Thermodynamic Study on the Ag–Pb–O System at 1273 K

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The phase relations for the Ag–Pb–O system saturated with alumina and the activity coefficient of $\text{AgO}_{0.5}$ in the PbO melt were investigated at 1273 K. A chemical equilibrium technique and an EMF method were applied to the measurement. In this system, there is a miscibility gap between a molten Ag–Pb alloy phase and a Pb–Ag–O oxide phase. The solubility of Ag in the oxide phase and that of Pb in the metal phase were studied as a relation of the partial oxygen pressure. These results suggest that component of silver oxide in liquid PbO phase should be represented as $\text{AgO}_{0.5}$. The activity coefficient of $\text{AgO}_{0.5}$ in the PbO based oxide melt at infinite dilution relative to pure solid $\text{AgO}_{0.5}$ is 0.602 at 1273 K.

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1. Introduction

Cupellation is a process of the selective oxidation for separating Ag and Pb, where a Pb based oxide melt containing considerable amount of Ag is generated. The production of Ag is an economically important part of the process. For an improvement of the operation, the thermodynamic properties of the Ag–Pb–O system are valuable information.

The system has a miscibility gap between a Ag–Pb melt and a Pb–Ag oxide melt. Various thermodynamic studies of liquid Ag–Pb alloys have been reported on the heat of mixing.^{1–3)} Iwase *et al.* reported the activity of Ag and Pb in the Ag–Pb alloy from 973 to 1273 K.⁴⁾ However, few researchers have investigated about the PbO– $\text{AgO}_{0.5}$ melt, except for Swinbourne *et al.*⁵⁾ who reported the activity coefficient of $\text{AgO}_{0.5}$ in the PbO based melt under the oxygen partial pressure from 1 to 10^5 Pa.

In present study, firstly the phase relations and oxygen partial pressure for the Ag–Pb–O system at 1273 K are investigated by a chemical equilibrium technique and an EMF method, respectively. Secondly, the distribution ratio of Ag between the Ag–Pb alloy and the Ag–Pb–O oxide melt, the activity coefficient of $\text{AgO}_{0.5}$ in the PbO based melt and that at infinite dilution relative to pure solid are discussed.

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 controlled to within 3 K.

Eight grams of Ag and Pb mixture, and 10 g of PbO were loaded into an aluminum crucible. Reagent grade Ag, Pb and PbO 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 argon gas at 100 mL/min was used to exclude oxygen from the system. After flushing the reaction tube for half hour, 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 slag phases was confirmed as 4 h in advance. After holding 4 h at the set temperature, the oxygen potential in the liquid alloy was indirectly determined with the following oxygen-concentration cell:

where, the connecting point of Re and Pt wire was set within the hot zone of the furnace. The dissolution of Re into the alloy phase was not observed. The crucible was removed from the furnace and quenched in the flushing Ar gas and the content was separated into two phases, namely metal and slag. Special care was taken in preparing the metal for chemical analysis to ensure that the specimen was not contaminated by slag particles. Compositions of the separated metal and slag were determined by analyzing Ag, Pb and Al with the inductively coupled plasma emission spectrometry (ICP-AES).

The oxygen partial pressure (P_{O_2} in atmospheres) was calculated from the electromotive force of the cell and the standard free energy of formation of NiO(s) ⁵⁾ as follows,

$$\log P_{\text{O}_2} = 20,171 \cdot E/T - 24,409/T + 8.869 \quad (1)$$

where E and T (in degrees Kelvin) are voltage and the absolute temperature, respectively.

3. Results and Discussion

3.1 Results of the experiment

Table 1 shows results of the present study. There is a miscibility gap between the liquid metal and oxide phases. Because of the limit of the analytical stability of the ICP-AES method, the concentration of oxygen in the metal was not evaluated by the mass balance of Ag, Pb, Al and O in the metal. On the assumption that the oxides components are $\text{AgO}_{0.5}$, PbO and $\text{AlO}_{1.5}$, the mole fractions of $\text{AgO}_{0.5}$, PbO and $\text{AlO}_{1.5}$ were determined from the concentration of Ag, Pb and Al in the oxide phase.

