Activity Coefficient of $\text{AgO}_{0.5}$ in the PbO-SiO$_2$ Melt at 1273 K

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Activity coefficient of $\text{AgO}_{0.5}$ in PbO-SiO$_2$ melt equilibrated with Ag-Pb alloy in an alumina or a magnesia crucible was investigated at 1273 K. A chemical equilibrium technique was applied to the measurement. The oxygen partial pressure was also measured by an EMF method. The activity coefficient of $\text{AgO}_{0.5}$ in the PbO-SiO$_2$ melt was derived.

The addition of SiO$_2$ in the PbO melt decreases dissolution of Ag into the oxide phases. However, the activity coefficient of $\text{AgO}_{0.5}$ increases slightly with an increase in the concentration of SiO$_2$ in the PbO melt. [doi:10.2320/matertrans.MRA2006251]

Keywords: activity coefficient of $\text{AgO}_{0.5}$, PbO-SiO$_2$ melt, silver-lead alloy

1. Introduction

Cupellation is a process of selective oxidation for separating Pb from Ag; however, PbO-based oxides entrain Ag as $\text{AgO}_{0.5}$. It is difficult to recover the Ag that is distributed in the oxide phase. The slag loss of Ag is a key issue of the process from the economical point of view. The equilibrium of Ag between metal and slag is expressed as follows:

$$\text{Ag(l)} + \frac{1}{4}\text{O}_2(\text{g}) = \text{AgO}_{0.5} (\text{l, in slag}). \quad (1)$$

In the last stage of cupellation, nearly the entire metal phase is composed of Ag. Thus the activity coefficient of Ag is nearly unity. For efficient separation, it is preferable to increase the activity coefficient of $\text{AgO}_{0.5}$ and decrease that of PbO in the oxide phase.

In a previous study it was reported that Ag dissolves in the PbO melt as $\text{AgO}_{0.5}$ in the oxygen partial pressure range from $P_{\text{O}_2} = 10^{-8}$ to $10^{-4.1}$ ($P_{\text{O}_2}$ is in the partial pressure). $P_{\text{O}_2} = 1$ in atmospheric pressure is $1.013 \times 10^5 \text{ Pa}$ The solubility of Ag in PbO slag is also reported; however, its solubility in PbO-based multicomponent slags has not been observed. The slags generated in actual operations contain sulfur and other oxides such as SiO$_2$. The other contents will cause a decrease in the activity coefficient of PbO and may change the activity coefficient of $\text{AgO}_{0.5}$ in the slag. For an improvement in the operation, the thermodynamic properties of Ag in the PbO-based oxides such as a PbO-SiO$_2$ melt should provide important information. The purposes of the present study are to measure the distribution of Ag between the metal and slag phases, and to investigate the influence of the addition of SiO$_2$ to a PbO based slag on the activity coefficient of $\text{AgO}_{0.5}$.

2. Experimental Procedure

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

Five grams of a Ag and Pb mixture, and 10 g of PbO and SiO$_2$ were loaded into an alumina crucible and a magnesia crucible. Reagent grade Ag, Pb, PbO, and SiO$_2$ were used to prepare the specimens. At the start of the experiment, the crucible was suspended at the top of a reaction tube. A continuous flow of Ar gas at 100 ml/min was used to exclude O$_2$ 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 as 4 h in advance. After being maintained 4 h at the set temperature, the oxygen partial pressure in the liquid alloy was measured with the following oxygen-concentration cell:

$$\text{Pt}/\text{Ni, NiO/ZrO}_2\text{-CaO/specimen/Re/Pt}$$

where the connecting point of the Re and Pt wire was set within the hot zone of the furnace. The dissolution of Re into the alloy phase was not observed. Then, the crucible was removed from the furnace and quenched in flushing Ar gas and the content was separated into two phases, namely, metal and slag. Special care was taken while preparing the metal for chemical analysis to ensure that the specimen entrains no slag particles. The compositions of the separated metal and slag were determined by the chemical analysis. The Ag, Pb, Al, and Mg contents in the metal and slag phases were determined by inductively coupled plasma (ICP) emission spectrometry, while the SiO$_2$ content was determined by gravimetry.

