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Calorimetric investigation of the Pb–In binary system

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Abstract

Results of the calorimetric investigations in the Pb–In binary system are presented in this paper. Activities, activity coefficients, partial and integral molar quantities for lead and indium at temperatures 673, 773, 873 and 973 K are determined. A good agreement between the experimental and literature values is reached.

Keywords: Alloy thermodynamics; Binary Pb–In system; Calorimetry

1. Introduction

Lead and lead alloys have frequently been the subject [1,2] of many research studies including the binary system Pb–In. The alloys of Pb–In are used as contact alloys for metal–glass or metal–ceramics connections because of their relatively low melting temperatures.

There are considerable informations on the phase diagram of this system [3–8]. First, it was thought to have continuous solid solution between In and Pb, but Hansen [3] doubted this as because indium has a tetragonal body centred crystal lattice. Further research by Valentiner [4], Klein and Volk [5], and Moore et al. [6], proofed this and the phase boundaries of the Pb–In system were determined. Also Evans and Prince [7] using DTA determined the liquidus and solidus curves. The most complete determination of the Pb–In phase diagram was made by Nabot and Ansara [8].

In the solid state, the accepted phase diagram exhibits an In-rich and an extended Pb-rich single-phase region, which are separated by an intermediate (αIn) phase. The phase diagram of the Pb–In system [8], is presented in Fig. 1.

There is much information on the thermodynamic parameters of this binary system [9–15]. Hultgren et al. [9], and Kubaschewski and Alcock [10] list partial and integral molar parameters for the whole concentration range at 673 K. Selected free mixing energies have been obtained from EMF measurements by Terpilowski and Gregorczyk [11]. Wittig and Scheidt [12], and Miller [13] determined the heats of formation at calorimetrically at 664 and 623 K, respectively. Sommer et al. [14] measured the activities of lead and indium at 1000 K by Knudsen method, and Shiu and Munir [15] performed vapour pressure measurements at 1070 K. A complete review of the thermodynamics of the Pb–In system together with thermodynamic values in this system obtained by optimisation, is described in Nabot and Ansara's work [8].

As a contribution to the better understanding of the Pb–In thermodynamics, a calorimetric investigation

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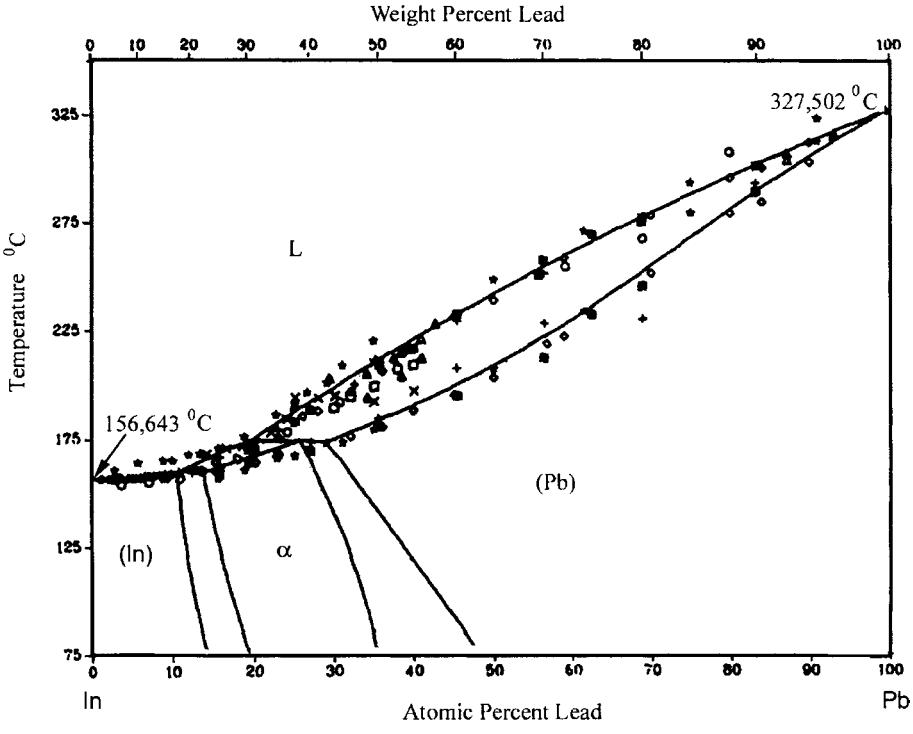

Fig. 1. Phase diagram of the Pb–In system.

over the complete concentration range and in the temperature interval 673–973 K are presented in this paper.

