Reductive Removal of Solutes in Molten Iron by Using Immiscibility of Iron and Ca-Alloy

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Abstract
In order to produce high purity iron (or high clean steel) from low grade ores and/or iron scraps in steel industry, it is necessary to develop a new method to remove the impurities in molten iron, which can improve the refining ability dramatically. In this work, we focus on the impurities in molten iron, which can improve the refining ability dramatically. In this work, we focus on the reductive removal by using immiscibility of iron and calcium. The oxygen partial pressure is expected to be kept under 10⁻²⁰ atm by the introduction of calcium alloy phase, which can enhance the reductive removal of impurities in molten iron. In this work, we examine the possibility of the reductive removal of impurities by the use of the calcium alloy phase.

Key words
Reductive Removal, Steelmaking, Refining, Calcium, Molten Iron, Dephosphorization

1. Introduction
In order to use calcium to refining effectively, it is necessary to decrease the calcium activity. The calcium activity is related to the calcium partial pressure as follows: aCa=αCaPCaCaM alloy/PCa(pure liquids), where αCa denotes the calcium activity relative to the pure liquid, PCa(Ca-M alloy) the partial pressure of calcium in Ca-M alloy and PCa(pure liquid) the partial pressure of calcium in the pure liquid. We examined the use of solvent suitable for calcium. The dependence of the calcium partial pressure on the composition of Ca-M (Mg, Ba, Sn, Pb or Ag) alloy at 1823K is calculated. It is found that the use of those solvents enables to control the calcium vapor pressure by adjusting the alloy composition. In this work, the possibility of a new reductive dephosphorization method is examined, which utilizes calcium as a new third phase in addition to slag and metal phases.

2. Suitable Conditions for the Reductive Dephosphorization Treatment by Calcium
Because the boiling point of Ca, 1757 K, is lower than the melting point of iron, 1812 K, the direct Ca treatment of molten steel is difficult. For this reason, the Ca treatment of molten pig-iron, the melting point of which become lower than 1757K, is considered in this work. For the Ca treatment of molten pig-iron, it is necessary to consider the formation of CaC₂, which is expressed by Eq.(1).

Ca(l) + 2C(in Fe) = CaC₂(s)  (1)

The standard Gibbs energy for Eq.(1) equals to the standard Gibbs energy of formation of CaC₂, which is expressed by Eq.(3) [1], when the reference state of the carbon activity is set to the pure solid.

Ca(l) + 2C(s) = CaC₂(s)  (2)

ΔG°(2) = −90100 − 11.0T  [J/mol]  (3)

The equilibrium constant for Eq.(1) is expressed by Eq.(4).

K(1) = aCaC₂  (4)

where αCa and aC denote the activities of CaC₂ and C relative to the pure solids, and aCa denotes the activity of Ca relative to the pure liquid. The formation condition of CaC₂ is represented as Eq.(5) by the condition of αCaC₂=1 in Eq.(4).

aC = 1/αCa exp(−5419/T − 0.66)  (5)

The activity of carbon, aC, is expressed by Eq.(6).

aC = γC C X  (6)

The activity coefficient of carbon, γC, in Eq.(6) is expressed by Eq.(7) by using the activity coefficient of carbon at infinite dilute solution, γC₀, and the first-order interaction parameter of carbon against carbon, εC C, and the second-order interaction parameter of carbon against carbon, ρC C.

lnγC = lnγC₀ + εC X + ρC X  (7)

where it is known that γC₀ = 0.538 [2], εC C = 11 [3] and ρC C = −5.6 [3] at 1873 K. From Eq.(7), the value of γC at 1873 K is calculated. The carbon content of iron in equilibrium with CaC₂ is determined from Eqs.(5) through (7) at each temperature and at each calcium activity by a regular solution approximation. Here, we assume the carbon solubility of Ca is negligibly small. The evaporation reaction of Ca is expressed by Eq.(8). The standard Gibbs energy for Eq.(8) [4] is represented by Eq.(9).