The oxygen partial pressure was calculated from the EMF of the cell and the standard free energy of the formation of NiO(s)$^{13}$ is as follows:

$$\log P_{\text{O}_2} = 20.171 \cdot E/T - 24.409/T + 8.869 \quad (2)$$

where $E$ and $T$ are the voltage and the absolute temperature, respectively.

3. Results and Discussion

3.1 Results of the experiment

Tables 1 and 2 show the results of the experiment in the alumina and magnesia crucibles, respectively. Assuming that the metal elements in oxide exist as oxide, namely $\text{AgO}_{0.5}$,
Determined from the concentration of the metal element in the PbO melt is reported in a previous study. The oxygen partial pressure and the concentration of AgO in the PbO melt are important factors. The activity coefficient of AgO in the PbO melt is given by the equation:

$$ \log \gamma_{\text{AgO}} = \frac{1}{C_0} \left( \frac{X_{\text{AgO}}}{X_{\text{PbO}}} \right) $$

where $X_{\text{AgO}}$ and $X_{\text{PbO}}$ are the mole fractions of AgO and PbO, respectively, in the melt.

Table 1: Equilibrated composition of Ag-Pb and PbO-SiO$_2$ melts in alumina.

<table>
<thead>
<tr>
<th>No.</th>
<th>$\log P_{O_2}$</th>
<th>$X_{\text{Pb}}$</th>
<th>$X_{\text{Ag}}$</th>
<th>$X_{\text{Si}}$</th>
<th>$X_{\text{Mg}}$</th>
<th>$X_{\text{AgO}}$</th>
<th>$X_{\text{PbO}}$</th>
<th>$X_{\text{SiO}_2}$</th>
<th>$X_{\text{MgO}}$</th>
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<tr>
<td>1</td>
<td>−6.84</td>
<td>0.104</td>
<td>0.896</td>
<td>0.00005</td>
<td>0.00005</td>
<td>0.522</td>
<td>0.00225</td>
<td>0.240</td>
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<td>2</td>
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<td>0.00047</td>
<td>0.00042</td>
<td>0.383</td>
<td>0.00357</td>
<td>0.565</td>
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<td>0.975</td>
<td>0.00013</td>
<td>0.00027</td>
<td>0.423</td>
<td>0.00206</td>
<td>0.511</td>
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<td>0.00095</td>
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<td>0.509</td>
<td>0.00230</td>
<td>0.244</td>
<td>0.244</td>
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<td>0.00099</td>
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<td>0.607</td>
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<td>0.396</td>
<td>0.00217</td>
<td>0.532</td>
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<td>7</td>
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<td>0.0135</td>
<td>0.986</td>
<td>0.00066</td>
<td>0.00020</td>
<td>0.421</td>
<td>0.00350</td>
<td>0.462</td>
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<tr>
<td>8</td>
<td>−5.58</td>
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<td>0.979</td>
<td>0.00116</td>
<td>0.00199</td>
<td>0.469</td>
<td>0.00433</td>
<td>0.385</td>
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<td>0.986</td>
<td>0.00015</td>
<td>0.00015</td>
<td>0.487</td>
<td>0.00502</td>
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<td>−4.74</td>
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<td>0.974</td>
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<td>0.00429</td>
<td>0.597</td>
<td>0.00809</td>
<td>0.142</td>
<td>0.253</td>
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<tr>
<td>11</td>
<td>−3.79</td>
<td>0.00238</td>
<td>0.994</td>
<td>0.00122</td>
<td>0.00240</td>
<td>0.461</td>
<td>0.0158</td>
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<td>0.215</td>
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<tr>
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<td>0.998</td>
<td>0.00006</td>
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<td>0.513</td>
<td>0.0138</td>
<td>0.225</td>
<td>0.248</td>
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<tr>
<td>13</td>
<td>−2.47</td>
<td>0.00044</td>
<td>0.999</td>
<td>0.00008</td>
<td>0.00053</td>
<td>0.475</td>
<td>0.0227</td>
<td>0.250</td>
<td>0.253</td>
</tr>
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Table 2: Equilibrated composition of Ag-Pb and PbO-SiO$_2$ melts in magnesia.

