Behavior of Vanadium and Niobium during Hot Metal Dephosphorization by CaO–SiO₂–Fe₂O₃ Slag

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(Received on April 19, 2011; accepted on July 4, 2011)

V and Nb are key elements for the production of high-grade steel. These elements are produced by few countries, and V has been nominated as a national stockpile element in Japan. Despite the importance of these elements, there are no strategies to obtain stable resources for them. Some types of iron ore that contain V and Nb can be used as sources of these elements. This study clarified the possibility of extracting V and Nb by means of a conventional hot metal dephosphorization process without using CaF₂ as a flux. First, the influences of V and Nb oxides on the distribution ratio of P₂O₅ between the solid solution and liquid phases in slag were measured. Then, the behaviors of V and Nb in hot metal dephosphorization by CaO–SiO₂–Fe₂O₃ slag were investigated. Finally, a previously described hot metal simulation model was modified and the behaviors of various elements, including V and Nb, during hot metal dephosphorization were simulated, and the results were compared with experimental ones. The results are summarized as follows: (1) The addition of V and Nb oxides slightly increases the distribution ratio of P₂O₅ between the solid solution and liquid phases in slag. (2) The decreasing rate of the elements by the flux addition can be expressed as Nb > Mn > P > V, and these decreasing rates increase as the basicity increases. (3) The simulation results for the behavior of P and V or Nb are in good agreement with the experimental results; that is, the decreasing rate for Nb is greater than that for P, and the separation of Nb leaving P in the hot metal is easier than the separation of V.

KEY WORDS: hot metal dephosphorization; vanadium; niobium; kinetic simulation.

1. Introduction

Vanadium (V) and niobium (Nb) are key elements in the production of high-grade steel; in fact, V has been designated as a national stockpile element in Japan. At present, over 95% of V is produced by only three countries—China, Russia, and South Africa—so Japan imports about 90% of its V from China. Similarly, about 90% of Nb is produced by Brazil, and Japan imports nearly all its Nb from Brazil. Over 70% of imported V and almost 100% of imported Nb are used as alloying materials in the steelmaking process; however, there are still no strategies to obtain stable resources for these elements.

However, some types of iron ore are known to contain 0.1%–0.5% V or Nb. For example, iron ore produced at Taharoa mine, New Zealand, contains about 0.3% V; that produced at Kiruna mine, Sweden, 0.1% V; that produced at Savage River mine, Australia, 0.46% V; that produced at Panzhihua mine, P. R. China, 0.21% V; and that produced at Baotou mine, P. R. China, 0.28% Nb. It is important to clarify the possibility of extracting these elements by using the metallurgical principles involved in the conventional ironmaking and steelmaking processes.

In the early 1980s, several researches were carried out on the distribution of V and Nb between hot metal and slag. Inoue et al.¹¹ pointed out that the distribution ratio of V ([V]/[V]) was more than one order of magnitude higher than that of P ([P]/[P]) in a CaO–MgO–FeO₃–SiO₂ system. Their results also showed that the influence of slag composition and temperature on the distribution ratio of V was comparably smaller than that of P. Tsukihashi et al.² studied the effect of Na₂O addition on the distribution ratios of V and Nb. They found that by adding small amounts of Na₂O to the CaO–CaF₂–SiO₂ flux, the distribution ratio of V increased from 0.4 to 5 and that of Nb increased from 6 to 100.

Additionally, several researches were focused on the difference between oxidation by soda- and lime-based fluxes. Inoue et al.²⁶ pointed out that oxidation of Si or P occurred to a similar degree in Na₂CO₃–Fe₂O₃ flux and CaO–CaF₂–Fe₂O₃ flux, while oxidation of V hardly occurred in the latter flux. This result suggests the possibility of removing P and Si while retaining V in the metal phase. Moreover, Inoue et al. also clarified that Nb oxidizes much more easily than V, and it is possible to remove Nb and Si while leaving P in the metal.

In Japan, hot metal dephosphorization is a commonly used process in steelmaking. Originally, this process is started using slag with CaF₂ of high basicity and low oxygen potential. Because of the environmental problem to reuse the slag, CaF₂ becomes difficult to use as a flux. Therefore, dephosphorization has recently been carried out by basic
oxygen furnace (BOF), using slag which has relatively low basicity and high oxygen potential. In this process the importance of dicalcium-silicate is stresses.

