

CALORIMETRIC INVESTIGATIONS OF THE SYSTEM Pb–Bi–Mg–Sb WITH OELSEN'S METHOD Part 2. Comparison of experimentally obtained values for lead activity with results of thermodynamic predicting

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(Received January 12, 2001; in revised form May 18, 2001)

Abstract

Results of the comparative thermodynamic analysis of the Pb–Bi_xMg_ySb_z section ($x:y:z=8:1:1$, in mole ratio) in the Pb–Bi–Mg–Sb system, obtained experimentally by Oelsen calorimetry and predicted by general solution model in the temperature range 600–1100 K, are given in this paper.

Keywords: alloy thermodynamics, calorimetry, Pb–Bi–Mg–Sb system, thermodynamic predicting methods

Introduction

Although thermodynamic investigations are very important for description and determination of the phenomena occurring in the Pb–Bi–Mg–Sb system, characteristic of the Kroll–Betterton process of lead refining from bismuth [1], relatively high investigating temperatures and oxidation of the constituents, make difficulties in experimental measurements. Thermodynamic data for constitutional binary and ternary systems have been determined and reported in literature [2–14], while the only data for multicomponent Pb–Bi–Sb–Mg system are the results of calorimetric investigations in the section Pb–Bi_xMg_ySb_z ($x:y:z=8:1:1$, mole ratio), which include the integral mixing enthalpies in the temperature interval 450–1100°C, and were given in work of Ivković *et al.* [15]. In order to continue and complete thermodynamic research of this section in the Pb–Bi–Mg–Sb system, results of comparison between data obtained experimentally by Oelsen calorimetry [16–18] and calculated by general solution model predicting [19], are presented in this paper.

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Experimental

As was stated in the previous part of this work [15], Oelsen calorimetry was used for the experimental measurements of thermodynamic data in Pb–Bi_xMg_ySb_z section ($x:y:z=8:1:1$, mole ratio) in Pb–Bi–Mg–Sb system. Eleven samples, chosen along the line of constant mole ratio given (with $x_{\text{Pb}}=0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$ and 1) and with constant total volume of 1 cm³, were investigated.

The water equivalent for the used calorimeter was determined to be 3453 J °C⁻¹ by a standard method using dissolved Na₂CO₃ [15], while all experiments were carried out in an air atmosphere with metals of the analytical grade.

Theoretical fundamentals

General solution model was used for the thermodynamic predicting in the investigated quaternary system based on the known thermodynamic properties for the constitutive binaries. This model for the thermodynamic predicting of multicomponent systems ($n>3$, n – number of components), developed by Chou and Wei [19], is confirmed as reasonable in theoretical considerations and more reliable in the practical use than the other known traditional models.

The main theoretical interpretation of this thermodynamic predicting model is given as follows:

$$\Delta G^E = \sum_{i,j=1}^m x_i x_j \left[A_{ij}^0 + A_{ij}^1 \left((x_i - x_j) + \sum_{k=1}^m A_{ij}^1 x_k (2\xi_{i(ij)}^k) - 1 \right) \right] \quad (1)$$

where A_{ij}^0 and A_{ij}^1 are binary regular parameters, $x_{i,j,k,\dots,m}$ is molar content for the constitutive components, and $\xi_{i(ij)}^{(k)}$ are the adequate similarity coefficients. It should be stated that the binary regular parameters are obtained by fitting the expression of ΔG_{ij}^E dependence on composition, according to the relation:

$$\Delta G_{ij}^E = X_1 X_2 (A_{ij}^0 + A_{ij}^1 (X_1 - X_2) + \dots + A_{ij}^n (X_1 - X_2)^n) \quad (2)$$

The similarity coefficients could be obtained by using the following expression:

$$\xi_{i(ij)}^{(k)} = \eta(ij, ik) / (\eta(ij, ik) + \eta(ji, jk)) \quad (i, j, k = 1, 2, 3 \dots n \quad i \neq j \neq k) \quad (3)$$

where $\eta(ij, ik)$ is a function related to the excess Gibbs energy of ij and ik binaries as follows:

$$\eta(ij, ik) = \int_{x_i=0}^{x_i=1} (\Delta G_{ij}^E - \Delta G_{ik}^E)^2 dX_i \quad X_i = X_{i(ij)} = X_{i(ik)} \quad (4)$$

and

$$X_{i(ij)} = x_i + \sum_{\substack{k=1 \\ k \neq i, j}}^m x_k \xi_{i(ij)}^{(k)} \quad (5)$$

In all equations given, ΔG^E and ΔG_{ij}^E are related to the integral molar Gibbs excess energies for multicomponent system and binary constitutive systems, respectively, X are the molar contents of components in the adequate binary systems, while x is related to the compositions in the investigated multicomponent system.