<table>
<thead>
<tr>
<th>No.</th>
<th>$\log P_{O_2}$</th>
<th>$X_{\text{Pb}}$</th>
<th>$X_{\text{Ag}}$</th>
<th>$X_{\text{Si}}$</th>
<th>$X_{\text{Mg}}$</th>
<th>$X_{\text{AgO}}$</th>
<th>$X_{\text{PbO}}$</th>
<th>$X_{\text{SiO}_2}$</th>
<th>$X_{\text{MgO}}$</th>
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<td>0.0575</td>
<td>0.940</td>
<td>0.0018</td>
<td>0.00059</td>
<td>0.440</td>
<td>0.00158</td>
<td>0.515</td>
<td>0.0429</td>
</tr>
<tr>
<td>2</td>
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<td>0.0615</td>
<td>0.937</td>
<td>0.0014</td>
<td>0.00046</td>
<td>0.459</td>
<td>0.00225</td>
<td>0.498</td>
<td>0.0402</td>
</tr>
<tr>
<td>3</td>
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<td>0.0248</td>
<td>0.972</td>
<td>0.0033</td>
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<td>0.487</td>
<td>0.00353</td>
<td>0.459</td>
<td>0.0505</td>
</tr>
<tr>
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<td>0.0320</td>
<td>0.967</td>
<td>0.0007</td>
<td>0.00005</td>
<td>0.672</td>
<td>0.00464</td>
<td>0.291</td>
<td>0.0322</td>
</tr>
<tr>
<td>5</td>
<td>−5.23</td>
<td>0.0200</td>
<td>0.979</td>
<td>0.0011</td>
<td>0.00000</td>
<td>0.680</td>
<td>0.00567</td>
<td>0.285</td>
<td>0.0302</td>
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<td>0.00000</td>
<td>0.630</td>
<td>0.00591</td>
<td>0.329</td>
<td>0.0343</td>
</tr>
<tr>
<td>7</td>
<td>−5.40</td>
<td>0.0765</td>
<td>0.925</td>
<td>0.0000</td>
<td>0.00013</td>
<td>0.985</td>
<td>0.00520</td>
<td>0.000</td>
<td>0.0091</td>
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</table>

Fig. 1: Activity coefficient of AgO$_{0.5}$ in the PbO-SiO$_2$ melt at 1273 K.

3.2 Activity coefficient of AgO$_{0.5}$ and PbO in PbO-SiO$_2$ melt

Ag dissolves in the PbO melt as AgO$_{0.5}$. The oxidation reaction of Ag in oxide is expressed as eq. (3).

$$ \text{Ag(1)} + \frac{1}{4}\text{O}_2(\text{g}) = \text{AgO}_{0.5}(\text{s}) $$

$$ \Delta G^\circ = 27,620 \text{J at 1273 K} $$

where eq. (4) is the Gibbs energy change for the reaction in eq. (3) at 1273 K. In fact, silver oxide decomposes into Ag and O$_2$ at the experimental temperature. The Gibbs energy change in eq. (4) was extrapolated from a lower temperature. The oxygen partial pressure and the concentration of AgO$_{0.5}$ in the slag are measured in the present study. The activity coefficient of Ag in an Ag-Pb melt is reported in a previous literature.$^3$ Applying these data to eqs. (3) and (4), the activity coefficient of AgO$_{0.5}$ in the PbO-SiO$_2$ melt can be obtained. The activity coefficient of AgO$_{0.5}$ is shown in Fig. 1. Here, the open circles and solid circles are the results obtained using the alumina and magnesia crucibles, respectively. The open square shows the activity coefficient of AgO$_{0.5}$ in the PbO melt.$^4$

The activity coefficient of AgO$_{0.5}$ in the PbO-SiO$_2$ melt in the magnesia crucible is slightly higher with the mole fraction of SiO$_2$. Since the EMF in the alumina crucible was relatively unstable, the results are scattered. However, the activity coefficient of AgO$_{0.5}$ in the PbO-SiO$_2$ melt is higher than that in a previous work. The PbO-SiO$_2$ melt in the alumina crucible entrains a considerable amount of AlO$_1$. The mole fraction of MgO in the PbO-SiO$_2$ melt is less than 0.05. The influence of MgO on the activity coefficient of AgO$_{0.5}$ may be relatively small. The activity coefficient of AgO$_{0.5}$ in the alumina crucible is higher than that in the magnesia crucible. The addition of AlO$_1$ in the PbO-SiO$_2$
melt is likely to increase the activity coefficient of AgO in Pb. The previous work was carried out in an alumina crucible. Further, the activity coefficient of AgO was 0.6 with $X_{AlO_2} = 0.15$ in the PbO phase. Without the influence of alumina, the activity coefficient of AgO in the PbO melt should be less than 0.6. The activity coefficients of AgO in the PbO-SiO$_2$ melt in the magnesia crucible are about 0.5, 0.6, and 0.6-0.9 at $X_{SiO_2} = 0$, 0.3, and 0.5, respectively. Therefore, the addition of SiO$_2$ causes an increase in the activity coefficient of AgO. Based on the assumption that MgO and AgO do not influence the activity coefficient of AgO, it can be expressed as a function of SiO$_2$ as follows:

