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Enthalpies of mixing of liquid systems for lead free soldering: Al–Cu–Sn system

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ABSTRACT

The present work refers to high-temperature drop calorimetric measurements on liquid Al–Cu, Al–Sn, and Al–Cu–Sn alloys. The binary systems have been investigated at 973 K, up to 40 at.% Cu in case of Al–Cu, and over the entire concentrational range in case of Al–Sn. Measurements in the ternary Al–Cu–Sn system were performed along the following cross-sections: x_{Al}/x_{Cu} = 1:1, x_{Al}/x_{Sn} = 1:1, x_{Cu}/x_{Sn} = 7:3, x_{Cu}/x_{Sn} = 1:1, and x_{Cu}/x_{Sn} = 3:7 at 1273 K. Experimental data were used to find ternary interaction parameters by applying the Redlich–Kister–Muggianu model for substitutional solutions, and a full set of parameters describing the concentration dependence of the enthalpy of mixing was derived. From these, the isoenthalpy curves were constructed for 1273 K. The ternary system shows an exothermic enthalpy minimum of approx. −18,000 J/mol in the Al–Cu binary and a maximum of approx. 4000 J/mol in the Al–Sn binary system. The Al–Cu–Sn system is characterized by considerable repulsive ternary interactions as shown by the positive ternary interaction parameters.

1. Introduction

Since soft solders with lead had to be replaced by new materials which are safe for the environment the search for lead-free solders has started in Europe several years ago. Whereas several suitable replacements have been developed for low temperature soft soldering there is still a lack of lead-free solders applicable at higher temperatures {240 to 350- °C}. Among the potential new materials are systems based on Cu–Sn alloys, whereas Cu is also a frequently used contact material. Al is under discussion as an additive in order to enhance the melting temperature of the solder. Moreover, Al electrodes with thin layers of Cu and Ni appear as contact materials in electronic soldering. To obtain the necessary knowledge on phase diagram and melting behavior of Al–Cu–Sn alloys, new experimental data are needed. Thermochemical measurements make an invaluable contribution to the understanding and calculation of phase equilibria, interfacial reactions and diffusion processes. Recently, thermodynamic data of Al–Cu–Sn from Knudsen effusion Mass Spectrometry (KEMS) have been published by Bencze *et al.* [1]. The aim of this work is a direct determination of the enthalpy of mixing of the liquid alloys and the comparison of these data to those derived from the KEMS measurements. In the literature one can find a number of results of calorimetric measurements in the binary systems Al–Cu, Al–Sn, and Cu–Sn, at various temperatures. They are summarized as follows:

1.1. Al–Cu system

Thermodynamic data for the binary system have been collected by Hultgren *et al.* [2] and Predel [3]. The data given for the integral enthalpy of mixing of liquid alloys are based on the work of Yazawa and Itagaki [4], who performed direct mixing calorimetry x_{Cu} = 0.11 to 0.90, at 1375 K. The minimum of the enthalpy was reported to be 10,200 J/mol at x_{Cu} = 0.62. In Hultgren *et al.* [2] it was mentioned that there are two other experimental works available which give much more exothermic values [5,6], with a minimum at approx. −23,000 J/mol at 1473 K and −20,000 J/mol at 1373 K, respectively. Later experiments from four different sources have been reviewed and assessed by Witusiewicz *et al.* [7]. These data are very consistent and show a minimum of approx. −17,500 J/mol at x_{Cu} = 0.62. A thermodynamic assessment for the Al–Cu system was published by Ansara *et al.* [8], reproducing the values given by Witusiewicz *et al.* [7].

1.2. Al–Sn system

This binary constituent system clearly shows endothermic mixing behavior of liquid alloys. Various experimental data have been collected and assessed by Hultgren *et al.* [2]. ΔH shows a maximum

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of approx. 4100 J/mol at $x_{Sn} = 0.43$. The direct reaction calorimetry done by Kawakami [5] at 1073 K for $x_{Sn} = 0.20$ to 0.76 resulted in a maximum of ΔH of approx. 6520 J/mol at $x_{Sn} = 0.4$. A study of Schmiedl and Stofko [9] yielded even more endothermic values with a maximum of approx. 7200 J/mol at $x_{Sn} = 0.4$. However, this value is based on an extrapolation of experimental values from a vapor pressure method for $x_{Sn} = 0$ to 0.3. A thermodynamic assessment for the Al–Sn system was published by Ansara *et al.* [8], reproducing the values given in Hultgren *et al.* [2].

1.3. Cu–Sn system

The heat of mixing in the liquid binary Cu–Sn system was determined by several authors. Experimental values have been published by Kleppa *et al.* [10], Takeuchi *et al.* [11], Itagaki and Yazawa [4], Iguchi *et al.* [12], Pool *et al.* [13], and Lee *et al.* [14] measured $\Delta_{mix}H$ at 723, 1363, 1373, 1393, 1440, and 997 K, respectively. Hultgren *et al.* summarized selected values of the integral enthalpies of mixing. Gierlotka *et al.* [15] used a substitutional solution model to describe the liquid phase. By comparing the data of Itagaki and Yazawa [4] at 1373 K and Lee *et al.* [14] at 997 K, they suggested a temperature dependence of the enthalpy of mixing for liquid Cu–Sn alloys. Moreover, Flandorfer *et al.* [16] measured the enthalpy of mixing of liquid Cu–Sn alloys at (773, 973, 1173, 1373, and 1523) K. The results were described by the Redlich–Kister model and also using an association model. The temperature dependence supposed by several authors before could be confirmed.

As far as the ternary Al–Cu–Sn system is concerned, there are only two thermodynamic studies by Bencze *et al.* [1] and Miettinen [17]. Bencze *et al.* [1] performed KEMS on the liquid ternary system whereas the latter author did a thermodynamic optimization of the copper-rich part of Al–Cu–Sn.

2. Experimental procedure

A Calvet-type twin micro-calorimeter HT 1000 (Setaram, Lyon, France) with two thermopiles consisting of more than 200 thermocouples each, a wire wound resistance furnace and an automatic drop device for up to 30 drops was used. Control of the entire equipment and data evaluation is performed with LabView and HiQ as described by Flandorfer *et al.* [18]. The measurements were performed under Ar-flow (approximately 30 ml/min). At the end of each series the calorimeter was calibrated by five additions (approximately 40 mg each) of NIST standard α-Al_2O_3 (National Institute of Standards and Technology, Gaithersburg, MD).

Drop calorimetry in the binary systems Al–Cu and Al–Sn at 973 K. Pieces of Cu have been added to pure liquid Al or Al–Cu alloys up to approx. 40 at.% Cu where the formation of solid (ε-phase) occurs. Three runs have been performed to check the reproducibility. Pieces of Sn have been added to pure liquid Al or Al–Sn alloys up to approx. 60 at% Sn and *vice versa*, Al to liquid Sn or Al–Sn alloys in the same way. Three runs have been performed in Al–Sn at all. In the ternary Al–Cu–Sn system heats of mixing have been measured along the five cross-sections $x_{Al}/x_{Cu} = 1{:}1$, $x_{Al}/x_{Sn} = 1{:}1$, $x_{Cu}/x_{Sn} = 7{:}3$, $x_{Cu}/x_{Sn} = 1{:}1$, and $x_{Cu}/x_{Sn} = 3{:}7$ at 1273 K, see also figure 1. Each section was measured twice in order to check the reproducibility. Starting materials for all experiments were Al rod (99.999%; Puratronic®, Alfa Aesar), Cu wire (99.98+%; Alfa Aesar), and Sn rod (99.9985%; Alfa Aesar). Al was surface cleaned by grinding, the Cu wire was treated under flowing H_2 at 250 °C for 2 h to remove oxide layers and Sn was used without further purification.

