Thermodynamics of Phosphorus in the MnO–SiO$_2$–Fe$_7$O System

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Phosphorus, one of typical impurities in steel, has been traditionally tried to be removed to the refining slag in the conventional steel making process. On the other hand, the inverse-utilization of impurities in steel was introduced recently to provide a resource circulating society. In these processes, phosphorus can be and must be restored in the steel during the deoxidation and solidification. The usage of elements with high deoxidizing and low dephosphorizing abilities such as manganese and silicon will be beneficial for obtaining such kind of steel. However, the thermodynamic behavior of phosphorus in such oxide fluxes has not been established. Therefore, the phosphate capacity as the phosphorus containing ability for the MnO–SiO$_2$–Fe$_7$O system, one of the typical slags for deoxidation, has been investigated by measuring the phosphorus partition between the slag and solid or molten iron. The phosphate capacities for the present system were determined to be from $8.5 \times 10^{14}$ to $3.8 \times 10^{18}$ at temperatures from 1 673 to 1 923 K. The present system has shown a much smaller phosphate capacity by several orders of magnitude compared to the conventional CaO bearing systems and provides the estimation of a very low phosphorus distribution ratio between the slag and the steel. In addition, the heats of the phosphate formation reaction were derived from the temperature dependence of phosphate capacities.

KEY WORDS: recycle process; steel scrap; phosphorus; deoxidation; MnO–SiO$_2$–Fe$_7$O system; thermodynamics; phosphate capacity.

1. Introduction

The inverse-utilization of recycle barriers has been attempted to create a resource circulating society. One of the recycle barriers in steel is impurities in steel scraps. Hence, a feasibility study on the creation of ultra-steel containing high impurities such as phosphorus has been carried out.1) Many favorable results with high phosphorus have been reported in the as-cast condition after rapid solidification or with the ultra fine-grained structure.2–4)

The behavior of impurities should be well known to create a steel with good properties from steel scraps. For example, thermodynamic properties of the oxide systems equilibrated with high impurities are necessary for establishing the proper deoxidation and solidification process. In the conventional refining process, phosphorus is aimed to concentrate itself into the slag. From this aspect, the thermodynamic properties of phosphorus in a basic oxide flux such as the CaO-bearing system have been investigated quite widely and well established covering a wide range of composition and temperature regarding various systems such as CaO–CaCl$_2$,5) CaO–CaF$_2$,6) CaO–FeO–SiO$_2$,7) CaO–CaF$_2$–SiO$_2$,8) and CaO–AlO$_1$–SiO$_2$.$^9$ Successfully, very little phosphorus content has been obtained in conventional steel making.

On the other hand, as is stated above, for the process to make high property steel by the utilization of impurities such as phosphorus, phosphorus can be restored in steel during the melting and deoxidation step. From this point of view, the elements with high deoxidizing and low dephosphorizing abilities such as manganese and silicon, which are typical deoxidizing elements, will be suitable for adding reagents. However, the behavior of phosphorus in the deoxidation slag such as manganese silicate has not been studied much. Therefore, the thermodynamic property of phosphorus in the MnO–SiO$_2$–Fe$_7$O system was investigated by focusing on the phosphorus partition between the slag and solid or molten iron in the present study. The phosphate capacities for the present system were derived, and the behavior of phosphorus during the intended process was estimated.

