Iron Making and Steel Making
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Module – 08
Lecture – 38
Secondary Steel Making: Vacuum Techniques for refining steel

In this lecture I will talk about the Vacuum Techniques for secondary refining of steel.

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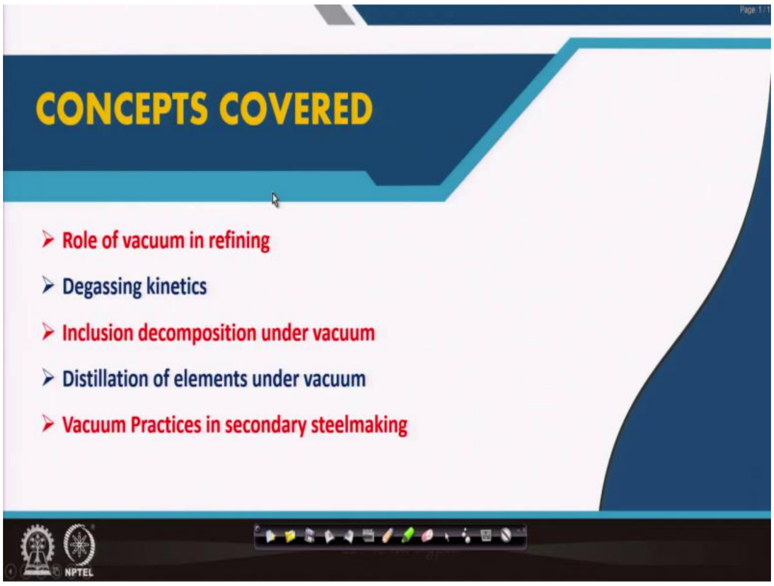

CONCEPTS COVERED

- Role of vacuum in refining
- Degassing kinetics
- Inclusion decomposition under vacuum
- Distillation of elements under vacuum
- Vacuum Practices in secondary steelmaking

So, the topics that will be covered here include role of vacuum in refining, degassing thermodynamics and kinetics, inclusion decomposition and distillation of elements under vacuum, and the vacuum practices used in secondary steelmaking.

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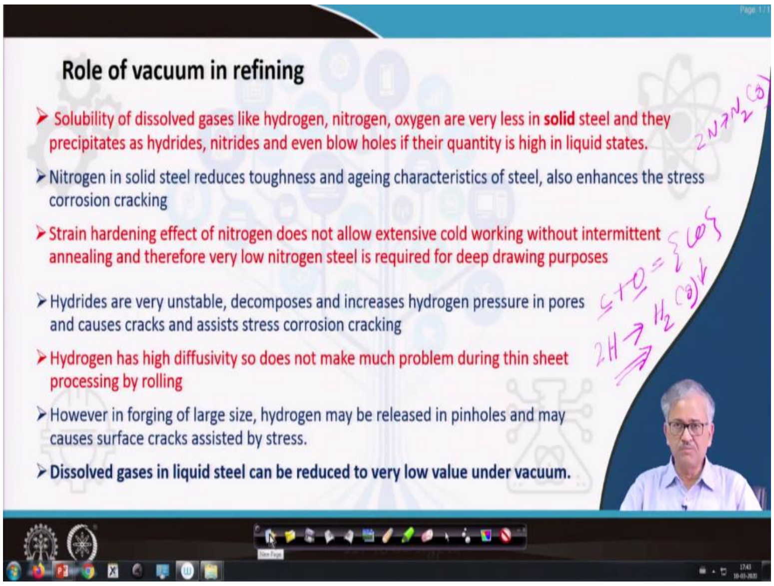

Role of vacuum in refining

- Solubility of dissolved gases like hydrogen, nitrogen, oxygen are very less in **solid** steel and they precipitates as hydrides, nitrides and even blow holes if their quantity is high in liquid states.
- Nitrogen in solid steel reduces toughness and ageing characteristics of steel, also enhances the stress corrosion cracking
- Strain hardening effect of nitrogen does not allow extensive cold working without intermittent annealing and therefore very low nitrogen steel is required for deep drawing purposes
- Hydrides are very unstable, decomposes and increases hydrogen pressure in pores and causes cracks and assists stress corrosion cracking
- Hydrogen has high diffusivity so does not make much problem during thin sheet processing by rolling
- However in forging of large size, hydrogen may be released in pinholes and may causes surface cracks assisted by stress.
- **Dissolved gases in liquid steel can be reduced to very low value under vacuum.**

$2N \rightarrow N_2(g)$

$\underline{C} + \underline{O} = \{CO\}$

$2H \rightarrow H_2(g)\uparrow$

Three major gaseous impurities in steel are like hydrogen, nitrogen, and oxygen. Due to limited solute solubility in solid, during solidification, these gaseous impurities will be ejected from the liquid steel at the solid – liquid interface, leading to supersaturation and precipitation of undesirable nitrides, hydrides and oxides inclusions. When their concentration is high in liquid, they will form gas bubbles and those will be partially entrapped in the form of blow holes.

