Thermodynamic Investigations and Characterization of Some Alloys in Ternary Pb-Au-Bi System

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The results of thermodynamic investigations and characterization of some alloys in ternary Pb-Au-Bi system are presented in this paper. Partial and integral molar quantities were determined in the temperature range of 873 - 973 K, based on the comparative thermodynamic analysis done experimentally using Oelsen calorimetry and analytically using Redlich-Kister-Muggianu model. Characterization of chosen lead-based ternary alloys were done using DTA, XRD and SEM analysis.

1. INTRODUCTION

For their good mechanical and thermal properties, as well as corrosion resistivity, gold and gold alloys are widely applied in modern technologies, such as electronics, aero and space technologies, etc.1 Specially interesting are gold alloys with In, Bi, Sn, Pb, Ga, Si and P, characterized by a low temperature eutectics, low melting temperatures, low concentrations of gold and formation of intermetallic compounds. One among such systems, usually used as solder materials in electronics or jewelry,1 is ternary Pb-Au-Bi system, whose alloys with mercury has also been investigated recently for the application as amalgams for fluorescent lamps.2

Literature data on thermodynamic properties and phase equilibria in Pb-Au-Bi system and its constituent binaries are numerous.1-8,9-16 Considering references on binary subsystems Pb-Au,3-8) Au-Bi9-16) and Bi-Pb17-19) the best review on their thermodynamic values is given in Hultgren's book20 and book "Noble Metal Alloys" by Massalski et al.21 Thermodynamics of ternary Pb-Au-Bi system has been investigated by some authors.22-24 Chao22) did EMF measurements of alloys in different sections of Pb-Au-Bi system in temperature range 700 - 1200 K, while Rebouillon et al.23,24) determined enthalpies of mixing and partial excess Gibbs energies of lead at different temperatures in various sections of the system using EMF method and Hoch-Arpshofen model, respectively.

In order to contribute to the more complete knowledge of the Pb-Au-Bi system, the results of the experimental and analytical thermodynamic investigations of some Pb-Au-Bi alloys in the section going from the lead corner to the eutectics in Au-Bi system (occurring at $x_{Bi}=0.868$ and the temperature of 514.4 K, according to Ref.31) are presented in this paper, as well as the results of characterization of these alloys.

2. EXPERIMENTAL

Oelsen calorimetry was used for the thermodynamic analysis of Pb-AuBieut section in the ternary Pb-Au-Bi system. Detailed descriptions of this experimental technique are reported in.22-24 Schematic representation of the used Oelsen water calorimeter is given in Fig.1.

Such calorimeter consists of a Dewar flask with water, a stirrer and a thermometer. It also contains a housing from copper sheet into which the iron holder with the sample is added, after these have been heated in a separate oven to the initial temperature. The temperature of the sample is followed with NiCr-Ni thermocouple during cooling and simultaneously the temperature of the water is measured.

The water equivalent was determined by standard
method using dissolved Na$_2$CO$_3$, adopting the value of the heat of solution of Na$_2$CO$_3$ of -23.442 kJ mol$^{-1}$ for the calibration. For the calorimeter used, the value of the water equivalent was 3314 J K$^{-1}$.

Differential thermal analysis (DTA) was done on derivatograph MOM, Budapest (Hungary), at the heating rate of 10 K min$^{-1}$ in an air atmosphere, while Al$_2$O$_3$ was used as a referent material during measurements.

X-ray diffraction (XRD) analysis was performed on Siemens apparatus, using Cu-anticathode and Ni-filters (40kV, 20mA).

Scanning electron microscopy (SEM) analysis was performed on electronic microscope Philips XL-300 with energetic dispersion spectrometer (EDX). Solution (40 ml HNO$_3$+30 ml CH$_3$COOH+160 ml H$_2$O+2-3 drops of H$_2$O$_2$) was used as an etching agent for the samples prepared according to the standard metallographic procedure.

All experiments were carried out in an air atmosphere, with Pb, Au and Bi metals of 99.99 mass% purity. Composition and masses of the alloys in the Pb-AuBicut section, investigated using Oelsen calorimetry, are given in Table 1, having constant total volume for all samples according to the requirements of the method used.

For the purpose of characterization, a few additional samples were investigated, having molar content of lead equal to 0.2; 0.4; 0.62; 0.68; 0.75; 0.8 and 0.85.