Ca(l) = Ca(g)  (8)
Fig. 1 Liquidus of Fe-C system and the condition of CaC$_2$ formation ($a_{CaC_2}=1$) at $a_{Ca}=1$

Fig. 2 Liquidus of Fe-C system and the condition of CaC$_2$ formation ($a_{CaC_2}=1$) at $a_{Ca}=0.8$

Fig. 3 Liquidus of Fe-C system and the condition of CaC$_2$ formation ($a_{CaC_2}=1$) at $a_{Ca}=0.7$

Fig. 4 Liquidus of Fe-C system and the condition of CaC$_2$ formation ($a_{CaC_2}=1$) at $a_{Ca}=0.6$
\[ \Delta G_{0}^{(8)} = 157800 - 87.11T \quad [\text{J/mol}] \]  

The equilibrium constant for Eq. (8) is expressed by Eq. (10) from \( P_{Ca} \) and the Ca activity relative to the pure liquid.

\[ K_{(8)} = \exp\left(-\frac{\Delta G_{0}^{(8)}}{RT}\right) = \frac{P_{Ca}}{a_{Ca}} \]  

\( P_{Ca} \) is expressed by Eq. (11) from Eqs. (9) and (10).

\[ P_{Ca} = a_{Ca} \cdot \exp\left(-18980/T + 10.48\right) \]  

From Eq. (11), \( P_{Ca} \) is determined from temperature and the Ca activity. The relationship of Eq. (5) is shown in Fig. 1 under the condition of \( a_{Ca}=1 \) together with the liquidus of Fe-C system. From Fig. 1, the coordinate of the intercept of the \( \text{CaC}_2 \) saturated line and the liquidus of Fe-C system is 1758 K and [mass%C]=0.70. At this time, the high value of \( P_{Ca}=0.69 \) [atm] is obtained, and it may be possible but difficult to react calcium directly. Accordingly, to lower the calcium activity using a solvent is considered. The relationships similar to Fig. 1 at \( a_{Ca}=0.8, 0.7, 0.6 \) are shown in Figs. 2 through 4, respectively. From Figs. 1 through 4, as the suitable condition for the Ca treatment, for example, the coordinate of the intercept of the \( \text{CaC}_2 \) saturated line and the liquidus of Fe-C system at \( a_{Ca}=0.7 \) (Fig. 3), 1750 K and [mass%C]=0.78, is considered. At this time, \( P_{Ca}=0.48 \) [atm] is derived. In this work, the use of Ca phase around this condition is considered. Subsequently, the candidate of the solvent to lower the calcium activity is examined.

### 3. Solvent of Calcium for the Ca Reductive Dephosphorization

It is necessary to lower the Ca activity by the solvent in the use of Ca phase. The suitable solvent of Ca is examined.

![Fig. 5 Ca activity for the Ca-M alloys at 1753K](image)

From the foregoing results on the suitable conditions for the Ca treatment, the temperature is set to be 1753 K. The activity diagrams for Ca-M alloys at 1753 K is shown in Fig. 5 [5 - 7]. As the candidate of the solvent, Mg, Ba, Sn, Pb and Ag are chosen in this work, and the calculation is conducted. From Fig. 5, it is found that Mg and Ba behave ideally with Ca and Sn, Pb and Ag show strong negative deviation from ideality. Using the data in Fig. 5, the calculated results of Ca vapor pressure are shown in Fig. 6 [4]. The vapor pressure of pure Ca is about 0.69 atm at 1753 K. It is possible to control the vapor pressure from 0 to 0.7 atm by diluting Ca with solvent.

### 4. Distribution Ratio of Phosphorus between Molten Iron and Slag by the Reductive Dephosphorization with Calcium

The distribution ratio of phosphorus between molten iron and slag by the reducive dephosphorization with calcium is calculated. The reductive dissolution reaction of gaseous phosphorus, \( P_2 \), in slag is expressed by

\[ \frac{1}{2}P_{2}(g) + \frac{3}{2}(O^{2-}) = (P^{5+}) + \frac{3}{4}O_{2}(g) \]  

The phosphide capacity is defined as

\[ C_{p^{[5+],e}} = \frac{K_{(12)}}{f_{P^{[5+]}}} = \frac{a_{Ca}^{3/2}}{P_2^{1/2}} \]  

The dissolution reaction of \( P_2 \) in molten iron, the standard Gibbs energy of the reaction and the equilibrium constant are expressed as follows:

\[ \frac{1}{2}P_{2}(g) = P \quad \text{(in Fe)} \]
\[ \Delta G_{f(14)}^0 = -157700 - 5.4T \text{ (J/mol)} \]  

\[ K_{(14)} = \frac{f_p \text{[mass\%P]}}{P_{O_2}^{1/2}} \]  

\[ \log f_p = e_p^f \text{[mass\%P]} + e_p^c \text{[mass\%C]} \]  

\[ e_p^f = 0.054 \]  

\[ e_p^c = 0.126 \]  

