Effect of Atmosphere and Slag Composition on the Evolution of PH₃ Gas during Cooling of Reducing Dephosphorization Slags

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The distribution ratio of phosphorous between the CaO–CaF₂ (–SiO₂) flux 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 (phosphine) gas. 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 was in good accordance to the saturation content of CaO in the CaO–CaF₂ flux at 1823 K. When the Vee ratio (= CaO/SiO₂) of the dephosphorization slag was greater than about 1.35, the lime and dicalcium silicate phases precipitated during solidification, resulting in an increase in the evolution rate of PH₃ gas under wet and dry conditions due to an increase in the reaction area. However, when the Vee ratio of the slag was lower than about 1.35, fluorite, cuspidine, and wollastonite phases precipitated from the phase diagram, resulting in less amount of PH₃ evolution during cooling because the reaction between Ca₃P₂ and H₂O was restricted to the surface of bulk slag.

KEY WORDS: phosphorus distribution ratio; CaO–CaF₂ (–SiO₂) slag; SiMn alloy; Ca₃P₂ stability; PH₃ (phosphine) gas; slag disintegration.

1. Introduction

High manganese steels (10 to 25 mass% Mn) are of interest due to their good mechanical properties including superior strength and good ductility.^{1–3)} Accordingly, the demand for ultra-low phosphorous manganese alloys such as FeMn and SiMn alloys has recently increased. However, the conventional oxidizing dephosphorization technique is not applicable to manganese alloys because silicon or manganese will be oxidized before phosphorous under oxidizing conditions.^{4–8)} Therefore, the dephosphorization should be carried out under a strongly reducing atmosphere to produce a low phosphorus manganese alloys. The mechanism of reducing dephosphorization using lime-based highly basic fluxes has been reported by several authors,^{4–11)} and recently reviewed and experimentally confirmed by the present authors in previous study.¹²⁾

However, because the calcium phosphide (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.^{5,9)} The equilibrium reaction of the evolution of phosphine gas is as follows:

Figure 1 shows the Gibbs free energy changes of the formation of phosphine gas, which is calculated using FactSageTM 6.2 software, which is a commercial thermochemical computing program.^{13,14)} The evolution 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.^{15,16)} Inhalation is the most likely route of exposure to phosphine gas. Symptoms are

Fig. 1. Gibbs free energy change of the formation reaction of PH₃ gas by the reaction between Ca₃P₂ and H₂O in atmosphere.

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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.^{15,16)}

Therefore, this study consists of the distribution behavior of phosphorous between the CaO–CaF₂ (–SiO₂) flux and SiMn alloy melts at 1 823 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 Procedure

A super-kanthal electric furnace was used for the equilibration of the CaO–CaF₂ flux and Si–Mn alloy melts. The temperature was controlled within ± 2 K using a B-type thermocouple and a proportional integral differential controller. The slag samples were prepared using reagent grade CaF₂ and CaO calcined from CaCO₃ at 1 273 K for 10 hours. The initial composition of the slag in the CaO–CaF₂ system ranged from 5 to 25 mass% CaO. The schematic diagram of the experimental apparatus is shown in previous articles.^{17,18)}

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:¹⁹⁾

With a CO/(CO + Ar) ratio of 0.25, the oxygen partial pressure is about 1.7×10^{-17} atm at 1 823 K. The CO gas was passed through Drierite (W. A. Hammond Drierite Co. Ltd., Xenix, OH), Mg(ClO₄)₂, silica gel, and soda lime to eliminate moisture and impurities. The time to establish equilibrium was preliminarily determined. 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 1 823 K. Then, the samples were rapidly crushed for chemical analysis

under inert atmosphere.

The composition of metal samples was determined using inductively coupled plasma atomic emission spectroscopy (iCAP6500; Thermo Scientific) excluding carbon content which was determined by combustion analyzer (CS-200; LECO). The equilibrium composition of slag was determined using X-ray fluorescence spectroscopy (S4 Explorer; Bruker AXS Inc.). The crystalline phases of solidified slags were identified using X-ray diffraction analysis (RAD-3C; Rigaku). The final compositions of the alloys and slags are listed in **Table 1**.

