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Thermodynamic Properties of Liquid Bismuth—Lead Alloys*

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On liquid Bi—Pb alloys emf measurements were carried out. From the emf data the thermodynamic properties were calculated. In the temperature range between 643 to 923 K no anomalies in the thermodynamic properties were found. The emf varies linearly with temperature and the activity of Pb shows a slight negative deviation from *Raoult*'s law. However, when $\Delta H^M/x$ is plotted against $(1-x)$ the results are two staight lines which intersect at approximately 35 at% Bi. This could be interpreted that Bi—Pb melts change from one regular behaviour to another.

(Keywords: Bismuth—Lead, Thermodynamic properties of liquid alloys)

Thermodynamische Eigenschaften flüssiger Wismut—Blei-Legierungen

An flüssigen Wismut—Blei Legierungen wurden EMK-Messungen durchgeführt. Aus den EMK-Daten wurden die thermodynamischen Größen berechnet. Im Temperaturbereich zwischen 643 und 923 K konnte kein anomales Verhalten der thermodynamischen Eigenschaften festgestellt werden. Die EMK steigt linear mit der Temperatur und die Aktivität von Pb zeigt eine geringe negative Abweichung vom *Raoult*'schen Gesetz. Wird jedoch $\Delta H^M/x$ gegen $(1-x)$ aufgetragen, werden zwei Gerade erhalten, die bei ca. 35 At% Bi einen Schnittpunkt aufweisen. Das kann dahin gedeudet werden, daß die Bi—Pb-Schmelze von einer regulären Lösung in eine andere übergeht.

Introduction

The determination of thermodynamic properties and structural properties of liquid Bi—Pb alloys has been the subject of numerous investigations. A critical analysis of earlier thermodynamic studies has

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[*] Herrn Prof. Dr. *K. L. Komarek* mit den besten Wünschen zum 60. Geburtstag gewidmet.

been presented by *Hultgren* et al. [1]. An extensive calorimetric investigation of this system was carried out by *Kleppa* [2]. More recently *Moser* [3] studied this system using an emf method. *Mehrotra* et al. [4] determined the activities with a different emf method using a solid electrolyte.

Prasad et al. [5] used vapour pressure measurements to evaluate the thermodynamic data, and mass spectrometric studies were carried out by *Fruehan* [6]. The density and temperature dependence of the surface tension was measured by *Abdel-Aziz* and *Kirshah* [7].

The structure of liquid Bi—Pb alloys was determined by neutron and X-ray diffraction measurements by *Sharrah* et al. [8] and by *Waseda* et al. [9]. The electrical resistivity was measured by *Roll* and *Biswas* [10], and *Flinn* et al. [11] carried out viscosity measurements in the liquid Bi—Pb system. The diffusion coefficients were determined by *Kohl* and *Predel* [12] and by *Kohl* [13].

Sharrah et al. [8], *Roll* and *Biswas* [10], *Flinn* et al. [11], *Kohl* and *Predel* [12], and *Kohl* [13] reported some anomalies in the melt in the composition range between 20 to 40 at% Bi and around 60 at% Bi which were in part explained by cluster formation. A careful investigation of thermodynamic properties using quasi-continuous emf measurements, similar to those used in the investigations of Sb—Zn [14], As—Cd [15] and Bi—Zn [16] were therefore thought to be of interest.

