$ was either measured directly by calorimetry [14–20] or calculated from the temperature dependences of activities measured by emf or other methods [21–24]. *Kleppa* [14] was the only one to find a temperature

Table 1. Binary and ternary interaction parameters of Bi–Sn–Zn

Interaction parameter	Temperature/°C	Source	ν, α	J mol^{-1}
$L_{\mathrm{Bi:Sn}}{}^{(\nu)}$	450	[5]	0	442
			1	−298
$L_{\mathrm{Bi:Sn}}{}^{(\nu)}$	470–570	this work	0	17782
			1	−4775
$L_{\mathrm{Sn:Zn}}{}^{(\nu)}$	422–577	[25]	0	12558
			1	−5623
			2	4149
$M_{\mathrm{Bi:Sn:Zn}}{}^{(\alpha)}$	500	this work	0	−15489
			1	−10785
			2	−12528

dependence of the enthalpy of mixing. A detailed review of all experimental data can be found in the work of *Lee* [25]. The binary Sn–Zn interaction parameters from his generally accepted assessment were used for this work (see Table 1).

To the best knowledge of the authors no calorimetric data are available for liquid Bi–Sn–Zn alloys in the literature. However, *Malakhov et al.* [26] and later *Moelans et al.* [27] presented thermodynamic assessments of the system based on emf and phase diagram data available at that time. *Muzaffar* [28] measured the freezing points and thermal arrests of 104 Bi–Sn–Zn alloys by thermal analysis using the cooling curves (cooling rates: approx. $10\,\mathrm{K\,min^{-1}}$). *Jänecke* [29] presented a sketch of the liquidus surface based on detailed investigations of the Bi–Cd–Pb–Sn–Zn quinary system. *Pelton et al.* [30] calculated the liquidus surface of Bi–Sn–Zn using thermodynamic data obtained by an emf method. Several authors [31–36] performed emf measurements in the temperature range between 450 and 650°C. However, no further experimental data on the melting behavior and the invariant reaction temperatures in the Bi–Sn–Zn ternary system are available from the literature.

Results and Discussion

Experimental Calorimetric Results

The original experimental data of the six measurement series (see Fig. 1) in the ternary Bi–Sn–Zn system can be found in Table 2, which contains information on

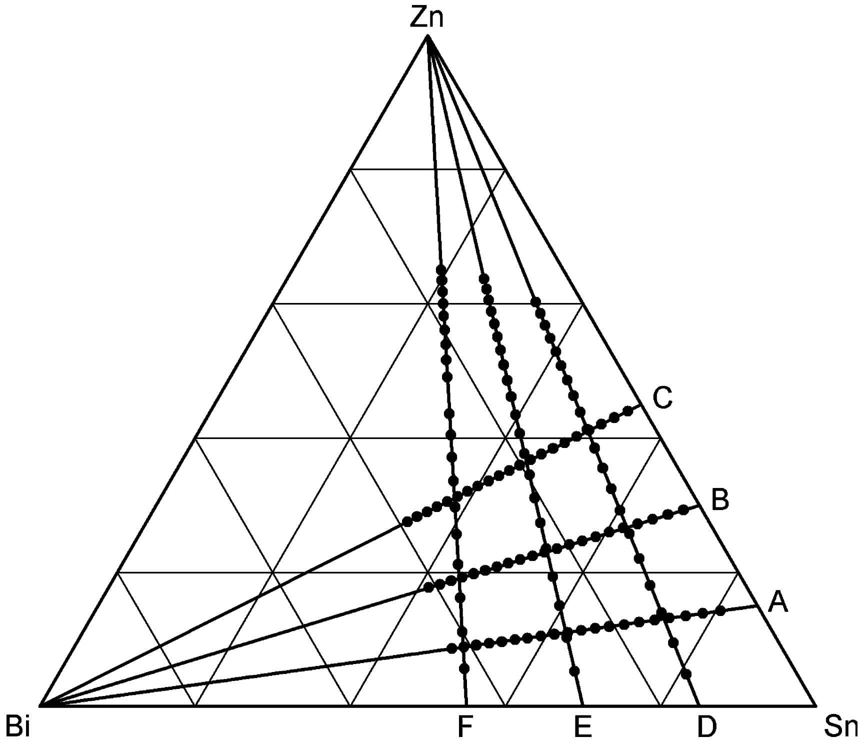

Fig. 1. Measured sections and alloy compositions in the ternary Bi–Sn–Zn system (500°C); grid in at.%

Table 2. Partial and integral enthalpies of mixing of liquid Bi–Sn–Zn alloys, 500°C, standard states: liquid pure components, *DT* denotes the drop temperature

