Thermodynamic Properties of Selenium in Ag-Pb Alloy and Lead Oxide Phases at 1273 K

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The distribution ratio of Se between Ag-Pb alloy and PbO phases was investigated at 1273 K. A chemical equilibrium technique was used for the measurement. The oxygen partial pressure was in equilibrium with both the phases, and it was measured by an EMF method. The distribution ratio, defined as the mole fraction of Se in PbO to the mole fraction of Se in metal, was plotted against the oxygen partial pressure. The distribution ratio decreased with an increase in the oxygen partial pressure. The slope of the plot indicates that Se dissolves in the PbO phase as oxide, which is unreasonable. The activity coefficient of Se in the Ag-Pb alloy was also measured, and it was found to decrease with an increase in the concentration of Ag. Se dissolved in the PbO phase in the non-oxide form. The activity coefficient of Se in Ag was estimated as 0.0009 at 1273 K. [doi:10.2320/matertrans.M2009021]

1. Introduction

In industries, selective oxidation of Pb is carried out for separating Ag and PbO. The thermodynamic properties of the Ag-PbO system have been investigated,[1–7] it is important information to improve this process. Some minor elements are present in the source material, and they are extracted from the Ag or PbO phase by separation. Therefore, the thermodynamic properties of these minor elements have to be taken into consideration. The thermodynamic properties of Se in the Ag-Pb alloy and the PbO phase have been described in this paper. Firstly, the distribution ratio of Se between the Ag-Pb alloy and PbO phase is measured as function of the oxygen partial pressure by a chemical equilibrium technique and an electro motive force (EMF) method. Se is mainly distributed in the Ag-Pb phase. Minor elements are generally dissolved in the oxide phase in the form of oxides. Therefore, the distribution ratio increases with an increase in the oxygen partial pressure. However, the distribution ratio of Se, defined as the mole fraction of Se in PbO to the mole fraction of Se in metal cannot be explained by oxidation-dissolution. Then, the activity coefficient of Se in Ag-Pb alloy is measured by an isothermal isopiestic method in a closed silica cell. The activity coefficient of Se in the Ag-Pb alloy is determined from a report on the activity coefficient of Se in Pb.[8] The structure of Se in the PbO phase is also discussed.

2. Distribution Ratio of Se between Ag-Pb Alloy and PbO Phases at 1273 K

2.1 Experimental procedure

A SiC 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 at 1273 K within ±3 K.

5 g of a mixture of Ag, Pb, and Se and 10 g of PbO were placed in an alumina or magnesia crucible. Reagent-grade Ag, Pb, Se, 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 Ar gas at 100 ml/min was used to prevent oxygen entering 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 predetermined as 4 h. After 4 h, the oxygen potential in the liquid alloy was indirectly determined with the following oxygen concentration cell:

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

where the point at which the Re and Pt wires were connected was within the hot zone of the furnace. There was no influence of Re on the EMF. The dissolution of Re into the alloy phase was not observed. The crucible was then removed from the furnace and quenched in flushing Ar gas and the contents were separated into two phases, namely, metal and oxide phases. Special care was taken in preparing the metal for chemical analysis, in order to ensure that the specimen did not contain any slag particles. The compositions of the separated metal and oxide were determined by chemical analysis. The Ag, Pb, Se, Al, and Mg contents of the metal and slag phases were determined by inductively coupled plasma (ICP) emission spectrometry.

The oxygen partial pressure was calculated from the EMF of the cell and the standard free energy of formation of NiO(s)[9] as follows:

$$\log P_{O_2} = 20{,}171 \cdot E/T - 24{,}409/T + 8.869 \qquad (1)$$

where E and T are the voltage and absolute temperature, respectively. P_{O_2} is the oxygen partial pressure and is expressed as $P_{O_2} = (P_{O_2}/\text{Pa})/(P_{O_2}{}^0/\text{Pa})$, where $P_{O_2}{}^0 = 101{,}325\,\text{Pa}$.

2.2 Distribution ratio of Se

Table 1 shows the results of Se distribution between Ag-Pb alloy and PbO phase at 1273 K. Under the assumption that the oxide components were $AgO_{0.5}$, PbO, $AlO_{1.5}$, MgO, and

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Table 1 Equilibrated composition for Se distribution between Ag-Pb and PbO at 1273 K.

