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Thermodynamic Properties of Liquid Al–Sn–Zn Alloys: A Possible New Lead-Free Solder Material

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Because of its potential to be used as a lead free solder material the thermodynamic properties of the liquid Al–Sn–Zn system were investigated. Using an appropriate galvanic cell, the partial free energies of Al were determined as a function of concentration and temperature. Thermodynamic properties were obtained for 30 alloys. Their composition was situated on three cross-sections with constant ratios of Sn:Zn = 2:1, 1:1 and 1:2. The integral Gibbs energy and the integral enthalpy for the ternary system at 973 K were calculated by Gibbs-Duhem integration.

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1. Introduction

Since public awareness of environmental and health issues has never been greater, lead and lead containing alloys cause great environmental concern and health hazards. One of the main driving forces to eliminate lead in solder joints is the fact that the disposal of great amounts of electronic equipment (mobile phones, computers, TV-sets, and so on) in landfills can cause lead to leach out and contaminate the underground water and subsequently find its way into the human body. In this case it is more economical to replace lead in solder materials instead of cleaning up the electronic waste. Therefore the development of Pb-free solders has become an important issue in the electronic industry.

Soldering will remain a very important technology, unless there will be a sudden improvement in the adhesive joining technology, which anyway is unlikely to replace the soldering completely. It is safe to say that tin will remain the major component in solder. Looking at the periodic table of elements lead can be substituted in solders only by a few elements. The new alloys should have a similar melting temperature as Pb–Sn solders. Of course, melting temperature will not be the only criterion a substitute solder has to fulfill. Some other criteria for the substitute solder would be: Wetting properties, joint strength, fatigue resistance, non-toxicity, corrosion resistance and low cost.

Currently a great number of research activities are going on worldwide aiming at the replacement of lead in solder materials by other, less toxic or non-toxic elements. In the ideal case, this should be done without decrease in quality and without increase in costs. A literature review on the possible binary or ternary systems of lead free solders for electronic assembly is given by Hua and Glazer[1] and a report *Lead-free Soldering (1999)*[2] and the corresponding *Update (2000)*.[3] A database for soldering alloys was established by Ishida *et al*.[4] At our institute the thermodynamic properties of the following systems Ag–Sn–Zn,[5] Au–Sn–Zn,[6] Cu–Sn–Zn[7] and In–Sn–Zn[8] were investigated.

The discussion also includes the use of zinc. Zinc is sufficiently available, but it is well known that zinc causes problems with wettability and corrosion.[9] The eutectic Sn–Zn solder exhibits a better fatigue life than that of the conventional Pb–Sn eutectic solders.[10] The melting temperature of the eutectic Sn–Zn solder is 199°C which is very close to the eutectic temperature of Pb–Sn.

Because zinc is very liable to oxidation a protective atmosphere might be needed for soldering when the solder material contains zinc. From the application point of view an enhancement in oxidation resistance will be necessary should Zn be considered as a soldering element. One possibility to improve the oxidation resistance is the alloying with a third element. This alloying element must have a low melting point and should form an oxidation resistance phase with tin or zinc. In a series of investigations aluminum is considered as a possible choice as an alloying element. Aluminum is very effective to improve the corrosion resistance of steel.[11] Extensive experimental studies of the ternary phase diagrams were carried out by Vincent and Sebaoun[12] and Sebaoun *et al*.[13] An assessment of the Al–Sn–Zn system was carried out by Fries *et al*.[14] and an evaluation of all the literature data is given by Hubert-Protopopescu and Hubert.[15] The microstructure of some Al–Sn–Zn alloys were measured by Lin and coworkers[16] and the oxidation resistance of 91Sn–8.55Zn–0.45Al (mass%) and some other alloys were determined also by Lin *et al*.[17]

Since there are no thermodynamic data of the liquid phase available in the literature we decided to measure these properties by using an emf method. The thermodynamic properties of Al were measured at three cross-sections with a constant Sn to Zn ratio of 2:1, 1:1 and 1:2. A Gibbs-Duhem integration was carried out to determine the integral thermodynamic properties of the whole ternary system.