2. Experimental

A SiC electric resistance furnace was employed as the experimental apparatus with a proportional-integral-differential (PID) controller using a Pt–Pt/6 % Rh thermocouple. The temperature was controlled within ±2 K over a length of 50 mm in an alumina tube (65-mm in outer diameter, 60-mm in inner diameter, and 1 000-mm in length) set in the center of the furnace. A MnO–SiO$_2$–Fe$_7$O slag was prepared as follows. A mixture of calcined MnO from the reagent grade MnCO$_3$ (99.9 % in purity), powder of reagent grade SiO$_2$ (99.9 % in purity) and Fe$_3$O$_4$ (99 % in purity), and dehydrated 2MgO · P$_2$O$_5$ was pre-melted in an iron crucible (26-mm in outer diameter, 19-mm in inner diameter, and 70-mm in length) for 3.6 ks at 1 723 K in an argon atmosphere. In the present study, iron oxide was added to the
slag to control the partial pressure of oxygen in the systems. Experiments have been conducted that cover the temperatures of both molten and solid iron states because the behavior of phosphorus between metal and slag during de-oxidation and that between metal and inclusion during solidification are both important. Hence, experiments were conducted by two methods according to the temperature range in terms of the melting point of iron. For the low temperature range below the melting point, m.p., 1812 K, 1 g of electrolytic iron (a 1 mm thick plate) and 10 g of pre-melted slag were placed in an iron crucible and equilibrated in an argon atmosphere at temperatures from 1673 K to m.p. For the high temperature range above the melting point of iron, 2 g of electrolytic iron and 3.5 g of a similar slag were set in a fused MgO crucible (21-mm in outer diameter, 17-mm in inner diameter, and 30-mm in length) and equilibrated at temperatures from m.p. to 1923 K. The equilibration times were determined to be 43.2 ks for the former experiments and 10.8 ks for the latter ones respectively from the results of the preliminary experiments. After the equilibration, the crucible was removed from the furnace and cooled in a jetting argon gas. The metal and the slag were separated from the sample and subjected to a chemical analysis. The slag was magnetically selected to eliminate the contamination of metallic iron. The phosphorus contents of metal and slag were analyzed by a molybdenum blue colorimetry. The oxygen content of the metal was determined with a LECO† oxygen analyzer. A conventional titration technique was applied for MnO, FeO, and total iron, and gravimetry for SiO2 in the slag. Inductively coupled plasma spectroscopy was used for the analysis of MgO in the slag and manganese in the metal.

3. Results and Discussion

Table 1 lists all experimental results, including slag and metal composition for the MnO–SiO2–FeO and MnO–SiO2–FeO–MgO systems. These are the results of the chemical analysis for the slag and metal after each experiment.

3.1. Experimental Composition

Figure 1 shows the slag composition that was investigated in the low temperature range from 1673 K to m.p. with solid iron. The value of the mole fraction of FeO is around 0.1, and may not cause drastic changes in the MnO–SiO2 basic system regarding the thermodynamic properties of phosphorus. For the experiments conducted at high temperatures from m.p. to 1923 K with molten iron, the slag composition will move to the MnO–MgO solid solution saturation according to the phase diagram for the MnO–SiO2–MgO system10) since a MgO crucible was used. Magnesium oxide solubilities for the present slag are plotted on the phase diagram for the MnO–SiO2–MgO system as shown in Fig. 2 by assuming a pseudo ternary system without iron oxide whose concentrations are almost the same as those in Fig. 1. The solubilities are in fairly good agreement with the liquidus lines that are equilibrated with the oxide solid solution over the temperature range.

3.2. Phosphate Capacities of the Slag

The reaction of the present system regarding phosphorus is expressed by Eq. (1):

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

where O2 and PO43− in the parentheses denote the components in the slag.

The ability of a slag to contain phosphorus as a phosphate ion is defined by the phosphate capacity11) as expressed by Eq. (2), according to Eq. (1):

\[ C_{PO_4} = \frac{\text{mass\% PO}_4^{3-}}{P_{PO_4^{3-}}^{\text{f}}} = \frac{K_1 \cdot a^{3/2}}{f_{PO_4^{3-}}} \]  

where (mass% PO43−) and fPO43− are the concentration in mass% and the activity coefficient relative to 1 mass% of phosphate ion in the slag, PPO43− and PO43− are the partial pressures of phosphorus and oxygen, aPO43− is the activity of oxide ion, and K1 is the equilibrium constant of Eq. (1), respectively.

