ELSEVIER
Thermochimica Acta 362 (2000) 113–120
thermochimica acta
www.elsevier.com/locate/tca

Comparative thermodynamic study of the Pb–Bi_2Mg_3 system

Dragana Živković*, Živan Živković, Irena Tasić
University of Belgrade, Technical Faculty VJ 12, 19210 Bor, Yugoslavia

Received 28 February 2000; accepted 27 June 2000

Abstract

Results of the comparative thermodynamic study of the Pb–Bi_2Mg_3 system, obtained experimentally by Oelsen calorimetry and calculated by different predicting methods (general solution model, Toop, Hillert, Kohler, Muggianu) are given in this paper. Corresponding analytical expressions for the lead partial molar thermodynamic quantities were obtained by using Krupkowski method and Margules power series, comparatively. The phase diagram of the investigated system is also presented. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Alloy thermodynamics; Calorimetry; Thermodynamic predicting methods; Ternary system Pb–Bi–Mg

1. Introduction

One of the important parts of the refining process in the extractive metallurgy of lead is the separation of bismuth, because bismuth content higher than 0.05% causes the lower corrosion resistance of lead to sulfuric acid and has negative influence to the application of such quality lead in the accumulators production [1].

Kroll [2] discovered in 1922 that bismuth may be separated from lead by the addition of calcium, while Betterton and Lebedeff [3] pointed out the possibility of the mutual addition of calcium and magnesium in the lead refining process. It is also known that magnesium only could be used for the separation of bismuth from lead in the case of the refining lead with the bismuth content higher then 0.5% [4].

The correct theoretical interpretation of the phenomena occurring in the process of lead refining from bismuth is based on the knowledge of the ternary system Pb–Bi–Mg [1]. The basic fundamental aspect of this process was given by Davey [5,6], Betterton and Lebedeff [3], Silina and Ponomarev [4], Mallaley and Morris [7], who gave an important contribution to the Pb-rich region in the ternary Pb–Bi–Mg system.

The complete explanation of the investigated process is also connected with the knowledge of the Pb–Bi–Mg system thermodynamics, and for that reason, determination of the characteristic thermodynamic properties is important from the scientific and practical point of view. Relatively high investigating temperatures and magnesium oxidation make the experimental measuring difficult, so there is no complete experimentally obtained data for the whole system. Thermodynamic data are available in literature for the binaries Pb–Bi, Bi–Mg and Mg–Pb in Ref. [8], as well as the limited data for certain sections in the ternary system Pb–Bi–Mg [9–14].

In order to have a more complete knowledge of the Pb–Bi–Mg thermodynamics, results of the comparative study of the Pb–Bi_2Mg_3 system, obtained experimentally by Oelsen calorimetry and calculated by

---

* Corresponding author. Tel.: +381-30-424-547; fax: +381-30-424-547.
E-mail address: jmm@eunet.yu (D. Živković).

0040-6031/00/$ – see front matter © 2000 Elsevier Science B.V. All rights reserved.
PII: S0040-6031(00)00576-1

different predicting methods, such as general solution model [15], Toop [16], Hillert [17], Kohler [18] and Muggianu [19], are presented in this paper.

2. Experimental

Oelsen calorimetry was used for the thermodynamic analysis of the Pb–Bi_2Mg_3 system. Descriptions of this experimental technique are reported in Refs. [20–22].

The eight samples were chosen in the ternary system Pb–Bi–Mg, shown in Fig. 1, along the line of a constant molar ratio Bi:Mg=2:3. According to the requirements of the method used, the total volume of all samples was constant — 1 cm^3, and their composition and masses are given in Table 1.

Used metals were of the analytical grade.

The water equivalent was determined by a standard method using dissolved Na_2CO_3 and for the calorimeter used it was found to be 3868 J/°C.

All experiments were carried out in an air atmosphere.

3. Results and discussion

The calorimetric measurements and thermodynamic calculations were carried out in the Pb–Bi_2Mg_3 system, whose phase diagram is presented in the Fig. 2.

