Journal of Thermal Analysis, Vol. 52 (1998) 393-401

COMPARATIVE THERMODYNAMIC STUDY OF THE Pb–Al BINARY SYSTEM

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(Received November 4, 1997)

Abstract

The results of a comparative thermodynamic study of the Pb–Al binary system: activities, activity coefficients, partial and integral molar quantities at 1000 K, obtained by experimental Oelsen calorimetry and thermodynamic predicting according to Chou for systems with miscibility gap are presented in this paper. Also, infinite dilution constants and interaction parameters at the mentioned temperature were determined by means of the Hajra method.

Keywords: alloy thermodynamics, binary systems with miscibility gap, Pb–Al system

Introduction

Although widely used in batteries, lead alloys are heavy and have poor creep properties. To develop a lighter, more resistant battery alloy, the possibility of alloying lead with aluminium has been explored recently [1], and there are literature data about the production of Pb–Al alloys [2–5].

The phase diagram of the Pb–Al binary system characterized by the existence of a miscibilty gap in the greatest composition field (phase boundaries at x_{Pb}=0.012 and 0.942), was first determined by Hansen (1958) and then modified by investigations of several authors [6]. It is shown in Fig. 1.

A compilation of known data on the thermodynamics of the Pb–Al system important from the scientific and practical points of view, is given in Hultgren's book [6]. It includes the results of: direct reaction calorimetric measurements by Wittig and Keil (1963) at 1105 K in the two-phase region x_{Pb}=0.1–0.77; emf measurements by Martin-Garin and Desrè (1967) at temperatures 623–1273 K in the composition range x_{Pb}=0.01–0.05 and direct reaction calorimetric measurements by Predel and Sandig (1969) in the one-phase liquid region x_{Pb}=0.1–0.9 [6].

As a contribution to the better knowledge of the thermodynamic behaviour of the Pb–Al binary system, thermodynamic data on the Pb–Al binary system ob-

1418-2874/98/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

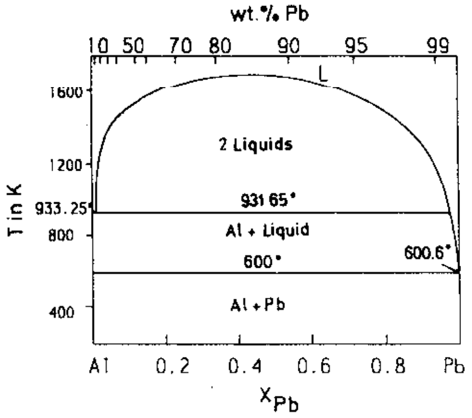

Fig. 1 The Pb–Al binary system

tained by experimental Oelsen calorimetric measurements [7–9] as well as by the thermodynamic predicting method for binary systems with a miscibility gap [10, 11] are presented in this work.

Experimental

Oelsen calorimetry was used for the experimental part of the comparative thermodynamic studies on the Pb–Al binary system. Full description of this experimental technique is given in Refs [7–9].

All the metals used were of analytical grade.

Compositions and masses of samples chosen for further experimental investigation are given in Table 1. According to the requirements of the method used the total volume of all samples was constant – 1 cm^3.

Table 1 Composition of the investigated samples

Sample	Composition/wt%		Molar content		Mass of samples/g		
N°	Pb	Al	x_{Pb}	x_{Al}	m_{Pb}	m_{Al}	m_{Total}
L1	0	100	0	1	0	2.7000	2.7000
L2	10	90	0.014	0.986	0.2869	2.6320	2.9189
L3	30	70	0.053	0.947	1.0532	2.4506	3.5038
L4	50	50	0.115	0.885	2.1792	2.1839	4.3631
L5	70	30	0.233	0.767	4.0570	1.7391	5.7961
L6	90	10	0.54	0.460	7.7637	0.8612	8.6249
L7	97	3	0.808	0.192	10.0830	0.3120	10.3950
L8	100	0	1	0	11.4000	0	11.4000

The water equivalent was determined by a standard method using dissolved Na_2CO_3 and for the calorimeter used it was found to be 4297 J K^{-1}.
All experiments were carried out in an air atmosphere.

