

EQUILIBRIUM BETWEEN CaO-SATURATED Fe_1O -CaO- P_2O_5 - CaF_2 SLAG AND LIQUID IRON

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Synopsis: Equilibrium between molten Fe_1O -CaO- P_2O_5 - CaF_2 slags and liquid iron were studied under a CaO-saturated condition at 1873K to clarify a role of CaF_2 in the molten slags. An increase of CaF_2 in the slags containing 10mass% P_2O_5 , increases the activity coefficient of iron oxide, γ_{Fe_1O} and also decreases the $\gamma_{P_2O_5}$ as follows,

$$\log \gamma_{P_2O_5} = 2.52N_{Fe_1O} - 1.32N_{CaF_2} - 19.4$$

Under a CaO-saturated condition, CaF_2 is effective to dephosphorization of liquid iron and most suitable slags for the dephosphorization of iron are those containing 40-50mass% CaF_2 .

Key words: CaO-saturated slag, dephosphorization, effect of CaF_2 , $\gamma_{P_2O_5}$, γ_{Fe_1O} , solubility of CaO, oxygen distribution.

1. Introduction

Calcium fluoride (CaF_2) has been used as an additive to promote slagging of fluxes in steelmaking processes. However, a role of CaF_2 in fluxes is not entirely clear yet. Some reports showed that the addition of CaF_2 promoted dephosphorization of liquid iron, but others didn't so, in other words, the CaF_2 helps only to decrease slag viscosity and hence its addition results in increase of the dephosphorization rate of steel.

In the present work, we measured equilibria of oxygen and phosphorus between Fe_1O -CaO- P_2O_5 - CaF_2 slags and iron under a CaO-saturated condition at 1873K to clarify a role of CaF_2 in the molten slags.

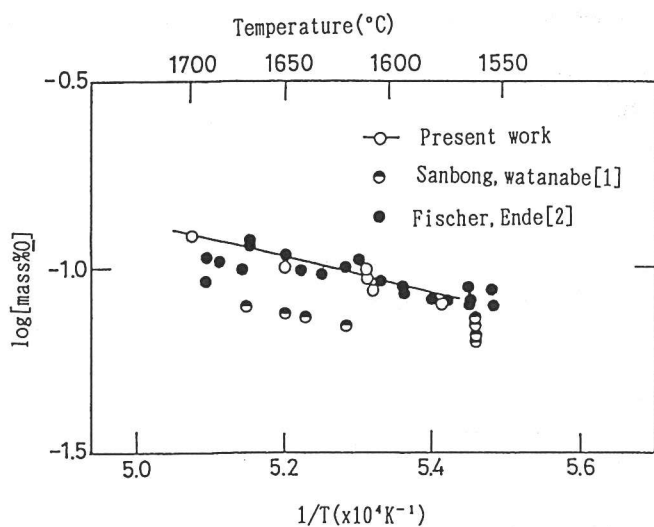


Fig.1 Change of oxygen content in liquid iron equilibrated with CaO-saturated iron oxide melt with temperature.

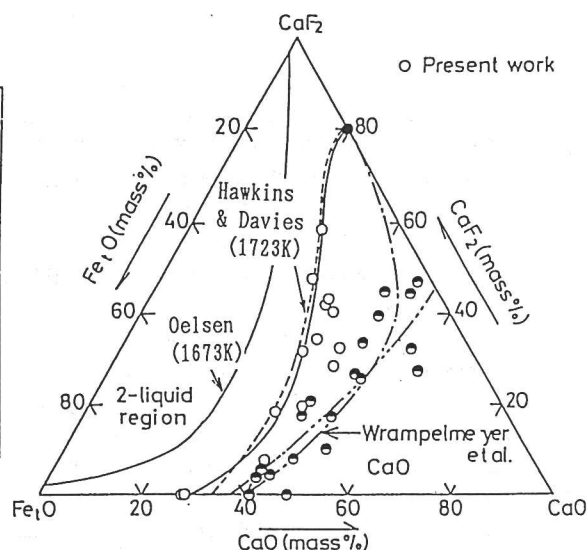


Fig.2 Solubility line of CaO in Fe_1O -CaO- CaF_2 system equilibrated with liquid iron at 1873K.

2. Experimental procedures

About 20 to 25 g of iron sample and 10g of slag sample were melted in a sintered CaO crucible under Argon. A molybdenum crucible was used a susceptor for a induction heating furnace, that provided for a uniform temperature in the CaO crucible. Metal samples are electrolytic iron for phosphorization run and an iron-0.03mass%P alloy for dephosphorization run. Slag samples were prepared by Ar-arc-melting of mixtures of chemical reagents. Usually, more than 30min. was required to established the slag-metal equilibria.