There is an excellent agreement between the literature [4] and experimental data based on the cooling curves obtained by Oelsen calorimetry. Eutectic type of the phase diagram is noticed, with the eutectic reaction at the temperature of 573 K, the eutectic point appearing at 98 wt.% Pb, 1.703 wt.% Bi and

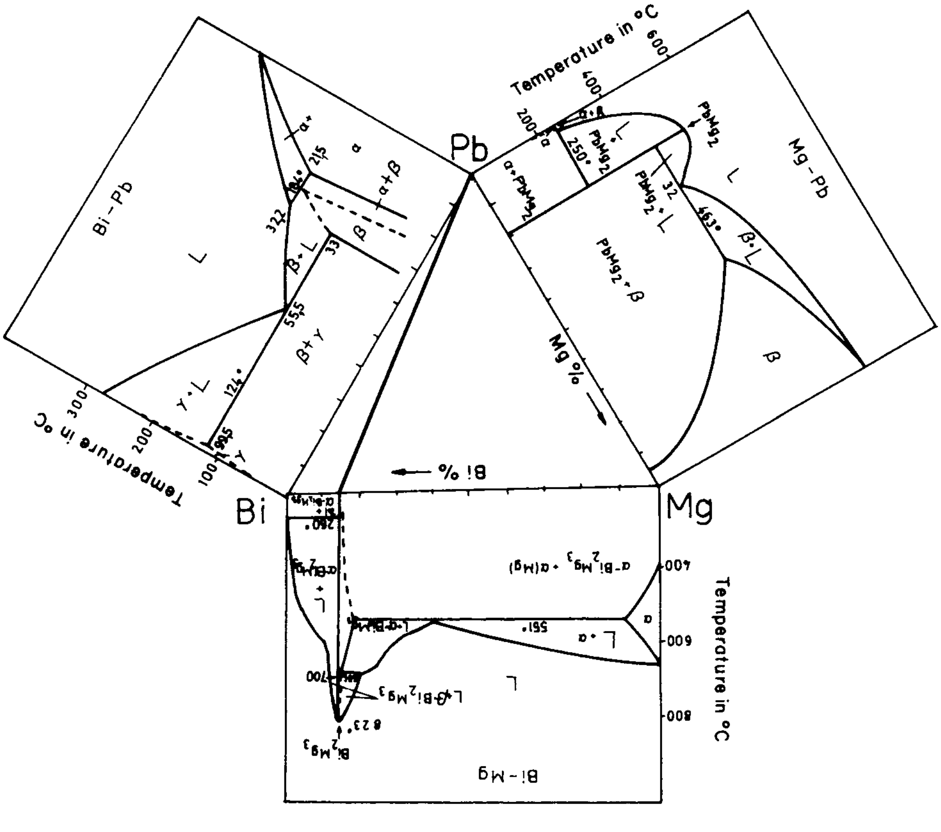

Fig. 1. The ternary system Pb–Bi–Mg with the indicated section Pb–Bi_2Mg_3.

Table 1
Composition and masses of the investigated samples

Alloy	Molar content			Weight percent (wt.%)			Mass, *m* (g)		
	Pb	Bi	Mg	Pb	Bi	Mg	Pb	Bi	Mg
A1	1	0	0	100	0	0	11.4	/	/
A2	0.959	0.016	0.025	98	1.703	0.297	10.961	0.191	0.033
A3	0.810	0.076	0.114	90	8.515	1.486	9.358	0.885	0.154
A4	0.487	0.205	0.308	60	25.544	4.456	5.752	2.449	0.427
A5	0.241	0.303	0.456	40	51.087	8.913	2.889	3.690	0.644
A6	0.02	0.392	0.588	4	81.739	14.261	0.237	4.840	0.845
A7	0.005	0.398	0.597	1	84.294	14.706	0.058	4.918	0.858
A8	0	0.4	0.6	0	85.146	14.854	/	4.943	0.862

0.297 wt.% Mg, and the occurrence of the ternary δ-solid solution based on lead below the eutectic temperature, as well as the phases αBi_2Mg_3 and βBi_2Mg_3.

Further, according to the recorded cooling curves, the temperature changes of the calorimeter used were determined for all samples in the investigated temperature interval 320–1073 K, which enabled the determination of the dependence of the calorimeter temperature change on the composition and temperature, given in Fig. 3, and the construction of the enthalpy isotherm diagram for the investigated temperature interval 320–1073 K presented in Fig. 4.

