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CALORIMETRIC INVESTIGATIONS OF THE SYSTEM Pb–Bi–Mg–Sb WITH OELSEN'S METHOD

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Abstract

The results of calorimetric investigations in the section $Pb–Bi_x–Mg_y–Sb_z$ (mole ratio Bi:Mg:Sb=8:1:1) of the system Pb–Bi–Mg–Sb with Oelsen's method are presented. The constructed space diagram and enthalpy isotherm diagram were used to determine integral mixing enthalpies for the investigated section in the temperature interval 450–1100 K.

Keywords: calorimetry, lead refining, Oelsen's method, Pb–Bi–Mg–Sb alloys

Introduction

During the Kroll-Betterton process, known in the extractive metallurgy of lead as the process of refining from bismuth by using calcium, magnesium and antimony, many processes take place in the system Pb–Bi–Mg–Sb [1–3].

Although there are literature data relating to the technological problems or fundamental aspects of the phenomena occurring in the systems Pb–Bi–Mg and Pb–Bi–Sb [1–5], no thermodynamic data are available on the system Pb–Bi–Mg–Sb. Determination of the thermodynamic properties of this system is therefore important from both scientific and practical points of view.

Thermodynamic data on the constitutional binary and ternary systems have been determined and reported [6–19]. All six binaries, except the liquid alloys Bi–Sb [11, 12], possess negative enthalpies of mixing and exhibit negative deviations from ideal behaviour in the whole concentration range, which is characteristic for strong interactions between constituent components and the existence of intermetallic compounds, presented in the phase diagrams of the systems Mg–Pb [7, 8], Mg–Bi [9, 10] and Mg–Sb [13, 14]. Similar thermodynamic trends for the constitutional ternary systems were indicated by the given thermodynamic data: the results of calorimetric measurements [15], thermodynamic

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predictions [16], MICT and LCPT model application [17, 18] in the system Pb–Bi–Mg, and the results of thermodynamic predictions in the system Pb–Bi–Sb [19].

As a contribution to the knowledge on the thermodynamics of the system Pb–Bi–Mg–Sb, the present paper reports results of Oelsen calorimetric measurements in the section Pb–$Bi_xMg_ySb_z$ (mole ratio Bi:Mg:Sb=8:1:1).

Experimental

Oelsen's calorimetry was used for the thermodynamic analysis of the investigated system. Descriptions of this experimental technique are to be found in [20–22]. The water equivalent was determined by a standard method involving dissolved Na_2CO_3, and for the calorimeter used it has a value of 3453 $J K^{-1}$.

The calorimetric measurements and thermodynamic calculations of the section Pb–$Bi_xMg_ySb_z$ in the system Pb–Bi–Mg–Sb were carried out along the line of a constant mole ratio Bi:Mg:Sb=8:1:1, which is presented in Fig. 1, while the compositions of the eleven samples investigated are given in Table 1.

The metals used were of analytical grade. All experiments were carried out in air.

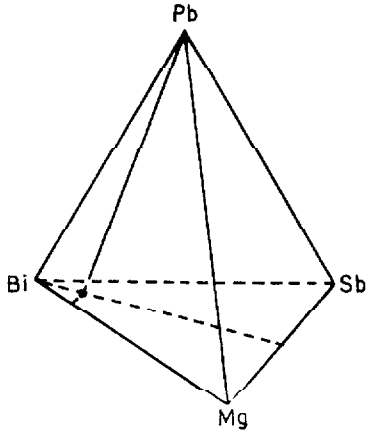

Fig. 1 Graphic presentation of the investigated section in the system Pb–Bi–Mg–Sb

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 450–1100 K (Table 2). With these data, the following step in Oelsen's thermodynamic analysis is the construction of the en-

thalpy space diagram: the dependence of the calorimeter temperature change on the composition and temperature (Fig. 2).

Table 1 Compositions of the investigated samples

Alloy	*x*Pb	*x*Bi	*x*Mg	*x*Sb	*m*Pb/g	*m*Bi/g	*m*Mg/g	*m*Sb/g
L0	1	0	0	0	11.4	0	0	0
L1	0.9	0.08	0.01	0.01	10.142	0.9093	0.0132	0.0662
L2	0.8	0.16	0.02	0.02	8.9137	1.798	0.0261	0.1309
L3	0.7	0.24	0.03	0.03	7.7122	2.6669	0.0388	0.1942
L4	0.6	0.32	0.04	0.04	6.5374	3.5165	0.0511	0.2561
L5	0.5	0.4	0.05	0.05	5.3882	4.3476	0.0632	0.3166
L6	0.4	0.48	0.06	0.06	4.2639	5.1606	0.075	0.3758
L7	0.3	0.56	0.07	0.07	3.1637	5.9563	0.0866	0.4338
L8	0.2	0.64	0.08	0.08	2.0868	6.7351	0.0979	0.4905
L9	0.1	0.72	0.09	0.09	1.0325	7.4975	0.109	0.546
L10	0	0.8	0.1	0.1	0	8.2442	0.1199	0.6004

