Estimation of Slag–Metal Interfacial Oxygen Potential in Phosphorus Reaction between Fe_tO Containing Slag and Molten Iron of High Carbon Concentration

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In this report, oxygen potential, $P_{\text{O}_2}^*$, at the interface between slag and molten iron of high carbon concentration is estimated from the experimental results of the authors' previous kinetic study of phosphorus reaction. The method of the estimation of $P_{\text{O}_2}^*$ is based on an assumption that a quasi-equilibrium is established in the slag–metal system at the time point when the phosphorus reaction changes its direction from dephosphorization to rephosphorization.

The estimated $P_{\text{O}_2}^*$ ranges in the order of 10^{-11} – 10^{-10} Pa. The $P_{\text{O}_2}^*$ increases with the increase in $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ in the slag and decreases with increasing the intensity of mechanical stirring employed in the experiments. The oxygen potential of the bulk slag, $P_{\text{O}_2,s}$, is calculated with a regular solution model, and the comparison of the bulk slag's $P_{\text{O}_2,s}$ with the interfacial oxygen potential, $P_{\text{O}_2}^*$, shows that $P_{\text{O}_2}^*$ is 2–3 order of magnitude smaller than $P_{\text{O}_2,s}$. The slag–metal interfacial oxygen potentials, $P_{\text{O}_2}^*$, obtained from the experimental data, are also compared with those calculated from a mathematical model which simulates the simultaneous reactions in the gas/slag/metal reaction system including Ar– O_2 atmosphere. The calculated interfacial oxygen potentials agree with the experimental data reasonably well.

KEY WORDS: oxygen potential; interface; phosphorus reaction; phosphate capacity; slag–metal reaction; hot metal dephosphorization.

1. Introduction

It is a well accepted idea for metallurgists that an interfacial oxygen potential affects seriously the simultaneous reactions between Fe_tO containing slag and molten iron of high carbon concentration. The quantitative aspects of the interfacial oxygen potential has however not yet been established since no method has been available for the direct measurement of the interfacial oxygen potential. An indirect method in which the interfacial oxygen potential is estimated by the equilibrium data of the slag–metal reactions is not applicable to the Fe_tO containing slag/molten Fe–C systems where the slag–metal reactions are accompanied by CO evolution at the slag–metal interface and the equilibrium data of the slag–metal reactions are hardly obtained experimentally. Because of the inapplicability of the thermodynamic methods, we should try kinetic approaches which may lead to quantitative estimation of the interfacial oxygen potential from rate data of the reactions on some reasonable assumptions.

In the present study, we estimate the interfacial oxygen potential from the authors' kinetic data¹⁾ of a phosphorus transfer reaction between a Fe_tO containing slag and a molten Fe–C–P metal on the assumption of

a quasi equilibrium of the reaction. On the basis of the estimated data of the interfacial oxygen potential, we investigate detailed mechanism of the phosphorus transfer reaction in conjunction with the theoretical reaction model which has been developed by the authors in the previous report.¹⁾

2. The Method of Estimation of the Interfacial Oxygen Potential

2.1. Principle

In the previous study,¹⁾ the authors made kinetic experiments of the simultaneous P and C oxidation reactions in the system of Fe_tO –CaO– Li_2O – SiO_2 – $\text{PO}_{2.5}$ slag and molten Fe–C–P alloy ($[\%C] \approx 4$) being stirred mechanically under Ar– O_2 atmosphere at 1573 K. In the study, they investigated the effects of P_{O_2} in the atmosphere, Fe^{2+} and Fe^{3+} concentration in the slag, and stirring speed on the oxidation reaction of P in the metal. In the analysis of the experimental results, the phosphorus transfer rate in the reaction has been represented by

$$-\frac{d[\%P]}{dt} = \frac{Ak_m\rho_m}{W_m}([\%P] - [\%P]_i)$$

$$= \frac{A k_s \rho_s}{W_m} ((\%P)_i - (\%P)), \dots\dots\dots(1)$$

where t is time; k is the mass transfer coefficient; A is the interfacial area; W is the mass; ρ is the density; the subscripts i , m and s represent the slag-metal interface, the metal phase and the slag phase, respectively.

A typical example of the experimental results in the previous study is illustrated in Fig. 1, where the phosphorus transfer reaction changes from dephosphorization to rephosphorization at $t \cong 15$ min.

At this time point, $[\%P]$ takes a minimum value, $[\%P]_{\min}$, while $(\%P)$ takes a maximum value, $(\%P)_{\max}$, and the phosphorus transfer rate, $d[\%P]/dt$, equals to zero. We can hence assume that

$$\begin{aligned} [\%P] &= [\%P]_{\min} = [\%P]_i, \text{ and} \dots\dots\dots(2) \\ (\%P) &= (\%P)_{\max} = (\%P)_i, \end{aligned}$$

at this time point. Here, on the assumption of interfacial equilibrium at the slag-metal interface, we have the following ratio of the phosphorus distribution between the slag and metal phases.

$$L_P = \frac{(\%P)_i}{[\%P]_i} = \frac{(\%P)_{\max}}{[\%P]_{\min}} \equiv \left(\frac{(\%P)}{[\%P]} \right)_{\max} \dots\dots\dots(3)$$

The phosphate capacity is represented by

$$C_{\text{PO}_4^{3-}} = \frac{(\% \text{PO}_4^{3-}) P_{\text{O}_2}^{-5/4}}{P_{\text{P}_2}^{1/2}} \dots\dots\dots(4)$$