The concentrations of phosphate ion in the slag can be

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† LECO is a trademark of Leco Corporation, St. Joseph, MI.
generated experimentally. The partial pressures of phosphorus and oxygen in the high temperature range can be determined by the concentrations in the molten iron according to the following thermodynamic data:

\[ \frac{1}{2} P_2(g) = P(\text{mass\% in Fe}) \] ..........................(3)

\[ \Delta G_f^\circ = -157700 + 5.4T \text{ J/mol} \] ..........................(4)

\[ \log f_p = e_p^0 \cdot [\text{mass\% P}] + e_p^0 \cdot [\text{mass\% O}] \] ..........................(5)

\[ e_p^0 = 0.054 \ (1873 \text{ K}) \] ..........................(6)

\[ e_p^0 = 0.13 \ (1873 \text{ K}) \] ..........................(7)

\[ \frac{1}{2} O_2(g) = O(\text{mass\% in Fe}) \] ..........................(8)

\[ \Delta G_f^\circ = -117110 + 3.39T \text{ J/mol} \] ..........................(9)

\[ \log f_p = e_o^0 \cdot [\text{mass\% O}] + e_p^0 \cdot [\text{mass\% P}] \] ..........................(10)

\[ e_o^0 = -1750/T + 0.76 \] ..........................(11)

\[ e_o^0 = 0.07 \ (1873 \text{ K}) \] ..........................(12)

In the low temperature range with solid iron, the phosphorus partial pressure was derived by Eq. (13) and the standard Gibbs energy for the phosphorus transformation reaction which is expressed by Eq. (15) after Barin:

\[ P(1) = P(X_p, \alpha-\text{Fe}) \] ..........................(13)

\[ \Delta G_f^\circ = -140400 + 34.7T \text{ J/mol} \] ..........................(14)

\[ 1/2 P_2(g) = P(1) \] ..........................(15)

In addition, the oxygen partial pressure was estimated by the activity data of Fe\text{O} in the MnO–SiO\text{2}–Fe\text{O} system investigated by Ban-ya et al.\text{19)} They reported the activity coefficient of stoichiometric Fe\text{O} as the function of composition expressed by Eq. (16) assuming a regular solution, and the conversion equation from activity of stoichiometric Fe\text{O} to that of Fe\text{O} expressed by Eq. (17). By using these equations, the activity of Fe\text{O} in the present system has been estimated from the obtained data in Table 1, and by combining those values and Eq. (19) derived from Eqs. (21) and (23), the oxygen partial pressure has been calculated.

\[ RT \ln a_{FeO} = -4460 X_1^{FeO} - 10000 X_2^{FeO} + 700 X_3^{FeO} - 22260 X_4^{FeO} + 10740 X_5^{FeO} + 9700 X_6^{FeO} \] ..........................(16)

\[ RT \ln a_{FeO} = RT \ln a_{FeO} \] ..........................(17)

\[ \Delta G_f^\circ = -217000 + 36.6T \text{ J/mol} \] ..........................(18)

\[ \frac{1}{2} Fe(s) + 1/2 O_2(g) = FeO(1) \] ..........................(18)

\[ H_2O(g) + 1/2 O_2(g) = H_2(g) \] ..........................(20)

\[ \Delta G_f^\circ = -30400 + 19.3T \text{ J/mol (1665 to 1809 K)} \] ..........................(21)

\[ H_2O(g) = H_2(g) + 1/2 O_2(g) \] ..........................(22)