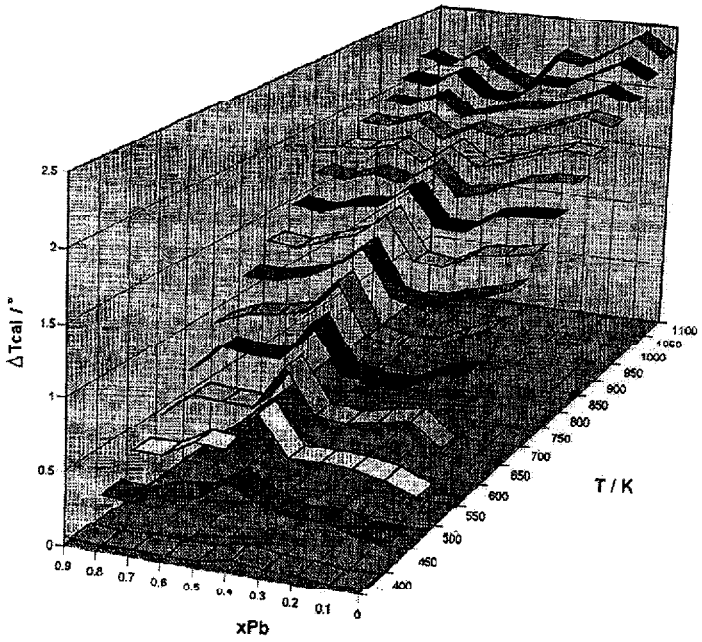

Fig. 2 The enthalpy space diagram: calorimeter temperature change *vs.* composition and temperature

Table 2 Calorimeter temperature changes for all samples in the investigated temperature interval 450–1100 K

ΔT_{cal} (o) at different temperatures / K															
*x*Pb	400	450	500	550	600	650	700	750	800	850	900	950	1000	1050	1100
1	0.042	0.211	0.388	0.565	0.79	1.074	1.227	1.357	1.523	1.688	1.854	1.996	2.102	2.208	2.315
0.9	0.017	0.174	0.331	0.46	0.654	0.894	1.116	1.291	1.457	1.623	1.734	1.836	1.928	2.03	2.131
0.8	0.005	0.156	0.33	0.633	0.86	0.98	1.12	1.261	1.424	1.586	1.738	1.825	1.911	1.998	2.074
0.7	0.021	0.238	0.454	0.617	0.833	1.007	1.169	1.343	1.505	1.668	1.798	1.906	2.014	2.112	2.198
0.6	0.014	0.252	0.436	0.609	0.837	1.065	1.267	1.417	1.529	1.609	1.68	1.771	1.859	1.957	2.05
0.5	0.019	0.398	0.737	0.932	1.124	1.311	1.462	1.585	1.689	1.771	1.835	1.879	1.918	1.943	1.964
0.4	0.061	0.277	0.445	0.62	0.79	0.947	1.113	1.276	1.42	1.556	1.693	1.836	1.978	2.106	2.235
0.3	0.035	0.221	0.451	0.6	0.747	0.909	1.066	1.243	1.42	1.603	1.76	1.884	2.005	2.103	2.188
0.2	0.032	0.229	0.443	0.644	0.753	0.92	1.15	1.375	1.56	1.706	1.844	1.978	2.092	2.21	2.307
0.1	0.008	0.172	0.404	0.684	0.869	1.024	1.202	1.397	1.586	1.757	1.907	2.061	2.196	2.325	2.455
0	0.018	0.174	0.323	0.508	0.922	1.123	1.284	1.446	1.596	1.759	1.891	2.013	2.116	2.22	2.309

The enthalpy isotherm diagram for the investigated temperature interval 450–1100 K is presented in Fig. 3.

