

Lecture 7: Oxidation of manganese and carbon

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Key words: Solidification of steel, decarburization, BOF steelmaking

Behaviour of manganese in iron-carbon melt:

- Mn is soluble in iron in any proportion
- Mn forms ideal solutions in iron
- Carbon lowers the activity of Mn in Fe-Mn-C system by forming Mn_3C .

Oxidation of Manganese:

Mn is oxidized readily at relatively low temperatures and can form oxides like MnO , MnO_2 , Mn_2O_3 etc. But MnO is stable at high temperature.



The reaction 1 occurs with dissolved oxygen in metal, whereas reaction 2 is a slag/metal reaction. Both reactions are exothermic. Lower temperature favours oxidation of Mn from metal to slag; whereas higher temperature favours reduction of MnO of slag and there occurs reversal of Mn. Reduction of MnO in slag is important; we consider reaction 2

$$K = \frac{a_{(MnO)} a_{[Fe]}}{h_{[Mn]} a_{(FeO)}} \quad (3)$$

Replacing activity by mole fraction and using $a_{[Fe]} = 1$, we get,

$$K = \frac{N_{(MnO)} Y_{(MnO)}}{f_{Mn} [wt\% Mn] \times \gamma_{(FeO)} N_{(FeO)}} \quad (4)$$

Grouping all activity coefficient terms and putting $N_{(MnO)} \approx (wt\% Mn)$

We get,

$$K^* = \frac{K (Y_{FeO}) f_{Mn}}{\gamma_{MnO}} = \frac{(wt\% Mn)}{[wt\% Mn] \times N_{FeO}} \quad (5)$$

Where K^* is an equilibrium quotient and it depends on composition of slag. Distribution of Mn between slag and metal can be written as

$$\varphi = \frac{(wt\% Mn)}{[wt\% Mn]} = K^* N_{FeO} \quad (6)$$

$$\log K^* = \frac{7940}{T} - 3.17 \quad (7)$$

According to equation 7 K^* increases with decrease in temperature ($K^* = 9.1, 11.72$ and 20.33 at temperatures $1923K, 1873K$ and $1773K$ respectively)

Condition for oxidation of Mn according to equation 6

- High activity of FeO in slag which means an oxidizing slag
- Decrease in temperature increases K^* according to equation 7.

Reduction of Mn in slag

Conditions for reduction of MnO, that is reversal of reaction 2 is important. The reduction of MnO in slag transfers Mn from slag to metal and increases the concentration of manganese. The following are the conditions for the reduction of MnO in slag

- Low activity of FeO in slag which means a reducing slag
- High temperature which decreases K^*

Illustration:

Consider a slag of basicity 1.8. At this basicity the activity coefficient of MnO in slag is 1.6. The mole fraction of FeO and MnO in slag is 0.25 and 0.05 respectively. Determine the equilibrium content of Mn and O in steel at 1873K. Given



Using equilibrium constant definition, we can write

$$\ln[\% Mn] = \frac{\Delta G^\circ}{RT} + \ln \frac{a_{Fe} \gamma_{MnO} N_{MnO}}{a_{FeO}} \quad (8)$$

Substituting the values, we get at 1873K

$$[\% \text{ Mn}] = 0.048\%$$

Using equations

$$\Delta G^\circ = -6880$$

$$a_{\text{FeO}} = 0.514 (N_{\text{FeO}})^{0.2665}$$

$$\text{We get } a_{\text{FeO}} = 0.36$$

$$\text{Hence } [\text{wt}\% \text{ O}] = [\text{wt}\% \text{ O}]_{\text{sat}} \times a_{\text{FeO}}$$

$$= 0.233 \times 0.36$$

$$= 0.084\%$$

Calculations performed at 1773K shows that [wt% Mn] is 0.032. This means that decrease in temperature favours removal of manganese from metal to slag. The reader may perform calculations at 1973K and interpret the calculations.