Following the basic equation in Oelsen's thermodynamic analysis [20–22] given as

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

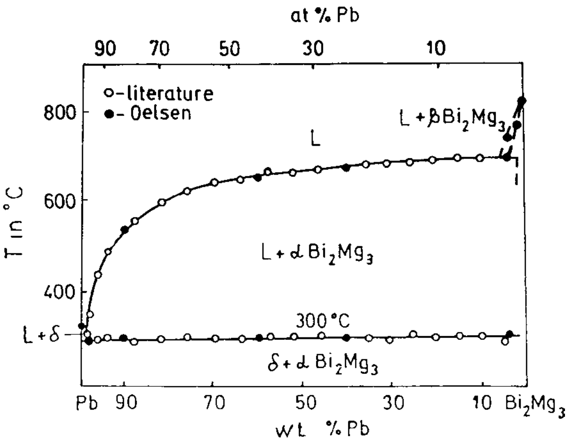

Fig. 2. Phase diagram of the $Pb–Bi_2Mg_3$ system.

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 the component *i*, further calculations in the thermodynamic analysis was done.

Based on Eq. (1) and the results of graphic planimetry, the tangent was constructed for the calculation of $-R \ln a_{Pb}$ at 973, 1023 and 1073 K, which enabled the determination of thermodynamic parameters for lead. Review of the results obtained by Oelsen's quantitative thermodynamic analysis, which include activities, activity coefficients and partial molar quantities for lead in the investigated composition range in the temperature interval 973–1073 K, are given in Table 2.

Positive deviation from the Raoult's law can be noticed for lead activities in all investigated samples at given temperatures, which causes the positive values for the partial molar excess Gibbs energies. This indicates the immiscibility existence in the system, characteristic for the behavior of lead. Having in mind the phase diagram of $Pb–Bi_2Mg_3$ system (Fig. 2), it is clear that the interactions between bismuth and magnesium, which form the intermetallic compound, are much stronger, comparing to the interactions between lead and other two components.

Beside the experimental investigation, different thermodynamic predicting models were used for the determination of the partial and integral thermodynamic properties in the $Pb–Bi_2Mg_3$ system, such as general solution model [15], Toop [16] and Hillert [17] asymmetric models, Kohler [18] and Muggianu [19]

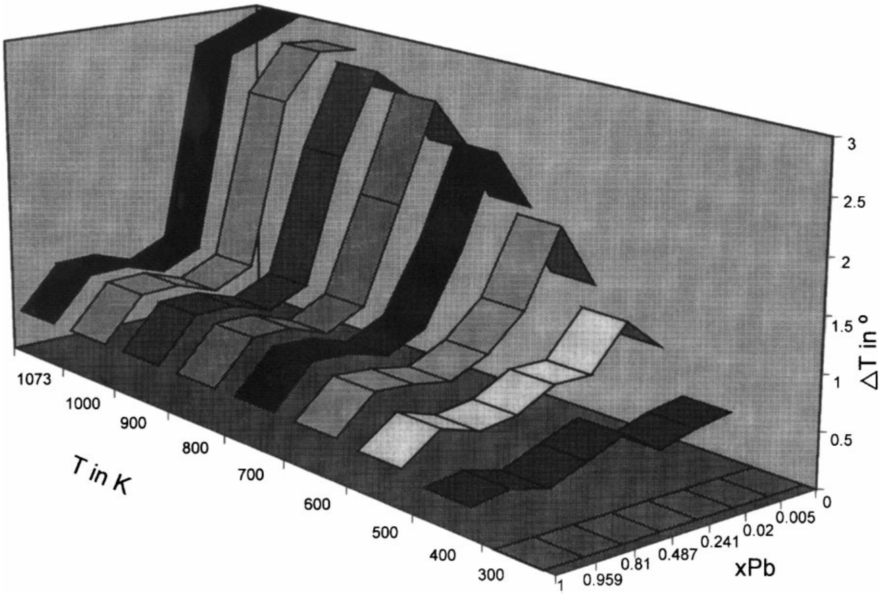

Fig. 3. The dependence of the calorimeter temperature change on composition and temperature.

