Thermodynamics and characterisation of alloys in Sb–PbBi_eut section in ternary Pb–Bi–Sb system

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Abstract

The results of thermodynamic investigation and characterisation of alloys in the Sb–PbBi_eut section in ternary Pb–Bi–Sb system are presented in this paper. Experimental calorimetric investigations were done according to Oelsen's method, while general solution model was applied for thermodynamic predicting. Activities, activity coefficients, partial molar quantities for antimony and integral molar quantities were obtained at temperature of 873 and 973 K. Also, characterisation of the obtained alloys was done according of DTA and optic microscopy.
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Keywords: Thermodynamics; Ternary systems; Pb–Bi–Sb alloys; Characterisation

1. Introduction

Beyond the systems Pb–Bi–Ca and Pb–Bi–Mg, ternary system Pb–Bi–Sb is the important one in the process of lead refining from bismuth [1]. The basic fundamental aspects of the processes occurring in these systems was already given in literature [2–9], as well as the results of investigation of the technological parameters typical for the separation of bismuth by addition of calcium, magnesium or antimony in the extractive metallurgy of lead [1–3,10].

Although complete explanation of the investigated process is connected with the knowledge of the Pb–Bi–Sb system thermodynamics, relatively high investigating temperatures and oxidation of the constituent components make the experimental measuring

difficult, so there is a lack of experimentally obtained data for this system. Thermodynamic data are available in literature for the binaries Pb–Bi, Bi–Sb and Sb–Pb in [11], while data for the ternary Pb–Bi–Sb system, determined by Živković et al. [12] for certain sections in the ternary system Pb–Bi–Sb, were obtained analytically by thermodynamic predicting.

As a part of the experimental investigations of Pb–Bi–Sb thermodynamics, results of the comparative study of the Sb–PbBi_eut section (PbBi_eut occurs at the molar ratio of Pb:Bi = 0.44:0.56), obtained experimentally by Oelsen calorimetry [13–15] and calculated by general solution model [16], are presented in this paper. Investigated alloys were characterised by means of DTA and optic microscopy.

2. Experimental

Oelsen calorimetry was used for the thermodynamic analysis of the Sb–PbBi_eut section in the ternary

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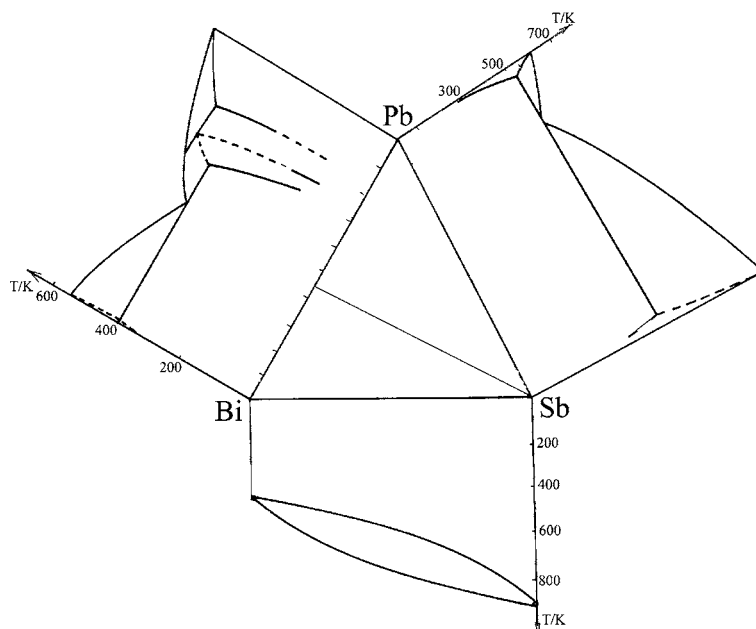*E-mail address:* jmm@eunet.yu (D. Živković).

Fig. 1. The ternary system Pb–Bi–Sb with the indicated section Sb–PbBi$_{eut}$.

system Pb–Bi–Sb. Description of this experimental technique is reported in [13–15].

The nine samples were chosen in the investigated section, along the line from antimony corner to the eutectic point in binary Pb–Bi system, which occurs at the molar ratio of Pb:Bi = 0.44:0.56, Fig. 1. 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.