We have Eq. (8) by the use of Eqs. (5)–(7).

$$\frac{1}{2} P_2 = \underline{P}, \dots\dots\dots(5)$$

$$\Delta G^\circ = -157700 + 5.4T \quad (\text{J}),^{2)} \dots\dots\dots(6)$$

$$a_P = f_P [\%P], \dots\dots\dots(7)$$

$$C_{\text{PO}_4^{3-}} = 2.759 \times 10^5 \cdot \frac{(\%P)_e P_{\text{O}_2}^{-5/4}}{f_P [\%P]_e} \dots\dots\dots(8)$$

Here, a_P and f_P represent the activity and the activity coefficient of $\underline{P}$ in the metal, respectively; the subscript e represents the equilibrium between the slag and metal. Substituting the $((\%P)/[\%P])_{\max}$ in the Eq. (3) for

$(\%P)_e/[\%P]_e$ in Eq. (8), and rewriting the P_{O_2} and f_P in Eq. (8) as $P_{\text{O}_2}^*$ and $f_{P,i}$ which are the corresponding values at the interface, we obtain

$$P_{\text{O}_2}^* = 2.252 \times 10^4 C_{\text{PO}_4^{3-}}^{-4/5} \left\{ \frac{1}{f_{P,i}} \left(\frac{(\%P)}{[\%P]} \right)_{\max} \right\}^{4/5} \dots\dots\dots(9)$$

Since, under the experimental conditions of the present and/or the previous study, interfacial concentration of $\underline{C}$, $[\%C]_i$, is nearly equal to $[\%C]$,^{1,3)} $f_{P,i}$ is given by

$$\log f_{P,i} = e_P^P [\%P]_{\min} + e_P^C [\%C], \dots\dots\dots(10)$$

where e_P^i represents the interaction parameter.

Extrapolating the value available in literature,²⁾ we have

$$e_P^P = 0.0643, \dots\dots\dots(11)$$

at the experimental temperature, 1573 K.

For carbon saturated molten iron, Tsukihashi *et al.*⁴⁾ measured the activity coefficient of $\underline{P}$ and obtained the relation between e_P^C and temperature, T , in the range of $T = 1473$ – 1673 K. From the equation, we have $e_P^C = 0.139$ at 1573 K. Besides Tsukihashi *et al.*, several research groups^{15–17)} measured the interaction parameter at higher temperature ranges and proposed somewhat scattered values for e_P^C . Among those, Hadrys, Froberg and Elliott with appendix B by Lupis¹⁵⁾ reported $e_P^C = 0.126$ at $T = 1873$ K. Extrapolating the value to $T = 1573$ K, we have $e_P^C = 0.150$ which is very close to Tsukihashi *et al.*'s result. The $e_P^C = 0.242$ in carbon saturated iron melt at $T = 1788$ K measured by Schenck *et al.*¹⁶⁾ leads to a higher value of $e_P^C = 0.275$ for $T = 1573$ K. Ban-ya and Suzuki¹⁷⁾ extracted markedly different e_P^C values from their own experimental results at $T = 1773$ K for low and high $\underline{C}$ concentration ranges respectively. With the $e_P^C = 4.72$ for the low $[\underline{C}]$ range and the $e_P^C = 10.6$ for the high $[\underline{C}]$ range, we obtain $e_P^C = 0.089$ and $e_P^C = 0.223$, respectively, at $T = 1573$ K. The reason of the change in e_P^C with $\underline{C}$ concentration, however, is not evident in the literature. Taking the scattering of the e_P^C data into consideration, we average the e_P^C values obtained from the investigations of Tsukihashi *et al.*,⁴⁾ Hadrys *et al.*¹⁵⁾ and Schenck *et al.*¹⁶⁾ We thus have

$$e_P^C = 0.19 \dots\dots\dots(12)$$

If the $C_{\text{PO}_4^{3-}}$ of the slag is known, from Eqs. (9)–(12), we can estimate the interfacial oxygen potential, $P_{\text{O}_2}^*$, using the measured value of $((\%P)/[\%P])_{\max}$ which is obtained experimentally at the time point when the phosphorus reaction changes from dephosphorization to rephosphorization.

2.2. The Measurement of $C_{\text{PO}_4^{3-}}$ of the Slag

When the carbon concentration of the metal is high, Fe_2O concentration is lowered considerably at the slag-metal interface. We can hence adopt the $C_{\text{PO}_4^{3-}}$ value of the Li_2O – CaO – SiO_2 primary slag (composition: Li_2O 20.5 mass%, CaO 38.4 mass%, SiO_2 41.1 mass%) employed in the previous studies^{1,3,5)} for the calculation of $P_{\text{O}_2}^*$ with Eq. (9). To estimate the $C_{\text{PO}_4^{3-}}$ value of the Fe_2O free slag, the present authors have measured the

Fig. 1. Changes in $[\%P]$ and $(\%P)$ with time.

phosphorus distribution ratio between the slag and the carbon saturated molten iron under the condition of $P_{\text{CO}}/P^0=1$, where $P^0=1.01325 \times 10^5$ Pa.