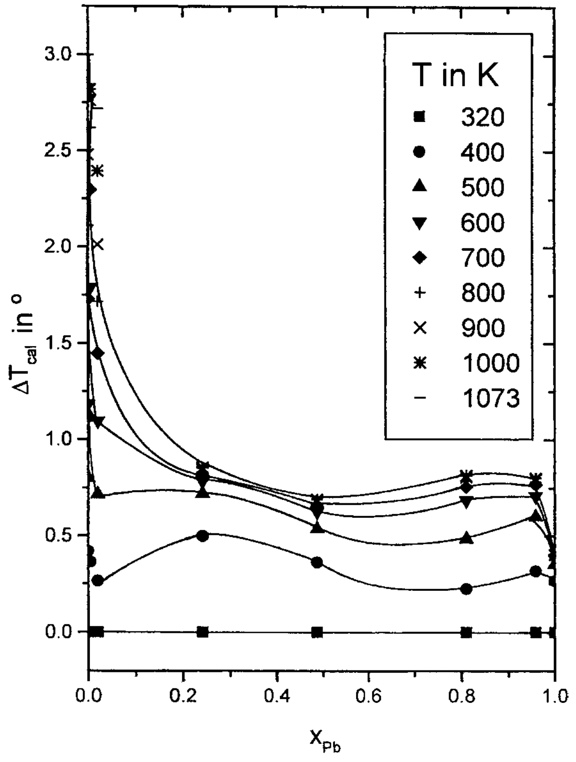

Fig. 4. The enthalpy isotherm diagram for the temperature interval 400–1100 K.

symmetric models. The main expressions for the thermodynamic calculation according to the mentioned models are given in Appendix A (Eqs. (A.1)-(A.10)).

Table 2
Results of the Oelsen's quantitative thermodynamic analysis (energies in J/mol)

T (K)	Alloy	a_{Pb}	γ_{Pb}	G^M_{Pb}	G^E_{Pb}
973	A2	0.970	1.011	−246	92
	A3	0.835	1.031	−1459	246
	A4	0.561	1.152	−4676	1144
	A5	0.300	1.245	−9740	1771
	A6	0.052	2.600	−23918	7730
	A7	0.022	4.400	−30875	11985
1023	A2	0.968	1.009	−277	79
	A3	0.815	1.006	−1740	52
	A4	0.541	1.118	−5225	894
	A5	0.289	1.199	−10558	1545
	A6	0.051	2.530	−25378	7895
	A7	0.021	4.260	−32737	12326
1073	A2	0.965	1.006	−318	56
	A3	0.805	1.015	−1749	131
	A4	0.535	1.099	−5579	834
	A5	0.286	1.187	−11167	1527
	A6	0.049	2.450	−26905	7994
	A7	0.021	4.200	−34464	12802

Table 3
Binary regular-solution parameters for Pb–Bi, Bi–Mg and Mg–Pb binaries at 973 K

Parameters (J/mol)	Pb–Bi	Bi–Mg	Mg–Pb
A^0_{ij}	−4977.71	−79266.8	−27215
A^1_{ij}	−126.553	43829	−14573.6
A^2_{ij}	555.979	27413.7	0
A^3_{ij}	217.803	42579.9	0

Thermodynamic data needed for the further calculations, for three constitutive binaries Pb–Bi, Bi–Mg and Mg–Pb at the temperature of 973 K, were taken from Hultgren book [8]. Binary regular-solution parameters and similarity coefficients for these systems at the investigated temperature were calculated according to (Eqs. (A.2) and (A.4)-(A.6)), respectively. The values of the parameters are shown in Table 3, while the values of the similarity coefficients are $\xi_{\mathrm{Pb-Bi}}$= 0.094, $\xi_{\mathrm{Bi-Mg}}$=0.683 and $\xi_{\mathrm{Mg-Pb}}$=0.818.

Based on these starting data, calculations were carried out according to the different predicting methods for all alloys in the investigated system Pb–Bi_2Mg_3 at a temperature of 973 K. The results of thermodynamic predictions according to different used models are given in Table 4, and good mutual agreement could be noticed from Fig. 5.

For the purpose of comparison between the experimental and predicted results, partial thermodynamic quantities for lead were calculated at the temperature 973 K based on the integral excess Gibbs energies determined from Kohler, Muggianu, Toop, Hillert and Chou results. The comparison is given by the dependence of ln γ_{Pb} on composition, and shown in Fig. 6.