The water equivalent was determined by a standard method using dissolved Na$_2$CO$_3$ and for the calorimeter used it was found to be 3314 J/K.

All experiments were carried out in an air atmosphere, with metals of the analytical grade.

DTA curves have been recorded on derivatograph MOM, Budapest (Hungary), at heating rate of 10°/min in an air atmosphere, while Al$_2$O$_3$ was used as a referent material during measurements.

Microstructure analysis of the investigated samples was examined by optical microscopy, using a Reichert MeF2 microscope. Solution of (8 ml H$_2$SO$_4$ + 2 g K$_2$Cr$_2$O$_7$) was applied for structure development.

Table 1
Composition and masses of the investigated samples

| Alloy	Pb (wt.%)	Bi (wt.%)	Sb (wt.%)	x_{Pb}	x_{Bi}	x_{Sb}	m_{Pb} (g)	m_{Bi} (g)	m_{Sb} (g)	m_{tot} (g)
A1	43.8	56.2	0	0.44	0.56	0	4.5736	5.8683	0	10.4419
A2	39	51	10	0.366	0.474	0.16	3.8529	5.0385	0.9879	9.8793
A3	31	39	30	0.257	0.32	0.423	2.7704	3.4853	2.681	8.9367
A4	22	28	50	0.163	0.206	0.631	1.7927	2.2816	4.0743	8.1486
A5	13	17	70	0.087	0.113	0.8	0.9735	1.273	5.2418	7.4883
A6	4.4	5.6	90	0.027	0.034	0.939	0.3049	0.3881	6.2368	6.9298
A7	2.2	2.8	95	0.013	0.017	0.97	0.1497	0.1905	6.4625	6.8027
A8	1.3	1.7	97	0.008	0.01	0.982	0.0878	0.1148	6.5503	6.7529
A9	0	0	100	0	0	1	0	0	6.68	6.68
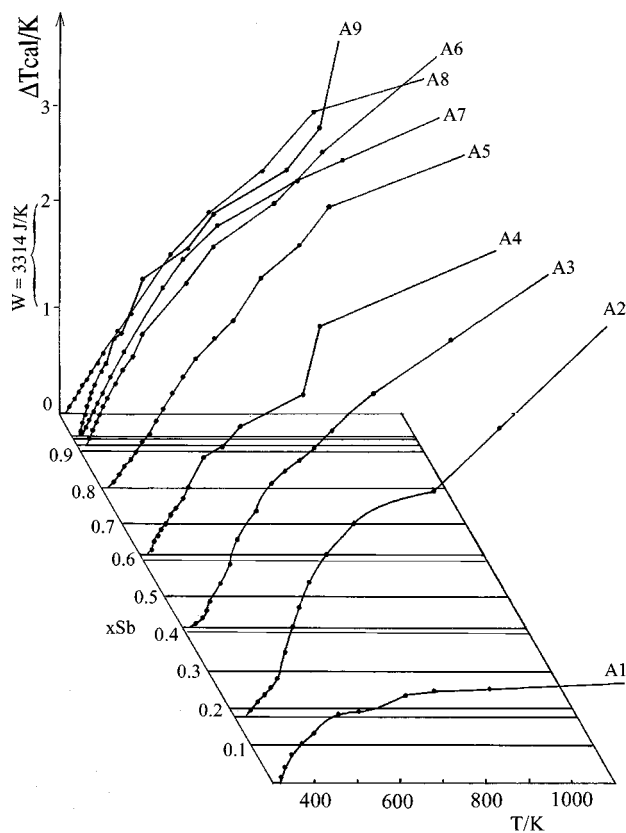
Fig. 2. Space enthalpy diagram for the investigated section.

3. Results and discussion

Based on the cooling curves obtained by Oelsen's calorimetry, the temperature changes of the calorimeter used were determined for all samples in the investigated temperature interval 350–1100 K. That enabled the determination of the dependence of the calorimeter temperature change on the composition and temperature, shown in Fig. 2, and the construction of the enthalpy isotherm diagram for the investigated temperature interval 350–1100 K, presented in Fig. 3.

