Distributions of Sn, Sb, and Bi between Ag-Pb Alloy and PbO Based Melt at 1273 K

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Distributions of Sn, Sb, and Bi between Ag-Pb alloy and PbO based melt were investigated at 1273 K. A chemical equilibrium technique was used in order to measure the distributions. The oxygen partial pressure equilibrated with the melts was measured by an EMF method. The distribution ratios were defined as the weight ratios of Sn, Sb, and Bi in PbO divided by those in the Ag-Pb phase. The obtained distribution ratios were plotted against the logarithm of the oxygen partial pressure. The plots showed that the distribution ratios of Sn, Sb, and Bi increased with an increase in the oxygen partial pressure. Taking the slope of these plots, the oxide forms of the minor elements dissolved in the PbO based melt could be estimated. Sn dissolves in PbO based melts as SnO₁₂ in the oxygen partial pressure range, \( P_{O_2} = 10^{-5} - 10^{-4} \). Depend on the concentration of Sn in PbO and that in Ag, the activity coefficient of SnO₂ in the PbO based melt at 1273 K was determined to be 62,000. The activity coefficient of BiO₁₂ decreases with increasing oxygen partial pressure and that of SbO₁₂ increases with increasing oxygen partial pressure. The distribution behavior of such minor elements was compared with that of Ag, and the efficiency of oxidation in the removal of such impurities from Ag was investigated. [doi:10.2320/matertrans.M2009117]

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1. Introduction

In industry, Ag and PbO are separated by the selective oxidation of Pb. The thermodynamic properties of the Ag-Pb-O system play an important role in this process of separation and have been investigated in order to improve this process. In this process, there are minor elements that coexist in the source material, and these are extracted from the Ag or PbO phase after the separation of Ag and PbO. Therefore, it is important to consider the distribution behaviors of minor elements in the Ag-Pb-O system. Generally, elements dissolve in the oxide phase in their corresponding oxide form; therefore, the distribution ratios of Ag and other minor elements vary with changing equilibrated oxygen partial pressure. It has been determined that Ag dissolves in PbO as an oxide, namely, AgO₂. Se oxide is stable as SeO₂ however, Se dissolves in the non-oxide form. The dissolution form of a minor element in the oxide phase provides important thermodynamic information that can help to estimate the distribution ratio between the metal and oxide phases.

In this study, the distribution behaviors of Sn, Sb, and Bi between Ag-Pb alloy and PbO based melt were investigated. First, the distribution ratios of Sn, Sb, and Bi in Ag-Pb and PbO based melt were measured as functions of the oxygen partial pressure by a chemical equilibrium technique and an EMF method. By examining the relationship between the oxygen partial pressure and distribution ratios, it was found that Sn dissolved in PbO as SnO₂. On the basis of the reported activity coefficients of Sn, Sb, and Bi and the standard free energy of formation of SnO₂, SbO₁₂, and BiO₁₂, it was possible to determine the activity coefficients of SnO₂, SbO₁₂, and BiO₁₂. The activity coefficient of SbO₁₂ increased and that of BiO₁₂ decreased with an increase in the oxygen partial pressure.

2. Experimental Procedure

A silicon carbide electric resistance furnace connected to a PID controller with a Pt/Pt-13%Rh thermocouple was employed. The temperature of the hot zone of the furnace was maintained at 1273 ± 3 K.

Five grams of Ag, Pb, Sn, and Sb mixture or Ag, Pb, and Bi mixture and 10 g of PbO were loaded into an alumina crucible. Reagent grade Ag, Pb, Sn, Sb, Bi, and PbO were used to prepare the specimens. The weights of Sn, Sb, and Bi were set in the range of 0.1–0.2 g. At the start of the experiment, the crucible was suspended at the top of a reaction tube. A continuous flow of argon gas at 100 ml/min was used to remove oxygen from the system. After flushing the reaction tube for 30 min, the crucible was slowly lowered into the reaction tube and placed on a support stage located in the hot zone. The time required to achieve equilibrium between the liquid alloy and the slag phases was confirmed in advance as 4 h. After maintaining the set temperature for 4 h, the oxygen partial pressure in the liquid alloy was indirectly determined using the following oxygen-concentration cell:

\[
\text{Pt/ Ni, NiO/ZrO}_2/\text{CaO} / \text{specimen/ Re/Pt}
\]

where the point at which Re and Pt wires were connected was set within the hot zone of the furnace. There was no influence of Re on the emf, and the dissolution of Re into the alloy phase was not observed. The crucible was then removed from the furnace and quenched in Ar gas, and its contents were separated into two phases, namely, metal and oxide. The metal phase was carefully prepared for chemical analysis by ensuring that it did not entrain any slag particles. The compositions of the separated metal and oxide phases were determined by chemical analysis. The concentrations of Sn, Sb, and Bi in the metal and oxide phases were determined by inductively coupled plasma atomic emission spectrometry.
The distribution of Sn and Sb between Ag-Pb alloy and PbO based melt at 1273 K is discussed in the next section.