Results and discussion

In the previous part of this work [15], temperature changes for the calorimeter used were determined for all samples in the temperature interval 450–1100 K, which enabled determination of the dependence of calorimeter temperature change on composition and temperature, as well as the enthalpy isotherm diagram construction.

In Oelsen thermodynamic analysis [16–18], thermodynamic properties are determined by so-called Oelsen integral, which enables calculation of partial molar Gibbs energy of mixing from directly measured values of enthalpies, and further, activities of the components of the system. Since determination of activities is conceived on knowledge of enthalpy and entropy article, under equilibrium conditions and constant pressure, it can be written that $dS_{x,T}^M$ is equal to $dH_{x,T}^M / T$ or

$$S_{x,T}^M = S_{x,T=0}^M + \int_{H_{x,T=0}^M}^{H_{x,T}^M} dH_{x,T}^M / T \quad (6)$$

If one use Nernst theorem, the term $S_{x,T=0}^M$ is equal to zero, so the following expression could be given:

$$S_{x,T}^M = \int_{H_{x,T=0}^M}^{H_{x,T}^M} dH_{x,T}^M / T \quad (7)$$

and further, integral molar Gibbs energy of mixing could be expressed as:

$$\Delta G_{x,T}^M = H_{x,T}^M - T \int_{H_{x,T=0}^M}^{H_{x,T}^M} dH_{x,T}^M / T \quad (8)$$

Because of a better survey, Oelsen introduced the mark $I_{x,T}$, which represents the enthalpy value directly measured in calorimeter: $I_{x,T} = H_{x,T}^M - H_{x,V}^M$ where V is room temperature. Multiplying Eq. (8) with $(-T)$ and using Eq. (9), one obtains:

$$-G_{x,T}^M / T = \int_{I_{x,V}}^{I_{x,T}} dI_{x,T} / T - \int_{1/V}^{1/T} I_{x,T} d(1/T) \quad (9)$$

which represents important Oelsen integral. This integral enables determination of partial molar Gibbs energy of mixing by directly measured values of enthalpies, while according to the relationship $G_i^M = RT \ln a_i$ activity of component could be calculated. Solution of Oelsen integral is done by graphical method of planimetry the areas below cooling curves.

Therefore, the basic equation used in Oelsen thermodynamic analysis [16–18] is

$$-G_i^M / T = \int_{1/T_0}^{1/T} H_{x,T} d\left(\frac{1}{T}\right) = -R \ln a_i \quad (10)$$

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 .

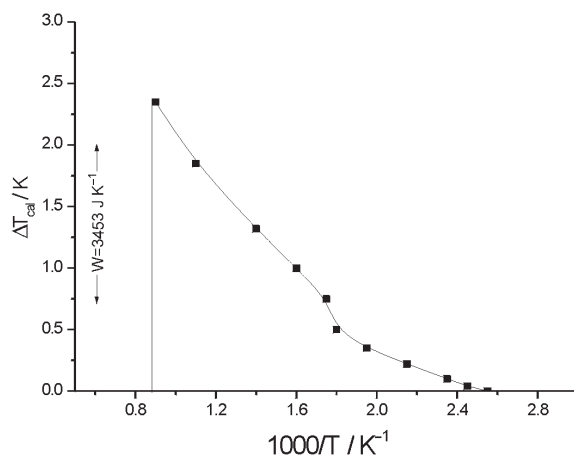


Fig. 1 Representation of graphic planimetry for sample with $x_{Pb}=0.9$

Based on these theoretical fundamentals, the next step in quantitative determination of lead activities in the researched section of Pb–Bi–Mg–Sb system, is graphic planimetry. Example of graphic planimetry for one investigated sample is given in Fig. 1.

