Lecture 25: Principles of degassing

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Key words: Degassing, gases in steel, ladle steelmaking

Introduction

During steelmaking gases like oxygen, hydrogen and nitrogen dissolve in steel. The term degassing is employed to remove nitrogen and hydrogen from steel. Dissolved oxygen from steel melt cannot be removed as molecular oxygen. Removal of oxygen is termed deoxidation and is discussed in lecture 24. This lecture concerns with degassing.

Both nitrogen and hydrogen impair the mechanical properties of steel. The maximum solubility of nitrogen in liquid iron is 450ppm and less than 10ppm at room temperature. During solidification excess nitrogen is rejected which may form either blow holes or nitrides. Excess nitrogen causes embrittlement of heat affected zone of welded steels and impair cold formability. Hydrogen in steel impairs steel properties. Solubility of hydrogen in steel is low at ambient temperature. Excess hydrogen is rejected during solidification and results in pinhole formation and porosity in steel. Few ppm of hydrogen causes blistering and loss of tensile ductility. Thus removal of nitrogen and hydrogen from steel is necessary.

Principles

Consider removal of hydrogen and nitrogen from liquid steel

$$[H] = \frac{1}{2}\{H_2\} \tag{1}$$

$$[N] = \frac{1}{2}\{N_2\} \tag{2}$$

$$[Wt\% \ N] = \frac{P_{N_2}^{\frac{1}{2}} \times K_N}{f_N} \tag{3}$$

$$[Wt\% \ H] = \frac{P_{H_2}^{\frac{1}{2}} \times K_H}{f_H} \tag{4}$$

f_N and f_H are activity coefficient of nitrogen and hydrogen in steel, P_{N_2} and P_{H_2} are equilibrium partial pressure of nitrogen and hydrogen in steel.

$$\log f_N = e_N^i (\% \, i) + e_N^J (\% \, J) + \cdots \tag{5}$$

$$\log f_H = e_H^i (\% \, i) + e_H^J (\% \, H) + \cdots \tag{6}$$

Some values of interaction parameters are given below.

Alloying elements i =	C	Cr	Ti	P	Si
e_H^i	0.045	+0.005	-0.22	0.011	0.027
e_N^i	0.13	- 0.045	-	0.051	0.047

$$\log k_N = -\frac{518}{T} + 2.937 \tag{8}$$

$$\log k_H = -\frac{1905}{T} + 2.409 \tag{9}$$

Let us calculate value of $[Wt\% \, H]$ when molten steel is degassed at 1850 K under vacuum. The pressure above the melt is reduced in one case to 1mm Hg and in other cases to 0.1 mm Hg and 10 mm Hg. Steel contains $C = 0.05\%$, Cr 6% Ti 0.6%, Ni 2% rest iron. Assume $e_H^{Ni} = 0$.

$$\log f_H = 0.05 \times 0.045 + 0.005 \times 6 + 0.22 \times 0.6$$

$$f_H = 0.795$$

$$k_H = 23.94$$

| Pressure (mmHg)	[ppm H]
0.1	0.218
1.0	1.092
10	3.450

We note that with the decreasing pressure above the melt dissolved hydrogen in steel decreases. At 10 mm Hg pressure above the melt, dissolved hydrogen is 3.450 ppm which decreases to 0.218 ppm at 0.1mm Hg pressure, which is 6% of hydrogen at 10mm Hg pressure. Higher degree of vacuum is beneficial with reference to degassing. But higher degree of vacuum requires proper selection of ladle refractory material to avoid decomposition of the refractory and vacuum equipment. Also side reactions may occur at higher degree of vacuum.

Side reactions

During vacuum degassing the following reaction may occur. Nitride and oxide inclusions can decompose according to

$$Al\ N = [Al] + [N]$$

Application of vacuum decreases nitrogen which favors decomposition of $Al\ N$. Oxide inclusions can react with C

$$SiO_2 + C = \{Si\} + 2\{CO\}$$
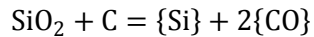
Lowering of CO pressure favours the forward reaction. Reaction between lining and carbon of liquid steel or decomposition of lining may occur:

$$SiO_2 + C = \{SiO\} + \{CO\}$$

$$MgO = Mg(g) + [O]$$

$$CaO = Ca(g) + [O]$$

$$MgO + C = Mg(g) + \{CO\}$$
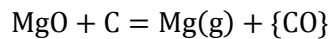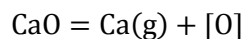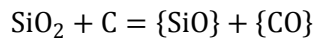
Note that SiO is a highly reactive gas at the steelmaking temperature. All reactions generate one or more gaseous species, hence lowering of pressure promotes the occurrence of side reactions. Mg and Ca are stable gases at steelmaking temperatures.