Severe strain hardening effect of nitrogen does not allow extensive cold working without intermittent annealing. Repeatedly annealing disperse the nitrogen avoiding local supersaturation and nitride precipitation on the grain boundary. So, nitrogen steel are not suitable for deep drawing purpose.

So, hydrogen form hydrides that are not very stable. Hydride dissociate into hydrogen and the hydrogen gas can build up inside the pores, develop pressure leading to crack formation; specially, if it is near surface region, they can make the hair line cracks. Such developed pressure inside the pores also might lead to the stress corrosion cracking. But hydrogen has a very high diffusivity. So, in case of a very thin sheet hydrogen could diffuse away easily to the atmosphere. So hydrogen is not a problem for rolling of thin sheet; but it causes a lot of problem for thick sheet, especially during forging. During forging of large size, hydrogen may be released in the pinholes and may cause the surface crack assisted by stress during forging.

Similarly, oxygen can form undesirable harmful oxide inclusions besides oxygen also can form the blow holes of CO. So, all this gaseous impurities have to be brought down to a very low level not only for casting, but also for post casting downstream applications. Such low level specification of gaseous impurities in liquid steel is possible only by application of vacuum.

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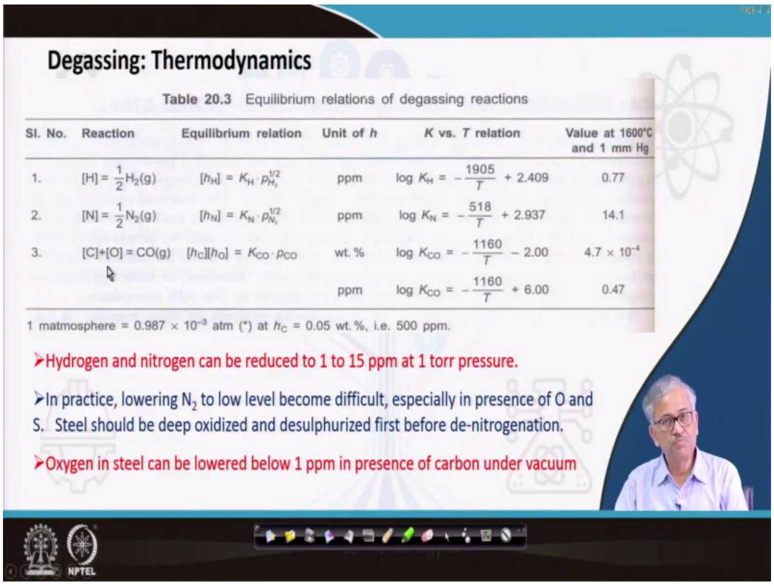


Degassing: Thermodynamics

Table 20.3 Equilibrium relations of degassing reactions

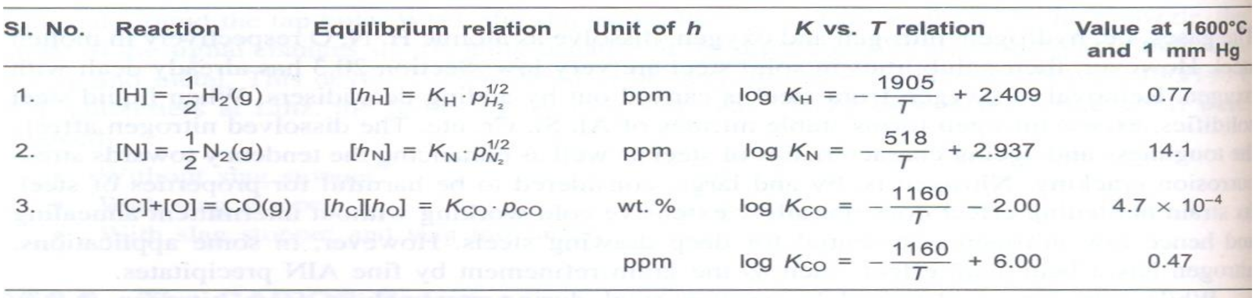
Sl. No.	Reaction	Equilibrium relation	Unit of *h*	*K* vs. *T* relation	Value at 1600°C and 1 mm Hg
1.	$[H] = \frac{1}{2}H_2(g)$	$[h_H] = K_H \cdot p_{H_2}^{1/2}$	ppm	$\log K_H = -\frac{1905}{T} + 2.409$	0.77
2.	$[N] = \frac{1}{2}N_2(g)$	$[h_N] = K_N \cdot p_{N_2}^{1/2}$	ppm	$\log K_N = -\frac{518}{T} + 2.937$	14.1
3.	$[C]+[O] = CO(g)$	$[h_C][h_O] = K_{CO} \cdot p_{CO}$	wt. %	$\log K_{CO} = -\frac{1160}{T} - 2.00$	4.7×10^{-4}
			ppm	$\log K_{CO} = -\frac{1160}{T} + 6.00$	0.47

1 matmosphere = 0.987×10^{-3} atm (*) at $h_C = 0.05$ wt. %, i.e. 500 ppm.