2. Experimental

To measure the thermodynamic analysis of Pb–In binary system, an Oelsen calorimetry was used. The experimental technique has been reported elsewhere [16–19].

Metallic Pb and In of p.a. purity were used in these experiments. The compositions of the samples investigated are given in Table 1. All experiments were carried out in air using a constant sample volume of 1 cm^3. The water equivalent was determined by a standard method using dissolved Na_2CO_3

Table 1
Composition of the investigated samples

Sample	Mass (%)		X_i		m (g)		m (total)
	Pb	In	Pb	In	Pb	In	
U1	0.0	100	0.0	1.0	0.0	7031	7.31
U2	7.786	92.214	0.0447	0.9523	0.5855	6.9345	7.52
U3	16.702	83.298	0.1	0.9	1.2987	6.4772	7.7759
U4	21.7248	78.2753	0.1333	0.8667	1.7223	6.2056	7.9279
U5	34.1589	65.8411	0.2233	0.7767	2.8485	5.4852	8.331
U6	54.608	45.392	0.4	0.6	4.9636	4.1272	9.0908
U7	73.023	26.977	0.6	0.4	7.2329	2.6721	9.905
U8	88.005	11.995	0.8026	0.1974	9.4017	1.2814	10.683
U9	100	0.0	1.0	0.0	11.4	0.0	11.4

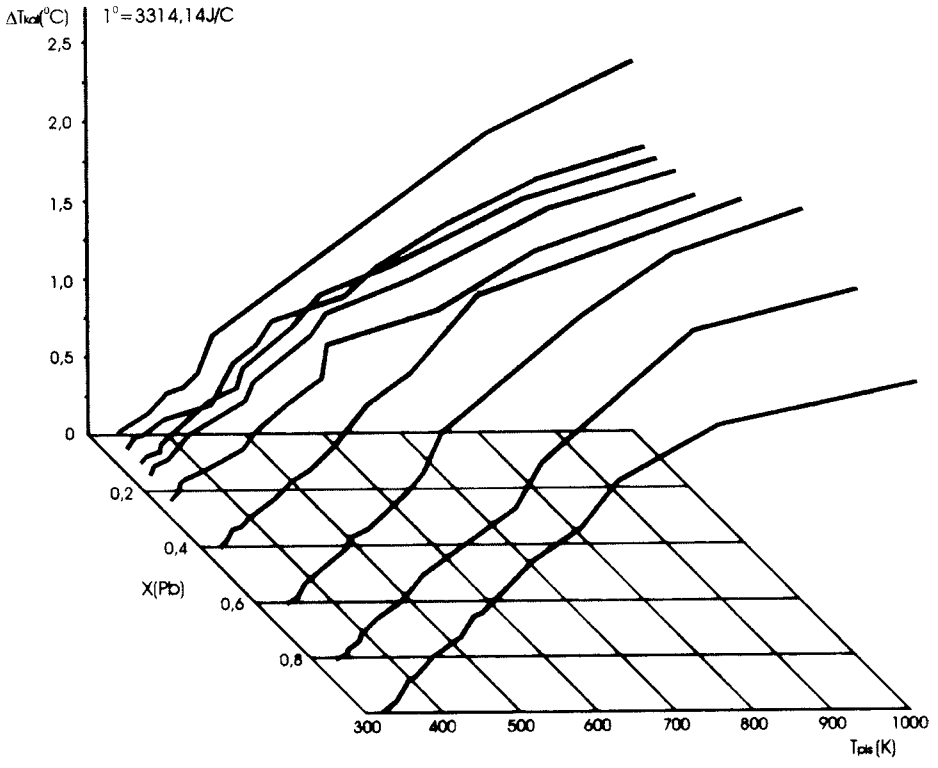

Fig. 2. Space enthalpy diagram–calorimeter temperature change vs. composition and temperature.

