TAMURA, T. and HINO, M. Interactions of two-liquid CaO-MgO-Fe_tO-P_2O_5 slag with MgO refractories. *VII International Conference on Molten Slags Fluxes and Salts,* The South African Institute of Mining and Metallurgy, 2004.

Interactions of two-liquid CaO-MgO-Fe_tO-P_2O_5 slag with MgO refractories

T. TAMURA and M. HINO
Graduate School of Engineering, Tohoko University, Japan

It is known that the CaO-Fe_tO-P_2O_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_tO and CaO and high amount of P_2O_5. The phosphorus distribution ratio between the two-liquid slag and molten steel was confirmed to be higher than that between $CaO_{sat.}$-Fe_tO-P_2O_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_tO-P_2O_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].

$$2\,[P] + 5Fe_tO = \left(P_2O_5\right) + 5t\,Fe \qquad [1]$$

Thereby, the dephosphorized slag consists of iron oxide which oxidizes phosphorus, phosphorus pentoxide which is a dephosphorization product, and lime which stabilizes P_2O_5 in slag. CaO-Fe_tO-P_2O_5 phase diagram was proposed by Muan and Osborn1) based on the work of Trömel *et al.*2–3).

In general, high values of both Fe_tO 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_tO and CaO are high in the two-liquid phase region in CaO-Fe_tO-P_2O_5 ternary system, because phase L_1 which is rich in iron oxide coexists with liquid L_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_tO form a complete solid solution. If a liquid miscibility gap exists in the CaO-Fe_tO-P_2O_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_tO-P_2O_5 quaternary system was estimated by Trömel *et al.*4) and MgO solubility in the system was measured by Nagabayashi *et al.*5) at steelmaking temperatures. It had been unknown, however, whether a miscibility gap exists or not in the CaO-MgO-Fe_tO-P_2O_5 system on the condition of (Mg,Fe)O saturation as shown in Figure 1. In our previous work6) using a chemical equilibrium technique, it was determined that a two-liquid region existed in CaO-MgO-Fe_tO-P_2O_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 $CaO_{sat.}$-Fe_tO-P_2O_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

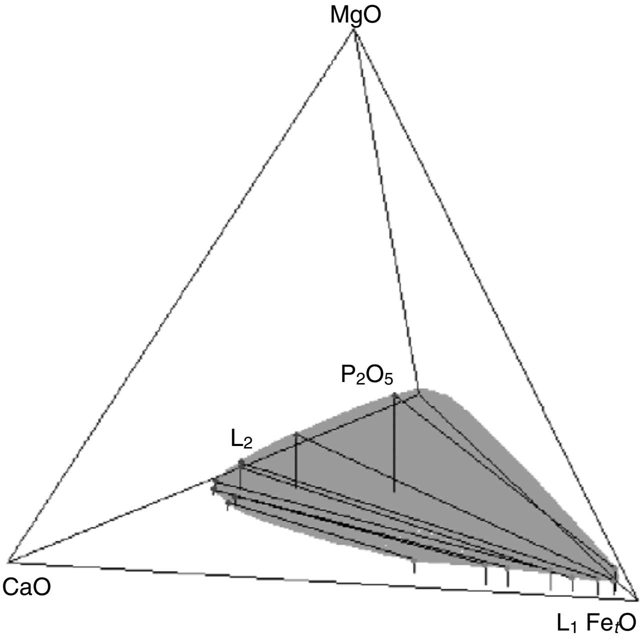

Figure 1. Two-liquid region saturated with (Mg,Fe)O in CaO-MgO-Fe_tO-P_2O_5 system at 1873 K[6]

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_tO-P_2O_5 slags at steelmaking temperatures are reported in the present study.

Experimental procedure

A vertical electric resistance furnace with $LaCrO_4$ heating elements was used (Figure 2). The reaction tube was of alumina, 60 mm in ID and 1000 mm length. CaO and Fe_tO were prepared by calcining $CaCO_3$ in a Pt crucible at 1473K for 10 hours in air and sintering the mixture of electrolytic iron and Fe_2O_3 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_tO-P_2O_5 quaternary slag was prepared from CaO, MgO, Fe_tO, $3CaO\cdot P_2O_5$, $CaHPO_4\cdot\cdot 2H_2O$ and $(NH_4)_2HPO_4$.