Experimental

The metals, 5 *N* bismuth and 5 *N* lead, were purchased from Ventron (Karlsruhe, F.R.G.), KCl, LiCl and $PbCl_2$ were p.A. products of E. Merck (Darmstadt, F.R.G.). Surface oxides of Bi and Pb were removed by melting the metals *in vacuum* and filtration through quartz wool. The metals were weighed on an analytical balance (± 0.05 mg), and the alloys were prepared in the emf cell. The electrolyte was a eutectic mixture of KCl—LiCl with 0.5 mol% $PbCl_2$ and was purified by passing Cl_2 gas through the melt followed by Ti-gettered Ar until the melt was colorless. The following cell arrangement was used:

$$Pb\,(l)/Pb^{2+}\,(KCl-LiCl)(l)/Pb_xBi_{1-x}\,(l)$$

The cell, the electrode containers and the capillaries were made of quartz. A W-electrode wire was sealed into the capillaries. Four electrodes, one pure lead, were used in each experiment. The cell arrangement was similar to that used previously [14–16]. The temperature was measured with a Ni/Ni—Cr thermocouple which was calibrated at the melting points of pure Cd, Zn and Sb.

The cell was heated in a vertical furnace (Heraeus ROK 6.5/60, Hanau, F.R.G.) which was controlled by a microprocessor (Jumo DPO-96, Fa. Jucheim, Fulda, F.R.G.). Measurements were carried out in the temperature range between 643 K to 923 K. The emf was continuously measured with a voltmeter combined with a small computer. The heating and cooling rate was 10 K per hour and the emf was measured every 5 minutes. At intervals the temperature was kept constant for an hour and so did the emf. The agreement between heating and cooling curves was excellent. Since no dedectable evaporation of the metals occurred the nominal composition was taken as actual composition.

Results and Discussion

Emf measurements were carried out on 21 bismuth-lead alloys. Their composition is given in Table 1. In the temperature range studied the emf varied linearly with temperature for all alloys. The emf was therefore expressed in an equation of the following form

$$E(\mathrm{mV}) = a + b\,T(\mathrm{K})$$

For each composition the coeffients a and b are given in Table 1. Also given are the activities (at 700 K) and partial molar properties of lead referred to liquid lead as standard state. The activities of lead exhibit a negative deviation from *Raoult*'s law.

The activities of bismuth (at 700 K) and the partial molar functions of Bi and the integral molar quantities were calculated by *Gibbs-Duhem* integration. The data are listed in Table 2 and refer to liquid bismuth as standard state.

Table 1. *Experimental results of the emf measurements on liquid* Bi—Pb *alloys*

Composition at% Pb	$E = a + bT$(K)	a_{Pb} (700 K)	$\Delta\bar{H}_{Pb}$ ($J\cdot$g-atom^{-1})	$\Delta\bar{S}_{Pb}$ ($J\cdot$g-atom^{-1}K^{-1})
5.46	19.5830 + 0.1290	0.0262	—3778.2	23.883
10.00	17.9810 + 0.1030	0.0504	—3468.5	19.886
14.88	17.5680 + 0.0840	0.0795	—3389.0	16.210
20.67	14.5805 + 0.0715	0.1173	—2811.7	13.801
26.93	12.5020 + 0.0593	0.1668	—2414.2	11.442
29.56	12.1215 + 0.0545	0.1889	—2338.9	10.515
34.96	10.3690 + 0.0470	0.2383	—2000.0	9.067
36.73	10.1700 + 0.0436	0.2596	—1962.3	8.409
39.74	8.6888 + 0.0413	0.2875	—1677.8	7.967
44.93	7.2720 + 0.0360	0.3406	—1401.6	6.953
49.68	6.1735 + 0.0305	0.4016	—1192.4	5.882
54.93	4.4655 + 0.0265	0.4664	—861.9	5.110
59.14	3.3670 + 0.0236	0.5172	—648.5	4.555
59.89	2.9393 + 0.0228	0.5342	—569.0	4.400
64.97	2.1948 + 0.0193	0.5942	—422.6	3.724
69.92	1.2908 + 0.0173	0.6413	—251.0	3.335
75.09	0.6780 + 0.0140	0.7066	—129.7	2.702
80.07	0.3383 + 0.0098	0.7877	—66.9	1.889
84.95	0.2525 + 0.0075	0.8337	—50.2	1.441
90.33	0.0715 + 0.0045	0.8984	—12.6	0.873
95.00	0.0194 + 0.0022	0.9489	—4.2	0.430