The hot metal dephosphorization slag in this case consists of a CaO–SiO2–FeO–P2O5 system, and the industrial operation is mainly carried out in the dicalcium silicate (C2S) saturated region. It is well known that C2S forms a solid solution with the main product of dephosphorization—tricalcium phosphate (C3P)—at the temperature treatment over a wide composition range.5–7) Measurements of the distribution ratio of P2O5 between the solid and liquid phases in the semi-solid slag (coexisting of solid solution phase in liquid slag phase) indicated that P2O5 is concentrated in the solid solution with a high distribution ratio.8,9) Kitamura et al.10,11) pointed out the importance of the solid solution in efficient dephosphorization. Based on their results, the solid solution can act as a sink for phosphorus, lowering the phosphorus content of the liquid phase and making it more capable of future dephosphorization.

This study aims to clarify the possibility of extracting V and Nb by means of a conventional hot metal dephosphorization process without using CaF2 as a flux. First, the influences of V and Nb oxides on the distribution ratio of P2O5 between the solid solution and liquid phases in slag were measured. Then, the behaviors of V and Nb in hot metal dephosphorization by CaO–SiO2–FeO slag were investigated. Finally, a previously described hot metal simulation model12,13) was modified and the behaviors of various elements, including V and Nb, during hot metal dephosphorization were simulated, and the results were compared with experimental ones.

2. Experimental Procedure

2.1. Effects of V and Nb Oxides on the Distribution Ratio of P2O5 between Solid Solution and Liquid Phases in Slag

The experimental procedure has already been described in a previous paper.14) Reagent-grade SiO2, Fe2O3, Fe, V2O5, Nb2O5, CaCO3, and 3[CaO·P2O5]·Ca(OH)2 were used to produce slag. First, CaCO3 was heated at 1273 K for 60 min in an Al2O3 crucible under air atmosphere to produce CaO. Next, Fe was mixed with Fe2O3 and heated at 1673 K for 60 min in an iron crucible under Ar atmosphere to produce FeO. Then, the reagents were mixed in various proportions, as shown in Table 1. The mixed reagents were put in a steel crucible. The crucible was heated in an electric resistance furnace up to 1673 K and kept for 60 min to produce a homogenous liquid-phase slag. The liquid slag was then cooled to 1573 K, at a cooling rate of 3 K/min, and kept for 60 min to produce a semi-solid slag (coexisting of solid solution with liquid slag). Finally, the sample was quenched in to the oil. The heat treatment was done under Ar atmosphere. The quenched sample was mounted and polished. The composition of each phase was measured by electron probe microanalyzer (EPMA). Then, the distribution ratio of P2O5 (LP) was calculated as follows:

\[ L_P = \frac{(%P_2O_5)_{SS} \cdot (%P_2O_5)_L}{(%P_2O_5)_S \cdot (%P_2O_5)_L} \]

where subscript SS and L indicates the solid solution and liquid phase respectively. It is known that V has the valence states of V\(^{5+}\), V\(^{4+}\) and V\(^{3+}\) and Nb has that of Nb\(^{5+}\) and Nb\(^{4+}\) in slag.12) However, in this research V-oxide and Nb-oxide is expressed as V2O5 and Nb2O5 respectively.

2.2. Behaviors of V and Nb in Hot Metal Dephosphorization by CaO–SiO2–FeO Slag

To produce flux for dephosphorization, FeO and CaO (produced as described in the previous section) were mixed with reagent-grade SiO2 and melted in an Fe crucible at 1673 K using an electrical resistance furnace under Ar atmosphere. After cooling, the flux was crushed and ground to under 2 mm. For hot metal dephosphorization, about 300 g of hot metal was melted at 1673 K using a resistance furnace; then, 30 g of dephosphorization flux was added eight times, at 180 s intervals. The initial composition ranges of the hot metal and flux are summarized in Tables 2 and 3. Metal was sampled with a quartz tube; the composition (except for carbon) was analyzed by fluorescence X-ray analysis, while the carbon content was analyzed by the combustion method. Slag was sampled by Mo wire and, after separating metallic iron by a bromine-methanol solution, a glass bead sample was analyzed by fluorescence X-ray analysis method. V-oxide and Nb-oxide is expressed as V2O5 and Nb2O5 respectively.

