Activity Coefficient of $\text{AgO}_{0.5}$ in $\text{PbO-NaO}_{0.5}$ and PbO-CaO Melts at 1273 K

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The equilibration of a Ag-Pb-based melt with $\text{PbO-NaO}_{0.5}$ and PbO-CaO melts at 1273 K was investigated. A chemical equilibrium technique was used to carry out measurements. The oxygen partial pressure was measured by an electromotive force (EMF) method. The activity coefficient of $\text{AgO}_{0.5}$ in the $\text{PbO-NaO}_{0.5}$ and PbO-CaO melts and that of PbO in the $\text{PbO-NaO}_{0.5}$ melt was derived. The addition of $\text{NaO}_{0.5}$ to the PbO-based melt resulted in a slight decrease in the activity coefficient of $\text{AgO}_{0.5}$. However, the activity coefficient of PbO decreased remarkably with an increase in the concentration of $\text{NaO}_{0.5}$ in the PbO-based melt. Therefore, improved phase separation of Ag from the PbO-based melt was achieved by the addition $\text{NaO}_{0.5}$. The addition of CaO in the PbO-based melt did not cause any change in the activity coefficient of $\text{AgO}_{0.5}$. [doi:10.2320/matertrans.M2009036]

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1. Introduction

Selective oxidation of Pb is carried out for phase separation between PbO and Ag. However, on oxidation, PbO-based oxides entrain Ag as $\text{AgO}_{0.5}$. It is difficult to recover Ag that is distributed in the oxide phase. The slag loss of Ag is a key problem with this oxidation process from an economical point of view. In a previous study, it was reported that Ag dissolved as $\text{AgO}_{0.5}$ in PbO-based melts under an oxygen partial pressure ranging from $P_{\text{O}_2} = 10^{-8}$ to 10^{-41} (P_{O_2} is the oxygen partial pressure and is expressed as $P_{\text{O}_2} = (P_{\text{O}_2}/\text{Pa})/(P_{\text{O}_2}^0/\text{Pa})$, where $P_{\text{O}_2}^0 = 101,325 \text{ Pa}$). The equilibrium of Ag between metal and slag phases is expressed as follows:¹⁾

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

The solubility of Ag in a PbO-SiO_2 slag was also reported.²⁾ Thus, efficient phase separation can be achieved by using PbO-based multicomponent slags. Oxides of alkali and alkali earths are known to improve the reactivity and capacity of slags generated in refining processes. The addition of these oxides might result in a decrease in the activity coefficient of PbO and a change in the activity coefficient of $\text{AgO}_{0.5}$ in oxide melts. For achieving improved phase separation, studying the thermodynamic properties of Ag in PbO-based melts such as $\text{PbO-NaO}_{0.5}$ and PbO-CaO melts can provide important information. The purposes of the present study were to measure the distribution of Ag between metal and oxide phases and to investigate the effect of $\text{NaO}_{0.5}$ (or CaO) addition on the activity coefficient of $\text{AgO}_{0.5}$ in a PbO-based melt.

2. Experimental Procedure

A silicon carbide electric resistance furnace connected to a PID controller with a Pt/Pt-13%Rh thermocouple was used for carrying out measurements. The temperature of the hot zone of the furnace was maintained within $\pm 3 \text{ K}$.

5 g of a Ag and Pb mixture and 10 g of PbO and NaOH (or CaO) mixture were loaded into an alumina crucible. Reagent grade Ag, Pb, PbO, NaOH, and CaCO_3 were used to prepare specimens. CaO was prepared in advance by decomposing CaCO_3 . According to the phase diagram of the $\text{NaO}_{0.5}$ -PbO system,³⁾ Na was stable as $\text{NaO}_{0.5}$ in the oxide melt at 1273 K. NaOH was decomposed on melting. At the beginning of the experiment, the crucible was suspended on top of a reaction tube. A continuous flow of Ar gas at 100 ml/min was used to exclude 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 metal and slag phases was confirmed as 4 h in advance. After maintaining equilibrium for 4 h at 1273 K, the oxygen partial pressure in the melt was measured using the following oxygen concentration cell:

where the connecting point between Re and Pt wires was set within the hot zone of the furnace. Dissolution of Re into the alloy phase was not observed. The crucible was then removed from the furnace and quenched in Ar gas, and the content was separated into two phases, namely, metal and oxide phases. Special care was taken while preparing the specimens for a chemical analysis by ensuring that they did not entrain any slag particles. The compositions of the separated metal and oxide phases were determined by the chemical analysis. The concentrations of Ag, Pb, Al, Na, and Ca in the metal and slag phases were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES).