No.	$\log P_{O_2}$	Metal phase (mole fraction)				Oxide phase (mole fraction)			
		Ag	Pb	Al	Se	$AgO_{0.5}$	PbO	$AlO_{1.5}$	Se
1	−7.70	0.795	0.198	0.0000	0.0066	0.0140	0.897	0.084	0.0047
2	−7.24	0.840	0.159	0.0001	0.0013	0.0080	0.906	0.0851	0.0012
3	−6.97	0.784	0.203	0.0104	0.0025	0.0041	0.885	0.108	0.0026
4	−6.60	0.873	0.102	0.0053	0.0191	0.0560	0.848	0.0835	0.0123
5	−6.40	0.894	0.081	0.0056	0.0191	0.0135	0.889	0.0896	0.0081
6	−6.21	0.829	0.160	0.0090	0.0014	0.0195	0.888	0.0914	0.0011
7	−6.19	0.916	0.058	0.0143	0.0116	0.0097	0.920	0.0673	0.0030
8	−6.02	0.898	0.100	0.0000	0.0024	0.0242	0.887	0.0874	0.0013
9	−5.54	0.978	0.012	0.0001	0.0100	0.0149	0.903	0.0799	0.0023
		Ag	Pb	Mg	Se	$AgO_{0.5}$	PbO	MgO	Se
10	−5.24	0.946	0.020	0.0002	0.0151	0.0150	0.916	0.0649	0.0042
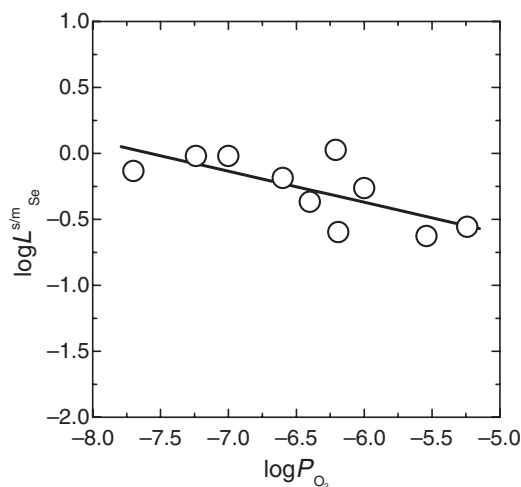
Fig. 1 Distribution ratio of Se between Ag-Pb alloy and PbO melt at 1273 K.

Fig. 2 Sketch of sample and crucibles sealed in a silica ampoule.

Se, the mole fractions of the oxides were determined from the concentration of the metal in the oxide phase. The distribution ratio ($L_{S/M}$) is defined as

$$L_{S/M} = \frac{X_{Se\ in\ Oxide}}{X_{Se\ in\ Metal}} \qquad (2)$$

where $X_{Se\ in\ Oxide}$ and $X_{Se\ in\ Metal}$ are the mole fractions of Se in the PbO based melt and the Ag-Pb alloy, respectively.

Figure 1 shows the distribution ratio of Se as a function of $\log P_{O_2}$. Se is mainly distributed in the Ag-Pb alloy phase. The distribution ratio decreases by a factor of 0.2–1 with an increase in the oxygen partial pressure in the range of $P_{O_2} = 10^{-8}$–10^{-5}. The influence of the crucible material was not observed in the present study.

Ag dissolved in the PbO melt as $AgO_{0.5}$; therefore, the distribution ratio increased with an increase in the concentration of Ag in the Ag-Pb melt.[6] Meanwhile, the behavior of Se between Ag-Pb melt and PbO based oxide disagrees with the behavior of Ag. The dissolution of Se in the PbO melt is discussed in the following section.

3. Activity Coefficient of Se in Ag-Pb Alloy

3.1 Experimental procedure
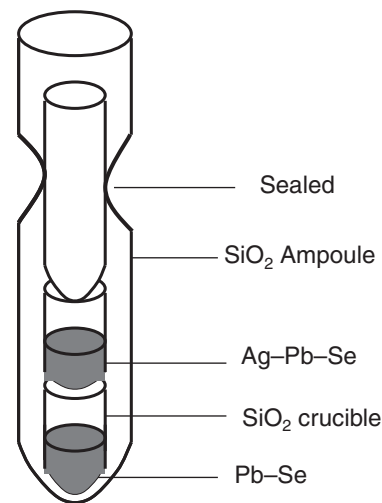
0.5 g of Pb-Se and Ag-Pb-Se mixtures were placed in silica

crucibles. The crucibles were vacuum-sealed in a silica ampoule. (Fig. 2) The ampoule was then placed in the hot zone of the electric resistance furnace. The time required to achieve equilibrium of Se was predetermined as 24 h. After 24 h, at the set temperature, the specimen was removed from the furnace and quenched. The Pb, Ag, and Se contents of the Pb melt and Ag-Pb alloy phases were determined by chemical analysis.

