Solubility of Silver in MO (M₂O)–B₂O₃ (M = Ca, Ba and Na) Slags

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The solubility of silver in MO–B₂O₃ (MO = CaO, BaO and Na₂O) slags at high temperatures was measured in order to understand the dissolution mechanism of silver in the slags, and the effects of CaO, BaO, and Na₂O on the solubility of silver. The solubility of silver in the Na₂O_{satd}–B₂O₃ system exhibits a minimum value as a function of oxygen partial pressure at about $p_{O_2} = 8.49 \times 10^{-9}$ Pa. Therefore, the dissolution reaction of silver in basic slags at higher oxygen potential can be estimated by the following equation:

The solubility of silver in B₂O₃–bearing slags also exhibits a minimum value as a function of slag composition. The minimum composition shifts to the acidic region following the order of CaO–, BaO–, and Na₂O–B₂O₃ slag. Based on these minimum compositions, *i.e.*, 65 (mol%) CaO, 45 (mol%) BaO, and 35 (mol%) Na₂O, the value of the CaO-equivalence of BaO and that of Na₂O are suggested as 1.44 (=mol% CaO/mol% BaO) and 1.86 (=mol% CaO/mol% Na₂O), respectively.

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1. Introduction

Basicity, defined as the activity of O^{2–} ions, is one of the most important thermodynamic properties in refining slags.¹⁾ It is, however, generally agreed that single ion activity can not be directly measured by the current thermodynamic technique.^{2,3)} Therefore, various indirect measures of basicity, such as capacity,⁴⁾ the redox equilibrium of transition metal ions,^{5–7)} the activity of basic oxides,^{8,9)} and theoretical optical basicity¹⁰⁾ have been applied as indirect measures of basicity. Recently, the solubility of a noble metal such as platinum or silver has been proposed as a new measure of basicity.^{11–16)} The Pt solubility, however, was measured at higher oxygen partial pressure, *i.e.*, in air. In addition, the dissolution mechanism of Pt was not clarified.^{11–13)} The present authors, therefore, had previously measured the solubility of silver at lower oxygen partial pressure in the acidic and the basic regions of the CaO–B₂O₃ and BaO–B₂O₃ slags.^{14–16)} As a result, it was suggested that the silver became stabilized as Ag⁺ ions in the acidic slags, while as Ag^{2–} ions in the basic slags at lower oxygen partial pressure.

In the present study, the effect of oxygen partial pressure on Ag solubility in highly basic slags is investigated to clarify the dissolution mechanism of silver in slags at higher oxygen potential. In addition, the influence of the basic oxides on Ag solubility is also discussed in MO–B₂O₃ (MO = CaO, BaO, and Na₂O) slags.

2. Experimental Procedure

A super-kanthal electric furnace was used for the equilibration of molten silver and the Na₂O–B₂O₃ melts. The temperature was controlled within ± 2 K by use of an R-type (Pt–13Rh/Pt) thermocouple, and a proportional-integral-differential (PID) controller. The slag samples were prepared using reagent-grade Na₂O and B₂O₃. A schematic diagram of the experimental apparatus has been illustrated in previous

articles.^{14–16)}

Slag samples weighing 10 g and 5 g of silver were maintained in graphite crucibles under a CO atmosphere to control oxygen partial pressure by the C/CO equilibrium, as given in eq. (1),¹⁷⁾ expressed as

In the case of Na₂O-rich slags, having a Na₂O content greater than 45 mol%, the Mo sleeve was inserted into the graphite crucible as schematically illustrated in Fig. 1(a). In addition, the Na₂O_{satd}–B₂O₃ system was equilibrated with molten silver in the Mo crucible (outer diameter 30 mm, inner diameter 25 mm, and height of 30 mm) within the porous alumina holder (outer diameter 50 mm, inner diameter 40 mm, and height of 150 mm) as illustrated in Fig. 1(b). Here, the oxygen partial pressure was controlled by the CO/CO₂ equilibrium, as expressed in eq. (2),¹⁷⁾ as

Impurities in the CO and CO₂ were removed by passing the gases through CaSO₄, Na₂O–CaO, silica gel, and H₂SO₄. The gas mixture was then introduced into the mullite reaction tube (outer diameter 70 mm, inner diameter 60 mm, and height of 1000 mm) by a mass flow controller (MFC, Matheson model 8284). The equilibration time was predetermined as 12 hours. After equilibrating, the samples were quenched in Ar gas and then crushed for chemical analysis. The content of sodium in the silver and slag melts was determined by atomic absorption spectrometry (Shimadzu, AA-6601 F/G).