Table 2. *Thermodynamic properties of liquid* Bi—Pb *alloys*

X_{Pb}	ΔG^M ($J \cdot$ g-atom^{-1})	ΔH^M ($J \cdot$ g-atom^{-1})	ΔS^M ($J \cdot$ g-atom^{-1} K^{-1})	a_{Bi} (700 K)	$\Delta \bar{H}_{Bi}$ ($J \cdot$ g-atom^{-1})	$\Delta \bar{S}_{Bi}$ ($J \cdot$ g-atom^{-1} K^{-1})
0.1	2 302.4	—348.7	2.791	0.898	—2.1	0.891
0.2	3 765.6	—661.1	4.435	0.763	—113.9	2.086
0.3	4 652.6	—920.5	5.332	0.650	—329.3	3.111
0.4	5 146.3	—1 092.0	5.792	0.519	—720.0	4.424
0.5	5 322.1	—1 150.6	5.959	0.392	—1 121.2	6.185
0.6	5 167.2	—1 083.6	5.834	0.278	—1 869.0	7.973
0.7	4 648.4	—920.5	5.326	0.196	—2 482.7	10.003
0.8	3723.8	—661.1	4.375	0.106	—3 037.9	14.320
0.9	2 301.2	—338.9	2.803	0.053	—3 272.0	19.749

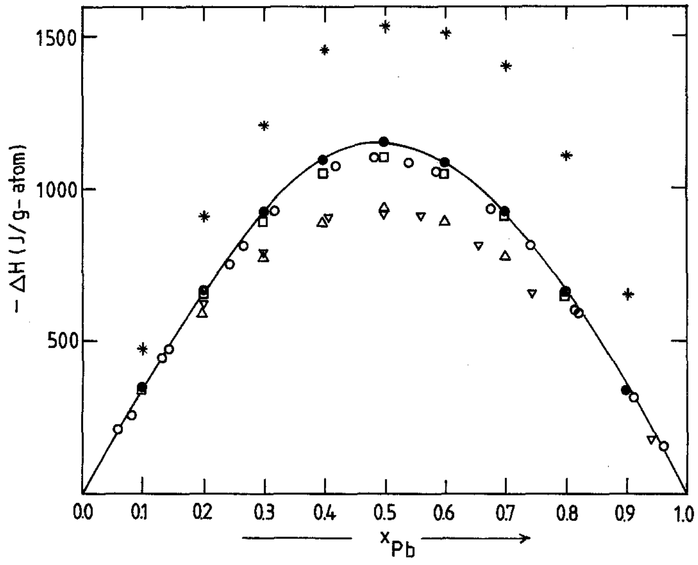

Fig. 1. Integral molar enthalpy of mixing: * *Fruehan*, ▽ *Prasad* et al., △ *Moser*, □ *Hultgren* et al., ○ *Kleppa*, ● present investigation

The integral molar enthalpy of mixing is shown in Fig. 1. The results are in very good agreement with the selected values by *Hultgren* et al. [1] and with the calorimetric data by *Kleppa* [2]. The data of *Moser* [3] also derived from emf studies are somewhat less positiv then the present data. This is also true for the results of *Prasad* et al. [5] who conducted vapour-pressure measurements. *Fruehan* [6] used a spectrometric technique to determine the activities of bismuth and lead at 1223 K and calculated $\Delta \bar{H}_{Bi}$, $\Delta \bar{H}_{Pb}$ and the integral molar enthalpy of mixing. Considering the small amount of heat involved, the uncertainty is rather large. It is estimated to be approximately 35 pct. This represents an uncertainty of about 500 J in the maximum value of ΔH. *Mehrota* et al. [4] represented $\ln \gamma_{Bi}$ and $\ln \gamma_{Pb}$ in a small graph from which no data could be taken.

