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Thermodynamic properties of liquid Cu–Sn–Zn alloys

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Abstract

Using an appropriate galvanic cell, the partial free energies of zinc in liquid Cu–Sn–Zn alloys were determined as a function of concentration and temperature. Thermodynamic properties were obtained for 40 alloys. Their composition was situated on four cross-sections with constant ratios Cu:Sn of 1:3, 1:2, 1:1 and 2:1. The integral free energy and the integral enthalpy for the ternary system at 1023 K were calculated by Gibbs–Duhem integration.

Keywords: Cu–Sn–Zn; Liquid alloys; Thermodynamic properties; E.m.f. measurements

1. Introduction

Owing to health concerns and environmental reasons, lead will be replaced in the near future in all solder materials. New lead-free solders must be developed, and for certain applications the ternary X–Sn–Zn alloys could be candidates. We have already investigated the Ag–Sn–Zn [1] and Au–Sn–Zn [2] systems. Since copper alloys have excellent electrical properties and high corrosion resistance, they are important materials for different industrial applications. However, data of thermodynamic properties and of the phase diagram are scarce for ternary copper alloys. Thermodynamic data are also needed for the calculation of phase diagrams and for the improvement of industrial processes.

In the present investigation the thermodynamic properties of zinc were measured with an e.m.f. method at four cross-sections with a constant Cu:Sn molar ratio of 2:1, 1:1, 1:2 and 1:3. A Gibbs–Duhem integration was applied to determine the integral thermodynamic properties for the whole ternary system. From the discontinuities in the slope of the e.m.f. versus temperature curves the liquidus temperature for most alloys was determined.

2. Experimental procedure

The ternary alloys were prepared from high purity metals (4 N copper from Fischer Scientific Co., NJ; 5 N tin and zinc from Johnson Matthey GmbH, Vienna,). In order to remove the oxide layer from the surface, Sn was polished with a fine emery paper and zinc was cleaned prior to its use by melting under vacuum and filtering through quartz wool under a purified argon atmosphere. Copper was used without further purification.

The metals were weighed and sealed in silica capsules under vacuum and melted together at 1300 K for several days. After heat treatment the alloys were quenched in ice water and approximately 3 g of each alloy composition was used for the e.m.f. measurements.

As electrolyte, the eutectic mixture KCl–LiCl with addition of 0.5 mol% $ZnCl_2$ was used. The preparation of the electrolyte and the assembly of the e.m.f. cell are described by Geffken et al. [3]. Measurements were carried out on heating and cooling. The heating and cooling rate was 8 to 10 K h^{-1}. Every 50 degrees the temperature was kept constant for a longer period of time to check the stability of the e.m.f. The temperature range of measurements was from the liquidus up to 1100 K.

The following arrangement for the experiment was used:

$$\mathrm{Zn(l)/Zn^{++}(KCl\text{–}LiCl)(l)/Cu\text{–}Sn\text{–}Zn\ alloy(l)}$$

Under reversible conditions, the Gibbs free energy change for the reaction is given by

$$\Delta\bar{G}_{Zn} = -2FE = RT \ln a_{Zn} \quad (1)$$

where F is the Faraday constant (96 486 C mol^{-1}), E the electromotive force of the cell, R the universal gas constant (8.31434 J mol^{-1} K^{-1}), T the absolute temperature and a_{Zn} the thermodynamic activity of zinc in the ternary alloy, with pure liquid zinc constituent as reference state. At all four cross-sections the e.m.f. versus temperature curves

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were straight lines. A least-squares fit was used, and the e.m.f. was expressed by the following equation:

$$E(\mathrm{mV}) = a + bT(\mathrm{K}) \tag{2}$$

For each experiment two cooling curves were recorded. The agreement between these two curves was very good. The deviation of the measured e.m.f. values from the fitted ones was ±0.7 mV at 5 and 10 at.% Zn, between ±0.1 and ±0.15 mV at all other compositions.

