Interactions of two-liquid CaO-MgO-Fe\textsubscript{t}O-P\textsubscript{2}O\textsubscript{5} slag with MgO refractories

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It is known that the CaO-Fe\textsubscript{t}O-P\textsubscript{2}O\textsubscript{5} slag system has a wide liquid miscibility gap at steelmaking temperatures and this two-liquid slag phase has many advantages such as high activities of both Fe\textsubscript{t}O and CaO and high amount of P\textsubscript{2}O\textsubscript{5}. The phosphorus distribution ratio between the two-liquid slag and molten steel was confirmed to be higher than that between CaO\textsubscript{sat.}-Fe\textsubscript{t}O-P\textsubscript{2}O\textsubscript{5} slag and molten steel. The two-liquid slag may be useful for dephosphorization of molten steel and reduction of slag volume. Furthermore, the phase equilibrium of two-liquid CaO-Fe\textsubscript{t}O-P\textsubscript{2}O\textsubscript{5} slag saturated with MgO was measured to determine the applicability of the two-liquid slag to dephosphorization in steelmaking process.

Keywords: slag, refractories, solid solution, two-liquid phase, dephosphorization, steelmaking, phase equilibrium.

Introduction

Since the impurities in steel are required to be extremely low to produce high quality steel, the amount of steelmaking slag as flux for refining is increasing. Consequently, it is extremely important to develop new refining techniques for the reduction of slag volume.

Dephosphorization is the oxidation reaction of phosphorus in liquid steel and is expressed by Equation [1].

\[ 2[P] + 5FeO = (P\textsubscript{2}O\textsubscript{5}) + 5Fe \]  

Thereby, the dephosphorized slag consists of iron oxide which oxidizes phosphorus, phosphorus pentoxide which is a dephosphorization product, and lime which stabilizes P\textsubscript{2}O\textsubscript{5} in slag. CaO-Fe\textsubscript{t}O-P\textsubscript{2}O\textsubscript{5} phase diagram was proposed by Muan and Osborn\textsuperscript{1)} based on the work of Trömel et al.\textsuperscript{2–3).}

In general, high values of both Fe\textsubscript{t}O and CaO activity are required for effective dephosphorization. A homogeneous liquid phase cannot achieve such a condition, because increase of the content of one slag component to raise its activity leads to decrease of that of the other, thus lowering its activity. Both the activities of Fe\textsubscript{t}O and CaO are high in the two-liquid phase region in CaO-Fe\textsubscript{t}O-P\textsubscript{2}O\textsubscript{5} ternary system, because phase L\textsubscript{1} which is rich in iron oxide coexists with liquid L\textsubscript{2} whose composition is close to liquid saturated with CaO. Therefore, the two-liquid phases are thermodynamically suitable for dephosphorization.

Slag and molten steel are held in a furnace lined with MgO-based refractories in practice. The slag is saturated with (Mg,Fe)O, since MgO and Fe\textsubscript{t}O form a complete solid solution. If a liquid miscibility gap exists in the CaO-Fe\textsubscript{t}O-P\textsubscript{2}O\textsubscript{5} slag at (Mg,Fe)O solid solution saturation, it would be expected that effective dephosphorization could be carried out utilizing this system. The (Mg,Fe)O-liquidus surface of CaO-MgO-Fe\textsubscript{t}O-P\textsubscript{2}O\textsubscript{5} quaternary system was estimated by Trömel et al.\textsuperscript{4)} and MgO solubility in the system was measured by Nagabayashi et al.\textsuperscript{5)} at steelmaking temperatures. It had been unknown, however, whether a miscibility gap exists or not in the CaO-MgO-Fe\textsubscript{t}O-P\textsubscript{2}O\textsubscript{5} system on the condition of (Mg,Fe)O saturation as shown in Figure 1. In our previous work\textsuperscript{6)} using a chemical equilibrium technique, it was determined that a two-liquid region existed in CaO-MgO-Fe\textsubscript{t}O-P\textsubscript{2}O\textsubscript{5} system on the condition of (Mg,Fe)O saturation, the phosphorus distribution ratio between the slag system and molten iron was higher than that of CaO\textsubscript{sat.}-Fe\textsubscript{t}O-P\textsubscript{2}O\textsubscript{5} system at steelmaking temperatures and the two-liquid slag phase was very useful for dephosphorization of molten steel and reduction of slag volume. On the other hand, information of (Mg,Fe)O composition in contact with steelmaking slag is necessary for further study.

![Figure 1. Two-liquid region saturated with (Mg,Fe)O in CaO-MgO-Fe\textsubscript{t}O-P\textsubscript{2}O\textsubscript{5} system at 1873 K\textsuperscript{6)}](image-url)
extremely important to limit damage to MgO refractories caused by slag penetration.

Keeping such background in mind, compositions of (Mg,Fe)O solid solutions equilibrated with two-liquid CaO-MgO-Fe\textsubscript{t}O-P\textsubscript{2}O\textsubscript{5} slags at steelmaking temperatures are reported in the present study.

**Experimental procedure**

A vertical electric resistance furnace with LaCrO\textsubscript{4} heating elements was used (Figure 2). The reaction tube was of alumina, 60 mm in ID and 1000 mm length. CaO and Fe\textsubscript{t}O were prepared by calcining CaCO\textsubscript{3} in a Pt crucible at 1473K for 10 hours in air and sintering the mixture of electrolytic iron and Fe\textsubscript{t}O powders at mole partition of 1:1 at 1373K for 6 hours in an iron crucible under a purified Ar stream, respectively. CaO-MgO-Fe\textsubscript{t}O-P\textsubscript{2}O\textsubscript{5} quaternary slag was prepared from CaO, MgO, Fe\textsubscript{t}O, 3CaO-P\textsubscript{2}O\textsubscript{5}, CaHPO\textsubscript{4}·2H\textsubscript{2}O and (NH\textsubscript{4})\textsubscript{2}HPO\textsubscript{4}.