3. Results and Discussion

3.1. Influence of V and Nb Oxides on the Distribution Ratio of P2O5

The experimental results are summarized in Table 4. The authors have already shown that the distribution ratio is influenced by the CaO content of the liquid phase.16) Further, Ito et al.8) have shown a good correlation with the T-Fe content of the liquid phase. Figures 1 and 2 show the influ-

Table 1. Mixture conditions of slags (mass%).

| Sample | CaO | SiO2 | FeO | P2O5 | V2O5 | Nb2O5 |
|--------|-----|------|-----|------|------|-------|
| V1     | 38.7| 29.3 | 21  | 6    | 5    | –     |
| V2     | 26.6| 20.4 | 42  | 6    | 5    | –     |
| V3     | 17.6| 10.7 | 60.7| 6    | 5    | –     |
| Nb1    | 38.7| 29.3 | 21  | 6    | –    | 5     |
| Nb2    | 26.6| 20.4 | 42  | 6    | –    | 5     |
| Nb3    | 17.6| 10.7 | 60.7| 6    | –    | 5     |

Table 2. Initial composition ranges of hot metals (mass%).

| V series | C | Si | Mn | P | V | Nb |
|----------|---|----|----|---|---|----|
| 4.29–4.77| 0.17–1.24 | 0.054–0.080 | – | 0.086–0.109 | – |
| Nb series| 3.36–4.29 | 0.19–0.45 | 0.051–0.080 | – | 0.065–0.092 | – |

Table 3. Mixture conditions of slags for dephosphorization (mass%).

| Slag | FeO | CaO | SiO2 | CaO/SiO2 |
|------|-----|-----|------|----------|
| P1   | 38  | 31  | 31   | 1.00     |
| P2   | 38  | 34  | 28   | 1.21     |
| P3   | 45  | 30  | 25   | 1.20     |
| P4   | 44  | 31  | 25   | 1.24     |
| P5   | 30  | 40  | 30   | 1.33     |
ences of V and Nb oxides on the distribution ratio, that is, the addition of V and Nb oxides results in a slightly larger distribution ratio.

As the distribution ratio can be expressed by Eq. (2), its value is controlled by the activity coefficients of \( \text{P}_2\text{O}_5 \) in the solid solution and the liquid phase.

\[
L_P = \frac{\text{P}_2\text{O}_5 (SS)}{\text{P}_2\text{O}_5 (L)} = \frac{k \gamma_{\text{P}_2\text{O}_5 (SS)}}{\gamma_{\text{P}_2\text{O}_5 (L)}} \quad \text{(2)}
\]

where \( a \) is the activity, \( \gamma \) is the activity coefficient, and \( k \) is the coefficient for conversion of mass percentage to mole fraction. The subscripts \( \text{P}_2\text{O}_5 \) (L) and \( \text{P}_2\text{O}_5 \) (SS) denote \( \text{P}_2\text{O}_5 \) in the liquid phase and the solid solution, respectively.

The activity coefficient of \( \text{P}_2\text{O}_5 \) in the solid solution can be calculated using the following empirical relation:

\[
\log \gamma_{\text{P}_2\text{O}_5 (SS)} = 0.0409 \times (\% \text{P}_2\text{O}_5)_{\text{SS}} + (1.4305 \times W^{1/2} - 17.567) - 1.227 \quad \text{(3)}
\]

where \( W \) is the total dissolved oxide content of the solid solution.

According to this equation, the addition of oxides, which can be dissolved in the solid solution, increases the activity coefficient of \( \text{P}_2\text{O}_5 \) in the solid solution and decreases the distribution ratio. The \( \text{V}_2\text{O}_5 \) or \( \text{Nb}_2\text{O}_5 \) content of the solid solution increases with the increase of \( \% \text{V}_2\text{O}_5 \) or \( \% \text{Nb}_2\text{O}_5 \) in the liquid phase.