- ➤Hydrogen and nitrogen can be reduced to 1 to 15 ppm at 1 torr pressure.
- ➤In practice, lowering N_2 to low level become difficult, especially in presence of O and S. Steel should be deep oxidized and desulphurized first before de-nitrogenation.
- ➤Oxygen in steel can be lowered below 1 ppm in presence of carbon under vacuum

Now, let us discuss the thermodynamics of degassing under vacuum. The Table 38.1 presents some equilibrium data indicating the minimum level of gaseous impurities achievable at 1 torr pressure (1 mm of Hg) and 1600°C.

Table 38.1 Equilibrium relations of degassing reactions[1]



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3.	$[C]+[O] = CO(g)$	$[h_C][h_O] = K_{CO} \cdot p_{CO}$	wt. %	$\log K_{CO} = -\frac{1160}{T} - 2.00$	4.7×10^{-4}
			ppm	$\log K_{CO} = -\frac{1160}{T} + 6.00$	0.47

Activity has been expressed with respect to 1wt% standard state and Henry’s has been assumed to be valid for the gaseous imputities in liquid steel. Finally, activity has been expressed in terms of concentration (either in ppm or wt%). 1 torr pressure represent 1 mm of mercury or, 10^{-3} atmosphere.

Using the equilibrium relationship provided, amount of hydrogen dissolved in liquid steel at 1 torr pressure and 1600oC can be calculated as 0.77 ppm (<1ppm!). Similarly, the nitrogen amount can be lowered at 14 ppm. Oxygen also can be lowered to less than 1 ppm(0.44 ppm), but in presence of carbon with a product gas CO. It has been found that oxygen can not be removed reasonably from pure liquid iron without any carbon in it.

Although thermodynamically nitrogen can be lowered to a value of 14 ppm, but in practice lowering nitrogen to a very low level become difficult, specially in presence of oxygen and sulfur. Because oxygen and sulphur are surface active elements and interact unfavorably for the surface adsorption and desorption of nitrogen. Therefore, steel should be deep deoxidized or deep desurphurdized first before the denitrogenation of the liquid bath.

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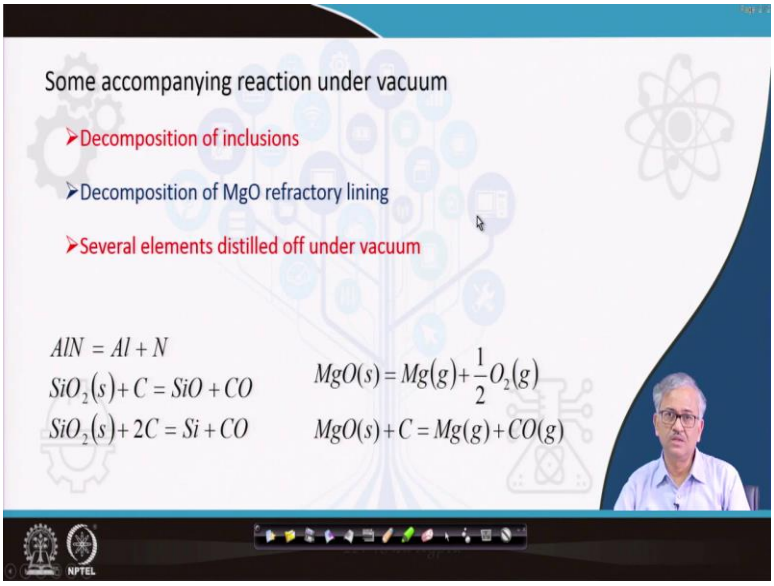

Some accompanying reaction under vacuum

- Decomposition of inclusions
- Decomposition of MgO refractory lining
- Several elements distilled off under vacuum

$$AlN = Al + N$$
$$SiO_2(s) + C = SiO + CO$$
$$SiO_2(s) + 2C = Si + CO$$
$$MgO(s) = Mg(g) + \frac{1}{2}O_2(g)$$
$$MgO(s) + C = Mg(g) + CO(g)$$

