EXPERIMENTAL STUDY ON THERMODYNAMICS OF Cu-Pb-Ti AND Cu-Pb-V ALLOYS

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Summary
The thermodynamic activity of Pb in liquid Cu-Pb-Ti and Cu-Pb-V alloys has been determined by the equilibrium saturation method at T = 1473K. The Cu-Pb alloy was accepted as a reference mixture. The interaction parameters of titanium and vanadium on the lead activity, $\varepsilon_{\text{T} \text{Pb}}$ and $\varepsilon_{\text{V} \text{Pb}}$, were calculated on the basis of experimental results. Negative values of these parameters suggest that titanium and vanadium decrease lead activity in the studied alloys.

Keywords: copper alloys, thermodynamic activity, interaction parameter

1. Introduction

Lead shows a very negative influence on the physical properties of copper, because it is insoluble in the alloy matrix. Microadditions of metals, which effectively increase the solubility of lead in copper or fix it into high-melting compounds, will allow the neutralization of that negative influence. Nevertheless, usually copper makes intermetallic phases with the same metals as lead [1-3].

It has been decided to make a selective study by the determination of the thermodynamic properties of ternary Cu-Pb-Ti and Cu-Pb-V alloys. Lead activity and the influence of titanium and vanadium on lead activity in the investigated alloys were analyzed. Metal, that the most effectively decreases Pb activity should be the most efficient neutralizer.
2. Experimental

The analyzed alloys show considerable differences between vapour pressures of their elements. For instance at $T = 1473K$: $p_{Cu} = 3.95 \times 10^{-3}$ hPa, $p_{Pb} = 19.32$ hPa, $p_{Ti} = 1.16 \times 10^{-4}$ hPa, $p_{V} = 4.1 \times 10^{-6}$ hPa, [4]. As the vapor pressure of Pb is much higher than that of other elements, the activity measurements of Pb were carried out by the comparative method of equilibrium vapor saturation [5-8]. Apparatus used in experiments is presented in Figure 1.

![Fig. 1. Apparatus for equilibrium saturation, 1 – [Ni-(Ni-Cr)] thermocouple and alundum sheath for thermocouple, 2– graphite cover, 3 – graphite blocks with grooves for alloys, 4 – vacuum chamber.](image)

The studied Cu-Pb-Ti and Cu-Pb-V alloys and the reference Cu-Pb alloy were placed inside a graphite cells in a isothermal zone of a resistance furnace under a reduced argon pressure and saturated with the lead vapor until equilibrium was reached. At the equilibrium state, the activity of Pb is the same in all alloys inside a closed system. If the activity of Pb in the reference Cu-Pb alloy is known, it is possible to calculate the activity of Pb in the Cu-Pb-Ti and Cu-Pb-V alloys:

$$a_{Pb}(Cu-Pb) = a_{Pb}(Cu-Pb-Ti)$$  \quad (1)

$$\gamma_{Pb}(Cu-Pb-Ti) = x_{Pb}(Cu-Pb) \cdot \gamma_{Pb}(Cu-Pb) / x_{Pb}(Cu-Pb-Ti)$$  \quad (2)

$$a_{Pb}(Cu-Pb) = a_{Pb}(Cu-Pb-V)$$  \quad (3)
The activity of Pb was determined experimentally, i.e. the experimental assigning of the equilibrium mole fraction of Pb in the reference and the studied alloys. The vapor pressure of lead is more than 100 times higher, than the pressure of the remaining elements. Therefore, the weighing method was accepted for the determination of the composition of alloys.
3. Results

The activity of lead in Cu-Pb-Ti and Cu-Pb-V at 1473 K was determined by the equilibrium saturation method. The activity coefficient of lead, $\gamma_{\text{Pb}}$, in those alloys was calculated on the basis of equation (2) or (4). Experimental values of Pb activity coefficient are presented in Tables 1 and 2. For describing the activity coefficient of lead $\gamma_{\text{Pb}}$ in the reference alloy Cu-Pb the equations proposed by Wypartowicz [9] and Esdaile et.al. [10] were accepted:

$$\ln \gamma_{\text{Pb}} = (3360/T - 0.6) (1 - x_{\text{Pb}})^2$$

(5)

$$\log \gamma_{\text{Pb}} = [-1.1293 + 263.5/T + (1.156 - 2375/T) x_{\text{Pb}}] x_{\text{Cu}}$$

(6)

Table 1. Experimental values of $\ln \gamma_{\text{Pb}}$ in Cu-Pb-Ti alloys calculated on the basis of equation 2. Values of Pb activity in the reference Cu-Pb mixture calculated according to equations (5) and (6)

