4th International Conference on Molten Slags and Fluxes, 1992, Sendai, ISIJ

THE REFINING OF STEEL WITH CALCIUM-BASED SLAGS

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Synopsis: Calcium and calcium-calcium halide melts have been considered for the dephosphorization of high chromium steels and for the removal of tramp elements introduced with contaminated scrap. The thermodynamic behavior of calcium-based slags and their interaction with liquid iron alloys are reviewed.

Key words: Calcium-based slags, dephosphorization, high chromium steels, tramp elements.

Calcium-based slags have been considered for the dephosphorization of high chromium steels and for the removal of tramp elements introduced with contaminated scrap. The phase diagram for the system Ca-$Ca_{1.5}P$, as determined by Kohler and Engell [1], is shown in Fig. 1. The data were obtained by differential thermal analysis using iron crucibles, and hence are limited to temperatures less than 1400°C The activity coefficients of $Ca_{1.5}P$ calculated from the liquidus line in Fig. 1 are fitted by

$$\ln\gamma_{Ca_{1.5}P} = \frac{10720}{T} - 4.31 \tag{1}$$

The free energy change for the reaction

$$1.5Ca_{(l)} + P_{(1wt\%\ in\ Fe)} = Ca_{1.5}P_{(s)}$$

has been determined by Min and Sano to be [2]

$$\Delta G^\circ = -204{,}730 + 91.0T\ \text{J} \tag{2}$$

Kitamura et al [3] conducted a study of the dephosphorization of high chromium steels with calcium metal and one of their melts will be considered. They found that the addition of 1 wt% Ca (1 part by weight of Ca to 100 parts by weight of steel) to a melt of composition 2.26 wt% C, 0.048 wt% P and 23.7 wt% Cr (their alloy *G*) at 1420°C decreased the phosphorus content to 0.018 wt%. A mass balance and the requirements of equilibrium give $\gamma_{Ca_{1.5}P} = 5.5$ and $X_{Ca_{1.5}P} = 0.04$ in the calcium slag. This value of $\gamma_{Ca_{1.5}P}$ is in good agreement with the value of 7.5 obtained from Eq. (1) at 1420°C. Fig. 2 shows the calculated variation of the final phosphorus content of a melt containing 23.7 wt% Cr with carbon content of the melt for 1 wt% addition of Ca to the melt at 1420°C. The initial decrease in the final phosphorus content with increasing carbon content, from *A* to *B* is caused by the influence of carbon on the activity coefficient of phosphorus in the melt, and at 2.16 wt% C ($a_{C(1wt\%)} = 0.78$), the activity of calcium carbide reaches unity and hence solid CaC_2 is precipitated in the calcium slag.

The variations of wt% C and partial pressure of Ca for CaC_2 in contact with an Fe-C alloy at 1600°C are shown in Fig. 3. Contact between CaC_2 and an Fe-C melt containing less than 0.79 wt% C causes the CaC_2 to decompose to form liquid calcium at its saturated vapor pressure of 1.41 atm and carbon in iron at $a_{C(gr)} = 0.3$ (wt% C = 0.79). If the initial carbon content of the Fe-C melt is greater than 0.79 wt% calcium vapor is produced at a pressure lower than the saturated value and the carbon content of the melt increases with decreasing vapor pressure of calcium as shown in Fig. 3. Thus, in Fig. 2, when the carbon content of the Fe-Cr melt is greater than 2.16 wt% the metallic Ca phase disappears and solid CaC_2 is formed. With increasing carbon content in the Fe-Cr melt the activity of Ca decreases and hence the degree of dephosphorization of the melt decreases. Presumably the phosphorus which has been removed from the alloy occurs in solid solution in the CaC_2. The portion of the curve *BC* in Fig. 2 was drawn using the experimental data of Kitamura et al. Behavior similar to that shown in Fig. 2 was observed by Katayama et al [4] who dephosphorized 100 kg melts of 18% Cr steel using CaF_2-CaC_2 fluxes. Their results are shown in Fig. 4, which shows that maximum dephosphorization is attained when the initial carbon content of the steel melt is about 1.2 wt%.