$$\gamma_{AgO} = 0.46X_{SiO_2} + 0.49$$

(5)

It is represented as a solid line in Fig. 1.

The oxidation reaction of Pb and the Gibbs energy change are

$$Pb(l) + \frac{1}{2}O_2(g) = PbO(l)$$

(6)

$$\Delta G^o = -184440 + 69.79T J$$

(7)

The equilibrium constant of eq. (6) is

$$K = \frac{\gamma_{PbO} \cdot X_{PbO}}{a_{Pb} \cdot P_{O_2}}$$

(8)

where $K$, $a_{Pb}$, $\gamma_{PbO}$, $X_{PbO}$ and $P_{O2}$ are the equilibrium constant, activity of Pb, activity coefficient of PbO, mole fraction of PbO and oxygen partial pressure, respectively.

The activity of Pb in Ag-Pb alloy can be found in the literature. Therefore, the activity coefficient of PbO is derived from the composition of PbO in the oxide phase, and that of Pb in the metal phase and the oxygen partial pressure.

Figure 2 shows the relationship between the mol fraction of SiO$_2$ in the PbO-SiO$_2$ melt and the activity coefficient of PbO. The activity coefficient of PbO in the PbO based melt decreases with an increase in the concentration of SiO$_2$. The oxide melt contains a small amount of AgO$\delta$ and AlO$_{1.5}$ or MgO at $X_{SiO_2} = 0$. Thus $X_{PbO}$ is nearly unity, and the activity coefficient of PbO would be almost unity at this point.

### 3.3 Solubility of AlO$_{1.5}$ and MgO in the PbO melt

Figure 3 shows the relationship between the mol fraction of SiO$_2$ and AlO$_{1.5}$ in the oxide phase. The open circles represent the results of the present study. The solid circles and open square represent the mol fraction of AlO$_{1.5}$ in PbO liquid saturated with the AlO$_{1.5}$ solid phase at 1273 K. In the present study, the mol fraction of AlO$_{1.5}$ decreases with an increase in the mol fraction of SiO$_2$. Mullite may be formed on the surface of the alumina crucible as follows:

$$4/3AlO_{1.5}(s) + SiO_2(l) = 1/3Al_6Si_2O_{13}(s)$$

(9)

The equilibrium constant of eq. (9) is

$$K = \frac{a_{1/3}^{Al_6Si_2O_{13}}}{a_{AlO_{1.5}} \cdot a_{SiO_2}}$$

(10)

In case the specimens were saturated with the mullite phase, $a_{Al_6Si_2O_{13}}$ would be unity and $a_{AlO_{1.5}}$ would be variable. The increase in the concentration of SiO$_2$ in the oxide phase causes a decrease in the activity and concentration of AlO$_{1.5}$ in the oxide.

The mol fraction of AlO$_{1.5}$ represented by the solid circle is lower than that represented by the open circles from $X_{SiO_2} = 0.15$ to 0.3. In the region with lower SiO$_2$ concentration the saturating phase is AlO$_{1.5}$. The concentration of AlO$_{1.5}$ will increase with the concentration of SiO$_2$ in the PbO saturated with AlO$_{1.5}$. Further, the concentration of PbO saturated with mullite will decrease with the increasing concentration of SiO$_2$. The mol fraction of AlO$_{1.5}$ in the PbO-SiO$_2$ melt saturated with mullite is shown as a function of the mol fraction of SiO$_2$ in eq. (11).

$$X_{AlO_{1.5}} in PbO-SiO_2 melt = -0.54X_{SiO_2} + 0.37$$

at 1273 K (0.2 < $X_{SiO_2}$ < 0.6)

(11)

Figure 4 shows the relationship between the mol fraction of MgO and SiO$_2$ in the oxide phase. The concentration of MgO increases with the increasing concentration of SiO$_2$. The mol fraction of MgO in the PbO-SiO$_2$ melt may be expressed as follows:

![Diagram](image-url)
The addition of SiO$_2$ in the PbO-based slag may cause a melting loss of the MgO-based refractory.