### Table 4. Compositions of liquid and solid phases in slag (mass%).

| Sample name | Phase       | Composition (mass%) | \( L_P \) |
|-------------|-------------|---------------------|----------|
|             | CaO | SiO\(_2\) | FeO | \( \text{V}_2\text{O}_5 \) | \( \text{Nb}_2\text{O}_5 \) | \( \text{P}_2\text{O}_5 \) |
| V1          | Solid solution | 54.21 | 11.76 | 2.7 | 0.75 | 30.59 | 12.49 |
|             | Liquid      | 32.85 | 34.78 | 29.03 | 0.87 | 2.45 |
|             | average     | 32.01 | 23.97 | 33.92 | 1.94 | 8.15 |
| V2          | Solid solution | 55.37 | 11.82 | 1.6 | 0.98 | 30.23 | 12.14 |
|             | Liquid      | 36.96 | 35.23 | 22.84 | 2.48 | 2.49 |
|             | average     | 38.41 | 33.59 | 19.81 | 3.62 | 4.56 |
| V3          | Solid solution | 53.35 | 11.42 | 4.2 | 0.36 | 30.66 | 10.43 |
|             | Liquid      | 26.6  | 34.85 | 35.04 | 0.56 | 2.94 |
|             | average     | 21.16 | 19.58 | 52.38 | 1.19 | 5.77 |
| Nb1         | Liquid      | 55.39 | 9.8   | 1.36 | 0.05 | 31   | 13.08 |
|             | average     | 35.3  | 31.74 | 22.07 | 0.07 | 2.59 |
| Nb2         | Liquid      | 46.44 | 11.65 | 3.28 | 0.17 | 30.65 | 15.48 |
|             | average     | 29.91 | 23.42 | 30.28 | 0.14 | 9.14 |
| Nb3         | Liquid      | 54.62 | 11.55 | 4.02 | 0.23 | 29.6 | 7.69 |
|             | average     | 26.54 | 11.02 | 31.80 | 0.22 | 7.69 |

**Fig. 1.** \( \% \text{CaO} \) in liquid solution with respect to CaO content in the liquid phase for a plain CaO–SiO\(_2\)–FeO–P\(_2\)O\(_5\) system (circles), plain slag with about 5 mass\% of \( \text{V}_2\text{O}_5 \) (triangles), and plain slag with about 5 mass\% of \( \text{Nb}_2\text{O}_5 \) (diamonds).

**Fig. 2.** \( \% \text{P}_2\text{O}_5 \) in liquid solution with respect to T·Fe content in the liquid phase for a plain CaO–SiO\(_2\)–FeO–P\(_2\)O\(_5\) system (circles), plain slag with about 5 mass\% of \( \text{V}_2\text{O}_5 \) (triangles), and plain slag with about 5 mass\% of \( \text{Nb}_2\text{O}_5 \) (diamonds).
solution was low, as shown in Table 3. Therefore, the addition of V₂O₅ and Nb₂O₅ decreased the activity coefficient of P₂O₅ in the solid solution and increased the distribution ratio.

The activity coefficient of P₂O₅ in the liquid phase cannot be calculated from a regular solution model for slag containing V₂O₅ and Nb₂O₅. If the activity coefficient of P₂O₅ in the solid solution can be evaluated using Eq. (3), the activity coefficient of P₂O₅ in the liquid phase for slag containing V₂O₅ and Nb₂O₅ can be estimated by Eq. (2). Figure 3 shows the relation between the estimated values and those calculated from the regular solution model without considering the effects of V₂O₅ and Nb₂O₅. Since a good correlation was found, the activity coefficient of P₂O₅ in the liquid phase is not affected by the V₂O₅ and Nb₂O₅ content and can be estimated from the regular solution model without considering their content.

3.2. Behaviors of V and Nb in Hot Metal Dephosphorization by CaO–SiO₂–Fe₂O₃ Slag

Figure 4 shows the relation between [%P] and [%V] in the hot metal. Clearly, there is a linear relation between the oxidation of V and P in the hot metal, which indicates that the decreasing rates of V and P are very close. Conversely, in the region of high P content, the Nb content decreases at a higher rate than the P content, as shown in Fig. 5. From these results, it can be inferred that Nb will be oxidized far more easily than P and V.

