The Influence of Basicity on the Solubility of Platinum in Oxide Melts

SHIGEKO NAKAMURA, KOKORO IWASAWA, KAZUKI MORITA, and NOBUO SANO

The solubility of platinum in molten BaO-CuO_x, BaO-MnO_x, CaO_{satd}-SiO_2-FeO_x, $KO_{0.5}$-SiO_2, $NaO_{0.5}$-SiO_2, and $NaO_{0.5}$-$PO_{2.5}$ fluxes has been measured in order to seek a measure of the basicity of highly basic fluxes containing transition metal ions and to clarify the chemical behavior of platinum in those melts. The solubility of platinum increases with increasing content of basic oxide in highly basic fluxes, suggesting that it may be a good indicator of the basicity of highly basic fluxes containing transition metal ions. The solubility of platinum in the $KO_{0.5}$-SiO_2, $NaO_{0.5}$-SiO_2, and $NaO_{0.5}$-$PO_{2.5}$ melts has a minimum value, and it is suggested that a platinum is amphoteric: it exists as a platinum cation in an acidic flux and does as a platinate ion in a basic flux.

I. INTRODUCTION

In a previous article,[1] the authors reported the solubility of platinum in several oxide fluxes. The solubility of platinum has been found to increase with increasing content of basic oxide, suggesting that it may be a good indicator of the basicity of highly basic fluxes. Platinum exists in highly basic fluxes as a platinate ion. An investigation of the dependence of the solubility of platinum on oxygen partial pressure and of the relationship between the solubility of platinum and other refining indexes, such as carbonate, sulfide, and phosphate capacities, has shown that the ionic form of platinum in highly basic fluxes is PtO_2^{2-}. Then, the reaction of platinum oxidation and dissolution of platinum into basic fluxes can be written as follows:

$$\mathrm{Pt\ (s)} + \frac{1}{2}\,\mathrm{O_2\ (g)} + (\mathrm{O^{2-}}) = (\mathrm{PtO_2^{2-}})\ \text{(in flux)} \qquad [1]$$

On the basis of those results, the purpose of this study is to seek a measure of the basicity of highly basic fluxes containing transition metal ions and to clarify the chemical properties of fluxes by investigating the solubility of platinum as a function of the flux composition in BaO-MnO_x, BaO-CuO_x, $KO_{0.5}$-SiO_2, and $NaO_{0.5}$-$PO_{2.5}$ melts. The correlation between the solubility of platinum and the phosphate capacity for a CaO_{satd}-SiO_2-FeO_x melt, simulating an industrial converter slag, has been investigated. In addition, the variation of chemical behavior of the platinum in molten fluxes with varying the flux composition has been examined.

II. EXPERIMENTAL PROCEDURE

The experimental procedure for solubility of platinum is similar to that described elsewhere.[1]

III. RESULTS AND DISCUSSION

A. *Solubility of Platinum in Molten Fluxes as a Measure of Basicity*

1. *Dependence of the solubility of platinum on the flux composition*

In Figure 1, the solubility of platinum at 1873 K in the BaO-MnO_x and BaO-CuO_x melts in air is plotted as a function of the BaO content on a molar basis, together with the previously reported results for the BaO-Al_2O_3 melt.[1] The solubility of platinum in these melts increases with increasing content of BaO, and for any particular BaO content, the BaO-CuO_x melt has the highest solubility followed by the BaO-MnO_x melt and then the BaO-Al_2O_3 melt. The solubility is very high, indicating that they are very basic and could have a strong refining capacity for manganese or copper containing alloys. The results of the investigation of the valences of manganese and copper in these fluxes are listed in Table I. As may be seen in Table I, the valences of manganese and copper in these fluxes are essentially Mn^{3+} and Cu^{+}, respectively.

2. *Correlation between the solubility of platinum and the phosphate capacity for the CaO_{satd}-SiO_2-FeO_x melt, simulating an industrial steelmaking slag*

The experimental results suggest that the solubility of platinum may be a good indicator of the basicity of highly basic fluxes containing transition metal ions. Then, the application of the solubility of platinum to the CaO_{satd}-SiO_2-FeO_x melt, simulating an industrial steelmaking slag, was attempted, and the correlation between the solubility of platinum and the phosphate capacity was determined.

The dephosphorization of steel by a slag-metal reaction can be expressed by Eq. [2].

$$\underline{\mathrm{P}} + \frac{5}{2}\,\underline{\mathrm{O}} + \frac{3}{2}\,(\mathrm{O^{2-}}) = (\mathrm{PO_4^{3-}}) \qquad [2]$$

where the underscore and the parentheses denote the component in the metal and the slag, respectively.