Volatilization of elements of high vapor pressure may occur. Mn and Fe have high vapor pressures and their losses occur during vacuum treatment. Loss of Al and Si is negligible.

General considerations

1) The desorption of gases is a gas/ metal interfacial reaction. The atomic nitrogen from the molten steel has to diffuse at the gas/metal interface, where it is converted to molecular nitrogen which can then be desorbed. The effectiveness of vacuum treatment increases with increase in surface area of liquid exposed to vacuum. The increased surface area of molten steel exposed to vacuum e.g. in the form of a thin stream or gas induced stirring will accelerate the degassing process.

2) Temperature of molten steel drops during vacuum treatment. More is the surface area of stream exposed to vacuum higher will be the temperature drop. To compensate for the loss of heat, the following alternative may be considered.
   i.   Tapping of steel at a higher temperature. This requires increased heat load in BOF/EAF
   ii. Additional heating during vacuum treatment.

3) The degassing time must be kept to minimum.

4) The degree of degassing increases with the degree of vacuum. Vacuum of the order of 1mm or even less than 1mm Hg (1mmHg=1torr) is employed in the practice. Vacuum pumping capacity should be adequate.

Fluid Flow in degassing

Degassing can be carried out either by placing ladle containing molten steel under vacuum or by recirculation of molten steel in vacuum.

In ladle degassing, the effectiveness of degassing decreases from top to bottom of the molten steel bath. Bottom layers of steel are very much less affected by vacuum since these layers are under the influence of ferrostatic pressure due to column of liquid steel. Hence bath agitation would help exposing the entire content of molten steel to the vacuum. Argon stirring is commonly employed during degassing. Argon bubbling during degassing of molten steel leads to massive volumetric expansion of bubbles due to temperature.(volume of gas becomes 6.3 times at 1873K). Moreover rising gas bubbles absorb dissolved gases. Radial expansion of gas bubble in vacuum processing impart to a radial motion to the surrounding fluid.

In recirculation degassing argon is also bubbled through porous plugs located at the bottom of the ladle. The speed of degassing increases with the increased rate of circulation (R) of liquid steel through the vacuum chamber. Typically R ranges in between 10t/min to 100t/min. Circulation velocity increases with an increasing argon gas flow rate.

The circulation rate (R) can be determined by

$$R = 7.42 \times 10^3 \ Q^{1/3} d^{1/3} \left\{ \ln \left(\frac{P1}{P2} \right) \right\} \qquad\qquad (9)$$

Here R= circulation rate Kg/s

Q= argon injection rate $Nm^3/min.$

$P_1 =$ Pressure at the base of downleg

$P_2 =$ Pressure in vacuum chamber

D= internal diameter of leg (m)

Material balance in degassing

Consider removal of hydrogen in recirculation degassing i.e. during circulation of molten steel in vacuum.

Hydrogen balance

Rate of hydrogen removal from steel $\left(\dot{M}_1 \right) =$ rate at which hydrogen is transferred in vacuum$\left(\dot{M}_2 \right)$

If weight of steel is m in tones, t is time in minutes and ppmH is hydrogen concentration at any instant of time.

$$\left(\dot{M}_1\right) = -m \times 10^6 \frac{d[PPmH]\times 10^{-6}}{dt} = -m \times \frac{d[PPmH]}{dt} \tag{10}$$

$$\left(\dot{M}_2\right) = R \times 10^6 \{[PPmH] - [PPmH]^*\} \times 10^{-6} \tag{11}$$

R is circulation rate in tone /min, and $[PPmH]^*$ is hydrogen concentration at equilibrium.

By 10 and 11

$$\frac{R}{m} dt = -\frac{d[PPmH]}{[PPmH] - [PPmH]^*} \tag{12}$$

Integrating equation 12 and using boundary conditions

$$[PPmH] = [PPmH]_1 \text{ at } t = 0$$
$$[PPmH] = [PPmH]_2 \text{ at } t = t \tag{13}$$

$$R = \frac{m}{t} \ln \frac{[PPmH]_1 - [PPmH]^*}{[PPmH]_2 - [PPmH]^*} \tag{14}$$

In lecture 30, some problems related to degassing are discussed

References:

1) A. Ghosh: Principles of secondary processing and casting of liquid steel.
2) A. Ghosh: Secondary steelmaking