REDDUCING DEPHOSPHORIZATION OF SiMn ALLOY BY CaO-CaF₂ SLAG AND THE STABILITY OF Ca₃P₂ IN SLAG UNDER ATMOSPHERIC COOLING CONDITIONS

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ABSTRACT

This study consists of experimental measurement of the phosphide capacity of the CaO-CaF₂ (-SiO₂) slag in equilibrium with SiMn alloy at 1823 K, and includes the thermodynamic analysis for the stability of reducing refining slags under various cooling conditions. Because Ca₃P₂, which is a reaction product of the reducing dephosphorization mechanism, is very active, the phosphine gas (PH₃), which is hazardous to environment as well as to human being, is evolved when it contacts to moisture. The phosphide capacity increased with increasing CaO concentration in the slag, followed by a constant value. The composition for the saturating capacity is in good accordance to the saturation content of CaO in the CaO-CaF₂ slag at 1823 K. When the slag disintegrated into fine powders not only due to the formation of dicalcium silicate but also due to the hydration of lime in the highly basic slags, the evolution of phosphine gas during cooling increased. When the Vee ratio (=CaO/SiO₂) of the dephosphorization slag is greater than about 1.35, lime and dicalcium silicate phases appeared during cooling cycle based on the CaO-SiO₂-CaF₂ phase diagram, resulting in an increase in the evolution rate of PH₃ gas due to an increase in the reaction area. However, when the Vee ratio of the slag is lower than about 1.35, the CaF₂, Ca₄Si₂F₂O₇ (cuspidine), and CaSiO₃ (wollastonite) phases appeared from the phase diagram, resulting in negligible amount of PH₃ evolution during cooling because the reaction between Ca₃P₂ and H₂O was restricted to the surface of bulk slag. Alternatively, the Ca₃P₂ phase was successfully transformed to the stable 3CaO-P₂O₅ phase by oxygen injection into the molten dephosphorization slag at high temperatures.

KEYWORDS: Phosphide capacity, CaO–CaF₂ (-SiO₂) slag, SiMn alloy, Ca₃P₂ stability, Phosphine (PH₃) gas, Slag disintegration, Vee ratio, 3CaO-P₂O₅, Oxygen injection.

1. INTRODUCTION

High manganese steels (10–25% Mn) are of interest due to their good mechanical properties including superior strength and good ductility [1]. Accordingly, the demand for ultra-low phosphorous manganese ferroalloys such as FeMn and SiMn alloys has recently increased. However, the conventional oxidizing dephosphorization technique is not applicable to Mn alloys because silicon or manganese will be oxidized before phosphorous under oxidizing conditions [2-4]. Therefore, the dephosphorization should be carried out under a strongly reducing atmosphere to produce a low phosphorus Mn alloys. The mechanism of reducing dephosphorization using lime-based highly basic fluxes has been reported by several authors [2-6].

However, because the calcium phosphate (Ca₃P₂), which is a reaction product of the reducing dephosphorization mechanism, is very active when it is exposed to moisture, the hazardous phosphine gas (PH₃) evolves [3, 5]. The equilibrium reaction of the emission of phosphine gas is as follows:

\[ \text{Ca}_3\text{P}_2(s) + 3\text{H}_2\text{O}(g) = 3\text{CaO}(s) + 2\text{PH}_3(g) \]  \hspace{1cm} (1)
The Gibbs free energy changes of the formation of phosphine gas were calculated by using FactSage™6.2 software, which is a commercial thermochemical computing program [7, 8]. The emission of phosphine gas dominantly originates from the formation of CaO at temperature higher than about 803 K, whereas from the formation of Ca(OH)₂ at temperature lower than about 803 K. However, even in any cases, it is inevitable to evolve the PH₃ gas during cooling of slags containing Ca₃P₂ under moist atmosphere. Phosphine gas is hazardous to environment as well as to human being [9]. Inhalation is the most likely route of exposure to phosphine gas. Symptoms are non-specific and include irritation of the respiratory tract, headaches, dizziness, abdominal pain, sickness, and vomiting. Severe phosphine poisoning can cause convulsions, damage to the lungs, heart, liver and kidney, and death [9].

Therefore, this study consists of the distribution behavior of phosphorous between the CaO-CaF₂ (-SiO₂) slag and SiMn alloy melts at 1823 K, and includes the thermodynamic and kinetics analyses for the environmental stability of reducing refining slags under wet and dry cooling conditions based on the effect of slag composition on the evolution of PH₃ gas.