The mole fraction of Ag in the molten Ag–Pb alloy and PbO based slag is shown in Fig. 1. () and [] refer to an element in the oxide and metal phase, respectively. The

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Table 1 Composition of the metal and slag phases and oxygen partial pressures.

No	Metal phase			Slag phase			$\log P_{O_2}$	$\gamma_{AgO_{0.5}}$
	X_{Pb}	X_{Ag}	X_{Al}	X_{PbO}	$X_{AgO_{0.5}}$	$X_{AlO_{1.5}}$		
1	0.973	0.024	0.0029	0.844	0.0003	0.156	—	—
2	0.935	0.062	0.0039	0.817	0.0003	0.182	—	—
3	0.890	0.106	0.0038	0.836	0.0006	0.164	—	—
4	0.800	0.196	0.0038	0.838	0.0016	0.161	—	—
5	0.636	0.361	0.0032	0.811	0.0009	0.188	—	—
6	0.522	0.474	0.0041	0.826	0.0017	0.172	—	—
7	0.335	0.663	0.0026	0.833	0.0018	0.165	—	—
8	0.187	0.811	0.0024	0.833	0.0022	0.165	—	—
9	0.108	0.884	0.0075	0.818	0.0020	0.180	—	—
10	0.034	0.955	0.0115	0.797	0.0047	0.198	—	—
11	0.001	0.998	0.0002	0.821	0.0118	0.167	—	—
12	0.416	0.583	0.0015	0.835	0.0010	0.164	−8.06	0.465
13	0.309	0.688	0.0028	0.837	0.0010	0.162	−7.73	0.627
14	0.207	0.792	0.0011	0.845	0.0022	0.153	−7.21	0.420
15	0.152	0.847	0.001	0.824	0.0019	0.174	−6.89	0.618
16	0.110	0.888	0.0021	0.833	0.0023	0.165	−6.39	0.720
17	0.090	0.908	0.0018	0.838	0.0024	0.160	−6.35	0.720
18	0.050	0.950	0.0003	0.849	0.0044	0.147	−5.55	0.657
19	0.027	0.972	0.0004	0.838	0.0049	0.157	−5.61	0.577
20	0.024	0.969	0.0071	0.847	0.0060	0.147	−5.15	0.614
21	0.013	0.987	0.00004	0.846	0.0077	0.147	−4.39	0.749
22	0.001	0.999	0.0007	0.810	0.0243	0.165	−3.25	0.465
23	0.001	0.999	0.0002	0.807	0.0275	0.166	−3.09	0.450
24	0.001	0.999	0.00007	0.787	0.0667	0.146	−1.68	0.419

Fig. 1 The distribution of Ag in molten Ag–Pb alloy and PbO based slag at 1273 K.

solubility of Ag in oxide phase increases remarkably with increasing Ag concentration in the Ag–Pb alloy in over $X_{Ag} = 0.9$ region.

The relationship between the concentration of Pb in the Ag–Pb phase and Ag in the oxide phase is shown in Fig. 2.

Fig. 2 The relationship between the concentration of Pb in the molten Ag–Pb alloy and Ag in PbO based slag.

That shows liner relationship from -3 to -1 $\log X_{Pb}$ and the slope is negative $1/2$.

In order to compare with the literature values, the distribution ratio for Ag (L_{Ag}) is defined as

$$L_{Ag} = (\text{mass\%Ag})/[\text{mass\%Ag}] = \frac{X_{AgO_{0.5}} \cdot (n_T)}{X_{Ag} \cdot [n_T]} \quad (2)$$

where n_T is total mole number of constituents in 100 g of each phase. The logarithmic relationship between oxygen partial pressure and the L_{Ag} are shown in Fig. 3. The L_{Ag} increases with increasing oxygen partial pressure. The line was obtained by a chemical equilibrium technique in controlled atmosphere. The present result shows good agreement with that of the literature⁶⁾ at $P_{O_2} = 10^3$ Pa, however that shows lower value in lower oxygen pressure region.