In the present study, the SiC was possibly formed at metal/crucible interface due to very low Gibbs free energy of the formation of SiC under present experimental conditions. However, not only because it is the same to both experimental conditions, viz. wet-cooled and dry-quenched experiments, but also because the SiC was not detected in bulk slag phase by XRD analysis, which will be discussed later, the SiC formation would not significantly affect the present 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:

$$L_P = \frac{(\text{mass\% P})_{\text{slag}}}{[\text{mass\% P}]_{\text{metal}}} \quad (4)$$

In case of solidified samples under fully wet conditions, *i.e.* 100% relative humidity, the equilibrium content of phosphorous in slag phase (mass% P)_{slag} was calculated from Eq. (5), assuming that the loss of phosphorous in slag phase fully originated from the formation of PH₃ 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.

$$(\text{mass\% P})_{\text{slag}} = \frac{[W_P^i - W_P^f]_{\text{metal}}}{W_S} \times 100 \quad (5)$$

Table 1. Initial composition of slag and equilibrium compositions of the slag and SiMn alloys in the present study.

Elemental contents (mass%)														
Initial slag	Equilibrium composition of slag				P in slag after cooling (ppm)**		$\Delta\text{PH}_3^{\#}$ (10 ⁻⁵ mole)	Equilibrium composition of metal						L _P
CaO	CaF ₂	SiO ₂	CaO	P (ppm)*	W ⁺	Q ⁺		Si	Mn	Fe	Ca	C	P (ppm)	
5	96.5	3.6	0	40.6 (±3.8)	16	23	0.14	41.1 (±1.9)	42.8 (±1.8)	13.6 (±0.6)	0.48 (±0.40)	1.95 (±0.01)	499 (±8)	0.08 (±0.01)
10	93.7	3.9	1.2	121.1 (±2.4)	51	97	0.95	41.1 (±0.2)	42.7 (±0.7)	13.5 (±0.2)	0.78 (±0.68)	1.90 (±0.04)	338 (±5)	0.36 (±0.01)
15	86.0	5.2	7.7	157.5 (±0.8)	36	110	1.52	40.0 (±0.2)	43.8 (±0.2)	13.9 (±0.2)	0.34 (±0.24)	1.94 (±0.02)	233 (±30)	0.76 (±0.16)
20	75.8	8.4	14.1	202.2 (±4.9)	26	130	2.14	38.9 (±0.5)	44.5 (±0.7)	14.2 (±0.1)	0.42 (±0.24)	1.92 (±0.04)	180 (±10)	1.13 (±0.09)
25	<75	>9	>15	214.7 (±21.4)	96	160	1.31	35.9 (±2.1)	46.9 (±1.5)	14.9 (±0.3)	0.39 (±0.31)	1.96 (±0.03)	181 (±40)	1.28 (±0.40)

Initial content of phosphorous in metal: 580 ppm.

⁺ W: wet-cooled, Q: dry-quenched.

* obtained from Eq. (5).

** obtained by chemical analysis.

[#] PH₃: (amount of PH₃ gas evolved under wet condition) – (amount of PH₃ gas evolved under dry condition)_{reference}.

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.

However, for the evaluation of phosphorus distribution ratio, the phosphorous concentration of slag should be estimated only in the homogeneous liquid phase. Thus, numerator of Eq. (4) was corrected to Eq. (6).

$$(\text{mass\% P})_{\text{slag}} = \frac{[W_P^i - W_P^f]_{\text{metal}}}{W_S \cdot F_{\text{liquid}}} \times 100 \quad \text{..... (6)}$$

where F_{liquid} is the fraction of liquid phase of slag which was calculated by lever rule from CaO–CaF₂ binary phase diagram.²⁰⁾ Consequently, when the CaO content are 20 and 25 mass%, F_{liquid} was estimated to be 0.99 and 0.93, respectively.

Figure 2 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:^{4–11)}

$$K_{(7)} = \frac{a_{P^{3-}} \cdot p_{O_2}^{0.75}}{a_P \cdot a_{O^{2-}}^{1.5}} = \frac{f_{P^{3-}} \cdot (\text{mass\% P}^{3-})}{f_P \cdot [\text{mass\% P}]} \cdot \frac{p_{O_2}^{0.75}}{a_{O^{2-}}^{1.5}} \quad \text{..... (8)}$$

where $a_{P^{3-}}$ and $f_{P^{3-}}$ are the activity and the activity coefficient of the phosphide ions in the slag phase, respectively, a_P and f_P are the activity and the activity coefficient of phosphorous in the SiMn alloy phase, respectively, p_{O_2} is the oxygen partial pressure, and $a_{O^{2-}}$ is the activity of free oxygen, *i.e.* the basicity of the slag. The phosphide capacity can be determined from Eq. (8) as follows:

$$C_{P^{3-}} = \frac{K_{(7)} \cdot a_{O^{2-}}^{1.5}}{f_{P^{3-}}} = \frac{p_{O_2}^{0.75}}{f_P} \cdot \frac{(\text{mass\% P}^{3-})}{[\text{mass\% P}]} \quad \text{..... (9)}$$