The oxygen partial pressure was calculated from the EMF of the cell, and the standard free energy of formation of NiO(s) ⁴⁾ is as follows:

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Table 1 Equilibrium compositions for the Ag-Pb-O system with NaO_{0.5} at 1273 K.

No.	log P_{O_2}	Metal phase				Oxide phase			
		X_{Pb}	X_{Ag}	X_{Na}	X_{Al}	X_{PbO}	$X_{AgO_{0.5}}$	$X_{NaO_{0.5}}$	$X_{AlO_{1.5}}$
1	-8.63	0.235	0.753	0.0001	0.012	0.601	0.0001	0.375	0.023
2	-8.45	0.227	0.760	0.0001	0.014	0.637	0.0013	0.338	0.023
3	-8.16	0.245	0.738	0.0001	0.017	0.691	0.0013	0.277	0.031
4	-8.08	0.400	0.600	0.0001	0.000	0.772	0.0012	0.224	0.003
5	-8.08	0.304	0.696	0.0001	0.000	0.722	0.0012	0.270	0.006
6	-7.24	0.074	0.927	0.0003	0.000	0.734	0.0022	0.254	0.010
7	-7.02	0.214	0.786	0.0000	0.000	0.861	0.0023	0.127	0.010
8	-6.89	0.109	0.892	0.0002	0.000	0.725	0.0016	0.267	0.006
9	-5.94	0.047	0.953	0.0000	0.000	0.731	0.0044	0.262	0.003
10	-5.69	0.011	0.989	0.0002	0.000	0.713	0.0060	0.276	0.005

Table 2 Equilibrium compositions for the Ag-Pb-O system with CaO at 1273 K.

No.	log P_{O_2}	Metal phase				Oxide phase			
		X_{Pb}	X_{Ag}	X_{Ca}	X_{Al}	X_{PbO}	$X_{AgO_{0.5}}$	X_{CaO}	$X_{AlO_{1.5}}$
1	-5.36	0.033	0.967	0.0000	0.0001	0.943	0.007	0.021	0.030
2	-5.51	0.036	0.964	0.0000	0.0001	0.942	0.007	0.032	0.021
3	-4.92	0.015	0.985	0.0002	0.0001	0.945	0.006	0.014	0.034
4	-4.45	0.012	0.988	0.0001	0.0001	0.930	0.011	0.008	0.052
5	-4.19	0.009	0.991	0.0003	0.0002	0.930	0.012	0.015	0.043

$$\log P_{O_2} = 20171 \times E/T - 24409/T + 8.869 \quad (2)$$

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 measured equilibrium values between the Ag-Pb-based and PbO-NaO_{0.5} melts and the Ag-Pb-based and PbO-CaO melts. Because of the limitation on the analytical stability of the ICP-AES method, the concentration of oxygen in the specimens was not evaluated from the mass balance of Ag, Pb, Na, Ca, Al, and O in the metal phase. Assuming that the metal elements in the oxide phase existed as oxides, namely, AgO_{0.5}, PbO, AlO_{1.5}, NaO_{0.5}, and CaO, the mole fractions of the oxides were determined from the concentration of the metal element in the oxide phase.

3.2 Phase separation between Ag-Pb-based melt and PbO-NaO_{0.5} or PbO-CaO melt

The relationship between the mole fraction of Ag in the Ag-Pb-based melt and that of AgO_{0.5} in the PbO-based melt is shown in Fig. 1. The vertical and horizontal axes represent the mole fractions of the elements in the oxide and metal phases, respectively. Open and solid circles represent the PbO-NaO_{0.5} and PbO-CaO-based melts, respectively. The solid line represents the mole fraction of AgO_{0.5} in the PbO-based melt.¹⁾ The solubility of Ag in the oxide phase increased remarkably with the concentration of Ag in the Ag-Pb-based melt over $X_{Ag} = 0.9$. It can be observed in Fig. 1 that the solubility of Ag in the PbO-NaO_{0.5} and PbO-CaO melts was almost the same as that in the PbO-based melt. The addition of NaO_{0.5} (or CaO) to the PbO-based melt did not

Fig. 1 Solubility of Ag in PbO-MO_x system.

cause a significant change in the concentration of Ag in the metal phase and that of AgO_{0.5} in the oxide phase.