Let us now see some of the accompanying reactions that take place under vacuum. Equations (38.1) to (38.5) shows some of the accompanying reaction during vacuum degassing.

$$AlN = Al + N$$

(38.1)

$$SiO_2(s)+C=SiO+CO$$

(38.2)

$$SiO_2(s)+2C=Si+CO$$

(38.3)

$$MgO(s)=Mg(g)+\frac{1}{2}O_2(g)$$

(38.4)

$$MgO(s)+C=Mg(g)+CO(g)$$

(38.5)

You can see some inclusions decompose under vacuum right. For example, aluminum nitride, which is an inclusion, decomposes under vacuum to aluminum and nitrogen; nitrogen is gaseous and this reaction responds favorably under vacuum. For example, silica, also a solid inclusion, may react with carbon in steel forming either SiO and CO gas (Equation 38.2), or Si (which dissolves in steel) and CO (Equation 38.3).

Magnesium refectory may also decompose under vacuum. It may decompose to Mg(g)and O2(g) (Equation 38.4), or in presence of dissolved carbon it can decompose as Mg(g) and CO(g) (Equation 38.5). It may be shown through thermodynamic calculations that later is more feasible under vacuum.

Some elements could be distilled off under vacuum . Table 38.2 shows the calculated data of equilibrium vapour pressure of some elements at 1600^{o}C and 1 torr pressure.

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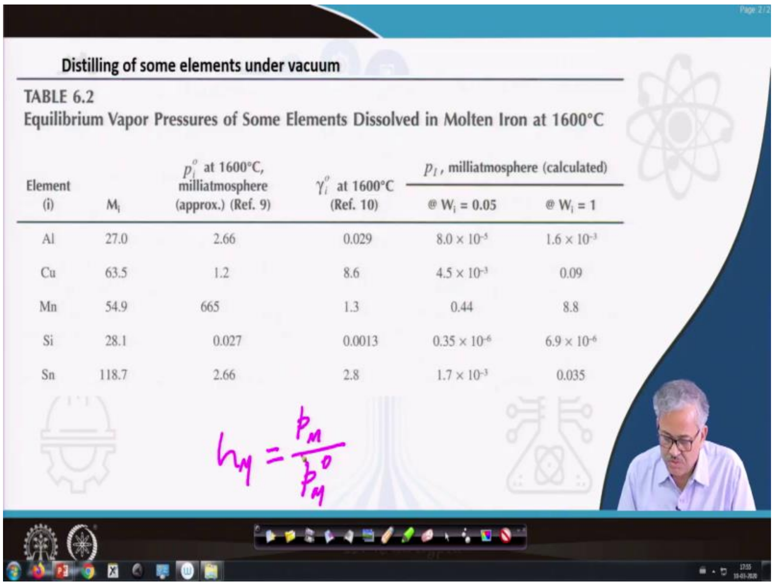


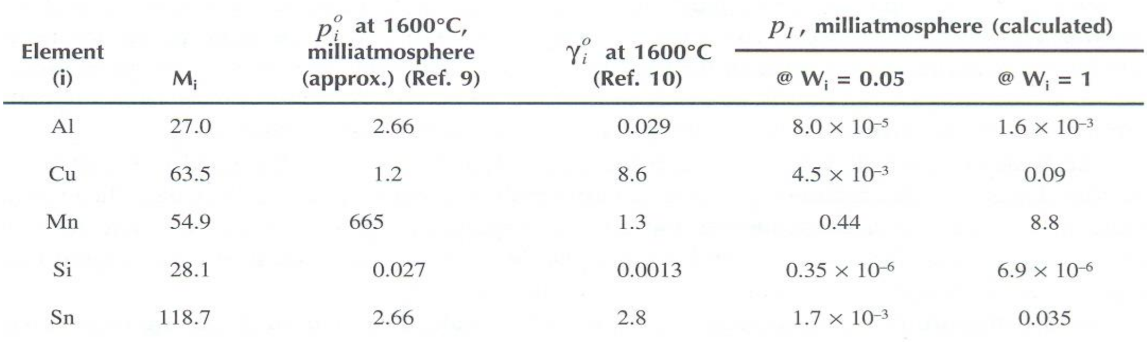
Distilling of some elements under vacuum

TABLE 6.2
Equilibrium Vapor Pressures of Some Elements Dissolved in Molten Iron at 1600°C

Element (i)	M_i	p_i^o at 1600°C, milliatmosphere (approx.) (Ref. 9)	γ_i^o at 1600°C (Ref. 10)	p_I, milliatmosphere (calculated)	
				@ W_i = 0.05	@ W_i = 1
Al	27.0	2.66	0.029	8.0×10^{-5}	1.6×10^{-3}
Cu	63.5	1.2	8.6	4.5×10^{-3}	0.09
Mn	54.9	665	1.3	0.44	8.8
Si	28.1	0.027	0.0013	0.35×10^{-6}	6.9×10^{-6}
Sn	118.7	2.66	2.8	1.7×10^{-3}	0.035

$$h_M = \frac{p_M}{p_M^0}$$

Table 38.2: Equilibrium vapour pressure of some elements dissolved in molten iron at 1600°C[1].