### 3. RESULTS AND DISCUSSION

Oelsen method, presenting a combination of simple classical thermal analysis with classical calorimetry at room temperature, is applied to determine the mixing enthalpies of liquid alloys, based on which further quantitative thermodynamic analysis$^{25}$ (including graphical planimetry and indirect determination of activities for constitutive components) is done.

The main fundamentals of Oelsen's approach are presented here for the binary system A-B. Concerning the alloy of the composition x$_B$=x at the temperature $T$, the integral Gibbs energy of mixing is given as$^{25}$

$$
\Delta G^M_{x,T} = (1-x)G^M_{A,T} + xG^M_{B,T} = (1-x)RT\ln a_{A,T} + xRT\ln a_{B,T} \quad (1)
$$

and according to the Gibbs-Helmholtz equation, the following expression is obtained

$$
\Delta H^M_{x,T} - T\Delta S^M_{x,T} = (1-x)RT\ln a_{A,T} + xRT\ln a_{B,T} \quad (2)
$$

Further determination of the activities for the constitutive components is conceived on the knowledge of the enthalpy and entropy term. Under equilibrium conditions and constant pressure, the entropy term can be written as

$$
dS^M_{x,T} = \frac{dH^M_{x,T}}{T} \quad (3)
$$

and

$$
S^M_{x,T} = S^M_{x,T=0} + \int_{x_{T=0}}^{x_T} \frac{dH^M_{x,T}}{T} \quad (4)
$$

and having in mind that $S^M_{x,T=0} = 0$, it follows that $S^M_{x,T} = \int_{x_{T=0}}^{x_T} \frac{dH^M_{x,T}}{T}$, based on which one could obtain that:

<table>
<thead>
<tr>
<th>Alloy</th>
<th>xPb</th>
<th>xAu</th>
<th>xBi</th>
<th>mPb,g</th>
<th>mAu,g</th>
<th>mBi,g</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>11.4000</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.9</td>
<td>0.0132</td>
<td>0.0868</td>
<td>9.2053</td>
<td>0.2343</td>
<td>1.7687</td>
</tr>
<tr>
<td>3</td>
<td>0.7</td>
<td>0.0396</td>
<td>0.2604</td>
<td>5.9430</td>
<td>0.5859</td>
<td>4.4036</td>
</tr>
<tr>
<td>4</td>
<td>0.5</td>
<td>0.066</td>
<td>0.4340</td>
<td>3.6244</td>
<td>0.8334</td>
<td>6.2684</td>
</tr>
<tr>
<td>5</td>
<td>0.3</td>
<td>0.0924</td>
<td>0.6076</td>
<td>1.8998</td>
<td>1.0193</td>
<td>7.6652</td>
</tr>
<tr>
<td>6</td>
<td>0.1</td>
<td>0.1188</td>
<td>0.7812</td>
<td>0.5615</td>
<td>1.1615</td>
<td>8.7318</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>0.1320</td>
<td>0.8680</td>
<td>0</td>
<td>1.2204</td>
<td>9.1746</td>
</tr>
</tbody>
</table>

*Table 1 Composition and masses of the investigated samples.*
Thermodynamic Investigations and Characterization of Some Alloys in Ternary Pb-Au-Bi System

\[ f_{GMx,T} = H_{Mx,T} - T \int_{H_{Mx,T}}^{H_{Mx,V}} dH_{Mx,T} \]  

(5)

For a better survey, Oelsen\(^{25}\) introduced the quantity \( I_{x,T} \), which represents the value of the enthalpy, directly determined in a calorimeter:

\[ I_{x,T} = H_{Mx,T} - H_{Mx,V} \]  

(6)

where \( V \) is the room temperature of 298 K. Rearranging Eqs. (5) and (6), it follows

\[ (1/T) - G_{Mx,T} = \int_{I_{x,T}}^{1/T} dI_{x,T} / T - \int_{1/V}^{1/T} I_{x,T} d(1/T) \]  

(7)

which presents the important Oelsen integral. Solution of this integral is done using a graphical planimetry of the area below the cooling curve.\(^{25}\)

Based on cooling curves obtained by calorimetric measurements, according to the Oelsen procedure described in Refs.\(^{25,27}\), temperature changes of the used calorimeter were determined for all chosen samples in the investigated temperature range up to 973 K. According to these data, the enthalpy space diagram and enthalpy isotherm diagram were constructed and presented in Figs. 2 and 3, respectively. (Note: in presented diagrams 1 K correspond to the water equivalent determined to be 3314 J K\(^{-1}\).)

