Dephosphorisation of Iron–Chrome Alloy with Ca–CaF₂ Melt during Electro Slag Refining

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Calcium–calcium fluoride melt was used to remove phosphorus from the ferro-chrome alloy (64.5 wt% Cr, 0.15 wt% P) during electro slag refining process. The effect of atmosphere and deoxidisers, viz. Al, Fe–Mo and misch metal were also studied during dephosphorisation reaction. The thermodynamic properties of Ca–CaF₂ melt is calculated from a known phase diagram and these results are discussed in relation with the dephosphorisation reaction.

KEY WORDS: dephosphorisation; refining; ferro-chrome alloy; Ca–CaF₂ melt; phosphorus removal; stainless steel making.

1. Introduction

Indian chromite ores have a relatively high phosphorus content which makes it undesirable for their use in stainless steel making, particularly for special applications where formability and strength of this alloy are desired.

The modern technology of stainless steel making, e.g., AOD and VOD processes, though capable of utilising low grade ferrochrome alloys produced from these chromite ores, is unable to reduce a high level of phosphorus. In an electric arc furnace, phosphorus is removed by using a basic oxidising slag but to bring down its level of phosphorus up to 0.04–0.045 wt% also results into a high loss of chromium from the alloy phase as chromium oxide which goes into the slag phase.¹)

In order to achieve a very low level of phosphorus in the Fe–Cr alloy without any loss of chromium as an oxide in the slag phase, we have studied the dephosphorisation reaction during electro slag refining process, capable of generating high temperatures, using Ca–CaF₂ flux. The present investigation was also aimed to achieve a similar condition either in an electric arc furnace or in a controlled ladle treatment of hot metal, the latter being very much suited to the AOD or VOD process.

This work originally began in Research Laboratory, Nippon Steel Corp. and some of their results were published towards the end of the last decade.²–⁵) Removal of impurities, both from iron base and Fe–Cr alloys were studied and it was reported that elements from groups VA and VB in the periodic table can be removed by using M–MX₂ melts (M=Ca, Mg; X=Cl, F). In one of these studies, diffusivities of P and N₂ gas dissolved in the Fe–Cr alloy were determined by Nakamura et al.⁶) Subsequently, their work was extended and the removal of oxygen, carbon and sulphur were also studied. Using these melts, tramp elements (Sb, As, Bi, etc.) in liquid iron were also removed simultaneously. Usually, these elements form compounds with metallic calcium and are transferred in the slag phase.

The mechanism of removal of an impurity (Z) from a given liquid metal, as suggested by Nakamura et al.,⁷,⁸) is described in the following chemical reaction:

\[ x(Ca) + y(Z) = (Ca, Z) \]

Based on the above equilibrium, in general, the distribution of phosphorus in the slag and alloy phase is given below:²,⁶)

\[ (\%P)/(\%P) = A(\%Ca)^b \]

Here both A and b depend upon the composition of alloy and vary between 2.4 to 4 and 1.94 to 2, respectively. A similar kind of distribution ratio for carbon in the flux as CaC₂ and C as dissolved in the alloy phase was obtained by Katayama et al.⁹)

Little is known about the co-ordination of phosphorus either in Ca–CaF₂ or in CaF₂–CaC₂ melts and regarding this a few suggestions have been made by Tokumitsu et al.⁵) and Bredig,¹) the latter suggesting that the metal imparts its metallic characteristics to the solvent in this mixture. Such solutions, therefore demonstrate both the ionic and electronic conductions. It has been also suggested that the metallic calcium in its parent halide melt (e.g., Ca–CaX₂, \( X=F, Cl, Br, I \)) can also assume a valence state between zero and +2. This new valence state of Ca in the solution, as proposed by Tokumitsu et al.,¹) facilitates the removal of phosphorus, nitrogen and other elements of this group from liquid iron.¹) Such a state was called "subhalide" by Bredig.¹)
2. Thermodynamic Properties of Ca–CaF₂ and CaC₂–CaF₂ Solutions

Thermodynamic properties of Ca–CaF₂ melts are calculated from the published phase diagram which is shown in Fig. 1. In order to calculate the activities of either components in a Ca–CaF₂ melt, the Clapeyron equation, which is given below, was used. The following equation yields the thermodynamic activity of calcium fluoride (a₁CaF₂) in this melt, i.e.,

\[
\ln a_{\text{CaF}_2} = -\frac{\Delta H_f (T_f - T)}{RT_f} \tag{3}
\]

where, \(\Delta H_f\), \(T_f\): enthalpy of fusion and the melting point, respectively

\(R\): the universal gas constant.