Figures 6 and 7 show the effects of basicity ((%CaO)/(%SiO₂)) and (%T·Fe) on the decreasing rate of each component. The decreasing rate of element M can be described by the K value, as follows:

\[-d[\%M]/dt = K[\%M].\] ......................... (4)

The average values of the basicity and (%T·Fe) during the period of flux supply were used for each condition. From these data, the decreasing rate of the elements can plainly be expressed as Nb > Mn > P > V, regardless of the basicity and (%T·Fe). As the basicity increases, the decreasing rate of Nb, P, and Mn also increase. However, the influence of the basicity on the decreasing rate of V is relatively weak. Inoue et al. pointed out that the influence of the basicity on the equilibrium partition ratio is no stronger for V than...
it is for P. The kinetic result of this experiment shows a similar trend. The effect of (%T-Fe) on the decreasing rate of each element is unclear. Generally, a (%T-Fe) increase results in an increase in the oxygen potential and a decrease in the basic oxide content (i.e., %CaO). Because these tendencies have opposite effects on the kinetics of the decreasing rate, the change in (%T-Fe) content does not cause the clear difference.

Figure 8 shows the relation between (%T-Fe) and the supply rate of FeO (V_{FeO}, kg/(t·min)), which is calculated from the FeO content of the flux and amount of flux added. Clearly, (%T-Fe) increases as V_{FeO} increases, and (%T-Fe) is lower in hot metal with Nb than in that with V. In the case of hot metal with Nb, an increase in V_{FeO} does not lead to an increase in (%T-Fe), because the added FeO will be consumed by Nb oxidation.

4. Simulation of the Behaviors of V and Nb during Dephosphorization

4.1. Outline of the Simulation Model

Details about the model can be found elsewhere; therefore, in this study, we only provide a brief description.

In this model, three phases: solid slag, liquid slag, and liquid metal and the reaction between the solid slag and the liquid slag are considered as well as the reaction between the liquid slag and the liquid metal.

A coupled reaction model is used to calculate the reaction kinetics between the molten slag and metal phases. In this model, the reactions are described by the double-film theory, assuming equilibrium conditions at the interface. For example, for the oxidation reaction of element “M” in Eq. (5), the molar flux density is described by Eq. (6), and the equilibrium relation at the interface is represented by Eq. (7), as follows:

\[ J_M = (k_M \times \rho_M/(100M_M)) \left\{ [%M]^b - [%M]^* \right\} \] ............................ (6)

where \( J_M \) is the molar flux density of element M (mol/(m²·s)); \( k_M \) and \( \rho_M \) are the mass transfer coefficients in the film layer of the liquid metal and slag phases, respectively (m/s); \( \rho_M \) and \( \rho_s \) are the densities of the liquid metal and slag, respectively (kg/m³); \( M_M \) and \( M_M^{tot} \) are the atomic weight of M and the molecular weight of MO_n, respectively; \( a_0 \) is the oxygen activity; \( C \) is the total number of moles in the liquid slag phase; \( f \) is the activity coefficient; \( K_M \) is an equilibrium constant of Eq. (7); \( \gamma_{MO_n} \) is the activity coefficient of MO_n; and the superscripts b and * indicate the bulk and interface concentrations, respectively, while the subscript L indicates the liquid slag. In this calculation, the composition of each component in the liquid slag phase was used instead of the average over the liquid and solid slag phases.

Using the mass transfer rate in the metal phase and the CO gas formation rate, the decarburization reaction is expressed as follows:

\[ J_C = (k_C \times \rho_C/(100M_C)) \left\{ [%C]^b - [%C]^* \right\} = G_{CO}(P_{CO}^* - 1), \] ............................ (8)

where \( P_{CO}^* \) denotes the partial pressure of CO at the interface, and \( G_{CO} \) denotes the formation rate of CO gas bubbles (mol/(m²·s)). By the use of Eqs. (6), (7) and (8) for each element and the mass balance equation, the changes in the metal and slag compositions can be calculated simultaneously.