2. Experimental Procedure

The ternary alloys were prepared from starting materials of high purity 5N metals (from Johnson Matthey GmbH, Germany). In order to remove the oxide layer from the surface of Sn and Al both metals were polished with a fine emery paper and Zn was cleaned prior to its use by melting it under vacuum and filtering the liquid metal through

quartz wool under a purified argon atmosphere. The metals were weighed, put into alumina crucibles and these crucibles were sealed into a quartz tube and kept in a furnace for three days at 1023 K. Afterwards the samples were quenched in ice water. The liquid electrolyte for the emf measurements was a eutectic mixture of KCl and LiCl with the addition of 0.5 mol%$AlCl_3$. The preparation of the electrolyte and the assembling of the cell is described in.[18] For electrodes an Mo-wire from Fa. Plansee (Austria) with 0.50 mm diameter was used. It was stable against the liquid Al during the time of measurements. For aluminum, tantalum is most resistant to corrosion among refractory materials but in our experiment Ta wires became very brittle therefore we changed to Mo-wires.[19] Thermodynamically, molybdenum should be less resistant against liquid aluminum than tantalum but in our work no perturbation of the emf during the measurements were observed.

Measurements were carried out on heating and cooling. The temperature range of the experiment was from the liquidus temperature of the alloys up to 1000 K and the temperature gradient of the measurement was 10 K/h. The temperature and the emf were recorded automatically every five minutes. During the experiment the temperature was kept constant several times for a longer period in order to check

Table 1 Emf data of liquid Al–Sn–Zn alloys.

Sn:Zn = 2:1

x_{Al}	E (mV)
0.050	$-74.969 + 0.1323T$/K
0.100	$-23.969 + 0.0706T$/K
0.200	$-16.860 + 0.0485T$/K
0.300	$2.874 + 0.0221T$/K
0.400	$-9.952 + 0.0280T$/K
0.500	$-8.350 + 0.0219T$/K
0.600	$-6.978 + 0.0166T$/K
0.700	$-20.435 + 0.0274T$/K
0.800	$-8.167 + 0.0130T$/K
0.900	$-8.265 + 0.0106T$/K

Sn:Zn = 1:1

x_{Al}	E (mV)
0.050	$-38.801 + 0.1023T$/K
0.100	$-30.331 + 0.0739T$/K
0.200	$-20.324 + 0.0480T$/K
0.300	$-16.666 + 0.0366T$/K
0.400	$-17.083 + 0.0369T$/K
0.509	$-14.188 + 0.0342T$/K
0.600	$-13.766 + 0.0218T$/K
0.700	$-13.244 + 0.0196T$/K
0.800	$-9.090 + 0.0131T$/K
0.900	$-8.018 + 0.0103T$/K

Sn:Zn = 1:2

x_{Al}	E(mV)
0.050	$-66.253 + 0.1229T$/K
0.100	$-24.434 + 0.0711T$/K
0.186	$-17.075 + 0.0488T$/K
0.299	$-3.778 + 0.0285T$/K
0.399	$-12.017 + 0.0295T$/K
0.499	$-7.399 + 0.0211T$/K
0.598	$-6.625 + 0.0163T$/K
0.700	$-8.121 + 0.0149T$/K
0.799	$-9.207 + 0.0119T$/K
0.900	$-2.964 + 0.0050T$/K