2. EXPERIMENTAL

A super-kanthal electric furnace was used for the equilibration of the CaO-CaF₂ (-SiO₂) slag and SiMn alloy melts. The temperature was controlled within ±2 K using a B-type thermocouple and a PID controller. The slag samples were prepared using reagent grade CaF₂ and CaO calcined from CaCO₃ at 1273 K for 10 hours. The initial composition of the slag in the CaO-CaF₂ system ranged from 5 to 25% CaO. The schematic diagram of the experimental apparatus is shown in previous articles [10].

The slag (7.0 g) and SiMn alloy (3.5 g) were held in graphite crucibles under a CO atmosphere to equilibrate. For reducing removal of phosphorous under a very low oxygen potential, CO gas was diluted with Ar, which was purified using silica gel also in addition to Mg turnings at 723 K. The oxygen partial pressure can be calculated based on the following reaction [11]:

\[
C(s) + \frac{1}{2}O_2(g) = CO(g), \quad \Delta G^\circ = -114,450 - 85.8T \text{ (J/mol)}
\]  

(3)

With a CO/(CO+Ar) ratio of 0.25, the oxygen partial pressure is about 1.7\times10^{17} \text{ atm} at 1823 K. After equilibrating for 12 hours, the slag samples were cooled under fully moisturized condition (direct contact with water spray), whereas the other samples were quickly quenched from 1823 K. Then, the samples were rapidly crushed for chemical analysis under inert atmosphere. The composition of metal samples was determined using ICP-AES and the equilibrium composition of slag was determined using XRF. The crystalline phases of solidified slags were identified using XRD analysis.

3. RESULTS AND DISCUSSION

3.1. Thermodynamics of Reducing Dephosphorization

In the present study, the distribution ratio of phosphorous between the slag and metal phases \(L_p\) was calculated from the following equation:
In case of solidified samples under fully wet conditions, i.e. 100% relative humidity, the equilibrium content of phosphorous in slag phase \((%P)_{\text{slag}}\) was calculated from eq. [5], assuming that the loss of phosphorous in slag phase fully originated from the formation of \(\text{PH}_3\) gas by the reaction with moisture during solidification. The equilibrium content of phosphorous in dry-quenched slags was also estimated from eq. [5], because these samples also reacted with moisture, even though moisture was very small, i.e. lower than about 25% relative humidity.

\[
L_P = \frac{(%P)_{\text{slag}}}{(%P)_{\text{metal}}} 
\]

where, \(W_P\) is the weight of phosphorous and the superscripts ‘i’ and ‘f’, respectively, represent the initial and the final content of phosphorus in the metal, \(W_S\) is the weight of slag. \(F_{\text{liquid}}\) is the fraction of liquid phase of slag which was calculated by lever rule from CaO–CaF₂ binary phase diagram [12]. Consequently, when the CaO contents are 20 and 25%, \(F_{\text{liquid}}\) was estimated to be 0.99 and 0.93, respectively.

Figure 1 shows the effect of CaO content in the CaO–CaF₂ flux on the distribution ratio of phosphorous at 1823 K. Under the highly reducing conditions, phosphorous is expected to dissolve into the flux as phosphide ions as follows [2-6]:

\[
[P] + \frac{3}{2}(O^{2-}) = (P^{3-}) + \frac{3}{4}O_2(g) 
\]

The phosphide capacity \(C_{p^{3-}}\) can be determined from equilibrium constant of Eq. (7) as follows.

\[
C_{p^{3-}} = \frac{K_{(7)} \cdot f^{1.5}_{p^{3-}}}{f_{p^{3-}}} = \frac{P^{0.75}_{O_2}}{f_P} \cdot \frac{(%P)_{P^{3-}}}{(%P)} 
\]
of phosphorous in the SiMn alloy phase, \( P_{O_2} \) is the oxygen partial pressure, and \( a_{O^2-} \) is the activity of \( O^{2-} \) ion, i.e. basicity of the slag. From eq. [9], the phosphorus distribution ratio is a function of phosphide capacity, stability of phosphorus in metal, and oxygen potential as follows:

\[
L_p = \frac{f_p}{f_{P_{O_2}}} \cdot \frac{K_{[\gamma]} \cdot a_{O^2-}^{1.5}}{f_{P_{O_2}}^{0.75}} = \frac{f_p}{f_{P_{O_2}}} \cdot \frac{C_{P_{O_2}}}{} \tag{9}
\]

Thus, the distribution ratio of phosphorous increases with increasing phosphide capacity of slag at a fixed oxygen potential. The \( L_p \) increases with increasing \( CaO \) content up to about 20%, which is mainly due to an increase in the basicity of the flux. However, it remains constant at \( CaO \) content greater than about 20%, where the flux is saturated by solid lime from the CaO-CaF\(_2\) binary phase diagram, [12] indicating that the activity of free \( O^{2-} \) ions is approximately constant, assuming that \( a_{O^2-} \) is proportional to \( a_{CaO} \) in the flux [2-4, 6, 10, 13-15].

