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THERMODYNAMIC ANALYSIS OF THE SYSTEM Bi–Au_2Bi

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Abstract

Results of the experimental thermodynamic investigations of the system Bi–Au_2Bi obtained by using Oelsen calorimetry are presented in this paper. Activities, activity coefficients and partial molar quantities for bismuth in the temperature interval 600–1000 K are determined. Based on the values of the thermodynamic parameters, negative deviation from Raoult law was obtained for the investigated system. Also, bismuth activities and activity coefficients dependence on composition and temperature is calculated by the nonlinear programming using gradient method.

Keywords: alloy thermodynamics, Au–Bi system, calorimetry, gold and gold alloys

Introduction

For their good mechanical and thermal properties and corrosion consistency, gold and gold alloys are widely applied in numerous modern technologies such as electronics, aero and cosmic technologies, as well as in chemistry and medicine [1].

Specially interesting are gold alloys with Bi, Sn, Pb, In, Ga, Si and P, characterized by low temperature eutectics, low melting temperatures, low concentrations of gold and formation of intermetallic compounds, which are usually used in electronics as brazing alloys or in jewellery as brazing materials [1, 2].

Thermodynamic investigations of the binary systems based on gold are numerous, but the most complete literature data can be found in Hultgren's book [3] and in book 'Noble Metal Alloys' by Massalski and others [4].

Concerning binary Au–Bi system thermodynamics, there are data obtained by using EMF measurements by Kleppa [5], Kameda and Azakami [6], and calorimetric measurements by Kleppa [7], Predel and Eman [8], while in recent times thermodynamic data were obtained by using predicting methods by Chou and Wang [9]. The phase diagram of the Au–Bi system is presented in Fig. 1, according to the work of Okamoto and Massalski [10].

For the purpose of this work, Au–Bi alloys were investigated thermodynamically in the concentration range Bi–Au_2Bi, important for gold jewellery brazing, by using Oelsen's calorimetry in a wide temperature interval. Also, as a contribution to the

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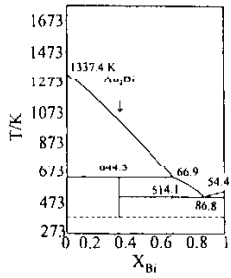

Fig. 1 Phase diagram of the Au–Bi system [10]

more complete thermodynamic description of this gold based binary system, activity coefficients dependence on composition and temperature is calculated by the non-linear programming using gradient method.

Experimental

Oelsen's calorimetry was used for the thermodynamic analysis. Descriptions of this experimental technique are reported in Refs [11–13].

Composition of the seven chosen samples in the investigated part Bi–Au_2Bi of the Au–Bi system, in the range of x_{Bi}=0.343–1, are given in Table 1. All samples had constant volume of 1 cm^3, according to the requirements of the used experimental method.

Table 1 Composition of the investigated samples

Alloy	Au	Bi	x_{Au}	x_{Bi}	$mAu \cdot 10^3$	$mBi \cdot 10^3$	$m_{tot} \cdot 10^3$
	mass %				kg		
B1	0	100	0	1	0	9.800	9.800
B2	4.51	95.49	0.045	0.959	0.452	9.578	10.030
B3	12.54	87.46	0.132	0.868	1.310	9.139	10.449
B4	19.07	80.93	0.200	0.800	2.064	8.759	10.823
B5	31.80	68.20	0.331	0.669	3.693	7.921	11.614
B6	48.52	51.48	0.485	0.515	6.253	6.634	12.887
B7	64.35	35.65	0.657	0.343	9.232	5.115	14.347

Used metals were of analytical grade. All experiments were carried out in an air atmosphere.

The water equivalent was determined by a standard method using dissolved Na_2CO_3 and for the calorimeter used, its value is 3453 J K^{-1}.

Results and discussion

Based on cooling curves obtained by Oelsen's calorimetry, temperature changes of the used calorimeter were determined for all samples in the investigated temperature interval 400–1000 K, and according to these data the enthalpy space diagram (dependence of the calorimeter temperature change on the composition and temperature) and enthalpy isotherm diagram, were constructed and presented in Figs 2 and 3, respectively.

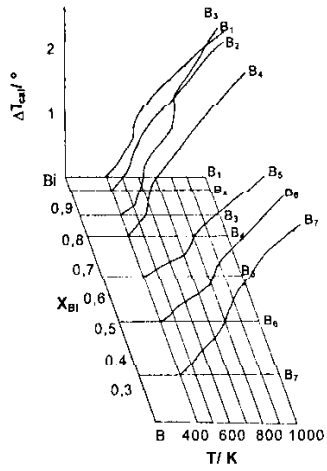

Fig. 2 The enthalpy space diagram – calorimeter temperature change *vs.* composition and temperature

Further quantitative thermodynamic analysis according to Oelsen is graphic planimetry, as shown in Fig. 4, while the final step of the calculation – construction of the tangent for determination of $-R\ln a_{Bi}$, is done according to the basic Oelsen equation:

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

and given in Fig. 5. In Eq. (1) are: μ – the partial molar Gibbs energy for the component i, T_0 – the starting temperature, T – the finite temperature, $H_{x,T}$ – the enthalpy values 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.