The details of this calculation are given by Richardson. The activity coefficients \(\gamma_{\text{CaF}_2}\) in this melt at various temperatures, were then calculated from the composition of the liquidus curve at that temperature and the calculated activities \(a_{\text{CaF}_2}\). Assuming the melt behaves as a regular solution, the activity coefficient at a constant temperature \(T_o\) greater than the melting point of CaF₂, was then calculated from Eqs. (4) and (5), i.e.,

\[
RT \ln \gamma_i = \text{constant} \tag{4}
\]

\[
\ln \gamma_{\text{CaF}_2} = \left(\frac{T}{T_o}\right) \ln \gamma_{\text{f}} \tag{5}
\]

From known values of \(\gamma_i\) at a temperature \(T_o > T_f\), the activity–composition diagram for components in the Ca–CaF₂ system was constructed and is shown in Fig. 2. Both components demonstrate a positive deviation from an ideal Raoultian behavior. The demonstration of a positive departure from ideality, therefore, contradicts the existence of a subhalide of calcium with CaF₂. The formation of a subhalide of metallic calcium with CaF₂ should demonstrate a negative deviation from ideality. The excess heat of mixing of this solution was then calculated using regular solution model which defines the excess partial heat of mixing (\(\Delta H_i\)) in Eq. (6).

\[
\Delta H_i = RT \ln \gamma_i = b(1 - X_i)^2 \tag{6}
\]

The above relationship given in Eq. (6) is shown in Fig. 3. The slope of this straight line gives the value of interaction heat \(b\) and is equal to 26.57 kJ for Ca–CaF₂ melt. Therefore, the free energy of mixing of Ca in the CaF₂ melt can be written as follows

\[
\Delta G_{\text{Ca}} = \Delta H_{\text{Ca}} - T \cdot \Delta S_{\text{Ca}} \tag{7}
\]

which from the regular solution model becomes

\[
RT \ln a_{\text{Ca}} = \Delta G_{\text{Ca}} = b(1 - X_{\text{Ca}})^2 + RT \ln X_{\text{Ca}}
\]

\[
= 26.57(1 - X_{\text{Ca}})^2 + 8.314 T \ln X_{\text{Ca}} \tag{8}
\]

From Eqs. (8) and (6), the values of \(RT \log a_{\text{Ca}}\) were calculated and a plot of \(RT \log a_{\text{Ca}}\ vs. \frac{1}{T}\) was constructed. From the slope and intercept of the straight line relationship of this plot, the Gibbs free energy equation for the dissolution of metallic Ca in CaF₂ melt was obtained and is given below in joules.

\[
\Delta G_{\text{Ca}}^\circ = 24787 - 19.78T \tag{9}
\]

\[\text{Fig. 2. Activity-composition diagram for Ca–CaF}_2\text{ system at 1973 K.}\]

\[\text{Fig. 3. } RT \ln \gamma_i = (1 - X_i)^2 \text{ plot.}\]
In the CaC$_2$–CaF$_2$ system, the melting point of CaC$_2$ is 2573 K$^{10}$ and its calculated enthalpy of fusion from the phase diagram, shown in Fig. 4 in the inset, is 16.91 kJ/mol. This data was obtained by calculating the slope of the straight line obtained from ln $X_{CaC_2}$ vs. $1/T$ relationship. Using a similar procedure as described above, the activity–composition diagram can be obtained. At 1973 K, however, the activity of CaC$_2$ is unity at $X_{CaC_2} = 0.52$ and beyond. For an efficient dephosphorisation, therefore it is the activity of CaC$_2$ in the melt which is more important here and it should be maintained at a maximum possible value.

3. Thermodynamic Properties of Fe–Cr Alloy

The thermochemical data for this alloy, both in solid and liquid states, have been obtained from Kubaschewski and Alcock. The heat of mixing curve for this alloy ($\Delta H_m$) is shown in Fig. 5 and is valid between 1748 to 2148 K. From the available data using Eq. (6) as shown above, the parameter, interaction heat ‘$b$’ is then calculated. From the partial heat of mixing data given in Ref. 10, the activity–mole fraction relationship for this alloy was drawn. Components of this alloy demonstrate a positive departure from an ideal Raoultian behaviour, see Fig. 6.