The ability of a slag to contain phosphorus as a phosphate ion is defined by the phosphate capacity, as defined by Eq. [4], according to Eq. [3].[2]

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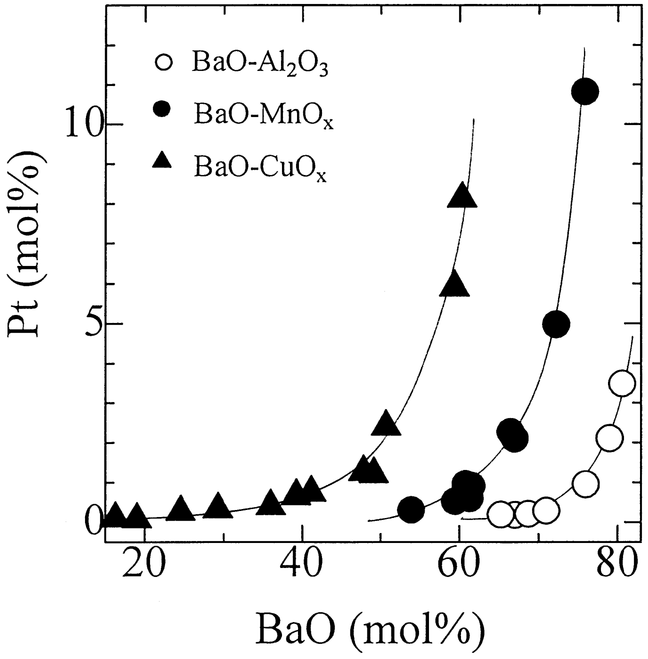

Fig. 1—Dependence of Pt solubility on content of BaO for the BaO-Al$_2$O$_3$, BaO-MnO$_x$, and BaO-CuO$_x$ melts at 1873K.

Table I. Determination of Valences of Mn and Cu in BaO Bearing Fluxes in Air at 1873 K

Flux Systems	
BaO-32.6 (mass pct) MnO$_x$	$Mn^{3+}/(Mn^{3+} + Mn^{2+}) = 0.99$
BaO-40.2 (mass pct) CuO$_x$	$Cu^{2+}/(Cu^{2+} + Cu^{+}) = 0.0036$

$$\frac{1}{2}\,P_2\,(g) + \frac{5}{4}\,O_2\,(g) + \frac{3}{2}\,(O^{2-}) = (PO_4^{3-}) \qquad [3]$$

$$C_{PO_4^{3-}} = \frac{(\text{mass pct } PO_4^{3-})}{P_{P_2}^{1/2}\cdot P_{O_2}^{5/4}} = K_{[3]}\,\frac{a_{O^{2-}}^{3/2}}{f_{PO_4^{3-}}} \qquad [4]$$

where $a_{O^{2-}}$, C_i, P_i, f_i, and $K_{[n]}$ are the activity of oxide ion, capacity, partial pressure, activity coefficient of species i, and equilibrium constant of Eq. [n], respectively.

Eliminating the $a_{O^{2-}}$ term from Eqs. [1] and [4], the relationship between the solubility of platinum and the carbonate capacity is derived as follows:

$$\log\,(\text{mass pct } PtO_2^{2-}) = \frac{2}{3}\log C_{PO_4^{3-}} + \log\frac{f_{PO_4^{3-}}^{2/3}}{f_{PtO_2^{2-}}} + \frac{1}{2}\log P_{O_2} + \log\frac{K_{[1]}}{K_{[3]}^{2/3}} \qquad [5]$$

The activity coefficients of the platinate ion, $f_{PtO_2^{2-}}$, and phosphate ion, $f_{PO_4^{3-}}$, are dependent upon the flux compositions. However, the second term of the right-hand side of Eq. [5] will be constant if the two activity coefficients have the same dependence on the flux composition. Then, the solubility of platinum may be expected to have a linear relationship with the phosphate capacity on a logarithmic scale, and the slope should be 2/3.

The authors[3] measured the phosphorus partition between the CaO$_{satd}$-SiO$_2$-FeO$_x$ melt and liquid iron at 1873 K. Figure 2 shows the solubility of platinum against phosphate capacity on a logarithmic scale for the CaO$_{satd}$-SiO$_2$-FeO$_x$ melt. The straight line is shown with a slope of 0.58, which is close to the expected value of 2/3.