3. Oxygen content in liquid iron equilibrated with CaO-saturated Fe_tO -CaO slag.

Figure 1 shows oxygen content in liquid iron equilibrated with CaO-saturated iron oxide melt. The results are as follows,

$$\log[\%O] = -5240/T + 1.743 \quad (1848 < T/K < 1933) \quad (1)$$

They were slightly higher than those reported by Sanbongi and Watanabe[1], but are in good agreement with those by Fischer and Ende[2].

4. Solubility of CaO in Fe_tO -CaO- CaF_2 melt at 1873K.

Solubility line of CaO in the system, Fe_tO -CaO- CaF_2 is shown in Fig. 2. Our result is fairly far from that reported by Wrampelmeyer et al.[3], especially in a higher CaF_2 region, but it is similar to that equilibrated with solid iron at 1723K reported by Hawkins and Davies[4]. Phase diagrams of the systems, CaO- Fe_tO and CaO- CaF_2 [5,6] indicate that by means of chemical analysis, it is very difficult to separate a suspended lime in the slag melts, namely exfoliated lime, from that crystallizing out from melts during the solidification. Although a very dense lime crucible we used, EDX-analysis of solidified slags showed that Ca in samples obtained near the crucible wall, was higher than that far from the wall. This suggests existence of the suspended CaO near the crucible wall, and hence slag compositions were determined for samples obtained from the central part of the solidified slag by chemical analysis, even if the slags were apparently seemed to be uniform.

5. Oxygen content in liquid iron equilibrated with molten Fe_tO - $CaO_{sat.}$ - CaF_2 slag at 1873K.

Figure 3 shows oxygen content in liquid iron equilibrated with Fe_tO - $CaO_{sat.}$ - CaF_2 slags at 1873K as a function of $F/(Fe+F)$ mass ratio, because solubility line of the CaO by Wrampelmeyer et al.[3] is differ from ours, as stated above. Activity of Fe_tO , a_{Fe_tO} in the slags (referred to iron saturated pure iron oxide) are calculated from the oxygen content in

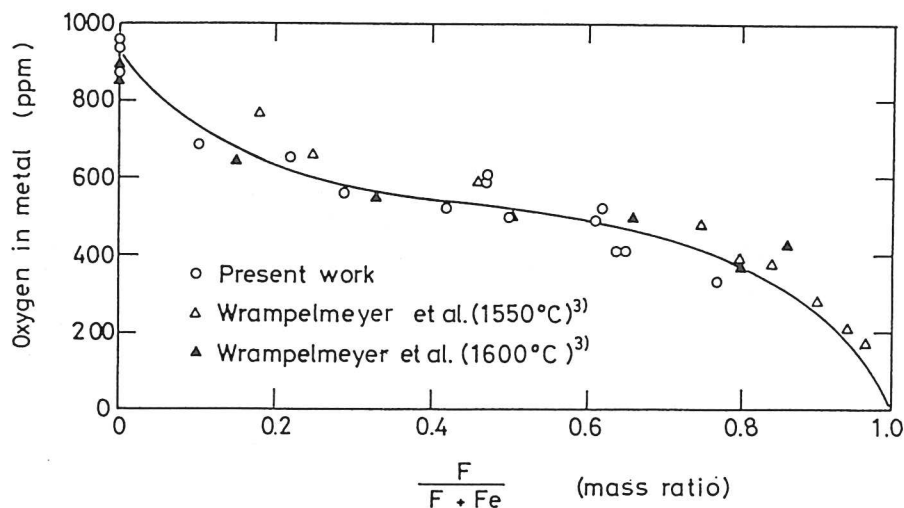


Fig.3 Oxygen content in iron equilibrated with Fe_tO - $CaO_{sat.}$ - CaF_2 slag at 1873K as a function of the mass ratio, $F/(Fe+F)$.

combination with thermo-chemical data[7,8,9] and is shown in Fig.4. The Wrampelmeyer's results are in fairly good agreement with ours. The figure also shows those reported by Iwase et al.[10] and Kay et al[11]. using different method at lower temperature, which are extrapolated to 1873K by the Masson's method[12]. The activity coefficient of Fe_tO , γ_{Fe_tO} in the CaO-saturated melts is shown in Fig. 5. It is concluded that CaF_2 in the melts contributes to increase the γ_{Fe_tO} .

