Lecture 6: Steel Making Reactions: Oxidation of Iron and Silicon

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Key words: Steel making, deoxidation, iron oxidation, desiliconization

Introduction

In steelmaking the impurities in hot metal like carbon, silicon, manganese, phosphorus and sulphur are removed through oxidation and slag formation so as to produce steel of desired chemistry and cleanliness. For this purpose oxygen is supplied and slag of desired chemistry is formed. When oxygen is supplied, oxidation of all impurities of hot metal including iron begins simultaneously.

To understand the conditions favourable for the removal of an impurity, we will first consider oxidation of an individual impurity. We will be using principles of thermodynamics to obtain the optimum conditions for the removal of an impurity. Note the following

- Carbon can oxidize to CO and CO_2 but at high temperature carbon oxidation to CO is highly probable. We will consider oxidation of C to CO.
- In expressing activity of solutes in molten steel, Henry's law is used by using 1 weight % standard state. Raoult's law is used to express activity of solutes in slag.
- Since impurities are dissolved in molten metal, reactions between impurity and oxygen occur with dissolved oxygen.
- Square brackets [ ] in a reaction denote impurity in metal, round brackets () in slag and curly {} in gas.

What are the oxidation reactions?

The principle reactions in steelmaking comprise of oxidation of impurity elements by oxygen dissolved in hot metal or FeO content of slag.

$$[Fe] + [O] = (FeO) \qquad\qquad (1)$$

$$[Mn] + [O] = (MnO) \qquad\qquad (2)$$

$$[Si] + [O] = (SiO_2) \tag{3}$$

$$[C] + [O] = (CO) \tag{4}$$

$$2[P] + 5[O] = (P_2O_5) \tag{5}$$
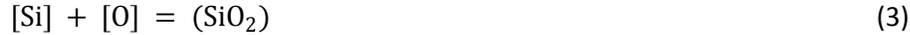
Note:

- All reactions are exothermic.
- C is removed as gas.
- Except C, all other impurities are removed as oxides and all these oxides float on the surface of the molten metal during refining of hot metal to steel.
- Iron oxidation is unavoidable. Oxidation of Fe is loss in productivity; hence its oxidation must be controlled.
- Oxygen must be dissolved to remove an impurity from the hot metal.

We begin with considering oxidation of an individual element and evolve the optimum conditions using thermodynamic principles.

Iron Oxidation:

Oxidation of iron i.e. reaction 1 is the most important since it controls

- FeO content of slag and oxygen content of steel
- Loss of iron in slag and hence affects productivity
- Oxidation potential of slag

In addition to the above FeO also helps in dissolution of lime in slag.

Consider the reaction

$$[Fe] + [O] = (FeO)$$
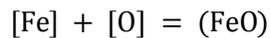
The equilibrium constant K_{Fe} is

$$K_{Fe} = \frac{a_{FeO}}{a_{Fe}\, h_O} = \frac{a_{(FeO)}}{a_{[Fe]} f_O\, [wt\%\, O]} \tag{6}$$

h is henrian and a is raoultian activity. Since Fe in steel is pure; $a_{Fe} = 1$, and

$$\log f_O = -0.17\, [wt\%\, O] \tag{7}$$

$$\log K_{Fe} = \frac{6150}{T} - 2.604 \tag{8}$$

In equation 8, T is in K. By equations 6, 7 and 8 we get

$$[wt\%\, O]\, 10^{-0.17\,[wt\%\,O]} = [a_{FeO}\{10^{(\frac{6150}{T} - 2.604)}\}^{-1}] \tag{9}$$

The equation 9 can be used to determine wt% O in steel at any temperature T, when a_{FeO} in slag is known.

When pure FeO is in contact with Fe; $a_{FeO} = 1$. We can determine [wt% O] at saturation for different temperatures:

T (K)	$[wt\% \ O]_{sat.}$
1873	0.233
1923	0.285

We note that increase in temperature increases oxygen dissolved in molten iron.

The above values of dissolved oxygen correspond when pure FeO is in contact with Fe pure. In steelmaking FeO is present along with other oxides like calcium oxide, magnesium oxide, silica, manganese oxide etc, hence activity of FeO is influenced by other solute oxides. Thus

$$a_{FeO} = \gamma_{FeO} \ N_{FeO}$$

where γ_{FeO} is activity coefficient and N_{FeO} mole fraction of FeO in slag,. γ_{FeO} depends on slag composition. In CaO- SiO_2-FeO system, as CaO/SiO_2 ratio increases a_{FeO} increases; physically it means that CaO replaces FeO from FeO. SiO_2. The following expression is used to express a_{FeO} :

$$a_{FeO} = 0.514 \ (N_{FeO})^{0.2665} \tag{10}$$

Consider a slag with N_{FeO} = 0.5 ; a_{FeO} according to equation 10 is 0.31; [wt% O] in steel would be 0.072 as calculated by equation 9.

Few other equations are available; i.e.

$$\log[\% \ O]_{sat.} = -\frac{6320}{T} + 2.734 \tag{11}$$

$$\log[\% \ O]_{sat.} = -\frac{6400}{T} + 2.756 \tag{12}$$

The calculations are made on [wt% O] by equations 9, 11 and 12 at different temperatures using $a_{FeO} = 1$.

T (K)	$[wt\% \ O]_9$	$[wt\% \ O]_{11}$	$[wt\% \ O]_{12}$
1873	0.233	0.229	0.220
1923	0.285	0.280	0.268

There is a slight difference in the values of dissolved oxygen content in steel. But all equations suggest that increase in temperature increases dissolved oxygen in iron which is in contact with pure FeO. This calculation indicates that control of temperature is important to limit the dissolution of oxygen in molten iron.

Oxidation of Silicon:

Consider reaction 2

$$[Si] + 2[O] = (SiO_2)$$
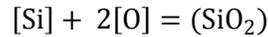
$$K_{Si} = \frac{a_{(SiO_2)}}{[wt\% \ Si][wt\% \ O]^2} \tag{13}$$

$$[wt\% \ Si] \times [wt\% \ O]^2 = \frac{a_{(SiO_2)}}{K_{Si}} \tag{14}$$

Different sources give the following expression for K_{Si}

$$\log K_{Si} = \frac{30110}{T} - 11.4 \tag{15}$$

$$\log K_{Si} = \frac{29700}{T} - 11.25 \tag{16}$$

Both equations predict that decrease in temperature increases K_{Si}. There is a slight difference in values of K_{Si}. Equation 15 predicts 15-17% higher K_{Si} than equation 16.

Conditions favourable for silicon oxidation are

- Low temperature
- Low a_{SiO_2} in slag. A basic slag favours silicon oxidation.

In a basic slag, silicon oxidation occurs practically to a very low value since SiO_2 reacts with CaO and decreases activity of silica in slag.

Another important feature of silicon reaction is very high affinity of silicon with oxygen, silicon can be used as a deoxidizing agent.

By equation 14

$$[wt\% \ O] = \sqrt{\frac{a_{SiO_2}}{K_{Si} \times [wt\% \ Si]}} \tag{17}$$

At 1773K, $K_{Si} = 3.24 \times 10^5$ by equation 16 and using $a_{SiO_2} = 1$, we get

$$[wt\% \ ] = \sqrt{\frac{0.308 \times 10^{-5}}{[wt\% \ Si]}} \tag{18}$$

Equation 18 shows drastic reduction in oxygen content of steel due to addition of silicon. This suggests that silicon is a very effective deoxidizer. Normally silicon is used as ferrosilicon in steelmaking.