Fig. 1 Schematic illustrations of the crucible and holder used in the present experiments for (a) the Na_2O -rich slags, and (b) $\text{Na}_2\text{O}_{\text{satd}}\text{-B}_2\text{O}_3$ slag.

Fig. 2 Dependence of Ag solubility on oxygen partial pressure in the $\text{Na}_2\text{O}_{\text{satd}}\text{-B}_2\text{O}_3$ system at 1373 K.

3. Results and Discussion

3.1 The mechanism for the dissolution of silver in molten slags

Dissolution mechanisms of silver in the slags at lower oxygen partial pressure can be found in the literature.¹⁴⁻¹⁶ Equations governing the dissolution mechanism can be written as

in the acidic region, and

in the basic region.

From these equations, it can be seen that the solubility of silver increases with increasing oxygen potential and decreasing slag basicity in the acidic slags, and *vice versa* in the basic slags. At a fixed temperature and slag composition, the solubility of silver and oxygen partial pressure exhibit a linear log-log relationship, having slopes of 1/4 and -1/2 in the acidic and basic regions of slags, respectively.¹⁴⁻¹⁶ The stability of many chemical species in molten slags, however, is influenced by the oxygen potential; for example, P^{3-} and PO_4^{3-} , and S^{2-} and SO_4^{2-} , among others. Therefore, understanding the reaction mechanism at higher oxygen partial pressure is required to gain accurate knowledge of the thermodynamic behavior of silver in molten slags.

In Fig. 2, the solubility of silver in the $\text{Na}_2\text{O}_{\text{satd}}\text{-B}_2\text{O}_3$ system at 1373 K is shown as a function of oxygen partial pressure at values higher than $p_{\text{O}_2} \cong 10^{-10}$ Pa. The solubility of silver ($\log(\text{mass}\%\text{Ag})$) in the $\text{Na}_2\text{O}_{\text{satd}}\text{-B}_2\text{O}_3$ system exhibits a minimum value as a function of oxygen partial pressure ($\log p_{\text{O}_2}$). Slopes of -0.382 and 0.409 are determined on either side of the minimum point. Based on these results, it is suggested that silver becomes stabilized in a different ionic form other than Ag^{2-} ion as shown in eq. (4) in highly basic slags, under conditions of higher oxygen partial pres-

sure. Hence, it is possible that a complex anion of silver, AgO_2^{2-} , exists in basic slags at higher oxygen partial pressure.^{18,19} Although the coordination state of silver-complex is not fully known, the dissolution reaction of silver in basic slags at higher oxygen potential can be approximated by eq. (5), as

This dissolution reaction of silver is very similar to that of platinum in basic slags, which can be found in the literature, given in eq. (6),¹¹⁻¹³ as

The dissolution mechanism of platinum in the acidic slags, however, is not exactly known.

The dependencies of the stability of sulfur on oxygen potential in $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ slag at 1773 K, of phosphorus in the 41 (mol%) $\text{CaO-Al}_2\text{O}_3$ system at 1823 K, of carbon in the $\text{BaO}_{\text{satd}}\text{-MnO}$ system at 1573 K, and of tin in the CaO-CaF_2 melt at 1773 K, as well as of silver in the $\text{Na}_2\text{O}_{\text{satd}}\text{-B}_2\text{O}_3$ system at 1373 K are shown in Fig. 3 for comparison purposes.^{1,20,21} It can be seen that in the basic slags the critical oxygen partial pressure of silver (solid line) is similar to those of carbon (dash-dot line) and tin (dash-dot-dot line). In addition, it is suggested that the thermodynamic behavior of silver and carbon is similar at oxygen partial pressure of less than $p_{\text{O}_2} \cong 10^{-8}$ Pa.