3.2 Distribution of Se between Pb melt and Ag-Pb alloy

Table 2 and Fig. 3 show the distribution ratio of Se between Pb melt and Ag-Pb alloy. The distribution ratio ($L_{Ag-Pb/Pb}$) is defined as

$$L_{Ag-Pb/Pb} = \frac{X_{Se\ in\ Ag-Pb}}{X_{Se\ in\ Pb}}. \qquad (3)$$

The concentration of Si in the metal samples was negligible. The distribution ratio increased with an increase in the concentration of Ag. The concentration of Se in Ag was 5.4 times its concentration in the Pb melt.

3.3 Activity coefficient of Se in Ag-Pb alloy at 1273 K

The equilibrated partial pressure of Se in the ampoule was uniform. Therefore, the activities of Se (a_{Se}) in the Pb melt and Ag-Pb alloy were also equal:

Table 2 The distribution ratio of Se between Pb and Pb-Ag alloy at 1273 K.

No.	Metal phase (mole fraction)				Oxide phase (mole fraction)			$L_{\text{Ag-Pb/Pb}}$
	X_{Ag}	X_{Pb}	X_{Se}	$\gamma_{\text{Se in Ag-Pb}}$	X_{Ag}	X_{Pb}	X_{Se}	
101	0.648	0.336	0.0160	0.0056	0.00002	0.985	0.0151	1.1
102	0.836	0.138	0.0261	0.0021	0.00003	0.991	0.0086	3.0
103	0.886	0.0896	0.0242	0.0014	0.0001	0.995	0.0054	4.5
104	0.951	0.0267	0.0225	0.0018	0.0003	0.993	0.0064	3.5
105	0.954	0.0237	0.0227	0.0021	0.0001	0.995	0.0050	4.5

Fig. 3 The distribution ratio of Se between Pb and Pb-Ag alloy at 1273 K.
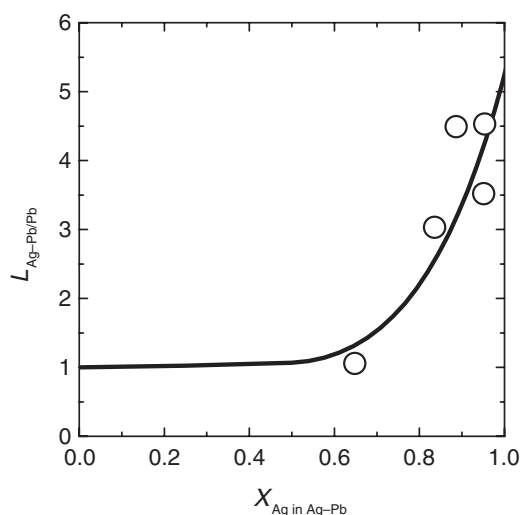
Fig. 4 The activity coefficient of Se in Ag-Pb alloy at 1273 K.

$$P_{\text{Se in Pb}} = P_{\text{Se in Ag-Pb}} \quad (4)$$

and

$$a_{\text{Se in Pb}} = a_{\text{Se in Ag-Pb}}. \quad (5)$$

The relationship between the distribution ratio and activity coefficient of Se (γ_{Se}) is derived from eq. (5) as

$$L_{\text{Ag-Pb/Pb}} = \frac{X_{\text{Se in Ag-Pb}}}{X_{\text{Se in Pb}}} = \frac{\gamma_{\text{Se in Pb}}}{\gamma_{\text{Se in Ag-Pb}}} \quad (6)$$

The activity coefficient of Se in the Ag-Pb alloy is determined by the distribution ratio and activity coefficient of Se in the Pb melt.

The activity coefficient of Se in the Pb phase was determined as 0.0060 on the basis of a report on the Gibbs free energy of mixing for the Pb-Se system at 1262 K.[8] The activity coefficient at 1273 K can also be determined by regular solution approximation as follows:

$$T \cdot \ln \gamma = \text{const.} \quad (7)$$

where T is the temperature. The activity coefficient at 1273 K was estimated as 0.0062. This value was substituted in eq. (6). In the present experiment, the concentration of Se in metals is very less; therefore, the above calculations were carried out under the assumption that the interaction parameters of Se on metals was negligible.