From Eq. (10), the phosphorus distribution ratio is a function of phosphide capacity, stability of phosphorus in metal, and oxygen potential as follows:

$$L_P = \frac{f_P}{p_{O_2}^{0.75}} \cdot \frac{K_{(7)} \cdot a_{O^{2-}}^{1.5}}{f_{P^{3-}}} = \frac{f_P}{p_{O_2}^{0.75}} \cdot C_{P^{3-}} \quad \text{..... (10)}$$

Fig. 2. Effect of CaO content on the distribution ratio of phosphorous between the CaO–CaF₂ flux and SiMn melt at 1823 K.

Thus, the distribution ratio of phosphorous increases with increasing phosphide capacity of slag at a fixed oxygen potential.¹²⁾ The distribution ratio of phosphorous increases with increasing CaO content up to about 20 mass%, which is mainly due to an increase in the basicity of the flux. However, the distribution ratio of phosphorous remained constant at CaO content greater than about 20 mass%, where the flux is saturated by solid lime from the CaO–CaF₂ binary phase diagram,²⁰⁾ indicating that the activity of free O²⁻ ions is approximately constant, assuming that $a_{O^{2-}}$ is proportional to a_{CaO} in the flux.^{21–28)}

3.2. Influence of CaO Content on the Evolution of PH₃ Gas under Wet Conditions

Assuming that the loss of phosphorous in slag phase is fully originated from the formation of PH₃ gas by the reaction with moisture during solidification, the quantity of phosphine gas evolved (N_{PH_3}) can be calculated by Eq. (11). That is, the evolution 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,

$$N_{PH_3} = \frac{W_S \cdot \{(\text{mass\% P})^{b/c} - (\text{mass\% P})^{a/c}\} \cdot 100}{M_P} \quad \text{..... (11)}$$

where the $(\text{mass\% P})^{b/c}$ (=before cooling) was obtained from Eq. (6) and $(\text{mass\% P})^{a/c}$ (=after cooling) was from chemical analysis, and M_P (= 30.97 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 H₂O, whereas it decreases with increasing the activity of CaO in slag. Thus, the evolution of phosphine gas is affected by these two factors.

Figure 3 shows the effect of CaO content on the amount of phosphine gas evolved which was normalized with reference to the dry-quenched samples. In the lower CaO content region, *viz.* $a_{CaO} < 1.0$, the phosphine gas was evolved due to the large potential of H₂O which is greater than that of CaO. However, even in the higher CaO content region, *viz.* $a_{CaO} = 1.0$, the phosphine gas is still evolved, which is contradictory to the thermodynamic expectation. The reason for this discrepancy is discussed in the following sections.

Fig. 3. Effect of CaO content on the evolution of phosphine gas under wet conditions.

3.3. Influence of Disintegration of Slag on the Evolution of PH₃ Gas

Figure 4 shows the morphology of slag samples after experiment. When the CaO content is greater than about 15 mass%, the slag was disintegrated into fine powders during cooling. The powdery slag in the CaO–CaF₂–SiO₂ 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.^{29,30} Secondly, if Ca₂SiO₄ (dicalcium silicate) is crystallized during solidification, the Ca₂SiO₄ also contributes to powdery slag because of the volume expansion by the phase transformation of Ca₂SiO₄ from β - to γ -phase at about 773 K.³¹

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:

$$-\frac{dC_{\text{Ca}_3\text{P}_2}}{dt} = \frac{1}{2} \cdot \frac{d(C_{\text{PH}_3})}{dt} = \frac{A}{V} \cdot k_m \cdot (C_{\text{Ca}_3\text{P}_2}^i - C_{\text{Ca}_3\text{P}_2}^e) \quad \dots (12)$$

where, k_m is rate constant, A and V are surface area and volume, respectively. $C_{\text{Ca}_3\text{P}_2}$ and C_{PH_3} are molar concentration of Ca₃P₂ and PH₃ gas, respectively, and the superscripts ‘i’ and ‘e’, respectively, represent the initial and the equilibrium conditions. In the present study, the equilibrium molar concentration of Ca₃P₂ is assumed to be zero.