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^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_2 was rich in CaO and the lower one L_1 was rich in Fe_tO.

Figure 3(b) shows typical examples of iron and magnesium images observed by EPMA at slag-crucible interface. It was monitored that Fe_tO 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_tO-P_2O_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_tO contents allowing Fe_tO 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_tO-P_2O_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_tO, reaction of oxygen and its equilibrium constant, K, can be represented by Equations. [2] and [3], respectively.

$$tFe(l) + \underline{O} = Fe_tO(\text{in liq. slag}) \qquad [2]$$

$$K = a_{Fe_tO(l)} / a^t_{Fe} \cdot a_O \qquad [3]$$

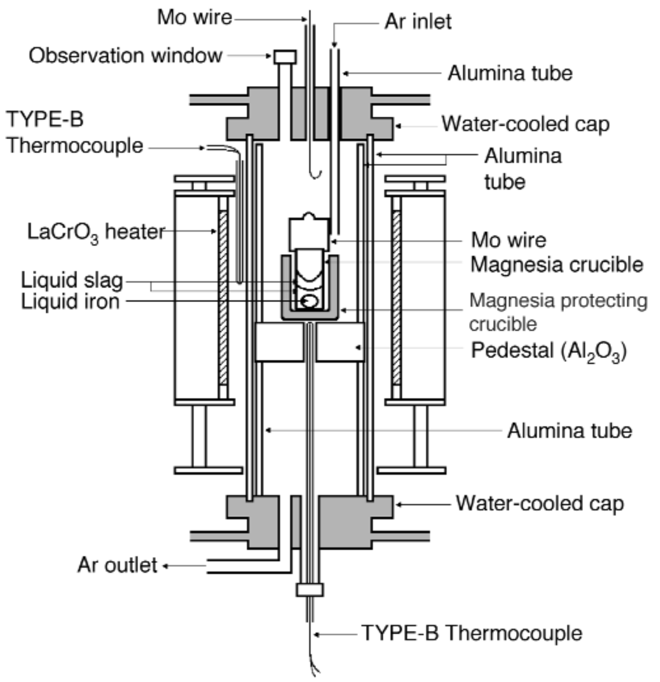

Figure 2. Arrangement of reaction chamber

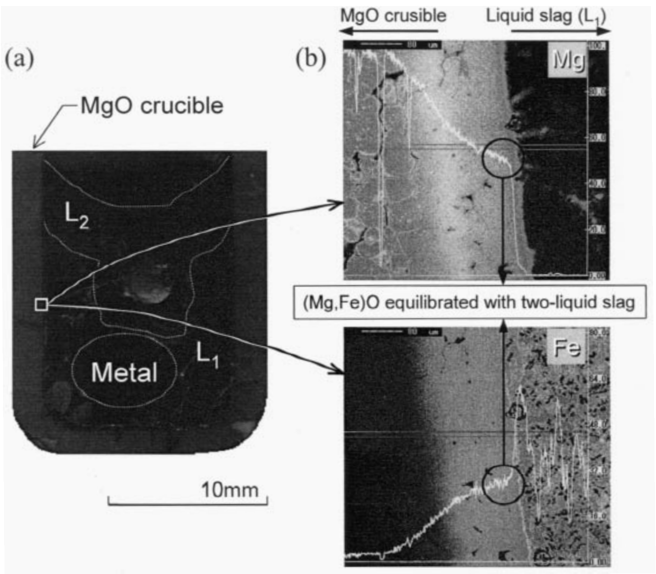

Figure 3. (a) Cross-section of a sample (b) the concentration profiles of Fe and Mg at MgO crucible/liquid slag interface