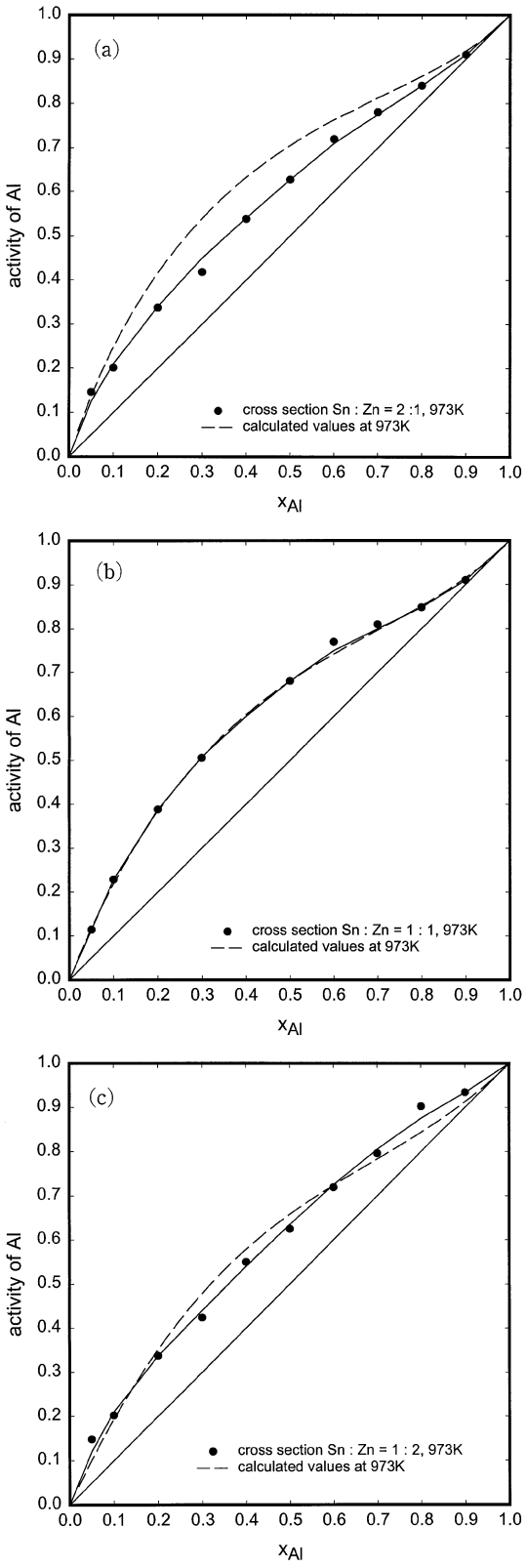

Fig. 1 Activity of Al, a_{Al}, for the three cross-sections Sn:Zn = 2:1, 1:1 and 1:2 at 973 K.

the stability of the emf. For the evaluation of the thermodynamic properties only the cooling curves were used. For these emf measurements the following cell arrangment was used:

$$\mathrm{Al}(l)/\mathrm{Al}^{+++}(\mathrm{KCl–LiCl–AlCl_3})(l)/\mathrm{Al–Sn–Zn}(l) \quad (1)$$

The transfer of Al^{3+} ions from the pure Al electrode, in which the chemical potential is G°_{Al}, to the alloy electrode in which aluminum is at a lower chemical potential $\bar{G}_{Al}$ occurs reversible in this cell. The free energy change for the transfer of one mole of Al^{3+} ions at temperature T is:

$$\Delta G = \bar{G}_{Al} - G^{\circ}_{Al} = RT \ln a_{Al} = -zFE$$

Where $z = 3$, F is the Faraday constant, R the universal gas constant, E the measured emf of the cell and a_{Al} the thermodynamic activity of aluminum in the ternary alloy.

Table 2 Activities and partial molar quantities of the Al–Sn–Zn system at 973 K.

Sn:Zn = 2:1

x_{Al}	a_{Al}	$\overline{\Delta G}_{Al}$ [J/g-atom]	$\overline{\Delta H}_{Al}$ [J/g-atom]	$\overline{\Delta S}_{Al}$ [J/g-atom × K]
0.050	0.146	−15575	21700	38.30
0.100	0.201	−12960	6938	20.45
0.200	0.337	−8793	4880	14.05
0.300	0.418	−7062	−832	6.40
0.400	0.538	−5009	2881	8.11
0.500	0.627	−3773	2415	6.36
0.600	0.719	−2668	2020	4.82
0.700	0.780	−1817	5915	7.95
0.800	0.840	−1298	2364	3.76
0.900	0.910	−601	2392	3.08

Sn:Zn = 1:1

x_{Al}	a_{Al}	$\overline{\Delta G}_{Al}$ [J/g-atom]	$\overline{\Delta H}_{Al}$ [J/g-atom]	$\overline{\Delta S}_{Al}$ [J/g-atom × K]
0.050	0.114	−17591	11231	23.59
0.100	0.229	−12037	8780	21.39
0.200	0.388	−7760	5883	13.92
0.299	0.506	−5494	4824	10.60
0.400	0.508	−5478	4945	10.71
0.509	0.680	−3120	4105	7.42
0.600	0.767	−2147	3984	6.30
0.700	0.810	−1709	3834	5.70
0.800	0.848	−1067	2631	3.80
0.900	0.910	−594	2321	3.03