Following the basic equation in Oelsen's thermodynamic analysis [13–15]:

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

(where G_i^M is the partial Gibbs energy of mixing for the component i, T_0 the starting temperature, T the fi-

nite 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 is the activity of the component i), further calculations in the thermodynamic analysis were done. Based on Eq. (1) and the results of graphic planimetry, the tangent was constructed for the calculation of $-R \ln a_{\mathrm{Sb}}$ at 873 and 973 K, which enabled the determination of antimony activities, activity coefficients and partial molar quantities. The results are given in Table 2.

Slight deviation from Raoult's law could be noticed in whole concentration area at both temperatures investigated. This deviation shows a negative trend for temperature of 873 K, while at temperature of 973 K negative trend is characteristic for higher contents of antimony. Further, partial molar excess Gibbs energies for antimony have negative values in whole concentration area at both temperatures.
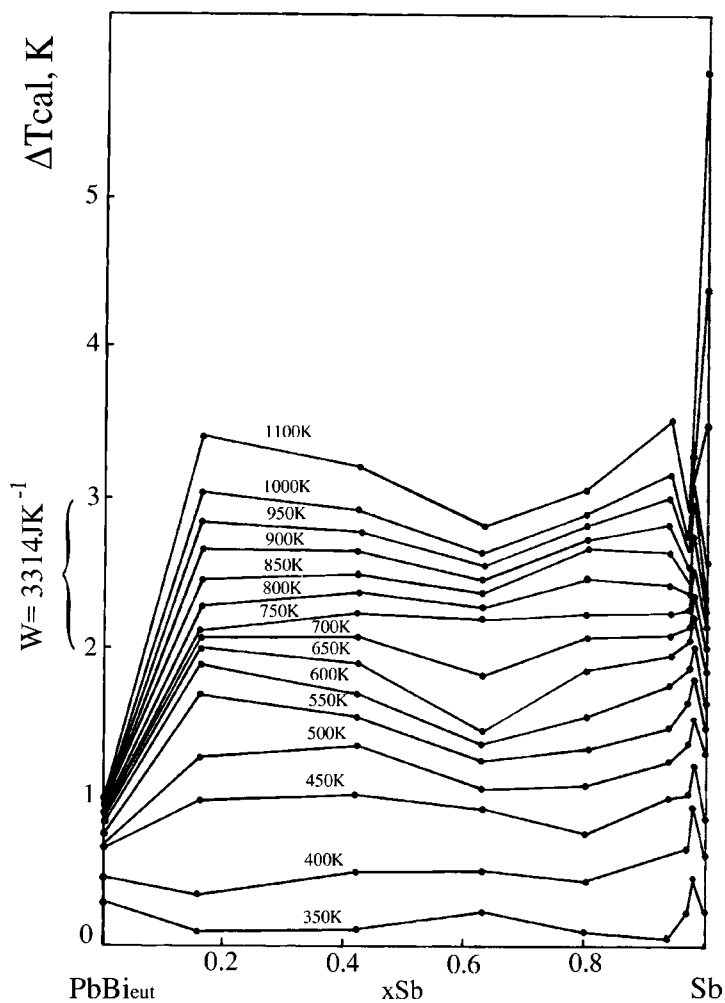
Fig. 3. The enthalpy isotherm diagram for the temperature interval 350–1100 K.

Table 2
Results of the Oelsen's quantitative thermodynamic analysis at 873 and 973 K (energies in J/mol)

Alloy	x_{Sb}	a_{Sb} (873 K)	γ_{Sb} (873 K)	G_{Sb}^{E} (873 K)	G_{Sb}^{M} (873 K)	a_{Sb} (973 K)	γ_{Sb} (973 K)	G_{Sb}^{E} (973 K)	G_{Sb}^{M} (973 K)
A1	0	0	–	–	–	0	–	–	–
A2	0.16	0.123	0.76875	−1908.81	−15209.9	0.184	1.15	1130.607	−13694.1
A3	0.423	0.373	0.881797	−913.026	−7157.79	0.421	0.995272	−38.339	−6998.43
A4	0.631	0.611	0.968304	−233.776	−3575.77	0.675	1.069731	545.289	−3179.53
A5	0.8	0.798	0.9975	−18.168	−1637.77	0.837	1.04625	365.7462	−1439.38
A6	0.939	0.876	0.932907	−504.072	−960.897	0.902	0.960596	−325.207	−834.359
A7	0.97	0.908	0.936082	−479.411	−700.488	0.939	0.968041	−262.752	−509.153
A8	0.982	0.959	0.976578	−172.019	−303.856	0.978	0.995927	−33.0185	−179.956
A9	1	1	1	0	0	1	1	0	0