Leal et al [5] studied the dephosphorization of 15 kg melts of chromium steel by injecting CaC_2 in an Ar-3%H_2 carrier gas. In this case dephosphorization proceeds according to

$$1.5CaC_{2(s)} + P_{(1wt\%)} = Ca_{1.5}P_{(s)} + 3C_{(1wt\%)}$$

for which, at 1600°C,

$$K_{1873} = \frac{a^3_{C(1wt\%)}}{a_{P(1wt\%)}} = 11.1$$

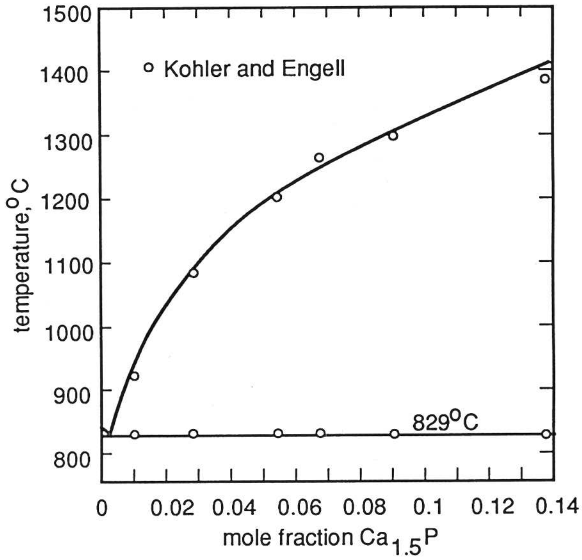

Fig. 1. The calcium phosphide liquidus in the system Ca–$Ca_{1.5}P^{(1)}$.

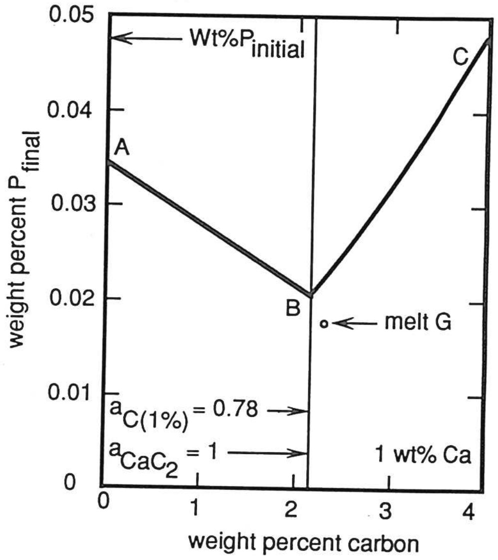

Fig. 2. The influence of carbon content on the dephosphorization of a melt containing 23.7 wt% Cr and an initial phosphorus 0.048 wt%.

or

$$\log a_{P(1wt\%)} = 3\log a_{C(1wt\%)} - 1.04 \tag{3}$$

Eq. (3) is shown in Fig. 5. During this process the CaC_2 in the carrier gas dissociates to form Ca vapor which acts as the dephosphorizing agent, forming solid $Ca_{1.5}P$ which rises to the surface with the bubbles. Leal et al used a CaO-CaF_2 slag cover on their melts, and, presumably, the $Ca_{1.5}P$ dissolved in this slag. Dephosphorization requires that the initial activity of C in the melt be less than $(11.1a_P)^{0.33}$ where a_P is the initial activity of P in the melt. Fig. 5 shows the calculated variations of wt% P with wt% C for Fe-C-P melts and for melts containing 10wt% Cr at 1600°C. The major effect of Cr is its influence on the activity of C. Leal et al found that the extent of dephosphorization achieved increases with increasing amount of CaC_2 injected (up to 29 kg CaC_2 per tonne), decreasing initial carbon content and increasing chromium content. Although the influences of C and Cr can be explained by thermodynamics, the cause of the variation of the extent of dephosphorization with rate of injection of CaC_2 is not apparent. The phosphorus content of a melt of 0.53 wt%C and 12 wt%Cr, injected with CaC_2 at the rate of 29 kg/tonne of metal decreased from 0.03 wt% to 0.006 wt% in 12 mins. Assuming that $Ca_{1.5}P$ is produced at unit activity, the calculated equilibrium phosphorus content is 0.00086 wt%. It was found that the degree of dephosphorization of melts contained in magnesia crucibles was three times greater than that achieved with alumina crucibles, which can only be due to the relative influences of dissolved MgO and Al_2O_3 on the activity of Ca_3P_2 in the CaO-CaF_2 slag.