According to Eq. (10) and graphic planimetry results, the tangents were constructed for the calculation of $-R \ln a_{Pb}$ at 600, 800 and 1100 K, which enabled the de-

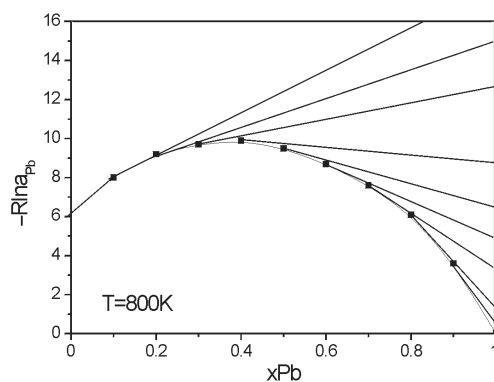


Fig. 2 Tangent construction for determination of $-R \ln a_{Pb}$ at 800 K

Table 1 Results of the Oelsen's quantitative thermodynamic analysis (energies in J mol⁻¹)

| x_{Pb} | $T=1100\text{ K}$ | | | $T=800\text{ K}$ | | | $T=600\text{ K}$ | | |
|-----------------|-------------------|----------------------|--|------------------|----------------------|--|------------------|----------------------|--|
| | a_{Pb} | γ_{Pb} | $G_{\text{Pb}}^{\text{E}}/\text{J mol}^{-1}$ | a_{Pb} | γ_{Pb} | $G_{\text{Pb}}^{\text{E}}/\text{J mol}^{-1}$ | a_{Pb} | γ_{Pb} | $G_{\text{Pb}}^{\text{E}}/\text{J mol}^{-1}$ |
| 0.1 | 0.049 | 0.49 | -6523.9 | 0.043 | 0.43 | -5613.4 | 0.038 | 0.38 | -4826.7 |
| 0.2 | 0.152 | 0.76 | -2509.8 | 0.131 | 0.655 | -2814.3 | 0.12 | 0.6 | -2548.2 |
| 0.3 | 0.236 | 0.78667 | -2194.4 | 0.229 | 0.76333 | -1796.2 | 0.217 | 0.72333 | -1615.7 |
| 0.4 | 0.348 | 0.87 | -1273.6 | 0.343 | 0.8575 | -1022.5 | 0.336 | 0.84 | -869.74 |
| 0.5 | 0.467 | 0.934 | -624.44 | 0.458 | 0.916 | -583.57 | 0.459 | 0.918 | -426.8 |
| 0.6 | 0.573 | 0.955 | -421.09 | 0.573 | 0.955 | -306.25 | 0.577 | 0.96167 | -194.98 |
| 0.7 | 0.689 | 0.98429 | -144.85 | 0.685 | 0.97857 | -144.07 | 0.688 | 0.98286 | -86.257 |
| 0.8 | 0.807 | 1.00875 | 79.6742 | 0.809 | 1.01125 | 74.4082 | 0.812 | 1.015 | 74.2704 |
| 0.9 | 0.912 | 1.01333 | 121.133 | 0.918 | 1.02 | 131.711 | 0.921 | 1.02333 | 115.059 |

termination of thermodynamic parameters for lead. Tangent construction at temperature of 800 K is shown in Fig. 2.

Review of the results obtained by the Oelsen's quantitative analysis, which includes activities, activity coefficients and partial molar quantities for lead in the investigated composition range in the temperature interval 600–1100 K, are given in Table 1.

Negative deviation from the Raoult's law can be noticed for lead activities in investigated samples up to the composition of $x_{\text{Pb}}=0.8$ at given temperatures. For higher lead concentrations, the slight positive deviation is observed. This indicates the existence of good miscibility in the greatest part of the system, characteristic of the behavior of lead, which can be explained by the interactions existing between lead and the other three components – bismuth, magnesium and antimony, as well as the known thermodynamic properties for the lead binary systems in the investigated Pb–Bi–Mg–Sb system. Since the chosen section is near to the lead–bismuth system, it is clear that the thermodynamic characteristics of this binary system will have a great influence on the thermodynamics of the Pb–Bi_xMg_ySb_z. That means, there are no such strong interactions in this case, as should be expected for the other sections in the investigated quaternary system, because intermetallic compounds are presented in Pb–Mg, Bi–Mg and Mg–Sb binaries, and also in constitutive ternaries.