Results and discussion

According to Oelsen's thermodynamic analysis [7–9], the first step was the construction of the space diagram and enthalpy isotherm diagram based on the cooling curves obtained in the temperature interval 500–1000 K; these are shown in Figs 2 and 3, respectively. Because of the investigated temperature interval, experimental measurements were made in the two-phase region of the Pb–Al binary system.

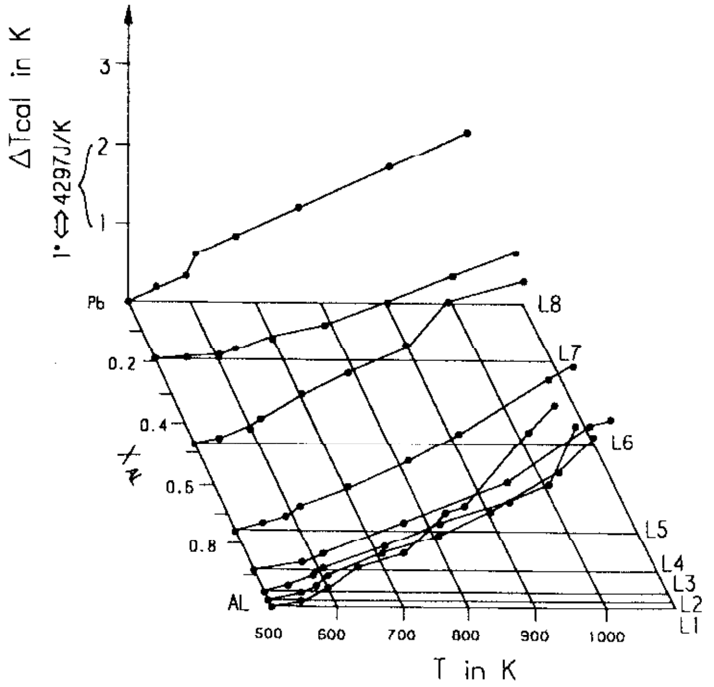

Fig. 2 Space diagram: the temperature change of the calorimeter *vs.* molar content and temperature

Following the basic equation in Oelsen's thermodynamic analysis [7–9] given as:

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

where G_i^M – is the partial molar Gibbs energy for component i, T_0 – is the starting temperature, T – is the final temperature, $H_{x,T}$ – is the enthalpy value measured in the Oelsen calorimeter for the temperature change from T_0 to T, R – is the gas constant and a_i – is the activity of the component i, the next step of thermodynamic analysis was graphic planimetry, as shown in Fig. 4, which permitted further calculations.

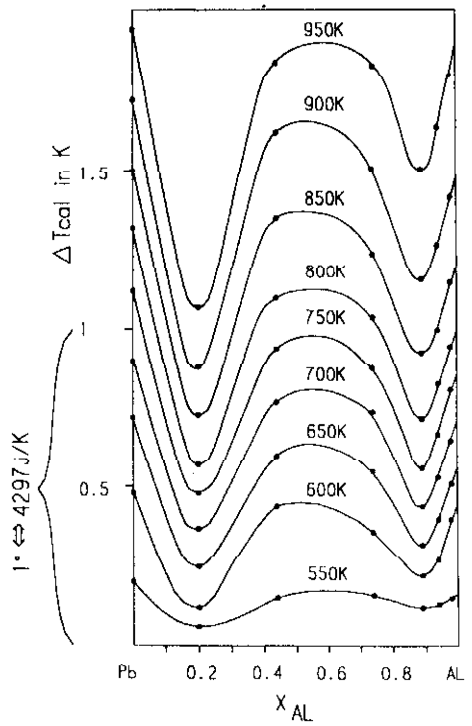

Fig. 3 Enthalpy isotherm diagram for the temperature interval 550–950 K

Table 2 Results of the Oelsen quantitative thermodynamic analysis at 1000 K (energies in J mol^{-1})