### 3.2. Influence of CaO Content on the Emission of PH\(_3\) Gas under Wet Conditions

Assuming that the loss of phosphorous in slag phase is fully originated from the formation of PH\(_3\) gas by the reaction with moisture during solidification, the quantity of phosphine gas evolved (\( N_{PH_3} \)) can be calculated by Eq. [10]. That is, the emission of phosphine gas was calculated by the difference in the phosphorous content in slag before and after cooling. Because one mole of phosphine gas corresponds to one mole of phosphorous,

\[
N_{PH_3} = \frac{W_S \cdot \{(mass\% P)^{b/c} - (mass\% P)^{a/c}\}}{M_P} \cdot 100 \tag{10}
\]

where the \((mass\% P)^{b/c}(=before\ cooling)\) was obtained from eq. [5] and \((mass\% P)^{a/c}(=after\ cooling)\) was from chemical analysis, and \( M_P (=30.97 \text{ g/mol}) \) is the atomic weight of phosphorous. According to eq [1], the driving force of the forward reaction increases with increasing partial pressure of \( H_2O \), whereas it decreases with increasing the activity of \( CaO \) in slag. Thus, the emission of phosphine gas is affected by these two factors.

Figure 2 shows the effect of CaO content on the amount of phosphine gas evolved which was normalized with reference to the dry-quenched samples.

**Figure 2:** Effect of CaO content on the evolution of phosphine gas under wet conditions
In the lower CaO content region, viz. $a_{\text{CaO}} < 1.0$, the phosphine gas was evolved due to the large potential of $\text{H}_2\text{O}$ which is greater than that of CaO. However, even in the higher CaO content region, viz. $a_{\text{CaO}} = 1.0$, the phosphine gas is still evolved, which is contradictory to the thermodynamic expectation. The reason for this discrepancy is discussed in the following sections.

### 3.3. Influence of Disintegration of Slag on the Emission of PH$_3$ Gas

When the CaO content is greater than about 15%, the slag was disintegrated into fine powders during cooling. The powdery slag in the CaO-CaF$_2$-SiO$_2$ slag is formed by two factors. Firstly, if CaO (lime) is crystallized during solidification under wet conditions, the hydration of CaO occurs, resulting in the volume expansion of slag [16]. Secondly, if Ca$_2$SiO$_4$ (dicalcium silicate) is crystallized during solidification, the Ca$_2$SiO$_4$ contributes to powdery slag because of the volume expansion by the phase transformation of Ca$_2$SiO$_4$ from $\beta$- to $\gamma$-phase at about 773 K [17].

Generally, the rate equation is functions of reaction surface area and driving force such as difference in concentration. Thus, the larger the surface area becomes, the faster the reaction will occur. That is, a disintegration of slag to fine powders results in a significant increase in surface area. The rate equation of the evolution of phosphine gas is as follows:

$$\frac{dC_{\text{Ca}_3\text{P}_2}}{dt} = \frac{1}{2} \cdot \frac{d(C_{\text{PH}_3})}{dt} = \frac{A}{V} \cdot k_m \cdot (C_{\text{Ca}_3\text{P}_2}^i - C_{\text{Ca}_3\text{P}_2}^e)$$

where, $k_m$ is rate constant, $A$ and $V$ are surface area and volume, respectively. $C_{\text{Ca}_3\text{P}_2}$ and $C_{\text{PH}_3}$ are molar concentration of Ca$_3$P$_2$ and phosphine gas, respectively, the superscripts ‘$i$’ and ‘$e$’, respectively, represent the initial and the equilibrium molar concentration of Ca$_3$P$_2$. In the present study, the equilibrium molar concentration of Ca$_3$P$_2$ is assumed zero.

The surface area of powdery slag, which is constituted by large and small spherical particles, can be calculated by eq. [12] as follows [18]:

$$A = \frac{X_S \cdot (V \times f)}{V_S} \cdot A_S + \frac{X_L \cdot (V \times f)}{V_L} \cdot A_L$$

$$f = 0.637 + 0.864X_S$$

where $X_{L\text{or}S}$ is weight fraction of large or small particles, $V$ is volume of bulk slag and $V_{L\text{or}S}$ and $A_{L\text{or}S}$ are unit volume and area of large or small particles, respectively. $f$ is the fractional packing density. For two spherical powders with a large difference in particle size with an ideal fractional packing density of 0.637 [18].