The ΔS^M curve for this system is a parabola with no signs of depression which would be an indication for associate formation. No unusual concentration and temperature dependence of the thermodynamic properties, like the one previously observed in the liquid Cd—Sb [17], Zn—Sb [14] and As—Cd [15] systems, could be dedected.

Kohl and *Predel* [12] measured the diffusion coefficient in molten Bi—Pb alloys and reported different mobilities of Bi in Pb in the concentration range of 20 to 40 at% Bi and Pb. Based on their results, on conductivity measurements by *Roll* and *Biswas* [10], neutron and X-ray

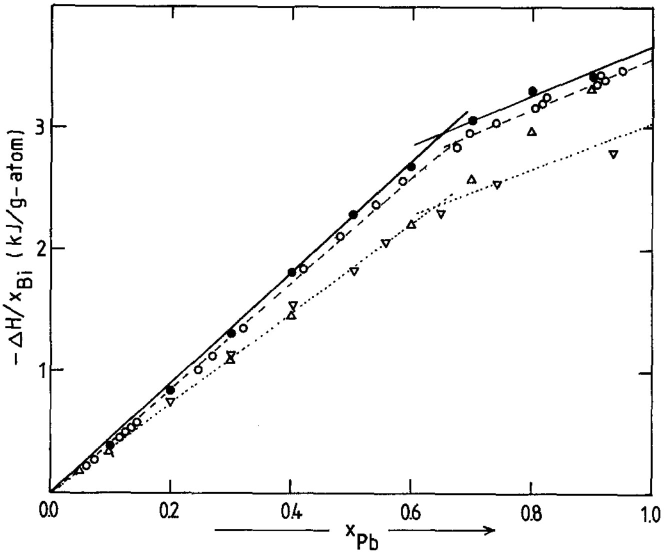

Fig. 2. Plot of $-\Delta H/x_{\mathrm{Bi}}$ vs. $(1-x_{\mathrm{Bi}})$: ▽ *Prasad* et al., △ *Moser*, ○ *Kleppa*, ● present investigation

diffraction measurements by *Sharrah* et al. [8] and viscosity measurements by *Flinn* et al. [11] they proposed the existence of some kind of ordering in the melt. Since compound formation was found in the solid at 33 at% Bi by *Predel* and *Schwermann* [18] and at 60–80 at% Bi by *Ponyatovskiy* and *Rabinkin* [19], *Kohl* [13] suggested that some associations may also occur in the melt at the same compositions. However, the results of *Sharrah* et al. [8] are in disagreement with the findings of *Wasada* et al. [9] who suggested that the structure of the crystalline compound. $BiPb_3$ does not influence the liquid structure of the alloys.

A smooth curve could be drawn through the thermodynamic data points, but assuming a regular solution there is a slight indication that ordering at approximately 35 at% Bi might occur in the melt. Based on the report of *Elliott* et al. [20], who discussed the regular solution behaviour of liquid alloys on the basis of H^M/x vs. x plots Fig. 2 was drawn.

For a regular solution the concentration dependence of ΔH^M can be described by $\Delta H = Cx(1-x)$ where C is a constant and x the mole fraction of one component. When $\Delta H^M/x$ is plotted against $(1-x)$ the plot is a straight line.

In Fig. 2 the results of *Kleppa* [2], *Moser* [3], *Prasad* et al. [5] and of the present investigation are shown. In all cases except for *Moser* [3] the results are two straight lines which intersect at ~35 at% Bi. The agreement between the calorimetric measurements of [2] and the present emf results are excellent. According to *Elliott* et al. [20] the Bi—Pb system obeys the regular solution theory in the composition range $x_{\mathrm{Bi}} = 0.0$ to 0.35 and $x_{\mathrm{Bi}} = 0.35$ to 1.0 and one could therefore argue that Bi—Pb melts change from one regular behaviour to another at $x_{\mathrm{Bi}} = 0.35$. No such unusual behaviour of the thermodynamic functions could be found between 60 and 80 at% Bi.

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