| No. | Temperature (K) | Slag Composition (mass\%) | Metal Composition (mass\%) | \[ P \] | \[ O \] | log f_{FeO} |
|-----|----------------|---------------------------|---------------------------|------|------|------------|
| 1   | 1673           | FeO                        | 25.2                      | 6.88 | 0.056| 0.058      |
| 2   | 1823           | FeO                        | 25.9                      | 6.18 | 0.055| 0.055      |
| 3   | 1873           | FeO                        | 26.5                      | 6.50 | 0.054| 0.056      |
| 4   | 2000           | FeO                        | 28.0                      | 6.99 | 0.053| 0.058      |
| 5   | 2123           | FeO                        | 29.5                      | 7.39 | 0.052| 0.058      |
| 6   | 2297           | FeO                        | 31.0                      | 7.79 | 0.051| 0.058      |
| 7   | 2473           | FeO                        | 32.5                      | 8.20 | 0.050| 0.058      |
| 8   | 2663           | FeO                        | 34.0                      | 8.61 | 0.049| 0.058      |
| 9   | 2873           | FeO                        | 35.5                      | 9.02 | 0.048| 0.058      |
| 10  | 3093           | FeO                        | 37.0                      | 9.43 | 0.047| 0.058      |
| 11  | 3323           | FeO                        | 38.5                      | 9.84 | 0.046| 0.058      |
| 12  | 3563           | FeO                        | 40.0                      | 10.25| 0.045| 0.058      |
| 13  | 3813           | FeO                        | 41.5                      | 10.66| 0.044| 0.058      |
| 14  | 4073           | FeO                        | 43.0                      | 11.07| 0.043| 0.058      |
| 15  | 4343           | FeO                        | 44.5                      | 11.48| 0.042| 0.058      |
| 16  | 4623           | FeO                        | 46.0                      | 11.89| 0.041| 0.058      |
| 17  | 4913           | FeO                        | 47.5                      | 12.30| 0.040| 0.058      |
| 18  | 5220           | FeO                        | 49.0                      | 12.71| 0.039| 0.058      |
| 19  | 5543           | FeO                        | 50.5                      | 13.12| 0.038| 0.058      |
| 20  | 5873           | FeO                        | 52.0                      | 13.53| 0.037| 0.058      |
| 21  | 6213           | FeO                        | 53.5                      | 13.94| 0.036| 0.058      |
| 22  | 6563           | FeO                        | 55.0                      | 14.35| 0.035| 0.058      |
| 23  | 6923           | FeO                        | 56.5                      | 14.76| 0.034| 0.058      |
| 24  | 7293           | FeO                        | 58.0                      | 15.17| 0.033| 0.058      |
| 25  | 7673           | FeO                        | 59.5                      | 15.58| 0.032| 0.058      |
| 26  | 8063           | FeO                        | 61.0                      | 15.99| 0.031| 0.058      |
| 27  | 8463           | FeO                        | 62.5                      | 16.40| 0.030| 0.058      |
| 28  | 8873           | FeO                        | 64.0                      | 16.81| 0.029| 0.058      |
| 29  | 9293           | FeO                        | 65.5                      | 17.22| 0.028| 0.058      |
| 30  | 9723           | FeO                        | 67.0                      | 17.63| 0.027| 0.058      |
| 31  | 10163          | FeO                        | 68.5                      | 18.04| 0.026| 0.058      |
| 32  | 10603          | FeO                        | 70.0                      | 18.45| 0.025| 0.058      |
Since the concentrations of phosphate ion in the slag in mass pct, \((\text{mass}% \text{ P}^{3-})\), are very low and less than 0.7 at highest, the activity coefficient is considered not to be affected by phosphate ion concentration in the slag. Therefore, the phosphate capacities are regarded to be constant at each slag composition within the concentration range of phosphate ion in the present study.

Figure 3 shows the relationship between the phosphate capacity obtained from the experimental data according to Eq. (2) and the molar ratio of MnO to SiO\(_2\) \((X_{\text{MnO}}/X_{\text{SiO}2})\) in the slag for the MnO–SiO\(_2–FeO\) system in the low temperature range from 1 673 to 1 773 K. The phosphate capacity increases remarkably with the molar ratio of MnO to SiO\(_2\) and seems to slightly decrease beyond composition of \(X_{\text{MnO}}/X_{\text{SiO}2}=2\) at all the temperatures. It indicates that the MnO acts as a basic oxide in the composition range of \(X_{\text{MnO}}/X_{\text{SiO}2}\) less than 2. With an increase in temperature, the phosphate capacity decreases over the slag composition. It is considered natural because the value for phosphate capacity defined by Eq. (2) depends intrinsically on the equilibrium constant of Eq. (1) which includes the exothermic phosphate formation reaction. A further discussion on the change of phosphate capacity by temperature will be made later.

