Iron Making and Steel Making
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Module - 08
Lecture – 37
Secondary Steel making: Introduction and de-oxidation (Continued)

In the previous lecture, we have discussed about the de-oxidation thermodynamics and kinetics. We have talked about factors influencing the deoxidation kinetics. We have mentioned that total oxygen in the bath can be estimated by chemical analysis; while dissolved oxygen can be measured by a solid electrolyte cell, called the cellox probe. In this lecture, we will discuss scientific principles of cellox probe, and various industrial deoxidation practices. Figure 37.1 shows the design of a cellox probe.

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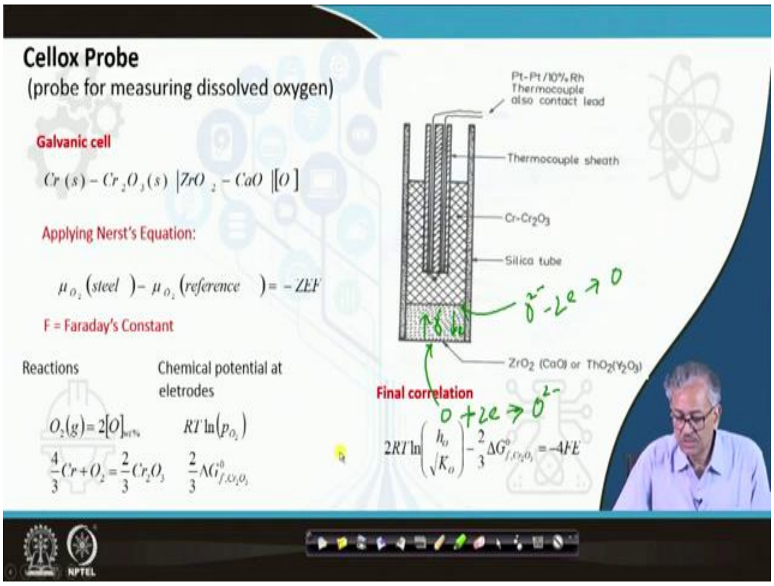

Cellox Probe

(probe for measuring dissolved oxygen)

Galvanic cell

$$Cr(s) - Cr_2O_3(s)\ |ZrO_2 - CaO\ \|[O]$$

Applying Nerst's Equation:

$$\mu_{O_2}(steel) - \mu_{O_2}(reference) = -ZEF$$

F = Faraday's Constant

Reactions	Chemical potential at eletrodes
$O_2(g) = 2[O]_{wt\%}$	$RT\ln(p_{O_2})$
$\frac{4}{3}Cr + O_2 = \frac{2}{3}Cr_2O_3$	$\frac{2}{3}\Delta G^0_{f,Cr_2O_3}$

Final correlation

$$2RT\ln\left(\frac{h_O}{\sqrt{K_O}}\right) - \frac{2}{3}\Delta G^0_{f,Cr_2O_3} = -4FE$$

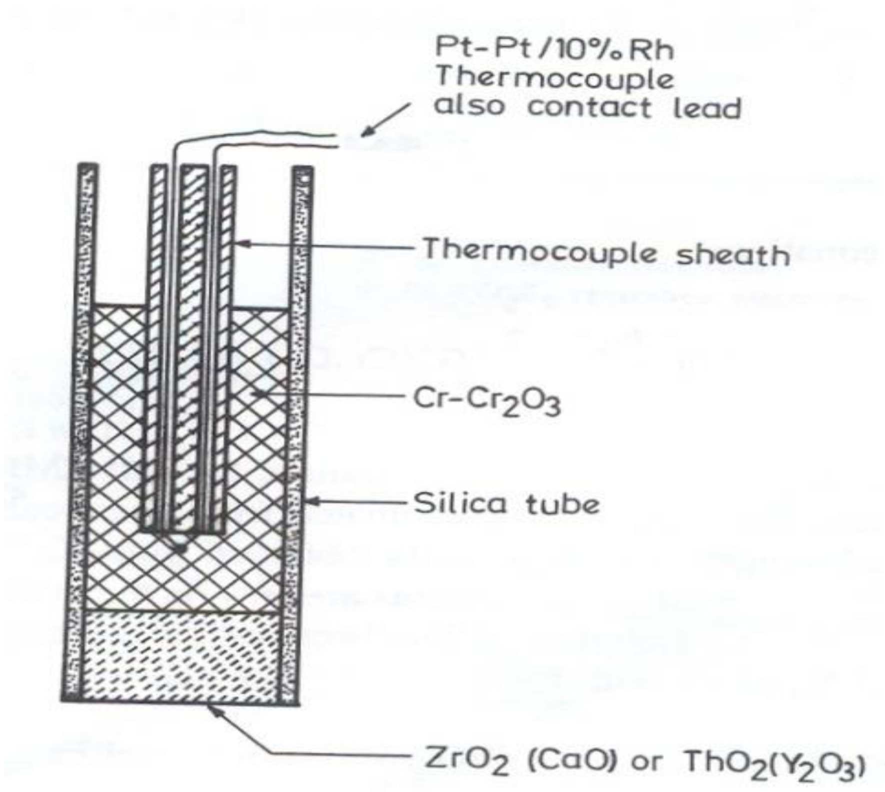

Figure 37.1: Schematics of a cellox probe[2].