Alloy	a_{Pb}	a_{Al}	γ_{Pb}	γ_{Al}	G_{Pb}^M	G_{Al}^M	G_{Pb}^{xs}	G_{Al}^{xs}	ΔG^M	ΔG^{xs}
L2	0.349	0.988	24.929	1.002	–8752	–100	26738	17	–221	391
L3	0.477	0.97	9	1.024	–6154	–253	18268	199	–565	1157
L4	0.586	0.953	5.096	1.077	–4443	–400	13538	615	–866	2101
L5	0.681	0.925	2.923	1.206	–3194	–648	8918	1557	–1241	3272
L6	0.772	0.866	1.429	1.883	–2151	–1196	2971	5259	–1711	4024
L7	0.866	0.681	1.072	3.547	–1196	–3194	576	10562	–1580	2487

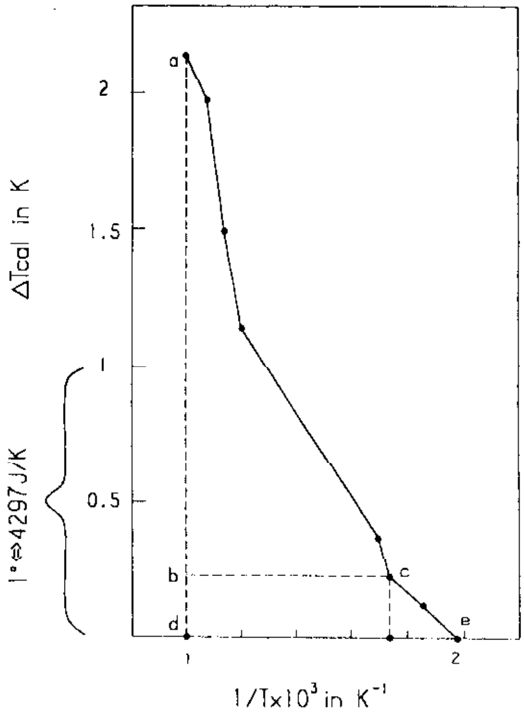

Fig. 4 Graphic planimetry (for sample L2)

Based on Eq. (1) and the results of graphic planimetry, the tangent was constructed for the determination of $-R\ln a_{Pb}$ and $-R\ln a_{Al}$ at 1000 K. This enabled determination of activities for both components, and indirectly, determination of other important thermodynamic properties of the Pb–Al binary system such as: activity coefficients, partial and integral molar quantities. The results are given in Table 2.

The strong positive deviation from Raoult's law indicates the immiscibility between the components of the Pb–Al systems and confirm thermodynamically the existence of the miscibility gap. It can be seen from Table 2 that lead deviates more irregularly than aluminium, if we have in mind that the activity of the component in the two-phase region tends to a constant value [12]. Such a thermodynamic behaviour could be explained by a non-homogeneous alloy state or limitations of the experimental technique used.

This is the main reason why thermodynamic predicting was applied, which has been described in the literature as an exact and precise method providing results consistent with experimental data [13, 14]. In our case, Chou's predicting method for binary systems with miscibility gap [10, 11] was used. The graphic representation of the method is given in Fig. 5.

The basic equations of the method [10] are:

$$d\ln\gamma_1^{\alpha} = \frac{1}{x_2^{\alpha} - x_2^{\beta}}\left(x_2^{\alpha}\sum\nolimits^{\beta} - x_2^{\beta}\sum\nolimits^{\alpha}\right) d\left(\frac{T}{T_0}\right) - d(T\ln x_1^{\alpha}) \qquad (2)$$

$$\ln\gamma_1^{\beta} = \ln\gamma_1^{\alpha} - \frac{T(\ln x_1^{\beta})/(x_1^{\alpha})}{T_0}, \qquad (3)$$