In this model, the boundary lines between the regions of liquid phase and the coexisting phase of solid with liquid are considered on the basis of the CaO–SiO2–FeO phase diagram. When C2S precipitates because of a change in the slag composition or temperature, the distribution of P_2O_5 between the liquid slag and the newly precipitated C2S is calculated. Conversely, when a fraction of C2S melts, the increase in the P_2O_5 content of the liquid phase is calculated from the weight of C2S melted and the average P_2O_5 content of the C2S.

To apply this model for the hot metal with V or Nb, the following oxidation reactions of V and Nb are considered:

\[ [V] + 2.5[O] = VO_{1.5} \]

\[ \Delta G^0 = -402865 + 207.543 \times T \] ............................ (9)
activity coefficient of VO$_{2.5}$ is 2.4 \times 10^{-4}. This value is very close to that observed by Tsukihashi et al.$^{2)}$ for CaO–CaF$_2$–SiO$_2$ slag with CaO/SiO$_2 = 5.0$.

Figure 10 shows a comparison between the simulation and experimental results for dephosphorization of hot metal with Nb under experimental conditions P1 and P4. The results are also in good agreement with respect to the behaviors of P and Nb. In this calculation, the activity coefficient of NbO$_{2.5}$ was set to about 1, which is much higher than the reported value of about 10$^{-3}$ for CaO–CaF$_2$–SiO$_2$ slag with CaO/SiO$_2 = 5.0$. Again, this difference can be considered to reflect the difference in slag composition, as the basicity in these experiments was close to 1.0. As the influence of the basicity on the partition ratio of Nb was not observed, we cannot confirm the validity of this value.

The purpose of this study is to clarify the possibility of extracting V and Nb by means of a conventional hot metal dephosphorization process without using CaF$_2$ as a flux. Therefore, a feasibility study was carried out using the simulation program. The basic conditions for the calculation are summarized in Table 5. In this calculation, Eq. (13) was used to estimate the activity coefficient of VO$_{2.5}$, while the influence of the basicity on the activity coefficient of NbO$_{2.5}$ was ignored.

Figure 11 shows the relation between P and V by changing the flux basicity and by changing changes in the FeO supply rate. In both cases, the decreasing rate of V is similar to that of P. To leave more V in the hot metal during dephosphorization, the difference in reaction rate must be enlarged. As shown in Fig. 6, the difference in the decreasing rate between P and V becomes greater when the basicity increases. In this simulation, to leave more V in the hot metal during dephosphorization, an increased basicity and

![Figure 10: Comparison of simulation results (cal.) with experimental results (exp.) for changes in P and V content during the experiment on hot metal dephosphorization.](image)

![Figure 11: Comparison of simulation results (cal.) with experimental results (exp.) for changes in P and Nb content during the experiment on hot metal dephosphorization.](image)

### Table 5. Basic conditions to calculate feasibility.

| Initial composition of hot metal (mass%) | C | Si | Mn | P | V or Nb |
|----------------------------------------|---|----|----|---|--------|
|                                        | 4.57 | 0–0.5 | 0.3 | 0.075 | 0.075 |

| Flux composition (mass%) | Weight of flux, kg/t | FeO supplying rate, kg/(min·t) |
|-------------------------|-----------------------|-------------------------------|
| FeO | CaO | SiO$_2$ | 46 | 29 | 25 | 30 | 2.2 |

| Calculation conditions | $k_m$ | $k_0/k_m$ | $G_{O_2}$ | Weight of metal | Interfacial Area |
|-----------------------|------|----------|---------|----------------|-----------------|
| m/s | mol/(m$^2$·s) | kg | m$^2$ | $1.2 \times 10^{-4} | 5 | 7.5 \times 10^{-4} | 300 \times 10^{-3} | 8 \times 10^{-4} |
decreased FeO supply rate are favorable. Nevertheless, the separation of V and P is difficult. Figure 12 shows the relation between P and Nb. The decreasing rate Nb is larger than that of P, and decreased FeO supply rate is favorable to leave more P in the hot metal. A separation that leaves P in the hot metal is easier for Nb than for V. Figure 13 shows the influence of the initial Si content on the relation between P and V or Nb. In the case of a high initial Si content, the phosphorization rate decreases greatly as the slag basicity decreases. Therefore, when the initial Si content is raised, it becomes easier to leave P in the hot metal but decrease the Nb content.