Samples of pure metals (Al, Cu, or Sn) were introduced into a bath of liquid Al, Sn or binary alloys (Al–Cu, Al–Sn, or Cu–Sn) of chosen starting compositions (see figure 1). All measurements

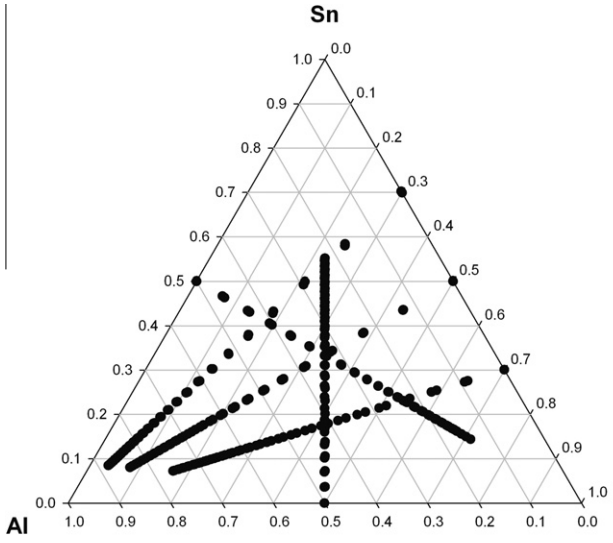

FIGURE 1. Sections chosen for drop calorimetric measurements in the ternary Al–Cu–Sn system performed at 1273 K; concentrations given in mole fractions.

were carried out in a graphite crucible ($Ø_i = 9$ mm, $h = 90$ mm) which was heated at 973 K for 10 min before using it to remove surface impurities.

The furnace temperature was set at (973 or 1273) K, respectively. The time interval between individual drops was usually 40 min. The obtained signals were recorded and integrated. The measured enthalpy (integrated heat flow at constant pressure) is

$$\Delta H_{drop} = n_i(H_{m,i,T_M} - H_{m,i,T_D}) + \Delta H_{Reaction}, \quad (1)$$

where n_i is the number of moles of the added sample, H_m denotes molar enthalpies, T_D is the drop temperature, and T_M is the calorimeter temperature of the respective measurement in K. The molar enthalpy difference $(H_{m,i,T_M} - H_{m,i,T_D})$ was calculated using the SGTE database [19]. Because of the relatively small masses added, the partial enthalpies can be directly given as

$$\Delta_{mix}\bar{H}_i = \Delta H_{Reaction;i}/n_i. \quad (2)$$

The integral enthalpy of mixing was calculated by summarizing the respective reaction enthalpies and division by the total molar amount of substance

$$\Delta_{mix}H = \sum_i \Delta H_{Reaction;i} \Big/ \left(n_{crucible} + \sum_i n_{drop;i}\right). \quad (3)$$

Random errors as well as systematic errors of calorimetry depend on the construction of the calorimeter, calibration procedure, signal integration and "chemical errors", *e.g.* incomplete reactions or impurities. Considering many calibration measurements done by dropping NIST standard sapphire, the standard deviation can be estimated to be less than ±1% for the HT-1000. The systematic errors are mainly caused by parasitic heat flows, base line problems at signal integration and dropping and mixing problems. One can estimate that the overall error is ±150 J/mol.

3. Results and discussion

3.1. Experimental results

The enthalpy of mixing of liquid alloys of Al–Cu and Al–Sn has been measured because of somewhat ambiguous literature data as described in the introduction. The drop enthalpy (ΔH_{drop}), the partial ($\Delta_{mix}\overline{H_i}$) and integral molar enthalpy of mixing ($\Delta_{mix}H$) of

TABLE 1
Partial and integral molar enthalpies of mixing of liquid Al–Cu and Al–Sn alloys at 700 °C; standard states: pure liquid components.

Dropped mole, n(i)/mmol	Drop enthalpy, ΔH_{drop}/J	Partial enthalpy		Integral enthalpy[a]	
		$x(i)$[b]	$\Delta_{mix}\bar{H}_i$/(J/mol)	$x(i)$	$\Delta_{mix}H$/(J/mol)
	Al–Cu; i = Cu; 1st run			*Starting amount: n(Al) = 11.6987 mmol*	
0.525	−4978	0.0214	−36,050	0.043	−1549
0.554	−5006	0.0637	−36,078	0.084	−3044
0.655	−5736	0.0645	−36,808	0.129	−4693
0.657	−5988	0.1494	−37,060	0.170	−6202
0.676	−6524	0.1887	−37,596	0.208	−7638
0.677	−7034	0.2250	−38,106	0.242	−8974
0.700	−7422	0.2589	−38,494	0.275	−10,253
0.741	−7290	0.2911	−38,362	0.307	−11,488
	Al–Cu; i = Cu; 2nd run			*Starting amount: n(Al) = 11.5394 mmol*	
0.605	−4517	0.0249	−35,589	0.0498	−1774
0.811	−5538	0.0796	−36,610	0.1093	−3955
0.828	−6077	0.0814	−37,149	0.1628	−5949
0.856	−6731	0.1873	−37,803	0.2118	−7811
0.871	−7487	0.1280	−38,559	0.2561	−9539
0.899	−7491	0.2764	−38,563	0.2968	−11,128
0.908	−7848	0.3152	−38,919	0.3337	−12,585
0.938	−7892	0.3508	−38,964	0.3679	−13,940
0.954	−7283	0.3836	−38,355	0.3993	−15,153
	Al–Cu; i = Cu; 3th run			*Starting amount: n(Al) = 11.6005 mmol*	
0.591	−5408	0.0242	−36,480	0.0485	−1769
0.606	−5863	0.0710	−36,935	0.0935	−3434
0.648	−6905	0.1154	−37,977	0.1373	−5100
0.675	−11,294	0.1579	−42,366	0.1785	−6882
0.698	−6747	0.1979	−37,819	0.2172	−8338
0.721	−7172	0.2354	−38,244	0.2535	−9727
0.723	−7617	0.2701	−38,689	0.2867	−11,015
0.751	−7214	0.3025	−38,286	0.3182	−12,218
0.837	−7808	0.3342	−38,880	0.3502	−13,468
0.850	−5727	0.3649	−36,799	0.3797	−14,529
	Al–Sn; i = Al; 1st run			*Starting amount: n(Sn) = 7.3196 mmol*	
0.4221	42,999	0.0545	706	0.0273	12,954
0.4641	42,198	0.1080	1354	0.0813	12,153
0.4905	40,872	0.1583	1888	0.1331	10,826
0.5287	40,352	0.2065	2370	0.1824	10,306
0.5986	39,200	0.2549	2784	0.2307	9155
0.6211	38,486	0.2992	3120	0.2770	8441
0.6526	37,979	0.3404	3403	0.3198	7934
0.7485	37,138	0.3821	3636	0.3613	7093
0.9464	36,470	0.4278	3843	0.4049	6425
0.9511	35,651	0.4674	3965	0.4476	5606
0.9664	35,032	0.5024	4032	0.4849	4987
0.9970	33,488	0.5340	3994	0.5182	3442
1.0135	34,161	0.5622	4002	0.5481	4116
1.0398	33,725	0.5879	3983	0.5750	3680
1.0758	33,368	0.6114	3945	0.5996	3323
1.1070	33,382	0.6330	3912	0.6222	3337
1.1479	33,021	0.6529	3861	0.6430	2976
1.1940	32,612	0.6715	3791	0.6622	2567
1.2348	32,426	0.6888	3717	0.6802	2381
1.2374	32,503	0.7043	3654	0.6966	2457
1.2584	32,245	0.7186	3584	0.7115	2200
1.3373	32,017	0.7324	3505	0.7255	1972
1.3810	31,848	0.7453	3423	0.7388	1802
1.5283	31,795	0.7581	3339	0.7517	1750
1.6035	31,716	0.7703	3255	0.7642	1670
	Al–Sn; i = Al; 2nd run			*Starting amount: n(Sn) = 7.4041 mmol*	
0.3948	42,330	0.0506	622	0.0253	12,285
0.4328	41,297	0.1005	1181	0.0756	11,252
0.5492	41,319	0.1568	1812	0.1287	11,274
0.5647	40,218	0.2077	2317	0.1823	10,173
0.6163	39,436	0.2568	2755	0.2323	9391
0.6251	37,832	0.3006	3052	0.2787	7787
0.6418	37,684	0.3406	3314	0.3206	7639
0.6516	36,588	0.3768	3491	0.3587	6543
0.7068	36,367	0.4118	3650	0.3943	6322
0.7208	35,410	0.4436	3743	0.4277	5365
0.7320	35,267	0.4726	3820	0.4581	5222
0.7509	34,730	0.4994	3864	0.4860	4685
0.7769	34,484	0.5244	3893	0.5119	4438
0.7990	34,140	0.5476	3903	0.5360	4095