Review of the results obtained by Oelsen's quantitative thermodynamic analysis, which include activities, activity coefficients and partial molar quantities for bismuth in the investigated composition range Bi–Au_2Bi of the Au–Bi system at temperatures 600–1000 K, are given in Table 2.

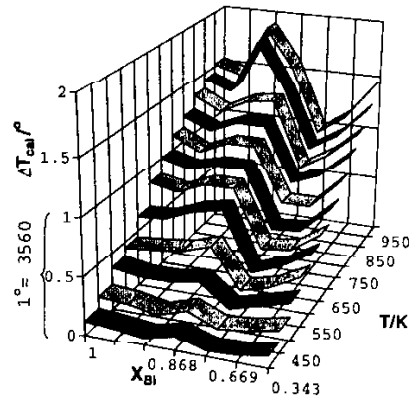

Fig. 3 The enthalpy isotherm diagram for the temperature interval 400–1000 K

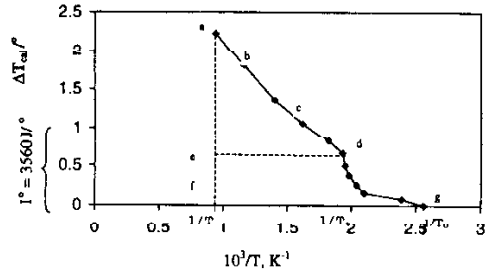

Fig. 4 Graphic planimetry (for sample B3)

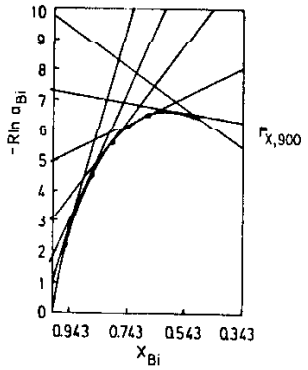

Fig. 5 Construction of the tangent for determination of $-R\ln a_{Bi}$ at 900 K

Table 2 Results of Oelsen's quantitative thermodynamic analysis

T/K	Alloy	a_{Bi}	γ_{oBi}	μ_{Bi}/J mol^{-1}	G^{xs}_{Bi}/J mol^{-1}
1000	B2	0.940	0.984	−514	−131
	B3	0.840	0.967	−1450	−279
	B4	0.767	0.959	−2205	−348
	B5	0.625	0.934	−3908	−568
	B6	0.509	0.988	−5615	−100
	B7	0.342	0.998	−8921	−17
900	B2	0.930	0.974	−543	−197
	B3	0.825	0.950	−1439	−384
	B4	0.758	0.948	−2073	−404
	B5	0.618	0.923	−3601	600
	B6	0.492	0.956	−5307	−337
	B7	0.342	0.997	−8028	−22
800	B2	0.887	0.929	−796	−490
	B3	0.786	0.906	−1602	−657
	B4	0.681	0.851	−2555	−1073
	B5	0.596	0.891	−3442	−768
	B6	0.486	0.944	−4799	−383
	B7	0.318	0.927	−7620	−504
700	B2	0.865	0.960	−844	−575
	B3	0.722	0.832	−1896	−1070
	B4	0.650	0.813	−2507	−1208
	B5	0.560	0.837	−3374	−1036
	B6	0.452	0.878	−4621	−757
	B7	0.300	0.875	−7007	−777
600	B2	0.855	0.895	−781	−553
	B3	0.715	0.824	−1673	−966
	B4	0.645	0.806	−2187	−1076
	B5	0.550	0.792	−2982	−1163
	B6	0.430	0.835	−4210	−900
	B7	0.280	0.816	−6350	−1014

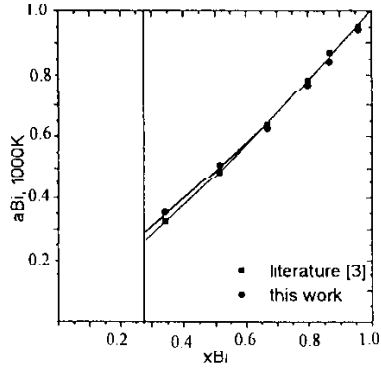

Fig. 6 Comparison between literature [3] and experimentally obtained values for a_{Bi} at 1000 K

According to the values of the obtained thermodynamic results, it can be concluded that negative deviation from Raoult's law is presented in the whole Bi–Au_2Bi part of the investigated Au–Bi system and at all investigated temperatures, which indicates good miscibility between components.