4. Experimental

4.1. Apparatus

A schematic diagram of ESR furnace is shown in Fig. 7. An extensive information in this area can be procured from Ref. 12). The temperature distribution in the ESR crucible has been measured by Oguti$^{10}$ and Sakata$^{11}$ and is shown in Fig. 8. For our present investigation with Ca–CaF$_2$ melt, the temperature considered during the dephosphorisation process was 1973 K and all thermodynamic calculations in this text are carried out at this temperature. A direct temperature measurement of a molten flux, however, could not be carried out with a thermocouple because of a very corrosive nature of this melt. On the other hand, an optical pyrometer can only measure temperature of the melt surface which is often cooler than the bulk. It is for this reason, that a temperature calibration based on the voltage input across the molten bath is being considered.

Fig. 5. Enthalpy of mixing vs. composition curve for Fe–Cr alloy. $^{10}$

Fig. 7. Schematic diagram of ESR furnace.

Fig. 8. Temperature profile in ESR crucible.$^{10,11}$
To initiate the melting and refining process, an arc was struck between the graphite plate [10] and a consumable impure electrode [2], see Fig. 7. Small amounts of metal scrap and CaF₂ flux were necessary to initiate the melting process. These two ingredients stabilise the initial arcing process which raises the temperature sufficiently high to melt CaF₂. Once CaF₂ is molten, its volume is raised by making more additions gradually followed by a gradual immersion of the consumable electrode. Maintenance of a significantly large volume of molten flux is necessary for the sustenance of a smooth melting and refining process. Necessary refining agents, e.g. metallic calcium etc., were added only after the argon gas was switched on to maintain an inert atmosphere over the melt. Also, prior to Ca addition, the molten bath was deoxidised either by aluminium or by mish metal addition. At the end of refining, the consumable electrode was withdrawn from the molten CaF₂ bath. Flux and the molten metal were then allowed to cool in a flowing stream of argon (approx. 500 ml/min) inside a water-cooled crucible [8].

Both the flux and alloy ingots were then chemically analysed for their constituents. Important parameters controlled during melting and other details of the melting process are shown in Tables 1 and 2.

### 4.2. Materials

Calcium fluoride of general purpose reagent purity (99 %) was used in this investigation. Prior to melting, it was dried at 673 to 723 K for about 2 h. Calcium metal of purity more than 99.95 % purity was used as a refining agent. Dry argon gas of commercial purity (1.5 % residual oxygen) was used to maintain an inert atmosphere during remelting of ferrochrome electrodes. The chemical analysis of a typical consumable electrode is given in Table 3.

#### Table 1. Remelting conditions of ferrochrome consumable electrodes.

| Ferrochrome electrodes | Slag composition (wt%) | Atmosphere | Voltage (V) | Amperage (A) | Calculated weight of a droplet |
|------------------------|------------------------|------------|-------------|--------------|-------------------------------|
|                        | %CaF₂  | %Ca  | %Al  |                      |                 |
| FeCr-1                 | 91.7   | 5.1  | 3.2  | Air              | 35–40           | 1000–1050                     |
| FeCr-2                 | 84.6   | 7.7  | 7.7  | Ar               | 35–40           | 1000–1050                     |
| FeCr-3                 | 81.8   | 9.1  | 9.1  | Ar               | 35–40           | 1000–1050                     |
| FeCr-4                 | 76.2   | 11.9 | 11.9 | Ar               | 35–40           | 1000–1050                     |
| FeCr-5                 | 72.7   | 18.2 | 9.1  | Ar               | 35–40           | 1000–1050                     |

* Contains 9.1 wt% (Fe-Mo) and 9.1 wt% mish metal.

#### Table 2. Dimension of ferrochrome ingots produced during remelting.

| Ferrochrome ingots | Weight (kg) | Diameter (mm) | Height (mm) | Remelting time (min) | No. of droplets | Calculated weight of a droplet |
|--------------------|-------------|---------------|-------------|----------------------|----------------|-------------------------------|
| FeCr-1             | 0.55        | 45.0          | 61.0        | 6.0                  | 35             | 1.96                          |
| FeCr-2             | 1.23        | 45.0          | 118.0       | 11.0                 | 36             | 3.11                          |
| FeCr-3             | 1.10        | 45.0          | 116.0       | 9.5                  | 37             | 2.84                          |
| FeCr-4             | 1.10        | 46.0          | 100.0       | 10.5                 | 35             | 2.99                          |
| FeCr-5             | 0.90        | 45.0          | 95.0        | 11.3                 | 50             | 2.21                          |

#### 4.3. Chemical Analysis

Standard procedures for a wet chemical analysis, as described in ASTM Handbook, were followed. An insignificantly small difference in the analysed values of Cr and Fe contents of electrode and ingot was observed. For this reason, chromium and iron were not analysed in each refined ingot and it was assumed to be constant before and after the refining step. A chemical analysis for carbon could not be done because of some experimental difficulties.

