

EFFECT OF ACTIVITY COEFFICIENT ON PHOSPHATE STABILITY IN MOLTEN SLAGS

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ABSTRACT

Recently, demands of special alloys which would be achieved with high chemical cleanness are on the increase because of high strength, high corrosion resistance and so on. Therefore the dephosphorization tendency toward lower basicity slag system for minimum of alloy loss. In relatively low basicity slags, the concept of forming pyrophosphate can be proposed pronounced effects for dephosphorization ability of slag. There are three factors for polymerizing phosphate ion in slag, high contents of phosphate ions, low basicity and low activity coefficient of pyrophosphate ion. In present study, basicity and activity coefficient are considered. First, effect of basicity is investigated in the slag having wide range of liquidus region. And effect of activity coefficient is examined in the slag containing high content of FeO, MnO and Al₂O₃. Through these studies, it was shown that they have an impact on increasing refining ability of phosphorus in low basic slags.

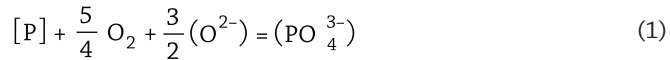
INTRODUCTION

Recently, demands of special alloy such as Mn TWIP, STS have been increased with increasing severe environments condition of materials. Current strong demands for high performance of special alloying steel have proposed the high cleanness from thermomechanical in point of view.

On the other hand, the scarcity of high quality of raw materials are generally held to be the principal disadvantages of current Ferro-alloying process, which was composed with EAF and low quality of coke. This current trend for deterioration of alloying raw material has focused on the new smelting reduction process with low quality of raw materials and reduction of process energy by using low melting temperature etc. In order to maximize the energy efficiency in low purity of raw material of ferro-alloy, slag volume and melting temperature should be minimized by control of basicity of slag. For example, The slag design for smelting reduction for Ferro-Alloy by emerging raw material such as Mn nodule, slag phase diagram of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MO}$ bearing slag plays a important role to design the slag system, was important to determine the recovery ratio of valuable elements and removal impurity such as phosphorus.

In established studies, it is known well that high basic slag has a high refining ability but high loss of alloy elements and high melting point. Thus, it is necessary to maximize the refining ability conventional slag system with low melting temperature by applying low basicity.

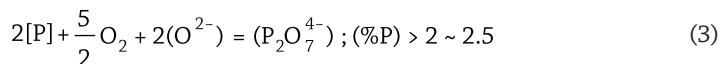
Generally, refining ability of slag would be quantified the Wagner's capacity concept, which was expressed by temperature, activity of oxygen ion and stability of reactant in molten slag as following Equation 1.



$$C_{\text{PO}_4^{3-}} = \frac{(\% \text{PO}_4^{3-})}{[\% \text{P}] \cdot p_{\text{O}_2}^{5/4} \cdot \gamma_{\text{P}}} = \frac{K_{(1)} \cdot a_{\text{O}^{2-}}^{3/2}}{\gamma_{\text{PO}_4^{3-}}} \quad (2)$$

For maximizing dephosphorization ability, it is necessary to satisfy the conditions of high partial pressure of oxygen, high basicity and ions having high affinity with phosphate ion. From Equation 2, dephosphorization ability, that is, phosphate capacity is affected by temperature, basicity and activity coefficient of phosphate ion. So far, in order to get a high phosphate capacity, the tendency of processing condition goes to high concentration of CaO because CaO is known to high basic oxide. And CaO produces Ca^{2+} ions having a strong coherence with phosphate ion. Thus, CaO is effective for dephosphorization both sides of slag basicity and activity coefficient of phosphate ion. However, most studies have been focused on only basicity without considering the activity coefficient of phosphate ion.

Recently, some studies show the possibility of effective dephosphorization by pyrophosphate ion, $\text{P}_2\text{O}_7^{4-}$ in high basic slags with high concentration of phosphorus [2, 3].



From these studies, dephosphorization ability depends on activity coefficient of phosphate ion as well as basicity.

Thus the influential factors of the activity coefficient of phosphate are contents of phosphorus in slag, interaction between phosphate and other ions, and slag basicity. First, effect of phosphorus contents in slag was already investigated by Sano and Selin as

above-mentioned. Second, interaction with ions has been mainly studied in case of Ca^{2+} ion. And effect of basicity is almost examined in high basic slag system near CaO saturated region.

Therefore, present study is intended to focus on effect of activity coefficient for increasing dephosphorization ability in different slag system. Especially, it is investigated effect of amphoteric oxide such as FeO, MnO and Al_2O_3 on phosphate stability in relatively low CaO containing slags.

