Steel Quality Role of Secondary Refining and Continuous Casting

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Module - 02
Lecture - 11
Secondary Refining Processes

I have started talking about the importance of secondary refining, in the last two or three sessions I have already covered some of them. I initially I talked about the limitation of primary why you know secondary refining is necessary.

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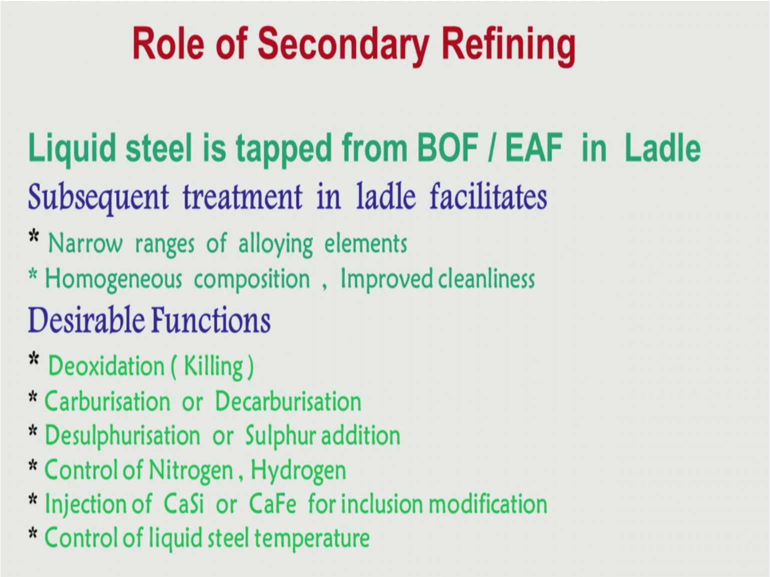

Role of Secondary Refining

Liquid steel is tapped from BOF / EAF in Ladle

Subsequent treatment in ladle facilitates

* Narrow ranges of alloying elements
* Homogeneous composition , Improved cleanliness

Desirable Functions

* Deoxidation (Killing)
* Carburisation or Decarburisation
* Desulphurisation or Sulphur addition
* Control of Nitrogen , Hydrogen
* Injection of CaSi or CaFe for inclusion modification
* Control of liquid steel temperature

Then what are the common secondary refining processes and some of them I had discussed what are the requirements and how you know different steel making process.

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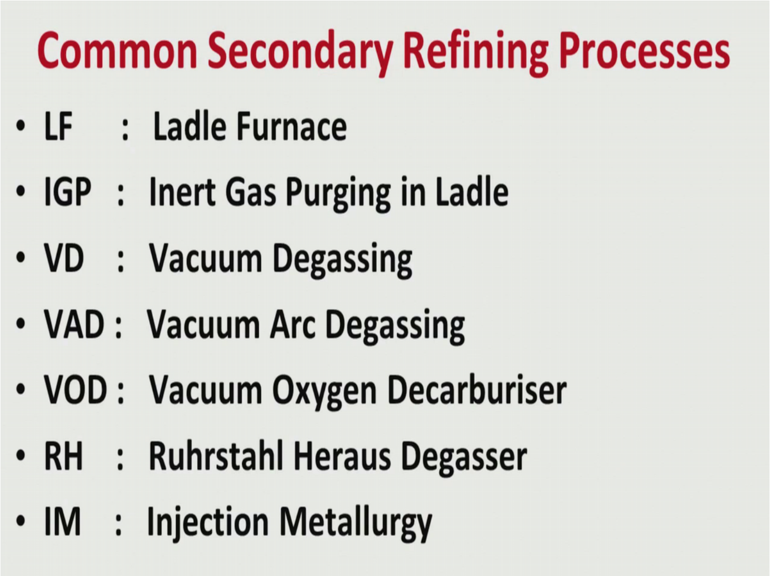

Common Secondary Refining Processes

- LF : Ladle Furnace
- IGP : Inert Gas Purging in Ladle
- VD : Vacuum Degassing
- VAD : Vacuum Arc Degassing
- VOD : Vacuum Oxygen Decarburiser
- RH : Ruhrstahl Heraus Degasser
- IM : Injection Metallurgy

They had fulfilled, then I have talked about in details about deoxidation what are the issues which element.