Laboratory study of Ca-based slags is made difficult by the problem of selecting a container material. For example CaC_2 equilibrated with carbon-saturated iron at 1600°C exerts a vapor pressure of calcium of 1.25×10^{-3} atm. At this pressure calcium vapor destroys both alumina and magnesia crucibles. Kohler and Engell [1] contained Ca-based slags in a CaO crucible at 1600°C and an argon pressure of 10 bars and obtained the activities of calcium by measuring the solubility of Ca in liquid iron. Their results are shown in Fig. 6. Matsumitsu et al [6] measured the activity of $Ca_{1.5}P$ in Ca–CaF_2 and Ca–$CaCl_2$ melts at 1350°, 1400° and 1450°C by equilibrating the Ca-based melts with a Ca-Ag alloy, which fixed the activity of Ca, and equilibrating a thin iron foil (which picked up phosphorus) with the Ca-based melt. Some of their results are shown in Fig. 7. They determined that $\gamma_{Ca_{1.5}P} = 11$ in a Ca–CaF_2 slag of $a_{Ca} = 0.2$ at 1450°C and $\gamma_{Ca_{1.5}P} = 16.4$ in a Ca–CaF_2 slag of $a_{Ca} = 0.13$ at 1400°C. The corresponding values obtained from Eq. (1) are 6.8 and 9.9, which indicates that phosphorus is less soluble in Ca–CaF_2 melts than in calcium metal. The deposphorization of an Fe alloy with an initial phosphorus content of 0.05 wt% by a 1% addition of a Ca–CaF_2 flux of $a_{Ca} = 0.2$ at 1600°C and a 10% addition of the same flux at 1500°C is shown as a function of carbon and chromium contents in Fig. 8. The activity coefficient of P in the iron melt is increased by carbon and is decreased by chromium. The distribution of P between iron and CaO-saturated Ca-based slags measured at 1600°C by Kohler and Engell is shown in Fig. 9. Although the activity of Ca can be varied independently in a Ca-Ca_3P_2-Ca halide melt, in a Ca-Ca_3P_2 melt it is determined by the ratio of Ca to Fe and the amount of P in the system and Fig. 9 shows that (%P)/[%P] has a value of approximately 400 in CaO-saturated Ca–Ca_3P_2 at 1600°C. The calculated distribution ratio for a 10% addition of Ca to Fe at 1600°C using Matsumitsu's estimate of $\gamma_{Ca_{1.5}P} = 2$ decreases from 238 when a trace of P is present to 80 at saturation with calcium phosphide.

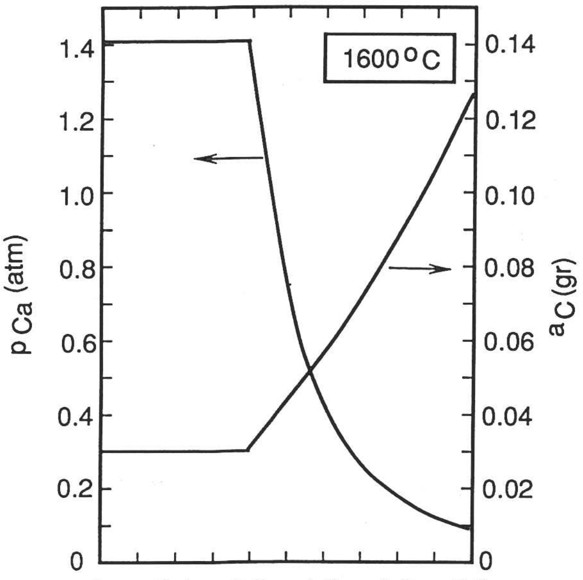

Fig. 3. The variations of the vapor pressure of calcium and the activity of carbon with carbon content in iron-carbon melts equilibrated with CaC_2 at 1600°C.