The experiments were made at 1573 K. A graphite crucible (O.D. 15 mm, I.D. 12 mm, 30 mm in length) containing Fe-C alloy (4 g) and the slag (2 g) was suspended with Mo wire in the hot zone of a reaction tube placed in a SiC resistance furnace (5.5 kW). The CO gas (gas flow rate: 300 cm³/min) was blown through an alumina tube onto the slag-metal bath surface. After a predetermined reaction time (1–14 hr), the crucible was removed quickly from the hot zone to a water-cooled copper cap which was located at the bottom of the reaction tube, and the slag-metal bath was thus quenched. The phosphorus contents of the slag and the metal were determined by a reduced molybdo-silicate spectrophotometric method. In the experiments, phosphorus was added initially to the slag phase, and hence the slag-metal reaction was the phosphorus transfer reaction from the slag phase to the metal phase.

The experimental results for the experimental time $t > \sim 12$ hr led to $(\%P)/[\%P]$ data which appeared independent of t . The average value of the data at $t > \sim 12$ hr is employed as the equilibrium phosphorus partition ratio at 1573 K under $P_{\text{CO}}/P^0=1$, and

$$\left(\frac{(\%P)}{[\%P]} \right)_e = 0.23. \quad (13)$$

We substitute the C(s)/CO(1.01325 $\times 10^5$ Pa) system's equilibrium oxygen partial pressure, $P_{\text{O}_2}/P^0=2.413 \times 10^{-17}$, which is calculated from thermodynamic data,⁶⁾ for the P_{O_2} in Eq. (8). We evaluate the activity coefficient, f_P , with Eqs. (10)–(12) and the following relation of carbon solubility,⁶⁾

$$[\%C]_{\text{sat}} = 1.34 + 2.54 \times 10^{-3} T/^{\circ}\text{C} - 0.33[\%P].$$

Substituting the f_P value for the f_P in Eq. (8), we have

$$C_{\text{PO}_3} = 4.89 \times 10^{24}. \quad (14)$$

From the phosphorus partition ratio, we can also obtain the Raoultian activity coefficient of $\text{PO}_{2.5}$ in the $\text{Li}_2\text{O}-\text{CaO}-\text{SiO}_2$ slag by using the thermodynamic relation,

$$P + \frac{5}{4} \text{O}_2(\text{g}) = \text{PO}_{2.5}(\text{l}), \quad (15)$$

$$\Delta G^{\circ} = -609541 + 247.732 T \quad (\text{J}),^{2,6,11,12} \quad (16)$$

as

$$\gamma_{\text{PO}_{2.5}} = 7.14 \times 10^{-11}. \quad (17)$$

3. $P_{\text{O}_2}^*$ in the Slag-Metal Phosphorus Reaction

3.1. Estimation of $P_{\text{O}_2}^*$ from the Results of the Kinetic Experiments

The data of the $(\%P)_{\text{max}}$, $[\%P]_{\text{min}}$ and the ratio $((\%P)/[\%P])_{\text{max}}$ observed in the course of the kinetic experiments in the previous study¹⁾ are listed in Table 1 together with the data of $(\% \text{FeO})$ and $(\% \text{FeO}_{1.5})$ in the slag. The experiments were made under various conditions of the oxygen partial pressure in the

Table 1. Data for estimating $P_{\text{O}_2}^*$.

Exp. No.	$[\%P]_{\text{min}}$	$(\%P)_{\text{max}}$	$((\%P)/[\%P])_{\text{max}}$	$(\% \text{FeO})$	$(\% \text{FeO}_{1.5})$
OPP- 2	0.0240	0.2940	12.26	7.07	2.30
OPP- 4	0.0268	0.2094	7.81	4.52	1.12
OPP- 7	0.0130	0.4250	32.69	4.98	3.47
OPP- 9	0.0056	0.3630	64.25	4.53	3.51
OPP-10	0.0083	0.3150	37.95	5.02	3.79
OPP-11	0.0053	0.3510	66.23	6.10	3.75
OPP-12	0.0067	0.3520	52.54	5.28	2.22
OPP-13	0.0054	0.3010	55.74	5.54	3.47
OPP-14	0.0118	0.3460	29.32	4.76	3.15
OPP-15	0.0113	0.3550	31.42	6.76	4.09
OPP-16	0.0052	0.3390	65.19	5.86	3.03
OPP-17	0.0020	0.4080	204.0	5.80	3.87
OPP-18	0.0146	0.4104	21.50	6.13	3.13
OPP-19	0.0042	0.3910	93.00	5.32	3.69
OPP-20	0.0110	0.3740	34.00	6.48	4.40
OPP-22	0.0046	0.3710	80.65	5.60	3.57
OPP-23	0.0048	0.3804	79.25	4.96	3.67

Fig. 2. Relation between slag-metal interfacial oxygen potential, $P_{\text{O}_2}^*$, and iron oxide mol fraction, X_{FeO} , in the slag.

atmosphere ($P_{\text{O}_2}/P^0=0-0.2$), the rotation speed of an eccentric alumina stirrer (30–300 min⁻¹), and the initial concentrations of the solutes in the metal and the slag phases ($(\% \text{FeO})_0$, $[\%P]_0$, and $(\%P)_0$). With the data in the Table 1, $P_{\text{O}_2}^*$ values are calculated on the basis of Eq. (9).