n_i/mmol	x(Bi)	x(Sn)	Heat effect ΔQ/J	Partial enthalpy h_i/J mol^{-1}	Integral enthalpy $\Delta_{\mathrm{mix}}H$/J mol^{-1}
Section A, $T = 501°\mathrm{C}$, $DT = 37°\mathrm{C}$, starting amount: $n(\mathrm{Sn}) = 6.1536$ mmol, $n(\mathrm{Zn}) = 1.0959$ mmol, $i = \mathrm{Bi}$					
0.0000	0.0000	0.8500			1359
0.3937	0.0515	0.8062	9767	448	1312
0.2024	0.0760	0.7854	4977	237	1284
0.2047	0.0995	0.7654	5079	446	1263
0.2123	0.1226	0.7458	5223	246	1237
0.1962	0.1430	0.7285	4853	378	1217
0.2216	0.1648	0.7099	5374	−112	1183
0.2224	0.1857	0.6922	5397	−91	1151
0.2289	0.2061	0.6748	5622	199	1127
0.2300	0.2256	0.6582	5569	−140	1096
0.2431	0.2452	0.6416	5885	−147	1065
0.2457	0.2640	0.6256	5989	17	1039
0.2578	0.2828	0.6096	6230	−194	1007
0.2710	0.3015	0.5937	6583	−63	979
0.2816	0.3200	0.5780	6825	−120	950
0.2886	0.3379	0.5628	6969	−214	920
0.3069	0.3560	0.5474	7456	−63	893
0.3232	0.3739	0.5322	7758	−357	858
0.3343	0.3915	0.5172	8014	−387	823
0.3497	0.4089	0.5025	8491	−79	797
0.3577	0.4256	0.4882	8621	−259	767
Section B, $T = 501°\mathrm{C}$, $DT = 39°\mathrm{C}$, starting amount: $n(\mathrm{Sn}) = 5.4488$ mmol, $n(\mathrm{Zn}) = 2.3050$ mmol, $i = \mathrm{Bi}$					
0.0000	0.0000	0.7000			2304
0.1898	0.0239	0.6833	5037	2180	2301
0.1957	0.0474	0.6668	5099	1753	2288
0.2039	0.0706	0.6506	5293	1651	2272
0.2053	0.0930	0.6349	5315	1581	2256
0.2112	0.1148	0.6196	5452	1507	2238
0.2163	0.1362	0.6047	5514	1179	2212
0.2232	0.1571	0.5900	5673	1105	2185
0.2249	0.1772	0.5759	5678	942	2156
0.2283	0.1967	0.5623	5750	876	2125
0.2332	0.2156	0.5490	5805	591	2089
0.2415	0.2344	0.5360	5975	437	2050
0.2516	0.2529	0.5230	6249	530	2013
0.2611	0.2712	0.5101	6503	597	1978
0.2707	0.2893	0.4975	6611	115	1932
0.2741	0.3067	0.4853	6837	632	1900
0.2909	0.3243	0.4730	7161	312	1860
0.3031	0.3417	0.4608	7473	347	1821

(*continued*)

Table 2 (*continued*)

n_i/mmol	x(Bi)	x(Sn)	Heat effect ΔQ/J	Partial enthalpy h_i/J mol^{-1}	Integral enthalpy $\Delta_{\text{mix}}H$/J mol^{-1}
0.3170	0.3590	0.4487	7793	275	1780
0.3319	0.3761	0.4367	8140	217	1739
0.3430	0.3928	0.4250	8400	179	1697
0.3694	0.4099	0.4131	9026	123	1652
Section C, $T = 501$°C, $DT = 39$°C, starting amount: n(Sn) = 4.6518 mmol, n(Zn) = 3.7999 mmol, $i =$ Bi					
0.0000	0.0000	0.5500			2979
0.1908	0.0221	0.5379	5420	4050	3003
0.1976	0.0439	0.5258	5571	3884	3022
0.2029	0.0654	0.5140	5602	3297	3029
0.2069	0.0863	0.5025	5639	2951	3027
0.2122	0.1068	0.4913	5721	2652	3018
0.2139	0.1265	0.4804	5738	2522	3007
0.2236	0.1463	0.4696	5975	2411	2994
0.2279	0.1655	0.4590	5999	2017	2972
0.2294	0.1840	0.4488	6011	1892	2948
0.2292	0.2016	0.4391	5903	1446	2916
0.2393	0.2193	0.4294	6197	1586	2886
0.2413	0.2363	0.4200	6158	1208	2850
0.2559	0.2536	0.4105	6510	1127	2811
0.2740	0.2712	0.4008	6977	1159	2772
0.2785	0.2883	0.3914	7085	1132	2733
0.2877	0.3051	0.3822	7256	908	2690
0.3015	0.3219	0.3729	7735	1346	2657
0.3244	0.3391	0.3635	8136	774	2610
0.3338	0.3559	0.3542	8387	816	2564
0.3489	0.3726	0.3451	8708	651	2514
0.3568	0.3888	0.3362	8890	604	2465
Section D, $T = 501$°C, $DT = 36$°C, starting amount: n(Bi) = 0.9123 mmol, n(Sn) = 5.1515 mmol, $i =$ Zn					
0.0000	0.1500	0.8500			83
0.3069	0.1428	0.8091	8969	8834	505
0.3285	0.1358	0.7694	9614	8871	915
0.3445	0.1291	0.7318	9946	8479	1285
0.3565	0.1229	0.6965	10117	7991	1608
0.3773	0.1170	0.6627	10592	7685	1903
0.3885	0.1114	0.6312	10692	7131	2151
0.3944	0.1063	0.6021	10796	6980	2374
0.4118	0.1014	0.5745	11104	6569	2566
0.4317	0.0967	0.5481	11502	6251	2736
0.4507	0.0923	0.5230	11852	5907	2881
0.4674	0.0881	0.4993	12155	5616	3004
0.4703	0.0843	0.4776	12084	5299	3104
0.4974	0.0806	0.4565	12483	4703	3175

(*continued*)