Therefore, the basic equation of the Oelsen quantitative thermodynamic analysis\(^{25}\) is

\[ -G_{Mx} = \int_{T_o}^{1/T} H_{x,T} d (1/T) = -R \ln a_i \]  

(8)

where are: \( G_{Mx} \) - the partial Gibbs energy of mixing for the component \( i \), \( T_o \) - the starting temperature, \( T \) - the final temperature, \( H_{x,T} \) - the enthalpy value measured in the Oelsen calorimeter for the temperature change from \( T_o \) to \( T \), \( R \) - the gas constant, and \( a_i \) - the activity of the component \( i \).

Considering previous diagrams, Eq.(8) and the results of graphic planimetry, indirect calculation of the activities, activity coefficients and partial molar quantities for lead at the temperatures of 873 and 973 K was done. Obtained thermodynamic data are presented in Table 2.

<table>
<thead>
<tr>
<th>T, K</th>
<th>Alloy No.</th>
<th>( x_{Pb} )</th>
<th>( a_{Pb} )</th>
<th>( G_{M_{Pb}} ), J mol(^{-1})</th>
<th>( \gamma_{Pb} ), J mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.9</td>
<td>0.860</td>
<td>0.955</td>
<td>-2088</td>
<td>-334</td>
</tr>
<tr>
<td>3</td>
<td>0.7</td>
<td>0.550</td>
<td>0.785</td>
<td>-4339</td>
<td>-1757</td>
</tr>
<tr>
<td>873</td>
<td>0.5</td>
<td>0.292</td>
<td>0.584</td>
<td>-8935</td>
<td>-3903</td>
</tr>
<tr>
<td>5</td>
<td>0.3</td>
<td>0.193</td>
<td>0.643</td>
<td>-11940</td>
<td>-3205</td>
</tr>
<tr>
<td>6</td>
<td>0.1</td>
<td>0.030</td>
<td>0.300</td>
<td>-25451</td>
<td>-8739</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>0</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.9</td>
<td>0.880</td>
<td>0.977</td>
<td>-1034</td>
<td>-188</td>
</tr>
<tr>
<td>3</td>
<td>0.7</td>
<td>0.640</td>
<td>0.914</td>
<td>-3610</td>
<td>-727</td>
</tr>
<tr>
<td>973</td>
<td>0.5</td>
<td>0.370</td>
<td>0.740</td>
<td>-8043</td>
<td>-2436</td>
</tr>
<tr>
<td>5</td>
<td>0.3</td>
<td>0.230</td>
<td>0.660</td>
<td>-11889</td>
<td>-2220</td>
</tr>
<tr>
<td>6</td>
<td>0.1</td>
<td>0.050</td>
<td>0.500</td>
<td>-24234</td>
<td>-5607</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>0</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
</tbody>
</table>

Table 2 Results of the Oelsen's calorimetry.
Negative deviation from ideal behavior was noticed, showing negative values of partial molar Gibbs excess energies obtained for the whole concentration range, which is in accordance with strong miscibility between constituent components in the investigated system.

Since Oelsen calorimetry results are related only to lead, thermodynamic calculation according to Redlich-Kister-Muggianu model was applied in order to obtain the integral thermodynamic quantities in the investigated section Pb-Au-Bi of the ternary system Pb-Au-Bi. Redlich-Kister-Muggianu model is one of the most frequently used calculation procedures for the determination of ternary integral molar excess Gibbs energy. Main expression of this model, in the case of a ternary system A-B-C, is given as follows:

$$
\Delta G_m^e = \sum_{i=1}^{3} x_i \sum_{k=1}^{2} L_{ijk} (x_i - x_j x_k) + 
\sum_{j=1}^{3} x_j \sum_{k=1}^{2} L_{jik} (x_j - x_k x_i) + 
\sum_{k=1}^{3} x_k \sum_{j=1}^{2} L_{jik} (x_k - x_j x_i) + 
\sum_{i=1}^{3} x_i \sum_{j=1}^{2} L_{ijk} (x_i - x_j x_k)
$$

(9)

where term $\varphi$ is related to the investigated phase; term $L_{ijk}$ presents a ternary interaction parameter and $x$ respond to the molar content of the component $i$.

$$
L_{ijk} = x_i x_j x_k L_{ijk}
$$

(10)

The calculation procedure, according to this model, is based on the known Redlich-Kister parameters for the constitutive binary systems, which are temperature dependent.