The solubility of silver in $\text{Na}_2\text{O-B}_2\text{O}_3$ slag (solid squares) under conditions of $p_{\text{O}_2} \cong 10^{-13}$ Pa is shown in Fig. 4, along with the results for $\text{CaO-B}_2\text{O}_3$ (solid circles) and $\text{BaO-B}_2\text{O}_3$ (open circles) slags.¹⁴⁻¹⁶ The solubility of silver in $\text{Na}_2\text{O-B}_2\text{O}_3$ slag, at a fixed oxygen partial pressure, decreases with increasing content of Na_2O , exhibits a minimum value, followed by an increase of solubility as the content of Na_2O increases in the slag. Therefore, it is confirmed that at a fixed

Fig. 3 Dependence of the stabilities of various elements in the molten slags on oxygen partial pressure (S: CaO–SiO₂–Al₂O₃ at 1773 K; P: 41 (mol%) CaO–Al₂O₃ at 1823 K; C: BaO_{satd}–MnO at 1573 K; Sn: CaO–CaF₂ at 1773 K; Ag: Na₂O_{satd}–B₂O₃ at 1373 K).

Fig. 4 Dependence of Ag solubility on the content of basic oxides in slags of CaO–B₂O₃ at 1773 K (solid circles), BaO–B₂O₃ at 1698 K (open circles), and Na₂O–B₂O₃ at 1373 K (solid squared).

oxygen partial pressure, the dissolution mechanism of silver in the slags is dependent on the slag composition, as given in eqs. (3) and (4). That is, the dominant ionic form of silver in the acidic region of the slag is Ag⁺, while being Ag²⁺ in the basic region of the slag.

The composition corresponding to the minimum Ag solubility shifts to the acidic region in the following order of CaO, BaO, and Na₂O–B₂O₃ slag. This means that Na₂O is qualitatively more basic than BaO and CaO. This tendency is very similar to that exhibited by platinum solubility. Nakamura *et al.* suggested that SiO₂ would be more basic than P₂O₅, as the result of the shift of the minimum composition of the Na₂O–SiO₂ melt to the more acidic composition, compared to the Na₂O–P₂O₅ melt.¹¹⁾ A more detailed discussion concerning these trends will be presented in §3.2.

In Fig. 5, the solubility of silver is shown as a function

Fig. 5 Dependence of Ag solubility on the activity of basic oxides in slags of CaO–B₂O₃ at 1773 K (solid circles), BaO–B₂O₃ at 1698 K (open circles), and Na₂O–B₂O₃ at 1373 K (solid squared).

of the activity of Na₂O (solid squares) with the results of the CaO–B₂O₃ (solid circles) and BaO–B₂O₃ (open circles) slags.^{14–16)} Although the activity of Na₂O in the limited composition range of less than 33 (mol%) Na₂O–B₂O₃ system can be found in the literature,²²⁾ the activity of Na₂O over the entire composition range of slag at 1373 K was measured by the present authors.^{23,24)} The –0.496 slope of the line in the acidic region is relatively close to the theoretical value of –1/2 as obtained by eq. (7) for the reaction shown in eq. (3), written as

$$\log(\text{mass\%Ag}^+) = -\frac{1}{2} \log a_{\text{O}^{2-}} - \frac{1}{4} \log p_{\text{O}_2} - \log f_{\text{Ag}^+} + \log K_{(3)} \quad (7)$$

where $a_{\text{O}^{2-}}$, p_{O_2} , f_{Ag^+} , and $K_{(3)}$ are the activity of the O^{2–} ion, the oxygen partial pressure, the activity coefficient of the Ag⁺ ion, and the equilibrium constant of eq. (3), respectively. The solubility of silver ($\log(\text{mass\%Ag}^+)$) is expected to be inversely proportional to the activity of the O^{2–} ion ($\log a_{\text{O}^{2-}}$), with the slope of 1/2 at a fixed temperature and oxygen partial pressure. This is true if the assumption that f_{Ag^+} is independent of the composition of the slag holds over the entire composition range. Therefore, the present results suggest that the f_{Ag^+} term in eq. (7) may be constant with slag composition in the acidic region. This may be due to the noble characteristics of silver, as has been reported for platinum.¹³⁾