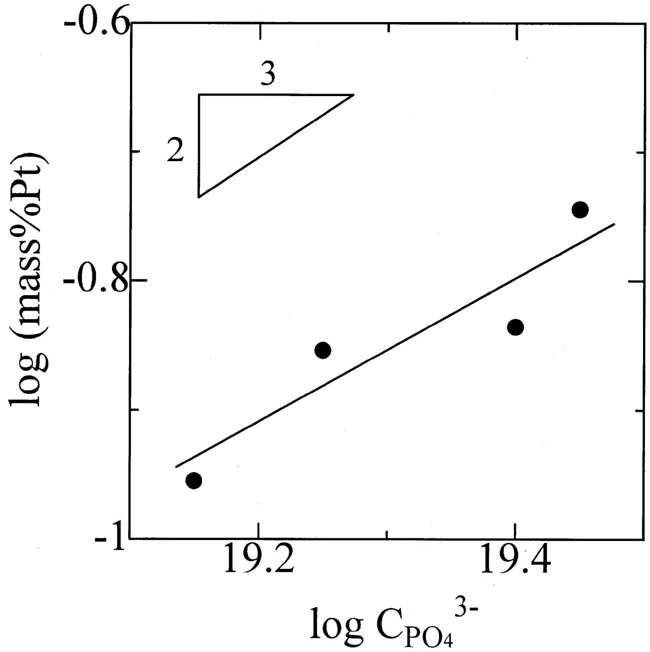

Fig. 2—Relationship between phosphate capacity and Pt solubility for the CaO$_{satd}$-SiO$_2$-FeO$_x$ melt at 1873K.

The basicity of fluxes may therefore be estimated by an easy method in which a flux is melted in a platinum crucible in air.

B. *Chemical Behavior of Platinum in Molten Fluxes*

1. *Dependence of the valences of platinum ion on the flux composition*

A comparison of the solubility of platinum at 1873 K in the KO$_{0.5}$-SiO$_2$ melt with that of the NaO$_{0.5}$-SiO$_2$ melt, which was reported in a previous article,[1] is shown in Figure 3. The KO$_{0.5}$-SiO$_2$ melt has a higher platinum solubility than the NaO$_{0.5}$-SiO$_2$ melt over the entire composition range of this study, indicating that K$_2$O is more basic than Na$_2$O, as is well known. Furthermore, in spite of increasing KO$_{0.5}$ content, the solubility of platinum decreases up to the point where the KO$_{0.5}$-SiO$_2$ melt has a minimum platinum solubility at about 50 mol pct of KO$_{0.5}$. In Figure 4, the solubility of platinum at 1373 K in the NaO$_{0.5}$-SiO$_2$ and NaO$_{0.5}$-PO$_{2.5}$ melts, as well as at 1873 K in the KO$_{0.5}$-SiO$_2$ melt is plotted on a logarithmic scale as a function of the basic oxide content. All those melts have a minimum point, suggesting that a platinum ion in a molten flux has a different form on either side of the minimum point. The reaction of the platinum oxidation and dissolution into molten fluxes may be written as Eqs. [1] and [6].

$$Pt\,(s) + mO_2\,(g) = (Pt^{4m+})\,(\text{in flux}) + 2m(O^{2-}) \qquad [6]$$

Beyond the minimum point, a platinum ionic form may be a platinate ion according to Eq. [1], as described in the previous report.[1] On the other hand, the solubility of platinum decreases with increasing basic oxide content up to the minimum point, indicating that the platinum in acidic fluxes exists as a platinum cation according to Eq. [6]. From these results, the platinum is amphoteric: it exists as