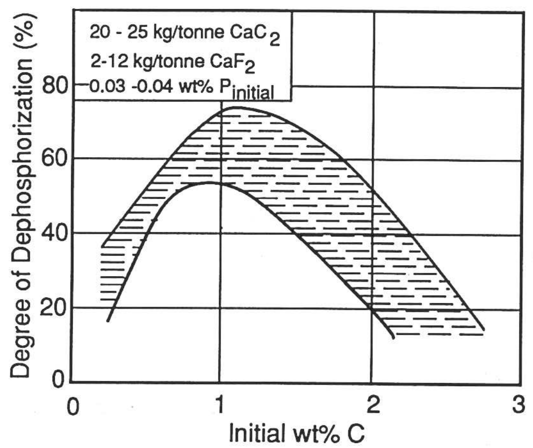

Fig. 4. The influence of initial carbon content on the dephosphorization of 18 wt% Cr steel by CaF_2–CaC_2 fluxes$^{(4)}$.

Knowledge of the removal of tramp elements such as Cu, Sn, and Pb from steel by treatment with Ca-based slags is not as advanced as that of removal of phosphorus. The partition of Sn between CaO-saturated Ca-based slags and liquid iron at 1600°C measured by Kohler and Engell is shown in Fig. 10. As is the case with P, the extent of the removal of Sn by Ca alone is determined by the mass ratio of Ca to Fe and to the amount of tin in the system. Fig. 10 shows a partition ratio of approximately 2000 for binary Ca-Sn slag, which means that a 10% addition of Ca to liquid iron containing 0.65 wt% Sn decreases the Sn content to 0.03 wt%. Kohler and Engell considered their results in terms of the equilibrium

$$2Ca + Sn = Ca_2Sn \tag{4}$$

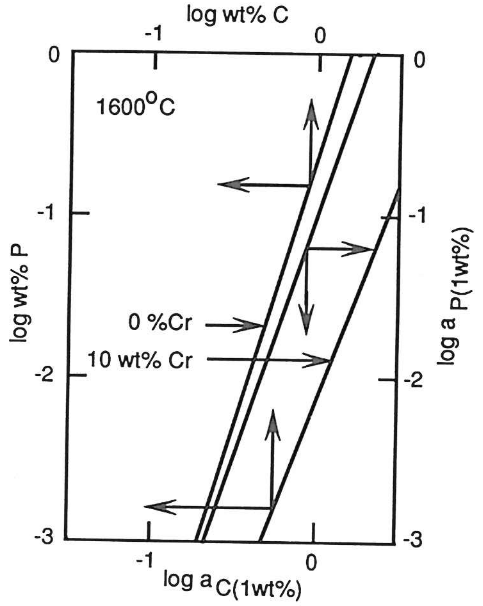

Fig. 5. The dependence of phosphorus content on the carbon content of liquid iron saturated with $Ca_{1.5}P$ and CaC_2 at 1600°C.

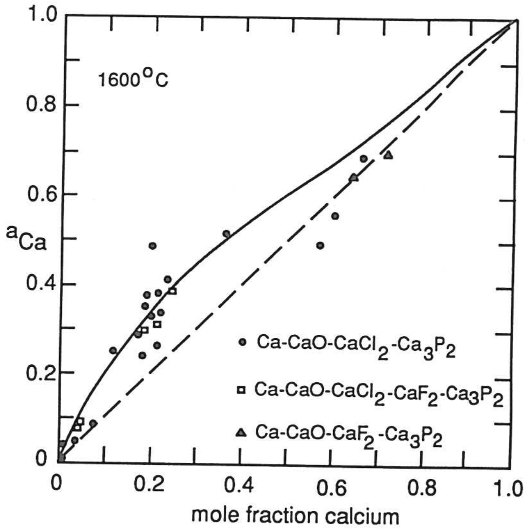

Fig. 6. The activity of Ca in CaO-saturated Ca- Ca halide melts at 1600°C[1].

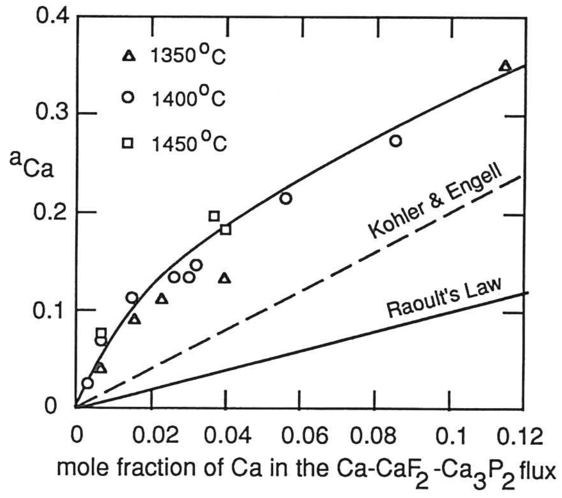

Fig. 7. The activity of Ca in $Ca\text{-}Ca_2\text{–}Ca_3P_2$ melts at 1350°, 1400° and 1450°C[6].