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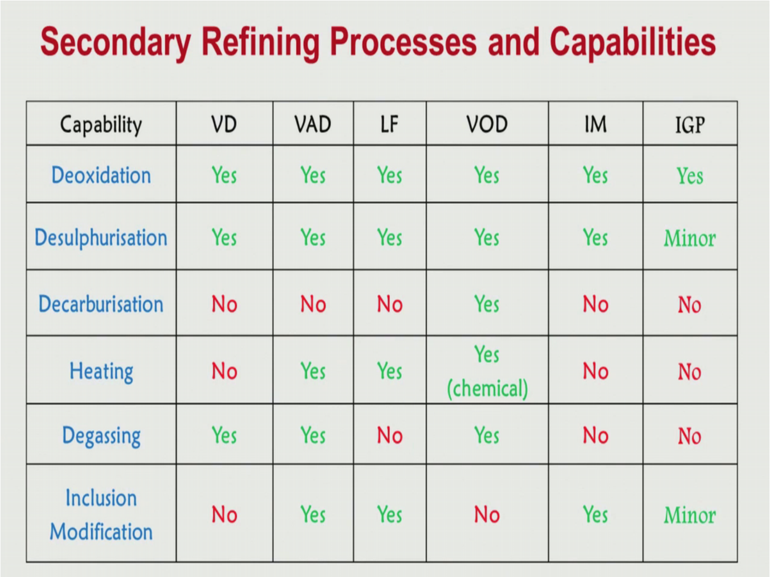

Secondary Refining Processes and Capabilities

Capability	VD	VAD	LF	VOD	IM	IGP
Deoxidation	Yes	Yes	Yes	Yes	Yes	Yes
Desulphurisation	Yes	Yes	Yes	Yes	Yes	Minor
Decarburisation	No	No	No	Yes	No	No
Heating	No	Yes	Yes	Yes (chemical)	No	No
Degassing	Yes	Yes	No	Yes	No	No
Inclusion Modification	No	Yes	Yes	No	Yes	Minor

We can theoretically know is a good dioxidiser, which one is a relatively moderate and which one is relatively be less dioxidiser.

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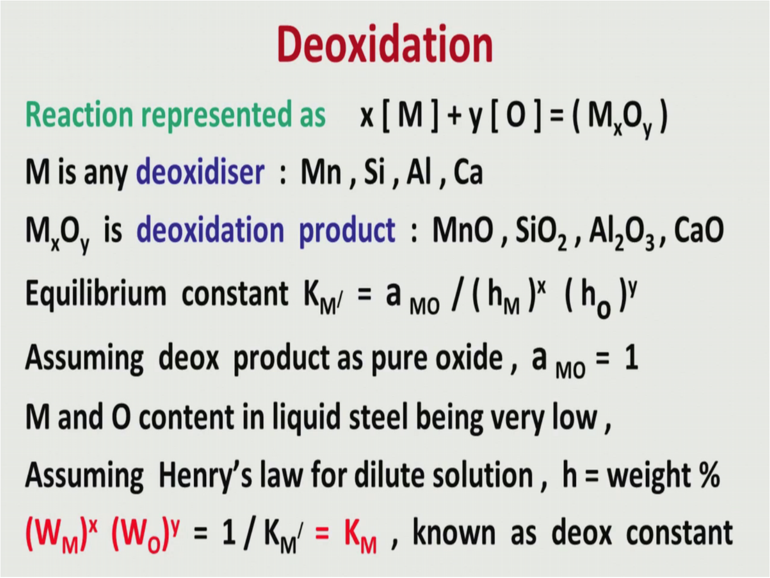

Deoxidation

Reaction represented as $x [M] + y [O] = (M_xO_y)$

M is any deoxidiser : Mn , Si , Al , Ca

M_xO_y is deoxidation product : MnO , SiO_2 , Al_2O_3 , CaO

Equilibrium constant $K_{M}' = a_{MO} / (h_M)^x \ (h_O)^y$

Assuming deox product as pure oxide , $a_{MO} = 1$

M and O content in liquid steel being very low ,

Assuming Henry's law for dilute solution , h = weight %

$(W_M)^x \ (W_O)^y = 1 / K_{M}' = K_M$, known as deox constant

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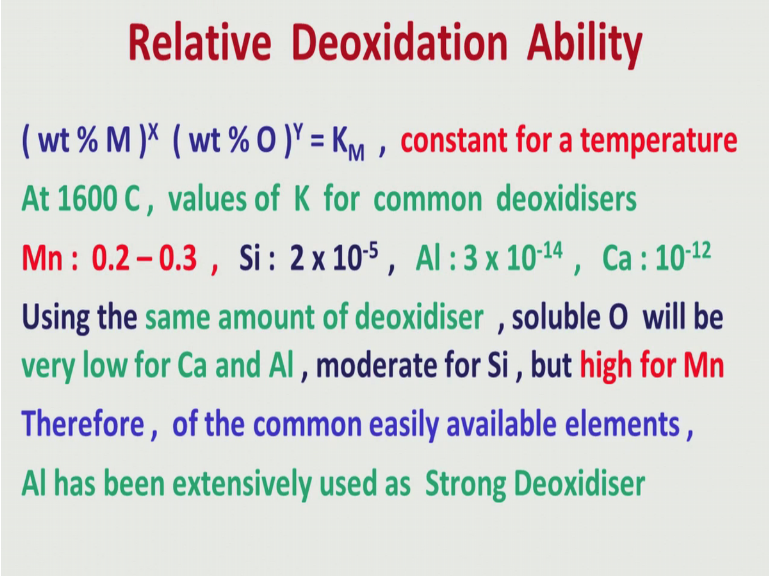