Table 2 (*continued*)

n_i/mmol	x(Bi)	x(Sn)	Heat effect ΔQ/J	Partial enthalpy h_i/J mol^{-1}	Integral enthalpy $\Delta_{\text{mix}}H$/J mol^{-1}
0.5073	0.0771	0.4369	12719	4681	3240
0.5178	0.0739	0.4185	12841	4407	3289
0.5458	0.0707	0.4008	13325	4023	3320
0.5707	0.0677	0.3837	13851	3876	3344
0.5910	0.0649	0.3676	14354	3896	3367
0.5948	0.0622	0.3526	14163	3421	3369
0.6235	0.0597	0.3382	14701	3184	3362
Section E, $T = 500°\text{C}$, $DT = 36°\text{C}$, starting amount: $n(\text{Bi}) = 1.6532$ mmol, $n(\text{Sn}) = 3.8599$ mmol, $i = \text{Zn}$					
0.0000	0.3000	0.7000			118
0.3060	0.2842	0.6632	9241	9845	629
0.3259	0.2692	0.6280	9692	9378	1093
0.3420	0.2550	0.5949	10092	9147	1518
0.3459	0.2421	0.5648	9868	8170	1855
0.3754	0.2294	0.5354	10598	7868	2168
0.3815	0.2179	0.5085	10798	7944	2458
0.4101	0.2067	0.4824	11174	6885	2685
0.4127	0.1966	0.4587	11309	7039	2899
0.4279	0.1871	0.4365	11372	6213	3059
0.4463	0.1781	0.4156	11837	6160	3208
0.4585	0.1697	0.3960	12017	5848	3332
0.4830	0.1617	0.3773	12369	5248	3423
0.4896	0.1543	0.3601	12471	5110	3500
0.5021	0.1474	0.3439	12583	4700	3554
0.5183	0.1409	0.3288	12802	4339	3588
0.5311	0.1348	0.3145	13062	4235	3616
0.5475	0.1290	0.3011	13109	3583	3615
0.5697	0.1235	0.2883	13607	3525	3611
0.5824	0.1184	0.2763	13857	3433	3604
0.5945	0.1136	0.2650	13877	2983	3578
0.6028	0.1091	0.2545	14028	2913	3552
Section F, $T = 501°\text{C}$, $DT = 36°\text{C}$, starting amount: $n(\text{Bi}) = 2.2653$ mmol, $n(\text{Sn}) = 2.7647$ mmol, $i = \text{Zn}$					
0.0000	0.4500	0.5500			117
0.2999	0.4247	0.5191	9229	10383	695
0.3292	0.4000	0.4889	10019	10039	1238
0.3426	0.3771	0.4610	10266	9573	1714
0.3768	0.3549	0.4337	11081	9019	2145
0.3853	0.3347	0.4090	11137	8514	2508
0.3912	0.3164	0.3867	11058	7876	2802
0.4184	0.2989	0.3653	11616	7373	3054
0.4286	0.2829	0.3457	11715	6942	3263
0.4416	0.2681	0.3276	11863	6472	3430
0.4753	0.2538	0.3102	12426	5752	3554

(*continued*)

Table 2 (*continued*)

n_i/mmol	x(Bi)	x(Sn)	Heat effect ΔQ/J	Partial enthalpy h_i/J mol^{-1}	Integral enthalpy $\Delta_{mix}H$/J mol^{-1}
0.9619	0.2291	0.2800	24883	5476	3741
0.5150	0.2177	0.2661	12986	4825	3795
0.5236	0.2073	0.2534	13029	4491	3828
0.5371	0.1976	0.2415	13214	4211	3846
0.5562	0.1884	0.2303	13576	4015	3854
0.5675	0.1799	0.2199	13647	3654	3845
0.5876	0.1719	0.2101	13983	3406	3825
0.5900	0.1645	0.2011	13939	3233	3800
0.6183	0.1574	0.1924	14461	2995	3765

the exact measurement and drop temperatures, starting amounts, added amounts, resulting heat effects, and the partial and integral enthalpies of mixing of the liquid alloys. 500°C was chosen as measurement temperature, because the ternary system is completely liquid at this temperature. The Bi–Zn binary system shows a large liquid miscibility gap with a critical point at 576°C [37], which also extends into