From Eqs. (13) and (16), Eq. (18) is derived.

\[ L_p = \left( \frac{\text{[mass\%P]} C_p}{\text{[mass\%P]}} \right) = \frac{f_p}{K_{(14)} P_{O_2}^{1/4}} \]  

Using Eq. (18), the phosphorus distribution ratio was calculated. The phosphate capacities for CaO-CaF₂ and CaO-Al₂O₃ slag are reported as follows:

CaOsatd.-CaF₂ slag:

\[ C_{p^\ast} = 2.24 \times 10^{-12} \text{ (at 1753K), } 7.94 \times 10^{-12} \text{ (at 1823K)} \]  

CaO-Al₂O₃(CaO-Al₂O₃satd.) slag:

\[ C_{p^\ast} = 2.33 \times 10^{-13} \text{ (at 1823K)} \]

The oxygen partial pressure, \( P_{O_2} \), is calculated from the following equation.

\[ \text{Ca(l)} + \frac{1}{2} \text{O}_2(g) = \text{CaO (s)} \]  

\[ \Delta G_{f(19)}^0 = -658000 + 1337T \text{ (J/mol)} \]  

The calculation is conducted under the conditions of \( a_{CaO} = 1 \) for CaOsatd.-CaF₂ slag and of \( a_{CaO} = 0.1 \) for CaO-Al₂O₃(CaO-Al₂O₃satd.). Here, we assume the carbon solubility of Ca-M (Mg, Ba, Sn, Pb or Ag) alloy is negligibly small. The dependence of the phosphorus distribution ratio on the calcium content is shown in Fig.7 for CaOsatd.-CaF₂ slag and in Fig.8 for CaO-Al₂O₃(CaO-Al₂O₃satd.), respectively. The value for \( C_{p^\ast} \) of CaO-Al₂O₃(CaO-Al₂O₃satd.) is not measured at 1753 K, and the value at 1823 K is used as it is. From these results, by using the element with strong affinity with Ca, such as Sn, Pb, and Ag, under the condition of \[ \text{[mass\%Ca]} = 40 \sim 60 \] (about \( P_{Ca} = 0.2 \sim 0.4 \) [atm]), it is found that the high distribution ratios, \( L_p = 100 \sim 600 \) and \( 500 \sim 2000 \), can be obtained for CaOsatd.-CaF₂ slag and for CaO-Al₂O₃(CaO-Al₂O₃satd.) slag, respectively. These high distribution ratios can be realized by the introduction of calcium alloy phase, by which the oxygen partial pressure is kept under \( 10^{-20} \) atm. In order to lower the oxygen partial pressure, Al is usually added in molten steel in steel refining. In this case, the oxygen partial pressure is
considered to become about $1 \times 10^{-17}$ atm, from which the distribution ratio of phosphorus only can be expected to be $L_P < 1$. Subsequently, the dissolution loss of solvent into molten iron is considered. The solubility of solvent M(Pb, Ag or Sn) in molten iron can be calculated from the activity coefficient of M in Fe [2], and the results are shown in Fig.9. It is known that the higher content of Sn (or Pb) than 0.04mass%Sn (0.001mass%Pb) causes adverse effect on the hot workability of steel. [11] For this reason, from Fig.9, it is necessary to use Ca-Sn (or Pb) alloy at [mass%Sn] < 50 (or [mass%Pb] < 75). Accordingly, Pb is concluded to be the most suitable and prospective element as the solvent of Ca.

5. Conclusions
The possibility of a new reductive dephosphorization method to utilize Ca as a third phase is examined. The conclusions are as follows:
(1) Ag, Pb and Sn are used as the solvent of Ca. From the viewpoint of dissolution loss into molten iron, Pb is the most suitable and prospective.
(2) If a third phase which is [mass%Ca] = 40~60 (about $P_{Ca} = 0.2 \sim 0.4$ [atm]) at [mass%C]$_{Fe}=0.8$ and at 1753K is used, the distribution ratios are expected to be $L_P=100 \sim 600$ for CaO$\cdot$h-CaF$_2$ slag and 500~2000 for CaO$\cdot$Al$_2$O$_3$(CaO$\cdot$Al$_2$O$_3$satd.) slag, respectively.

References