Hence, the reaction rate of phosphine gas emission from powdery slag is determined by combining eqs. [11] to [13],

$$\frac{1}{Q} \cdot \frac{d(C_{\text{PH}_3})}{dt} = \frac{(r_S + (r_L - r_S) \cdot X_S) \cdot (0.637 + 0.864X_S)}{r_L \cdot r_S}$$

where $Q$ is constant, and $r_{L\text{or}S}$ is radius of large or small particles.

Figure 3 shows the effect of size ratio of large to small particles and the fraction of small particles on the evolution of phosphine gas. The more the slags become powdery, the larger the reaction surface area is expected, and thus the rate of gas evolution increases as a quadratic function. Therefore, if CaO or Ca$_2$SiO$_4$ are precipitated during solidification even in highly dry
atmosphere, the evolution of PH₃ gas could not be negligible.

Figure 3: Effect of particle size ratio and fraction of small particle on the emission rate of PH₃ gas

The slag composition after dephosphorization is plotted on the CaO-CaF₂-SiO₂ ternary phase diagram as shown in figure 4 [19]. Solidification path can be predicted based on polythermal projection of the CaO-CaF₂-SiO₂ ternary phase diagram. Figure 4 also shows the schematic diagram of cooling path and the microstructure of solidified slag in each case ‘a’ and ‘b’ in phase diagram. For slags #1 and #2, the CaF₂ is primarily crystallized, followed by the nucleation and growth of SiO₂ (cristobalite). Finally the slag solidifies at the CaF₂-SiO₂-CaSiO₃ ternary eutectic composition. That is, the rate of phosphine gas emission is relatively low, because the solid compounds that contribute to the disintegration are not precipitated.

Figure 4: (a) Slag composition after de-P reaction plotted on the CaO-CaF₂-SiO₂ phase diagram and (b) schematics of cooling path and the solidification structure of dephosphorization slags

On the other hand, for slags #3 and #4, the CaF₂ is primarily crystallized, followed by the
nucleation and growth of Ca$_2$SiO$_4$. After that, slag solidifies at the CaF$_2$-Ca$_2$SiO$_4$-(3CaO·SiO$_2$)$_3$CaF$_2$ ternary eutectic composition. That is, the rate of phosphine gas emission is relatively high, because the solid compounds which contribute to the disintegration of slag, e.g. Ca$_2$SiO$_4$ are precipitated.

Consequently, when the Vee ratio (=CaO/SiO$_2$) of the dephosphorization slag is greater than about 1.35, the CaO (lime) and Ca$_2$SiO$_4$ (dicalcium silicate) phases precipitated during cooling cycle. This can be a reason for a decrease in between dry-quenched and wet-cooled 25% CaO samples in figure 2. That is, even it was directly quenched under dry atmosphere, the slag was disintegrated into fine powders, resulting in an emission of PH$_3$ gas before chemical analysis. Therefore, there was less difference in between dry-quenched and wet-cooled slag samples in highly basic compositions. However, when the Vee ratio of the slag is lower than about 1.35, the CaF$_2$, CaSiO$_3$ (wollastonite) and SiO$_2$ phases precipitated.

Figure 5 shows the result of XRD analysis of the dephosphorization slag of which initial composition is 5 and 25% CaO, respectively. The solid compounds at low CaO content slags were identified as mostly CaF$_2$ and CaSiO$_3$, whereas the compounds at high CaO content slags were confirmed as not only CaF$_2$ but also CaO, Ca(OH)$_2$ and Ca$_2$SiO$_4$. Thus, the present thermodynamics and kinetic discussions base on the phase equilibrium are in good agreement with the experimental result in this study.

Consequently, it is strongly recommended that reducing dephosphorization slags should be kept or treated under dry atmosphere. Furthermore, the Vee ratio of dephosphorization slag should be controlled to be lower than 1.35 during reducing refining reaction.

### 3.4. Conversion of Ca$_3$P$_2$ to 3CaO·P$_2$O$_5$ in Reducing Dephosphorization Slags by Oxygen Injection

Even though the above results are very useful to restrain the emission of phosphine gas from reducing dephosphorization slag during cooling, the problem due to phosphine emission at room temperature is still unsolved. Therefore, we tried to find a method to completely remove the Ca$_3$P$_2$ compound in reducing dephosphorization slag, which is the origin for the emission of PH$_3$ gas.