Table 3
Binary parameters and similarity coefficients at 873 K for systems Pb–Bi, Bi–Sb and Sb–Pb

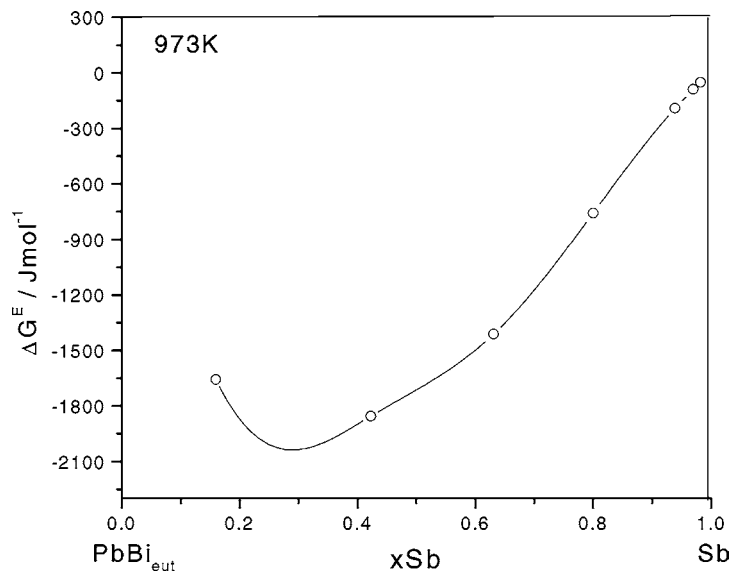| System ij	A_{ij}^0	A_{ij}^1	A_{ij}^2	A_{ij}^3	ξ_{ij}
Pb–Bi	−4977.66	−127.205	555.6138	218.9122	0.396
Bi–Sb	−9112.03	1129.861	6906.111	5063.605	0.24
Sb–Pb	−2106.21	5.9949	200.9536	−246.222	0.829

Table 4
Results of the thermodynamic predicting according to Chou's general solution model (energies in J/mol)

Alloy	x_{Sb}	f_{123}	ΔG_{123}^E	G_{Sb}^E	γ_{Sb}	a_{Sb}
A1	0					
A2	0.16	−2231.18	−1657	−3517	0.625	0.1
A3	0.423	643.0438	−1854	−1347	0.835	0.353
A4	0.631	2478.731	−1411	−194	0.974	0.615
A5	0.8	3822.487	−757	80	1.011	0.809
A6	0.939	5478.813	−192	29	1.004	0.943
A7	0.97	5837.347	−89	10	1.001	0.971
A8	0.982	5980.73	−51	5	1.0007	0.983
A9	1				1	1

For Oelsen's calorimetry results are related only to antimony, thermodynamic predicting according to Chou's general solution model [16] was applied in order to obtain the integral thermodynamic quantities in the investigated section of the ternary system Pb–Bi–Sb. This model is based on the knowledge of thermodynamic data for constituent binary subsystems. The basic theoretical interpretations of this method are given:

$$
\begin{aligned}
G^E = {} & x_1 x_2 (A_{12}^0 + A_{12}^1 (x_1 - x_2) + A_{12}^2 (x_1 - x_2)^2) \\
& + x_2 x_3 (A_{23}^0 + A_{23}^1 (x_2 - x_3) + A_{23}^2 (x_2 - x_3)^2) \\
& + x_3 x_1 (A_{31}^0 + A_{31}^1 (x_3 - x_1) \\
& + A_{31}^2 (x_3 - x_1)^2) + f x_1 x_2 x_3
\end{aligned}
\tag{2}
$$