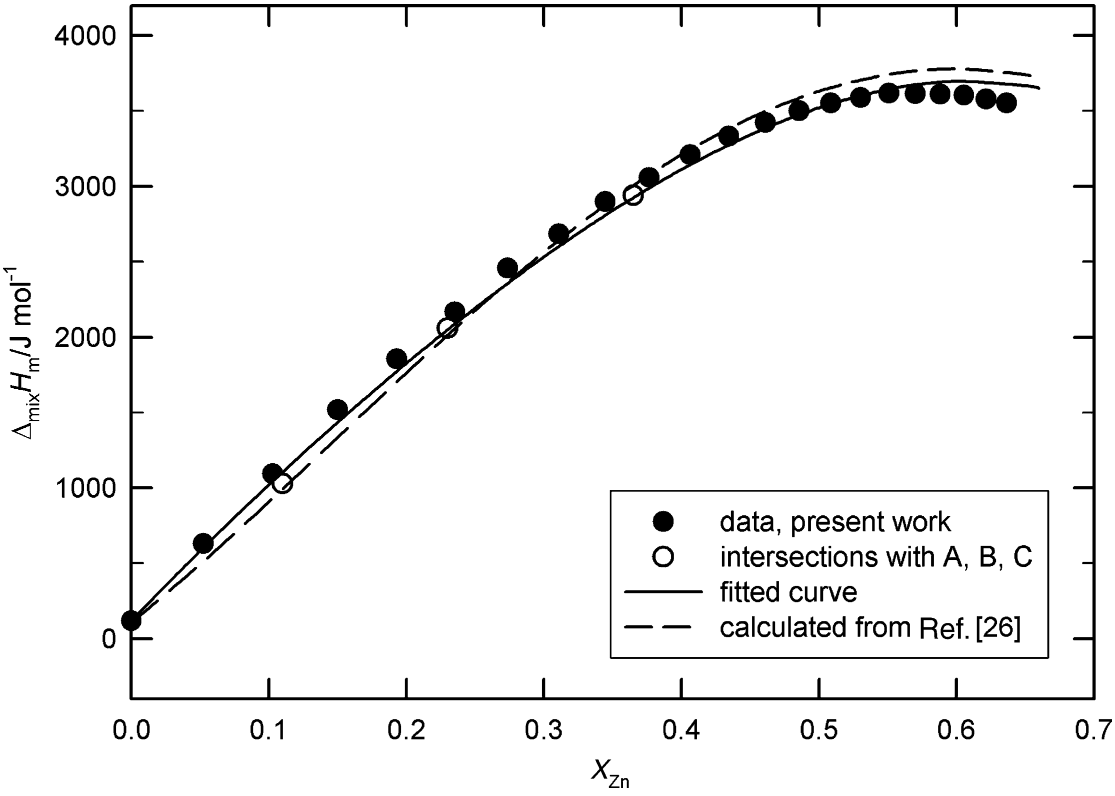

Fig. 2. Integral molar enthalpies of mixing of liquid Bi–Sn–Zn alloys, pure Zn dropped into molten $Bi_{30}Sn_{70}$ (Section E in Fig. 1) at 500°C; standard states: pure liquid metals; values from the other sections are marked by open symbols

the ternary system [26]. However, this miscibility gap did not affect our measurements as it is limited to approximately 10 at.% Sn at 500°C and our measurements were performed in the Sn-rich concentration range.

Figure 2 shows, as an example, the experimental data of the integral molar enthalpy of mixing of ternary Bi–Sn–Zn alloys, with pure Zn dropped into liquid $Bi_{30}Sn_{70}$ (corresponding to Section E in Fig. 1) at 500°C. The open symbols in Fig. 2 indicate experimental values from Sections A, B, and C. The positive starting value of $\Delta_{\mathrm{mix}}H_{\mathrm{m}}$ for the binary master alloy was calculated from Eq. (1) (see below) and the respective interaction parameters in Table 1. An analogous procedure was used for all six sections. From Fig. 2 it can be seen that the measured enthalpies of mixing in this section are all positive (*i.e.* endothermic) and run through a maximum at approximately 58 at.% Zn. By definition, $\Delta_{\mathrm{mix}}H_{\mathrm{m}}$ is 0 for pure Zn.

Binary and Ternary Modelling

The binary interaction parameters of Bi–Sn and Sn–Zn were directly taken from the literature [5, 25]. *Malakhov*'s recent assessment of the Bi–Zn system [13] was, however, not accepted as he used a model with seven interaction parameters to describe the liquid phase. So in a first step, the binary Bi–Zn experimental calorimetric data for the enthalpies of mixing from *Wittig et al.* [12] were treated by a least squares fit using the following *Redlich-Kister* polynomial, as proposed by *Ansara* and *Dupin* [38, 39] for substitutional solutions according to the CALPHAD method:

$$\Delta_{\mathrm{mix}}H_{\mathrm{m}} = \sum_{i}\sum_{j>i}\left[x_i x_j \sum_{\nu} L_{i:j}^{(\nu)}(x_i - x_j)^{\nu}\right] \tag{1}$$

where i and j are equal to 1 for Bi or 2 for Zn and ${L_{i:j}}^{(\nu)}(\nu = 0, 1, 2, \ldots)$ are the so called binary interaction parameters of the order ν. As Bi–Zn shows a rather simple course of the enthalpy of mixing curve with just one minimum, it was sufficient to use only $L^{(0)}$ and $L^{(1)}$ for a good description. In this case the polynomial has the form:

$$\Delta_{\mathrm{mix}}H_{\mathrm{m}} = L_{1:2}^{(0)}x_1x_2 + L_{1:2}^{(1)}x_1x_2(x_1 - x_2) \tag{2}$$

The result of the least squares fit for Bi–Zn is presented in Table 1 together with the literature values for the binary interaction parameters of Bi–Sn [5] and Sn–Zn [25]. Note that all three binary sub-systems show positive enthalpies of mixing in the entire composition range.

In a second step, the experimental data for the integral molar enthalpies of mixing of ternary Bi–Sn–Zn alloys were treated by a least squares fit. In this case the so-called *Redlich-Kister-Muggianu* polynomial was used which also takes the additional ternary interactions into account [38, 39]:

$$\Delta_{\mathrm{mix}}H_{\mathrm{m}} = \sum_{i}\sum_{j>i}\left[x_i x_j \sum_{\nu} L_{i:j}^{(\nu)}(x_i - x_j)^{\nu}\right] + x_i x_j x_k (M_{i:j:k}^{(0)}x_i + M_{i:j:k}^{(1)}x_j + M_{i:j:k}^{(2)}x_k) \tag{3}$$

Table 3. Measured and calculated enthalpies of mixing at the different intersections, Bi–Sn–Zn system at 500°C; standard states: Bi(l), Sn(l), Zn(l)