5. Conclusion

This study aims to clarify the possibility of extracting V and Nb by means of a conventional hot metal dephosphorization process without using CaF₂ as a flux. First, the influences of V and Nb oxides on the distribution ratio of P₂O₅ between the solid solution and liquid phases in slag were measured. Then, the behaviors of V and Nb in hot metal dephosphorization by CaO–SiO₂–FeO slag were investigated. Finally, a previously described hot metal simulation model was modified and the behaviors of various elements, including V and Nb, during hot metal dephosphorization were simulated, and the results were compared with experimental ones.

The results are summarized as follows:

1) The addition of V and Nb oxides slightly increases the distribution ration of P₂O₅ between the solid solution and liquid phase in slag. The content of V₂O₅ and Nb₂O₅ in the solid solution is low. Therefore, the activity coefficient of P₂O₅ in the solid solution is considered to be low.

2) The decreasing rates of the elements by the flux addition can be expressed as Nb > Mn > P > V, regardless of the basicity and (%T·Fe). Increasing the basicity increases the decreasing rate, but this effect is greater for Nb than for other elements. Similarly, increasing (%T·Fe) increases the decreasing rate, but again the effect is mainly for Nb.

3) The simulation and experimental results are in good agreement with respect to the behaviors of P and V or Nb. To leave more V in the hot metal during dephosphorization, increasing the basicity and decreasing the FeO supply rate are favorable, even though the separation of P and V remains difficult. The decreasing rate is greater for Nb than for P, and separation leaving P in the hot metal is easier for Nb than for V. As the Si content increases, it becomes easier to leave P in the hot metal and remove Nb.

Acknowledgment

The authors appreciate the financial support of a Grant-in-Aid for Scientific Research (B) from the Japan Society for the Promotion of Science.

REFERENCES

1) R. Inoue and H. Suito: Trans. Iron Steel Inst. Jpn., 22 (1982), 705.
2) F. Tsukihashi, A. Tagaya and N. Sano: Trans. Iron Steel Inst. Jpn., 28 (1988), 164.
3) R. Inoue and H. Suito: Trans. Iron Steel Inst. Jpn., 23 (1983), 586.
4) R. Inoue and H. Suito: Trans. Iron Steel Inst. Jpn., 23 (1983), 578.
5) W. Fix, H. Heymann and R. Henke: J. Am. Ceram. Soc., 52 (1969), 345.
6) K. Yokoyama, H. Kubo, K. Mori, H. Okada, S. Takeuchi and T. Nagasaka: Tetsu-to-Hagané, 92 (2006), 6.
7) S. Ohguchi, D. G. C. Robertson, B. Deo, P. Grieveson and J. H. E. Jeffes: Ironmaking Steelmaking, 11 (1984), 202.
8) K. Ito, M. Yanagisawa and N. Sano: Tetsu-to-Hagané, 68 (1982), 342.
9) R. Inoue and H. Suito: ISIJ Int., 46 (2006), 174.
10) S. Kitamura, H. Shibata and N. Maruoka: Steel Res., 79 (2008), 586.
11) K. Shimazu, S. Kitamura and H. Shibata: ISIJ Int., 49 (2009), 505.
12) S. Kitamura, K. Miyamoto, H. Shibata, N. Maruoka and M. Matsuo: ISIJ Int., 49 (2009), 1333.
13) F. Pahlevani, S. Kitamura, H. Shibata and N. Maruoka: Steel Res. Int., 81 (2010), 617.
14) F. Pahlevani, S. Kitamura, H. Shibata and N. Maruoka: ISIJ Int., 50 (2010), 822.
15) S. Kitamura, H. Shibata and N. Maruoka: Steel Res., 79 (2008), 586.
16) S. Kitamura and H. Shibata: Proc. 2nd Int. Conf. Simulation and Modeling of Metallurgical Processes in Steelmaking, ASMET, Graz, Austria, (2007), 72.
17) S. Kitamura, H. Shibata and N. Maruoka: Proc. 3rd Int. Conf. Process Development in Iron and Steelmaking, SCANMET III, MEFOS, Lulea, Sweden, (2008), 283.