Using the measured values of E, the a_{Zn} and $\Delta\bar{G}_{\mathrm{Zn}}$ at a given temperature were calculated. From the temperature dependence of E, the partial molar entropy $\Delta\bar{S}_{\mathrm{Zn}}$ and enthalpy $\Delta\bar{H}_{\mathrm{Zn}}$ were derived, using the following equations:

$$\Delta\bar{S}_{\mathrm{Zn}} = 2F(\partial E/\partial T)_{x,P} = 2bF \tag{3}$$

$$\begin{aligned}\Delta\bar{H}_{\mathrm{Zn}} &= 2F[T(\partial E/\partial T)_{x,P} - E] = \Delta\bar{G}_{\mathrm{Zn}} + T\Delta\bar{S}_{\mathrm{Zn}} \\ &= -2aF \end{aligned} \tag{4}$$

The Gibbs–Duhem equation given by Elliott and Chipman [4] (eq. (12) in their publication) was applied to determine the integral thermodynamic quantities for the whole ternary system from the e.m.f. data.

3. Experimental results and discussion

The thermodynamic data of the three binary systems were taken from the literature.

3.1. Tin–zinc system

In this system the thermodynamic properties were investigated with an e.m.f. method from Ref. [5], with calorimetric measurements from Ref. [6], and by a vapour pressure method [7,8]. The thermodynamic activities were determined with a thermal analysis by Itagaki and Yazawa [9] and a torque effusion method [10,11]. A review of this binary system is given by Moser et al. [12].

3.2. Copper–tin system

A new and very extensive review of the Cu–Sn system is given by Saunders and Miodownik [13]. E.m.f. measurements using a solid electrolyte were carried out by Sommer et al. [14] in the copper-rich solid solution region of this system. New calorimetric investigations of liquid Cu–Sn alloys are reported by Lee et al. [15]. Their data of the mixing enthalpy of liquid Cu–Sn alloys at 997 K are a little more negative than the values recommended by Saunders and Miodownik [13] and by Hultgren et al. [16].

3.3. Copper–zinc system

This system was evaluated by Hultgren et al. [16] and a thermodynamic re-evaluation is given by Kowalski and Spencer [17].

3.4. Copper–tin–zinc system

Some information on this ternary system is given by Tefelske et al. [18].

We started our investigation from the binary Cu–Sn system by adding zinc. The activity of Zn was measured along four cross-sections with a constant Cu:Sn ratio of

Table 1
Measured e.m.f. data

at.% Zn	E.m.f.	Liquidus temperature (K)
(a) Cu:Sn 1:3 cross-section		
5.01	$-14.090+0.13880T(\mathrm{K})$	785
10.01	$-12.600+0.11088T(\mathrm{K})$	805
19.99	$-12.180+0.07792T(\mathrm{K})$	863
30.01	$-10.180+0.06094T(\mathrm{K})$	893
39.99	$-9.273+0.04718T(\mathrm{K})$	919
49.99	$-8.429+0.03547T(\mathrm{K})$	917
59.99	$-9.079+0.02899T(\mathrm{K})$	883
70.00	$-8.284+0.02312T(\mathrm{K})$	880
79.99	$-4.563+0.01390T(\mathrm{K})$	843
90.01	$-0.693+0.00596T(\mathrm{K})$	—
(b) Cu:Sn 1:2 cross-section		
4.99	$5.748+0.12486T(\mathrm{K})$	790
9.99	$3.866+0.09311T(\mathrm{K})$	824
20.00	$0.804+0.06801T(\mathrm{K})$	878
29.99	$-2.643+0.05490T(\mathrm{K})$	912
40.01	$-3.397+0.04291T(\mathrm{K})$	933
50.00	$-4.376+0.03459T(\mathrm{K})$	940
60.00	$-5.663+0.02747T(\mathrm{K})$	923
70.00	$-4.467+0.01923T(\mathrm{K})$	885
80.00	$-3.931+0.01326T(\mathrm{K})$	830
89.99	$-0.729+0.00514T(\mathrm{K})$	833
(c) Cu:Sn 1:1 cross-section		
5.00	$22.670+0.12016T(\mathrm{K})$	873
10.01	$21.180+0.08874T(\mathrm{K})$	873
20.00	$14.290+0.06602T(\mathrm{K})$	903
30.00	$11.340+0.04825T(\mathrm{K})$	944
40.00	$6.692+0.03895T(\mathrm{K})$	952
50.01	$3.109+0.03138T(\mathrm{K})$	977
60.00	$1.848+0.02359T(\mathrm{K})$	943
69.99	$-0.216+0.01840T(\mathrm{K})$	905
80.00	$-0.450+0.01117T(\mathrm{K})$	838
90.00	$-0.363+0.00485T(\mathrm{K})$	790
(d) Cu:Sn 2:1 cross-section		
5.01	$42.000+0.11969T(\mathrm{K})$	912
10.01	$39.490+0.08915T(\mathrm{K})$	885
20.00	$32.300+0.05981T(\mathrm{K})$	903
30.01	$27.290+0.04128T(\mathrm{K})$	955
40.01	$22.470+0.03013T(\mathrm{K})$	973
50.02	$13.970+0.02533T(\mathrm{K})$	987
60.00	$6.432+0.02137T(\mathrm{K})$	990
70.00	$4.917.0.01410T(\mathrm{K})$	960
80.00	$1.226+0.01120T(\mathrm{K})$	902
90.00	$0.179+0.00523T(\mathrm{K})$	821