Table 4
Integral excess Gibbs free energies, G^E (in J/mol), for the Pb–Bi_2Mg_3 system at 973 K calculated by different predicting methods

ΔG^E (J/mol at 973 K)					
x_{Pb}	Toop	Hillert	Chou	Kohler	Muggianu
1	0	0	0	0	0
0.959	−540	−535	−422	−470	−349
0.81	−2870	−2797	−2501	−2634	−2539
0.487	−10320	−9905	−9237	−9712	−9499
0.241	−16710	−14148	−15286	−16346	−13099
0.02	−21187	−21156	−20372	−21261	−21331
0.005	−21620	−21598	−20681	−21715	−21644
0	−21767	−21767	−20783	−21767	−21767

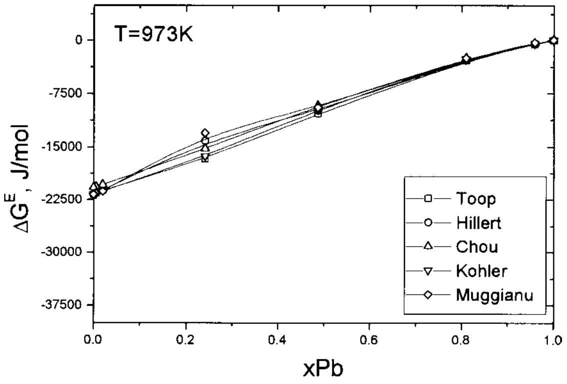

Fig. 5. Graphical representation of the predicted results.

As can be seen, different models results deviate differently from the experimental data. Relatively good agreement exists at the higher lead contents, but for the lower concentrations a greater deviation occurs for most of the used predicting models, except the Hillert model. Since the investigated system is an asymmetric system, according to the values of excess Gibbs energies for the constitutive binaries and values of the similarity coefficients, it could be expected that the asymmetric predicting models will give better results. Therefore, considering Fig. 6, the thermodynamic properties of lead in the Pb–Bi_2Mg_3 liquid alloys could be described mostly satisfactorily with the Hillert model.

In order to obtain the corresponding analytical expressions for the lead partial molar thermodynamic

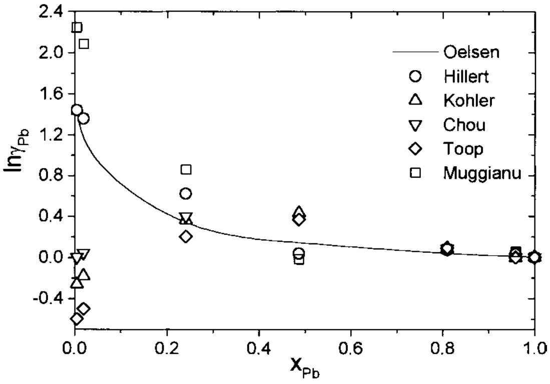

Fig. 6. The comparison between experimental and predicted results at 973 K.

Table 5
The comparasion between experimental, Margules and Krupkowski results for the lead activities

a_{Pb}									
T (K)	973			1023			1073		
x_{Pb}	Oelsen	Krupkow.	Margules	Oelsen	Krupkow.	Margules	Oelsen	Krupkow.	Margules
1	1	1	1	1	1	1	1	1	1
0.959	0.970	0.966	0.970	0.968	0.962	0.969	0.965	0.962	0.965
0.81	0.835	0.860	0.833	0.815	0.840	0.838	0.822	0.841	0.819
0.487	0.561	0.620	0.569	0.541	0.578	0.545	0.535	0.583	0.543
0.241	0.300	0.367	0.290	0.289	0.331	0.377	0.286	0.338	0.276
0.2	0.052	0.036	0.063	0.051	0.032	0.081	0.049	0.033	0.059
0.005	0.022	0.009	0.019	0.021	0.008	0.022	0.021	0.008	0.018
0	0	0	0	0	0	0	0	0	0

quantities, Margules power series [23] and Krupkowski method [24] were used comparatively. The main expressions for the mentioned methods are given in Appendix B Eqs. (B.1)-(B.4)).