The oxygen partial pressure changes with changing the composition of the Ag–Pb alloy. The solubility of Ag in the PbO based oxide and the composition of the Ag–Pb alloy are shown in Fig. 4 in a function of the oxygen partial pressure. The solid squares and circles indicate the concentration of Pb in the alloy and the solubility of Ag in the slag, respectively. The solubility of Ag increases with increasing oxygen partial pressure.

Fig. 3 Influence of the oxygen partial pressure on the L_{Ag} .

Fig. 4 The solubility of Ag in the PbO based oxide and the composition of the Ag–Pb alloy.

3.2 Thermodynamic analysis of the distribution ratio of Ag

In case that Ag solves in the oxide phase as $AgO_{0.5}$, the chemical reaction would be as follows:

$$\Delta G^0 = 27,620 \text{ J at } 1273 \text{ K}^{7)} \quad (4)$$

where Equation 4 is the Gibbs energy for the reaction eq. (3) at 1273 K. Actually, silver oxide decomposes into Ag and O_2 at the experimental temperature, the Gibbs energy change was obtained from the extrapolation of values at lower temperature. The equilibrium constant K is

$$K_3 = \frac{a_{AgO_{0.5}}}{a_{Ag} \cdot P_{O_2}^{1/4}} = \frac{\gamma_{AgO_{0.5}} \cdot X_{AgO_{0.5}}}{a_{Ag}} \cdot \frac{1}{P_{O_2}^{1/4}}, \quad (5)$$

where $a_{AgO_{0.5}}$, $\gamma_{AgO_{0.5}}$, $X_{AgO_{0.5}}$ and a_{Ag} are activity of $AgO_{0.5}$ relative to solid $AgO_{0.5}$, activity coefficient of $AgO_{0.5}$, mole fraction of $AgO_{0.5}$ and activity of Ag, respectively. Here Equation 5 can be rewritten as eq. (6)

$$\log X_{AgO_{0.5}} - \log a_{Ag} = \frac{1}{4} \log P_{O_2} + \log K_3 - \log \gamma_{AgO_{0.5}}. \quad (6)$$

Taking $\log X_{AgO_{0.5}} - \log a_{Ag}$ as the ordinate and $\log P_{O_2}$ as the abscissa, $1/4$ will be expressed by the slope of the straight line.

The relationship between the oxygen potential and $\log X_{AgO_{0.5}} - \log a_{Ag}$ is shown in Fig. 5. Activity of Ag is obtained from the composition of Ag–Pb alloy equilibrated with the slag. The activity of Ag in the Ag–Pb system at 1273 K is reported.⁴⁾ The results show a liner relationship. Using the least-squares method for the total experimental range, the line can be expressed as

$$\log X_{AgO_{0.5}} - \log a_{Ag} = 0.265 \cdot \log P_{O_2} - 0.802 \quad (7)$$

The slope is 0.265. A slight positive deviation from the line may be found in higher oxygen pressure region from 10^2 to $10^{3.3}$ Pa. The part of the results from 10^{-3} to 10 Pa seems liner and the slope is almost $1/4$. Because of the equilibrium

Fig. 5 The relationship between the oxygen potential and $\log X_{AgO_{0.5}} - \log a_{Ag}$.

Fig. 6 The relationship between $(1 - X_{\text{AgO}_{0.5}})^2$ and $\gamma_{\text{AgO}_{0.5}}$.

constant is a function only of temperature, the straight line suggests that $\log \gamma_{\text{AgO}_{0.5}}$ is almost a constant value under oxygen partial pressure from 10^{-3} to 10 Pa. Compared with eq. (6), it can be safely said that the component for Ag in PbO based oxide phase should be represented as $\text{AgO}_{0.5}$ under oxygen partial pressure from 10^{-3} to 10 Pa.