Beside experimental measurements, thermodynamic predicting was done in the investigated Pb–Bi_xMg_ySb_z section using general solution model for the multi-component systems. Thermodynamic data needed for the further calculation, for six constitutive binaries Pb–Bi, Pb–Mg, Pb–Sb, Bi–Mg, Mg–Pb, Mg–Sb, were taken from Hultgren book [2]. Binary regular – solution parameters and similarity coefficients for these systems at the investigated temperature were calculated according to Eq. (2) and Eqs (3–5), respectively.

Based on these data, calculations were carried out according to Eq. (1) for all chosen alloys in the investigated section in the system Pb–Bi–Mg–Sb at the investigated temperatures in the interval 600–1100 K. The results of thermodynamic predicting according to general solution model, which includes integral molar excess Gibbs energies and activities for all four components in the system are given in Ta-

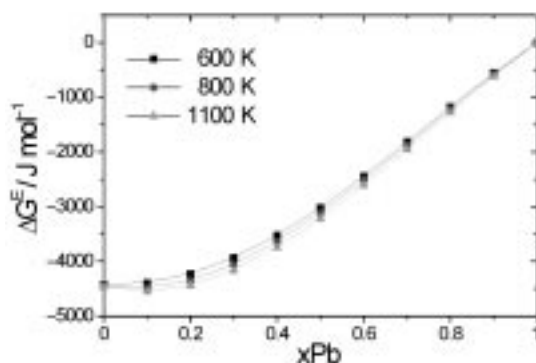


Fig. 3 ΔG^E dependence on composition at different temperatures

ble 2. The graphical presentation of ΔG^E vs. composition at different temperatures is shown in Fig. 3.

Table 2 Results of the thermodynamic predicting by general solution model

| x_{Pb} | $\Delta G^E/\text{J mol}^{-1}$ | a_{Pb} | a_{Bi} | a_{Mg} | a_{Sb} |
|-----------------|--------------------------------|-----------------|-----------------|-----------------|-----------------|
| a) $T=1100$ K | | | | | |
| 0.1 | -4552 | 0.0614 | 0.8349 | 0.0005 | 0.0347 |
| 0.2 | -4445 | 0.1463 | 0.6918 | 0.0005 | 0.0328 |
| 0.3 | -4165 | 0.2496 | 0.5543 | 0.0006 | 0.0304 |
| 0.4 | -3745 | 0.3639 | 0.4304 | 0.0006 | 0.0277 |
| 0.5 | -3216 | 0.4814 | 0.3238 | 0.0007 | 0.0246 |
| 0.6 | -2608 | 0.5962 | 0.2347 | 0.0008 | 0.0211 |
| 0.7 | -1952 | 0.7044 | 0.1613 | 0.0009 | 0.0172 |
| 0.8 | -1278 | 0.8058 | 0.1003 | 0.0009 | 0.0125 |
| 0.9 | -618 | 0.9026 | 0.0479 | 0.0008 | 0.0069 |
| b) $T=800$ K | | | | | |
| 0.1 | -4487 | 0.0545 | 0.8998 | 0.0001 | 0.0238 |
| 0.2 | -4351 | 0.1351 | 0.7263 | 0.0001 | 0.0237 |
| 0.3 | -4059 | 0.2382 | 0.5637 | 0.0001 | 0.0232 |
| 0.4 | -3638 | 0.3562 | 0.4222 | 0.0001 | 0.0222 |
| 0.5 | -3113 | 0.4794 | 0.3059 | 0.0001 | 0.0206 |
| 0.6 | -2514 | 0.5992 | 0.2138 | 0.0002 | 0.0184 |
| 0.7 | -1871 | 0.7100 | 0.1424 | 0.0002 | 0.0155 |
| 0.8 | -1215 | 0.8106 | 0.0866 | 0.0003 | 0.0117 |
| 0.9 | -580 | 0.9046 | 0.0411 | 0.0003 | 0.0067 |
| c) $T=600$ K | | | | | |
| 0.1 | -4394 | 0.0495 | 0.9860 | 0.0000 | 0.0162 |
| 0.2 | -4228 | 0.1243 | 0.7751 | 0.0000 | 0.0177 |
| 0.3 | -3934 | 0.2241 | 0.5824 | 0.0000 | 0.0185 |
| 0.4 | -3525 | 0.3434 | 0.4196 | 0.0000 | 0.0185 |
| 0.5 | -3020 | 0.4721 | 0.2908 | 0.0000 | 0.0177 |
| 0.6 | -2440 | 0.5988 | 0.1940 | 0.0000 | 0.0161 |
| 0.7 | -1814 | 0.7145 | 0.1236 | 0.0000 | 0.0137 |
| 0.8 | -1174 | 0.8159 | 0.0727 | 0.0001 | 0.0106 |
| 0.9 | -555 | 0.9070 | 0.0341 | 0.0001 | 0.0063 |