Based on the experimentally obtained data for the investigated system, the appropriate models were applied and the thermodynamic description for the lead activity coefficients in the temperature interval 973–1073 K was done. The adequate analytical expressions obtained according to Margules power series [23] and Krupkowski method [24], are given as follows:

Margules power series results:

$$T=973\ \text{K}\quad \ln\gamma_{Pb}=0.42957(1-x_{Pb})-1/2\ (4.39585)(1-x_{Pb})^2+1/3\ (21.5754)\ (1-x_{Pb})^3-1/4\ (36.89137)\ (1-x_{Pb})^4+1/5\ (20.65277)\ (1-x_{Pb})^5$$

$$T=1023\ \text{K}\quad \ln\gamma_{Pb}=0.42802\ (1-x_{Pb})-1/2\ (5.77692)\ (1-x_{Pb})^2+1/3\ (26.4031)(1-x_{Pb})^3-1/4\ (42.84505)\ (1-x_{Pb})^4+1/5\ (23.13479)\ (1-x_{Pb})^5$$

$$T=1073\ \text{K}\quad \ln\gamma_{Pb}=0.27651(1-x_{Pb})-1/2\ (3.62255)(1-x_{Pb})^2+1/3\ (18.76194)\ (1-x_{Pb})^3-1/4\ (32.97605)\ (1-x_{Pb})^4+1/5\ (18.87516)\ (1-x_{Pb})^5$$

Krupkowski method results:

$$T=973\ \text{K}\quad \ln\gamma_{Pb}=0.61890\ (1-x_{Pb})^{1.41072}$$

$$T=1023\ \text{K}\quad \ln\gamma_{Pb}=0.49162\ (1-x_{Pb})^{1.57387}$$

$$T=1073\ \text{K}\quad \ln\gamma_{Pb}=0.52410\ (1-x_{Pb})^{1.59670}$$

These results were compared with the experimentally obtained data (in the example of lead activities), as presented in Table 5, while the graphical representation made for the temperature of 1073 K is shown in Fig. 7.

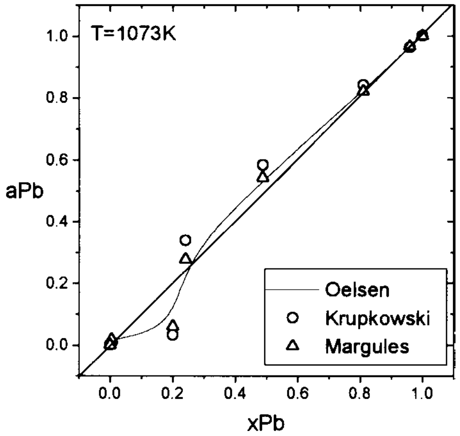

Fig. 7. Graphical review of the comparison at the temperature of 1073 K.

It can be concluded that the Margules power series results give better agreement with the experimental data, related to the applied Krupkowski method, for the investigated Pb–Bi_2Mg_3 system.

4. Conclusion

The thermodynamic properties of the Pb–Bi_2Mg_3 system were experimentally (Oelsen's calorimetry) and analytically (thermodynamic predicting models: Kohler, Muggianu, Toop, Hillert, Chou) determined and mutually compared. The obtained results show the most satisfying agreement between experimental data and data obtained by Hillert model, while the best approximation for the analytical expressions of the lead activity coefficient dependence on composition were done by Margules power series. Also, the phase diagram investigation confirmed the simple eutectic type of the investigated Pb–Bi_2Mg_3 system. All of these results could be useful in further interpretation of the phenomena occurring in the ternary Pb–Bi–Mg system, important in the lead refining from bismuth.

Appendix A.

The basic theoretical interpretations of the thermodynamic predicting models used in this paper are given as follows:

Chou model [15]

$$\begin{aligned} G^{\mathrm{E}} &= x_1x_2(A_{12}^0 + A_{12}^1(x_1 - x_2) + A_{12}^2(x_1 - x_2)^2) \\ &\quad + x_2x_3(A_{23}^0 + A_{23}^1(x_2 - x_3) + A_{23}^2(x_2 - x_3)^2) \\ &\quad + x_3x_1(A_{31}^0 + A_{31}^1(x_3 - x_1) + A_{31}^2(x_3 - x_1)^2) \\ &\quad + fx_1x_2x_3 \end{aligned} \qquad \text{(A.1)}$$

where $A_{ij}^0, A_{ij}^1, A_{ij}^2$ are parameters for binary system '*ij*' independent of composition, only relying on temperature, which have been used in the regular type equation:

$$\begin{aligned} G_{ij}^{\mathrm{E}} &= X_iX_j(A_{ij}^0 + A_{ij}^1(X_i - X_j) + A_{ij}^2(X_i - X_j)^2 \\ &\quad + \ldots + A_{ij}^n(X_i - X_j)^2) \end{aligned} \qquad \text{(A.2)}$$