In Fig. 2, $P_{\text{O}_2}^*$ is plotted against the mol fraction of the total iron oxide in the slag, i.e. $X_{\text{FeO}} = X_{\text{FeO}} + X_{\text{FeO}_{1.5}}$. The figure shows that the interfacial oxygen potential $P_{\text{O}_2}^*$ has the value of the order of 10^{-11} – 10^{-10} Pa, which is 10 – 10^2 times larger than the equilibrium oxygen partial pressure for C(s)/CO(1.01325 $\times 10^5$ Pa) system, i.e. $P_{\text{O}_2, \text{C/CO}}/P^0=2.413 \times 10^{-17}$ (at 1573 K). We cannot find however a simple linear relation between $P_{\text{O}_2}^*$ and X_{FeO} in the figure.

3.2. Change in $P_{\text{O}_2}^*$ with the Composition of the Ar-O₂ Atmosphere

In the previous study,¹⁾ the oxygen partial pressure, P_{O_2} , of the Ar-O₂ atmosphere was changed in a series

Fig. 3. Effect of oxygen partial pressure in the atmosphere, P_{O_2} , on the slag-metal interfacial oxygen potential $P_{O_2}^*$.

Fig. 4. Effect of mechanical stirring on the slag-metal interfacial oxygen potential $P_{O_2}^*$.

of experiments. The $P_{O_2}^*$ data estimated with the experimental results are plotted against P_{O_2} in Fig. 3. The experimental conditions other than P_{O_2} are also listed in the figure. Apparently $P_{O_2}^*$ increases with the increase in P_{O_2} . In the experiments, the rate of $\underline{P}$ oxidation increased with increasing P_{O_2} , which suggested an increase in the interfacial oxygen potential accompanied by the corresponding increase in L_p at the slag-metal interface. We regard that the results shown in Fig. 3 support the qualitative argument of the previous report¹⁾ quantitatively.

3.3. Relation between $P_{O_2}^*$ and Mechanical Stirring Condition

In one series of experiments in the previous study,¹⁾ the authors examined the effect of the mechanical stirring of the slag-metal bath on the phosphorus reaction rate. In the experiments, the rotation speed, R , of an alumina eccentric stirrer was changed in the range of 30–300 min^{-1} . Figure 4 shows the relation between $P_{O_2}^*$ and the stirring speed, R . The experimental conditions other than R are also listed in the figure. In the figure, $P_{O_2}^*$

Fig. 5. Relation between $P_{O_2}^*$ and $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$.

decreases slightly with R in the range of $R > \sim 50 \text{ min}^{-1}$. From the results of the authors' another investigation³⁾ on the rate of $\underline{C}$ oxidation between Fe_2O_3 containing slag and high carbon concentration iron, we can expect that the intensification of the mechanical stirring of the slag-metal bath accelerates CO bubbles' detachment from the slag-metal interface and the accelerated detachment of CO bubbles results in the improvement of $\underline{C}$ oxidation rate and coincident increase in FeO reduction rate, which may lead to a decrease in the interfacial oxygen potential. We consider that Fig. 4 demonstrates quantitatively the decrease in the interfacial oxygen potential and the lowering of L_p at the interface with the intensification of the stirring.

3.4. Relation between $P_{O_2}^*$ and Fe^{2+} and Fe^{3+} Concentrations in the Slag

Figure 5 shows the relation between $P_{O_2}^*$ and the ratio of Fe^{3+} to the total iron in the slag, $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$. In the figure, the data points represented by the symbol $\circ$ were estimated from the numerical values listed in Table 1 ($(\%P)_{\text{max}} < 0.8$; initial concentration of $\text{PO}_{2.5}$, $(\% \text{PO}_{2.5})_0 = 0$), while the data represented by $\bullet$ were estimated from the results ($(\%P)_{\text{max}} \geq 2-3$) of the additional experiments ($(\% \text{PO}_{2.5})_0 = 1.6-1.2$) made in the present study under Ar atmosphere.

In Fig. 5, $P_{O_2}^*$ at the interface tends to increase with $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ which is considered usually as an indication of the oxygen potential of bulk slag. Figure 5 thus shows that $P_{O_2}^*$ at the slag-metal interface tends to increase with the increase in the oxygen potential, $P_{O_{2,s}}$, of the bulk slag.

We can estimate $P_{O_{2,s}}$ of the bulk slag with the measured values of $(\% \text{FeO})$ and $(\% \text{FeO}_{1.5})$ on the basis of the following thermodynamic relations.

$$\Delta G^\circ = 126817 - 53.011T \quad (\text{J}), \quad \dots\dots\dots(19)$$

$$K = \frac{\gamma_{\text{FeO}}}{\gamma_{\text{FeO}_{1.5}}} \cdot \frac{X_{\text{FeO}}}{X_{\text{FeO}_{1.5}}} P_{\text{O}_2}^{1/4} \dots (20)$$

Here, X is the mol fraction. To determine the activity coefficients, γ_{FeO} and $\gamma_{\text{FeO}_{1.5}}$, we use the regular solution model of Ban-ya and Hino.⁷⁾ In the process of the calculation of the activity coefficients in the present slag, however, we have to estimate the numerical values of the interaction parameters, $\alpha_{\text{Li}^+ - \text{Ca}^{2+}}$, $\alpha_{\text{Li}^+ - \text{Si}^{4+}}$, $\alpha_{\text{Li}^+ - \text{P}^{5+}}$, $\alpha_{\text{Li}^+ - \text{Fe}^{2+}}$, and $\alpha_{\text{Li}^+ - \text{Fe}^{3+}}$, which have not been available in literature.