The activity coefficient for bismuth is less than unity in the investigated compositional range. With bismuth molar content decreasing, it decreases up to the sample B5 (at temperatures 600, 900 and 1000 K) and B4 (at 700 and 800 K), and then con-

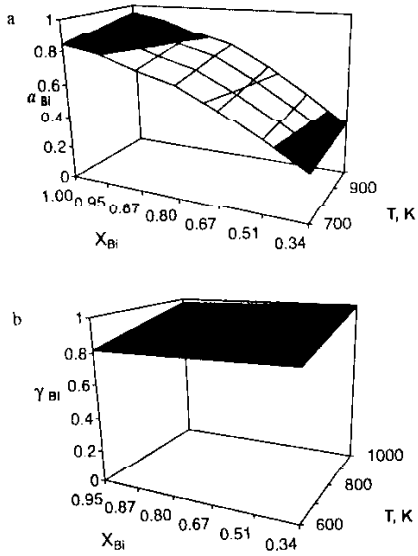

Fig. 7 3D-dependencies of bismuth activities (a) and activity coefficients (b) in the part Bi–Au_2Bi of the Au–Bi system for the temperature interval 600–1000 K

Table 3 The approximation errors (in %) for a_B and γ_{oBi}

Alloy	a_{Bi}/K					γ_{oBi}/K				
	600	700	800	900	1000	500	700	800	900	1000
E1	19.3	15.7	12.1	8.52	4.9	–	–	–	–	–
E2	9.99	7.06	5.5	6.18	3.52	8.56	5.31	3.39	3.79	0.75
B3	2.07	–1.3	2.97	3.77	1.77	0.47	–3.34	0.72	1.15	–1.22
B4	0	–3.7	–3.21	3.45	0.86	–1.93	–6.07	–5.88	0.66	–2.24
B5	1.89	–0.65	1.339	1.01	–1.74	–4.08	–3.25	–1.46	–2.26	–5.32
B6	3.61	4.21	7.11	4.48	4.04	0.89	1.19	3.86	0.88	0
B7	1.25	3.72	5.3	8.34	8.22	–1.85	0.42	1.67	4.55	3.7

tinues to increase up to the sample B7 at all investigated temperatures. Similarly, derived values for the bismuth partial molar Gibbs excess energies have also the negative values and the minimums at the same compositions, as can be seen in Table 2. Concerning the dependence of the bismuth activities on temperature, it can be noticed that temperature decreasing causes bismuth activities decrease for all investigated compositions.

Comparison between values for bismuth activities experimentally obtained by Oelsen calorimetry and taken from literature [3] for the temperature 1000 K is shown in Fig. 6.

There is a good agreement between literature [3] and experimentally obtained values for bismuth activities at 1000 K, so analogously good consistency can be expected for bismuth activity values at all other investigated temperatures, especially if one has in mind that there are no literature data for bismuth activities except for temperature of 1000 K.

In order to obtain the analytical expression for the bismuth activities and activity coefficients dependence on composition and temperature in the range of x_{Bi}=0.343–1 and in interval of 600–1000 K, the nonlinear programming gradient method was used [14, 15]. The following aim function was formed:

$$F(d_1, d_2, d_3, d_4) = \sum_{i}^{k}\sum_{l}^{j}\left[H(x_k, T_j) - G(x_k, T_j)\right]^2 \quad (2)$$

which should be minimized and values of parameters d_i (i=1, 2, 3, 4) should be determined so the aim function has the minimum. In this case, the function $G(x,T)$ has the following form, which describes the supposed linear dependence on temperature and composition:

$$G(x,T)=g_1(T)g_2(x) = (d_1 + d_2T)(d_3 + d_4x) \quad (3)$$

while $H(x_k,T_j)$ presents the experimental results, where k is the number of investigated alloys and j is the number of investigated temperatures in range.

Formation of the iterative process [14, 15] is defined as surely convergent process and it leads to the values of d_i (i=1, 2, 3, 4), so the approximation in this work gives the following results:

$$a_{Bi} = (0.421 + 0.0002563T)(-0.00054 + 1.4043x_{Bi}) \quad (4)$$

$$\gamma_{oBi} = (0.586 + 0.004T)(1.0153 - 0.0253x_{Bi}) \quad (5)$$

In Figs 7a and 7b, 3D-dependencies of bismuth activities and activity coefficients are given, respectively, while the approximation errors are presented in Table 3.

* * *

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