### 3.4 Solubility of Ag in PbO-SiO$_2$ melt

Figure 5 shows the relationship between the mole fraction of AgO$_{0.5}$ in the oxide and that of Ag in the metal. The solid circles and open circles represent the results obtained using the alumina and magnesia crucibles, respectively. The solid line represents the mole fraction of AgO$_{0.5}$ in PbO.$^1$ The mole fraction of AgO$_{0.5}$ in the PbO-SiO$_2$ melt is less than that of the PbO melt. The addition of SiO$_2$ in PbO decreases the dissolution of Ag in the PbO melt.

The influence of the oxygen partial pressure on the concentration of AgO$_{0.5}$ in the PbO-based melt is shown in Fig. 6. The concentration of AgO$_{0.5}$ does not depend on the addition of SiO$_2$. That means influence of SiO$_2$ on the activity coefficient of AgO$_{0.5}$ is relatively small. However, SiO$_2$ decreases the activity of PbO that causes a decrease in the partial pressure of oxygen; therefore, the phase separation is improved as shown in Fig. 5.

The redox reaction between Ag and Pb and the Gibbs energy change are expressed as follows:

$$2\text{Ag}(l) + \text{PbO}(l) \rightarrow \text{Pb}(l) + 2\text{AgO}_{0.5}(s)$$  \hspace{1cm} (13)

and

$$\Delta G^\circ = 150,800 \text{ J} \text{ at 1273 K.}$$  \hspace{1cm} (14)

The equilibrium constant of eq. (13) is expressed as

$$K = \frac{a_{\text{Pb}} \cdot a^{2}_{\text{AgO}_{0.5}}}{a_{\text{PbO}} \cdot a^{2}_{\text{Ag}}}.$$  \hspace{1cm} (15)

In the last stage of cupellation, the concentration of Ag in the metal is nearly unity. The activity of Ag in the metal phase is almost equal to the mole fraction of Ag. The mole fraction of PbO is defined as $X_{\text{PbO}} = 1 - X_{\text{SiO}_2} - X_{\text{MgO}} - X_{\text{AgO}_{0.5}}$ or $X_{\text{PbO}} = 1 - X_{\text{SiO}_2} - X_{\text{AlO}_{1.5}} - X_{\text{AgO}_{0.5}}$. The activity coefficient of PbO and AgO$_{0.5}$ can be derived from Figs. 1 and 2. The influence of SiO$_2$ on the solubility of Ag in the
slag is then shown as Fig. 7. The horizontal and vertical axes represent the mass pct of Pb in the Ag-Pb alloy and mass pct Ag in the oxide phase, respectively. It is assumed that the metal and slag are equilibrated at 1273 K. The phase separation is improved with increasing concentration of SiO_2 in the oxide phase. Addition of SiO_2 in the PbO-based melt increases the activity coefficient of AgO_{0.5} and decreases the activity of PbO in the oxide phase. This causes the effective separation of PbO and Ag.

4. Conclusions

The activity coefficient of Ag in the PbO-SiO_2 melt equilibrated with the Ag-Pb alloy in an alumina or a magnesia crucible was investigated at 1273 K and the following conclusions were obtained.

(1) SiO_2 increases slightly the activity coefficient of AgO_{0.5} in the PbO-SiO_2 melt.
(2) SiO_2 decreases the activity coefficient of PbO in the PbO-SiO_2 melt.
(3) The addition of SiO_2 in the oxide phase causes effective separation of PbO and Ag in the cupellation.

(4) SiO_2 increases the dissolution of MgO into PbO based melt.

Acknowledgement

The authors wish to thank Mr. Ryoju Obata for assistance with the measurement and chemical analysis. Ms. T. Kon of Iwate Univ. prepared experimental specimens.

REFERENCES