In the course of the present study, the authors measured the activities (standard state: corresponding pure liquids) of FeO and FeO_{1.5} in the Li₂O–CaO–SiO₂–Fe₂O slag under the condition of solid Fe saturation at the temperature of 1573 K by means of an electrochemical method developed by Iwase *et al.*⁸⁾ The experimental results are shown in Fig. 6, where $X_{\text{Fe}^{2+}}$ and $X_{\text{Fe}^{3+}}$ are the cation fractions of Fe²⁺ and Fe³⁺, respectively.

The regular solution model⁷⁾ leads to the following equation.

$$\begin{aligned} \alpha_{\text{Li}^+ - \text{Fe}^{2+}} - \alpha_{\text{Li}^+ - \text{Fe}^{3+}} &= X_{\text{Li}^+}^{-1} \{ RT \ln(\gamma_{\text{FeO}}/\gamma_{\text{FeO}_{1.5}}) \\ &+ (\alpha_{\text{Fe}^{3+} - \text{Si}^{4+}} - \alpha_{\text{Fe}^{2+} - \text{Si}^{4+}}) X_{\text{Si}^{4+}} \\ &+ (\alpha_{\text{Fe}^{3+} - \text{Ca}^{2+}} - \alpha_{\text{Fe}^{2+} - \text{Ca}^{2+}}) X_{\text{Ca}^{2+}} \\ &+ \alpha_{\text{Fe}^{2+} - \text{Fe}^{3+}} (X_{\text{Fe}^{2+}} - X_{\text{Fe}^{3+}}) \} \equiv -F \dots (21) \end{aligned}$$

Here, X_i is the cation fraction of i -component. Employing the interaction parameters available in literature, and using the γ_{FeO} and $\gamma_{\text{FeO}_{1.5}}$ data together with X_i extracted from the activity data in Fig. 6, we can determine the value of F in Eq. (21). We thus have

$$\alpha_{\text{Li}^+ - \text{Fe}^{3+}} = \alpha_{\text{Li}^+ - \text{Fe}^{2+}} + F \dots (22)$$

Applying the regular solution model to represent γ_{FeO} , and using the a_{FeO} data in Fig. 6, we have

$$RT \ln \gamma_{\text{FeO}} = F_1(\alpha_{\text{Li}^+ - \text{Fe}^{2+}}, \alpha_{\text{Li}^+ - \text{Ca}^{2+}}, \alpha_{\text{Li}^+ - \text{Si}^{4+}}), \dots (23)$$

where F_1 is a function of $\alpha_{\text{Li}^+ - \text{Fe}^{2+}}$, $\alpha_{\text{Li}^+ - \text{Ca}^{2+}}$, and $\alpha_{\text{Li}^+ - \text{Si}^{4+}}$. Previously, the authors measured the activity of iron oxide in (28%Li₂O–58%SiO₂–14%Al₂O₃)–Fe₂O slag at 1523 K,¹³⁾ and, in the course of the present study, they recalculated the Fe₂O activity from the previous experimental data by using the standard Gibbs free

Fig. 6. Activities of FeO and FeO_{1.5} in Li₂O–CaO–SiO₂–Fe₂O slag in equilibrium with Fe(s) at 1573 K.

energy for Fe₂O formation¹⁴⁾ employed in the regular solution model⁷⁾. We thus have $\gamma_{\text{FeO}} = 2.37$ for the slag at $N_{\text{FeO}} < 0.1$, where N_{FeO} is the mol fraction of Fe₂O in the slag. By the use of the thermochemical relation for the conversion of the iron oxide activity, a_{FeO} , to $a_{\text{FeO}_{1.5}}$,⁷⁾ together with a relation between the mol fraction of Fe₂O and the cation fraction of Fe²⁺, we have $\gamma_{\text{FeO}} = 3.01$ at $X_{\text{Fe}^{2+}} \rightarrow 0$ for this slag system. With this $\gamma_{\text{FeO}} = 3.01$, on the assumption of $X_{\text{Fe}^{2+}} = 0$, the terms relating to Al³⁺ being ignored because of the insignificant cation fraction of Al³⁺, i.e. $X_{\text{Al}^{3+}} < 0.1$, the regular solution model gives the following relation

$$0.549\alpha_{\text{Li}^+ - \text{Fe}^{2+}} - 0.187\alpha_{\text{Li}^+ - \text{Si}^{4+}} = 25769 \text{ (J)} \dots (24)$$

In the course of another previous study,⁵⁾ the authors measured the activity of SiO₂, a_{SiO_2} , in the present Li₂O–CaO–SiO₂ primary slag. With the a_{SiO_2} value (standard state: β -cristobalite) and necessary conversion of the standard state,⁷⁾ we have the following relation based on the regular solution model.

$$0.375\alpha_{\text{Li}^+ - \text{Si}^{4+}} - 0.125\alpha_{\text{Li}^+ - \text{Ca}^{2+}} = -52258 \text{ (J)} \dots (25)$$

Solving the simultaneous equations, Eqs. (23), (24) and (25), with respect to $\alpha_{\text{Li}^+ - \text{Fe}^{2+}}$, $\alpha_{\text{Li}^+ - \text{Ca}^{2+}}$, and $\alpha_{\text{Li}^+ - \text{Si}^{4+}}$, we can determine the numerical values of the three interaction parameters. For $\gamma_{\text{PO}_{2.5}}$, the regular solution model leads to

$$RT \ln \gamma_{\text{PO}_{2.5}}(\text{R.S.}) = F_2(\alpha_{\text{Li}^+ - \text{P}^{5+}}, \alpha_{\text{Li}^+ - \text{Ca}^{2+}}, \alpha_{\text{Li}^+ - \text{Si}^{4+}}), \dots (26)$$

where (R.S.) represents that the standard state of PO_{2.5} is PO_{2.5}(R.S.) of the regular solution.⁷⁾ Converting the $\gamma_{\text{PO}_{2.5}}$ value of Eq. (17) into $\gamma_{\text{PO}_{2.5}}(\text{R.S.})$ value in accordance with the free energy change reported by Ban-ya and Hino,⁷⁾ and substituting the value for $\gamma_{\text{PO}_{2.5}}(\text{R.S.})$ in Eq. (26), we can obtain $\alpha_{\text{Li}^+ - \text{P}^{5+}}$ from Eq. (26).

