THERMODYNAMIC MEASURES CALCULATION FOR Pb – Sb BINARY ALLOY SYSTEM USING REDLICH – KISTER THEORETICAL MODEL

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This paper aims to find a new thermodynamic model allowing the experimental data processing for the Pb – Sb binary system. The paper proposes a Redlich – Kister model as a kick off point for experimental data analysing. The obtained thermodynamic functions for the thermodynamic characterizing of the binary alloy system of Pb and Sb allowed the coverage of every interest point of temperature – concentration interconnection, with a high calculation precision.

Keywords: thermodynamic activity, activity coefficient, thermodynamic model, binary alloy system

1. Introduction

The publication number in the field of binary alloys thermodynamic revealed the importance of this type of binary system, Pb – Sb. Recent investigation on the Pb – Sb system had been realized by S. Hassam, D. Boa, Y. Fouque et.all in 2009 [1]. This research goup measured the mixing enthalpy of the Pb – Sb binary system at 973K in the interval $x_{Sb} = 0.2 - 0.6$. The integral molar energies values for the binary system In – Sb, Pb – Sb and In – Pb have been also calculated by Ansara respectively Ohtnai et all [2 – 4] and had been used as a starting point for the binary thermodynamic calculation. D. Manasijevic et all calculated the equilibrium phase in ternary In – Sb – Pb system [5 – 6].

The main objective of the paper is to find and apply a new thermodynamic model which allows a better experimental data processing. There was a huge concern regarding the determination of the thermodynamic measures of different

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binary or ternary [7-13] alloy system of Pb - Sb, resulting in a series of papers published in the scientific literature.

It is well known that the binary alloy system of the Pb – Sb present a high importance in the electro-technical industry, solder, hard lead, alloy for cable cover, used in printing, in the automobile industry as antifriction alloy. The thermodynamics of different alloys had been investigated by different researchers and the development of composite materials and high entropy alloys was based on the alloys thermodynamics and kinetics [17, 18, 19, 20].

The Pb – Sb with 90% Sn are used for soldering and for the typography Pb – Sn – Sb sometimes with 1.5%Bi increasing their fluidity in liquid state and time service. The most appreciated are babbit alloys having as a base Sb – Sn – Pb with 0.7% Cu, babbit alloys Pb – Sb with 0.25% - 1.1% Ca and 0.67 – 0.95% Na.

After a systematic study of the thermodynamic already known models [14 – 16] and using both some results for the scientific literature and the own experimental results the paper proposed an accurate analyze of the theoretical model Redlich – Kister.

This paper's novelty consist in working temperature (923K), a temperature not found the in the specialty literature.

The dependence of the thermodynamics' proprieties of the state parameter can t be accurate theoretical established, that's why the empirical relations (Margules formula) are used for describing these proprieties in the Pb-Sb system. Using the empirical relations is helpful in the practical solution of some elaboration problems for the alloys or for the metal thermic affinity, underlining more the conformity between the model and the experimental data and less the bound between the model and the interaction of elementary particles.

2. The theoretical model Redlich-Kister

In the *Redlich-Kister* model, the correlation between the coefficients is less than in the Margules model because the $q_p x_2^p$ are all null on $x_1 = x_2 = 0.5$, and their absolute values aren't at the x_2 concentration. This is the reason why the q_p coefficients aren't growing fast with high values in the same time with the growing of p and, as a result, the value of ΔG^E depends less on the total number of the terms of the series.

According to this model the Gibbs free energies for the integral molecular and partial molecular is calculated based on the relations (1-3):

$$\Delta G^E = x_1 x_2 \sum_{j=1}^{p} q_j \left(1 - 2x_2\right)^{j-1} \tag{1}$$

$$\Delta\overline{G}_1^E = x_2^2 \sum_{j=1}^{p} q_j \left[(2j-1-2jx_2)(1-2x_2)^{j-2} \right] \tag{2}$$

$$\Delta\overline{G}_2^E = x_1^2 \sum_{j=1}^{p} q_j \left[(1-2jx_2)(1-2x_2)^{j-2} \right] \tag{3}$$