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The vapour pressure of of elements in liquid iron may be calculated using the Equation 38.6, from the definition of activity.

$$a_i = \frac{p_i}{p_i^0} \tag{38.6}$$

Where, p_i^0 represents the vapour pressure of solute "i" under pure state. Now, assuming henry's law activity on Raoultian scale may be expressed as:

$$a_i = \gamma_i^0 x_i \tag{38.7}$$

Where, γ_i^0 is the Henry's law constant and x_i is the mole fraction of the solute i. The mole fraction of solute "i" may be expressed in terms of weight percentage of solvent (Fe) and solute in binary solution, as follows:

$$x_i = \frac{0.56 w_i}{M_i}$$

(38.8)

Contribution of solute in total mole fraction has been ignored.

Now, combining Equations (38.6) to (38.8), the vapor pressure of the solute "i", may be calculated as:

$$p_i = \frac{0.56 w_i \gamma_i^0 p_i^0}{M_i}$$

(38.9)

Equation (38.9), can be used to calculate the vapor pressure of the solute at a particular wt% of solute in the solvent. In Table 38.2, vapour pressure of solute (in milli-atmosphere) has been calculated at two different wt% in solution, namely at 0.05wt% and 1wt% at 1600°C. It is to be noted that 1 torr pressure represents 1 milli atmosphere. So if the vapor of the solutes become higher than 1 milliatmosphere, those are likely to be distilled off at 1 torr pressure. From the Table 38.2 it is seen that when manganese is present at 1wt% level in the liquid iron, its vapour pressure is 8.8 milliatmosphere at steelmaking temperature and therefore it will be distilled off at 1 torr pressure. Other solute (Al, Cu, Sn, Si) are unlikely to be distilled off.

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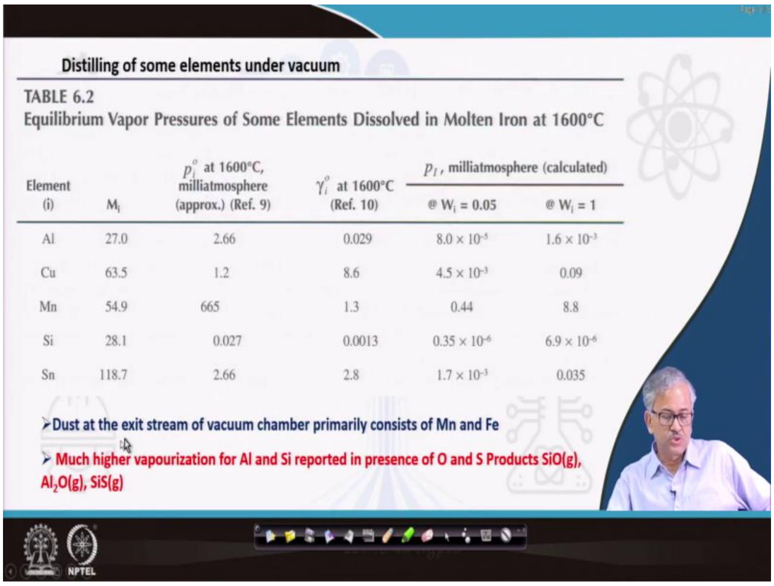

Distilling of some elements under vacuum

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- Dust at the exit stream of vacuum chamber primarily consists of Mn and Fe
- Much higher vapourization for Al and Si reported in presence of O and S Products SiO(g), Al_2O(g), SiS(g)

It is indeed found that the dust in the exit stream of vacuum chamber primarily consists of manganese and iron. Iron obviously, will vaporize because iron forms 95 percent of the iron melt.

Besides also aluminum and silicon is also reported to vaporize in presence of oxygen and sulfur; because in presence of oxygen aluminum forms Al_2O gas and silicon forms the SiS gas in presence of sulphur.