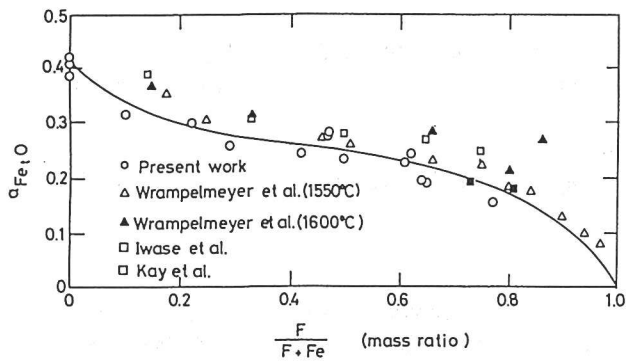


Fig.4 Activity of iron oxide, a_{Fe_tO} in $Fe_tO-CaO_{sat.}-CaF_2$ slag saturated with iron at 1873K.

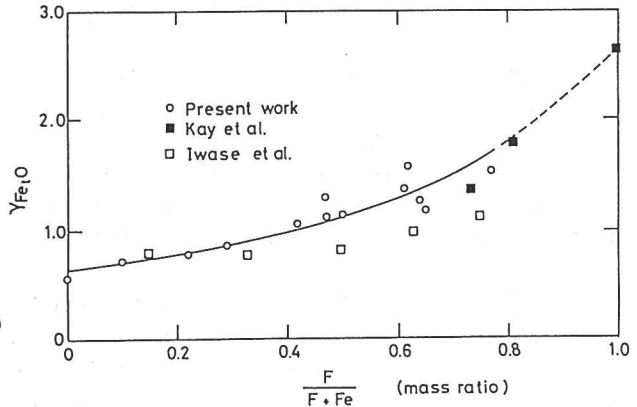


Fig.5 Activity Coefficient of iron oxide, γ_{Fe_tO} in $Fe_tO-CaO_{sat.}-CaF_2$ slag saturated with iron at 1873K.

6. Equilibrium phosphorus and oxygen content between liquid iron and $Fe_tO-CaO_{sat.}-P_2O_5-CaF_2$ slags at 1873K.

Figures 6 and 7 shows O and P contents in irons equilibrated with CaF_2 -free $Fe_tO-CaO_{sat.}-P_2O_5$ slags at 1873K. Solid and open circles in the figure are from dephosphorization and phosphorization runs, respectively. Below 10mass% P_2O_5 , oxygen in the metals decreased and phosphorus in it increased with increasing the P_2O_5 content. However, above 10mass% P_2O_5 , effect of P_2O_5 in the slags on the oxygen and phosphorus became small.

Effects of CaF_2 in slags containing 10mass% P_2O_5 on equilibrium O and P in metals are shown in Fig.8 and Fig.9. Under CaO saturation, increase of CaF_2 means decrease of Fe_tO in slags. These figures suggest that increase of CaF_2 contribute to decrease phosphorous in metals, instead of decrease of oxidation power of the slags.

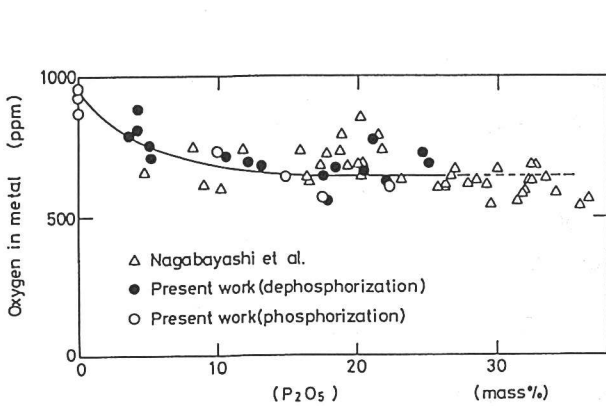


Fig.6 Oxygen content in liquid iron equilibrated with $Fe_tO-CaO_{sat.}-P_2O_5$ slag at 1873K.