METHODOLOGY

Experimental Apparatus

A schematic diagram of the experimental system is shown in Figure 1.

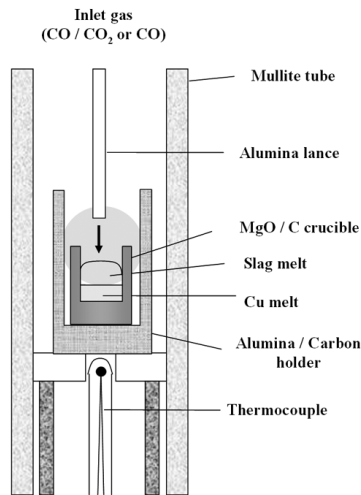


Figure 1: Experimental apparatus

The experiment consisted of equilibrating copper metals with a slag of varying composition in MgO or carbon crucible at 1723~1773 K. Since copper as metallic phase does not reduce MnO in slag, it is superior to carbon saturated iron melts. The temperature was controlled within ± 2 K using an R-type (Pt-13%Rh) thermocouple and a Proportional-Integral-Differential (PID) controller. The slag samples were prepared from mixtures of analytical grade CaCO_3 , B_2O_3 , Al_2O_3 , MgO, SiO_2 , FeO, MnO. Phosphorus was added to the slag as $\text{Ca}_3\text{P}_2\text{O}_8$. The equilibration times were 24 hours which were found to be sufficient to establish equilibrium in preliminary experiments. After equilibration, the crucible was quickly withdrawn from the furnace and quenched in an Ar stream. The slag sample was taken out after cracking the crucible and the surface layer contacted with crucible was removed by grinding. Then metal and slag samples were crushed for chemical analyses. Phosphorus in both metal and slag was analyzed by molybdenum blue colorimetry method (JIS G1311-1987) and other elements were analyzed by X ray fluorescence (XRF, Bruker-SRS340).

RESULTS AND DISCUSSION

Dephosphorization Mechanism in Low Basic Slag

Phosphorus species in the slag are known that phosphide, P^{3-} , orthophosphate, PO_4^{3-} , and pyrophosphate, $P_2O_7^{4-}$ anions [4]. In low basic slag system, acidic oxides are polymerized to various forms with acidic oxides rate. Phosphate is also polymerized in low basic slag because it acts the part of acidic oxide as following equation:



$$K_{(4)} = \frac{X_{P_2O_7^{4-}} \cdot \gamma_{P_2O_7^{4-}} \cdot a_{O^{2-}}}{X_{PO_4^{3-}}^2 \cdot \gamma_{PO_4^{3-}}^2} \quad (5)$$

In condition of low basic slag, effective dephosphorization can be obtained by stabilizing pyrophosphate phase, $P_2O_7^{4-}$. There are three factors for progressing Equation 4. First, the concentration of phosphate in slag is known by Sano *et al.* and Selin. Sano *et al.* obtained that a PO_4^{3-} is predominant up to 2 mass pct in a CaO-CaF₂-SiO₂ melt doubly saturated with CaO and 2CaO-SiO₂ at 1573 K [2]. And Selin reported that PO_4^{3-} is predominant up to 2.5 mass pct for CaO-MgO_{satd.}-SiO₂-FeO system at 1873 K [3].

Second, low basicity condition will progress the polymerization of phosphate. As lower basicity, i.e., lower oxygen ion activity, the reaction (4) goes to left-hand side, $P_2O_7^{4-}$ is more stable than PO_4^{3-} .

Third, the activity coefficient of phosphate is influential with polymerization. That is, stabilizing phosphate is fixed with activity coefficient is interaction between other ions in slag. And slag structure changing with slag composition is also one of the factors as phosphate is polymerized with existing acidic oxide in slag. Thus, pyrophosphate can be produced by increasing pyrophosphate stability with the ions having high affinity with phosphate and decreasing basicity.

Effect of Basicity

First, to estimate effect of basicity, it needs slag systems having wide liquidus region. B₂O₃ systems have low melting point and double saturate composition of B₂O₃ and MO.

Figure 3 shows effect of basicity in wide composition range of Na₂O-B₂O₃, CaO-B₂O₃ and CaO-SiO₂-CaF₂ slag. Every case shows the continuous increase over whole range.