The probe consists of a solid electrolyte made of calcia stabilized zirconia or yettria stabilized thoria. It only allows oxygen ions to pass through it. On one side of the electrolyte is chromium that acts as reference electrode and on the other side is the liquid steel that acts as other electrode. A thermocouple is inserted in the Cr-Cr_2O_3 mix to measure the temperature. It forms a concentration cell and oxygen passes from liquid metal at higher oxygen potential to the chromium electrode at lower oxidation potential through the solid electrolyte. Since the oxidation potential at chromium electrode is fixed the oxygen potential at the liquid steel (or, dissolved oxygen) could be estimated by calculating emf induced by applying Nernst equation (Equation 37.1).

$$\mu_{O_2}(steel) - \mu_{O_2}(reference) = -ZEF \tag{37.1}$$

Where, Z is the number of electron exchanged between the electrodes, E is the EMF generated and F is the this the Faraday’s constant.

To understand the electron exchange, let us write the half-cell reaction at the cathode and anode.

At the anode:

$$\{O_2\} = 2[O]_{wt\%}$$

(37.2)

$$2[O] - 4e = 2O^{2-}$$

(37.3)

At the cathode:

$$2O^{2-} + 4e = \{O_2\}$$

(37.4)

$$\frac{4}{3}Cr(s) + \{O_2\} = \frac{2}{3}Cr_2O_3(s)$$

(37.5)

Obviously, when one mole of oxygen is exchanged between the electrodes, total four electron are exchanged (Z=4). Then, the chemical potential of oxygen in reference electrode is just 2/3 rd of the free energy of formation of Cr_2O_3. The chemical potential oxygen in the liquid bath may be given by Equation (37.6):

$$\mu_{O_2} = RTln\left(p_{O_2}\right) = 2RTln\left(\frac{W_O}{\sqrt{K_O}}\right)$$

(37.6)

Where, K_O represent the equilibrium constant for the reaction given by equation (37.2). Henry's law has been assumed to be valid for dissolved oxygen in the bath ($h_O = W_O$).

Finally, the equation (37.1) can be written as:

$$2RTln\left(\frac{W_O}{\sqrt{K_O}}\right) - \frac{2}{3}\Delta G_f\big]_{Cr\rightarrow Cr_2O_3} = -4EF$$

(37.7)

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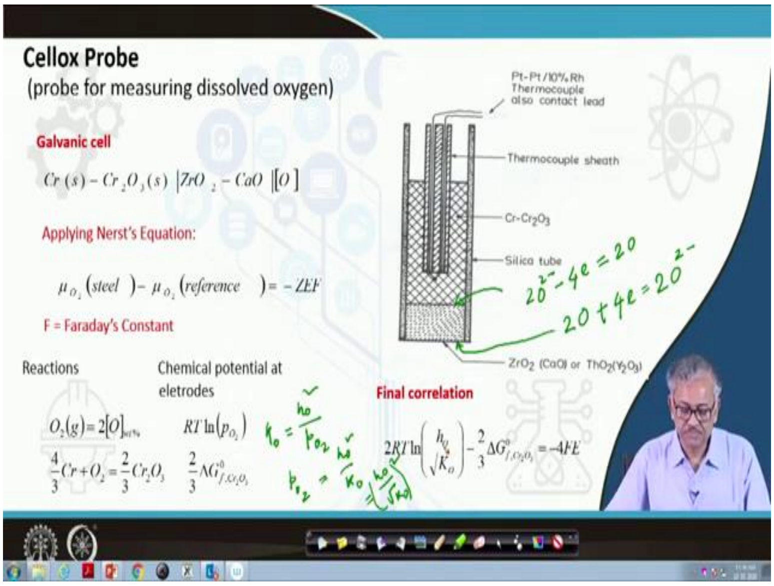

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$\frac{4}{3}Cr + O_2 = \frac{2}{3}Cr_2O_3$	$\frac{2}{3}\Delta G^0_{f,Cr_2O_3}$

$K_O = \frac{h_O}{p_{O_2}}$ ✓

$p_{O_2} = \frac{h_O}{K_O}$ ✓ $= \frac{h_O}{\sqrt{K_O}}$

Final correlation

$2RT\ln\left(\frac{h_O}{\sqrt{K_O}}\right) - \frac{2}{3}\Delta G^0_{f,Cr_2O_3} = -4FE$

$2O^{2-} - 4e = 2O$

$2O + 4e = 2O^{2-}$

In equation (37.7), the only unknown is W_O, which can be calculated, from the measured emf of the cell.