3.3 Activity coefficient of $\text{AgO}_{0.5}$ in the PbO based melt

To obtain the activity coefficient of $\text{AgO}_{0.5}$ in molten PbO saturated with $\text{AlO}_{1.5}$ at infinite dilution relative to pure solid $\text{AgO}_{0.5}$ ($\gamma_{\text{AgO}_{0.5}}^\circ$), a typical graphic expression is employed. $(1 - X_{\text{AgO}_{0.5}})^2$ and $\gamma_{\text{AgO}_{0.5}}$ are taken as the abscissa and the ordinate in Fig. 6. The activity coefficient of $\text{AgO}_{0.5}$ at infinite dilution relative to pure solid $\text{AgO}_{0.5}$ ($\gamma_{\text{AgO}_{0.5}}^\circ$) can be obtained from the extrapolated line at $(1 - X_{\text{AgO}_{0.5}})^2 = 1$. The result shows no tendency with the $(1 - X_{\text{AgO}_{0.5}})^2$ over 0.98, namely the oxygen partial pressure under 10 Pa. Therefore, the activity coefficient at infinite dilution is derived as 0.602 that is average of the activity coefficient of $\text{AgO}_{0.5}$ in the $(1 - X_{\text{AgO}_{0.5}})^2 > 0.98$ region. The activity coefficient of $\text{AgO}_{0.5}$ decreases in higher mole fraction of $\text{AgO}_{0.5}$. Using same standard condition of $\text{AgO}_{0.5}$ [eqs. (3) and (4)], $\gamma_{\text{AgO}_{0.5}}^\circ$ obtained by present study is 1.3 times as large as that measured by Swinbourne *et al.* The activity coefficient is constant up to $X_{\text{AgO}_{0.5}} = 0.03$.

The solubility of $\text{AlO}_{1.5}$ in the PbO phase is almost constant within $X_{\text{AgO}_{0.5}} = 0.14\text{--}0.16$. So the influence of $\text{AlO}_{1.5}$ on the activity coefficient of $\text{AgO}_{0.5}$ in PbO would not be ignored. However, the solubility has no tendency to be affected with the experimental condition. Therefore, the effect of $\text{AlO}_{1.5}$ on the activity coefficient is not found in the present study.

4. Conclusions

The phase relations for the Ag–Pb–O system saturated with alumina and the activity coefficient of $\text{AgO}_{0.5}$ in PbO melts were investigated at 1273 K and the following conclusions were obtained.

- (1) Distribution ratio of Ag increases remarkably with increasing concentration of Ag in the Ag–Pb alloy over $X_{\text{Ag}} = 0.9$.
- (2) Ag solves in the PbO based oxide as $\text{AgO}_{0.5}$ in the range of oxygen pressure from $P_{\text{O}_2} = 10^{-3}$ to 10 Pa.
- (3) The activity coefficient of $\text{AgO}_{0.5}$ in molten PbO saturated with $\text{AlO}_{1.5}$ at infinite dilution relative to pure solid is 0.602 based on which is derived from the following reaction

$$\Delta G^0 = 27,620 \text{ J at } 1273 \text{ K.}$$

The activity coefficient is constant up to $X_{\text{AgO}_{0.5}} = 0.03$.

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REFERENCES

- 1) M. Kawakami: Sci. Rep. Tohoku Univ. **19** (1930) 521–549.
- 2) Z. Kouzuka, T. Oishi and J. Moriyama: Trans. JIM **32** (1968) 136–142.
- 3) K. Itagaki and A. Yazawa: Trans. JIM **33** (1969) 259–266.
- 4) M. Iwase, K. Fujimura and T. Mori: Trans. JIM **39** (1975) 1118–1127.
- 5) G. G. Charette and S. N. Flengas: J. Electrochem. Soc. **115** (1968) 796–804.
- 6) D. R. Swinbourne, S. Yan, G. Hoang and D. Higgings: Trans. Inst. Min. Metall. C **112** (2003) C69–74.
- 7) O. Knacke, O. Kubaschewski and K. Hesselmann: *Thermochemical Properties of Inorganic Substances*, 2nd ed. (Springer-Verlag, Verlag Stahleisen, 1991).