Approximately 3 g slag of tablet shape with given composition and about 1 g of electrolytic iron plate were charged in a MgO crucible. The MgO crucible charged with the slag and metal was heated to and maintained of 1823, 1873 or 1923K under a purified Ar stream for 6 hours in the furnace. The holding time was determined by preliminary work. It was withdrawn from the furnace after attainment of equilibrium and quenched by impinging He and dipping in water bath.

Slag composition was determined by an electron probe micro analyzer (EPMA). To minimize the analytical error caused by segregation during solidification, the average intensities of elements (Ca, Mg, Fe, P) in each liquid slag phase were employed in 0.256 × 0.256 mm\textsuperscript{2} EPMA mapping to determine the slag compositions. Concentration profiles of elements in a MgO crucible were scanned from slag-crucible interface to the bulk of crucible by EPMA to examine the composition of solid phase equilibrated with liquid phase by assuming local equilibrium between slag and crucible at the interface. The phosphorus and oxygen contents in iron were determined by induction coupled plasma spectroscopy (ICP) and inert gas impulse infrared absorption spectroscopy (LECO), respectively.

**Experimental results**

A cross-sectional view of a typical sample is shown in Figure 3(a). The slag separated into two liquids, and metal existed in an elliptical morphology at the bottom. Upper liquid slag phase L\textsubscript{2} was rich in CaO and the lower one L\textsubscript{1} was rich in Fe\textsubscript{t}O.

Figure 3(b) shows typical examples of iron and magnesium images observed by EPMA at slag-crucible interface. It was monitored that Fe\textsubscript{t}O diffused into MgO crucible, and (Mg,Fe)O solid solution was formed at the interface. (Mg,Fe)O solid solution and slag at the interface were presumed to be in local equilibrium, and the composition of (Mg,Fe)O solid solution formed at the slag interface was identical.

Figure 4 shows phase equilibria among (Mg,Fe)O solid solution and the two-liquids in CaO-MgO-Fe\textsubscript{t}O-P\textsubscript{2}O\textsubscript{5} quaternary system at steelmaking temperatures. The triangles indicate relations among each equilibrium phase. The shaded triangles indicate that (Mg,Fe)O solid solution have higher Fe\textsubscript{t}O contents allowing Fe\textsubscript{t}O to diffuse into MgO refractories more easily.

Figure 5 shows low concentrations of CaO contained in (Mg,Fe)O solid solution equilibrated with two-liquid CaO-MgO-Fe\textsubscript{t}O-P\textsubscript{2}O\textsubscript{5} slag at steelmaking temperatures. CaO content increased with increase of MgO content in (Mg,Fe)O as shown in Figure 5. CaO content in (Mg,Fe)O increased at lower temperature.

When slag contains Fe\textsubscript{t}O, reaction of oxygen and its equilibrium constant, \( K \), can be represented by Equations. [2] and [3], respectively.

\[
\dot{\text{Fe}}(\text{g}) + \text{O} = \text{Fe}_\text{t}O(\text{in liq. slag})
\]

\[
K = \frac{a_{\text{Fe}_\text{t}O}}{a_{\text{Fe}} a_{\text{O}}}.
\]
where $a_{FeO(1)}$ denotes Raoultian activity of $FeO$ of which reference state is pure liquid $FeO$ equilibrated with iron, and $a_0$ is Henrian activity of oxygen in 1mass% standard state. As pure liquid iron is taken as a standard state of iron, the activity of iron, $a_0$, is considered to be unity because impurity levels in the molten iron are low. Hence, $a_{FeO(1)}$ can be calculated by

$$a_{FeO(1)} = a_0 / [a_0]_{sat}. \quad [4]$$

where $[a_0]_{sat}$ denotes activity of oxygen in iron equilibrated with pure $FeO$, and $[a_0]_{sat}$ and $[a_0]$ can be calculated using oxygen solubility in pure liquid iron and the related interaction

$$
\log [mass\%O]_{sat} = -6320/T + 2.734 \quad [5]
$$

$$
\log f^O_O = (-1750/T + 2.734)[mass\%O] \quad [6]
$$

$$
\log f^P_P = 0.006[mass\%P] \quad [7]
$$

To determine the activity of $FeO$ in $(Mg,Fe)O$ solid solution, standard state of activity of $FeO$ described above is converted from liquid to solid state by Equations [8] and [9].

$$
[Fe,O(O(s)) = [Fe,O(1)] \quad [8]
$$

$$
\Delta G^0_{FeO} = 33470 - 20.30 T / J \quad [9]
$$

The activity of $FeO$ in $(Mg,Fe)O$ solid solution is shown in Figure 6. The value of activity of $FeO$ exhibits ideally in this work. Hahn and Muan also measured activity of $FeO$ in $(Mg,Fe)O$ solid solution by chemical equilibration method, and their values exhibits positive deviation from ideality. The reason of this discrepancy in activity of $FeO$ in $(Mg,Fe)O$ solid solution is not clear.

Conclusions

Metal-slag equilibration experiment was carried out using magnesia crucible, and compositions of $(Mg,Fe)O$ in contact with two liquid $CaO-MgO-FeO-P2O5$ slags were measured at steelmaking temperatures. $(Mg,Fe)O$ compositions changed significantly according to compositions of two-liquid $CaO-MgO-FeO-P2O5$ slags.
References


Figure 6. Activity of FeO in (Mg,Fe)O