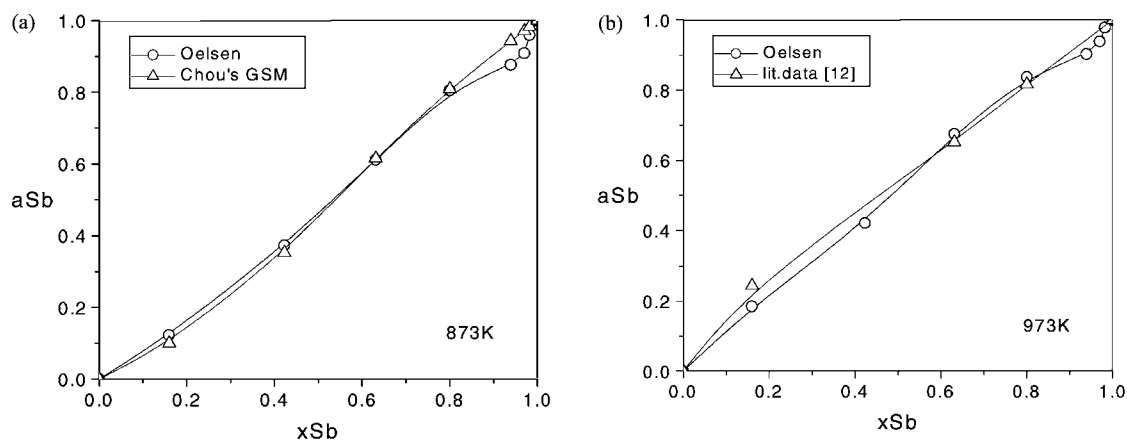Fig. 4. Dependence of predicted ΔG^E on x_{Sb} at 873 K.

Fig. 5. Comparison between experimentally obtained, predicted and literature data for antimony activities: (a) at 873 K; (b) at 973 K.

where A_{ij}^0, A_{ij}^1, A_{ij}^2 are parameters for binary system "*ij*" independent of composition, only relying on temperature, and x_1, x_2, x_3 correspond to the mole fraction of components in investigated ternary system, which

have been used in the regular type equation:

$$G_{ij}^E = X_i X_j (A_{ij}^0 + A_{ij}^1 (X_i - X_j) \\ + A_{ij}^2 (X_i - X_j)^2 + \cdots + A_{ij}^n (X_i - X_j)^2) \quad (3)$$
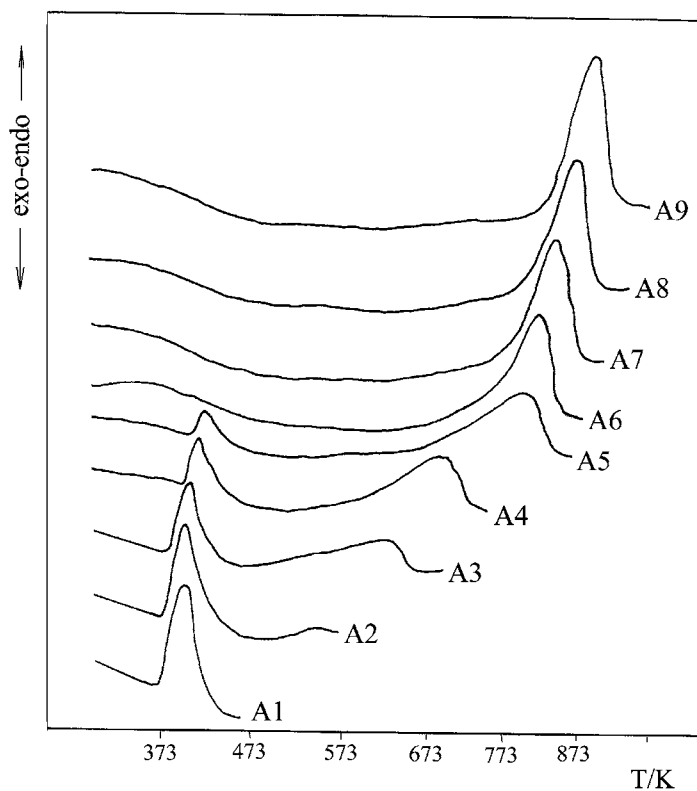

Fig. 6. DTA curves for samples with $x_{Sb} = 0.1$–0.9 obtained at the heating rate of $10\,°C\,min^{-1}$ in an air atmosphere.

where X_i and X_j indicate the mole fraction of component "i" and "j" in "ij" binary system and function f is the ternary interaction coefficient [16], while in given Eqs. (2) and (3), G^E and G_{ij}^E correspond to the integral molar excess Gibbs energies for ternary and binary systems, respectively.