The obtained negative values for integral molar Gibbs excess energies point out to the miscibility in the system and interactions between the components, as confirmed experimentally. But, if one derives the activity coefficients for lead by using

predicting results, the slight positive deviation from the ideal behavior could be noticed for the lead thermodynamic behavior, at the same higher concentrations of lead, as for the experimentally obtained results. More detailed information on the phase

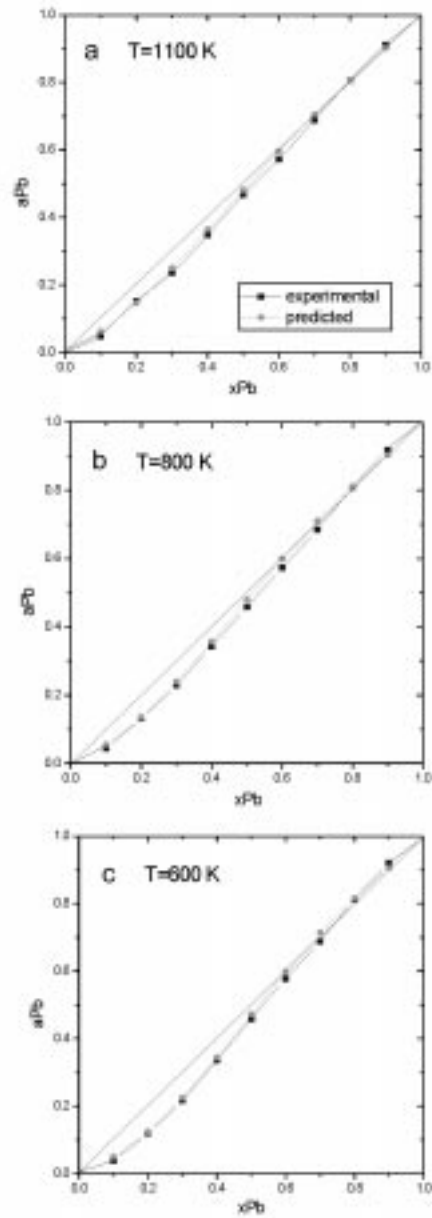


Fig. 4 The graphical comparison between experimental and predicted results different temperatures

equilibrium in the investigated section is needed for the explanation of the previous statement, but since there are no reports on the phase diagram of this section in the Pb–Bi–Mg–Sb system, further investigations should be done.

For the purpose of comparison between the experimental and predicted results, the activities for lead were compared at the temperatures 600, 800 and 1100 K. The graphical presentation is given in Fig. 4, where good mutual agreement could be noticed.

It can be concluded that, in cases of multicomponent systems, when the thermodynamic properties for only one, main component can be experimentally obtained, the comparative use of experimental measurements and thermodynamic predicting models gives more complete set of data, which enables the determination of the thermodynamic properties for all constituents as well as the integral molar quantities.

For this specific case of the Pb–Bi_xMg_ySb_z ($x:y:z=8:1:1$, mole ratio) section in the Pb–Bi–Mg–Sb quaternary system, concerning the lack of the reference thermodynamic data, such a comparative approach is of great importance for the knowledge of this system thermodynamics, and also for better understanding of the Kroll–Betterton process in the lead refining from bismuth by using magnesium and antimony.

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