2:1, 1:1, 1:2 and 1:3. At each fixed composition the temperature versus e.m.f. curves were straight lines and the e.m.f. is expressed by Eq. (2).

In Table 1(a) and (b) the parameters *a* and *b* are given for all measured alloys. The activity of Zn in the Cu–Zn system shows a negative deviation from Raoult's law. At the Cu:Sn 2:1 cross-section the deviation is less negative and at Cu:Sn 1:1 it is only slightly negative. At a higher tin content the activity of zinc becomes more and more positive. The results of our investigation in the ternary system are presented in Fig. 1, and in Table 2 the activities of zinc, the partial Gibbs free energy, partial enthalpies and partial entropies are listed.

The integral Gibbs free energy and the enthalpy of mixing for the ternary Cu–Sn–Zn system were calculated using an equation given by Elliott and Chipman [4]. The integration was carried out along the line of a constant Cu to Sn ratio, and for the integration constant $G^{xs}_{\text{binary Cu-Sn}}$ the values of Hultgren et al. [16] calculated for 1023 K were used.

The results are given in Table 3 and the iso-Gibbs free energy curves for the ternary system are plotted in Fig. 2.

Table 2
Activities and partial molar quantities of Cu–Sn–Zn system

x_{Zn}	a_{Zn}	$\Delta\bar{G}_{Zn}$ (J mol^{-1})	$\Delta\bar{H}_{Zn}$ (J mol^{-1})	$\Delta\bar{S}_{Zn}$ (J K^{-1} mol^{-1})
(a) Cu:Sn 1:3 and 1:2 cross-sections at 1023 K				
Cu:Sn 1:3				
0.0500	0.0549	−24682	2719	26.785
0.1001	0.1015	−19457	2431	21.397
0.1999	0.2160	−13032	2350	15.037
0.3001	0.3062	−10065	1964	11.759
0.3999	0.4128	−7525	1789	9.105
0.4999	0.5315	−5376	1627	6.845
0.5999	0.6270	−3971	1752	5.594
0.7000	0.7057	−2965	1599	4.461
0.7999	0.8033	−1863	881	2.682
0.9001	0.8921	−971	134	1.080
Cu:Sn 1:2				
0.0499	0.0484	−25758	−1109	24.094
0.0999	0.1055	−19128	−746	17.968
0.2000	0.2026	−13581	−155	13.123
0.2999	0.2969	−10328	510	10.594
0.4001	0.3990	−7815	656	8.280
0.5000	0.4948	−5985	844	6.675
0.6000	0.6010	−4331	1093	5.302
0.7000	0.7082	−2935	862	3.711
0.8000	0.8036	−1860	759	2.560
0.8999	0.9024	−873	141	0.991
(b) Cu:Sn 1:1 and 2:1 cross-sections at 1023 K				
Cu:Sn 1:1				
0.0500	0.0368	−28096	−4375	23.188
0.1001	0.0789	−21605	−4087	17.124
0.2000	0.1562	−15791	−2758	12.740
0.3000	0.2523	−11713	−2188	9.310
0.4000	0.3479	−8981	−1291	7.517
0.5001	0.4499	−6794	−600	6.055
0.6000	0.5546	−5014	−357	4.553
0.6999	0.6557	−3590	42	3.550
0.8000	0.7796	−2118	87	2.155
0.9000	0.9009	−888	70	0.936
Cu:Sn 2:1				
0.0501	0.0240	−31733	−8105	23.097
0.1001	0.0516	−25220	−7620	17.203
0.2000	0.1199	−18041	−6233	11.542
0.3001	0.2066	−13414	−5266	7.965
0.4001	0.2985	−10283	−4336	5.813
0.5000	0.4046	−7696	−2696	4.888
0.6000	0.5263	−5459	−1241	4.123
0.7000	0.6447	−3733	−949	2.722
0.8000	0.7499	−2448	−237	2.162
0.9000	0.8893	−998	35	1.009