while

$$\sum\nolimits^{\alpha} = x_1^{\alpha}\ln x_1^{\alpha} + x_2^{\alpha}\ln x_2^{\alpha} \qquad \sum\nolimits^{\beta} = x_1^{\beta}\ln x_1^{\beta} + x_2^{\beta}\ln x_2^{\beta} \qquad (4)$$

where $\gamma_i^{\alpha,\beta}$ and $x_i^{\alpha,\beta}$ – are the activity coefficient and molar content of the component "i" in the α and β phases in the miscibility gap, respectively; T – is the temperature along the miscibility gap line and T_0 – is the temperature investigated. (Equations for calculation of the activity of component 2 can be derived analogously.)

In view of Eqs (2–4) and the known phase diagram taken from Hultgren *et al.* [6] (Fig. 1), a complete set of thermodynamic properties was obtained for Pb–Al binary system at 1000 K. The results of calculation are presented in Table 3.

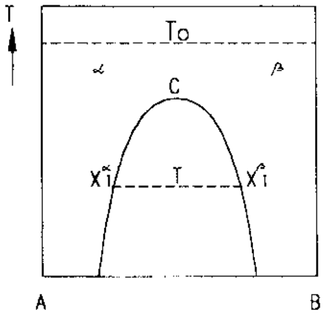

Fig. 5 Graphic representation of Chou's predicting method for binary systems with miscibility gap

Conclusions similar to those given for the experimental results could be drawn in the case of predicting calculation. A strong positive deviation from Raoult's law characterizes the behavior of lead in the investigated binary system, but some differences connected with the aluminium data are also noticed. The activity coefficient of aluminium is smaller than 1 in the region of L2–L4 alloys (x_{Pb}=0.014–0.115). The explanation for this behaviour could be the small solubility of Al in Pb, reported in the literature [6]. Also, there is a visible deviation between experimental and predicted results for the lead activities in the same composition range (L2–L4 alloys).

Table 3 Results of the predicting method applied at 1000 K

Alloy	a_{Pb}	a_{Al}	γ_{Pb}	γ_{Al}	G^{M}_{Pb}	G^{M}_{Al}	G^{xs}_{Pb}	G^{xs}_{Al}	ΔG^{M}	ΔG^{xs}
L2	0.943	0.984	67.357	0.998	–488	–134	35002	–17	–139	474
L3	0.851	0.924	16.057	0.976	–1341	–657	23080	–206	–693	1029
L4	0.714	0.875	6.209	0.989	–2801	–1110	15181	–94	–1305	1662
L5	0.789	0.917	3.386	1.196	–1970	–720	10141	1485	–1012	3502
L6	0.698	0.878	1.293	1.909	–2989	–1082	2134	5374	–2112	3624
L7	0.75	0.9	0.928	4.688	–2392	–876	–619	12844	–2101	1966