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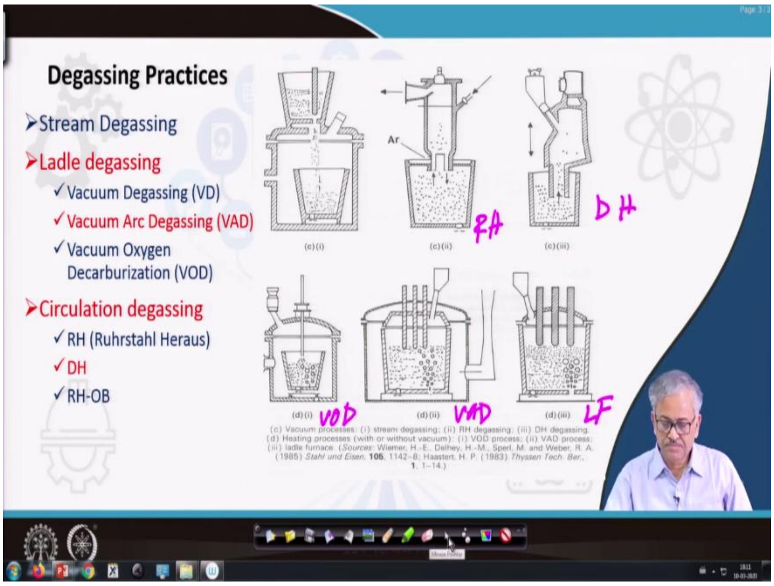
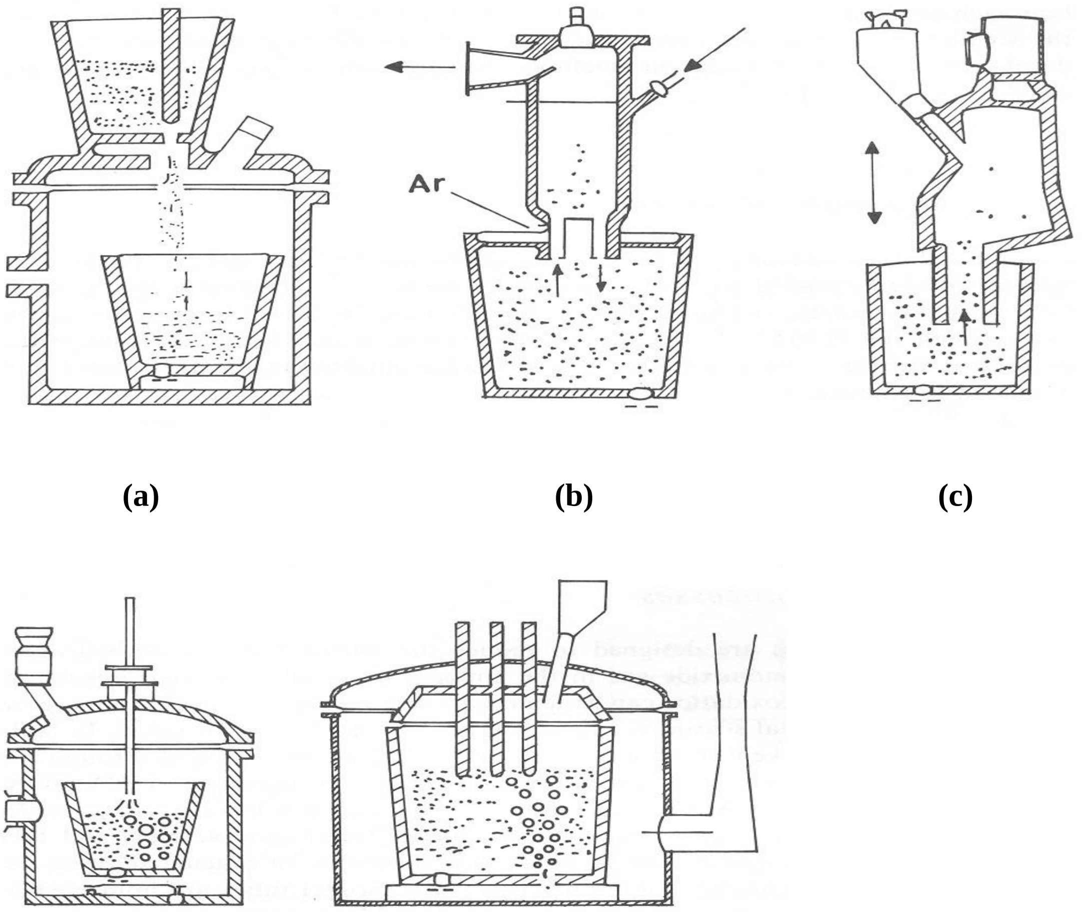


Degassing Practices

- Stream Degassing
- Ladle degassing
  - ✓ Vacuum Degassing (VD)
  - ✓ Vacuum Arc Degassing (VAD)
  - ✓ Vacuum Oxygen Decarburization (VOD)
- Circulation degassing
  - ✓ RH (Ruhrstahl Heraus)
  - ✓ DH
  - ✓ RH-OB

(c) Vacuum processes: (i) stream degassing; (ii) RH degassing; (iii) DH degassing. (d) Heating processes (with or without vacuum): (i) VOD process; (ii) VAD process; (iii) ladle furnace. (*Sources*: Wiemer, H.-E., Delhey, H.-M., Sperl, M. and Weber, R. A. (1985) *Stahl und Eisen*, **105**, 1142–8; Haastert, H. P. (1983) *Thyssen Tech. Ber.*, **1**, 1–14.)