For the calculation of the coefficients q_p the relation (2), for example, is transformed into the relation (4), as below:

$$\Delta\overline{G}_1^E = q_1 z_1 + q_2 z_2 + \cdots + q_p z_p, \tag{4}$$

In which:

$$z_1 = x_2^2, \quad z_2 = x_2^2(3-4x_2), \ldots, z_p = x_2^2(2p-1-2px_2)(1-2x_2)^{p-2} \tag{5}$$

It results the function:

$$\Phi = \sum_{i=1}^{n} (\tilde{y}_i - y_i)^2 \tag{6}$$

where $\tilde{y}_i = \sum_{j=1}^{p} q_j z_{j,i}$ is given by the relation (4) in"*i" point*, and y_i is referring to the experimental value of the excess molar partial quantities of the free energy ($\Delta\overline{G}_{1,i}^E$) in "*i"* point.

$$\Phi = \sum_{i=1}^{n} \left(q_1 z_{1,i} + q_2 z_{2,i} + \cdots + q_p z_{p,i} - \Delta\overline{G}_{1,i}^E \right)^2 \tag{7}$$

The partial derivate of the (7) function in connection with q_j, $j = 1,2,\ldots,p$ it is cancelled

$$\frac{\partial\Phi}{\partial q_1} = 2\sum_{i=1}^{n} z_{1,i} \left(q_1 z_{1,i} + q_2 z_{2,i} + \cdots + q_p z_{p,i} - \Delta\overline{G}_{1,i}^E \right) = 0 \tag{8}$$

$$\frac{\partial\Phi}{\partial q_2} = 2\sum_{i=1}^{n} z_{2,i} \left(q_1 z_{1,i} + q_2 z_{2,i} + \cdots + q_p z_{p,i} - \Delta\overline{G}_{1,i}^E \right) = 0 \tag{9}$$

$$\frac{\partial\Phi}{\partial q_p} = 2\sum_{i=1}^{n} z_{p,i} \left(q_1 z_{1,i} + q_2 z_{2,i} + \cdots + q_p z_{p,i} - \Delta\overline{G}_{1,i}^E \right) = 0 \tag{10}$$

And it is obtained a system of *p* equations with *p* unknowns:

$$q_1 \sum_{i=1}^{n} z_{1,i}^2 + q_2 \sum_{i=1}^{n} z_{1,i} z_{2,i} + \cdots + q_p \sum_{i=1}^{n} z_{1,i} z_{p,i} = \sum_{i=1}^{n} z_{1,i} \Delta\overline{G}_{1,i}^E \tag{11}$$

$$q_1 \sum_{i=1}^{n} z_{1,i} z_{2,i} + q_2 \sum_{i=1}^{n} z_{2,i}^2 + \cdots + q_p \sum_{i=1}^{n} z_{2,i} z_{p,i} = \sum_{i=1}^{n} z_{2,i} \Delta\overline{G}_{1,i}^E \tag{12}$$

$$q_1\sum_{i=1}^{n} z_{1,i}z_{p,i} + q_2\sum_{i=1}^{n} z_{2,i}z_{p,i} + \cdots + q_p\sum_{i=1}^{n} z_{p,i}^2 = \sum_{i=1}^{n} z_{p,i}\Delta\overline{G}_{1,i}^{E} \tag{13}$$

of which solutions q_j, $j = 1,2,...,p$ is allowing the determination of the excess thermodynamic measures .

3. The experimental method

For the determination of the thermodynamic activities in the binary alloy system of Pb-Sb the authors used the measurement of the electromotive force. The choice to use this method is made due to its high precision and reproducibility of the proven experimental data in other researches concerning the thermodynamic of the metallurgical melts.

The method is based on the measurement of the electromotive force in a galvanic cell having a reversible concentration with a liquid or solid electrolyte at a temperature in which weren't found available data in the scientific literature (923K). After the achievement of the measurement the data obtained were compared with the data obtained through the measurement of the electromotive force method of Seltz and DeWitt at 900 K and the data were certified with the Cochran measure.

For this criteria I obtained the calculate value G = 0.205 less than the tabled value $G_T = G_{0.05(1-10)} = 0.602$. This result indicates a better precision of the measurements and the relative average error is only of 4.09%, providing an adequate confidence in the used values.