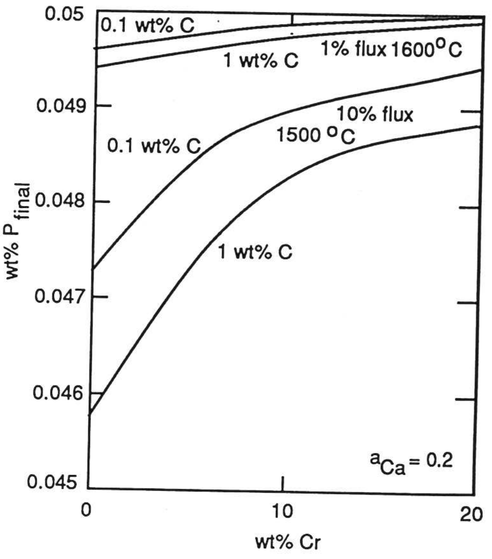

Fig. 8. Calculated dependence of the variation of the dephosphorization of a steel melt with an initial phosphorus content of 0.05 wt% on the carbon and chromium contents.

for which

$$K_4 = \frac{a_{\mathrm{Ca_2Sn}}}{a^2_{\mathrm{Ca}}\ a_{\mathrm{Sn}}}$$

Kohler and Engell showed that a log-log plot of weight percent of Sn in the iron against the weight percent of Ca in the iron produced a straight line with a slope of - 2.4, which, being close to the stoichiometric value of 2 in Eq. (4), lead them to suggest that Sn exists as Cu_2Sn clusters in Ca-Sn melts. As the activity of Ca_2Sn in a Ca-Sn melt is simply proportional to the product $a^2_{Ca}a_{Sn}$ it is not apparent that consideration of the removal of Sn from Fe by treatment with Ca in terms of Eq. (4) is useful. Equilibrium is achieved when calcium has been transfered to the iron and tin has been transfered to the calcium to the extents that the activities of each of Ca and Sn are the same in both phases.

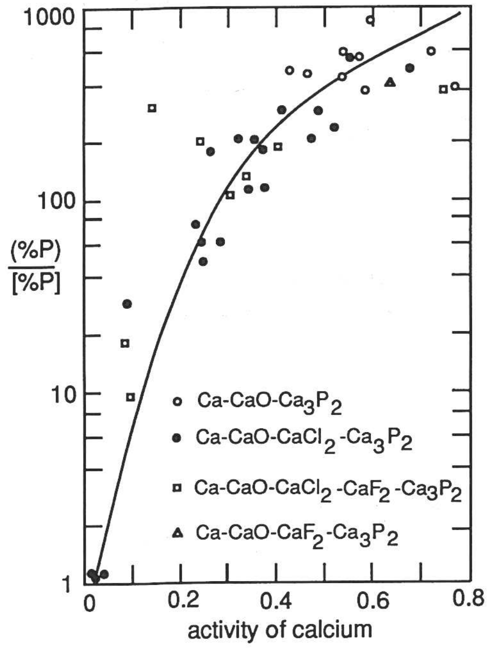

Fig. 9. The phosphorus distribution ratio between liquid iron and Ca-Ca halide slags as a function of the activity of calcium 1600°C(1).

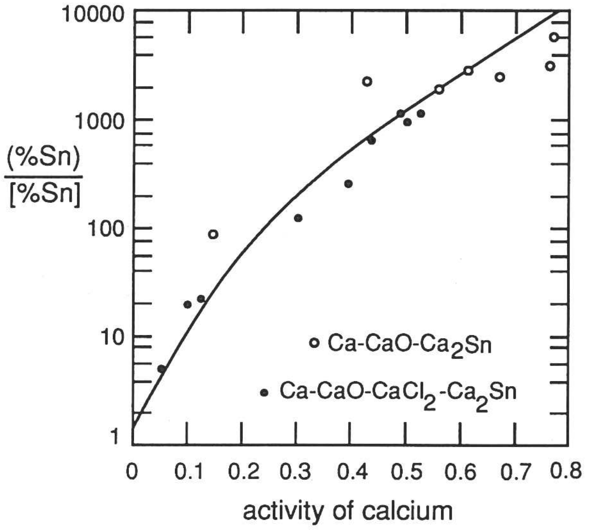

Fig. 10. The tin distribution ratio between liquid iron and calcium slags at 1600°C°.