### 5. Results and Discussion

#### 5.1. Removal of Phosphorus

A small amount of chromium was lost as Cr₂O₃ in the slag phase when electrodes were remelted in air. Although the removal of phosphorus is feasible in an oxidising atmosphere, and can only be achieved at a relatively high basicity, in the present situation, however, such an atmosphere is not desirable. Any presence of oxygen in the molten flux aids the oxidation of metallic calcium to CaO and consequently prevents the formation of phosphide. In the absence of a deoxidiser, oxygen transfer occurs from am-
bient through the molten flux into the liquid alloy. The enrichment of alloy phase with oxygen therefore causes chromium oxide to form. The presence of a deoxidiser also retards the exchange of oxygen from the atmosphere with fluorine in the molten flux. It is for these reasons that the addition of a deoxidiser was essential during the dephosphorisation process.

Dephosphorised melts, for reasons stated above, have therefore a larger proportion of $P$ in the molten flux as phosphide. The distribution of phosphorus in the flux and in the metal phase is shown in Fig. 9. This plot also shows the data of other workers\(^1\) for which it is evident that the extrapolated straight line passes through the origin and it only holds good for a low carbon Fe–Cr alloy. It is perhaps reasonable to assume that the mechanism of dephosphorisation in two independent works could have been similar in spite of a large difference in the chromium content of electrodes (cf., 18–8 stainless steel in Ref. 2)). The equation for a straight line relationship shown in Fig. 9 is given below. Other set of data seem to vary quite considerably perhaps because of an obvious temperature variation during each set of experiments of Nakamura et al.\(^2\)

\[
\log \left( \frac{[\% P]}{[\% Fe]} \right) = 0.24 \text{ (wt\% Ca)} \quad \text{.........(10)}
\]

The compositions of refined ingots, electrodes and various fluxes used in the melting process are given in Table 3. The data, in this table, shows that the removal of phosphorus is possible even in the absence of metallic calcium. When deoxidisers such as Al, misch metal and Fe–Mo are used, it seems that the dephosphorisation reaction perhaps proceeds by forming aluminium phosphide as shown in Eq. (11) for which the value of $\Delta G$ in Joules is given below:

\[
\Delta G_{\text{AlP}}^o = -127331 + 121.3 T \text{ J} \quad \text{.........(11)}
\]

The value of equilibrium constant \( K(\text{AlP}) = 1.08 \times 10^{-8} \) at 1973 K. This means that the removal of phosphorus with Al is only possible if the activity of AIP in the fluoride melt is less than unity. The free energy term in Eq. (11) excludes the effect of mixing of AIP and Al in CaF\(_2\) melts. These data could not be incorporated in this equation because neither the phase diagram nor the free energy mixing of data is available. However, the addition of Al prior to that of calcium in a CaF\(_2\) melt deoxidises it by forming alumina as shown below.

\[
2(\text{Al}) + 3(\text{O}) = \text{Al}_2\text{O}_3(l)
\]

\[
\Delta G_{\text{AlP}}^o = -127938 + 288.92 T \text{ J} \quad \text{.........(12)}
\]

The value of $K(\text{AlO}) = 2.5 \times 10^{17}$ at 1973 K.

In the dephosphorised bath, therefore, the dephosphorisation reaction occurs according to the following equilibrium.

\[
3(\text{Ca}) + 2[\text{P}] = (\text{CaP}_2)
\]

\[
\Delta G_{\text{CaP}}^o = -504003 + 291.14 T \text{ J} \quad \text{.........(13)}
\]

This equation also includes a contribution for the free energy of mixing of metallic Ca in the CaF\(_2\) melt but neither the free energy of mixing of phosphide nor its free energy change at the fusion temperature is included here. The value of $K_{\text{CaP}}$ can be therefore calculated from the $\Delta G^o$ value in Eq. (13) which can be written as follows:

\[
K_{\text{CaP}} = a_{\text{CaP}}^o/(a_{\text{Ca}}^2 \cdot a_{\text{P}}^2) = \exp (\Delta G_{\text{CaP}}/RT)
\]

\[
\text{.........(14)}
\]

In this equation, $[a_i]$ in Fe–Cr–C–P alloy is not known and in order to determine its value, we have made a rather simplified assumption and have treated this metallic liquid as it is made of Fe–C–P alloy. This approximation facilitates us to use Wagner's interaction parameters known for some iron base alloys,\(^{10}\)

\[
\ln f_i = \ln (\eta_i/\eta_{\text{inl}}) = X_i \cdot e_i^0 + X_j \cdot e_j^0 \quad \text{.........(15)}
\]

where,

\[
\eta_i = 239 \left( \frac{M_i}{M} \right) e_i^0 + \left( \frac{M - M_i}{M} \right) \quad \text{.........(16)}
\]

\[
\eta_j = 230 \left( \frac{M_j}{M} \right) e_j^0 + \left( \frac{M - M_j}{M} \right) \quad \text{.........(17)}
\]

\(M_i\): the atomic weight of the \(i\)-th minor solute in this alloy, e.g., for a P and C containing melt $M$ is the atomic weight of the alloy (solvent), e.g., Fe–Cr or Fe.