Values for the integral molar excess Gibbs energies for the constituent binary systems Pb–Bi, Bi–Sb and Sb–Pb, available in the literature for the tempera-

ture of 873 K [11], were used as starting data for the calculation, and their binary parameters calculated by Eq. (3) are presented in Table 3. Also, similarity coefficients for three constituent binary systems, calculated according to Chou's analytical procedure [16], are presented in the same table.

Based on these data and according to Eq. (2), thermodynamic prediction was done for the selected alloys (Table 1) in the Sb–PbBi$_{eut}$ section of the Pb–Bi–Sb
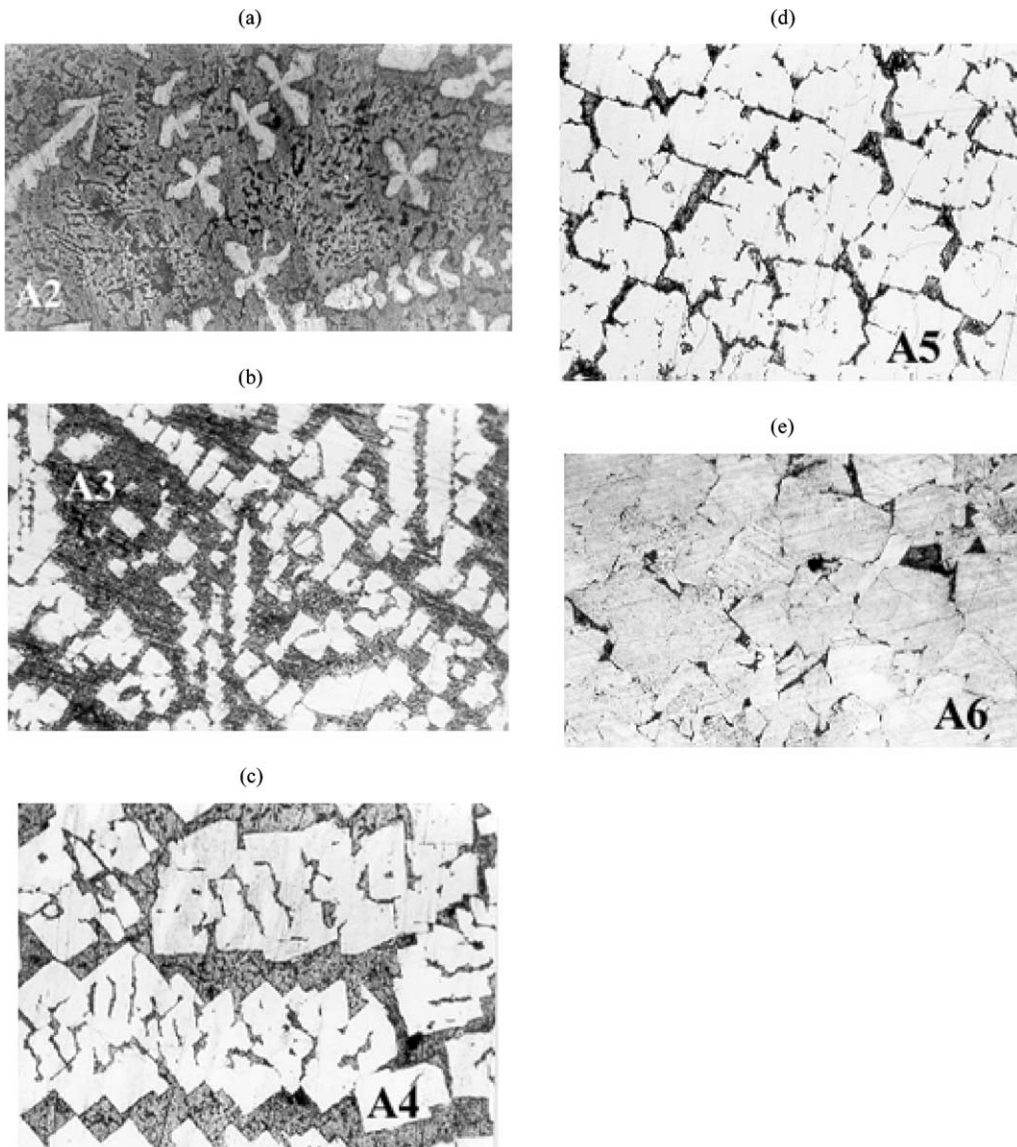

Fig. 7. Microphotographs for samples A2 (a), A3 (b), A4 (c), A5 (d) and A6 (e).

system, and values of the integral molar excess Gibbs energies and ternary interaction coefficients were determined. In order to compare the experimental results with the predicted ones, partial thermodynamic quantities for antimony were derived according to the following equation: $G^{\mathrm{E}}_{\mathrm{Sb}} = G^{\mathrm{E}} + (1 - x_{\mathrm{Sb}})(\partial G^{\mathrm{E}} / \partial x_{\mathrm{Sb}})$.