So, the application of a mentioned model was done next in the thermodynamic investigation of Pb-Au-Bi alloys, using literature values for the Redlich-Kister parameters of the constitutive binaries in liquid phase, presented in Table 3.

The calculation of thermodynamic properties of liquid Pb-Au-Bi alloys was performed according to the Eq.(9). Because no complete thermodynamic information about this ternary system was reported, direct extrapolation was undertaken and the ternary interaction parameter was neglected for the lack of sufficient data.

Thermodynamic calculation according to Redlich-Kister-Muggianu model was applied in order to check the agreement with experimental Oelsen results, on one hand, and the agreement with literature experimental data, on the other hand. The calculation was done as follows: a) for the investigated section at the temperatures of 873 and 973 K, and b) for the sections with molar ratio Au/Bi = 1:1, 1:3 and 1:2 for which literature data exist at the temperature of 973 K. The results, including calculated integral molar excess Gibbs energies, are presented in Table 4.

Further, a comparison of the results for partial excess Gibbs energy of lead was done at the temperature of 973K - first, between the results of Oelsen calorimetry and calculation (given in Fig.4), and second, between literature data and calculation (given in Fig.5).

Mutual agreement could be noticed in both cases - between calculation and Oelsen calorimetry, and also between calculation and experimental literature data, which may lead to the conclusion that most probably results of the calorimetric research presented in this work are in the accordance with EMF results from literature, too.

Besides thermodynamic analysis, the samples in the section Pb-AuBi Hart were characterized using DTA, XRD and SEM method.

The temperatures for the phase transformations in the temperature range up to 973K were obtained by DTA measurements. Characteristic peaks, showing endothermic

<table>
<thead>
<tr>
<th>System $y$</th>
<th>$L_{\infty}(T)$</th>
<th>$L_{\infty}'(T)$</th>
<th>$L_{\infty}''(T)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au-Pb</td>
<td>-8204.5 + 5 145492T - 1.15561271T</td>
<td>27543.3 - 275 99041T + 35 526571T</td>
<td>/</td>
</tr>
<tr>
<td>Au-Bi</td>
<td>2769 55 - 6.307577T</td>
<td>-1495 3 + 1 133275T</td>
<td>-3850.95 + 3.69306T - 810 - 0.344775T</td>
</tr>
<tr>
<td>Bi-Pb</td>
<td>-4330.3 - 2.0421T + 0.06542T11T</td>
<td>1.53 - 1 02298T</td>
<td>896.7 - 1.2644T</td>
</tr>
</tbody>
</table>

Table 3 Redlich-Kister parameters for the constitutive binaries in liquid phase

<table>
<thead>
<tr>
<th>T, K</th>
<th>$\Delta G^e = a + b \cdot x_{Pb} + c \cdot x_{Pb}^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>873</td>
<td>$-256.83$</td>
</tr>
<tr>
<td>973</td>
<td>$-313.29$</td>
</tr>
<tr>
<td></td>
<td>$-5835.8$</td>
</tr>
<tr>
<td></td>
<td>$6100.2$</td>
</tr>
</tbody>
</table>

Table 4 The results of Redlich-Kister-Muggianu model application.
Thermodynamic Investigations and Characterization of Some Alloys in Ternary Pb-Au-Bi System

The results of XRD analysis, obtained using available ASTM reflections for the constituent binary systems in the ternary Pb-Au-Bi system, are presented in Table 5 for the chosen samples in the Pb-Au-Bi section. Also, SEM image for the sample with \( x_{\text{Pb}} = 0.8 \) is shown in Fig. 7.

Fine grains in a multiphase heterogenic mixture could be observed. Since EDX analysis did not give any authentic data on the composition of the present phases, isothermal solidification of the eutectic type could be supposed only by the shape shown in a SEM image.

The results of the characterization of alloys in the Pb-Au-Bi section should be taken as an unpretentious contribution to the experimental investigation of the phase equilibria in Pb-Au-Bi system, but only as an assumption which needs more detailed observation and research.

Fig. 4 Comparison between \( G_{\text{Pb}}^{x_{\text{Pb}}} \) obtained by Oelsen calorimetry and calculation at 973 K.

Fig. 6 The results of DTA measurements.

Fig. 7 SEM image of the investigated sample with \( x_{\text{Pb}} = 0.8 \) (Enlargement: x2000).

Pb-AuBi cut (Fig. 6).

The results of XRD analysis, obtained using available ASTM reflections for the constituent binary systems in the ternary Pb-Au-Bi system, are presented in Table 5 for the chosen samples in the Pb-Au-Bi section. Also, SEM image for the sample with \( x_{\text{Pb}} = 0.8 \) is shown in Fig. 7.