Relative Deoxidation Ability

$(wt \% \ M)^X \ (wt \% \ O)^Y = K_M$, constant for a temperature

At 1600 C , values of K for common deoxidisers

Mn : 0.2 – 0.3 , Si : 2×10^{-5} , Al : 3×10^{-14} , Ca : 10^{-12}

Using the same amount of deoxidiser , soluble O will be very low for Ca and Al , moderate for Si , but high for Mn

Therefore , of the common easily available elements ,

Al has been extensively used as Strong Deoxidiser

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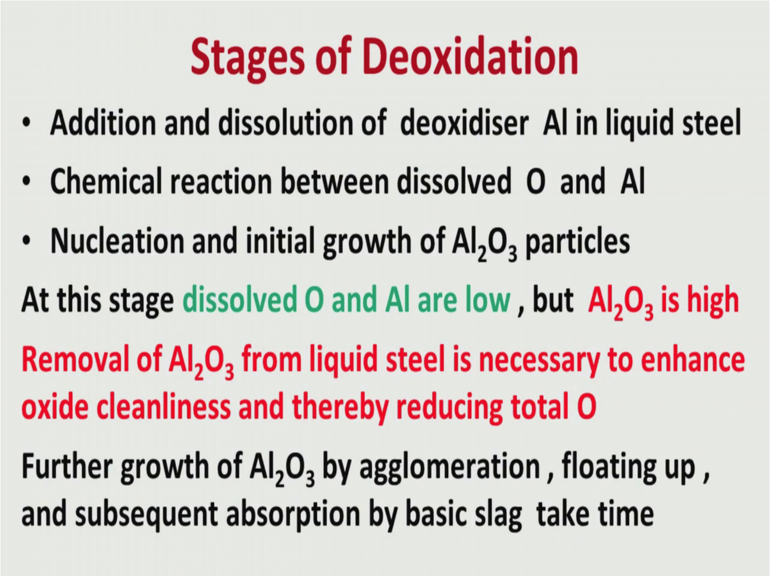

Stages of Deoxidation

- Addition and dissolution of deoxidiser Al in liquid steel
- Chemical reaction between dissolved O and Al
- Nucleation and initial growth of Al_2O_3 particles

At this stage dissolved O and Al are low, but Al_2O_3 is high

Removal of Al_2O_3 from liquid steel is necessary to enhance oxide cleanliness and thereby reducing total O

Further growth of Al_2O_3 by agglomeration, floating up, and subsequent absorption by basic slag take time

So, what are the dioxidation stages? You know like do you require inclusions to float up for decreasing the you know alumina or silica whatever inclusions have formed.

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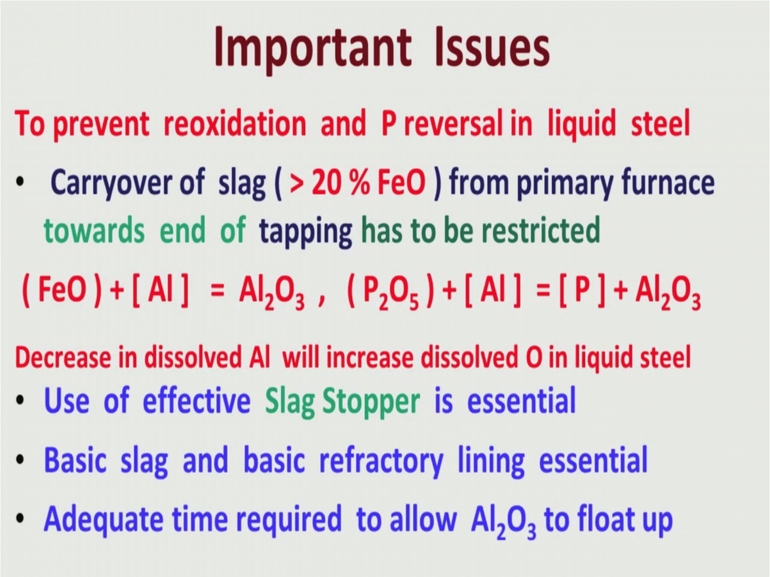