3.3 Effect of dissolution of AlO_{1.5}

Figure 2 shows the relationship between the mole fraction of AlO_{1.5} and NaO_{0.5} (or CaO) in the oxide phase. Solid and open circles represent the PbO-NaO_{0.5} and PbO-CaO melts, respectively. The solid square represents the concentration of AlO_{1.5} in the PbO-based melt saturated in AlO_{1.5} crucible.¹⁾ The addition of AlO_{1.5} to the PbO-based melt resulted in an increase in the activity coefficient of AgO_{0.5}.²⁾ The concentration of AlO_{1.5} in the PbO-NaO_{0.5} and PbO-CaO melts was less than 0.03 and 0.05, respectively. The dissolution of AlO_{1.5} (mole fraction = 0.15) resulted in an increase in the activity coefficient of AgO_{0.5} by 1.2 times. Therefore, the effect of AlO_{1.5} addition was negligible. According to the

Fig. 2 Solubility of $\text{AlO}_{1.5}$ in PbO based melt.

phase diagram of the $\text{NaO}_{0.5}\text{-AlO}_{1.5}$ and $\text{CaO-AlO}_{1.5}$ systems, solid compounds such as NaAlO_2 ⁵⁾ and CaOAl_2O_3 ⁶⁾ were stable. Some of the compounds in the systems were formed on the surface of the alumina crucible. Therefore, the degree of dissolution of $\text{AlO}_{1.5}$ in the oxide phase decreased with increasing concentration of CaO and $\text{NaO}_{0.5}$.

3.4 Activity coefficient of PbO in $\text{PbO-NaO}_{0.5}$ melt

The oxidation reaction of Pb and the Gibbs free energy change can be expressed, respectively, as

$$\Delta G^\circ = -184440 + 69.79T \text{ J}^4). \quad (4)$$

Equilibrium constant of eq. (3), K_3 , is

$$K_3 = \frac{a_{\text{PbO}}}{a_{\text{Pb}} \times P_{\text{O}_2}^{1/2}} \quad (5)$$

where a_i and P_{O_2} are the activity of element i and the oxygen partial pressure in the atmosphere, respectively. The value of the activity of Pb in Ag-Pb -based systems can be derived from the literature.⁷⁾ Therefore, the activity of PbO was derived from the concentration of Pb in the metal phase and the oxygen partial pressure. The effect of $\text{NaO}_{0.5}$ addition on the activity of PbO in the PbO -based melt saturated with $\text{AlO}_{1.5}$ at 1273 K is shown in Fig. 3. Solid circles and broken line represent the activity coefficients of PbO measured in the present study. The line is activity in the ideal solution. The broken line is estimated from present data and activity of ideal solution in below $X_{\text{NaO}_{0.5}} = 0.05$ region. The activity coefficient of PbO decreased remarkably with increasing concentration of $\text{NaO}_{0.5}$, and its value was considerably smaller than that of the ideal solution. Na_2PbO_2 is stable in the solid state at low temperature,³⁾ and thus, the affinity between PbO and $\text{NaO}_{0.5}$ is strong. Therefore, it was clear that $\text{NaO}_{0.5}$ addition resulted in the decrease in the activity coefficient of PbO .