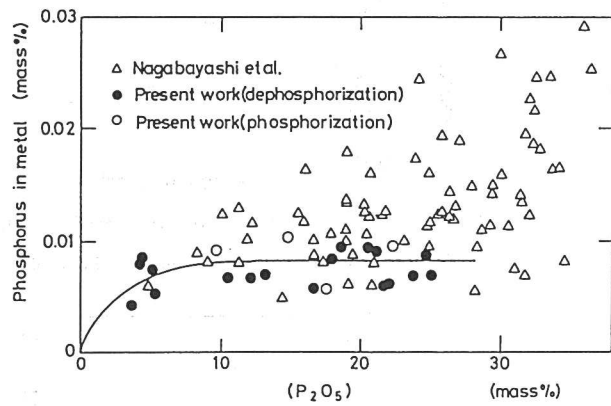


Fig.7 Phosphorus content in liquid iron equilibrated with $Fe_tO-CaO_{sat.}-P_2O_5$ slag at 1873K.

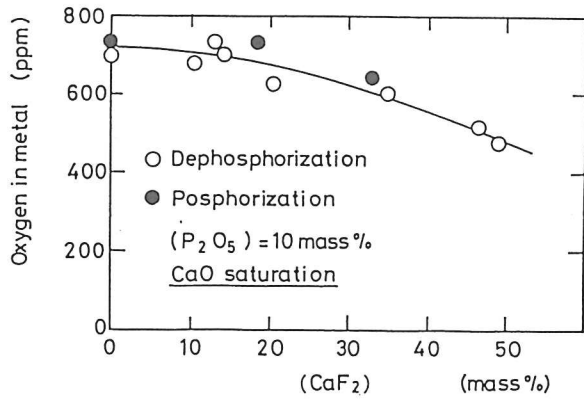


Fig. 8 Effect of CaF_2 content in $\text{Fe}_{10}\text{-CaO}_{\text{sat.}}\text{-10mass\%P}_2\text{O}_5\text{-CaF}_2$ slags on oxygen in iron.

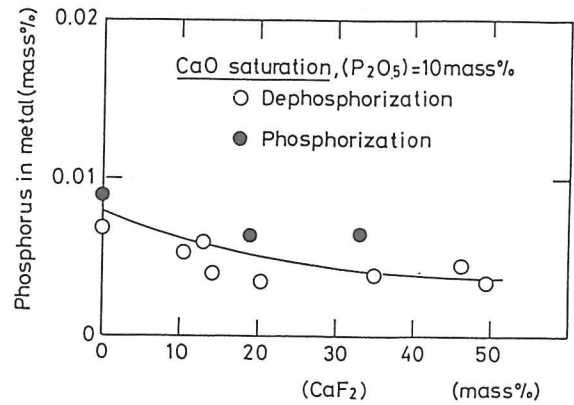


Fig. 9 Effect of CaF_2 content in $\text{Fe}_{10}\text{-CaO}_{\text{sat.}}\text{-10mass\%P}_2\text{O}_5\text{-CaF}_2$ slags on phosphorus in iron.

From these results, $a_{\text{Fe}_2\text{O}}$ in the slags was calculated and the results are shown in Fig. 10. The $\gamma_{\text{Fe}_2\text{O}}$ increases with increasing of CaF_2 content in the slags containing 10mass% P_2O_5 as well as in those of P_2O_5 -free $\text{Fe}_{10}\text{-CaO}(\text{sat.})\text{-CaF}_2$ system.

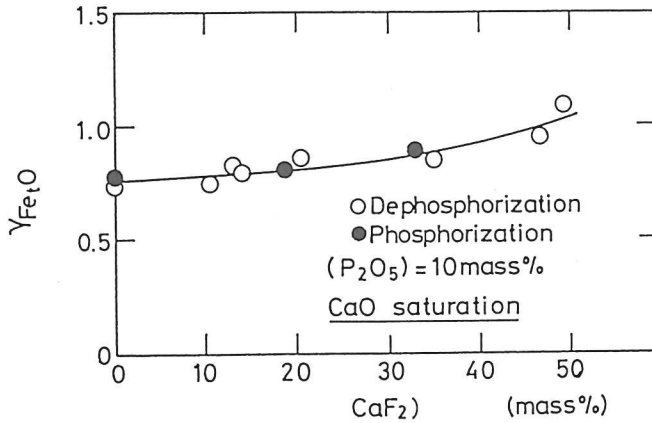


Fig. 10 Activity Coefficient of iron oxide, $\gamma_{\text{Fe}_2\text{O}}$ in $\text{Fe}_{10}\text{-CaO}_{\text{sat.}}\text{-10mass\%P}_2\text{O}_5\text{-CaF}_2$ slags saturated with iron at 1873K.