TABLE 1 (*continued*)

Dropped mole, n(i)/mmol	Drop enthalpy, ΔH_{drop}/J	Partial enthalpy		Integral enthalpy[a]	
		$x(i)$[b]	$\Delta_{mix}\bar{H}_i$/(J/mol)	$x(i)$	$\Delta_{mix}H$/(J/mol)
0.8229	33,788	0.5693	3895	0.5584	3743
0.8527	33,444	0.5896	3871	0.5794	3399
0.8829	33,209	0.6088	3838	0.5992	3164
0.8894	33,101	0.6263	3803	0.6175	3056
0.9617	32,738	0.6436	3752	0.6350	2693
0.9926	32,640	0.6599	3699	0.6518	2595
1.0142	32,426	0.6750	3640	0.6674	2381
1.1751	32,299	0.6910	3572	0.6830	2254
1.3727	32,152	0.7077	3493	0.6993	2106
1.5813	32,058	0.7249	3406	0.7163	2013
1.7953	31,792	0.7421	3302	0.7335	1747
	Al–Sn; i = Sn			*Starting amount: n(Al) = 8.4759 mmol*	
0.2457	49,838	0.0282	660	0.0141	23,423
0.2734	46,650	0.0577	1255	0.0429	20,234
0.2960	43,275	0.0877	1752	0.0727	16,859
0.2999	41,053	0.1163	2155	0.1020	14,638
0.3131	39,068	0.1442	2487	0.1302	12,653
0.3247	38,433	0.1714	2789	0.1578	12,018
0.3415	36,419	0.1981	3022	0.1847	10,004
0.3730	35,573	0.2255	3232	0.2118	9158
0.4443	34,692	0.2557	3428	0.2406	8277
0.4528	33,956	0.2841	3586	0.2699	7541
0.4925	33,154	0.3127	3712	0.2984	6739
0.5096	32,476	0.3400	3805	0.3264	6061
0.5449	31,867	0.3669	3872	0.3534	5452
0.5620	31,663	0.3924	3927	0.3796	5248
0.5875	30,932	0.4169	3951	0.4047	4517
0.5987	30,752	0.4400	3966	0.4285	4337
0.5998	29,767	0.4613	3943	0.4507	3352
0.6259	29,484	0.4820	3910	0.4716	3069
0.6265	29,597	0.5011	3883	0.4915	3182
0.6607	29,092	0.5197	3838	0.5104	2677
0.6744	28,906	0.5374	3788	0.5286	2491
0.7110	28,807	0.5547	3736	0.5461	2392
0.7748	28,347	0.5721	3665	0.5634	1932
0.7942	28,373	0.5886	3599	0.5804	1958
0.7994	27,746	0.6040	3515	0.5963	1331

[a] Per mole of binary mixture.
[b] Average of x_i before and after the drop.

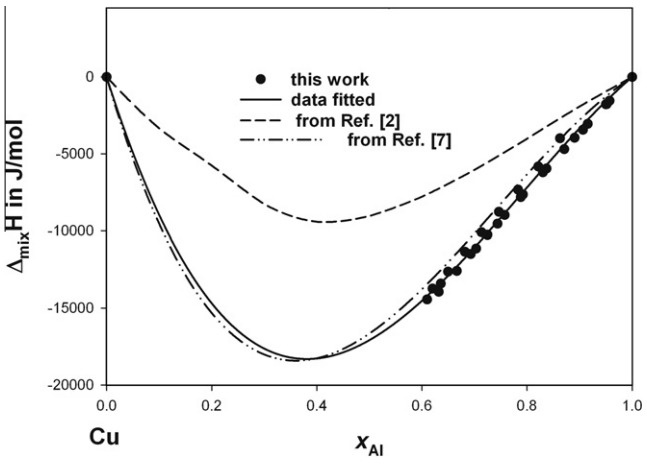

FIGURE 2. Measured integral enthalpy of mixing in Al–Cu at 973 K with fitted curve and comparison to Hultgren *et al.* [2] and Witusiewicz *et al.* [7].

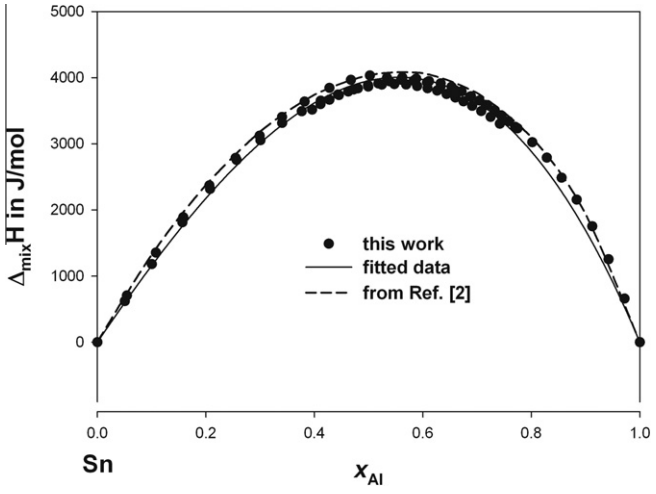

FIGURE 3. Measured integral enthalpy of mixing in Al–Sn at 973 K with fitted curve and comparison to Hultgren *et al.* [2].

liquid alloys obtained in three separate experiments for Al–Cu and three experiments in Al–Sn at a constant temperature of 973 K are given in table 1. It also provides information to the number of moles of pure metals dropped into the liquid alloys. The lower experimental temperature compared to the ternary system (1273 K, see below) was chosen in order to avoid evaporation of Al. No indication for significant temperature dependence of both systems was found in literature.

Figure 2 shows the experimental enthalpy of mixing of Al–Cu together with the fitted curve and literature values. Obviously, the values given in the compilation of Hultgren *et al.* [2], which

TABLE 2
Partial and integral enthalpies of mixing of liquid Al–Cu–Sn alloys, 1273 K; standard states: liquid pure components.