Figure 4 shows the activity coefficient of Se in the Ag-Pb alloy at 1273 K. It decreases immediately with an increase in the Ag content. The activity coefficient of Se in Ag at 1273 K was estimated as 0.001.
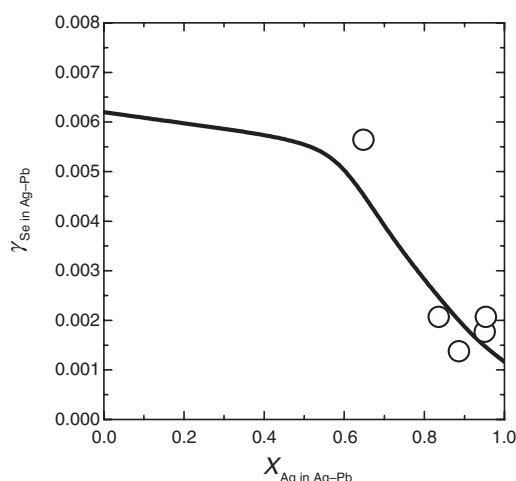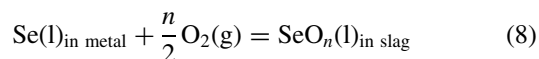
4. Discussion

4.1 Thermodynamic analysis of distribution of Se in PbO phase

Element is generally solved into metal and oxide phase as a form of the metal and the oxide, respectively. Equilibrium of Se between Ag-Pb alloy and PbO phase is given as:

$$\text{Se(l)}_{\text{in metal}} + \frac{n}{2}\text{O}_2(\text{g}) = \text{SeO}_n(\text{l})_{\text{in slag}} \quad (8)$$

where n is a positive number.
The equilibrium constant (K_8) of eq. (8) is

$$K_8 = \frac{a_{\text{SeO}_n}}{a_{\text{Se}} \cdot P_{\text{O}_2}^{n/2}} = \frac{\gamma_{\text{SeO}_n} \cdot X_{\text{SeO}_n}}{a_{\text{Se}} \cdot P_{\text{O}_2}^{n/2}} \quad (9)$$

where a_{SeO_n} is the activity of Se oxide relative to liquid Se oxide, a_{Se} is the activity of Se relative to liquid Se, and γ_{SeO_n} is the activity coefficient of Se oxide relative to liquid Se oxide. Here, eq. (9) can be rewritten as:

$$\log X_{\text{SeO}_n} - \log a_{\text{Se}} = \frac{n}{2} \log P_{\text{O}_2} + \log K_8 - \log \gamma_{\text{SeO}_n} \quad (10)$$

Taking $\log X_{\text{SeO}_n} - \log a_{\text{Se}}$ as the ordinate and $\log P_{\text{O}_2}$ as the abscissa for the result in Table 1, $n/2$ may be expressed by the slope of a straight line. The activity coefficient of Se can be derived from Fig. 4 and the mole fraction of Se in the specimen. Since the concentration of Se in the oxide phase was diluted, γ_{SeO_n} may be assumed as constant for all experimental results. Therefore, the calculated mole fraction of SeO$_n$ is approximately equal to the mole fraction of Se in the oxide. The relationship between $\log P_{\text{O}_2}$ and $\log X_{\text{SeO}_n} -$
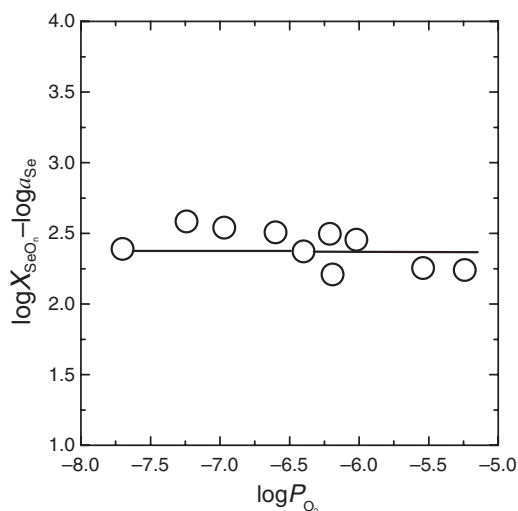
Fig. 5　The relationship between $\log P_{O_2}$ and $\log X_{SeO_n} - \log a_{Se}$.