\(e_i, e_j\): the interaction parameters of the \(i\)-th and \(j\)-th solute on \(i\), respectively.

\(X_i, X_j\): the mole fractions of solutes.

\(\eta_i\): the activity coefficient of the solution at infinite dilution.

For phosphorus–phosphorus interaction in an iron base alloy, we have considered the following values and have assumed that phosphorus behaves very similarly to nitrogen in this alloy. In that situation, $e_i^0 = e_j^0 = 0$. Then from Eqs. (16) and (17) and from the available data in reference,\(^9\) we have the value of $\eta_i$.

![Fig. 9. Variation of phosphorus distribution ratio in flux and alloy phase with calcium content of flux at 1973 K.](image)
and $\tau_n$ in Eq. (18) at 1 873 K. The calculation of $\gamma_C$ and $\tau_n$ also requires the values of $\tau_{\text{dil}}$ at an infinite dilution of phosphorus and carbon which have been obtained from Ref. 1. At 1 873 K,

$$
\ln \gamma_C = 0.302 + 7.23 \chi_p
$$

$$
\ln \gamma_n = -3.1696 + 0.419 \chi_p 
$$

These activity coefficients can then be calculated at 1 973 K using regular solution approximation. Once the value of $\gamma_p$ is known, it is possible to calculate the activity of calcium phosphide in CaF$_2$ melt. These values are given in Table 4. The equilibrium relationship between the phosphorus content of flux and alloy phase at 1 973 K is shown in Fig. 10. We have also attempted a separate approach to calculate the activity of calcium phosphide in the molten flux. Assuming an ideal mixing of cations and anions in the CaF$_2$ flux, according to Temkin model

$$
a_{CaP_2} = (X_{Ca})^{\lambda} \times (X_p)^{\beta} 
$$

where, $X_{Ca}$, $X_p$: the mole fractions of metallic Ca and phosphide ion in the CaF$_2$ melt, respectively. The ideal Temkin activity of calcium phosphide is then compared with the values of activity of Ca$_3$P$_2$ calculated from Eq. (14), the latter being a few orders larger than the ideal Temkin model. This may perhaps suggest that the melt upon addition of Ca$_3$P$_2$ demonstrates a positive departure from an ideal Temkin behaviour.

In order to test the validity of calculated activity of Ca$_3$P$_2$ in the CaF$_2$ melt from Eq. (14), we have performed a test on our experimental data. By assuming ideal Temkin model, the value of $a_{CaP_2}$ (e.g. =8.23x10^{-9}) in the melt was used in Eq. (14) to calculate the activity of phosphorus ($a_p$=0.018, cf. see $a_p$ for FeCr-1) in the liquid Fe–Cr alloy. These values are about three orders of magnitude larger than the calculated thermodynamic activity of phosphorus from Wagner's interaction parameter. A large difference in these two values of $a_p$ in Fe–Cr alloy can therefore be explained in terms of a non-Temkin type activity of the phosphide in CaF$_2$ melt, i.e.,

$$
a_{CaP_2} \neq a_{CaP_2}(\text{ideal})
$$

It should be noted that in this verification, the ideal Temkin’s activity of phosphide was calculated on the basis of mole fraction of metallic Ca in the solution. If the ionic fraction of Ca$^{2+}$ in the flux is considered for the Temkin model, the activity of phosphorus in the alloy [$a_p$] will be much larger.

It is therefore evident that the removal of phosphorus from Fe–Cr depends upon the activity of metallic Ca in the CaF$_2$ melt. The removal of impurities is thermodynamically more efficient where Ca in the CaF$_2$ melt obeys Henry’s law. It is in this region that the activity coefficient of Ca in the melt is maximum. As the solute concentration increases, the magnitude of positive departure gradually approaches to a Raoultian behaviour, see Fig. 2, thus bringing the activity coefficient of Ca closer to unity.

5.2. Removal of Carbon from Fe–Cr Alloy

Nakamura et al.* have considered the dissolved carbon in Fe–Cr alloy during decarburisation reaction. They defined the following equilibrium for the removal of carbon.