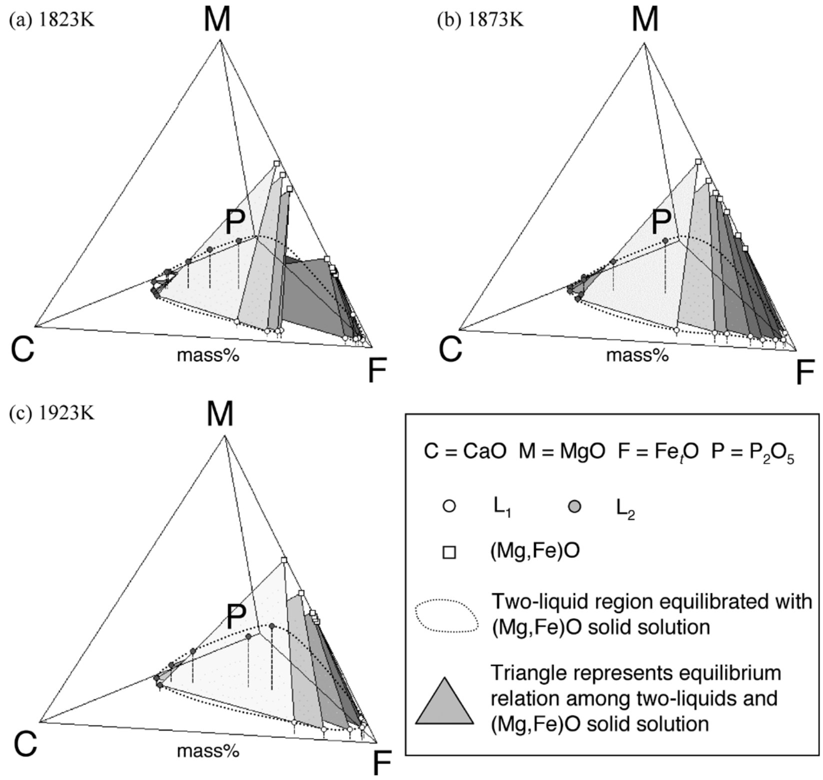

Figure 4. Phase equilibria of two-liquids and (Mg,Fe)O solid solution in CaO-MgO-Fe$_t$O-P$_2$O$_5$ system at steelmaking temperatures

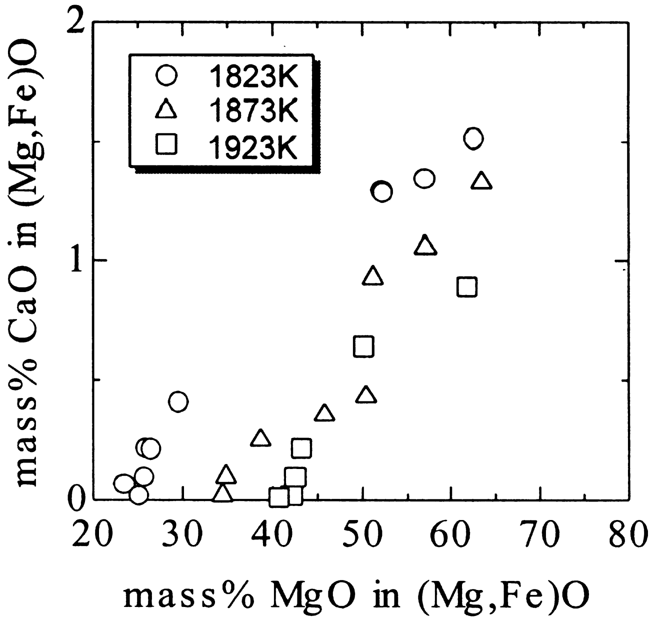

Figure 5. CaO concentration in (Mg,Fe)O solid solution in contact with two-liquid CaO-MgO-Fe$_t$O-P$_2$O$_5$ slag at steelmaking temperatures

where $a_{Fe_tO(1)}$ denotes Raoultian activity of Fe$_t$O of which reference state is pure liquid Fe$_t$O equilibrated with iron, and a_O 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_{Fe}, is considered to be unity because impurity levels in the molten iron are low. Hence, $a_{Fe_tO(1)}$ can be calculated by