Mole dropped, n_i/mmol	Drop enthalpy, ΔH_{Signal}/J	Partial enthalpy		Integral enthalpy		
		x_i[a]	$\Delta_{mix}\overline{H_i}$/(J/mol)	x_{Al}	x_{Cu}	$\Delta_{mix}H$/(J/mol)
x_{Al}/x_{Cu} = 1:1; 1st run; i = Sn; starting amounts: n_{Al} = 4.5494 mmol; n_{Cu} = 4.5370 mmol						
0		0		0.5007	0.4993	−16,640
0.3402	80,107	0.0180	45,129	0.4826	0.4813	−14,411
0.3445	70,640	0.0531	35,663	0.4656	0.4643	−12,645
0.3453	62,708	0.0859	27,730	0.4497	0.4485	−11,267
0.3503	59,367	0.1168	24,389	0.4347	0.4335	−10,073
0.3554	56,330	0.1461	21,352	0.4204	0.4192	−9041
0.3656	54,179	0.1741	19,202	0.4066	0.4055	−8118
0.3721	51,309	0.2009	16,332	0.3936	0.3925	−7332
0.3910	50,067	0.2268	15,089	0.3807	0.3796	−6598
0.4077	48,738	0.2522	13,760	0.3681	0.3671	−5926
0.4164	47,815	0.2768	12,837	0.3561	0.3551	−5315
0.4166	47,829	0.3000	12,851	0.3449	0.3439	−4741
0.4262	44,271	0.3220	9293	0.3341	0.3332	−4302
0.4331	43,960	0.3430	8982	0.3238	0.3229	−3892
0.4497	44,879	0.3633	9901	0.3137	0.3129	−3465
0.4533	41,705	0.3829	6727	0.3042	0.3034	−3156
0.4587	41,781	0.4014	6803	0.2952	0.2944	−2859
0.4718	42,938	0.4192	7960	0.2864	0.2856	−2538
0.4722	43,173	0.4362	8195	0.2781	0.2774	−2228
0.5143	40,776	0.4529	5798	0.2697	0.2689	−1983
0.5172	40,156	0.4694	5178	0.2616	0.2609	−1770
0.5210	40,965	0.4850	5987	0.2540	0.2533	−1545
0.5222	40,568	0.4998	5590	0.2468	0.2462	−1343
0.5223	39,840	0.5138	4862	0.2400	0.2394	−1172
0.5271	39,832	0.5271	4854	0.2335	0.2329	−1009
0.5422	39,029	0.5399	4051	0.2272	0.2266	−872
x_{Al}/x_{Cu} = 1:1; 2nd run; i = Sn; starting amounts: n_{Al} = 4.5216 mmol; n_{Cu} = 4.5321 mmol						
0		0		0.4994	0.5006	−16,669
0.3449	87,964	0.0183	52,986	0.4811	0.4822	−14,113
0.3640	67,467	0.0547	32,489	0.4632	0.4642	−12,376
0.3824	55,105	0.0893	20,127	0.4465	0.4475	−11,171
0.3824	55,105	0.1222	20,127	0.4303	0.4313	−10,032
0.4017	61,136	0.1543	26,158	0.4144	0.4154	−8699
0.4322	62,839	0.1860	27,861	0.3986	0.3996	−7306
0.4337	53,927	0.2165	18,949	0.3839	0.3848	−6339
0.4448	39,203	0.2452	4225	0.3700	0.3708	−5955
0.4493	57,546	0.2723	22,568	0.3569	0.3577	−4943
0.4632	48,470	0.2981	13,492	0.3443	0.3451	−4293
0.4750	48,800	0.3227	13,822	0.3322	0.3330	−3661
0.4795	46,088	0.3460	11,110	0.3209	0.3217	−3158
0.4882	46,800	0.3681	11,822	0.3102	0.3109	−2656
0.4885	39,734	0.3890	4756	0.3001	0.3008	−2416
0.4909	44,373	0.4085	9395	0.2907	0.2913	−2043
0.4953	46,244	0.4270	11,266	0.2817	0.2824	−1633
0.4978	47,136	0.4444	12,158	0.2732	0.2739	−1218
0.4995	42,666	0.4609	7688	0.2652	0.2658	−957
0.5024	45,010	0.4765	10,032	0.2576	0.2582	−642
0.5185	32,722	0.4915	−2256	0.2502	0.2508	−689
0.5191	39,216	0.5059	4238	0.2432	0.2438	−551
0.5246	38,115	0.5196	3137	0.2366	0.2371	−450
0.5307	33,660	0.5327	−1318	0.2302	0.2307	−473
0.5328	40,929	0.5452	5951	0.2241	0.2246	−304
x_{Al}/x_{Sn} = 1:1; 1st run; i = Cu; starting amounts: n_{Al} = 2.5944 mmol; n_{Sn} = 2.5999 mmol						
0		0		0.4995	0	4081
0.3748	19,431	0.0337	−20,544	0.4659	0.0673	2424
0.4175	18,922	0.0998	−21,053	0.4334	0.1324	787
0.4205	19,083	0.1608	−20,892	0.4049	0.1893	−655
0.4560	19,702	0.2162	−20,273	0.3780	0.2432	−2099
0.4768	19,624	0.2677	−20,351	0.3535	0.2923	−3335
0.4798	20,583	0.3140	−19,392	0.3318	0.3358	−4387
0.4814	21,674	0.3550	−18,301	0.3125	0.3743	−5261
0.5004	21,085	0.3921	−18,890	0.2948	0.4098	−6049
0.5096	22,199	0.4260	−17,776	0.2786	0.4421	−6773
0.5262	22,761	0.4571	−17,214	0.2637	0.4720	−7399
0.5361	22,519	0.4856	−17,456	0.2501	0.4993	−7928
0.5418	23,409	0.5117	−16,566	0.2377	0.5241	−8413
0.5448	23,935	0.5354	−16,040	0.2264	0.5468	−8806
0.5733	24,292	0.5576	−15,683	0.2156	0.5683	−9208
0.5790	24,656	0.5783	−15,319	0.2057	0.5882	−9586
0.5865	25,365	0.5973	−14,610	0.1966	0.6065	−9881
0.5996	25,176	0.6150	−14,799	0.1880	0.6236	−10,154

TABLE 2 (*continued*)

Mole dropped, n_i/mmol	Drop enthalpy, ΔH_{Signal}/J	Partial enthalpy		Integral enthalpy		
		x_i[a]	$\Delta_{mix}\overline{H_i}$/(J/mol)	x_{Al}	x_{Cu}	$\Delta_{mix}H$/(J/mol)
0.6156	25,931	0.6316	−14,044	0.1800	0.6396	−10,396
0.6200	26,595	0.6471	−13,380	0.1726	0.6545	−10,612
0.6295	27,012	0.6614	−12,963	0.1656	0.6684	−10,773
		x_{Al}/x_{Sn} = 1:1; 2nd run; i = Cu; starting amounts: n_{Al} = 2.5977 mmol; n_{Sn} = 2.5962 mmol				
0		0		0.5001	0	4083
0.4081	19,744	0.0364	−20,231	0.4637	0.0728	2312
0.4228	19,195	0.1054	−20,780	0.4312	0.1379	691
0.4351	19,343	0.1669	−20,632	0.4021	0.1960	−745
0.4362	19,169	0.2214	−20,806	0.3767	0.2468	−2014
0.4690	19,435	0.2708	−20,540	0.3527	0.2948	−3194
0.4795	19,655	0.3163	−20,320	0.3311	0.3379	−4241
0.4918	19,998	0.3574	−19,977	0.3116	0.3770	−5169
0.4960	20,225	0.3945	−19,750	0.2941	0.4119	−5988
0.4998	20,927	0.4277	−19,048	0.2784	0.4434	−6687
0.5026	21,584	0.4577	−18,391	0.2641	0.4719	−7285
0.5031	21,926	0.4847	−18,049	0.2513	0.4976	−7809
0.5130	22,359	0.5095	−17,616	0.2394	0.5213	−8273
0.5280	22,726	0.5324	−17,249	0.2283	0.5435	−8689
0.5384	23,622	0.5539	−16,353	0.2180	0.5642	−9036
0.5642	23,227	0.5740	−16,748	0.2081	0.5839	−9384
0.5774	24,280	0.5931	−15,695	0.1989	0.6023	−9663
0.5829	24,469	0.6108	−15,506	0.1904	0.6193	−9913
0.5876	24,757	0.6271	−15,218	0.1826	0.6350	−10,132
0.5881	25,450	0.6422	−14,525	0.1753	0.6495	−10,306
0.6026	25,932	0.6563	−14,043	0.1685	0.6632	−10,452
0.6051	26,420	0.6695	−13,555	0.1621	0.6759	−10,569
0.6155	27,035	0.6819	−12,940	0.1561	0.6879	−10,657
0.6630	27,544	0.6939	−12,431	0.1501	0.6998	−10,725
0.7234	28,539	0.7059	−11,436	0.1441	0.7119	−10,754
		x_{Cu}/x_{Sn} = 7:3; 1st run; i = Al; starting amounts: n_{Cu} = 6.0794 mmol; n_{Sn} = 2.6138 mmol				
0		0		0	0.6993	−4079
0.8695	11,651	0.0455	−28,009	0.0909	0.6357	−6255
0.8736	17,490	0.1290	−22,170	0.1670	0.5825	−7587
0.8776	22,565	0.1993	−17,095	0.2316	0.5373	−8324
0.8784	26,707	0.2593	−12,953	0.2870	0.4986	−8658
0.9240	29,983	0.3121	−9677	0.3372	0.4635	−8730
0.9347	32,632	0.3593	−7028	0.3813	0.4327	−8617
0.9521	34,443	0.4009	−5217	0.4206	0.4052	−8401
0.9936	35,766	0.4386	−3894	0.4566	0.3800	−8121
1.0159	36,757	0.4728	−2903	0.4890	0.3573	−7809
1.0177	37,343	0.5034	−2317	0.5179	0.3372	−7499
1.0600	37,883	0.5312	−1777	0.5446	0.3185	−7182
1.0629	38,099	0.5566	−1561	0.5686	0.3017	−6885
1.0952	38,262	0.5798	−1398	0.5909	0.2861	−6602
1.1019	38,692	0.6010	−968	0.6110	0.2720	−6324
1.1412	38,369	0.6205	−1291	0.6299	0.2588	−6080
1.1708	39,031	0.6387	−629	0.6475	0.2465	−5821
1.2575	39,050	0.6561	−610	0.6646	0.2345	−5568
1.3342	39,256	0.6728	−404	0.6810	0.2231	−5316
1.3361	39,358	0.6885	−302	0.6959	0.2126	−5081
1.3569	39,452	0.7028	−208	0.7097	0.2030	−4860
1.3884	39,500	0.7161	−160	0.7226	0.1940	−4652
1.4280	39,629	0.7286	−31	0.7347	0.1856	−4451
1.4503	39,507	0.7403	−153	0.7459	0.1777	−4269
1.4540	39,629	0.7511	−31	0.7563	0.1704	−4096
		x_{Cu}/x_{Sn} = 7:3; 2nd run; i = Al; starting amounts: n_{Cu} = 6.0751 mmol; n_{Sn} = 2.6175 mmol				
0		0		0	0.6989	−4071
0.7942	11,333	0.0419	−28,327	0.0837	0.6404	−6102
0.7998	16,953	0.1193	−22,707	0.1550	0.5906	−7393
0.8091	21,520	0.1858	−18,140	0.2166	0.5475	−8176
0.8202	25,397	0.2435	−14,263	0.2705	0.5098	−8595
0.8346	28,712	0.2944	−10,948	0.3183	0.4765	−8749
0.8943	31,481	0.3406	−8179	0.3629	0.4452	−8712
0.9347	33,693	0.3834	−5967	0.4038	0.4167	−8536
0.9773	35,323	0.4225	−4337	0.4412	0.3905	−8272
1.0188	36,261	0.4584	−3399	0.4756	0.3665	−7973
1.0329	37,023	0.4910	−2637	0.5063	0.3450	−7660
1.0500	37,612	0.5202	−2048	0.5341	0.3256	−7344
1.0785	38,064	0.5469	−1596	0.5596	0.3078	−7030
1.0974	38,190	0.5712	−1470	0.5828	0.2916	−6737
1.1059	38,464	0.5933	−1196	0.6038	0.2769	−6458
1.1078	38,782	0.6133	−878	0.6229	0.2636	−6189