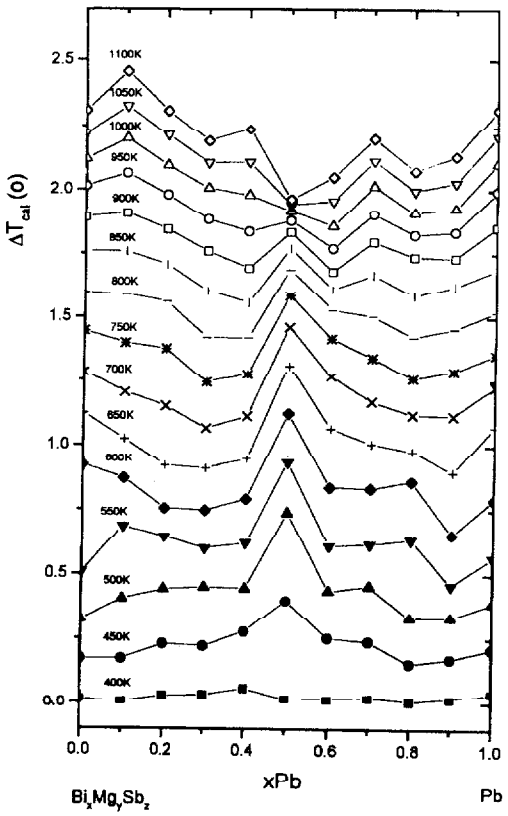

Fig. 3 The enthalpy isotherm diagram for the temperature interval 450–1100 K

From the enthalpy isotherm diagram, integral mixing enthalpies for the investigated section $Pb–Bi_xMg_ySb_z$ in the system Pb–Bi–Mg–Sb at temperatures in the interval 450–1100 K were determined according to Oelsen [20]:

$$\Delta H^{M} = \frac{\Delta\Delta T_{cal} W}{\sum \frac{m_i}{M_i}} \quad (1)$$

where ΔH^{M} is the integral mixing enthalpy (J mol^{-1}), W is the water euqivalent (J K^{-1}), m_i is the mass of component i, and M_i is the atomic mass of component i (g mol^{-1}). The value of $\Delta\Delta T_{cal}$ can be obtained as follows: for the isotherm in Fig. 3, the points for x_{Pb}=0 and x_{Pb}=1 are connected by a straight line; $\Delta\Delta T_{cal}$ is then obtained as the height from each point to the connecting straight line. By

means of such a calculation, integral mixing enthalpies at the investigated temperatures were determined (Table 3).

Table 3 Integral mixing enthalpies at temperatures in the interval 450–1100 K

Alloy	ΔH^M J mol^{-1}								
	L1	L2	L3	L4	L5	L6	L7	L8	L9
xPb→ T/K	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1
450	−635	−6421	1299	1313	11950	5369	2035	1371	1386
500	−1270	−1284	6494	5253	23901	6712	4071	4114	4158
550	−5079	3853	3247	1313	25229	5369	3392	5486	7623
600	−5079	5779	1948	−1313	17262	−4027	−9498	−9600	−2772
650	−4821	−6421	−5195	−1313	11950	−12081	−14926	−17828	−9702
700	−3809	−6421	−1299	2627	11950	−9396	−13569	−12343	−8316
750	−3809	−7705	−1299	0	9295	−10739	−13569	−8228	−5544
800	−6349	−10274	−6494	−5253	4027	−16108	−14926	−6857	−2772
850	−2539	−7705	−3247	−6567	1328	−12081	−12212	−4114	0
900	−6349	−8990	−5195	−11820	−5975	−14766	−10855	−4800	0
950	−7618	−10274	−7793	−15760	−10623	−10739	−9498	−2743	0
1000	−6349	−10274	−5195	−15760	−14606	−8054	−10177	−2743	4158
1050	−8888	−11558	−6494	−17073	−15934	−6712	−8141	0	6930
1100	−11427	−15411	−7143	−16416	−23901	−4027	−9498	1371	11780

At lower temperatures, 450–550 K, the sign of the integral mixing enthalpies is positive in the composition range x_{Pb}=0.1–0.7, while at 600 K it starts to become negative in the greatest composition part. This trend of negative integral mixing enthalpies is present up to the highest investigated temperatures for liquid Pb–Bi–Mg–Sb alloys.

A negative integral mixing enthalpy is characteristic for systems with stronger interactions between the constitutional components, i.e. systems involving the existence of an intermetallic compound or an equilibrium between solid and liquid solutions. As mentioned earlier, the binaries Pb–Bi, Pb–Mg, Pb–Sb, Bi–Mg and Mg–Sb exhibit negative deviations from ideal behaviour and have negative integral mixing enthalpies [6]; intermetallic compounds are present in Pb–Mg, Bi–Mg and Mg–Sb, and also in constitutive ternaries [15], which all suggest the similar behaviour of the quaternary system Pb–Bi–Mg–Sb. Thus, on the basis of the konwn phase diagrams of the constitutional ternary systems [15] and the results obtained for the investigated section Pb–$Bi_xMg_ySb_z$ (mole ratio Bi:Mg:Sb=8:1:1), it can be predicted that the occurrence of intermetallic compounds in the system is probable.

As there are no reports on the phase diagram of this section in the quaternary system Pb–Bi–Mg–Sb, further investigations are needed for the phase diagram construction in order to furnish more complete and precise information than that obtained by Oelsen's calorimetry.

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