3. Distribution Behaviors of Sn, Sb, and Bi between Ag-Pb alloy and PbO based Melt at 1273 K

3.1 Distribution ratios of Sn and Sb

Figures 1 and 2 show the results of the experiment for determining the distribution behaviors of Sn and Sb between Ag-Pb and PbO based oxide at 1273 K. The distribution ratio of M ($L_M^{s/m}$) is defined as

$$L_M^{s/m} = \frac{[\text{mass}\%M]}{[\text{mass}\%M]}$$ (2)

where M, (mass\%M) and [mass\%M] denote an element, its concentration in slag, and its concentration in metal, respectively.

The distribution ratios of Sn and Sb increased by a factor of 30–1000 and 100–300, respectively, with an increase in the oxygen partial pressure $P_{O_2}$ in the range of $10^{-6.5}$–$10^{-5.0}$. Sn and Sb were mainly distributed in the oxide phase, and their concentration was less than 1 mass\%. Concentrations of Sn and Sb in metal are low, therefore data are slightly scattered. Since the melt was equilibrated with the AlO$_{1.5}$ crucible, the solubility of AlO$_{1.5}$ in the PbO phase was almost constant approximately 4 mass\%. The addition of AlO$_{1.5}$ in the PbO melt did not cause any remarkable change in the activity coefficient of AgO$_{0.5}$ but increased it slightly. In this case, the influence of AlO$_{1.5}$ on the activity coefficient of minor elements could not be established; hence, it was excluded from the following thermodynamic analysis.

The distribution ratios can be represented graphically by the least square method:

$$\log L_{Sn}^{s/m} = 1.0 \cdot \log P_{O_2} + 8.2$$ (3)

and

$$\log L_{Sb}^{s/m} = 0.40 \cdot \log P_{O_2} + 4.5$$ (4)

3.2 Distribution ratio of Bi

Figures 3 shows results of the experiment for determining the distribution behavior of Bi in Ag-Pb and PbO at 1273 K. The distribution ratio increased by a factor of 1–100 with an increase in the oxygen partial pressure $P_{O_2}$ in the range of $10^{-6.5}$–$10^{-4}$. The concentration of Bi in the oxide phase was less than 2 mass\%. The distribution ratio of Bi can also be represented graphically by plotting the equation

$$\log L_{Bi}^{s/m} = 0.96 \cdot \log P_{O_2} + 6.2$$ (5)

The distribution ratios of all three elements, Sn, Sb, and Bi, between Ag-Pb and the PbO based melt increased with an increase in the oxygen partial pressure, that is agree with distribution phenomena of Ag which dissolved into the PbO melt as oxide. The dissolution of the elements in the PbO based melt is discussed in the next section.

4. Discussions

4.1 Dissolution of Sn, Sb, and Bi in PbO based melt

Generally, an element dissolved into a metal and oxide phase in its metallic and oxide form, respectively. The oxidation and reduction of element M between Ag-Pb alloy and the PbO based melt can be described as
Table 1 Thermodynamic data relating with distribution equilibria of minor elements (1273 K).

<table>
<thead>
<tr>
<th>Element</th>
<th>Reaction</th>
<th>( P_{O_2} )</th>
<th>( K ) at 1273 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>Ag(l)+1/4O_2(g) = AgO_{0.25}(s)</td>
<td>3.42 × 10^6</td>
<td>7.36 × 10^{-2}</td>
</tr>
<tr>
<td>Pb</td>
<td>Pb(l)+1/2O_2(g) = PbO(l)</td>
<td>1.42 × 10^{-4}</td>
<td>8.37 × 10^2</td>
</tr>
<tr>
<td>Bi</td>
<td>Bi(l)+3/4O_2(g) = BiO_{0.75}(l)</td>
<td>2.53 × 10^{-7}</td>
<td>8.86 × 10^4</td>
</tr>
<tr>
<td>Sn</td>
<td>Sn(l)+O_2(g) = SnO_2(l)</td>
<td>8.93 × 10^{-14}</td>
<td>1.12 × 10^{11}</td>
</tr>
<tr>
<td>Sb</td>
<td>Sb(l)+3/4O_2(g) = SbO_{1.5}(l)</td>
<td>7.18 × 10^{-12}</td>
<td>2.28 × 10^8</td>
</tr>
<tr>
<td>Se</td>
<td>Se(l)+O_2(g) = SeO_2(s)</td>
<td>2.98 × 10^{-3}</td>
<td>3.36 × 10^4</td>
</tr>
</tbody>
</table>

\( \text{M(l)} + \frac{n}{2} \text{O}_2(g) = \text{MO}_n(l) \) (6)

where \( n \) is a positive number.