(*continued on next page*)

TABLE 2 (*continued*)

Mole dropped, n_i/mmol	Drop enthalpy, ΔH_{Signal}/J	Partial enthalpy		Integral enthalpy		
		x_i[a]	$\Delta_{mix}\overline{H_i}$/(J/mol)	x_{Al}	x_{Cu}	$\Delta_{mix}H$/(J/mol)
1.1152	38,794	0.6316	−866	0.6403	0.2514	−5944
1.1904	39,035	0.6487	−625	0.6572	0.2396	−5694
1.2219	39,092	0.6650	−568	0.6729	0.2286	−5458
1.2379	39,180	0.6802	−480	0.6875	0.2184	−5237
1.2549	39,234	0.6942	−426	0.7010	0.2090	−5029
1.3027	39,392	0.7074	−268	0.7138	0.2000	−4825
1.3572	39,311	0.7199	−349	0.7260	0.1915	−4633
1.4165	39,330	0.7319	−330	0.7377	0.1833	−4449
1.4362	39,407	0.7432	−253	0.7486	0.1757	−4275
1.5462	39,451	0.7540	−209	0.7594	0.1682	−4101
	x_{Cu}/x_{Sn} = 1:1; 1st run; i = Al; starting amounts: n_{Cu} = 2.5180 mmol; n_{Sn} = 2.5261 mmol					
0		0		0	0.4992	−2149
0.7472	26,538	0.0645	−13,122	0.1290	0.4348	−3565
0.7750	30,169	0.1804	−9491	0.2318	0.3835	−4264
0.7805	33,470	0.2726	−6190	0.3134	0.3427	−4469
0.8191	35,914	0.3479	−3746	0.3823	0.3084	−4396
0.8454	37,415	0.4113	−2245	0.4402	0.2794	−4195
0.8554	38,327	0.4645	−1333	0.4888	0.2552	−3947
0.8754	38,790	0.5096	−870	0.5304	0.2344	−3696
0.8832	39,075	0.5483	−585	0.5661	0.2166	−3459
0.8980	39,214	0.5817	−446	0.5972	0.2011	−3243
0.8995	39,331	0.6107	−329	0.6242	0.1876	−3048
0.9125	39,304	0.6362	−356	0.6481	0.1757	−2877
0.9229	39,463	0.6588	−197	0.6694	0.1650	−2715
0.9462	39,343	0.6791	−317	0.6887	0.1554	−2575
0.9684	39,674	0.6975	14	0.7063	0.1466	−2429
0.9807	39,476	0.7142	−184	0.7221	0.1387	−2307
1.0589	39,679	0.7298	19	0.7375	0.1311	−2179
1.1089	39,654	0.7446	−6	0.7518	0.1239	−2061
1.1360	39,550	0.7584	−110	0.7649	0.1174	−1957
1.1515	39,517	0.7709	−143	0.7769	0.1114	−1865
1.1860	39,669	0.7825	9	0.7880	0.1058	−1771
1.2219	39,470	0.7932	−190	0.7984	0.1007	−1694
1.2334	39,754	0.8031	94	0.8078	0.0959	−1610
1.2842	39,652	0.8123	−8	0.8168	0.0915	−1535
1.3024	39,751	0.8209	91	0.8251	0.0873	−1462
1.3413	39,697	0.8290	37	0.8329	0.0834	−1395
	x_{Cu}/x_{Sn} = 1:1; 2nd run; i = Al; starting amounts: n_{Cu} = 2.5275 mmol; n_{Sn} = 2.5303 mmol					
0		0		0	0.4997	−2155
0.7557	26,064	0.0650	−13,596	0.1300	0.4348	−3642
0.7928	29,824	0.1822	−9836	0.2344	0.3826	−4385
0.8213	33,695	0.2767	−5965	0.3191	0.3403	−4560
0.8350	35,966	0.3535	−3694	0.3879	0.3059	−4473
0.8610	37,102	0.4168	−2558	0.4456	0.2770	−4292
0.8724	38,044	0.4698	−1616	0.4940	0.2528	−4058
0.9121	38,459	0.5152	−1201	0.5363	0.2317	−3819
0.9418	39,916	0.5548	256	0.5732	0.2133	−3495
0.9440	38,830	0.5889	−830	0.6047	0.1976	−3299
0.9621	37,901	0.6185	−1759	0.6323	0.1837	−3191
0.9996	38,083	0.6448	−1577	0.6572	0.1713	−3082
1.0125	38,441	0.6682	−1219	0.6792	0.1603	−2962
1.0344	39,247	0.6891	−413	0.6990	0.1504	−2805
1.0570	39,606	0.7079	−54	0.7168	0.1415	−2642
1.0922	38,507	0.7250	−1153	0.7331	0.1334	−2557
1.1575	39,512	0.7408	−148	0.7485	0.1257	−2418
1.1604	39,232	0.7553	−428	0.7622	0.1188	−2309
1.2149	39,743	0.7686	83	0.7751	0.1124	−2180
1.2305	38,793	0.7809	−867	0.7867	0.1066	−2112
1.2527	40,245	0.7921	585	0.7974	0.1012	−1977
1.2853	39,837	0.8024	177	0.8073	0.0963	−1871
1.2972	39,267	0.8119	−393	0.8164	0.0917	−1802
1.3068	39,759	0.8206	99	0.8247	0.0876	−1716
1.3187	39,196	0.8286	−464	0.8324	0.0838	−1661
1.3324	39,885	0.8359	225	0.8395	0.0802	−1581
	x_{Cu}/x_{Sn} = 3:7; 1st run; i = Al; starting amounts: n_{Cu} = 1.1057 mmol; n_{Sn} = 2.5669 mmol					
0		0		0	0.3011	−432
0.7568	37,539	0.0854	−2121	0.1709	0.2496	−721
0.7794	38,865	0.2329	−795	0.2949	0.2123	−732
0.7846	39,855	0.3411	195	0.3872	0.1845	−611
0.8246	40,113	0.4243	453	0.4613	0.1622	−482
0.8254	40,824	0.4904	1164	0.5195	0.1447	−304
0.8372	40,284	0.5432	624	0.5669	0.1304	−213