For the experiment in the high temperature range from 1 823 to 1 923 K, the solubility of MgO is considerably large and changes much along with the slag composition. Therefore, the value of \((X_{\text{MnO}}+X_{\text{MgO}})/X_{\text{SiO}2}\) was adopted as the index of the slag composition for higher temperature experiments assuming that the basicities of MnO and MgO are comparable in the present system. Figure 4 shows the relationship between the phosphate capacity and the value of \((X_{\text{MnO}}+X_{\text{MgO}})/X_{\text{SiO}2}\) in the MnO–SiO\(_2–FeO–MgO\) system from 1 823 to 1 923 K. The phosphate capacity increases with the value of \((X_{\text{MnO}}+X_{\text{MgO}})/X_{\text{SiO}2}\) and decreases with an increase in temperature over all slag composition. It indicates that MgO and MnO act as basic oxides comparably together in the present system.

Dephosphorization of steel has been conventionally carried out by mainly using CaO bearing fluxes. Figure 5 shows the phosphate capacities versus the content of the basic oxide for various CaO-bearing systems, together with the present results at 1 723 K. The \(C_{\text{PO}3}\) value for the present system is extremely small compared to all the CaO bearing systems. In particular, it is two and a half orders of magnitude smaller than that for the CaO–Al\(_2\)O\(_3\) system in the similar range of basic oxide content and temperature. It indicates that the basicity of MnO is very much lower than CaO as a flux component.

Based on the phosphate capacity obtained for the present system, the phosphorus distribution ratio between the MnO–SiO\(_2–FeO–MgO\) slag and the phosphorus containing steel, \(L_p\), defined by the following Eq. (24) can be estimated.

\[
L_p=\frac{(\text{mass}% \text{ P} \text{ in slag})}{(\text{mass}% \text{ P} \text{ in metal})} \quad \text{(24)}
\]

In the conventional steel making process, much effort has been made to increase the \(L_p\) as high as possible. However, in recent studies, phosphorus has been revealed to be useful for refining the microstructure and improving the mechani-
Based on these facts, phosphorus can be beneficial from the viewpoint of the reduction in the environmental load. Namely, a lower phosphorus distribution ratio is preferable in the proposed process. The phosphorus distribution ratio of Eq. (24) can be calculated by combining Eqs. (2), (3), and (8).

For example, when the oxygen concentration of steel was 200 mass ppm and the molar ratio of MnO to SiO2 in the slag was 2 in the Mn–Si deoxidation, a very low phosphorus distribution ratio of 0.021 was obtained. From the viewpoint of the material balance, the amount of the slag generated during the deoxidation will be only less than 0.1 mass% of the molten steel in case of initial oxygen concentration of 500 ppm, assuming that no residual slag from the previous step has not been carried over to the deoxidation process. It means that very little amount of phosphorus will be removed to the deoxidation slag and the most part of it remains in the molten steel when the Mn–Si deoxidation is applied to the phosphorus containing steel. In other words, steel making from steel scraps without dephosphorization by using CaO can be a promising candidate for the process towards a resource circulating society, and also beneficial from the viewpoint of the reduction in the environmental load.

3.3. Temperature dependence of phosphate capacity

Figure 6 shows the temperature dependence of phosphate capacity at the slag composition of \( X_{\text{MnO}}/X_{\text{SiO2}} = 2.5 \) from 1 673 to 1 773 K by the extrapolation in Fig. 3 and that of \( (X_{\text{MnO}} + X_{\text{MgO}})/X_{\text{SiO2}} = 2.5 \) from 1 823 to 1 923 K in Fig. 4, in the viewpoint of the same molar ratio of basic oxide to acid one. The phosphate capacity increases with a decrease in temperature and a very good linear correlation is evident for each temperature range. The temperature dependence of phosphate capacity for these systems can be expressed as Eqs. (25) and (26) by linear regression.

\[
\log C_{P(2.5)} = 44.500(\pm 6.300)T - 8.45(\pm 0.15) \\
(\text{MnO–SiO2–FeO system, 1 673 to 1 773 K})
\]

\[
\log C_{P(2.5)} = 47.700(\pm 7.000)T - 9.87(\pm 0.14) \\
(\text{MnO–SiO2–FeO–MgO\textsubscript{satd.} system, 1 823 to 1 923 K})
\]

Two straight lines are almost parallel to each other with a distance of a half order of magnitude. In other words, the phosphate capacity in the high temperature range is larger than that in the low temperature range. This can be attributed to the replacement of MnO with MgO by the MgO saturation in the slag for the high temperature range. It indicates that MgO is a preferable component for dephosphorization to MnO in the present slag system.