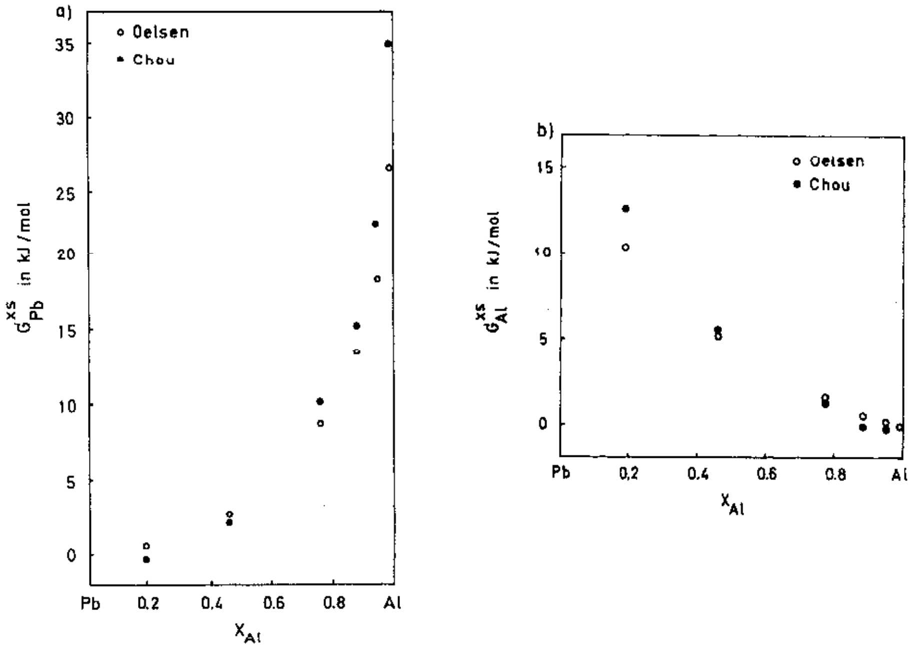

Fig. 6 Comparison of partial molar excess Gibbs energies for lead (a) and aluminium (b) obtained by Oelsen calorimetry and Chou predicting

A comparison of partial molar excess Gibbs energies for lead and aluminium obtained by means of Oelsen's experimental method and those yielded by the predicting method is shown in Fig. 6.

It can be concluded that in general there is good agreement between calculated and experimental thermodynamic quantities, except in the mentioned composition range L2–L4 (x_{Pb}=0.014–0.115), where some disagreement occurs – probably caused by a non-homogeneous alloy state or limitations of the experimental technique used. However, predicted results are in better agreement with the mentioned fact about the value of the activity in the two-phase region, and also with available literature data [6], so these results must be taken as more reliable.

Recently, a new consistent methodology has been developed by Hajra [15] for the determination of the thermodynamic quantities related to infinite dilution state based on the Maclaurin infinite series expressed by the integral property of the system. So, in the last part of the present study of the Pb–Al binary system, the results of the determination of infinite dilution constants and interaction parameters by Hajra's method are described.

This model is presented as a four-parameter function [15]

$$\frac{\Delta G^{xs}}{RT}=x_1(1-x_1)(a_1+a_2x_2+x_2(1-x_2)(a_3+a_4x_2)) \tag{5}$$

in which are:

$$\begin{aligned} a_1 &= \ln\gamma_2^o \\ a_2 &= \ln\gamma_1^o-\ln\gamma_2^o \\ a_3 &= 1/2\varepsilon_2^2-\ln\gamma_1^o+\ln\gamma_2^o \\ a_4 &= 1/2(\varepsilon_1^1-\varepsilon_2^2)+3(\ln\gamma_1^o-\ln\gamma_2^o), \end{aligned} \tag{6}$$

where γ_i^o and ε_i^i are the corresponding infinite dilution constants and interaction parameters of the first order.

Based on Eqs (5–6) and known experimental values for the integral molar excess Gibbs energy (Table 2), adequate parameters a_i (i=1–4), infinite dilution constants γ_{Pb}^o and γ_{Al}^o as well as the interaction parameters ε_{Pb}^{Pb} and ε_{Al}^{Al} at 1000 K were determined and are shown in Table 4.

Table 4 Results of Hajra's method applied at 1000 K

a_1	a_2	a_3	a_4	γ_{Pb}^o	γ_{Al}^o	ε_{Pb}^{Pb}	ε_{Al}^{Al}
1.7295	1.2553	1.3193	6.4873	5.638	10.48	−16.268	0.423

Values of the calculated interaction parameters point out to the thermodynamic behaviour of the components in the Pb–Al binary system especially in the explanation of the more irregular deviations of the thermodynamic quantities for lead than for aluminium, as it was mentioned earlier. These results complete the thermodynamic study presented for the Pb–Al binary system and are useful in interpreting thermodynamic properties of the investigated system.

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The authors acknowledge the contribution of Mr. Miroslav Ćirić, Met. Eng. and Mr. Saša Simić, Mech. Eng. to the realization of this work.

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