TABLE 2 (*continued*)

Mole dropped, n_i/mmol	Drop enthalpy, ΔH_{Signal}/J	Partial enthalpy		Integral enthalpy		
		x_i[a]	$\Delta_{mix}\overline{H_i}$/(J/mol)	x_{Al}	x_{Cu}	$\Delta_{mix}H$/(J/mol)
0.8428	40,227	0.5865	567	0.6061	0.1186	−142
0.9384	40,090	0.6241	430	0.6421	0.1077	−90
0.9614	39,857	0.6574	197	0.6728	0.0985	−65
0.9696	39,198	0.6858	−462	0.6988	0.0907	−97
0.9922	39,989	0.7101	329	0.7215	0.0839	−65
1.0088	39,971	0.7314	311	0.7413	0.0779	−38
1.0155	40,200	0.7499	540	0.7585	0.0727	0
1.0581	39,835	0.7664	175	0.7742	0.0680	12
1.0896	40,372	0.7813	712	0.7884	0.0637	56
1.0900	40,385	0.7947	725	0.8009	0.0599	95
1.1274	39,628	0.8066	−32	0.8124	0.0565	88
1.1686	40,469	0.8177	809	0.8229	0.0533	129
1.2030	40,024	0.8278	364	0.8327	0.0504	142
1.2064	40,323	0.8370	663	0.8414	0.0478	169
1.2227	40,203	0.8454	543	0.8493	0.0454	187
1.2371	39,800	0.8530	140	0.8566	0.0432	185
1.2642	39,947	0.8600	287	0.8634	0.0411	190
1.2946	40,081	0.8665	421	0.8696	0.0392	201
1.3698	40,103	0.8727	443	0.8757	0.0374	212
x_{Cu}/x_{Sn} = 3:7; 2nd run; i = Al; starting amounts: n_{Cu} = 1.0854 mmol; n_{Sn} = 2.5594 mmol						
0		0		0	0.2978	−414
0.7394	36,800	0.0843	−2860	0.1687	0.2476	−827
0.7427	38,194	0.2289	−1466	0.2891	0.2117	−919
0.7891	39,224	0.3365	−436	0.3839	0.1835	−855
0.8169	39,712	0.4213	52	0.4587	0.1612	−745
0.8421	39,922	0.4887	262	0.5188	0.1433	−633
0.8825	39,803	0.5439	143	0.5690	0.1283	−552
0.8954	39,800	0.5897	140	0.6103	0.1160	−486
0.9366	39,574	0.6280	−86	0.6458	0.1055	−449
0.9369	39,664	0.6606	4	0.6753	0.0967	−411
0.9688	40,485	0.6882	825	0.7011	0.0890	−313
1.0044	40,005	0.7125	345	0.7239	0.0822	−263
1.0389	40,075	0.7339	415	0.7440	0.0762	−214
1.0511	40,156	0.7528	496	0.7616	0.0710	−165
1.1085	39,834	0.7697	174	0.7777	0.0662	−142
1.1260	39,812	0.7849	152	0.7920	0.0619	−123
1.1348	39,375	0.7983	−285	0.8047	0.0582	−133
1.1815	39,893	0.8105	233	0.8163	0.0547	−111
1.1860	40,110	0.8215	450	0.8267	0.0516	−79
1.1971	39,580	0.8313	−80	0.8360	0.0488	−80
1.2294	40,049	0.8403	389	0.8446	0.0463	−55
1.2850	40,952	0.8486	1292	0.8527	0.0439	15
1.2998	39,724	0.8563	64	0.8600	0.0417	17
1.3594	39,514	0.8635	−146	0.8670	0.0396	9
1.3947	40,204	0.8702	544	0.8734	0.0377	35
1.4087	41,837	0.8764	2177	0.8793	0.0359	135

[a] Average value before and after the drop.

are based on calorimetric experiments done by Itagaki and Yazawa [4] are much less exotherm than values from our experiments and all other literature data.

Figure 3 shows the experimental enthalpy of mixing of Al–Sn together with the fitted curve and literature values. We have measured over the entire concentration range with an overlap along 40 at.% $\leqslant x_{Al} \leqslant$ 60 at.%. The rather consistent literature values and the asymmetry of the enthalpy of mixing curve (with a maximum of approx. 4000 J/mol at 60 at.% Al) could be nicely reproduced.

In the same way, the experimental results for the ternary system Al–Cu–Sn obtained in 10 separate measurements are given in table 2. The starting values of $\Delta_{mix}H$ for the binary systems, necessary for the evaluation of the measurements, were taken from this work and literature, see table 3. All measured alloy concentrations correspond to the liquid state of the ternary system at 1273 K.

In figures 4 to 8 experimental data for all five section x_{Al}/x_{Cu} = 1:1 (figure 4), x_{Al}/x_{Sn} = 1:1 (figure 5), x_{Cu}/x_{Sn} = 7:3 (figure 6), x_{Cu}/x_{Sn} = 1:1 (figure 7), and x_{Cu}/x_{Sn} = 3:7 (figure 8) are shown together with calculated values (see section 3.2). The experimental results of the two runs for each section are in very good agreement to each other, indicating satisfying reproducibility of the measurements. A further proof of the quality of our data is the good agreement of values from different experiments close to the intersection points of the five concentrational sections (see table 4 and figure 1). The maximum deviation is 500 J/mol, however, it goes down to 50 J/mol and the average deviation is approx. 200 J/mol. Considering the estimated error of ±150 J/mol the deviation is insignificant and a chemical systematic error can be thus excluded.

3.2. Binary and ternary modeling

The experimental results of the binary systems Al + Cu and Al + Sn were described by a least square fit to the well-known Redlich–Kister polynomial [20] for substitutional solutions which is given by the following equation:

$$\Delta_{mix}H = \sum_i \sum_{j>i} \left[x_i x_j \sum_v {}^v L^H_{ij} (x_i - x_j)^v \right], \quad (4)$$

TABLE 3
Binary and ternary interaction parameters in liquid Al–Cu–Sn system.

Calorimetry (this work)				KEMS [1]		
System	Temperature/K	Literature	Interaction parameters/(J/mol)	Temperature/K	Literature	Interaction parameters/(J/mol)
Al–Cu	973	This work	${}^{0}L^{H}_{Al,Cu} = -68334$ ${}^{1}L^{H}_{Al,Cu} = 39088$	Various temp.	[8]	${}^{0}L^{H}_{Al,Cu} = -66622$ ${}^{1}L^{H}_{Al,Cu} = 46800$ ${}^{2}L^{H}_{Al,Cu} = -2812$
Al–Sn	973	This work	${}^{0}L^{H}_{Al,Sn} = 15809$ ${}^{1}L^{H}_{Al,Sn} = 3691$	Various temp.	[8]	${}^{0}L^{H}_{Al,Sn} = 16329.85$ ${}^{1}L^{H}_{Al,Sn} = 4111.97$ ${}^{2}L^{H}_{Al,Sn} = 1765.43$
Cu–Sn	1273	[16]	${}^{0}L^{H}_{Cu,Sn} = -8620$ ${}^{1}L^{H}_{Cu,Sn} = -21735$ ${}^{2}L^{H}_{Cu,Sn} = -13125$	Various temp.	[22]	${}^{0}L^{H}_{Cu,Sn} = -9002.8$ ${}^{1}L^{H}_{Cu,Sn} = -20100.4$ ${}^{2}L^{H}_{Cu,Sn} = -10528.4$
Al–Cu–Sn	1273	This work	${}^{(0)}L^{H}_{Al,Cu,Sn} = 48744$ ${}^{(1)}L^{H}_{Al,Cu,Sn} = 156862$ ${}^{(2)}L^{H}_{Al,Cu,Sn} = 5207$	1273	[1]	${}^{(0)}L^{H}_{Al,Cu,Sn} = 29253$ ${}^{(1)}L^{H}_{Al,Cu,Sn} = 165408$ ${}^{(2)}L^{H}_{Al,Cu,Sn} = 96707$