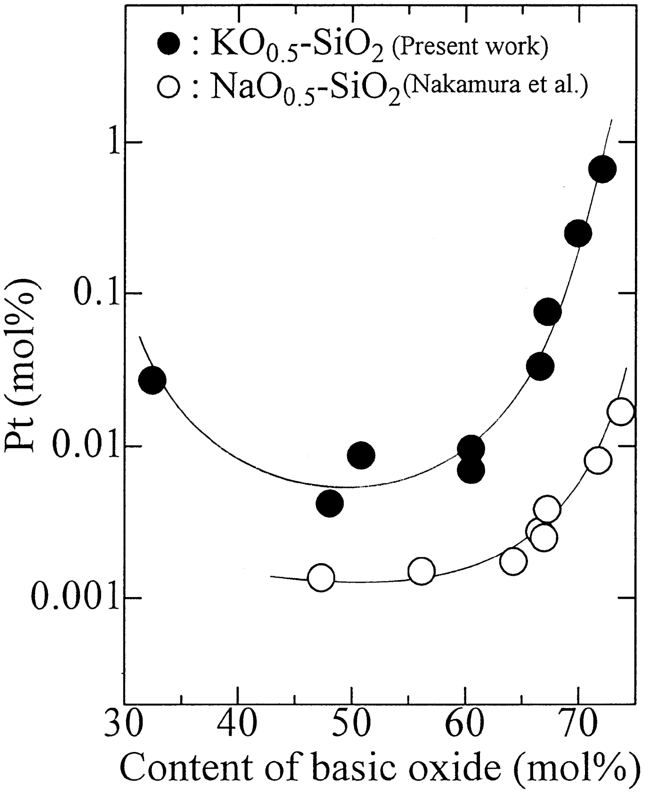

Fig. 3—Dependence of Pt solubility on content of basic oxides for the $KO_{0.5}$-SiO_2 and $NaO_{0.5}$-SiO_2 melts at 1873K.

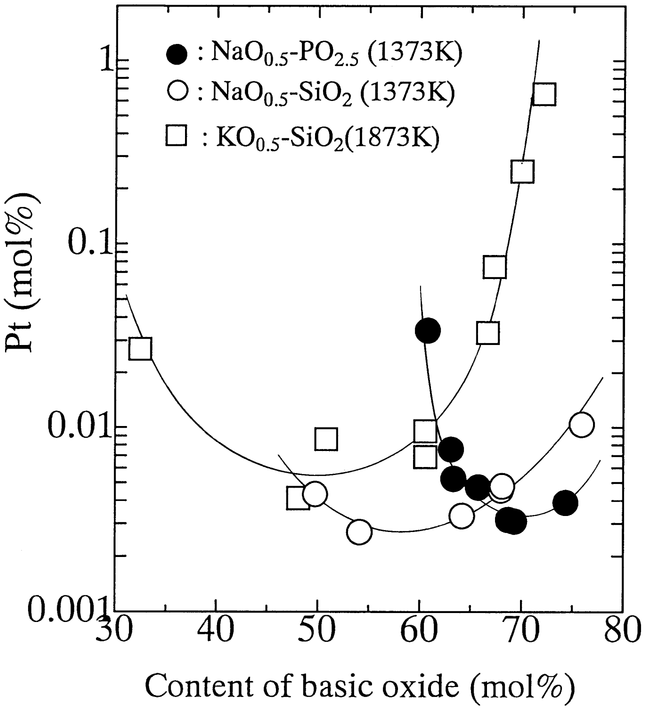

Fig. 4—Dependence of Pt solubility on content of basic oxides for the $NaO_{0.5}$-SiO_2 and $NaO_{0.5}$-$PO_{2.5}$ melts at 1373K and $KO_{0.5}$-SiO_2 melt at 1873K.

a platinum cation and behaves as a basic substance in an acidic flux, whereas it exists as a platinate ion and behaves as an acidic substance in a basic flux.

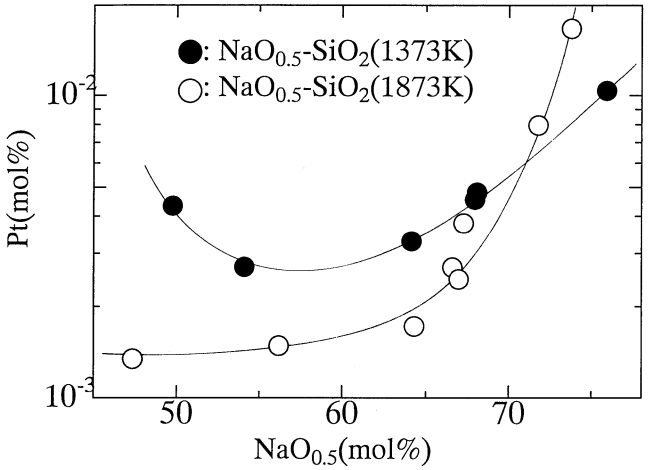

Fig. 5—Dependence of Pt solubility on content of $NaO_{0.5}$ for the $NaO_{0.5}$-SiO_2 melts at 1373K and 1873K.