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The results of the characterization of alloys in the Pb-AuBi cut section should be taken as an unpretentious contribution to the experimental investigation of the phase equilibria in Pb-Au-Bi system, but only as an assumption which needs more detailed observation and research.
4. CONCLUSION

Thermodynamics of the Pb-AuBi\text{cut} section in ternary Pb-Au-Bi system was studied using Oelsen calorimetry and Redlich-Kister-Muggianu model. Thermodynamic properties were obtained for the temperature interval 873 - 973 K and compared mutually, showing good agreement. Negative deviation from Raoult law in the whole concentration range indicated to the strong miscibility of the constituent elements. Also, DTA, XRD and SEM analysis of the chosen samples was done in the frame of the characterization of the investigated Pb-Au-Bi alloys.

References


\begin{table}
\centering
\caption{The results of XRD investigations.}
\begin{tabular}{|c|c|c|c|c|c|}
\hline
\hline
\(x_{Pb} = 0.20\) & \(x_{Pb} = 0.62\) & \(x_{Pb} = 0.68\) & \(x_{Pb} = 0.75\) & \(x_{Pb} = 0.80\) & \(x_{Pb} = 0.85\) \\
\hline
(nm) & (nm) & (nm) & (nm) & (nm) & (nm) \\
\hline
0.3884 & 0.4076 & 0.3509 & 0.3267 & 0.5646 & 0.3944 \\
0.3640 & 0.3929 & 0.3234 & 0.2898 & 0.4795 & 0.3232 \\
0.3263 & 0.3600 & 0.3095 & 0.2786 & 0.3958 & 0.3083 \\
0.3081 & 0.3252 & 0.2863 & 0.2651 & 0.3522 & 0.2851 \\
0.2912 & 0.2793 & 0.2783 & 0.2525 & 0.3240 & 0.2785 \\
0.2780 & 0.2674 & 0.2660 & 0.2497 & 0.3077 & 0.2666 \\
0.2344 & AuBi & 0.2351 & AuBi & 0.2536 & Pb & 0.2350 & AuBi & 0.2896 & Pb & 0.2493 & Pb \\
0.2253 & Bi & 0.2258 & Bi & 0.2346 & AuBi & 0.2251 & Bi & 0.2792 & Bi & 0.2376 & AuBi \\
0.2186 & 0.2014 & Au & 0.2248 & Bi & 0.2001 & Au & 0.2761 & Bi & 0.2267 & Bi \\
0.2113 & 0.1958 & Bi & 0.2076 & AuBi & 0.1959 & Bi & 0.2669 & Bi & 0.2175 \\
0.2012 & Au & 0.1854 & Bi & 0.2013 & Au & 0.1853 & Bi & 0.2589 & Bi & 0.2109 \\
0.1959 & Bi & 0.1623 & AuBi & 0.1959 & Bi & 0.1664 & Pb & 0.2489 & Pb & 0.2075 \\
0.1851 & Bi & 0.1484 & Bi & 0.1853 & Bi & 0.1619 & AuBi & 0.2375 & AuBi & 0.2033 & Au \\
0.1627 & AuBi & 0.1430 & AuBi & 0.1736 & & 0.1488 & PbBi & 0.2270 & Bi & 0.1971 & Bi \\
0.1610 & & & & 0.1617 & AuBi & 0.1453 & AuBi & 0.2111 & Bi & 0.1849 & Bi \\
0.1547 & & & & 0.1486 & PbBi & 0.1434 & AuBi & 0.1991 & & 0.1736 & Pb \\
0.1503 & & & & & & 0.1853 & Bi & 0.1655 & & & & \\
0.1480 & Bi & & & & & & 0.1739 & Pb & 0.1618 & & & \\
0.1433 & AuBi & & & & & & 0.1661 & & & 0.1540 & & \\
0.1394 & AuBi & & & & & & 0.1538 & AuBi & 0.1488 & PbBi & \\
0.1379 & AuBi & & & & & & 0.1488 & PbBi & 0.1459 & & \\
0.1393 & AuBi & & & & & & 0.1431 & AuBi & 0.1437 & AuBi & \\
0.1393 & AuBi & & & & & & & & 0.1393 & AuBi & \\
\hline
\hline
\end{tabular}
\end{table}
29) Version 1.1 of the COST 531 Database for Lead Free Solders.

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