Let us now discuss the various degassing practices. Figure 38.1 shows the various degassing practices that are followed in the industries.



(a) **(b)** **(c)**

(d) **(e)**

Figure 38.1: Various degassing Practices in Industries: (a) stream degassing, (b) RH degassing, (c) DH degassing, (d) VOD, (e) VAD [1]

In stream degassing (Figure (38.1(a)), liquid steel fall in the form of a stream through vacuum chamber into a ladle, placed inside the chamber. The exposed area of the stream allows degassing of liquid. The RH degassing (Figure 38.1(b)) is the most popular degassing unit, where liquid from the ladle circulate through the vacuum chamber placed above the ladle at a certain flow rate through two snorkels (uptake and downtake) , as shown in the figure. It is also call the circulation degassing. The name RH is derived from German name Ruhrstahl Heraus. A lifter gas (normally argon) is used to drag the liquid from the ladle through the uptake snorkel by creating a buoyancy force. After degassing the comparatively heavier liquid come down through the downtake snorkel under gravity.

Since small amount of liquid is taken to the vacuum chamber, the liquid in the vacuum chamber may be assumed to achieve equilibrium concentration under vacuum.

Finally, there is also another device called the VAD (Vacuum Arc Degassing), where both degassing and temperature compensation is met up. Argon stirring is done from the bottom to agitate the bath and improve the kinetics of the process.

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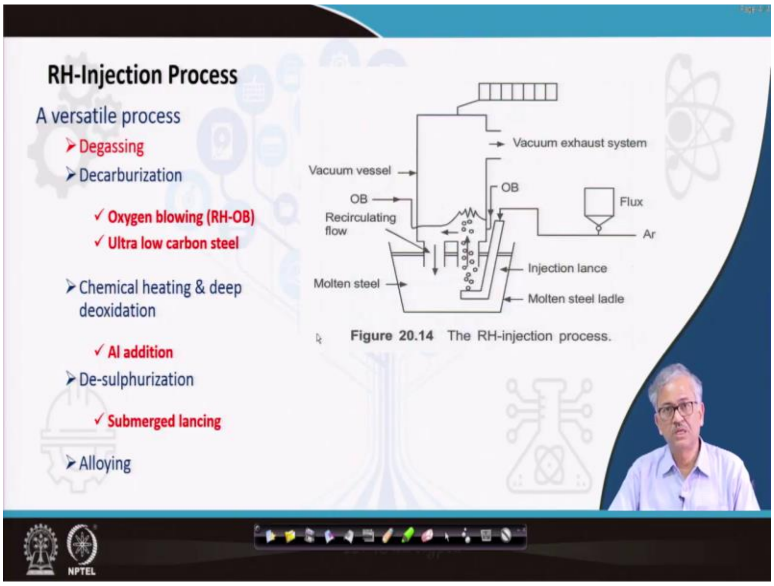

RH-Injection Process

A versatile process

- Degassing
- Decarburization
  - ✓ Oxygen blowing (RH-OB)
  - ✓ Ultra low carbon steel
- Chemical heating & deep deoxidation
  - ✓ Al addition
- De-sulphurization
  - ✓ Submerged lancing
- Alloying

Figure 20.14 The RH-injection process.

RH process is not only used for degassing, today it is used for various other processes and called the RH injection process. Figure 38.2 shows the RH injection process.

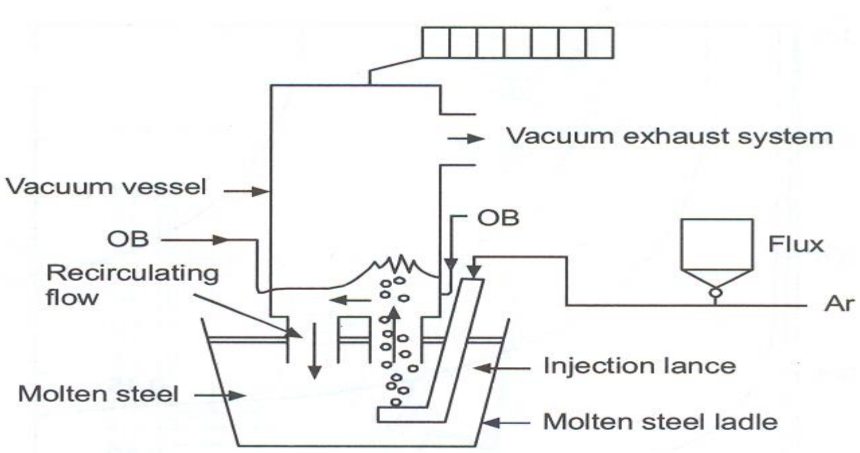

Figure 38.2: RH injection process[1]