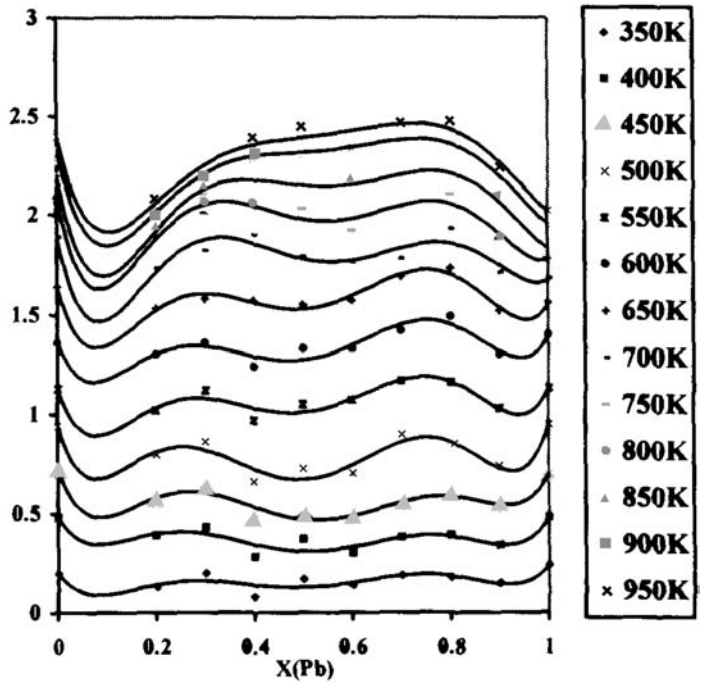

Fig. 3. Enthalpy isotherm diagram for the investigated temperature interval 673–973 K.

and for the calorimeter used it was found to be $\pm 3314.14\ \mathrm{J\ K^{-1}}$.

3. Results and discussion

From the Oelsen's thermodynamic analysis based on the cooling curves, temperature change of the calorimeter was determined for all samples investigated over the temperature interval 673–973 K. Based on this, enthalpy diagram (dependence of change calorimeter temperature on composition and temperature) and enthalpy isotherm diagrams were constructed. These diagrams are shown in Figs. 2 and 3, respectively.

Further analysis by the Oelsen method involved graphic planimetry (Fig. 4) and tangent construction to determine $R \ln a_{X,T}$ terms. Following the basic equation in the analysis

$$\frac{G_i^{\mathrm{M}}}{T} = \int_{1/T_0}^{1/T} H_{X,T}\, \mathrm{d}\left(\frac{1}{T}\right) = -R \ln a_i$$

where G_i^{M} is the partial molar Gibbs energy for component "i", T_0 the starting temperature, T the final temperature, $H_{X,T}$ the enthalpy value measured in the Oelsen calorimeter for the temperature change from T_0 to T, R the gas constant and a_i the activity of component "i".

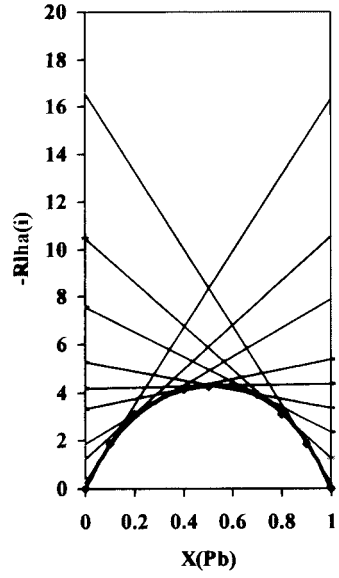

Fig. 5. Tangent construction for determination of $-R \ln a_{X,T}$.

From these results, activities for Pb and In at 673, 773, 873 and 973 K were determined. These activities values are shown in Fig. 5, from which positive deviation from Raoult law can be observed consistent with immiscibility of the constituent components (Fig. 6). All results obtained by the Oelsen's quantitative thermodynamic analysis (activities, activity

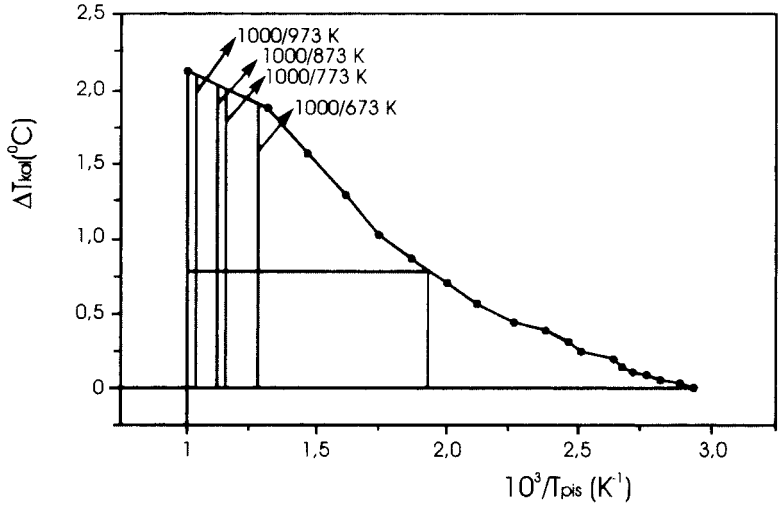

Fig. 4. Graphic planimetry (for sample 2).