3.5 Activity coefficient of $\text{AgO}_{0.5}$ in $\text{PbO-NaO}_{0.5}$ and PbO-CaO melts

The oxidation reaction of Ag to $\text{AgO}_{0.5}$ can be represented as follows:

Fig. 3 Activity of PbO for the $\text{PbO-NaO}_{0.5}$ melt. Fig. 4 Activity coefficient of $\text{AgO}_{0.5}$ for the $\text{PbO-NaO}_{0.5}$ melt.

$$\Delta G^\circ = 27620 \text{ J at } 1273 \text{ K}^4) \quad (7)$$

$$K_6 = \frac{a_{\text{AgO}_{0.5}}}{a_{\text{Ag}} \cdot P_{\text{O}_2}^{1/4}} \quad (8)$$

where eq. (7) is the Gibbs free energy change at 1273 K for the reaction shown in eq. (6). In fact, $\text{AgO}_{0.5}$ decomposed into Ag and O_2 at the experimental temperature; therefore, the Gibbs free energy change was obtained from the extrapolation of values at lower temperature. The activity of Ag in Ag-Pb -based melts can be derived from the literature.⁷⁾ The oxygen partial pressure was measured by the EMF method. The concentration of Ag in the oxide melt was sufficiently low to assume that the activity coefficient of $\text{AgO}_{0.5}$ was constant. Substitutions the measured concentration of $\text{AgO}_{0.5}$ in oxide and Ag in metal for eq. (8) derive the activity coefficient of $\text{AgO}_{0.5}$. In Fig. 4, the activity coefficient of $\text{AgO}_{0.5}$ in the $\text{PbO-NaO}_{0.5}$ melt is shown as a function of the mole fraction of $\text{NaO}_{0.5}$. The activity coefficient of $\text{AgO}_{0.5}$ in the slag without $\text{NaO}_{0.5}$ and $\text{AlO}_{1.5}$ was 0.49.²⁾ As shown in Fig. 2, concentration of $\text{AlO}_{1.5}$ in the melt is small, the effect of $\text{AlO}_{1.5}$ addition on the activity coefficient of $\text{AgO}_{0.5}$ was assumed to be negligible.

Fig. 5 Activity coefficient of $\text{AgO}_{0.5}$ for the PbO-CaO melt.

The activity coefficient of $\text{AgO}_{0.5}$ in the oxide phase decreased with increasing concentration of $\text{NaO}_{0.5}$. The relationship between the mole fraction of $\text{NaO}_{0.5}$ and the activity coefficient of $\text{AgO}_{0.5}$ can be derived from Fig. 4 as

$$\gamma_{\text{AgO}_{0.5}} = -0.21 \cdot X_{\text{NaO}_{0.5}} + 0.49. \quad (9)$$

The activity coefficient of $\text{AgO}_{0.5}$ in the Pb-CaO melt is shown in Fig. 5 as a function of the mole fraction of CaO ; it remained almost constant across the varying concentrations of CaO . Calcium aluminate was formed on surface of the crucible. The activity of $\text{AlO}_{1.5}$ is inversely proportional to that of CaO , and thus, the concentration of $\text{AlO}_{1.5}$ in the slag decreased with the addition of CaO . The effect of $\text{AlO}_{1.5}$ addition on the activity coefficient of $\text{AgO}_{0.5}$ was negligible. Therefore, the addition of CaO to the PbO -based melt did not cause a change in the activity coefficient of $\text{AgO}_{0.5}$.

3.6 Solubility of $\text{AgO}_{0.5}$ in PbO -based melt

The effect of the oxygen partial pressure on the concentration of $\text{AgO}_{0.5}$ in the $\text{PbO-NaO}_{0.5}$ melt and that of the oxygen partial pressure on the concentration of Pb in the Ag-Pb -based melt is shown in Fig. 6. Solid and open circles indicate the mole fractions of Pb in the metal phase and those of $\text{AgO}_{0.5}$ in the oxide phase, respectively.

Specimens were prepared from the $\text{PbO-NaO}_{0.5}$ melt with the mole fraction of $\text{NaO}_{0.5}$ ranging from 0.13 to 0.38. The concentration of $\text{AgO}_{0.5}$ in the $\text{PbO-NaO}_{0.5}$ melt was higher than that in the PbO -based melt. However, the concentration of Pb in the $\text{PbO-NaO}_{0.5}$ melt was lower than that in the PbO -based melt. The addition of $\text{NaO}_{0.5}$ to the PbO -based melt resulted in a decrease in the activity coefficients of both $\text{AgO}_{0.5}$ and PbO .