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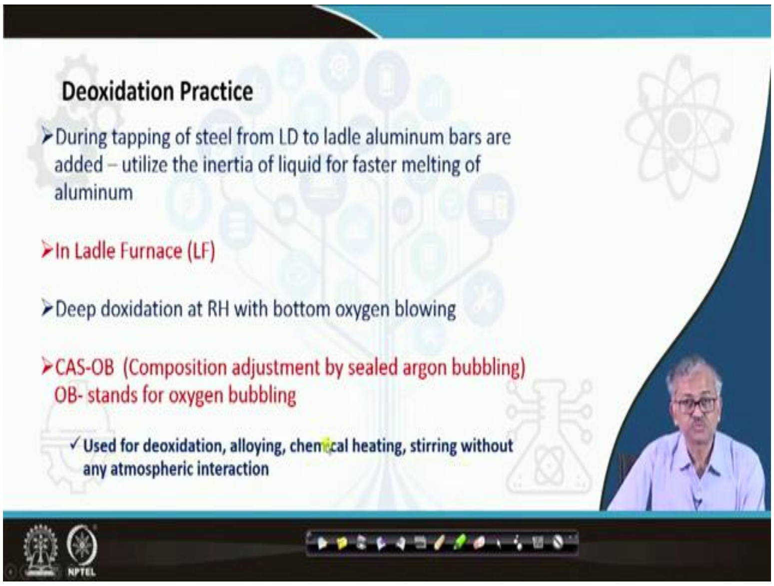

Deoxidation Practice

- During tapping of steel from LD to ladle aluminum bars are added – utilize the inertia of liquid for faster melting of aluminum
- In Ladle Furnace (LF)
- Deep doxidation at RH with bottom oxygen blowing
- CAS-OB (Composition adjustment by sealed argon bubbling) OB- stands for oxygen bubbling
  - ✓ Used for deoxidation, alloying, chemical heating, stirring without any atmospheric interaction

Now we will discuss the various de-oxidation practices.

During the tapping, de-oxidation is done utilizing the inertia of tapping stream. Aluminum bars are laid on the ladle bottom and liquid steel is tapped directly over the aluminum bars in the ladle. Required bath stirring to facilitate aluminum melting and its dissolution into the liquid bath is derived from the inertia of the falling stream.

Deoxidation can be carried out in the in Ladle Furnace. Since it has electric arc heat source and bottom gas stirring, aluminum addition could be done here. It may be noted that melting of aluminum is controlled by heat transfer at the solid-liquid interface. Besides aluminum being lighter than steel it will float to the top and a strong circulation in the bath would help it immersed till it melts.

Deep deoxidation can be carried out under vacuum in presence of carbon in the bath. Oxygen blowing is done to oxidize the carbon and both carbon and oxygen from the bath is removed as CO under reduced partial pressure of CO in vacuum. Since the solubility product of dissolved oxygen and carbon goes very low under vacuum, RH-OB, CAS-OB are used to deep decarburized as well as deoxidize the bath. OB stands for oxygen blowing. CAS stands for compositional adjustment under sealed argon bubbling. It is a Japanese technology, where argon is purged from the bottom of the ladle and the eye of the bubble plume is covered by inserting an cylindrical hood, that protects the eye opening from atmospheric interaction and lots of operations including, alloying, deoxidation, decarurization, chemical heating could be carried out under inert atmosphere with a higher yield. It will be discussed later in details.

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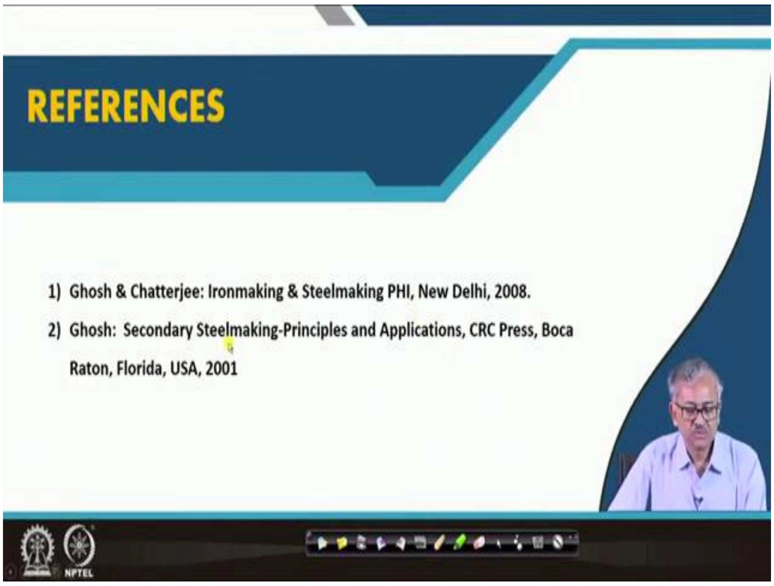