<table>
<thead>
<tr>
<th>$x_{\text{Pb}}$ (Cu-Pb)</th>
<th>$x_{\text{Pb}}$ (Cu-Pb-Ti)</th>
<th>$x_{\text{Ti}}$ (Cu-Pb-Ti)</th>
<th>$\ln \gamma_{\text{Pb}}$ acc.to eq.(5)</th>
<th>$\ln \gamma_{\text{Pb}}$ acc.to eq.(6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0044</td>
<td>0.0099</td>
<td>0.0204</td>
<td>0.848</td>
<td>0.862</td>
</tr>
<tr>
<td>0.0074</td>
<td>0.0260</td>
<td>0.0198</td>
<td>0.373</td>
<td>0.398</td>
</tr>
<tr>
<td>0.0134</td>
<td>0.0225</td>
<td>0.0206</td>
<td>1.115</td>
<td>1.180</td>
</tr>
<tr>
<td>0.044</td>
<td>0.0116</td>
<td>0.0302</td>
<td>0.705</td>
<td>0.668</td>
</tr>
<tr>
<td>0.0109</td>
<td>0.0159</td>
<td>0.0297</td>
<td>1.266</td>
<td>1.337</td>
</tr>
<tr>
<td>0.0015</td>
<td>0.0067</td>
<td>0.0416</td>
<td>0.186</td>
<td>0.078</td>
</tr>
<tr>
<td>0.0033</td>
<td>0.0139</td>
<td>0.0386</td>
<td>0.227</td>
<td>0.255</td>
</tr>
<tr>
<td>0.0023</td>
<td>0.0096</td>
<td>0.0598</td>
<td>0.265</td>
<td>0.265</td>
</tr>
</tbody>
</table>

Table 2. Experimental values of $\ln \gamma_{\text{Pb}}$ in Cu-Pb-V alloys calculated on the basis of equation 2. Values of Pb activity in the reference Cu-Pb mixture calculated according to equations (5) and (6)

<table>
<thead>
<tr>
<th>$x_{\text{Pb}}$ (Cu-Pb)</th>
<th>$x_{\text{Pb}}$ (Cu-Pb-V)</th>
<th>$x_{\text{V}}$ (Cu-Pb-V)</th>
<th>$\ln \gamma_{\text{Pb}}$ acc.to eq.(5)</th>
<th>$\ln \gamma_{\text{Pb}}$ acc.to eq.(6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0081</td>
<td>0.0107</td>
<td>0.0081</td>
<td>1.374</td>
<td>1.381</td>
</tr>
<tr>
<td>0.0274</td>
<td>0.0291</td>
<td>0.0274</td>
<td>1.525</td>
<td>1.545</td>
</tr>
<tr>
<td>0.0078</td>
<td>0.0078</td>
<td>0.0078</td>
<td>1.649</td>
<td>1.645</td>
</tr>
<tr>
<td>0.0062</td>
<td>0.0066</td>
<td>0.0062</td>
<td>1.589</td>
<td>1.579</td>
</tr>
<tr>
<td>0.0092</td>
<td>0.0101</td>
<td>0.0092</td>
<td>1.555</td>
<td>1.493</td>
</tr>
<tr>
<td>0.0042</td>
<td>0.0075</td>
<td>0.0042</td>
<td>1.093</td>
<td>0.978</td>
</tr>
<tr>
<td>0.0049</td>
<td>0.0074</td>
<td>0.0049</td>
<td>1.256</td>
<td>1.323</td>
</tr>
</tbody>
</table>

As the solutions, are diluted ones, they can be described by means of the Wagner equation [1, 2]:

$$\ln \gamma_{\text{Pb}} = (3360/T - 0.6) (1 - x_{\text{Pb}})^2$$

(5)
\[ \ln \gamma_{Pb} = \ln \gamma_{Pb}^0 + \varepsilon_{Pb}^{Pb} x_{Pb} + \varepsilon_{Pb}^{Ti} x_{Ti} \]  
(7)

\[ \ln \gamma_{Pb} = \ln \gamma_{Pb}^0 + \varepsilon_{Pb}^{Pb} x_{Pb} + \varepsilon_{Pb}^{V} x_{V} \]  
(8)

where \( \gamma_{Pb}^0 \) is the activity coefficient of Pb in Cu-Pb-Ti or Cu-Pb-V at \( x_{Pb} \to 0 \), 
\( \varepsilon_{Pb}^{Pb} = (\partial \ln \gamma_{Pb} / \partial x_{Pb}) \) \( x_{Pb} \to 0 \), \( x_{Ti} \to 0 \), or \( x_{V} \to 0 \) is the interaction parameter of Pb in Cu-Pb-Ti or Cu-Pb-V, 
\( \varepsilon_{Pb}^{Ti} = (\partial \ln \gamma_{Pb} / \partial x_{Ti}) \) \( x_{Pb} \to 0 \), \( x_{Ti} \to 0 \) is the interaction parameter of Ti in Cu-Pb-Ti and 
\( \varepsilon_{Pb}^{V} = (\partial \ln \gamma_{Pb} / \partial x_{V}) \) \( x_{Pb} \to 0 \), \( x_{V} \to 0 \), is the interaction parameter of V in Cu-Pb-V.

In equation (7, 8) values of mole fractions of components and lead activity coefficient were determined experimentally, whereas values of \( \ln \gamma_{Pb}, \varepsilon_{Pb}^{Pb}, \varepsilon_{Pb}^{Ti} \) 
and \( \varepsilon_{Pb}^{V} \) were calculated by means of the least–squares method.