Intersection between sections...	Concentration			Experimental values		Calculated values from polynomial (3) kJ mol^{-1}
	at.% Bi	at.% Sn	at.% Zn	1st section kJ mol^{-1}	2nd section kJ mol^{-1}	
A–D	13.0	74.0	13.0	1.23	1.24	1.24
A–E	27.0	62.0	11.0	1.03	1.07	1.11
A–F	41.0	50.0	9.0	0.80	1.02	0.95
B–D	11.0	62.0	27.0	2.23	2.21	2.23
B–E	23.0	54.0	23.0	2.06	2.15	2.05
B–F	36.5	44.5	19.0	1.77	1.94	1.82
C–D	9.0	50.0	41.0	3.03	2.95	3.00
C–E	19.0	44.5	36.5	2.94	3.01	2.93
C–F	31.0	38.0	31.0	2.68	2.89	2.73

where i and j are equal to 1, 2, or 3 for the elements Bi, Sn, and Zn, respectively, and ${L_{i:j}}^{(\nu)}$ ($\nu = 0, 1, 2, \ldots$) are the interaction parameters of the constituent binaries, which were taken from Table 1. The last term represents the additional mixing enthalpy due to ternary interactions, where ${M_{i:j:k}}^{(\alpha)}$ ($\alpha = 0$, 1, or 2) are the excess ternary interaction parameters. As the result of this least squares fit the ternary interaction parameters ${M_{\mathrm{Bi:Sn:Zn}}}^{(\alpha)}$ are also included in Table 1. The calculated enthalpies of mixing are represented by a solid line in Fig. 2.

The measured enthalpies of mixing close to the crossover of two different sections in the ternary Bi–Sn–Zn system together with the values calculated using the polynomial in Eq. (3) are listed in Table 3. The different sections are marked by capital letters as in Fig. 1. The values of $\Delta_{\mathrm{mix}}H_{\mathrm{m}}$ at the intersections are also shown in Fig. 2. The absolute deviations from the fitted values are on the average only 60 J mol^{-1} which is quite small in comparison with the experimental uncertainty ($\pm$150 J mol^{-1}).

Applying the polynomial (Eq. (3) and Table 1), a three-dimensional integral enthalpy of mixing *versus* ternary composition plot was constructed for liquid Bi–Sn–Zn alloys at 500°C (see Fig. 3). The darker the shade of grey in this graphic representation, the lower $\Delta_{\mathrm{mix}}H_{\mathrm{m}}$. Furthermore, isoenthalpy curves of the integral molar enthalpy of mixing for the ternary liquid alloys were calculated and plotted on a *Gibbs* triangle (see Fig. 4). From both figures it can be seen that the enthalpy of mixing is positive (*i.e.* endothermic) over the entire composition range. The global maximum of the Bi–Sn–Zn system can be found in the binary Bi–Zn bordering system ($\Delta_{\mathrm{mix}}H_{\mathrm{m}} = +4523$ J mol^{-1} at 44 at.% Bi and 56 at.% Zn).

In Fig. 2 a comparison of the $\Delta_{\mathrm{mix}}H_{\mathrm{m}}$ values calculated from the binary and ternary interaction parameters published by *Malakhov et al.* [26] with our experimental data is included. The agreement is quite satisfying, although the maximum in the curve from their fit is slightly shifted towards more endothermic values. However, the set of parameters presented in this work does not only fit better to the experimental values in the ternary Bi–Sn–Zn system but is also much simpler than the one presented by *Malakhov et al.* [26].

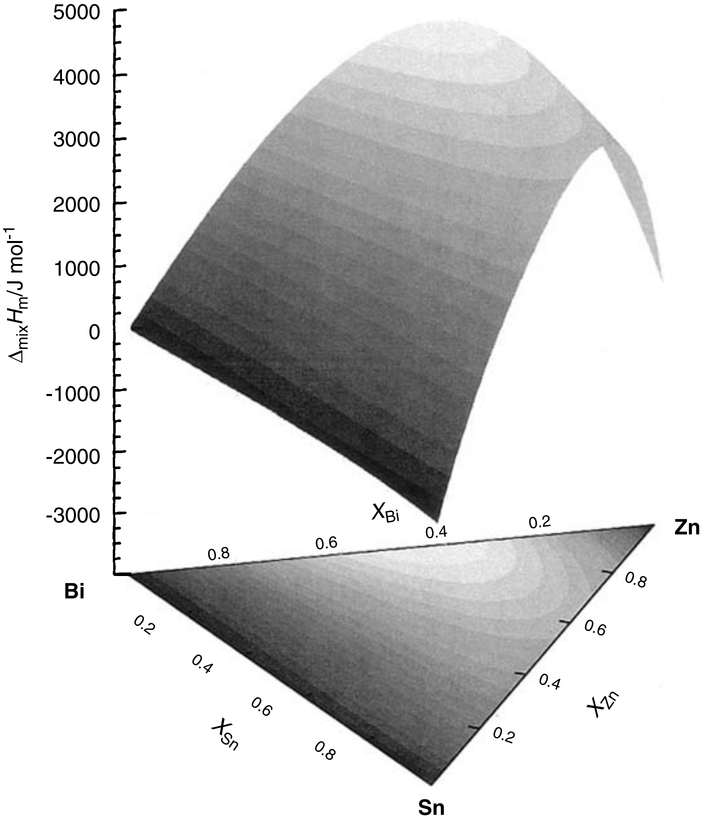

Fig. 3. Three-dimensional enthalpy of mixing *vs.* concentration plot of liquid Bi–Sn–Zn alloys at 500°C; standard states: pure liquid metals