Degassing is obviously, one of the major aim of the RH process; but nowadays deep decarburization is done in this reactor with oxygen blowing in vacuum chamber, called the RH-OB process. RH-OB also help in deep-oxidation of the bath. Deslphurization can be carried out by injecting flux powder (primarily calcium powder) along with argon gas through submerged lance. Enhanced stirring in small amount of liquid in the vacuum chamber favors the kinetics to achieve equilibrium.

Controlled alloying with higher yield is also possible in RH under vacuum. Micro-alloying of IF steel could be done in the same reactor following the RH-OB process for deep decarburization.

Reference: [1]. Ghosh and Chatterjee: Ironmaking & Steelmaking-Theory & Practice, PHI, New Delhi, 2008.

[2] Ahindra Ghosh: Secondary Steelmaking-Principles and Applications, CRC Press, USA, 2001

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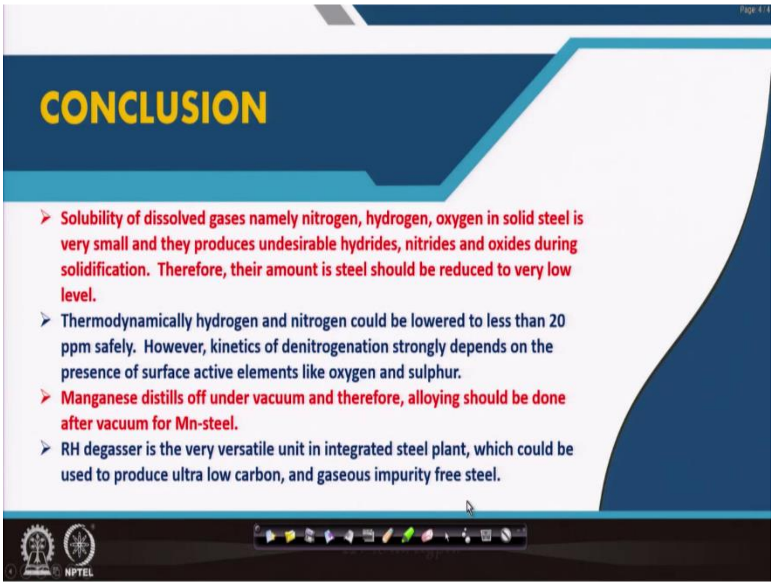

CONCLUSION

- Solubility of dissolved gases namely nitrogen, hydrogen, oxygen in solid steel is very small and they produces undesirable hydrides, nitrides and oxides during solidification. Therefore, their amount is steel should be reduced to very low level.
- Thermodynamically hydrogen and nitrogen could be lowered to less than 20 ppm safely. However, kinetics of denitrogenation strongly depends on the presence of surface active elements like oxygen and sulphur.
- Manganese distills off under vacuum and therefore, alloying should be done after vacuum for Mn-steel.
- RH degasser is the very versatile unit in integrated steel plant, which could be used to produce ultra low carbon, and gaseous impurity free steel.

Conclusion: Solubility of dissolved gases mainly nitrogen, hydrogen, oxygen in solid steel is very limited and large presence of these gaseous impurities in liquid steel produce undesirable hydrides, nitrides and oxides during solidification. Therefore, their amount in steel should be reduced to a very low level.

Thermodynamically, hydrogen and nitrogen could be lowered even below that 20 ppm safely; but in actual practice it is not. Especially nitrogen removal becomes difficult in presence of surface active elements like oxygen and sulfur. Therefore, bath has to be deoxidized and desulphurized deeply denitrogenation can proceed to a very low value. Oxygen and sulfur unfavorably interact with the adsorption and desorption of nitrogen.

Under vacuum, some impurities like AlN and SiO_2 are likely to decompose. Manganese is likely to distilled off under 1 torr pressure. Therefore, Mn-alloyng shouldbe done after vacuum treatment.

RH degassing unit is versatile and can be used for deep de-oxidation, and decarburization using oxygen blowing. Desulphurization can be carried by flux powder lancing with argon gas. Microalloying can be done with high yield. Microalloyed IF steel can preferably made in RH reactor.