$$a_{Fe_tO(1)} = a_O / [a_O]_{sat.} \qquad [4]$$

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

$$\log[\text{mass\%O}]_{sat.} = -6320/T + 2.734^{7)} \qquad [5]$$

$$\log f_O^O = (-1750/T + 2.734)[\text{mass\%O}]^{8)} \qquad [6]$$

$$\log f_O^P = 0.006[\text{mass\%P}]^{9)} \qquad [7]$$

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

$$Fe_tO(s) = Fe_tO(1) \qquad [8]$$

$$\Delta G^o_{(8)} = 33470 - 20.30\ T \quad / J^{10)} \qquad [9]$$

The activity of Fe$_t$O in (Mg,Fe)O solid solution is shown in Figure 6. The value of activity of Fe$_t$O exhibits ideally in this work. Hahn and Muan**11**) also measured activity of Fe$_t$O 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 Fe$_t$O 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-Fe$_t$O-P$_2$O$_5$ slags were measured at steelmaking temperatures. (Mg,Fe)O compositions changed significantly according to compositions of two-liquid CaO-MgO-Fe$_t$O-P$_2$O$_5$ slags.

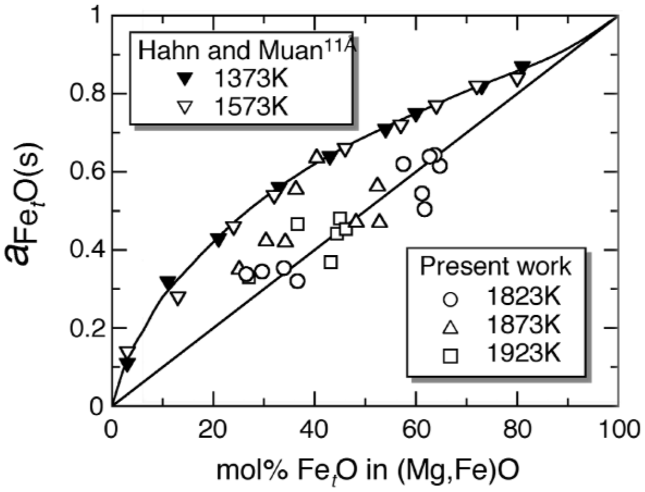

Figure 6. Activity of Fe_tO in (Mg,Fe)O

References

1. MUAN, A. and OSBORN, E.F. Phase equilibria among oxides in steelmaking, Addison-Wesley 1965, p. 122.
2. TRÖMEL, G., FIX, W., and FRITZE, H.W. Archiv. Eisenhüttenwes., 32, 1961, p. 353.
3. TRÖMEL, G. and FRITZE, H.W. Archiv Eisenhüttenwesen., 30, 1959, p. 461.
4. TRÖMEL, G., FIX, W., and KAUP, K. Archiv. Eisenhüttenwes., 38, 1967, p. 595.
5. NAGABAYASHI, R., HINO, M., and BAN-YA, S. Tetsu-to-Hagané, 74, 1988, p. 1577.
6. TAMURA, T., NAGASAKA, T., and HINO, M. ISSTech Conference Proceedings, 2003, p. 943.
7. *Steelmaking Data Sourcebook*, Part 1, ed. by The 19th Committee on Steelmaking, The Japan Society for the Promotion of Science, Gordon and Breach Science Pub., New York, 1988.
8. TAYLOR, C.R. and CHIPMAN, J. Trans. *AIME*, 154, 1943, p. 228.
9. BAN-YA, S. and MATOBA, S. Tetsu-to-Hagané, 49, 1963, p. 753.
10. SCHENCK, H., SCHMAHL, N.G., and BISWAS, A.K. Archiv. Eisenhüttenwes., 28, 1957, p. 517.
11. HAHN, W.C. Jr. and MUAN, A. *Transactions of the Metallurgical Society of AIME*, 224, 1962, p. 416.