Table 3
Calculated integral thermodynamic quantities of Cu–Sn–Zn system

at.% Zn	ΔG_{mix} (J mol^{-1})	ΔH_{mix} (J mol^{-1})	ΔS_{mix} (J K^{-1} mol^{-1})
(a) Cu:Sn 1:3 cross-section at 1023 K			
0.00	−6849	−144	6.554
5.00	−8176	−100	7.894
10.00	−8877	52	8.729
15.00	−9335	178	9.300
20.00	−9631	287	9.695
25.00	−9798	403	9.971
30.00	−9854	525	10.146
35.00	−9807	639	10.211
40.00	−9662	731	10.160
45.00	−9427	799	9.995
50.00	−9104	857	9.737
55.00	−8699	922	9.405
60.00	−8215	1002	9.011
65.00	−7653	1086	8.543
70.00	−7011	1143	7.971
75.00	−6280	1141	7.253
80.00	−5446	1068	6.367
85.00	−4485	950	5.312
90.00	−3357	827	4.090
95.00	−1983	646	2.570
(b) Cu:Sn 1:2 cross-section at 1023 K			
0.00	−8206	−628	7.407
5.00	−9465	−683	8.584
10.00	−10116	−693	9.212
15.00	−10527	−683	9.622
20.00	−10773	−659	9.887
25.00	−10891	−618	10.041
30.00	−10899	−560	10.106
35.00	−10808	−484	10.091
40.00	−10625	−397	9.998
45.00	−10353	−301	9.826
50.00	−9995	−201	9.574
55.00	−9550	−97	9.240
60.00	−9015	11	8.823
65.00	−8387	126	8.321
70.00	−7662	245	7.729
75.00	−6833	359	7.030
80.00	−5888	453	6.197
85.00	−4809	496	5.185
90.00	−3564	454	3.927
95.00	−2081	293	2.321
(c) Cu:Sn 1:1 cross-section at 1023 K			
0.00	−10233	−1975	8.072
5.00	−11558	−2141	9.205
10.00	−12237	−2245	9.767
15.00	−12659	−2327	10.099
20.00	−12904	−2384	10.284
25.00	−13007	−2406	10.363
30.00	−12984	−2393	10.353
35.00	−12844	−2350	10.257
40.00	−12593	−2283	10.079
45.00	−12238	−2193	9.819
50.00	−11785	−2080	9.487
55.00	−11236	−1940	9.087
60.00	−10593	−1773	8.622
65.00	−9852	−1584	8.082
70.00	−9003	−1380	7.452
75.00	−8032	−1167	6.710
80.00	−6915	−943	5.838
85.00	−5627	−696	4.820
90.00	−4130	−414	3.632
95.00	−2363	−128	2.184
(d) Cu:Sn 2:1 cross-section at 1023 K			
0.00	−10941	−3652	7.124
5.00	−12415	−3875	8.348
10.00	−13240	−4080	8.954
15.00	−13780	−4234	9.331
20.00	−14113	−4343	9.550
25.00	−14275	−4413	9.640
30.00	−14290	−4448	9.621
35.00	−14170	−4436	9.514
40.00	−13924	−4365	9.344
45.00	−13558	−4220	9.127
50.00	−13074	−3999	8.871
55.00	−12472	−3704	8.571
60.00	−11752	−3351	8.212
65.00	−10910	−2958	7.773
70.00	−9940	−2540	7.234
75.00	−8834	−2103	6.579
80.00	−7578	−1643	5.802
85.00	−6152	−1152	4.888
90.00	−4517	−640	3.791
95.00	−2591	−183	2.354

The minimum is at approximately 48 at.% Cu, 24 at.% Sn and 28 at.% Zn. The data for the binaries Cu–Zn were taken from Gerling and Predel [19] and for Sn–Zn from Moser and Gasior [5].