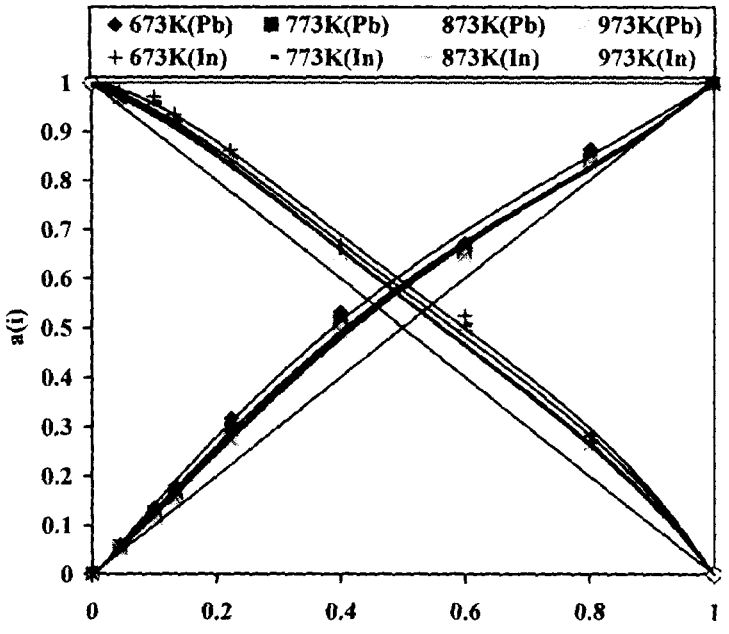

Fig. 6. Activities of Pb and In vs. composition at 673, 773, 873 and 973 K.

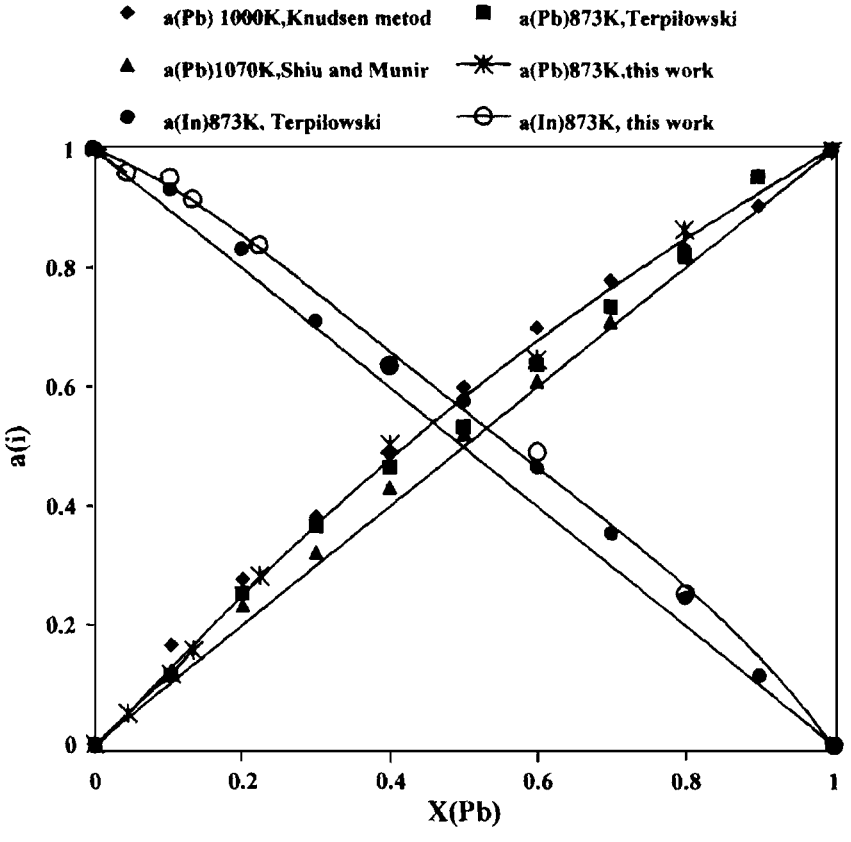

Fig. 7. Comparison of activities obtained experimentally and from literature data.