The equilibrium constant in eq. (6) \( (K_6) \) is

\[
K_6 = \frac{a_{\text{MO}_n}}{a_{\text{M}} \cdot P_{O_2}^{n/2}} = \frac{(\gamma_{\text{MO}_n}) \cdot (X_{\text{MO}_n})}{[\gamma_{\text{M}}] \cdot [X_{\text{M}}] \cdot P_{O_2}^{n/2}} \tag{7}
\]

where \( a_{\text{MO}_n} \), \( \gamma_{\text{MO}_n} \), and \( a_{\text{M}} \) are the activity of \( \text{MO}_n \), activity coefficient of \( \text{MO}_n \), and activity of \( \text{M} \) relative to pure liquid \( \text{M} \), respectively. Equation (7) can be rewritten as

\[
\log L_{\gamma_{\text{MO}_n}/\gamma_{\text{M}}/X_{\text{M}}/P_{O_2}^{n/2}} = \frac{n}{2} \log P_{O_2} + \log[\gamma_{\text{M}}] - \log(\gamma_{\text{MO}_n}) + \log \left( \frac{[\gamma]}{[\gamma]} \right) + \log K_6 \tag{8}
\]

where \( [\gamma] \) denotes the total mole number of constituents in 100 g of phase. Since the concentrations of Sn, Sb, and Bi in Ag-Pb and the PbO based melt were low, their activity coefficients could be assumed to be constant. The distribution ratios of Sn, Sb, and Bi are graphically illustrated in Figs. 1, 2, and 3, respectively, by taking \( \log L_{\gamma_{\text{MO}_n}/\gamma_{\text{M}}/X_{\text{M}}/P_{O_2}^{n/2}} \) as the ordinate and \( \log P_{O_2} \) as the abscissa. Then, the slope of the straight line gives \( n/2 \). The values of the slope in the case of Sn, Sb, and Bi are 1.0, 0.40, and 0.96, respectively. The stable oxides of Sn, Sb, and Bi; the corresponding oxygen partial pressure of the equilibrated pure metal; and the oxide and equilibrium constants are listed in Table 1. SnO_2, SbO_{1.5}, and BiO_{1.5} were the most stable oxides in the given temperature and oxygen partial pressure range. The slope of the line in Fig. 1 indicates that Sn dissolved in the PbO melt as SnO_2. In Figs. 2 and 3, the value of the slope in the case of Bi is slightly higher than 0.75, while that of Sb is considerably lower than 0.75.

4.2 Activity coefficients of SnO_2, SbO_{1.5}, and BiO_{1.5} in PbO melt at 1273 K

Using eq. (6), on the basis of the concentrations and activity coefficients of Sn, Sb, and Bi, equilibrated oxygen partial pressure, and the standard free energy of formation of the oxide, the activities of SnO_2, SbO_{1.5}, and BiO_{1.5} can be derived as follows:

\[
\gamma_{\text{MO}_n} = \frac{\gamma_{\text{M}} \cdot X_{\text{M}} \cdot P_{O_2}^{n/2} \cdot K_6}{X_{\text{MO}_n}} \tag{9}
\]

In this experiment, the mole fraction of \( \text{M} \) in metal and \( \text{MO}_n \) in oxide phase were determined from the concentrations of Sn, Sb, and Bi. The equilibrium constant \( K_6 \) was obtained from the standard free energy change expressed in eq. (6). When the concentrations of Sn, Sb, and Bi are low, then the activity coefficients of Sn and Bi in Ag-Pb alloy, based on regular solution approximation, can be expressed as follows:

\[
\ln \gamma_M = X_{\text{Ag}} \cdot \ln \gamma_{\text{MinAg}} + X_{\text{Pb}} \cdot \ln \gamma_{\text{MinPb}} - \frac{\Delta G_{\text{mix}}^{\text{xe}}}{RT} \tag{10}
\]