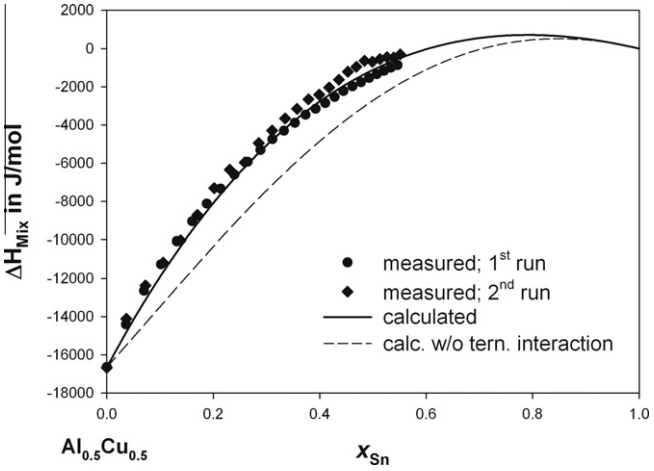

FIGURE 4. Integral molar enthalpies of mixing of liquid Al–Cu–Sn alloys at 1273 K for the section $x_{Al}/x_{Cu} = 1{:}1$; standard states: pure liquid metals; solid line: calculation with ternary interaction; dashed line: calculation without ternary interaction.

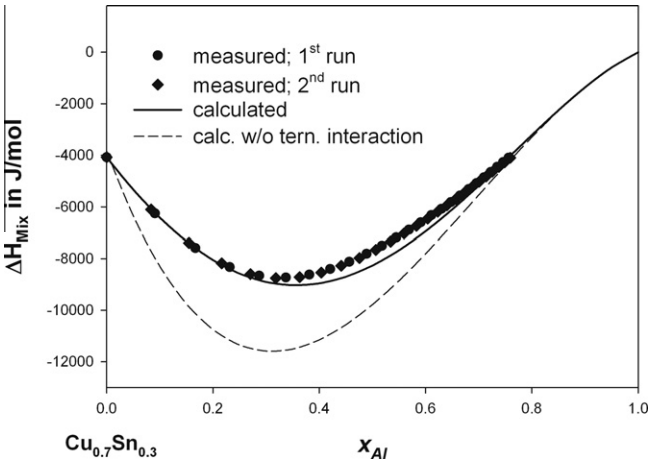

FIGURE 6. Integral molar enthalpies of mixing of liquid Al–Cu–Sn alloys at 1273 K for the section $x_{Cu}/x_{Sn} = 7{:}3$; standard states: pure liquid metals; solid line: calculation with ternary interaction; dashed line: calculation without ternary interaction.

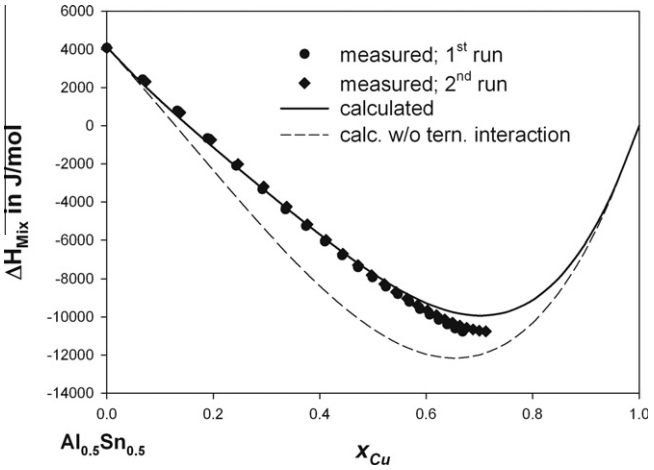

FIGURE 5. Integral molar enthalpies of mixing of liquid Al–Cu–Sn alloys at 1273 K for the section $x_{Al}/x_{Sn} = 1{:}1$; standard states: pure liquid metals; solid line: calculation with ternary interaction; dashed line: calculation without ternary interaction.

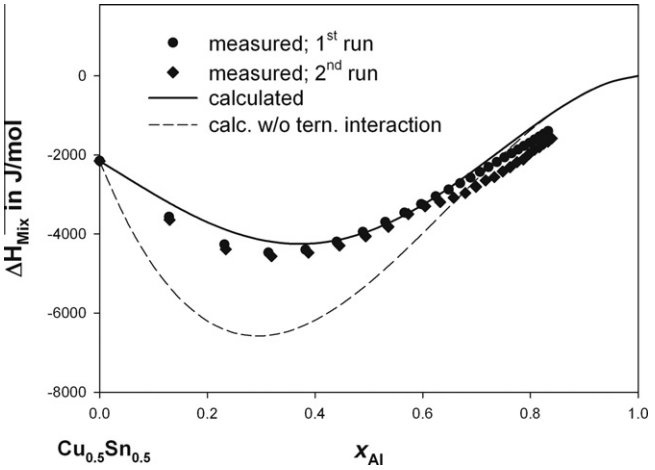

FIGURE 7. Integral molar enthalpies of mixing of liquid Al–Cu–Sn alloys at 1273 K for the section $x_{Cu}/x_{Sn} = 1{:}1$; standard states: pure liquid metals; solid line: calculation with ternary interaction; dashed line: calculation without ternary interaction.

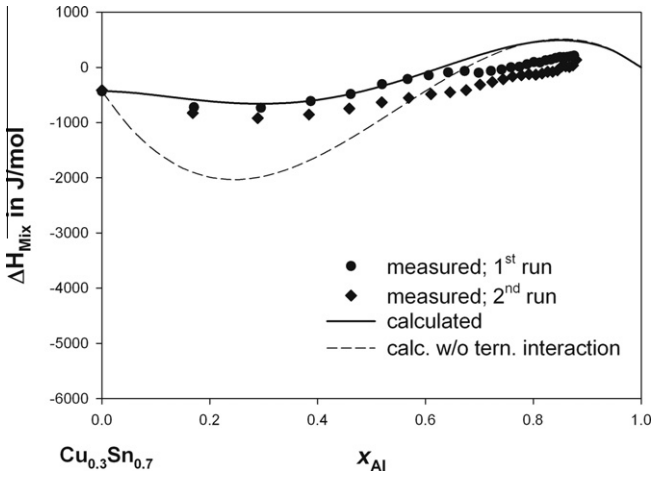

FIGURE 8. Integral molar enthalpies of mixing of liquid Al–Cu–Sn alloys at 1273 K for the section $x_{Cu}/x_{Sn} = 3{:}7$; standard states: pure liquid metals; solid line: calculation with ternary interaction; dashed line: calculation without ternary interaction.

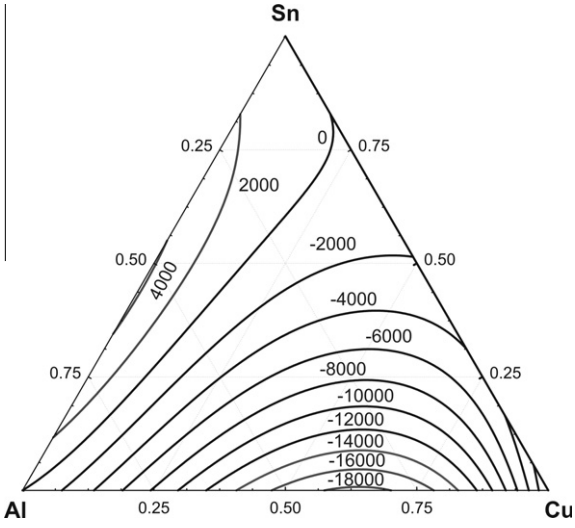

FIGURE 9. Iso-enthalpy curves of liquid Al–Cu–Sn alloys at 1273 K; standard states: pure liquid metals. Values in the Cu-corner refer to metastable liquid alloys; all concentrations given in mole fractions.

where i, j, are equal to element 1 and 2 according to the alphabetical order (Al; Cu and Al; Sn, respectively) and $v = 0, 1, 2, 3, \ldots$, *etc.* up to the maximal necessary power.