where X_i and X_j indicate the mole fraction of component '*i*' and '*j*' in '*ij*' binary system. The function *f* is the ternary interaction coefficient expressed by

$$\begin{aligned} f &= (2\xi_{12} - 1)\{A_{12}^2((2\xi_{12} - 1)x_3 + 2(x_1 - x_2)) + A_{12}^1\} \\ &\quad + (2\xi_{23} - 1)\{A_{23}^2((2\xi_{23} - 1)x_1 \\ &\quad + 2(x_2 - x_3)) + A_{23}^1\} + (2\xi_{31} - 1) \\ &\quad \times \{A_{31}^2((2\xi_{31} - 1)x_2 + 2(x_3 - x_1)) + A_{31}^1\}, \end{aligned} \qquad \text{(A.3)}$$

where ξ_{ij} are the similarity coefficients defined by η_i called the deviation sum of squares:

$$\xi_{ij} = \frac{\eta_i}{(\eta_i + \eta_j)} \qquad \text{(A.4)}$$

where

$$\begin{aligned} \eta_{\mathrm{I}} &= \int_{X_i=0}^{X_i=1} (\Delta G_{12}^{\mathrm{E}} - \Delta G_{13}^{\mathrm{E}})^2 \mathrm{d}X_1 \\ \eta_{\mathrm{II}} &= \int_{X_i=0}^{X_i=1} (\Delta G_{21}^{\mathrm{E}} - \Delta G_{23}^{\mathrm{E}})^2 \mathrm{d}X_2 \\ \eta_{\mathrm{III}} &= \int_{X_i=0}^{X_i=1} (\Delta G_{31}^{\mathrm{E}} - \Delta G_{32}^{\mathrm{E}})^2 \mathrm{d}X_3, \end{aligned} \qquad \text{(A.5)}$$

and

$$\begin{aligned} X_{1(12)} &= x_1 + x_3\xi_{12} \\ X_{2(23)} &= x_2 + x_1\xi_{23} \\ X_{3(31)} &= x_3 + x_2\xi_{31} \end{aligned} \qquad \text{(A.6)}$$

Toop model [16]

$$\begin{aligned} G^{\mathrm{E}} &= \frac{x_2}{1 - x_1}\Delta G_{12}^{\mathrm{E}}(x_1; 1 - x_1) \\ &\quad + \frac{x_3}{1 - x_1}\Delta G_{13}^{\mathrm{E}}(x_1; 1 - x_1) \\ &\quad + (x_2 + x_3)^2\Delta G_{23}^{\mathrm{E}}\left(\frac{x_2}{x_2 + x_3}; \frac{x_3}{x_2 + x_3}\right) \end{aligned} \qquad \text{(A.7)}$$

Hillert model [17]

$$\begin{aligned} G^{\mathrm{E}} &= \frac{x_2}{1 - x_1}\Delta G_{12}^{\mathrm{E}}(x_1; 1 - x_1) \\ &\quad + \frac{x_3}{1 - x_1}\Delta G_{13}^{\mathrm{E}}(x_1; 1 - x_1) \\ &\quad + \frac{x_2x_3}{v_{23}v_{32}}\Delta G_{23}^{\mathrm{E}}(v_{23}; v_{32}) \end{aligned} \qquad \text{(A.8)}$$

where v_{ij}=1/2 (1+x_i−x_j).

Kohler model [18]

$$\begin{aligned} G^{\mathrm{E}} &= (x_1 + x_2)^2\Delta G_{12}^{\mathrm{E}}\left(\frac{x_1}{x_1 + x_2}; \frac{x_2}{x_1 + x_2}\right) \\ &\quad + (x_2 + x_3)^2\Delta G_{23}^{\mathrm{E}}\left(\frac{x_2}{x_2 + x_3}; \frac{x_3}{x_2 + x_3}\right) \\ &\quad + (x_3 + x_1)^2\Delta G_{31}^{\mathrm{E}}\left(\frac{x_{31}}{x_1 + x_3}; \frac{x_1}{x_1 + x_3}\right) \end{aligned} \qquad \text{(A.9)}$$

Bonnier model [19]

$$G^{\mathrm{E}} = \left[\frac{x_2}{(1 - x_1)}\right]G_{12}^{\mathrm{E}} + \left[\frac{x_3}{(1 - x_1)}\right]G_{13}^{\mathrm{E}} + (1 - x_1)G_{23}^{\mathrm{E}} \qquad \text{(A.10)}$$

In all given equations, G^E and G^E_{ij} correspond to the integral molar excess Gibbs energies for ternary and binary systems, respectively, while x_1, x_2, x_3 correspond to the mole fraction of components in investigated ternary system.