Fig. 6　The relationship between activity of Se and mole fraction of Se in PbO based melt at 1273 K.

$\log a_{Se}$ is shown in Fig. 5. The dependence of the $\log X_{SeO_n} - \log a_{Se}$ value on $\log P_{O_2}$ is small. The value of n is approximately equal to zero. Therefore, eq. (8) can be rewritten as

$$Se(l)_{in\ metal} = Se(l)_{in\ slag} \qquad (11)$$

Se dissolves in the PbO phase in the non-oxide form. It was observed that the change in the distribution ratio of Se in Fig. 1 depends on the change in the activity coefficient of Se in the metal phase rather than the oxygen partial pressure.

In the case of selective oxidation of Se in order to separate it from the Ag-Pb alloy, the distribution ratio of Se between Ag and PbO melt is approximately 1 and decreases with an increase in the oxygen partial pressure. It is unreasonable to remove Se by oxidation since the slag phase does not entrain Se efficiently.

4.2　Gibbs free energy of dissolution of Se in PbO phase at 1273 K

The Gibbs free energy of dissolution of Se in the PbO phase can also be calculated from the present results. The dissolution reaction of Se in the PbO phase and the equilibrium constant are expressed as:

$$Se(l) = Se(X\ in\ PbO) \qquad (12)$$

$$K_{12} = \frac{a_{Se\ in\ PbO}}{a_{Se}} = \frac{f_{Se\ in\ PbO} \cdot X_{Se\ in\ PbO}}{a_{Se}} \qquad (13)$$

where f_i is the Henrian activity coefficient of Se in the PbO phase. Since the concentration of Se is dilute, f_i can be assumed as unity. The Gibbs free energy of dissolution of Se into PbO can be derived as

$$\Delta G^\circ = -RT \ln K_{12} \qquad (14)$$

The relationship between the activity of Se and the mole fraction of Se in PbO phase is shown in Fig. 6. The slope is 265, that is, $K = 265$. The Gibbs free energy of dissolution can be determined from eqs. (13) and (14)

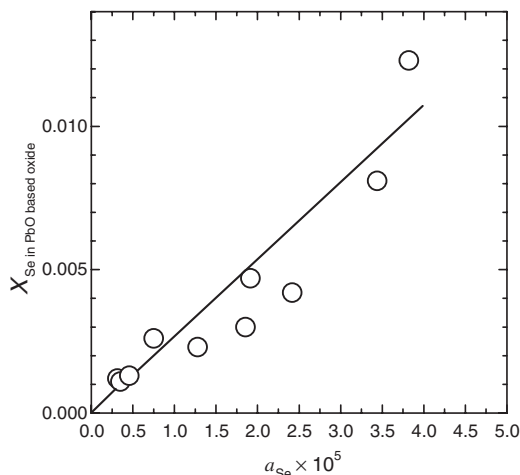$$\Delta G^\circ = -59,000\ J/mol \quad at\ 1273\ K. \qquad (15)$$

5.　Conclusions

The thermodynamic properties of Se in the Ag-Pb alloy and the PbO phase was investigated by a chemical equilibrium technique and an EMF method. The following conclusions were derived from the experiment.

(1) Se is mainly distributed in the Ag-Pb alloy phase. The distribution ratio decreases with an increase in the oxygen partial pressure.

(2) The activity coefficient of Se in the Ag-Pb alloy decreases with an increase in the Ag content.

(3) The activity coefficient of Se in Ag at 1273 K was estimated as 0.001.

(4) Se dissolves in the PbO phase in the non-oxide form.

(5) The Gibbs free energy of dissolution of Se in the PbO phase was derived as

$$\Delta G^\circ = -59,000\ J/mol \quad at\ 1273\ K$$

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) D. R. Swinbourne, S. Yan, G. Hoang and D. Higgings: Trans. Inst. Min. Metall. C **112** (2003) C69-74.
6) S. Ueda, T. Kumagai and K. Yamaguchi: Mater. Trans. **46** (2005) 1866–1869.
7) S. Ueda, T. Kumagai and K. Yamaguchi: Mater. Trans. **47** (2006) 1458–1462.
8) K. P. Kotchi, R. Castenet and J. C. Mathieu: J. Thermal Ana. (1987) 1477–1486.
9) O. Knacke, O. Kubaschewski and K. Hesselmann: *Thermochemical Properties of Inorganic Substances*, 2nd ed., (Springer-Verlag, Verlag Stahleisen, 1991) p. 1455.