The experimental results of the ternary systems Al–Cu–Sn were described by a least square fit to the Redlich–Kister–Muggianu polynomial [21] which is given by the following equation:

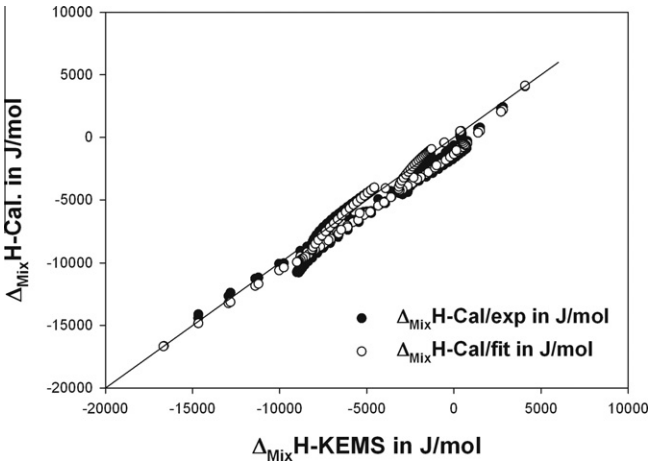

FIGURE 10. The measured integral molar enthalpies of mixing data derived from KEMS *vs.* the corresponding calorimetric data at 1273 K.

$$\Delta_{\mathrm{mix}}H = \sum_i \sum_{j>i} \left[x_i x_j \sum_v {}^{v}L^{\mathrm{H}}_{i,j}(x_i - x_j)^v \right] + x_i x_j x_k \left({}^{(0)}L^{\mathrm{H}}_{i,j,k} x_i + {}^{(1)}L^{\mathrm{H}}_{i,j,k} x_j + {}^{(2)}L^{\mathrm{H}}_{i,j,k} x_k \right), \quad (5)$$

where i, j, k are equal to 1, 2, 3 for the element Al, Cu, and Sn and $v = 0, 1, 2, 3, \ldots$, *etc.* up to the maximal necessary power. The binary parameters ${}^{v}L_{i,j}$ were determined from experimental enthalpies of mixing from this work (Al–Cu and Al–Sn) and literature (Cu–Sn [16]); see also table 3. The three ternary parameters $L^{\mathrm{H}}_{i,j,k}$ were obtained from the experimental enthalpies of mixing from the present investigation. The parameters $L^{\mathrm{H}}_{i,j,k}$ represent the additional mixing enthalpy due to ternary interactions. All binary and ternary interaction parameters are listed in table 3. An isenthalpic plot based on this calculation is shown in figure 9. The ternary system shows an exothermic enthalpy minimum of approx. −18,000 J/mol in the Al–Cu binary and a maximum of approx. 4000 J/mol in the Al–Sn binary system. Alloys at the very Cu-rich corner are not fully liquid at 1273 K and the plotted values have to be considered as an extrapolation to the metastable state.

The calculated values for the enthalpy of mixing in the liquid Al–Cu–Sn system along the sections measured are shown in figures 2 to 6 as solid lines, together with the experimental results. The calculated values based on the Redlich–Kister–Muggianu polynomial are in excellent agreement with the measured values for all sections. The dashed lines indicate calculated values neglecting the terms for ternary interactions in equation (5). For all section, these values fit much worse to our experiments and are generally too low (more exothermic or less endothermic) in comparison to the experiment. As a conclusion we suppose that in the Al–Cu–Sn system additional, repulsive ternary interaction occur if ternary

TABLE 4
Values of the integral enthalpy of mixing at the intersection points.

Concentration			Integral enthalpy of mixing in J/mol[a]				
x_{Al}	x_{Cu}	x_{Sn}	Al/Cu = 1:1	Al/Sn = 1:1	Cu/Sn = 7:3	Cu/Sn = 1:1	Cu/Sn = 3:7
0.41	0.41	0.18	−8700		−8400		
0.22	0.55	0.23		−8800	−8300		
0.33	0.33	0.34	−4300	−4250		−4500	
0.40	0.20	0.40		−650			−700
0.22	0.22	0.56	−450				−650

[a] Rounded to 50 J/mol.

liquid alloys are formed. This is as well indicated by the three positive ternary interaction parameters; see table 3.

3.3. Comparison to data obtained from KEMS measurements

The enthalpies of mixing data, obtained in this work, were compared to those obtained by Bencze *et al.* [1]. The authors of this paper investigated 31 compositions (41 samples) of the Al–Cu–Sn system in the liquid region {1273 to 1473 K} by KEMS. They presented data on excess Gibbs free energy, ternary L^{G}-parameters, activities, activity coefficients, partial equilibrium vapor pressures as well as partial and integral molar excess Gibbs Energy and fitted their data also to the Redlich–Kister–Muggianu model [20], *i.e.* in the form of equation (6), similar to equation (5):

$$G^{E} = \sum_{i}\sum_{j>i}\left[x_i x_j \sum_{v} {}^{v}L^{G}_{i,j}(x_i - x_j)^{v}\right] + x_i x_j x_k \left({}^{(0)}L^{G}_{i,j,k}x_i + {}^{(1)}L^{G}_{i,j,k}x_j + {}^{(2)}L^{G}_{i,j,k}x_k\right), \quad (6)$$

where G^{E} denotes the integral molar excess Gibbs energy. The excess Gibbs energy binary $({}^{v}L^{G}_{i,j})$ and ternary $({}^{(0\,or\,1\,or\,2)}L^{G}_{i,j,k})$ L-parameters certainly differ from the corresponding enthalpy type L^{H}-parameters $({}^{v}L^{H}_{i,j}$ and $ {}^{(0\,or\,1\,or\,2)}L^{H}_{i,j,k})$ present in equation (5). Though reference [1] did not present the excess enthalpy and entropy data of liquid Al–Cu–Sn alloy, all the excess or mixing data (both partial and integral) of these quantities can be evaluated from the reported ternary $G^{E}(T)$ functions where the various $L^{G}(T)$ terms include the temperature dependence. The binary and ternary $L^{G}(T)$ parameters present in equation (6) are given in the form of $L^{G} = A + B + C \cdot T\ln(T)$ in reference [1]. Therefore, using the well-known Gibbs–Helmholtz equation for the evaluation of $H^{E}(T)$ from $G^{E}(T)$, the following relationships can be obtained:

$$L^{H}_{i,j} = A_{i,j} - C_{i,j}T \quad \text{and} \quad L^{H}_{i,j,k} = A_{i,j,k} - C_{i,j,k}T. \quad (7)$$

It follows from equation (7) that L^{H} is equal to A if $C = 0$, *i.e.* the enthalpy data do not depend on temperature if all the corresponding C parameters in the polynomial are equal to 0. This holds (*i.e.* all $C = 0$) for the binary Al–Sn data [2,8], for the binary Al–Cu [8] and for the binary Cu–Sn [22]. Nevertheless, according to Flandorfer *et al.* [16], some of the C-parameters of the binary Cu–Sn system must depend on temperature causing temperature dependence of the integral excess enthalpy. Similarly, the ternary L^{H}-parameters must also depend on temperature according to both this work and reference [1]. The comparison of the ternary L^{H}-parameters obtained in this work and evaluated from the $L^{G}(T)$-functions of reference [1] can be seen in table 3 at 1273 K. The last three columns include the data of reference [1]. The agreement between the calorimetric and KEMS enthalpy of mixing data can be seen in figure 10 where both the directly measured calorimetric data and also the fitted calorimetric data are plotted against the KEMS data. One can see that the correlation is excellent in both cases but it is even better with the fitted calorimetric data. When comparing the calorimetric enthalpy of mixing data to those obtained by KEMS it should be noted that KEMS determines these data using the 2nd or 3rd law thermodynamic methods, *i.e.*, not directly. Therefore the uncertainty of the KEMS must be higher. The estimated uncertainty of the enthalpy data by KEMS is (~1 to 2) kJ/mol.

Acknowledgements

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