The Ca$_3$P$_2$ in molten reducing dephosphorization slag can be oxidized to the 3CaO·P$_2$O$_5$ phase at high temperature by oxygen injection as shown in eq. [15].

$$\text{Ca}_3\text{P}_2(s) + 4\text{O}_2(g) = 3\text{CaO} \cdot \text{P}_2\text{O}_5(s)$$  \(15\)

The reducing dephosphorization slag (300 g), which was supplied from an industrial SiMn
refining process, was initially melted in the graphite crucible (OD: 56 mm, ID: 50 mm, H: 96 mm) at 1773 K using a high frequency induction furnace with a graphite heater under a purified Ar-3%H2 atmosphere. After the slag was melted, the power of the furnace was switched off, after which the slag was slowly cooled down. At this time, the gas was switched from Ar-H2 gas mixture to O2 gas, and then a stainless steel lance (OD: 6mm, ID: 4mm) for injecting O2 gas (flow rate=1.0 l/min) was inserted into the molten slag and kept 5 mm above the bottom of the crucible. Strong agitation of the molten slag by O2 gas injection resulted in fast attainment of the oxidation of reducing dephosphorization slag during cooling. After cooling, the crystalline phases of the solidified slags were identified using an XRD analysis.

Figure 6 show the results of XRD analyses for the as-received reducing dephosphorization slag and oxygen-treated slag, respectively. Both of the slags were mainly composed of calcium fluoride (CaF2), wollastonite (CaSiO3), cuspidine (Ca2Si2F7O7), dicalcium silicate (Ca2SiO4), iron oxide (Fe2O3) and manganese oxide (MnO) based on the reference peak from a JCPDS. The reducing dephosphorization slag was mainly CaO-CaF2 system coupled with small amounts of SiO2, Fe2O3, and MnO, those were formed during SiMn refining process. The cuspidine phase is believed to crystallize during solidification of the reducing dephosphorization slag.

![XRD pattern](image)

**Figure 6:** XRD pattern for the (a) as-received reducing dephosphorization slag from Mn smelting company and (b) the oxygen-treated reducing dephosphorization slag in the present experiments.

It is very interesting in Figure 6 that the calcium phosphide (Ca3P2) was identified in the as-received reducing dephosphorization slag [20], whereas the tricalcium phosphate (3CaO·P2O5) compound was detected at the expense of Ca3P2 phase in the oxygen-treated slag. Consequently, from the present experiments, the Ca3P2 phase was successfully transformed to the 3CaO-P2O5 phase by oxygen injection into the molten dephosphorization slag. This process can be potentially practiced in slag pot with the O2-injection equipment in the ferroalloys smelter, resulting in the environmental friendly slag products instead of discarding or dumping the reducing dephosphorization slag at yard.

4. CONCLUSIONS

The distribution ratio of phosphorous between the CaO–CaF2 (~SiO2) slag and SiMn alloy melts at 1823 K was measured under strongly reducing atmosphere. Furthermore, thermodynamic and kinetics analyses were carried out for the environmental stability of reducing refining slags containing Ca3P2 under wet cooling conditions from the effect of slag composition on the evolution of PH3 gas. The results of this study can be summarized as follows.
1. The distribution ratio of phosphorous between the CaO–CaF₂ (–SiO₂) flux and SiMn metal phases increased with increasing CaO concentration in the flux, followed by a constant value. The composition for the saturating distribution ratio of phosphorous is in good accordance to the saturation content of CaO in the CaO–CaF₂ flux at 1823 K. This means that the reducing refining mechanism was confirmed due to transfer of Ca from slag to metal phase by the reaction between CaO in the flux and Si in the alloy under strongly reducing conditions.

2. Despite of activity of CaO in the flux was unity at CaO > 20%, the emission of phosphine gas was still high, which is mainly due to the fact that the basic dephosphorization slag was disintegrated into fine powders. When the slag was disintegrated not only due to the phase transformation of dicalcium silicate but also due to the hydration of lime during cooling under wet conditions, the emission of phosphine gas significantly increased.

3. When the Vee ratio (=CaO/SiO₂) of the reducing dephosphorization slags is greater than about 1.35, the lime and dicalcium silicate phases precipitated during solidification, resulting in an increase in the emission rate of PH₃ gas due to an increase in the reaction area. However, when the Vee ratio of the slags is lower than about 1.35, the fluorite, cristobalite, and wollastonite phases appeared from the phase diagram, resulting in less amount of PH₃ emission during cooling because the reaction between Ca₃P₂ and H₂O was restricted to the surface of bulk slag.

4. The Ca₃P₂ phase was successfully transformed to the 3CaO·P₂O₅ phase by oxygen injection into the molten dephosphorization slag. This process can be potentially practiced in slag pot with the O₂-injection equipment in the ferroalloys smelter, resulting in the environmental friendly slag products instead of discarding or dumping the reducing dephosphorization slag at yard.

5. REFERENCES