Oxidation of Carbon

It is important to note that amongst all steelmaking reactions, oxidation of carbon is the reaction whose product is gas i.e. CO. Therefore this reaction is of very much significance during steelmaking because

- CO gas during escape from the molten bath can induce stirring in metal and slag phases during steelmaking.
- CO gas can cause slag to foam which leads to increase in surface area.
- CO gas has a high calorific value and combustion of CO in steelmaking can contribute to energy efficiency.

Carbon oxidation is also known as “decarburizing” reaction



$$K_{\text{CO}} = \frac{p_{\text{CO}}}{h_{\text{C}} h_{\text{O}}} = \frac{p_{\text{CO}}}{[\text{wt}\% \text{ C}] \times f_{\text{C}} \times [\text{wt}\% \text{ O}] \times f_{\text{O}}} \quad (10)$$

$$[\text{wt}\% \text{ C}] \times [\text{wt}\% \text{ O}] = \frac{p_{\text{CO}}}{K_{\text{CO}}} \times \frac{1}{f_{\text{C}} \times f_{\text{O}}} \quad (11)$$

If we assume $f_{\text{C}} = f_{\text{O}} = \text{unity}$ that is at low concentration of carbon and oxygen in molten metal then

$$[\text{wt}\% \text{ C}] \times [\text{wt}\% \text{ O}] = \frac{p_{\text{CO}}}{K_{\text{CO}}} \quad (12)$$

According to eq. 12, the product $[\text{wt}\% \text{ C}] \times [\text{wt}\% \text{ O}]$ at a given temperature depends only on partial pressure of CO in equilibrium with melt. It is important to note that p_{CO} depends on the location of nucleation of CO in steel melt. If CO nucleates deep into the bath then p_{CO} will be greater than atmospheric pressure.

Let us calculate equilibrium content of carbon and oxygen at 1873K for $p_{\text{CO}} = 1 \text{ atm}$, 1.2 atm and 1.5 atm

The value of K_{CO} is calculated from

$$\log K_{\text{CO}} = \frac{1056}{T} + 2.13$$

[wt% C]	[wt% O]		
	$p_{\text{CO}} = 1$	$p_{\text{CO}} = 1.2$	$p_{\text{CO}} = 1.5$
0.05	0.0405	0.0486	0.0608
0.1	0.0202	0.0242	0.0303
0.5	0.0040	0.0048	0.0060
1.0	0.0020	0.0024	0.0030

From the table we note that

- Decrease in carbon content increases the oxygen dissolved in steel. This is important in connection with production of ultra low carbon steel for certain applications. Production of ultra low carbon steels will be accompanied with dissolved oxygen if precautions are not taken during steelmaking.
- Increase in p_{CO} increases [wt% O] in steel

Let us consider the evolution of CO gas. According to equation 9,

12 Kg C produces $22.4 \text{ m}^3 \text{ CO}$ (1 atm and 273K)

1 Kg C produces $1.87 \text{ m}^3 \text{ CO}$ (1 atm and 273K) which is equivalent to $12.83 \text{ m}^3 \text{ CO}$ (1 atm and 1873 K)

Now for 1000 Kg hot metal and 0.2% carbon in steel

CO production would be 488 m^3 (1atm, 1873 K) / ton of hot metal. This volume of CO will evolve no doubt over a period of time but at any time large amount of CO will be escaping the system. Escaping of this gas will agitate the bath and contribute to enhanced rates of mass transfer reactions. Also care must be taken for the easy and unhindered escape of CO gas from the vessel failing which foaming and eventually expulsion of slag may occur.

Rimming reaction

Other aspect of carbon reaction is the evolution of CO during solidification of steel. As the temperature of molten steel decreases from 1873K to 1773K, K_{CO} increases from 494 to 532 which results in decrease in $[wt\% C] \times [wt\% O]$ as steel cools. This will lead to CO evolution during solidification and is called rimming reaction. Rimming reaction induces stirring in the solidifying liquid steel and minimizes segregation of solutes.