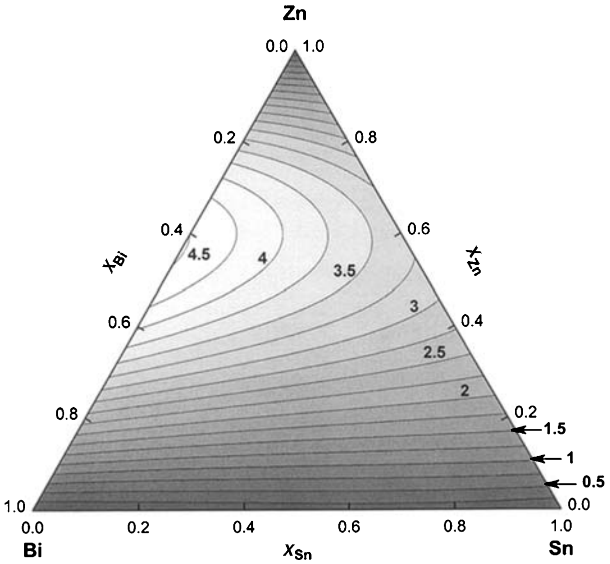

Fig. 4. Isoenthalpy curves for liquid Bi–Sn–Zn alloys at 500°C (in kJ mol^{-1}); standard states: pure liquid metals

Table 4. Results of DSC measurements

No.	Nominal composition	Thermal effect/°C	
		Ternary eutectic	Liquidus on heating
1	$Bi_{67}Sn_{30}Zn_3$	135.5	197.0
2	$Bi_{62}Sn_{35}Zn_3$	135.5	186.5
3	$Bi_{57}Sn_{40}Zn_3$	135.5	175.0
4	$Bi_{47}Sn_{50}Zn_3$	135.5	156.0
5	$Bi_{42}Sn_{55}Zn_3$	136.0	145.5
6	$Bi_{37}Sn_{60}Zn_3$	136.0	140.5
7	$Bi_{27}Sn_{70}Zn_3$	135.5	165.0
8	$Bi_{22}Sn_{75}Zn_3$	135.5	176.0
9	$Bi_{17}Sn_{80}Zn_3$	135.5	189.0
10	$Bi_{12}Sn_{85}Zn_3$	136.0	198.0
11	$Bi_{70}Sn_{25}Zn_5$	135.5	204.5
12	$Bi_{65}Sn_{30}Zn_5$	135.0	195.0
13	$Bi_{60}Sn_{35}Zn_5$	135.0	185.5
14	$Bi_{55}Sn_{40}Zn_5$	135.5	177.0
15	$Bi_{45}Sn_{50}Zn_5$	135.5	161.5
16	$Bi_{40}Sn_{55}Zn_5$	135.5	...
17	$Bi_{35}Sn_{60}Zn_5$	135.5	144.5
18	$Bi_{25}Sn_{70}Zn_5$	135.0	165.5
19	$Bi_{20}Sn_{75}Zn_5$	135.0	175.0
20	$Bi_{15}Sn_{80}Zn_5$	135.5	187.0
21	$Bi_{10}Sn_{85}Zn_5$	134.5	197.5
22	$Bi_{68}Sn_{25}Zn_7$	134.5	210.0
23	$Bi_{63}Sn_{30}Zn_7$	135.0	199.0
24	$Bi_{58}Sn_{35}Zn_7$	135.0	193.0
25	$Bi_{53}Sn_{40}Zn_7$	135.0	181.5
26	$Bi_{48}Sn_{45}Zn_7$	134.5	175.5
27	$Bi_{43}Sn_{50}Zn_7$	135.0	165.5
28	$Bi_{33}Sn_{60}Zn_7$	135.0	151.0
29	$Bi_{28}Sn_{65}Zn_7$	134.5	164.0
30	$Bi_{23}Sn_{70}Zn_7$	134.5	168.0
31	$Bi_{18}Sn_{75}Zn_7$	135.5	175.5
32	$Bi_{13}Sn_{80}Zn_7$	134.5	185.0

Results from DSC Measurements

Liquidus temperatures and the temperature of the ternary eutectic reaction $L \rightleftarrows (Bi) + (Sn) + (Zn)$ were determined by DSC measurements of samples with 3, 5, and 7 at.% Zn, annealed at 150°C. The nominal sample compositions can be found in Table 4, which also lists the liquidus temperatures and the temperatures of the ternary eutectic reaction E. Three different heating rates (10, 5, and 1 $K\,min^{-1}$) were employed and the thermal effects extrapolated to zero heating rate using a linear fit. Figure 5 shows, as an example, the liquidus and invariant reaction temperatures of the sample $Bi_{12}Sn_{85}Zn_3$ determined at different heating rates. It can be seen that the experimentally measured temperatures increase with increasing heating rate, *i.e.* tem-