The surface area of powdery slag, which is constituted by large and small spherical particles, can be calculated by Eq. (13) as follows:

$$A = \frac{X_s \cdot (V \times f)}{V_s} \cdot A_s + \frac{X_L \cdot (V \times f)}{V_L} \cdot A_L \quad \dots (13)$$

where X_L or X_s is weight fraction of large or small particles, V is volume of bulk slag and V_L or V_s and A_L or A_s are unit volume and area of large or small particles, respectively. f is the fractional packing density.³² For two spherical powders with a large difference in particle size with an ideal fractional packing density of 0.637,³² the fractional packing density f , which is a function of X_s is determined as follows:

$$f = 0.637 + 0.864 X_s \quad \dots (14)$$

Hence, the reaction rate of phosphine gas evolution from powdery slag is determined by combining Eqs. (12), (13) and (14).

Fig. 4. Morphology of (a) low (initial CaO = 5 mass%) (b) and high (initial CaO = 25 mass%) CaO-containing slag samples after solidification.

$$\frac{1}{Q} \cdot \frac{d(C_{\text{PH}_3})}{dt} = \frac{(r_s + (r_L - r_s) \cdot X_s) \cdot (0.637 + 0.864 X_s)}{r_L \cdot r_s} \quad \dots (15)$$

where Q is constant, and r_L or r_s is radius of large or small particles.

Figure 5 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 Ca₂SiO₄ are precipitated during solidification even in highly dry atmosphere, the evolution of PH₃ gas could not be negligible.

3.4. Solidification Path of Slag and the Evolution of PH₃ Gas

Table 1 shows the slag composition before and after dephosphorization reaction. The content of SiO₂ increased due to slag-metal reaction which is given in Eq. (16).

The slag composition after dephosphorization is plotted on the CaO–CaF₂–SiO₂ ternary phase diagram as shown in **Fig. 6**.³³

Fig. 5. Effect of particle size ratio and weight fraction of small particle on the evolution rate of phosphine gas.

Fig. 6. Slag composition after dephosphorization reaction plotted on the CaO–CaF₂–SiO₂ ternary phase diagram.³³

Fig. 7. Schematic diagram of cooling path and solidification structure of dephosphorization slags.

Solidification path can be predicted based on polythermal projection of the CaO–CaF₂–SiO₂ ternary phase diagram. **Figure 7** shows the schematic diagram of cooling path and the microstructure of solidified slag in each case ‘a’ and ‘b’ in Fig. 6. 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 evolution is relatively low, because the solid compounds that contribute to the disintegration are not precipitated.

On the other hand, for slags #3 and #4, the CaF₂ is primarily crystallized, followed by the nucleation and growth of Ca₂SiO₄. After that, slag solidifies at the CaF₂–Ca₂SiO₄–(3CaO–SiO₂)₃CaF₂ ternary eutectic composition. That is, the rate of phosphine gas evolution is relatively high, because the solid compound which contributes to the disintegration of slag, *e.g.* Ca₂SiO₄ is precipitated.

Consequently, when the Vee ratio (= CaO/SiO₂) of the dephosphorization slag is greater than about 1.35, the CaO (lime) and Ca₂SiO₄ (dicalcium silicate) phases precipitated during cooling cycle. This can be a reason for a decrease in between dry-quenched and wet-cooled 25 mass% CaO samples in Fig. 3. That is, even it was directly quenched under dry atmosphere, the slag was disintegrated into fine powders, resulting in an evolution of PH₃ gas before chemical analysis as discussed in Section 3.3. Therefore, there was less difference in between dry-quenched and wet-cooled slag samples in highly basic compositions.

Figure 8 shows the result of X-ray diffraction analysis of the dephosphorization slag of which initial composition is 5 and 25 mass% CaO, respectively. The solid compounds at low CaO content slags were identified as mostly CaF₂ and

Fig. 8. XRD analysis of the dephosphorization slag of which initial composition is (a) 5 and (b) 25 mass% CaO.

CaSiO₃, whereas the compounds at high CaO content slags were confirmed as not only CaF₂ but also CaO, Ca(OH)₂ and Ca₂SiO₄. Thus, the present thermodynamic and kinetic discussions based on the phase equilibria 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 process.

4. Conclusions

The distribution ratio of phosphorous between the CaO–CaF₂ (–SiO₂) flux and SiMn alloy melts at 1 823 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 1 823 K. This means that the reducing refining mechanism was con-

firmed 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 mass%, the evolution 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 evolution 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 evolution 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 evolution during cooling because the reaction between Ca₃P₂ and H₂O was restricted to the surface of bulk slag.

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