Tsukihashi *et al.*[4] measured the distribution of antimony between carbon-saturated iron and a Na_2O-SiO_2 melt in an extremely low oxygen partial pressure (8.4×10^{-18} atm) at 1473 K. They reported that the valence of the antimony species changes from two to four as the melts become more basic, and the activity coefficient of $SbO_{1.5}$ increases with increasing Na_2O content up to 57 mass pct, beyond which it decreases. They concluded that the antimony oxide is amphoteric, that is, it behaves as a basic oxide up to 57 mass pct of Na_2O content and as an acidic oxide in a more basic composition.

As can be seen in Figure 4, the compositions at the minimum are about 70 and 50 mol pct of $NaO_{0.5}$ content for the $NaO_{0.5}$-$PO_{2.5}$ and $NaO_{0.5}$-SiO_2 melts, respectively. The minimum composition of the $NaO_{0.5}$-$PO_{2.5}$ is shifted to the more basic one compared to the $NaO_{0.5}$-SiO_2 melt, indicating that $PO_{2.5}$ is a more acidic oxide than SiO_2.

Kawahara *et al.*[5] measured the solubility of CO_2 in $NaO_{0.5}$-$PO_{2.5}$ and $NaO_{0.5}$ -SiO_2 melts at 1473 K. They reported that the solubility of CO_2 in the $NaO_{0.5}$-SiO_2 melt is much larger than that of the $NaO_{0.5}$-$PO_{2.5}$ melt, suggesting that $PO_{2.5}$ is more acidic than SiO_2.

2. *Dependence of the solubility of platinum on temperature in the $NaO_{0.5}$-SiO_2 melt*

The solubility of platinum in the $NaO_{0.5}$-SiO_2 melt at 1373 and 1873 K is shown in Figure 5. The solubility of platinum in the melt at 1373 K is much larger than that of 1873 K, up to about 68 mol pct of $NaO_{0.5}$ content, beyond which it is reversed. For both Eqs. [1] and [6], the reaction of platinum oxidation and that of dissolution may be rewritten in a molecular form as follows:

$$\text{Pt (s)} + m\text{O}_2\text{ (g)} = \text{PtO}_{2m}\text{ (in flux)} \qquad [7]$$

The enthalpy change of Eq. [7] is determined by a sum of the standard enthalpy change of Eq. [8] and the enthalpy change of dissolving PtO_{2m} into molten fluxes.

$$\text{Pt (s)} + m\text{O}_2\text{ (g)} = \text{PtO}_{2m}\text{ (s)} \qquad [8]$$

The standard enthalpy change of Eq. [8] is not available, but it may have slightly negative values, similar to the standard enthalpy change of the oxidation of gold as Eq. [9], because of the noble nature of platinum.

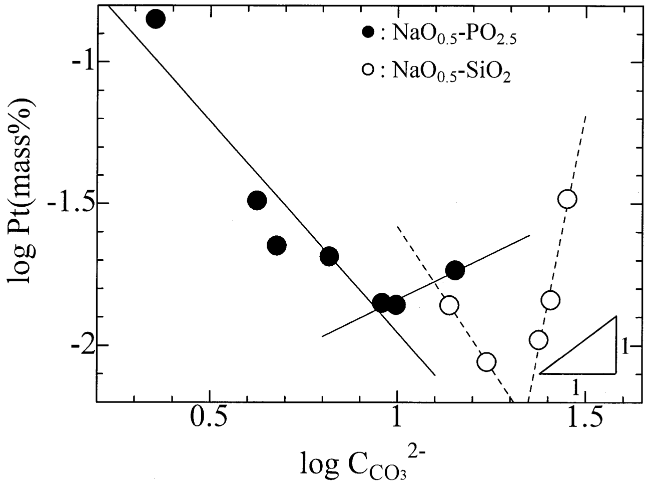

Fig. 6—Relationship between carbonate capacity and Pt solubility for the $NaO_{0.5}$-SiO_2 and $NaO_{0.5}$-$PO_{2.5}$ melts at 1373K.

$$\mathrm{Au\ (s)} + \frac{3}{4}\mathrm{O_2\ (g)} = \mathrm{AuO_{3/2}\ (s)} \qquad [9]$$

$$\Delta G^\circ = -410 + 32.55T \quad \mathrm{J/mol}^{[6]}$$

Therefore, the enthalpy change of Eq. [7] would easily changes from negative to positive in sign depending on the enthalpy change of dissolution PtO_{2m}. The experimental results indicate that the enthalpy change of dissolving PtO_{2m}, $\Delta\overline{H}_{PtO_{2m}}$, may have positive values for PtO_2^{2-} in basic fluxes, whereas it has negative values for Pt^{4m+} in acidic fluxes.