Here, \( \gamma_{\text{MinAg}} \) and \( \gamma_{\text{MinPb}} \) denote the activity coefficients of M, Ag, and Pb, in Ag-Pb alloy, respectively, and \( \Delta G_{\text{mix}}^{\text{xe}} \) denotes the excess energy of mixing of Ag and Pb. Concentrations of Ag and Pb in metal phase can be derived from equilibration of Ag-Pb-O system. The activity coefficients of Sn in Ag and Pb are 1.49 at 1250 K and 6.82 at 1050 K, respectively. The activity coefficients of Sn in liquid Ag and Pb at 1273 K were derived from the reported values based on the regular solution approximation as 1.48 and 4.87, respectively. Similarly, the activity coefficients of Sb in Ag and Pb and Bi in Pb were determined as 0.057, 0.84, and 0.68, respectively. The activity coefficient of Bi in pure Ag could not be determined; however, in the case of Ag-Bi alloy at 1000 K on the liquidus saturated with Ag it was determined to be 1.1. The partial enthalpy of Bi in Ag-Bi alloy decreased with a decrease in the concentration of Bi, and therefore, the activity coefficient of dilute Bi shifts to 1 in Ag at 1273 K. In the following analysis, the activity coefficient of Bi in Ag was assumed to be unity. Using the regular solution approximation, the excess energy of mixing of Ag and Pb at 1273 K was found out from literature. Since the concentrations of SnO_2, SbO_{1.5}, and BiO_{1.5} were less than 2 mass%, the self-interaction parameter of SnO_2, SbO_{1.5}, and BiO_{1.5} on the activities could be ignored. The activity coefficients of Sn, Sb, and Bi could be obtained from eq. (9). Activities of SnO_2, SbO_{1.5}, and BiO_{1.5} are plotted as a function of the oxygen partial pressure in Fig. 4. It appears that the activity coefficient of SnO_2 does not vary with changing oxygen partial pressure. However, the activity coefficient of SbO_{1.5} shows an increase with an increase in the oxygen partial pressure. In the case of BiO_{1.5}, the activity coefficient slightly...
decreases with an increase in the oxygen partial pressure. The difference of oxide form between a stable oxide and its solution in PbO can be understood by observing the slopes in Fig. 2 and Fig. 3, which are lower and higher than 0.75, respectively. The difference causes the change in the activity coefficients of SbO
\textsubscript{1/5} and BiO
\textsubscript{1/5}. According to eqs. (4) and (5), SbO
\textsubscript{0/8} and BiO
\textsubscript{1/9.6} might be stable oxides in PbO melt. If they are taken to reference states, the activity coefficients of them are constant values in various oxygen partial pressure.

4.3 Phase separation of minor elements

The distribution ratios of Sn, Sb, Bi, Se,\textsuperscript{7) and Ag\textsuperscript{4)} are shown in Fig. 5. The equilibrium partial pressure of oxygen between the metals and the oxides is shown in Table 1. The distribution ratios of the minor elements are much higher than that of Ag. Typically, the distribution ratio increases with a increase in the equilibrium oxygen partial pressure between pure metal elements and pure oxides. Sn and Sb are oxidized more easily than Pb; hence, they have high distribution ratios. Both AgO
\textsubscript{0.5} and SeO\textsubscript{2} are unstable at 1273 K; however, Ag oxide and Se in the non-oxide form are stable in the PbO based melt.

The distribution ratios of Sn, Sb, Bi, and Se are plotted as functions of the mole fraction of Ag in the PbO based melt equilibrated with Ag-Pb alloy (Fig. 6). The relationship between the partial pressure of oxygen and the mole fraction of Ag in PbO can be derived from the equilibration of the Ag-Pb-O system.\textsuperscript{4)} Since the concentration of AgO\textsubscript{0.5} in PbO increases with increasing oxygen partial pressure, the distribution ratios of the minor elements, except for Se, also increase.

Therefore, in order to increase the distribution ratios of Sn, Sb, and Bi, the oxygen partial pressure should be increased. This leads to an increase in the concentration of Ag in the PbO based oxide phase and a decrease in the concentration of Pb in the Ag phase.

5. Conclusions

The distribution ratios of Sn, Sb, and Bi between Ag-Pb alloy and the PbO based melt in an alumina crucible were investigated by a chemical equilibrium technique and an EMF method. The conclusions are as follows:

(1) Sn, Sb, and Bi are mainly distributed in the PbO based phase. The distribution ratios increase with an increase in the oxygen partial pressure.

(2) Sn dissolves in PbO as SnO\textsubscript{2} in the oxygen partial pressure range of 10\textsuperscript{-7.5} – 10\textsuperscript{-6}.

(3) The activity coefficients of SnO\textsubscript{2}, SbO\textsubscript{1/5}, and BiO\textsubscript{1/5} in PbO based melt were determined to be approximately 62,000, 2.3, and 0.40, respectively.

REFERENCES