Appendix B.

The main expressions for the methods used in the analytical representation of the experimentally obtained results are given as follows:

Margules power series [23]

$$G_i^E = RT\ln\gamma_i = RT\{\alpha_1(1-x_i) + \tfrac{1}{2}\alpha_2(1-x_i)^2 + \tfrac{1}{3}\alpha_3(1-x_i)^3 + \tfrac{1}{4}\alpha_4(1-x_i)^4 + \ldots\} \tag{B.1}$$

Krupkowski equation [24]

$$G^E = RT(\ln\gamma_i + \ln\gamma_j) \tag{B.2}$$

where are

$$\ln\gamma_i = \omega(T)(1-x_i)^m$$
$$\ln\gamma_j = \omega(T)\left\{\frac{[(1-x_i)^m - m(1-x_i)^{m-1}]}{[(m-1)+(m-1)^{-1}]}\right\} \tag{B.3}$$

and where m is the parameter, which has values in the interval (1–2) for systems with positive deviation from Raoult law and $\omega(T)$ is the temperature function in form:

$$\omega(T) = \frac{C_1}{(T-C_2)} \tag{B.4}$$

where C_1 and C_2 are constants independent of temperature and composition.

References

[1] M.P. Smirnov, Rafinirovanie svinca i pererabotka poluproduktov, Metallurgia, Moscow, 1977.
[2] W.J. Kroll, Metall und Erz 19 (1922) 317.
[3] J.A. Betterton, J. Lebedeff, Trans. Am. Inst. Min. Eng. 121 (1936) 205.
[4] J.K. Silina, V.D. Ponomarev, IZVUZ Cvetnaya Metallurgia 1 (1960) 91.
[5] T.R.A. Davey, J. Metals 3 (1956) 341.
[6] T.R.A. Davey, Z. Erz. Metallhuttenwes 2 (1957) 87.
[7] K. Mallaley, D.R. Morris, Canad. Metall. Quart. 29 (1990) 67.
[8] R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, K. Kelley, The Selected Values of the Thermodynamic Properties of Binary Alloys, ASM, Metals Park, OH, 1973.
[9] M.M. Alger, C.A. Eckert, Ind. Eng. Chem. 25 (3) (1986) 416.
[10] W.J. Howel, C.A. Eckert, Z. Metallknd. 81 (5) (1990) 335.
[11] D. Živković, Z. Živković, J. Šestak, Thermochim. Acta 230 (1993) 65.
[12] D. Živković, Z. Živković, J. Šestak, Thermochim. Acta 230 (1993) 77.
[13] D. Živković, Z. Živković, J. Šestak, J. Therm. Anal. 42 (1994) 521.
[14] Z. Živković, D. Živković, Min. Metall. Quart. 43 (3-4) (1996) 209.
[15] K.C. Chou, CALPHAD 19 (3) (1995) 315.
[16] G.W. Toop, Trans. Met. Soc. AIME 233 (1965) 850.
[17] M. Hillert, CALPHAD 4 (1980) 1.
[18] F. Kohler, Monatsh. Chem. 91 (1960) 738.
[19] Y.M. Muggianu, M. Gambino, J.P. Bross, J. Chimie Physique 72 (1975) 83.
[20] W. Oelsen, P. Zuhlke, Arch. Eisenhuttenwess 27 (1956) 743.
[21] W. Oelsen, E. Schurmann, H.J. Weigt, O. Oelsen, Arch. Eisenhuttenwess 27 (1956) 487.
[22] W. Oelsen, F. Bieret, G. Schwabe, Arch. Eisenhuttenwess 27 (1956) 607.
[23] M. Margules, Akad. Wiss. Vienna 104 (1895) 1243.
[24] A. Krupkowski, Bull. Acad. Polon. Sci. Lett. A 1 (1950) 15.