![Fig. 10. Relationship between equilibrium phosphorus content of alloy and flux at 1 973 K.](image)

Table 4. Calculated thermodynamic activity of Ca$_3$P$_2$ in the molten flux.

| Ferrochrome | Metal phase | Slag phase |
|-------------|-------------|------------|
| wt% P       | log wt% P   | $\tau_n$  |
| FeCr-1      | 0.021       | 1.678      | 0.499 | 0.2987 | 0.095 | 0.373 | 0.411 | -0.386 | 5.225 x 10^{-8} | 8.23 x 10^{-8} |
| FeCr-2      | 0.013       | 1.886      | 0.499 | 0.3196 | 0.149 | 0.470 | 0.727 | -0.138 | 4.07 x 10^{-8} | 7.47 x 10^{-8} |
| FeCr-3      | 0.005       | 2.301      | 0.499 | 0.6111 | 0.1633 | 5.512 | 0.895 | -0.048 | 1.706 x 10^{-8} | 1.83 x 10^{-8} |
| FeCr-4      | 0.002       | 2.699      | 0.499 | 0.011  | 0.208 | 0.381 | 1.167 | -0.067 | 7.719 x 10^{-7} | 6.31 x 10^{-8} |

Data of Nakamura et al.* for low C ferrochrome alloy

A) 0.0135 | -1.87  | 0.499 | -3.18   | 0.063 | 0.288 | 0.09  | -1.05  | 2.589 x 10^{-8} |
B) 0.0105 | -1.96  | 0.499 | -3.29   | 0.045 | 0.25  | 0.07  | -1.15  | 1.741 x 10^{-8} |
C) 0.016   | -1.796 | 0.499 | -3.11   | 0.031 | 0.21  | 0.046 | -1.34  | 1.055 x 10^{-8} |
D) 0.0155 | -1.81  | 0.499 | -3.12   | 0.056 | 0.223 | 0.051 | -1.292 | 2.29 x 10^{-8} |

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\((\text{Ca})+2[\text{C}]=(\text{CaC}_2)\)

\[
K_{\text{CaC}_2} = \frac{a_{\text{CaC}_2}}{a_\text{Ca} \sqrt{a_C}} = \exp\left(\frac{\Delta G^\circ}{RT}\right) = 0.334
\]

\[
\Delta G^\circ = -153.906 + 71.88 T \text{ J} \quad \ldots \ldots \ldots (20)
\]

The above relationship shows that at equilibrium, the carbon content of alloy phase is inversely proportional to the calcium content of flux. However, the relationship shown in Fig. 11 obtained from their work\(^2\) has a positive slope. Nakamura et al.,\(^3\) however, varied the carbon content of alloy phase simultaneously with calcium content of the molten flux. For calculating the activity of CaC\(_2\) we have assumed that \(\gamma_C=0.144\) in this alloy.\(^6\) Values of \(a_{\text{CaC}_2}\) can then be calculated for different calcium content in the flux and these values are shown in Table 5.

In Fe-Cr alloy containing carbon, we have now assumed that carbon is present as a chromium carbide phase (Cr\(_2\)C\(_2\)) because this phase does not melt at 1973 K. Therefore, we have considered the following decarburisation reaction.

\[
\langle \text{Cr}_2\text{C}_2\rangle + (\text{Ca}) = (\text{CaC}_2) + 3(\text{Cr})
\]

\[
\Delta G^\circ = 21752 - 10.79 T \text{ J} \quad \ldots \ldots \ldots (21)
\]

The thermodynamic activity of carbide phase for 3.5 wt% C in this alloy can be obtained from the following reaction

\[
3(\text{Cr}) + 2(\text{C}) = \langle \text{Cr}_2\text{C}_2\rangle
\]

\[
\Delta G^\circ = -175058 + 90.67 T \text{ J} \quad \ldots \ldots \ldots (22)
\]

This yields a value of \(a_{\text{Cr}_2\text{C}_2}=7\times10^{-3}\) in the alloy phase which in turn gives the value of \(a_{\text{CaC}_2}=8.17\times10^{-8}\) at 1973 K. This shows that carbon even in the form of Cr\(_2\)C\(_2\) can be removed from the alloy phase.

6. Conclusions

(1) Phosphorus can be efficiently removed from the ferro-chrome alloy using Ca–CaF\(_2\) melt.

(2) The extent of dephosphorisation depends upon the type of deoxidiser used prior to the addition of metallic calcium in the molten CaF\(_2\) flux.