A similar procedure was used to calculate the integral enthalpy of mixing. In this case the data, given by Hultgren et al. [16] at 1400 K, were used for the integration constant. The results for the enthalpy are presented in Fig. 3 and given in Table 3. ΔH_{mix} is negative at the Cu:Sn 2:1 and 1:1 cross-sections. For the 1:2 and 1:3 cross-

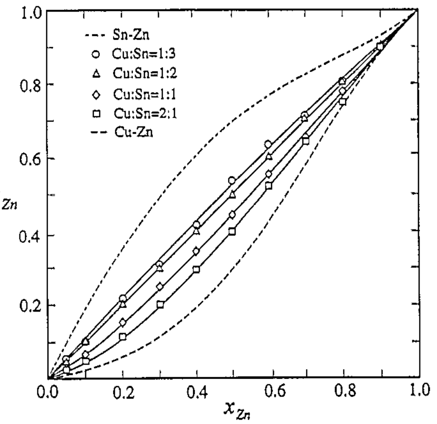

Fig. 1. Activity a_{Zn} of zinc with pure liquid zinc as a reference state for four Cu:Sn cross-sections 2:1, 1:1, 1:2 and 1:3 at 1023 K and for the binary Sn–Zn (Hultgren et al. [16] at 750 K) and Cu–Zn (Gerling and Predel [19] at 1173 K).

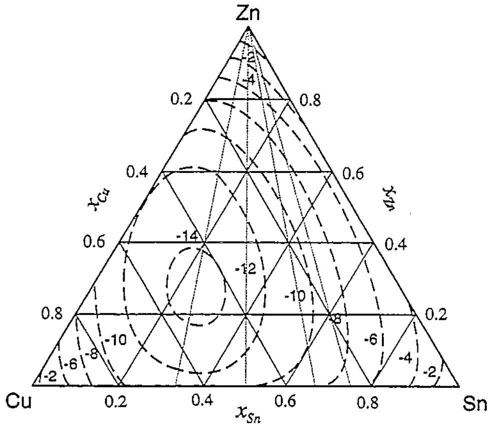

Fig. 2. Iso-Gibbs energy curves ΔG (kJ mol^{-1}) at 1023 K for the ternary Cu–Sn–Zn system.

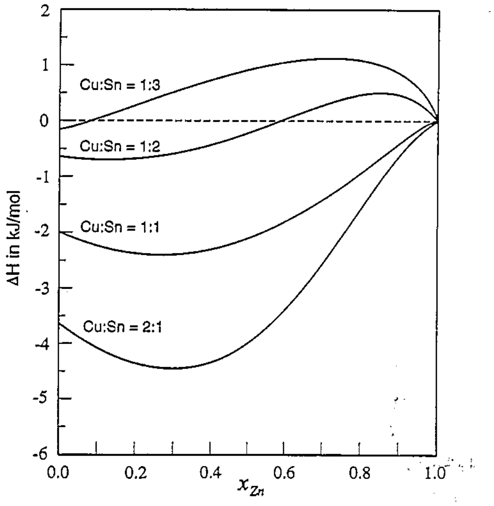

Fig. 3. Integral enthalpy of mixing ΔH for the four cross-sections at 1023 K.

sections the mixing enthalpy exhibits a change of sign. The integral enthalpy of mixing for the whole ternary system is plotted in Fig. 4. For the Cu–Zn system the data of Parameswaran and Healy [20] at 1400 K were used and the values of Hultgren et al. [16] at 750 K for the Sn–Zn system.

Since no data about the liquidus were found in the literature, Table 1 gives the liquidus temperature for most alloys which was taken from the distinct break in the e.m.f. versus temperature curves at the liquidus. The accuracy was estimated to be ±7 K.

The investigation of the ternary Cu–Sn–Zn system yields a consistent set of thermodynamic data of the liquid alloys, which are useful for the calculation of the ternary phase diagram. The data might also help to improve some industrial processes.

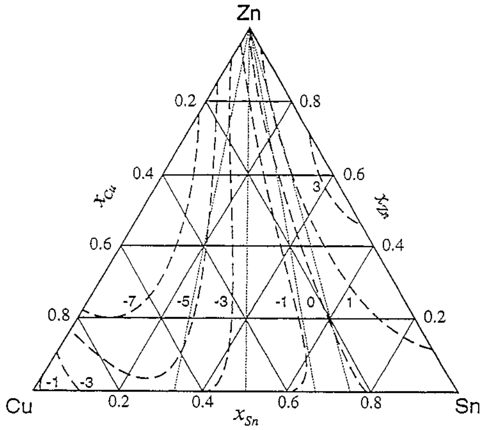

Fig. 4. Iso-integral molar enthalpy curves ΔH (kJ mol^{-1}) at 1023 K for the ternary Cu–Sn–Zn system.

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