3. *Correlation between the solubility of platinum and the carbonate capacity*

The CO_2 dissolution into molten fluxes may be expressed by Eq. [10], and the carbonate capacity is defined as Eq. [11],[2] according to the former equation.

$$CO_2 + (O^{2-}) = (CO_3^{2-}) \qquad [10]$$

$$C_{CO_3^{2-}} = \frac{(\text{mass pct } CO_3^{2-})}{P_{CO_2}} = K_{[10]} \cdot \frac{a_{O^{2-}}}{f_{CO_3^{2-}}} \qquad [11]$$

Eliminating the $a_{O^{2-}}$ term from Eqs. [1] or [6] and [11], the relationship between the solubility of platinum and the carbonate capacity is derived as follows:

$$\log\ (\text{mass pct } PtO_2^{2-}) = \log C_{CO_3^{2-}} + \log \frac{f_{CO_3^{2-}}}{f_{PtO_2^{2-}}} + \frac{1}{2}\log P_{O_2} + \log \frac{K_{[1]}}{K_{[10]}} \qquad [12]$$

$$\log\ (\text{mass pct } Pt^{4m+}) = -2m \log C_{CO_3^{2-}} + \log \frac{f^{2m}_{CO_3^{2-}}}{f_{Pt^{4m+}}} + m \log P_{O_2} + \log \frac{K_{[6]}}{K^{2m}_{[10]}} \qquad [13]$$

The activity coefficients of the platinate ion, $f_{PtO_2^{2-}}$, platinum cation, $f_{Pt^{4m+}}$, and carbonate ion, $f_{CO_3^{2-}}$, are dependent upon the flux compositions. However, the second term of the right-hand side of Eqs. [12] and [13] will be constant if the two activity coefficients have the same dependence on the flux composition. Then, the solubility of platinum may be expected to have a linear relationship with the carbonate capacity on a logarithmic scale, and the slope for Eq. [12] is expected to be unity and that for Eq. [13] to be $-2m$.

Kawahara *et al.*[5] measured the carbonate capacities of the $NaO_{0.5}$-SiO_2 and $NaO_{0.5}$-$PO_{2.5}$ melts at 1473 K. In Figure 6, the solubility of platinum measured in the present study at 1473 K is plotted against the carbonate capacity of the $NaO_{0.5}$-SiO_2 and $NaO_{0.5}$-$PO_{2.5}$ melts on a logarithmic scale. For the range used in Eq. [1], the straight lines are shown with slopes 6.67 and 0.65 for the $NaO_{0.5}$-SiO_2 and $NaO_{0.5}$-$PO_{2.5}$ melts, respectively. The slope of the line for the $NaO_{0.5}$-SiO_2 melt is far higher than the expected value of unity. Similarly, for the range used in Eq. [2], the slopes are -2.00 and -1.49 for the $NaO_{0.5}$-SiO_2 and $NaO_{0.5}$-$PO_{2.5}$ melts, respectively. The valences of the platinum cation in Eq. [2] are estimated using the experimental results and are found to be four and three for the $NaO_{0.5}$-SiO_2 and $NaO_{0.5}$-$PO_{2.5}$ melts, respectively. However, in order to decide the valences of the platinum cation, it is necessary to clarify the dependence of the solubility of platinum on the oxygen partial pressure.

IV. CONCLUSIONS

The solubility of platinum increases with increasing content of BaO in the BaO-MnO_x and BaO-CuO_x melts, suggesting that it may be a good indicator of the basicity of highly basic fluxes containing transition metal ions. The correlation between the phosphate capacity and the solubility of platinum for the CaO_{satd}-SiO_2-FeO_x melt, simulating an industrial converter slag, has been investigated. The solubility of platinum has a linear relationship with the phosphate capacity on a logarithmic scale, and the slope is close to the expected value of 2/3.

It is possible to estimate the dephosphorization ability of fluxes by measuring the platinum solubility in the fluxes, which is easy in fusing a flux in a platinum crucible.

The solubility of platinum in the $KO_{0.5}$-SiO_2, $NaO_{0.5}$-SiO_2, and $NaO_{0.5}$-$PO_{2.5}$ melts has a minimum value, and it is suggested that a platinum ion in a molten flux has a different form on either side of those minimum compositions. Platinum is amphoteric: it is stable as a platinum cation in an acidic flux and as a platinate ion in a basic flux.

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