The slope of the Na₂O–B₂O₃ line in the basic region is 1.19, slightly higher than the theoretical value of unity obtained from eq. (8) for the reaction shown in eq. (4), expressed as

$$\log(\text{mass\%Ag}^{2-}) = \log a_{\text{O}^{2-}} - \frac{1}{2} \log p_{\text{O}_2} - \log f_{\text{Ag}^{2-}} + \log K_{(4)} \quad (8)$$

The solubility of silver ($\log(\text{mass\%Ag}^{2-})$) will be proportional to the activity of the O^{2–} ion ($\log a_{\text{O}^{2-}}$), with the slope

of unity at a fixed temperature and oxygen partial pressure. This will be true if the assumption that $f_{\text{Ag}^{2-}}$ is independent of slag composition holds over the entire range of composition. Although the reason for the slightly greater slope is not clear, it may be caused by the effect of the slag composition on $f_{\text{Ag}^{2-}}$ in basic slags, or by the influence of the slag structure on the silver dissolution reaction. That is, the dissociation reaction of Na_2O and the modification reaction of the borate network may be in competition with each other.^{15,16)}

3.2 Influence of CaO, BaO and Na₂O on silver solubility

The present authors propose a simple definition of the CaO-equivalence of BaO (or Na₂O) by employing the minima found in the Ag solubility.

As was shown in Fig. 4, the compositions of 65 (mol%) CaO (solid circles), 45 (mol%) BaO (open circles), and 35 (mol%) Na₂O (solid squares) each exhibits a minimum Ag solubility, in each slag system. Hence, the CaO-equivalence of BaO and that of Na₂O are estimated as 1.44 (=mol% CaO/mol% BaO) and 1.86 (=mol% CaO/mol% Na₂O), respectively, based on the molar content of the basic oxides at the respective minimum Ag solubility.

The theoretical optical basicities of pure BaO and Na₂O, based on the Pauling electronegativity, are proposed to have the same value, namely 1.15.²⁵⁾ Therefore, BaO and Na₂O are considered oxides with the same basicity in the theoretical optical basicity of molten slags. This is probably one of the reasons for some of the discrepancy between the theoretical optical basicity and the actually measured refining indices in highly basic slags.^{10,12–16,26,27)} Therefore, this discrepancy may be explained by introducing the CaO-equivalence of BaO (1.44), and that of Na₂O (1.86), estimated by using the solubility of silver in the slags.

4. Conclusions

The solubility of silver in MO–B₂O₃ (MO = CaO, BaO, and Na₂O) slags at high temperatures was measured to help understand the dissolution mechanism of silver in the slags, and the effect of basic oxides on the solubility of silver in these slags. The results of the present study can be summarized as follows.

The solubility of silver in the basic slags exhibits a minimum value as a function of the oxygen partial pressure at about $p_{\text{O}_2} = 8.49 \times 10^{-9}$ Pa. Therefore, the dissolution reaction of silver in basic slags at higher oxygen potential is suggested by the following equation, expressed as

$$(p_{\text{O}_2} \geq 8.49 \times 10^{-9} \text{ Pa}).$$

The solubility of silver in B₂O₃–bearing slags exhibits a minimum value as a function of slag composition. The minimum composition shifts to the acidic region following the order of CaO–, BaO–, and Na₂O–B₂O₃ slag. Based on these minimum compositions, *i.e.*, 65 (mol%) CaO, 45 (mol%) BaO, and 35 (mol%) Na₂O, the CaO-equivalence of BaO and that of Na₂O are estimated as 1.44 and 1.86, respectively.

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