Sn:Zn = 1:2

x_{Al}	a_{Al}	$\overline{\Delta G}_{Al}$ [J/g-atom]	$\overline{\Delta H}_{Al}$ [J/g-atom]	$\overline{\Delta S}_{Al}$ [J/g-atom × K]
0.050	0.148	−15441	19177	35.57
0.100	0.202	−12955	7073	20.58
0.186	0.337	−8800	4943	14.11
0.300	0.424	−6934	1094	8.25
0.400	0.550	−4831	3479	8.54
0.499	0.625	−3801	2142	6.10
0.598	0.719	−2673	1918	4.72
0.700	0.796	−1846	2351	4.31
0.799	0.902	−687	2665	3.47
0.900	0.934	−550	858	1.44

Using the results of the measured emf the activity of aluminum and the change of the Gibbs free energy were calculated. From the temperature dependence of E the partial molar entropy $\overline{\Delta S}_{Al}$ and enthalpy $\overline{\Delta H}_{Al}$ were derived using the following equations:

$$\overline{\Delta S}_{Al} = zF\left(\frac{\partial E}{\partial T}\right)_{x,P}$$

$$\overline{\Delta H}_{Al} = -zF\left(E - T\left(\frac{\partial E}{\partial T}\right)_{x,P}\right) = \overline{\Delta G}_{Al} + T\overline{\Delta S}_{Al}$$

In order to calculate the integral thermodynamic properties of the ternary system, the Gibbs-Duhem equation given by Elliott and Chipman (eq. (12) in Ref. 20)) was applied.

3. Experimental Results

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

(1) Tin–Zinc System

In this system the thermodynamic properties were investigated by emf methods,[21–25] by calorimetric measurements[26–28] and by vapour pressure methods[29] and.[30] The thermodynamic activities were also measured by thermal analysis[31] and a torque effusion method.[32,33] The wetting properties were investigated by Suganuma and Niihara.[34] The phase diagram was determined by Moser *et al*.[35]

(2) Aluminum-Tin System

Calorimetric measurements were carried out by Wittig and Keil[36] and the phase diagram is given by McAlister and Kahan.[37]

(3) Aluminum-Zinc System

The thermodynamic properties were determined by calorimetric measurements[36] and with an emf method.[38] The phase diagram is given by Murray[39] and Chen and Chang[40] calculated the phase diagram.

(4) Aluminum-Tin-Zinc System

The ternary phase diagram was studied by Vicent and Seboun[12,13,41,42] and a critical evaluation of different reported investigations is given by Hubert-Protopopescu and Hubert.[15] Standard CALPHAD procedures were used to as-

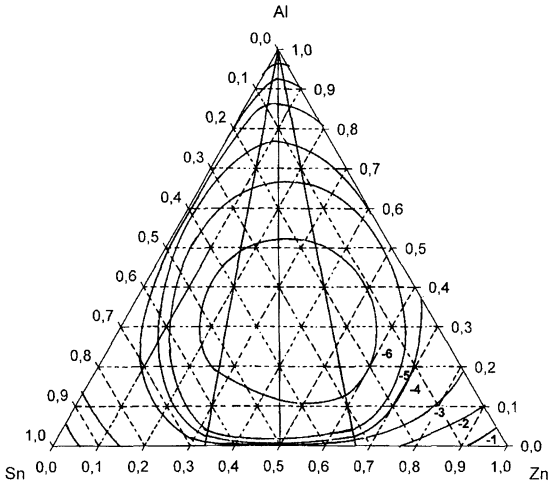

Fig. 2 Iso-Gibbs energy curves (ΔG in kJ/g-atom) of the ternary Al–Sn–Zn system at 973 K.

Table 3 Integral thermodynamic quantities of the Al–Sn–Zn system at 973 K.