The results of thermodynamic prediction, as well as the derived values for antimony thermodynamic quantities, are shown in Table 4, while dependence of integral molar Gibbs excess energies on composition is given in Fig. 4.

As can be seen, negative values for the integral molar excess Gibbs energies were obtained in the whole concentration range of the Sb–PbBi$_{\mathrm{eut}}$ section. Slight deviation from Raoult's law is noticed: negative trend at lower antimony contents and weak positive trend— almost ideal, at higher antimony contents.

Furthermore, comparison between the experimentally obtained, predicted and literature data [12] for activities of antimony at investigated temperatures shows relatively good agreement, as presented in Fig. 5.

For the characterisation of investigated alloys, DTA results and optic microscopy were used.

Results obtained by DTA for alloys with $x_{\mathrm{Sb}} = 0.1$, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 and 0.9 are shown in Fig. 6, while microphotographs of the samples A2–A6 are presented in Fig. 7.

Microstructure analysis of the investigated samples shows expected structure of primary solidified antimony crystals surrounded by $(\alpha + \varepsilon)$ eutectics. By increasing of antimony molar content, quantity of primary crystals with regular geometrical shapes is increased. For the samples with the highest content of antimony, structure consists of crystal base of antimony surrounded with precipitated secondary intermediate phases.

4. Conclusion

Comparative thermodynamic analysis of the Sb–PbBi$_{\mathrm{eut}}$ section in the Pb–Bi–Sb system was done based on the experimental calorimetric investigations according to Oelsen's method and thermodynamic prediction by Chou's general solution model. Values for the activities, activity coefficients, partial molar quantities for antimony at 873 and 973 K, and integral molar quantities at a temperature of 873 K were obtained and their comparison shows good agreement. Slight deviation from ideal behaviour is characteristic for the alloys in whole concentration area and at both investigated temperatures. Characterisation of the investigated alloys was done by DTA and optic microscopy.

References

[1] M.P. Smirnov, Rafinirovanie svinca i pererabotka polupro-duktov, Metallurgia, Moscow, 1977 (in Russian).
[2] W.J. Kroll, Metall und Erz 19 (1922) 317.
[3] J.A. Betterton, J. Lebedeff, Trans. Am. Inst. Miner. Eng. 121 (1936) 205.
[4] T.R.A. Davey, Z. Erz. Metallhuttenwes. 2 (1957) 87.
[5] J.K. Silina, V.D. Ponomarev, IZVUZ Cvetnaya Metal. 1 (1960) 91.
[6] K. Mallaley, D.R. Morris, Canad. Metall. Quart. 29 (1990) 67.
[7] D. Živković, Ž. Živkovic, J. Šestak, Thermochim. Acta 230 (1993) 65.
[8] D. Živković, Ž. Živković, D. Grujičić, J. Therm. Anal. 54 (1998) 41.
[9] D. Živković, Ž. Živković, I. Tasić, Thermochim. Acta 362 (2000) 113.
[10] T.R.A. Davey, J. Metals 3 (1956) 341.
[11] 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.
[12] D. Živković, Ž. Živković, N. Štrbac, J. Chem. Technol. Rep. Srp. 39 (1997) 103 (in Serbian).
[13] W. Oelsen, P. Zuhlke, Arch. Eisenhuttenwess. 27 (1956) 743.
[14] W. Oelsen, E. Schurmann, H.J. Weigt, O. Oelsen, Arch. Eisenhuttenwess. 27 (1956) 487.
[15] W. Oelsen, F. Bieret, G. Schwabe, Arch. Eisenhuttenwess. 27 (1956) 607.
[16] K.C. Chou, CALPHAD 19 (3) (1995) 315.