Table 2
Results of Oelsen's quantitative thermodynamic analysis

	γ(Pb)	α(Pb)	γ(In)	α(In)	G^{XS}(Pb)	G^{XS}(In)	ΔG^{XS}	G^{M}(Pb)	G^{M}(In)	ΔG^{M}
673 K										
U1	–	–	–	–	–	–	–	–	–	–
U2	1.348	0.060	21.94	0.981	1675.0	148.539	216.77	−15714	−107.33	−804.95
U3	1.35	0.135	9.72	0.972	1679.1	430.621	555.477	−11204.5	−158.9	−1263.4
U4	1.349	0.179	7.014	0.935	1677.4	424.42	591.45	−9597.9	−376.05	−1605
U5	1.421	0.317	3.855	0.861	1967.5	576.54	887.16	−6421.15	−837.4	−2084
U6	1.327	0.531	1.667	0.667	1585.1	592.32	989.45	−3541.8	−2265.9	−2776
U7	1.118	0.671	0.873	0.524	625.77	1510.88	979.82	−2232.4	−3616	−2785
U8	1.077	0.865	0.351	0.282	418.93	1995.7	730.19	−811.466	−7082	−2049
U9	–	–	–	–	–	–	–	–	–	–
773 K										
U1	–	–	–	–	–	–	–	–	–	–
U2	0.801	0.055	21.61	0.966	1425	71.58	132.1	−18547	−222.31	−1041
U3	1.25	0.125	9.6	0.96	1434	414.7	516.7	−13364	−262.3	−1572
U4	1.249	0.166	6.924	0.923	1433	404.4	541.5	−11517	−514.9	−1981
U5	1.319	0.294	3.788	0.846	1783	549.2	824.7	−7852	−1074	−2588
U6	1.275	0.51	1.627	0.651	1561	524.2	939.1	−4327	−2758	−3386
U7	1.088	0.653	0.843	0.506	544	1510	930.7	2738	−4378	−3358
U8	1.04	0.842	0.335	0.269	307.9	1988	639.8	−1105	8438	−2552
U9	–	–	–	–	–	–	–	–	–	–
873 K										
U1	–	–	–	–	–	–	–	–	–	–
U2	1.178	0.052	21.49	0.961	1194	43.17	94.66	−21361	−288.7	−1230
U3	1.18	0.118	9.53	0.953	1201	415.3	493.9	−15511	−349.4	−1865
U4	1.183	0.157	6.871	0.916	1220	401.5	510.6	−13406	−636.8	−2338
U5	1.246	0.282	3.752	0.838	1704	551.3	808.8	−9177	−1282	−3045
U6	1.26	0.504	1.59	0.636	1677	422.9	924.7	−4973	−3284	−3960
U7	1.077	0.646	0.82	0.492	541.7	1502	926	−3165	−5148	−3958
U8	1.042	0.836	0.315	0.253	297.6	1801	594	−1298	−9975	−3011
U9	–	–	–	–	–	–	–	–	–	–
973 K										
U1	–	–	–	–	–	–	–	–	–	–
U2	1.167	0.052	21.20	0.948	1254	−62.05	−3.192	−23885	−431.9	−1480
U3	1.17	0.117	9.46	0.946	1270	403.4	493.7	−17356	−449.07	−2139
U4	1.169	0.155	6.819	0.909	1266	385.4	511	−15034	−771.8	−2673
U5	1.231	0.275	3.748	0.837	1684	604.8	828.2	−10443	−1439	−3449
U6	1.237	0.495	1.582	0.633	1723	433.1	934.3	−5688	−3699	−4494
U7	1.076	0.646	0.808	0.485	597.5	1558	941.1	−3534	−5853	−4462
U8	1.042	0.836	0.310	0.249	338.5	1878	603.2	−1440	−11246	−3376
U9	–	–	–	–	–	–	–	–	–	–

coefficients, partial and integral molar quantities) are tested in Table 2.

From the thermodynamic analysis, it can be concluded that positive deviation from Raoult's law is present over the complete range of Pb–In binary system at all the temperatures investigated. With decreasing temperature, activities of lead increase, which is the opposite dependence to that observed with In. It may be seen from Fig. 7 that experimental data are in good agreement with the literature [11–15].

4. Conclusions

Results of the thermodynamic analysis of binary Pb–In system by Oelsen's quantitative calorimetry are

presented in the paper. Thermodynamic values were determined for this system at 673, 773, 873 and 973 K. Positive deviation from Raoult's law is confirmed. A good agreement between experiments and literature data for activities at 673 K was reached. With decreasing of temperature activities of lead are increasing and opposite for In.

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