Min and Sano [2] have measured the free energy of the reaction

$$2Ca_{(l)} + Sn_{(l)} = Ca_2Sn_{(s)} \tag{5}$$

by equilibrating an Ag-Ca-Sn melt with solid C, CaC_2 and solid Ca_2Sn and combining their results with the free energy of formation of CaC_2. They obtained

$$\Delta G^{\circ}_{5} = -353{,}970 + 79.28T \ \text{J/mole} \tag{6}$$

Min and Sano then combined Eq. (6) with the results of Kohler and Engell to obtain a value of $\gamma^{\circ}_{\mathrm{Ca_2Sn}}$ of 150 at 1600°C.

The efficiencies of removal of several elements from a high carbon high chromium steel by treatment with Ca at 1420°C are shown in Fig. 11 [3]. The complexity of the melt and the lack of fundamental thermodynamic data are such that the data are not amenable to quantitative interpretation. Leal et al found that injection of chromium steels with CaC_2 removes tramp elements as shown in Fig. 12. The rate of dephosphorization is decreased when, simultaneously, other elements are being removed from dilute solution in the melt. Nakamura [7] et al used Ca-CaF_2 melts as a flux for the electroslag remelting of 18-8 stainless steels. With a CaF_2 to Ca ratio of 24 the tin content of the melt decreased from 200 ppm to 70 ppm, the lead content decreased from 152 ppm to 35 ppm and the copper content decreased from 770 ppm to 710 ppm. The tramp elements were not removed when CaF_2 alone was used as the flux.

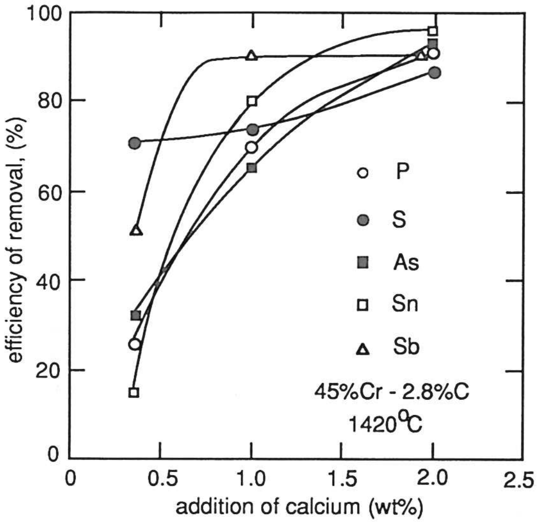

Fig. 11. The influence of the amount of calcium added to a 45% Cr steel on the removal of P, S, As, Sn and Sb(3)

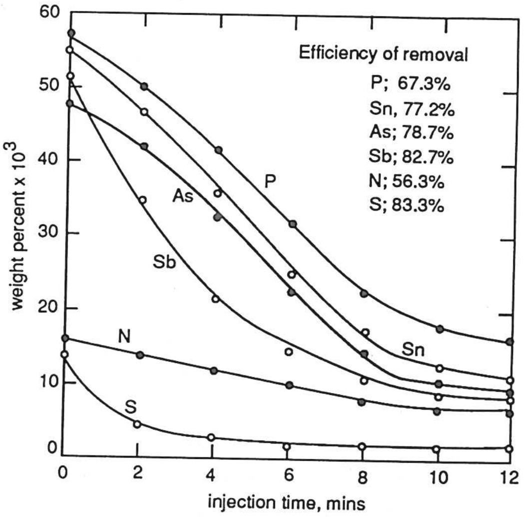

Fig. 12. The rates of removal of P, As, Sb, Sn and N from a 12% Cr steel by injecting CaC_2 at the rate of 24.5 kg/tonne(5).

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