From the tendency of phosphorus distribution ratio, basicity has a very slight effect on polymerization of phosphate ion. However, the slopes of each slag are different from general slope, 1.5. This phenomenon can be explained the difference of activity coefficient of phosphate ion in each slag system from Equation 2. Dephosphorization ability depends on the ratio of $a_{O^{2-}}$ and $\gamma_{PO_4^{3-}}$, and the slopes of Figure 2 include the effects both basicity and activity coefficient of phosphate ion.

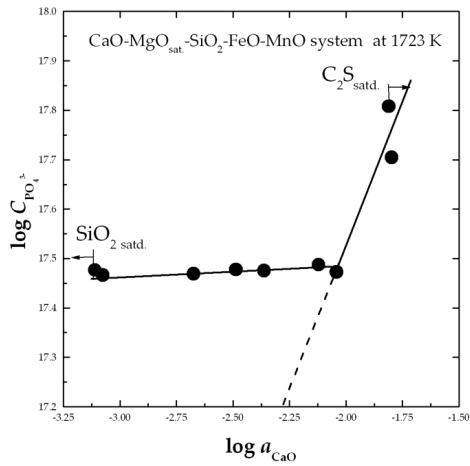


Figure 2: Effect of basicity on dephosphorization in wide range of slag

Figure 3 shows dependence of basicity on phosphate capacity in high FeO and MnO content and relatively low content of CaO slag. The tendency of dephosphorization increases in lower basic regions near SiO_2 saturated. This phenomenon is opposite to general dephosphorization mechanism in oxidizing condition, phosphate capacity decreases as decreasing basicity. And from this results, it can be supposed to possibility of effective dephosphorization in low CaO slag with high FeO and MnO.

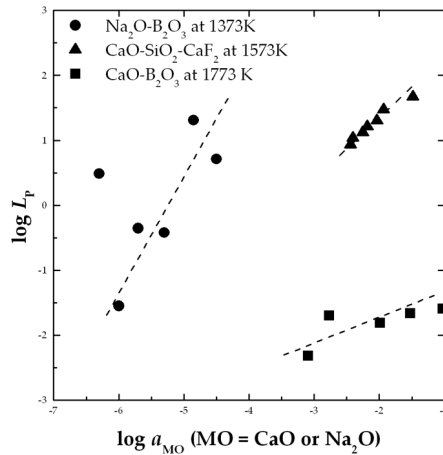
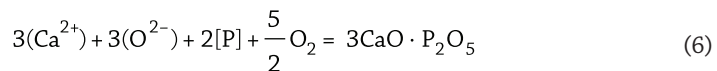


Figure 3: Phosphate capacity in low basic slag

Effect of Activity Coefficient

Phosphorus in metal moves to slag and it is mainly caught by Ca^{2+} ions because of high affinity between two ions. In relatively high basicity case, it is well known that very stable component calcium phosphate was formed;



Activity of Ca^{2+} ion is proportioned to activity of CaO as well as O^{2-} ion. However, current studies have been focused on CaO effect of high basicity.

In Figure 3, the tendency of dephosphorization shows a breaking curve with about unit a_{CaO} . It is not regular case like continuous decrease as going to low basicity, SiO_2 saturated region. The cause of this curvature may be changes of activity coefficient of $\text{PO}_{2.5}$ in slag as follows;

$$\text{PO}_{2.5} = [\text{P}]_{\text{Cu}} + \frac{5}{4} \text{O}_2 \quad (7)$$

$$\Delta G_{(7)}^0 = 161300 - 65.7 T \text{ (cal/mol)} \quad (8)$$

$$\log \gamma_{\text{PO}_{2.5}} = -\log K_{(7)} + \log f_{\text{P}} + \log [\% \text{P}] + \frac{5}{4} \log p_{\text{O}_2} - \log X_{\text{PO}_{2.5}} \quad (9)$$

The $\log \gamma_{\text{PO}_{2.5}}$ values are plotted against the activity of CaO in Figure 4.

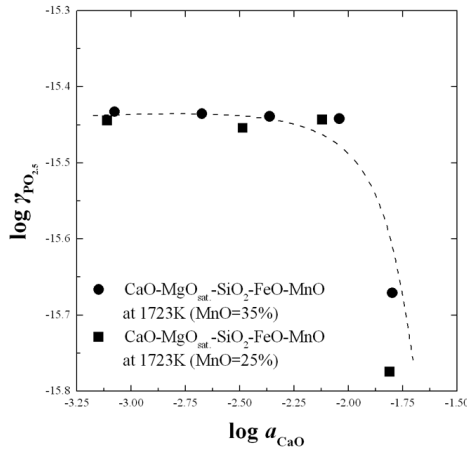


Figure 4: Relationship between $\gamma_{\text{PO}_{2.5}}$ and a_{CaO}

The $\log \gamma_{\text{PO}_{2.5}}$ values are constant up to $a_{\text{CaO}} \approx 10^{-2}$, unity basicity region ($\% \text{CaO} / \% \text{SiO}_2 \approx 1.0$), and they decrease linearly above this region. As mentioned, this is not caused by only CaO, but high content of FeO and MnO in slag. It can be considered that FeO and MnO act decreasing the activity coefficient of phosphate ion in low basic condition.