REFERENCES

1) Ghosh & Chatterjee: Ironmaking & Steelmaking PHI, New Delhi, 2008.
2) Ghosh: Secondary Steelmaking-Principles and Applications, CRC Press, Boca Raton, Florida, USA, 2001

The reference are mentioned above.

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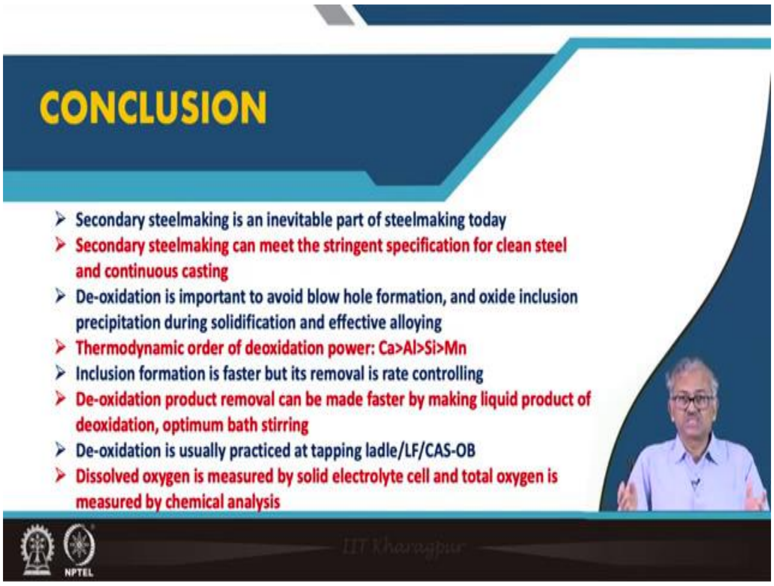

CONCLUSION

- Secondary steelmaking is an inevitable part of steelmaking today
- Secondary steelmaking can meet the stringent specification for clean steel and continuous casting
- De-oxidation is important to avoid blow hole formation, and oxide inclusion precipitation during solidification and effective alloying
- Thermodynamic order of deoxidation power: Ca>Al>Si>Mn
- Inclusion formation is faster but its removal is rate controlling
- De-oxidation product removal can be made faster by making liquid product of deoxidation, optimum bath stirring
- De-oxidation is usually practiced at tapping ladle/LF/CAS-OB
- Dissolved oxygen is measured by solid electrolyte cell and total oxygen is measured by chemical analysis

Conclusion: The conclusion from lectures 36 & 37 are summarized here.

Today secondary steelmaking is an essential unit to complete steelmaking for meeting up stringent compositional requirement, low tolerance for impurities during continuous casting, and inclusion removal and control for clean steel production. Primary steel making units are designed for faster production of crude steel and subsequent compositional adjustment are left to secondary steelmaking equipped with advanced instrumentation.

Secondary steelmaking starts with deoxidation. Other operations that follows are degassing, deep decarburization, de-sulphurization, inclusion control by injection of calcium powder, inclusion removal and bath homogenization by gas stirring, temperature compensation etc.

Some of the important units in secondary steel making are VD, VAD, VOD, AOD, RH, LF, CAS.

De-oxidation thermodynamics indicated that calcium is the strongest deoxidizer followed by aluminum, silicon and weakest is the manganese. Due to low yield and corrosive nature of Ca, it is not usually used for bulk deoxidation and aluminum is preferred. Also Si-Mn is also used sometimes as it favours deoxidation kinetics by producing liquid product of deoxidation.

De-oxidation kinetics has been found to be rate limited by the removal of oxidation products from the bath. Formation of bigger oxide particles, bath stirring, and liquid product of deoxidation have been found to favour the oxide removal rate.

Dissolved oxygen in the bath can be measured by solid electrolyte cell, called the cellox probe, by applying Nernst equation.

Deoxidation practice starts at the tapping ladle by laying aluminum bar at the bottom of the ladle and pouring liquid steel over it and the inertia of the tapping stream is utilized for aluminum melting and dissolution. De-oxidation is also carried out in ladle furnace with inert gas injection from bottom.

Deoxidation may be carried out along with decarburization in RH-OB, with oxygen blowing under vacuum.   CAS-OB can also be used to lower the carbon and oxygen at lower value.