Since the phosphate capacity is defined as Eq. (2), the slope of the linear regression line expressed by Eq. (28) corresponds to the heats of reaction of Eq. (27) including the dissolution of PO2.5 into the slag.

\[
\frac{1}{2} P_2(g) + \frac{5}{4} O_2(g) = (PO_{2.5})........................(27)
\]

\[
\frac{\partial \log C_{P(2.5)}}{\partial (1/T)} = \Delta H_{298}/2.303R ..............(28)
\]

where \( R \) is a gas constant. The heat of reaction of Eq. (27) for the MnO–SiO2–FeO and MnO–SiO2–FeO–MgO\textsubscript{satd.} system was determined to be \(-851(\pm 120)\) and \(-912(\pm 134)\) kJ/mol, respectively, according to Eqs. (25) and (26). It shows that PO2.5 is more stable in the MnO–SiO2–FeO–MgO\textsubscript{satd.} system than in the MnO–SiO2–FeO system. This fact agrees well with the result of comparison of the phosphate capacities for both systems.

4. Conclusions

The phosphate capacities for the MnO–SiO2–FeO (–MgO\textsubscript{satd.}) system have been investigated at temperatures from 1 673 to 1 923 K by two fashions of the chemical equilibrium technique. The findings obtained in the present study are summarized as follows:

(1) The phosphate capacity for the MnO–SiO2–FeO system from 1 673 to 1 773 K was determined ranging from \(1.5 \times 10^{16}\) to \(3.8 \times 10^{18}\). The values increased with the molar ratio of MnO to SiO2 and slightly decreased beyond the composition of \(X_{\text{MnO}}/X_{\text{SiO2}} = 2.5\), and decreased with increasing temperature.

(2) The phosphate capacity for the MnO–SiO2–FeO–MgO\textsubscript{satd.} system from 1 823 to 1 923 K was determined ranging from \(8.5 \times 10^{15}\) to \(3.8 \times 10^{18}\). The values increased with the increase in the ratio of \(X_{\text{MnO}} + X_{\text{MgO}})/X_{\text{SiO2}}\) and decreased with increasing temperature.

(3) The present system has very poor phosphorus containing ability compared to the conventional CaO bearing systems and provides a very low phosphorus distribution ratio between the steel and the slag in the Mn–Si deoxidation. The inverse-utilization of phosphorus in steel and the reduction of the environmental load become possible.

(4) The phosphate capacities as functions of temperature were obtained for the slag composition of \(X_{\text{MnO}}/X_{\text{SiO2}} = 2.5\) for the MnO–SiO2–FeO system and \(X_{\text{MnO}} + X_{\text{MgO}})/X_{\text{SiO2}} = 2.5\) for the MnO–SiO2–FeO–MgO\textsubscript{satd.} system and expressed as follows:

\[
\log C_{P(2.5)} = 44.500(\pm 6.300)T - 8.45(\pm 0.15) \\
(\text{MnO–SiO2–FeO system, 1 673 to 1 773 K})
\]

\[
\log C_{P(2.5)} = 47.700(\pm 7.000)T - 9.87(\pm 0.14) \\
(\text{MnO–SiO2–FeO–MgO\textsubscript{satd.} system, 1 823 to 1 923 K})
\]
log$C_{PO4}$ = 44 500(± 6 300)/$T$–8.45(± 0.15)  
(MnO–SiO$_2$–Fe$_2$O system, 1 673 to 1 773 K)  
log$C_{PO4}$ = 47 700(± 7 000)/$T$–9.87(± 0.14)  
(MnO–SiO$_2$–Fe$_2$O–MgO$_{satd.}$ system, 1 823 to 1 923 K)  

From the slopes of these function lines, the heats of the phosphate formation reaction including the dissolution into the slag were derived to be –851(± 120) and –912(± 134) kJ/mol, respectively. These results indicate that MgO is a preferable component for dephosphorization to MnO in the present slag system.

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