Sn:Zn = 2 : 1

x_{Al}	ΔG^M [J/g-atom]	ΔH^M [J/g-atom]	ΔS^M [J/g-atom·K]
0.000	−2773	2476	5.353
0.050	−5046	2375	7.626
0.100	−5516	2984	8.734
0.150	−5851	3180	9.280
0.200	−6067	3330	9.625
0.250	−6197	3439	9.902
0.300	−6270	3512	10.521
0.350	−6279	3556	10.569
0.400	−6210	3570	10.050
0.450	−6081	3558	9.905
0.500	−5895	3521	9.676
0.550	−5653	3436	9.340
0.600	−5349	3299	8.887
0.650	−4994	3129	8.347
0.700	−4592	2927	7.726
0.750	−4129	2678	6.995
0.800	−3609	2362	6.136
0.850	−3017	1982	5.137
0.900	−2315	1519	3.940
0.950	−1421	910	2.395

Sn:Zn = 1 : 1

x_{Al}	ΔG^M [J/g-atom]	ΔH^M [J/g-atom]	ΔS^M [J/g-atom·K]
0.000	−2824	3291	6.284
0.050	−5503	3138	8.922
0.100	−5970	3497	9.727
0.150	−6233	3768	10.277
0.200	−6373	3999	10.658
0.250	−6416	4192	10.900
0.300	−6388	4344	11.027
0.350	−6293	4452	11.042
0.400	−6204	4514	11.014
0.450	−6061	4524	10.877
0.500	−5771	4498	10.552
0.550	−5535	4421	10.231
0.600	−5192	4277	9.678
0.650	−4816	4067	9.128
0.700	−4404	3789	8.419
0.750	−3944	3447	7.594
0.800	−3445	3035	6.658
0.850	−2881	2535	5.565
0.900	−2220	1917	4.251
0.950	−1374	1154	2.598

Sn:Zn = 1 : 2

x_{Al}	ΔG^M [J/g-atom]	ΔH^M [J/g-atom]	ΔS^M [J/g-atom.K]
0.000	−2409	3208	5.772
0.050	−5397	3068	8.699
0.100	−5885	3581	9.727
0.150	−6161	3740	10.174
0.200	−6304	3838	10.422
0.250	−6454	3889	10.629
0.300	−6512	3904	10.703
0.350	−6501	3881	10.669
0.400	−6410	3818	10.510
0.450	−6257	3719	10.252
0.500	−6061	3589	9.917
0.550	−5796	3424	9.475
0.600	−5474	3218	8.932
0.650	−5086	2968	8.276
0.700	−4642	2681	7.525
0.750	−4133	2366	6.678
0.800	−3531	2003	5.687
0.850	−2854	1602	4.579
0.900	−2127	1151	3.368
0.950	−1236	641	1.929

sess the ternary system and both binary aluminum systems during the European COST 507 program.[43] Calorimetric measurements were done by Aragon *et al.*[44] The microstructure of some of these alloys with a low aluminum content were investigated by Lin and coworkers.[16]

We started our investigation from the binary Sn–Zn system by adding Al. The activity of Al was measured along three cross sections with a constant Sn:Zn ratio of 2:1, 1:1 and 1:2. At all cross sections the temperature vs. emf curves were straight lines. A least square fit was used and the emf is expressed by the following equation.

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

In Table 1 the parameters are given for all alloys. The activity of Al shows a positive deviation from Raoult's law. The results of our investigation in the ternary system are shown in Figs. 1(a), (b), (c) and are given in Table 2. We also tried to calculate the activity of aluminum by using the equations given by COST 507.[43] The agreement between our measured activities and the calculated ones is very good at the cross sections Sn:Zn = 1:1 and 1:2. A rather large deviation is found at the Sn:Zn = 2:1 cross section. The partial Gibbs energy,

partial enthalpy and entropy of aluminum are also listed in Table 2. The integral Gibbs energy and the integral enthalpy of mixing for the ternary Al–Sn–Zn system were calculated with an equation given by Elliott and Chipman.[20] The integration was carried out along the line of constant Sn:Zn ratios, and for the integration constant the values by Hultgren *et al*.[45] were used. The results are given in Table 3 and the integral Gibbs energy for the ternary system is plotted in Fig. 2.

4. Summary

The investigation of the ternary Al–Sn–Zn system yields a consistent set of thermodynamic data of the liquid alloys, which may be useful for the development of new lead-free solder materials and also for the calculation of the ternary phase diagram and to determine the surface tension and the wettability with different models as it was done by Prasad *et al*.[46–48]

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