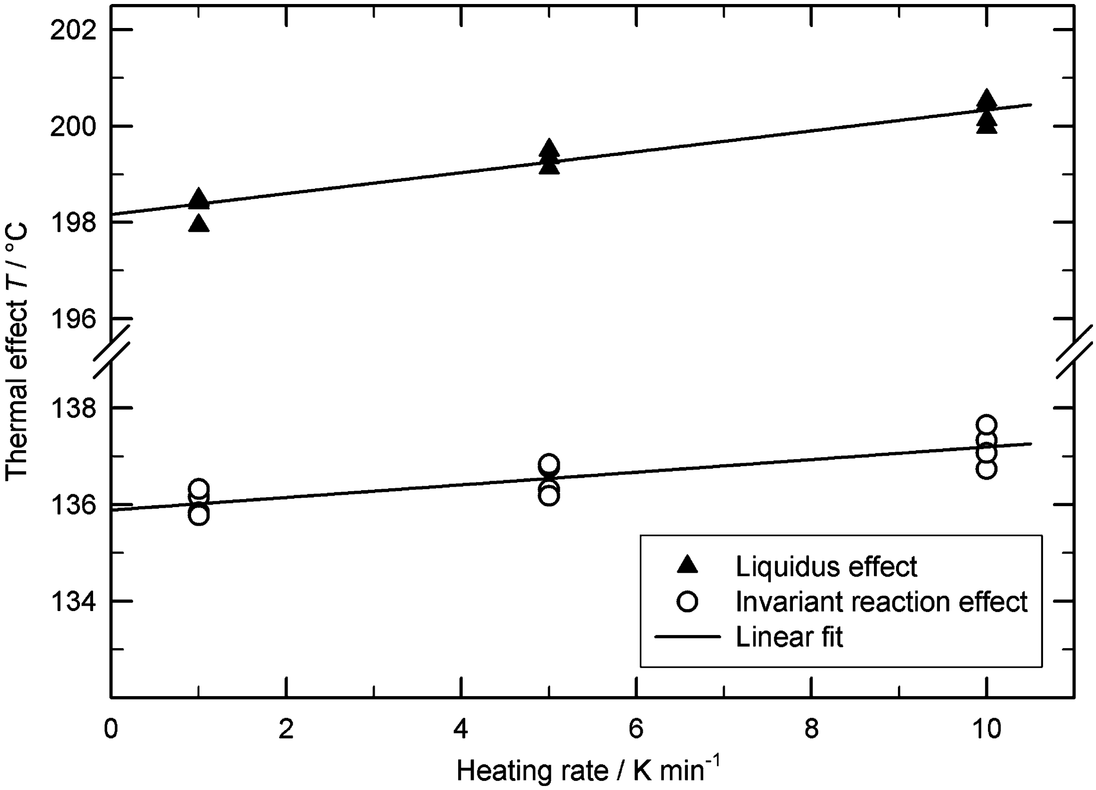

Fig. 5. Extrapolation of transformation temperatures from DSC to zero heating rate, sample No. 10 ($Bi_{12}Sn_{85}Zn_3$)

peratures determined at 10 K min^{-1} may be too high by 2°C. A reasonable heating rate combining both accuracy and reasonable measurement time would be 2 K min^{-1}.

The ternary invariant reaction E occurs in all 32 samples investigated. From the literature [26] it is known that it corresponds to the reaction $L \rightleftarrows (Bi) + (Sn) + (Zn)$. This ternary eutectic was investigated intensively by *Muzaffar* [28] in 1923, from thermal analyses using the cooling curves of 91 samples an average reaction temperature of 129.9°C was found. However, the cooling rate of approx. 10 K min^{-1} was quite high and supercooling phenomena might have occurred in addition. In the present work we find the invariant reaction temperature to be 135.0 ± 0.5°C, which is 5°C higher than the value reported by *Muzaffar* [28] and also higher than indicated in the recent assessments based on *Muzzafar*'s experimental data (126.1°C suggested by *Malakhov et al.* [26], and 131.2°C by *Moelans et al.* [27]). Our reaction temperature for E is in good agreement with *Jänecke*'s 136°C [29], however, this author did not give any experimental details. From the course of the liquidus temperatures in the three sections it can be estimated that the composition of the liquid in the ternary eutectic reaction is approximately 41 at.% Bi, 57 at.% Sn, and 2 at.% Zn. This is slightly shifted towards lower Zn content and higher Sn content as compared to the values calculated by *Malakhov et al.* [26] (39.4 at.% Bi, 54.4 at.% Sn, 6.2 at.% Zn) or *Moelans et al.* [27] (38.9 at.% Bi, 56.3 at.% Sn, 4.8 at.% Zn). This shift is also illustrated by Fig. 6 which shows a comparison of our experimentally determined