For observing FeO effect on dephosphorization, the phosphate capacities are compared with different slag with high FeO contents as Figure 5 [5, 6, 7, 8, 9]. Many experimental results show the common tendency of CaO activity dependence, they have a constant value of phosphate capacity in relatively low basicity. FeO changes its property with slag compositions, it acts polymerization former like SiO_2 in high basic slag and it acts structure modifier like CaO in high acidic slag. However, from this character, it is not reasonable to consider that increase of dephosphorization ability is due to FeO acting as an oxygen ion donor in relatively low basic region. Because the increasing ranges of dephosphorization ability are higher than that caused by CaO. Thus, as mentioned, activity coefficient of phosphate in slag move to lower states due to FeO existence in relatively low contents of CaO slag system.

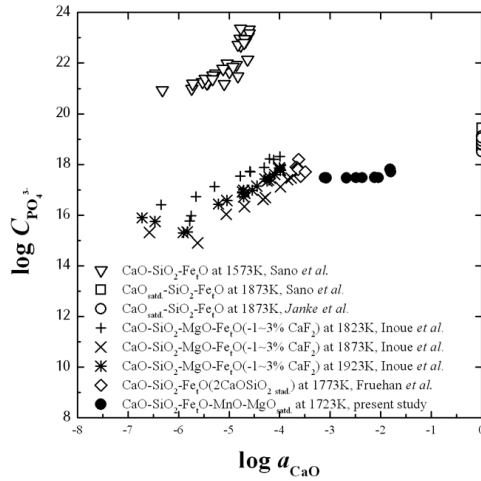


Figure 5: Phosphate capacities of FeO containing slags

Similar phenomenon shows in case of Al_2O_3 containing slag system like Figure 6. In $CaO-B_2O_3$ slag without Al_2O_3 , the phosphate capacity increases as higher content of CaO . However, phosphate capacity is nearly constant over whole composition even increasing CaO content both cases of $CaO-B_2O_3-Al_2O_3$ and $CaO-SiO_2-Al_2O_3$ slags. Al_2O_3 is also amphoteric oxide like FeO , and it acts as FeO in relatively low contents of CaO slag. Thus, it is certain that amphoteric oxide has some effect for dephosphorization in low CaO content, that is, low basic slag enough to form pyrophosphate ion. And this effect is considered that phosphate activity coefficient is changed by amphoteric oxide, but the mechanism is still uncertain.

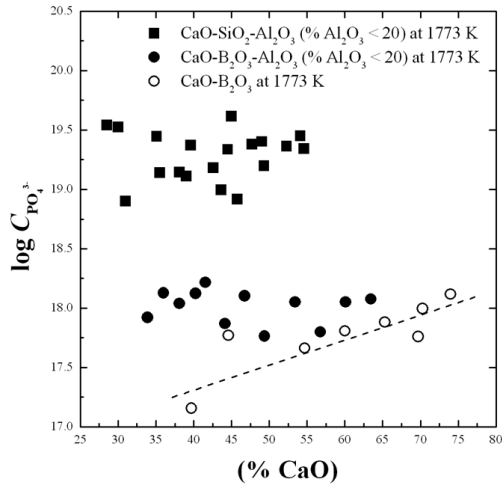


Figure 6: Effect of Al_2O_3 on dephosphorization

CONCLUSIONS

In relatively low CaO containing slags, the concept of low basicity and low activity coefficient of phosphate ion can be proposed to pronounce effects for dephosphorization ability of slag. First of the factors for increasing phosphorus refinability is low basicity with low content CaO; however, this shows very slight effect.

Second factor is low activity coefficient of pyrophosphate ion; for confirming this, influence of amphoteric oxides such as FeO and Al_2O_3 was determined. In low CaO content region, it is confirmed that FeO and Al_2O_3 have effect on increasing dephosphorization ability. From this result, the possibility of dephosphorization can be supposed in low basic slag.

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