Since the F value (Eq. (21)) obtained from the experimental results shown in Fig. 6 changes slightly with (%Fe₂O) as $-F \sim 120\text{--}80 \text{ kJ}$ in the range of (%Fe₂O) = 1–25, we take averaged F values for the Fe₂O concentration ranges of (%Fe₂O) = 5–10 and (%Fe₂O) = 10–20, respectively, to estimate appropriate sets of values of the interaction parameters relating to Li⁺, $\alpha_{\text{Li}^+ - j}$, which are applicable to the (%Fe₂O) range of ○ ((%Fe₂O) = 5–10) and ● ((%Fe₂O) = 10–20) in Fig. 5. The sets of $\alpha_{\text{Li}^+ - j}$ obtained in the present study are listed in Table 2.

Employing the $\alpha_{\text{Li}^+ - j}$ values in Table 2 and the other interaction parameters available in literature,⁷⁾ we can

Table 2. Interaction energies between cations.

ion-ion	Interaction energy, α_{i-j} (kJ)	
	(%Fe ₂ O) = 5–10	(%Fe ₂ O) = 10–20
Fe ²⁺ –Li ⁺	–1.37	–3.93
Fe ³⁺ –Li ⁺	–109.5	–85.6
Ca ²⁺ –Li ⁺	–8.49	–31.0
Si ⁴⁺ –Li ⁺	–142.1	–149.7
P ⁵⁺ –Li ⁺	–264.1	–271.7

Fig. 7. Relationship between the oxygen potential in the bulk slag and that at the slag-metal interface.

estimate the oxygen potential, $P_{O_{2,s}}$ of the bulk slag for the slags of $\circ$ and $\bullet$ in Fig. 5. The estimated $P_{O_{2,s}}$ is compared with the interfacial $P_{O_2}^*$ in Fig. 7, where the data represented by $\bullet$ are correspondent to those represented by $\bullet$ in Fig. 5. The other data in Fig. 7 correspond to those represented by $\circ$ in Fig. 5. We see in Fig. 7 that $P_{O_2}^*$ tends to increase slightly with the increase in $P_{O_{2,s}}$, which suggests that the transfer of oxygen from the bulk slag to the slag-metal interface affects the interfacial oxygen potential and influences the phosphorus oxidation reaction thereby. However, we should note the small change in $P_{O_2}^*$, i.e. $P_{O_2}^*/P^0 = 10^{-16}$ – 10^{-15} , compared with the large change in $P_{O_{2,s}}$, i.e. $P_{O_{2,s}}/P^0 = \sim 10^{-15}$ – 10^{-12} .

4. Calculation of the Interfacial Oxygen Potential with a Reaction Model

In the previous study¹⁾, the authors developed a mathematical model of $\underline{P}$ oxidation by FeO and Fe_2O_3 in a slag under oxidizing atmosphere and showed that the model could explain the results of an experiment under the condition of gas atmosphere of the oxygen partial pressure equal to 1.01325×10^4 Pa and the stirring speed of 200 min^{-1} . In the following parts of the present report, we estimate a slag-metal interfacial potential by the reaction model and compare the estimated value with the $P_{O_2}^*$ value obtained in the preceding parts of the present report.

4.1. Reaction Model

The details of the reaction model have been described in the previous report.¹⁾ In the model, the gas-slag and slag-metal reactions are represented as follows.

At the gas-slag interface;

At the slag-metal interface;

The $\underline{\text{C}}$ oxidation reaction proceeds through CO bubble at the slag-metal interface. The overall reaction of the $\underline{\text{C}}$ oxidation is

Assuming the slag-metal interfacial equilibrium, and using a slag-metal interfacial oxygen activity, $a_{O,i}$, we have the following relations for the reactions of Eqs. (28)–(30).

$$K'_{\text{FeO}} = \frac{a_{O,i}}{(\% \text{FeO})_i} \quad (32)$$

$$K'_{\text{FeO}_{1.5}} = \frac{a_{O,i}^{3/2}}{(\% \text{FeO}_{1.5})_i} \quad (33)$$

$$K'_P = \frac{(\% \text{PO}_{2.5})_i}{[\% \text{P}]_i a_{O,i}^{2.5}} \quad (34)$$

Here, K' 's are equilibrium parameters determined with thermochemical data and $a_{\text{Fe}} = 0.66$,¹⁾ and the subscript i denotes the slag-metal interface. The rate of the gas-slag reaction of Eq. (27), the mol flux of the FeO transfer to the gas-slag interface and the mol flux of the $\text{FeO}_{1.5}$ transfer from the gas-slag interface are represented by Eqs. (35)–(37), respectively.