The $[\text{Ag}]/(\text{AgO}_{0.5})$ ratio in Fig. 1 appears to have no change with the addition of $\text{NaO}_{0.5}$; that means that effect of the reduction of PbO activity for the oxide melt is almost same to the effect of the changing of activity coefficient of $\text{AgO}_{0.5}$ in that. However, Fig. 6 shows that the equilibrium oxygen partial pressure decreased with addition of $\text{NaO}_{0.5}$ for a given $[\text{Ag}]/(\text{AgO}_{0.5})$ ratio or $[X_{\text{Pb}}]$.

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

Fig. 6 The solubility of $\text{AgO}_{0.5}$ in PbO based oxide and Pb in Ag-Pb alloy. Fig. 7 Phase separation between Ag alloy and Pb based oxide.

and

$$\Delta G^\circ = 150800 \text{ J at } 1273 \text{ K}^4). \quad (11)$$

The equilibrium constant of eq. (10) is expressed as

$$K_{15} = \frac{a_{\text{Pb}} \cdot a_{\text{AgO}_{0.5}}^2}{a_{\text{PbO}} \cdot a_{\text{Ag}}^2}. \quad (12)$$

In the final stage of cupellation, the mole fraction of Ag in the metal phase was nearly unity. The activity of Ag in the metal phase was probably equal to the mole fraction of Ag . The concentration of PbO in the oxide phase was high; the mole fraction of PbO is defined as $X_{\text{PbO}} = 1 - X_{\text{NaO}_{0.5}} - X_{\text{AlO}_{1.5}} - X_{\text{AgO}_{0.5}}$. The activity coefficients of PbO and $\text{AgO}_{0.5}$ can be derived from Figs. 2, 3, and 4. The effect of $\text{NaO}_{0.5}$ addition on the solubility of Ag in the slag is shown in Fig. 7. The horizontal and vertical axes represent the mass pct of Pb in the Ag-Pb -based melt and the mass pct of Ag in the oxide phase, respectively. It was assumed that the metal and slag phases were equilibrated at 1273 K. Solid, broken, and thin broken lines represent the phase distribution of Ag

in PbO ,¹⁾ $\text{PbO-NaO}_{0.5}$ ($\text{NaO}_{0.5}$: 5 mass%), and PbO-SiO_2 (SiO_2 : 10 mass%),²⁾ respectively.

Improved phase separation was achieved by increasing the concentration of $\text{NaO}_{0.5}$ in the oxide phase. As shown in Figs. 3 and 4, the addition of $\text{NaO}_{0.5}$ to the PbO -based melt resulted in a slight decrease in the activity coefficient of $\text{AgO}_{0.5}$ and a remarkable decrease in the activity coefficient of PbO in the oxide phase. This helped achieve improved phase separation between PbO and Ag . The effect of $\text{NaO}_{0.5}$ addition on the separation was similar to that of SiO_2 addition.

As shown in Figs. 2 and 5, the concentrations of CaO and $\text{AlO}_{1.5}$ in the PbO-CaO melt investigated in the present study were sufficiently low. Therefore, the activity of PbO was probably equal to the mole fraction of PbO . The activity coefficient of $\text{AgO}_{0.5}$ remained constant across the varying concentrations of CaO . CaO addition resulted in a decrease in the concentration and activity of PbO in the oxide phase. Thus, slightly improved phase separation between Ag and PbO was achieved.

4. Conclusions

The activity coefficient of Ag in the $\text{PbO-NaO}_{0.5}$ and PbO-CaO melts equilibrated with the Ag-Pb -based melt at 1273 K in an alumina crucible was investigated, and the following conclusions were derived.

(1) The activity of PbO in the $\text{PbO-NaO}_{0.5}$ melt decreased significantly with increasing concentration of $\text{NaO}_{0.5}$.

(2) The activity coefficient of $\text{AgO}_{0.5}$ in the $\text{PbO-NaO}_{0.5}$ melt decreased slightly with increasing concentration of $\text{NaO}_{0.5}$.

(3) Improved phase separation was achieved with increasing concentration of $\text{NaO}_{0.5}$ in the oxide phase.

(4) The activity coefficient of $\text{AgO}_{0.5}$ in the PbO-CaO melt did not vary with increasing concentration of CaO .

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