4. Results and discussions

For the alloy system Pb-Sb the system solutions (11)-(13) leads to the following measurements of the activity coefficients (1–Pb; 2–Sb):

$$\ln\gamma_{Pb} = x_{Sb}^2\left[\begin{array}{c} -0.12265 - 0.03756(3-4x_{Sb}) - 0.05508(5-6x_{Sb})(1-2x_{Sb}) + \\ -0.01426(7-8x_{Sb})(1-2x_{Sb})^2 \end{array}\right] \tag{14}$$

$$\ln\gamma_{Sb} = x_{Pb}^2\left[\begin{array}{c} -0.11801 - 0.04067(1-4x_{Sb}) - 0.05378(1-6x_{Sb})(1-2x_{Sb}) + \\ -0.0207(1-8x_{Sb})(1-2x_{Sb})^2 \end{array}\right] \tag{15}$$

The values of the activity coefficients for Pb and Sb are measured with (14-15) and showed in the table1. Average square error of the *Redlich-Kister* model is $EMP_{\gamma Pb} = 3.403\times10^{-6}$.

Tabel 1

The values of the activity coefficients of Pb and Sb calculated with the Redlich-Kister model

Sb	.0	.1	.2	.3	.4	.5	.6	.7	.8	.9	.0
Pb	.00	.995	.986	.976	.968	.961	.954	.945	.931	.910	.882
Sb	.792	.877	.929	.958	.973	.981	.986	.991	.996	.999	.000

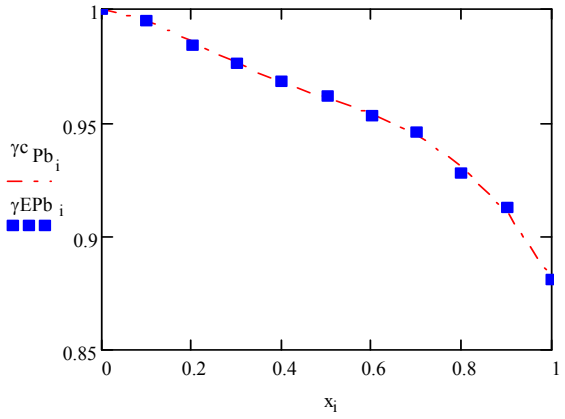

Fig. 1. Graphical comparison between the activity coefficient of Pb, experimental E and calculate value c realized with the help of the Redlich - Kister at temperature of 923K

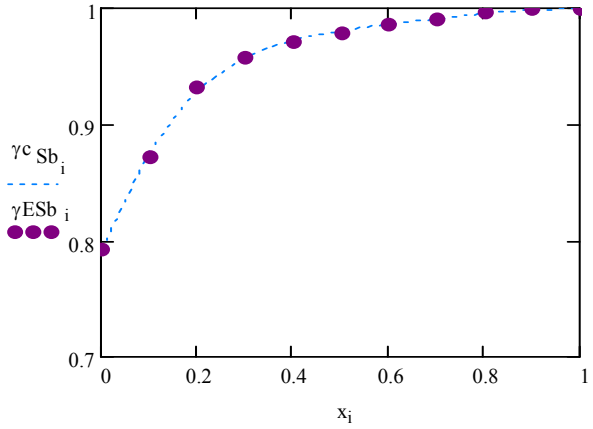

Fig. 2. Graphical comparison between the activity coefficient of Sb, experimental E and calculate value c realized with the help of the Redlich-Kister at temperature of 923K

The activity coefficient of Sb and Pb at 923K were calculated and a graphical comparios was realized with the data already known at the temperature of 900K

In Fig. 1 and 2 the graphical comparison between the activity coefficients experimentally determined and calculated with Redlich – Kister temperature at 923K of Pb and Sb are shown. The experimental data are following the calculated data meaning that the model used is very accurate.

This way of solving the problem is very useful for practical solving of some alloys production problems, to obtain composite materials, high entropy alloys or to thermal refining of the metals when the concordance between the model and the experimental data is very important.

5. Conclusions

The obtained Redlich – Kister models giving a better description of the thermodynamic proprieties of Pb and Sb and from the thermodynamic point of view both elements are acting similar.

The Redlich – Kister model is more precise for Pb and could be used as a reference model for other papers in this field.

The obtained thermodynamic functions for the thermodynamic characterizing of the binary alloy system of Pb and Sb, allow covering every interest point of temperature-concentration with a high precision through calculation.

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