$$J_{\text{FeO}_{1.5}}^{\text{sg}} = k'(\% \text{FeO})^{\text{sg}} P_{O_2}^{1/2} \quad (35)$$

$$J'_{\text{FeO}} = \beta_{\text{FeO}}((\% \text{FeO}) - (\% \text{FeO})^{\text{sg}}) \quad (36)$$

$$J'_{\text{FeO}_{1.5}} = \beta_{\text{FeO}_{1.5}}((\% \text{FeO}_{1.5})^{\text{sg}} - (\% \text{FeO}_{1.5})) \quad (37)$$

Here, k' is the apparent rate constant of the chemical reaction of Eq. (27);¹⁾ P_{O_2} is the oxygen partial pressure in the atmosphere; the superscript sg denotes the slag-gas interface. The mol fluxes of the components in the slag and metal phases are represented as follows.

$$J_P = \beta_P([\% \text{P}] - [\% \text{P}]_i) = \beta_{\text{PO}_{2.5}}((\% \text{PO}_{2.5})_i - (\% \text{PO}_{2.5})) \quad (38)$$

$$J_{\text{FeO}} = \beta_{\text{FeO}}((\% \text{FeO}) - (\% \text{FeO})_i) \quad (39)$$

$$J_{\text{FeO}_{1.5}} = \beta_{\text{FeO}_{1.5}}((\% \text{FeO}_{1.5}) - (\% \text{FeO}_{1.5})_i) \quad (40)$$

For $\underline{\text{C}}$ oxidation rate, the authors' previous study³⁾ gives

$$J_{\underline{\text{C}}} = \frac{k_{ov} a_{\text{FeO}}}{(1 + K a_{\text{PO}_{2.5}})} \quad (41)$$

Here, β_j is a rate constant expressed as

$$\beta_j = \frac{k_j \rho}{100 M_j} \quad (42)$$

where k_j , ρ and M_j represent the mass transfer coefficient of j -component, the density of slag or metal, molecular or atomic weight of j -component, respectively. The values of k_{ov} and K in Eq. (41) are the overall rate constant of $\underline{\text{C}}$ oxidation reaction in the absence of the influence of $\text{PO}_{2.5}$ in the slag and the apparent adsorption equilibrium constant of $\text{PO}_{2.5}$, respectively. On the assumption of steady state of the reaction process,

$$J_{\text{FeO}_{1.5}}^{\text{sg}} = J'_{\text{FeO}} = J'_{\text{FeO}_{1.5}} \quad (43-a)$$

Fig. 8. Comparison of changes in [%P], [%C], (%P), (%FeO) and (%Fe₂O₃) with time between experiments and calculations for various partial oxygen pressures in the atmosphere.

$$2.5J_P + J_C = J_{FeO} + 1.5J_{FeO_{1.5}} \quad (43-b)$$

We can determine the interfacial concentrations and the interfacial oxygen activity from the relations of Eqs. (32)–(43) and the initial conditions of the experiments. The solutes' concentration changes are then calculated with the interfacial concentrations and the rate equations¹⁾ for the components in the slag and metal phases. The interfacial oxygen potential, $P_{O_2, cal.}^*$, at the slag–metal interface is thus obtained by

$$\underline{O} = \frac{1}{2} O_2, \quad (44)$$

$$K = \frac{P_{O_2, cal.}^{*1/2}}{a_{O,i}} \quad (45)$$

The equilibrium constants, the chemical reaction rate constant and the mass transfer coefficients employed in the present calculation are essentially the same as those employed in the previous study.¹⁾ To take the effect of stirring on the mass transfer coefficient of P in the metal side interface, we estimate k_P with the following relation.⁵⁾

$$\frac{k_P}{k_{P, 200}} = \left(\frac{R}{200} \right)^{1/2} \quad (46)$$

Here, $k_{P, 200} = 0.05 \text{ cm/s}$.¹⁾ The slag side mass transfer coefficient is not affected by the mechanical stirring condition,⁵⁾ and hence we use $k_{FeO} = k_{FeO_{1.5}} = k_{PO_{2.5}} = 0.003 \text{ cm/s}$.¹⁾ The overall rate of $\underline{C}$ oxidation reaction becomes slightly larger with the increase in the rotation speed of the stirrer,^{1,3)} which enhances CO bubbles' detachment from the slag–metal interface. The enhancing effect of the mechanical stirring on the $\underline{C}$ oxidation rate, however, is not taken into consideration in the present model. To fit the model calculation to the experimental data, we thus change the overall reaction rate constant k_{ov} slightly as $k_{ov} = (2.3\text{--}3.5) \times 10^{-5} \text{ mol/cm}^2 \cdot \text{s}$.

4.2. Results of the Model Calculation

Figure 8 gives the examples of the calculated concentration changes, together with the experimental results, of the solutes in the slag and metal phases under the conditions of an initial concentration of iron oxide in the slag (%Fe₂O₃) = 15 and various oxygen partial

Fig. 9. Changes in $P_{O_2}^*$ with time.

pressures in the atmosphere, P_{O_2} . As shown in the figure, the model calculation fits the experimental data reasonably well.