Calculations were performed in two ways:

I. Values \( \gamma_{Pb}^0 \) and \( \varepsilon_{Pb}^{Pb} \) parameters were accepted from the binary Cu-Pb system.

According to equation (5):

\[ \ln \gamma_{Pb} = 1.681 - 3.55x_{Pb} \]  
(9)

According to equation (6):

\[ \log \gamma_{Pb} = 0.659 - 1.36x_{Pb} \]  
(10)

The \( \varepsilon_{Pb}^{Ti} \) and \( \varepsilon_{Pb}^{V} \) parameters were calculated on the basis of experimental results by the least-squares method.

II. Values of all parameters, that is \( \gamma_{Pb}^0, \varepsilon_{Pb}^{Pb}, \varepsilon_{Pb}^{Ti}, \) and \( \varepsilon_{Pb}^{V} \) were calculated on the basis of experimental results by the least-squares method.

Values of parameters calculated by both methods are presented in Table 3.

Values of interaction parameters \( \varepsilon_{Pb}^{Ti} \) and \( \varepsilon_{Pb}^{V} \) calculated by methods I and II do not differ significantly (see Tables 3 and 4). Moreover, the choice of the description of the reference alloy [9 or 10] does not influence values of interaction parameters in studied mixtures (see Table 3 and 4).

On the basis of experimental results the following the following expressions for the Pb activity in studied alloys were obtained.
\( T = 1473K: \)

Cu-Pb-Ti alloys

\[
\ln \gamma_{Pb} = 1.681 - 1.56x_{Pb} - 30.74x_{Ti}
\] (11)

Cu-Pb-V alloys

\[
\ln \gamma_{Pb} = 1.681 + 0.2x_{Pb} - 10.31x_{V}
\] (12)

Table 3. Values of \( \ln \gamma_{Pb}^0 \) and \( \varepsilon_{Pb}^\gamma \) parameters calculated by methods I and II. Values of \( \ln \gamma_{Pb} \) in Cu-Pb calculated according to equations (5) and (6)

<table>
<thead>
<tr>
<th>( \ln \gamma_{Pb} ) in Cu-Pb</th>
<th>( \varepsilon_{Pb}^\gamma ), method I</th>
<th>( \ln \gamma_{Pb}^0 ), method II</th>
<th>( \varepsilon_{Pb}^\gamma ), method II</th>
</tr>
</thead>
<tbody>
<tr>
<td>According to eq. (5)</td>
<td>-34.35</td>
<td>-1.56</td>
<td>-30.74</td>
</tr>
<tr>
<td>According to eq. (6)</td>
<td>-30.23</td>
<td>-1.27</td>
<td>-30.79</td>
</tr>
</tbody>
</table>

Table 4. Values of \( \ln \gamma_{Pb}^0 \) and \( \varepsilon_{Pb}^\gamma \) parameters calculated by methods I and II. Values of \( \ln \gamma_{Pb} \) in Cu-Pb calculated according to equations (5) and (6)

<table>
<thead>
<tr>
<th>( \ln \gamma_{Pb} ) in Cu-Pb</th>
<th>( \varepsilon_{Pb}^\gamma ), method I</th>
<th>( \ln \gamma_{Pb}^0 ), method II</th>
<th>( \varepsilon_{Pb}^\gamma ), method II</th>
</tr>
</thead>
<tbody>
<tr>
<td>According to eq. (5)</td>
<td>-9.24</td>
<td>0.20</td>
<td>-10.31</td>
</tr>
<tr>
<td>According to eq. (6)</td>
<td>-9.55</td>
<td>0.77</td>
<td>-10.67</td>
</tr>
</tbody>
</table>

The comparison between the calculated and experimental Pb activities in Cu-Pb-Ti and Cu-Pb-V alloys at 1473K are presented in Figs. 2, 3.

4. Conclusions

Using the vapor saturation method, the Pb activities in Cu-Pb-Ti and Cu-Pb-V alloys at the temperature 1473 K were determined and interaction parameters were calculated. Negative values of interaction parameters suggest that both titanium and vanadium decrease lead activity in the studied alloys. Values of interaction parameters calculated by two methods do not differ significantly (only 10 per cent), what speaks for consistency of the results.
Experimental study on thermodynamics...

Fig. 2. Activity coefficient of Pb in Cu-Pb-Ti alloys at $T = 1473$ K

![Graph showing activity coefficient of Pb in Cu-Pb-Ti alloys at 1473 K.]

Fig. 3. Activity coefficient of Pb in Cu-Pb-V alloys at $T = 1473$ K

![Graph showing activity coefficient of Pb in Cu-Pb-V alloys at 1473 K.]

References

[1] T. POMIANEK, J. MIDURA: Influence of Ce on the activity of Pb in $\{(1-x_1-x_2)Cu + x_1Pb + x_2Ce\}$ (l) for $x_1, x_2 < 1$ at the temperature 1473K. *J. Chem. Thermodynamics*, 22(1990), 949-956.
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