(3) The distribution of phosphorus in the metal and slag phase is linearly dependent on the calcium content of the molten flux.

(4) Calculated activities of Ca and CaF\(_2\) from the phase diagram demonstrate a positive deviation from an ideal Raoultian behaviour in Ca–CaF\(_2\) melt.

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Appendix I

Use of Fe-Ca-S-O Liquid for the Treatment of Hot Metal

Treatment of liquid iron base alloy outside the blast furnace has been recently a relatively new trend in steel making. For this reason, we shall investigate the usage of Fe-Ca-S-O liquid in external treatment of hot metal. In this regard, we have considered FeO-CaS phase diagram which was produced by Koch and Trommel[21] and this is shown in Fig. A-1-1(a). Predominant areas for various phases in equilibrium at 1173 K is shown in Fig. A-1-1(b). The evidence of this liquid was also found by Lapin et al.[17] and Yarigin et al.[19]. Very recently, the existence of this liquid has been confirmed by Jha.[20] during the investigation on the carbothemic reduction of pyrrhotite mineral in presence of lime. The reduction reaction was studied between 1073 to 1273 K. Turkdogan and Martonik[20] observed fairly large iron peak in Energy Dispersive X-ray (EDX) spectra of sample at the CaO-CaS pellet-liquid metal interface during the following reaction:

\[ \text{[S]} + \text{[C]} + \text{(CaO)} = \text{(CaS)} + \text{CO} \ (g) \]  

(A-1-1)

Their observations seem to suggest that for the existence of non-metallic iron in this pellet, it is necessary that Fe-Ca-S-O liquid must form at the interface during desulphurisation reaction. The proportion of this liquid, at the interface, at a given temperature will solely depend upon the amount of sulphur, oxygen and iron present in the pellet. These observations suggest that the desulphurisation reaction must have proceeded in the presence of Fe-Ca-S-O liquid as an intermediary. Under this section, we will therefore study the role of this liquid in removing various impurities from the liquid iron.

Blast furnace hot metal is, thermodynamically, an ideal liquid to treat it with Fe-Ca-S-O melt at its tap temperature. At 1873 K, when it is treated with a mixture containing more than 90 mol% FeS or with pure pyrrhotite mineral, the following reactions we expect to occur.

\[
\begin{align*}
\text{(FeS)}_2 &= \text{[Fe]} + \text{[S]} \\
\text{[Mn]} + \text{[S]} &= \text{(MnS)} \\
\Delta G'\text{(MnS)} &= -1515333 + 84.91 T J \\
2\text{[Cu]} + \text{[S]} &= \text{(Cu}_2\text{S)} \\
\Delta G'\text{(Cu}_2\text{S)} &= -21208 + 40.324 T J
\end{align*}
\]

(A-1-2)

The values of equilibrium constant \( K(\text{MnS}) \) and \( K(\text{Cu}_2\text{S}) \) at 1873 K are 0.617 and 0.03, respectively. For \( \alpha(\text{MnS}) \) and \( \alpha(\text{Cu}_2\text{S}) \) in the melt equal to \( 10^{-3} \), the sulphur content in the liquid metal at equilibrium is 0.315 and 0.039 wt%, respectively. Therefore, to initiate above reactions, the hot metal should contain a minimum of 0.315 wt%, i.e., \( \alpha_s = 1.127 \times 10^{-4} \) or \( \alpha_{FeS} = 4.81 \times 10^{-4} \). In this calculation, we have considered that the hot metal is constituted of Fe-Ca-S and Fe-Mn-S components for which \( \gamma_s \) at 1873 K is 0.161 and \( \gamma_{FeS} \) and \( \gamma_{Cu} \) are 1.25 and 9.26, respectively.[11]

These melts containing metal sulphides can then be separately treated for the recovery of Mn and Cu by adding lime and activated charcoal according to the following reaction.[20] Metal sulphide can be reduced to metal.

\[
\text{(MS)} + \text{CaO} + \text{C} \ (g) = \text{M} \ (l) + \text{CaS} \ (l) + \text{CO} \ (g)
\]

(A-1-3)

The removal of sulphur from the hot metal with CaO-containing slag has been extensively studied and hence will not be dealt with here any further.