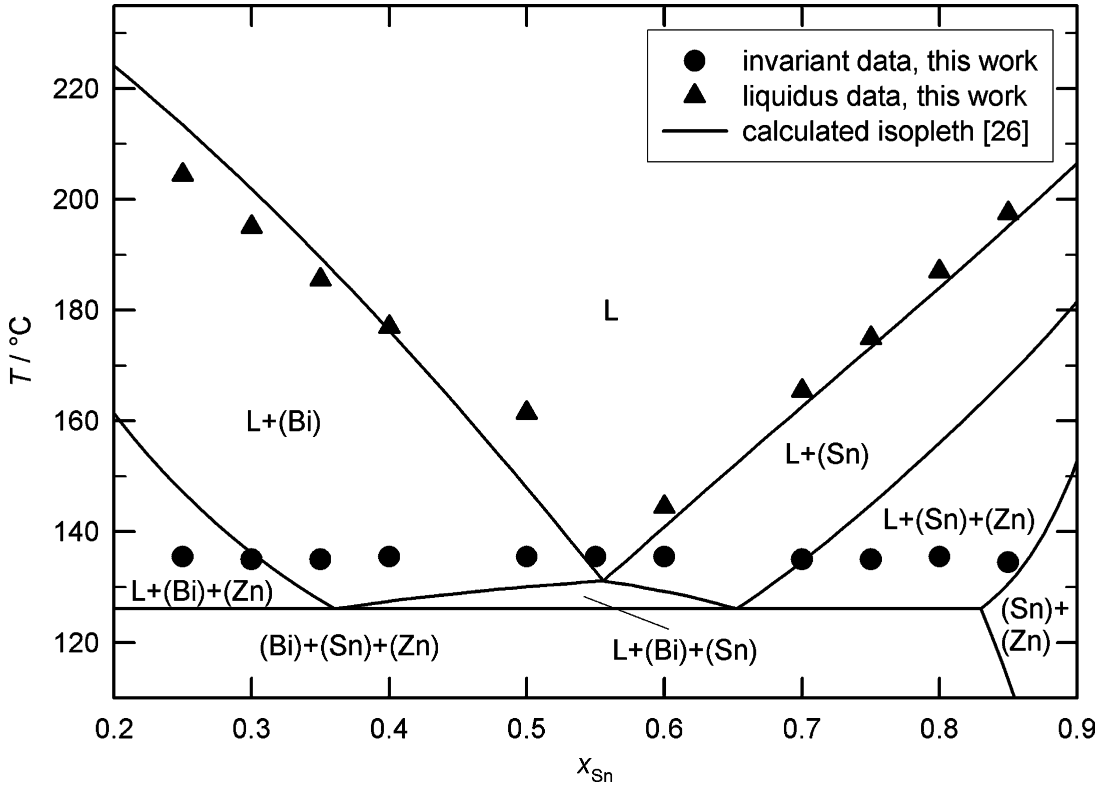

Fig. 6. Isoplethal section of the Bi–Sn–Zn system at 5 at.% Zn calculated from the assessed parameters of *Malakhov et al.* [26]; experimental transformation temperatures from the present work are included for comparison

transformation temperatures to the values calculated from the assessed parameters of *Malakhov et al.* [26] for the isopleth at 5 at.% Zn.

The liquidus temperatures as well as the ternary eutectic temperature reported in this work will be used for a further phase diagram optimization according to the CALPHAD method.

Experimental

The drop calorimetric measurements were carried out in a *Calvet*-type microcalorimeter (manufactured by SETARAM, Lyon, France; thermopile with more than 200 thermocouples, wire wound resistance furnace, suitable for temperatures up to 1000°C, automatic drop device for up to 30 drops, and control and data evaluation with LabView and HiQ as described by *Flandorfer et al.* [40]). To prevent oxidation, all measurements were carried out under Ar flow (approx. $30\,cm^3/min$). At the end of each series, the calorimeter was calibrated by six additions (approx. 40 mg each) of standard α-Al_2O_3 supplied by the National Institute of Standards and Technology (Gaithersburg, MD, USA). DT, the drop temperature and T, the measurement temperature (sample temperature in the furnace) were determined for each drop using thermocouples and thermoresistors. The accuracy was usually better than ±1°C. Generally, the mean values of DT and T for the different drops in one run were used for the data evaluation.

The samples for the calorimetric measurements were prepared from Bi pellets (99.999%, ASARCO, South Plainfield, NJ, USA), Sn rods (99.9985%), and Zn shot (99.999%; both Alfa

Johnson-Matthey, Karlsruhe, Germany). The Zn shot was melted under vacuum and filtered through quartz wool for further purification.

In the ternary Bi–Sn–Zn system the enthalpies of mixing of about 120 molten samples were determined at 500°C. Pieces of pure Bi (40 to 80 mg) were dropped into approx. 800 mg of molten $Sn_{85}Zn_{15}$, $Sn_{70}Zn_{30}$, and $Sn_{55}Zn_{45}$ alloys, respectively. To cross-check the enthalpies of mixing at several intersections, we also added pure Zn (20 to 40 mg each) to approx. 800 mg of liquid $Bi_{15}Sn_{85}$, $Bi_{30}Sn_{70}$, and $Bi_{45}Sn_{55}$ (see Fig. 1). All measurements were carried out in graphite crucibles (11 mm inner diameter, 70 mm height). The interval between individual drops was usually 40 min, and the data acquisition interval was approximately 0.7 s. The obtained signals were recorded and integrated. The measured enthalpy (integrated heatflow at constant pressure) can be expressed by

$$\Delta H_{\mathrm{Signal}} = n_i(H_{\mathrm{m},i,T} - H_{\mathrm{m},i,DT}) + \Delta H_{\mathrm{Reaction}} \tag{4}$$

where n_i is the number of mol of the added element i, $H_{\mathrm{m},i,T}$ denotes its molar enthalpy at the respective temperature of measurement T (in K) and $H_{\mathrm{m},i,DT}$ is the molar enthalpy at drop temperature. The molar enthalpy differences $H_{\mathrm{m},i,T} - H_{\mathrm{m},i,DT}$ were calculated using the polynomials published by *Dinsdale* [41]. Because of the rather small masses added, the partial enthalpies can be directly expressed as $h_i \approx \Delta H_{\mathrm{Reaction}}/n_i$. In a series of preceding articles [42–44] it was concluded that the precision of our drop calorimetric measurements was generally $\pm 150\,\mathrm{J\,mol^{-1}}$.

A differential scanning calorimeter (Pyris 1 DSC, Perkin Elmer) was used to determine the liquidus temperatures of a total of 32 samples in three sections (3, 5, and 7 at.% Zn) as well as the invariant reaction temperature of the ternary eutectic $L \rightleftarrows (Bi) + (Sn) + (Zn)$. The nominal sample compositions are listed in Table 4. The samples for DSC measurements were prepared from Bi (99.999 +%), Sn (99.999 +%), and Zn (99.9985%), all supplied by Alfa Aesar, Karlsruhe, Germany. Weighed amounts of the materials were sealed in quartz capsules under Ar atmosphere. Then they were melted in a vertical resistance furnace, quenched in water, and annealed at 150°C for 4 weeks. A sample mass of 80 to 100 mg was used for the measurements with Al as reference material. Three different heating rates (10, 5, and $1\,\mathrm{K\,min^{-1}}$) were employed to be able to extrapolate the temperatures to zero heating rate. Two different samples were used for each composition and the samples were cycled over the respective temperature range twice. Temperatures were determined with Pt resistance thermometers. As supercooling was observed frequently on cooling, the liquidus temperatures were determined from the heating curves maxima only. The temperatures of the invariant phase reaction were usually taken from the extrapolated peak-onset on heating. The accuracy of all given temperatures is ±0.5°C.

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