Figure 9 shows the time change in the interfacial oxygen potential, $P_{O_2, cal.}^*$, obtained from the model calculation for various P_{O_2} . In the figure, $P_{O_2, cal.}^*$ increases slightly in the initial period ($t < \sim 5 \text{ min}$) of the reaction. This initial increase in $P_{O_2, cal.}^*$ corresponds to the initial increase in $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ accompanying with the proceeding of FeO oxidation reaction at the slag–gas interface. In the whole time range of the figure, on the other hand, $P_{O_2, cal.}^*$ ranges from 10^{-10} – 10^{-9} Pa , which suggests that the interfacial oxygen potential of the slag/molten iron with high carbon concentration is affected strongly by the high $\underline{C}$ content in the metal phase. In the Fig. 9, however, $P_{O_2, cal.}^*$ increases with time at $t > \sim 15 \text{ min}$ apparently, which is due to the roughness of the approximation employed in the course of the derivation of the rate equation of Eq. (35) for the chemical reaction at the slag–gas interface. The authors are now investigating the details of the slag–gas reaction kinetics.

We compare in Fig. 10 the slag–metal interfacial oxygen potentials, $P_{O_2}^*$, obtained from the experimental results, with the calculated $P_{O_2, cal.}^*$ at the corresponding reaction time when the experimental data for $P_{O_2}^*$ have been obtained. The agreement between the experimental $P_{O_2}^*$ and the calculated $P_{O_2, cal.}^*$ is fairly well though

Fig. 10. Comparison of the slag-metal interfacial oxygen potential, $P_{O_2}^*$, between experiments and calculations.

$P_{O_2}^*, \text{cal.}$ appears slightly larger than $P_{O_2}^*$. We thus can conclude that the present model explains the reaction between Fe_2O_3 containing slag and molten iron with high carbon concentration reasonably well.

4.3. Comparison with Previous Reaction Model

Ohguchi *et al.*^{9,10)} proposed a multicomponent mixed-transport-control theory for kinetics of coupled slag/metal and slag/metal/gas reactions, and applied the model to analyze the kinetics of hot metal desiliconization, decarburization, desulfurization and dephosphorization reactions. In the model, Ohguchi *et al.* assumed that C oxidation reaction rate increases in proportion to a supersaturation pressure of CO gas, P_{CO}^* , at the slag-metal interface. As a value of the supersaturation pressure, they reported $P_{\text{CO}}^*/P^0 = \sim 50$ in the case of simultaneous dephosphorization, decarburization and desulfurization of hot metal of low Si concentration.⁹⁾ Here, taking $P_{\text{CO}}^*/P^0 = 50$ and $a_{\text{C}} \cong 1$, we have the equilibrium oxygen potential of $P_{O_2}^*/P^0 \geq 6 \times 10^{-14}$ at the slag-metal interface. This value, being 10 – 10^2 greater than the $P_{O_2}^*$ obtained in the present study, has the similar order of magnitude with the oxygen potential of the bulk slag in the present study. In spite of the difference in the slag composition between Ohguchi *et al.*'s and the present studies, we can consider that the large $P_{O_2}^*$ extracted from Ohguchi *et al.*'s P_{CO}^* value is not reasonable as an interfacial oxygen potential which is affected by high C content in the metal.

5. Conclusion

In the present study, we estimated the oxygen potential at the interface between FeO and Fe_2O_3 containing slag and molten iron with high carbon concentration on the assumption of establishment of a quasi-equilibrium of phosphorus reaction at the interface. We calculated the slag-metal interfacial oxygen potential, $P_{O_2}^*$, using the kinetic data of the experiments made under various conditions of the oxygen partial pressure of the atmosphere, the mechanical stirring intensity *etc.* We investigated the change in $P_{O_2}^*$ with the experimental conditions, focusing on the relation between $P_{O_2}^*$ and the

concentrations of Fe^{2+} and Fe^{3+} in the slag especially. The $P_{O_2}^*$ obtained from the experimental results was compared with the interfacial oxygen potential calculated from the present authors' reaction model.

The results of the present study are summarized as follows:

(1) The equilibrium partition ratio of phosphorus was measured between carbon saturated molten iron and 20.5% Li_2O –38.4% CaO –41.1% SiO_2 slag at 1573 K under CO (1.01325×10^5 Pa) atmosphere. From the results of the experiments, we obtained the phosphate capacity of the slag, $C_{\text{PO}_4^{3-}} = 4.89 \times 10^{24}$ and the activity coefficient of $\text{PO}_{2.5}$ in the slag, $\gamma_{\text{PO}_{2.5}} = 7.14 \times 10^{-11}$.

(2) In the present phosphorus reaction system, the interfacial oxygen potential, $P_{O_2}^*$, at the slag-metal interface ranges in the order of 10^{-11} – 10^{-10} Pa.

(3) The $P_{O_2}^*$ increases with the increase in the partial oxygen pressure in the atmosphere, and the $P_{O_2}^*$ decreases with intensifying the mechanical stirring.

(4) The $P_{O_2}^*$ increases apparently with $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ in the bulk slag. The comparison of $P_{O_2}^*$ with the bulk slag's oxygen potential, estimated from activity data calculated with a regular solution model, suggests a strong effect of high C concentration on $P_{O_2}^*$, while the bulk slag's oxygen potential also affects $P_{O_2}^*$.

(5) The present authors' reaction model, for the phosphorus oxidation by FeO and Fe_2O_3 in the slag, fits the experimental $P_{O_2}^*$ data reasonably well, which confirms the applicability of the model to the kinetics of the simultaneous reactions between Fe_2O_3 containing slag and molten iron of high C concentration.

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(Originally published in *Tetsu-to-Hagané*, **76** (1990), 1488, in Japanese)