The effect of Si and Al on the desulphurisation equilibria has been studied by Turkdogan and Martonik.[20] Their role in liquid metal brings out another mechanism of removal of phosphorus and sulphur simultaneously. It is also well-known for economic reasons that the steel making slag should be used for the external treatment of the blast furnace metal.[21,22] The removal of phosphorus with sulphur from liquid iron can be described by the following two equilibria:

\[
\begin{align*}
5\text{(CaO)} + 5\text{[S]} + 2\text{[P]} &= 5\text{(CaS)} + (P_2O_5) \\
\Delta G'\text{(PO)} &= -89307 + 398.85 T J \\
7\text{(CaO)} + 5\text{[S]} + 2\text{[P]} &= 5\text{(CaS)} + (Ca_3P_2O_7) \\
\Delta G'\text{(2CP)} &= -687665 + 421.35 T J
\end{align*}
\]

(A-1-4)
It has been suggested earlier\textsuperscript{16,21-23} that the dephosphorisation reaction is more efficient at lower temperatures because of a large exothermic heat of reaction. For slags saturated with lime and Ca\textsubscript{3}P\textsubscript{2}O\textsubscript{5}, determined the equilibrium constant for the following reaction\textsuperscript{23} is given below:

\[ 4(CaO) + 2[P] + 5[O] = Ca\textsubscript{3}P\textsubscript{2}O\textsubscript{5}(s) \]

\[ K_p = \frac{1}{[\%P][\%O]^5} \]

\[ \log K_p = \frac{75660}{T} \] \hspace{1cm} (A-I-5)

Using Eqs. (A-I-4) and (A-I-5) one can write

\[ (Ca\textsubscript{3}P\textsubscript{2}O\textsubscript{5}) + 2(CaO) = Ca\textsubscript{3}P\textsubscript{2}O\textsubscript{5}(s) \]

\[ \Delta G^\circ = -190431.1 + 31.62T J \] \hspace{1cm} (A-I-6)

The value of activity of \( a_{Ca_3P_2O_5} \) equals 2.187\times10^{-4} at 1873 K for lime and tetracalcium phosphate saturation. This also ascertains that the activity of \( P_2O_5 \) in the slag is extremely low. Therefore, in the hot metal containing \( S \) and \( P \) when \( Ca\textsubscript{3}P\textsubscript{2}O\textsubscript{5} \) slag is intimately mixed, the desulphurisation reaction should commence. It is also important for thermodynamic reasons that this step should follow the decopperisation step. In the following Fig. A-I-2, the sulphur content of hot metal is plotted against \( P \) content. This relationship is very similar to those of silicon and aluminium in iron plotted by Turkoğan and Martonik,\textsuperscript{23} This relationship suggests that during the dephosphorisation reaction phosphorus in the hot metal increases the activity coefficient of sulphur, thus making its removal more feasible.

For reasons stated above, the desulphurisation should be therefore carried out after dephosphorisation when the bath temperature has risen which will force equilibrium reaction (A-I-1) in the forward direction. At this stage, necessary thermodynamic conditions should be heeded, e.g., carbon addition in the hot metal to raise the activity coefficient of sulphur. The desulphurisation reaction also suggests that from a liquid Fe-Cr alloy containing C and S, both of them can be removed simultaneously in the AOD vessel by injecting lime with argon gas.

Appendix II

Removal of Silicon from the Blast Furnace Type Liquid Metal

For the removal of Si from iron base alloy with \( CaF_2-CaC_2 \) or \( Ca-CaF_2 \) flux, we consider the following reactions given in Table A-II-1. Calculated values of equilibrium constants, \( K \), at 1873 K are closer to unity in reactions (A-II-1) and (A-II-2). From these equilibria, the removal of silicon either as SiC or as CaSi will not only therefore depend upon the magnitude of individual equilibrium constant, but also it will be decided by the activities of calcium (\( a_{Ca} = 0.5 \)) in the flux and carbon in the liquid alloy for a given activities of silicon and CaC\textsubscript{2}. Also in Eqs. (A-II-1) and (A-II-2), \( a_{Si} \) is constant for a given silicon content of liquid alloy (\( e.g., 1 \text{ wt}\% Si \) and is equal to 2.57\times10^{-3}. This gives \( a_{Si}=1.22\times10^{-3} \) and \( a_{CaSi}=6.45\times10^{-4} \). Evidently, \( a_{Si}<a_{CaSi} \) and hence this sets up a condition for the formation of CaSi in the desiliconisation reaction. It should also be noted that a 3-condensed phase equilibria would make this system invariant at a given temperature. This will also limit the above equilibria to an extent to which either SiC or CaSi saturation can be achieved.

Apart from these thermodynamic factors, the nature of product will also depend upon the kinetic factors. If we assumed that the diffusivities of Si and C in the liquid alloy and the decomposition constant for CaC\textsubscript{2} are fixed at a given temperature, the nature of product will then be decided by the activation energy of chemical reaction at the flux metal interface.