Combined our results with equilibrium constant of the reaction, $5\text{O}+2\text{P}=(\text{P}_2\text{O}_5)$ by Turkdogan[11], the $\gamma_{\text{P}_2\text{O}_5}$ in the slags was calculated. Fig. 11 shows that the higher P_2O_5 in slags is (that means decrease of Fe_{10} content in slags), lower the $\gamma_{\text{P}_2\text{O}_5}$ in the slags is. Fig. 12 shows that at a constant P_2O_5 content of 10mass%, an addition of CaF_2 in slags contributes to decrease the $\gamma_{\text{P}_2\text{O}_5}$, which are as follows,

$$\log \gamma_{\text{P}_2\text{O}_5} = 2.52N_{\text{Fe}_2\text{O}} - 1.32N_{\text{CaF}_2} - 19.4 \quad (2)$$

((P_2O_5)=10mass%, at CaO saturation at 1873K)

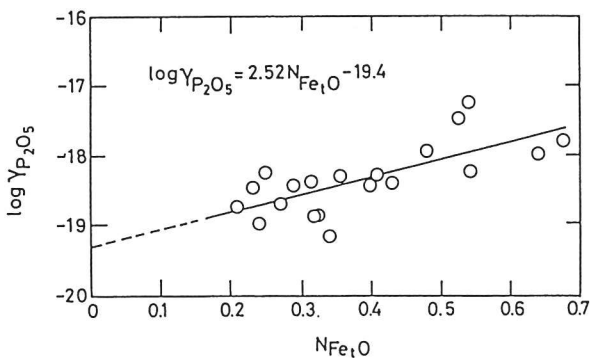


Fig. 11 Relation between $N_{\text{Fe}_2\text{O}}$ and $\log \gamma_{\text{P}_2\text{O}_5}$ in $\text{Fe}_{10}\text{-CaO}_{\text{sat.}}\text{-CaF}_2$ slags at 1873K.

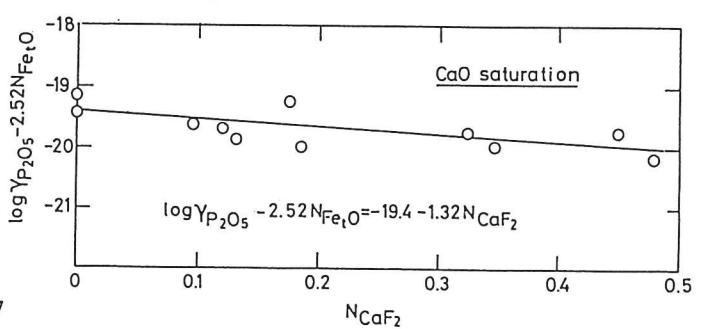


Fig. 12 Relation between $N_{\text{Fe}_2\text{O}}$ and $\log \gamma_{\text{P}_2\text{O}_5}$ in $\text{Fe}_{10}\text{-CaO}_{\text{sat.}}\text{-10mass\%P}_2\text{O}_5\text{-CaF}_2$ slags at 1873K.

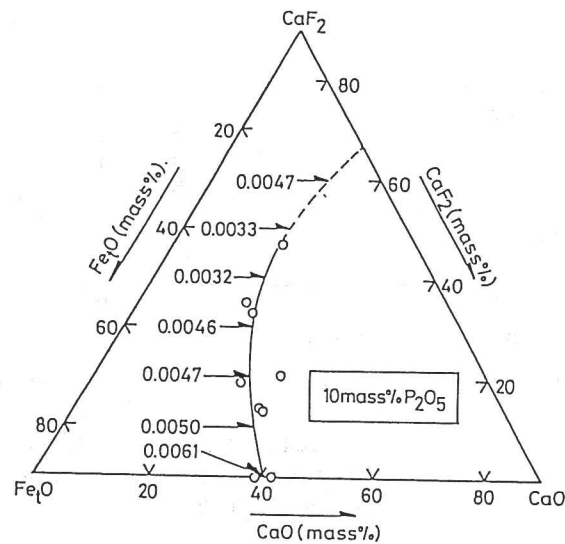


Fig.13 Calculated phosphorus content in liquid iron equilibrated with Fe₀-CaO...-10mass%P₂O₅-CaF₂ slags at 1873K.

Combined this equation with $\gamma_{\text{Fe}_t\text{O}}$, shown in Fig.10, we calculate phosphorus content in metals equilibrated with slags containing 10mass%P₂O₅ along the line of lime saturation, that is shown in Fig.13. From the figure, we can choose the most suitable composition of Fe_tO-CaOsat.-10mass%P₂O₅-CaF₂ slags for the dephosphorization, that contains 40-50mass%CaF₂.

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