Important Issues

To prevent reoxidation and P reversal in liquid steel

- Carryover of slag (> 20 % FeO) from primary furnace towards end of tapping has to be restricted

$(FeO) + [Al] = Al_2O_3$, $(P_2O_5) + [Al] = [P] + Al_2O_3$

Decrease in dissolved Al will increase dissolved O in liquid steel

- Use of effective Slag Stopper is essential
- Basic slag and basic refractory lining essential
- Adequate time required to allow Al_2O_3 to float up

Then I have talked about an important issue like we took prevent reoxidation and phosphorus reverse and liquid steel, carryover of slag from primary furnace towards end of tapping has to be restricted. Why I talked about this because primary slag has very large amount of iron oxide it may be about its much more than 20 percent, may be 25 percent moreover it has some amount of MnO manganese oxide, it has some amount of phosphorous oxide which by the way phosphorous has got transferred in primary steel making from metal to slag in the form of phosphorous oxide.

So, if these you know carryover slag; that means, primary furnace slag when if it is carried over to the ladle to during subsequent secondary refining stages, this will create problem this will have implications on the quality.

Iron oxide might react with aluminum in steel generating alumina phosphorous oxide might react with alumina aluminum in steel. So, there is a phosphorous chances of phosphorous reversal MnO if it which is there in the you know primary slag when it is coming to secondary stage if it comes it will also react with aluminum in liquid steel generating manganese oxide. So, in the process what is happening in this reoxidation is happening; that means the aluminum which is present in liquid steel is getting oxidized to alumina and phosphorous oxide which was in the slag.

So, there is it will react with the aluminum and there is a possibility of phosphorous revers and liquid steel. So, these have implications on quality and moreover this aluminum by the process of deoxidation aluminum which is present in liquid steel dissolve aluminum if it comes down. So, reaction with iron oxide or phosphorous oxide or manganese oxide then what is going to happen? The dissolved oxygen in liquid steel also will come down because dissolved aluminum is increasing or just that reverse dissolved aluminum is decreasing by these reactions. So, dissolved oxygen in liquid steel is going to increase which has lot of implication on the quality. So, affective slag stopper I had told is very important

Moreover I told you that basic slag and basic refractory why this are important because basic slag will be helpful in absorbing the inclusions which are floating up whether it is alumina or SiO2, and basic refractory lining is important because if you have less basic refractory lining that means, if there is SiO2 in the lining some amount of SiO2 has you know include as undesirable constituent in the refractory lining, it would react with aluminum in liquid steel and generate alumina which is a which has to be taken care of dissolved aluminum will come down. So, deoxidation is a problem.

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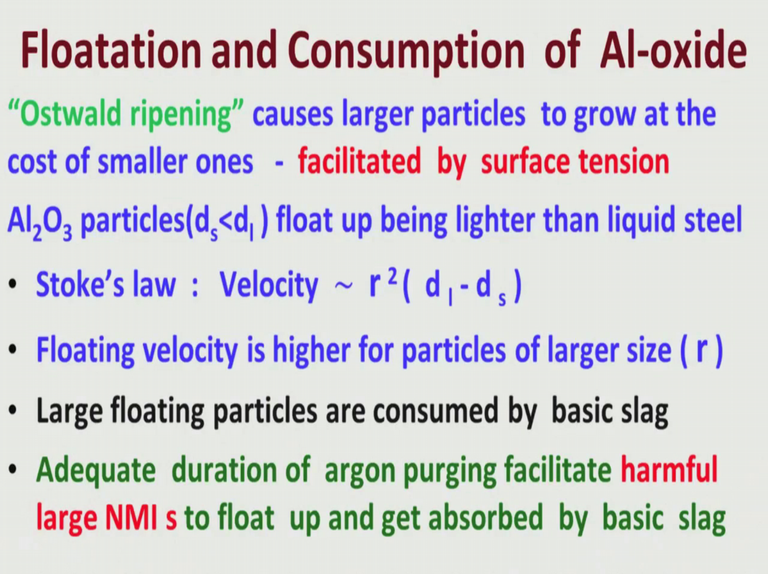

Floatation and Consumption of Al-oxide

"Ostwald ripening" causes larger particles to grow at the cost of smaller ones - facilitated by surface tension

Al_2O_3 particles($d_s<d_l$) float up being lighter than liquid steel

- Stoke's law : Velocity $\sim r^2(d_l - d_s)$
- Floating velocity is higher for particles of larger size (r)
- Large floating particles are consumed by basic slag
- Adequate duration of argon purging facilitate harmful large NMI s to float up and get absorbed by basic slag

Now, floatation of this you know aluminum oxide I have talked about stokes law how does it help, how does it you know how does it another explain, while inclusions which are larger in size should float up at higher velocity, because the density of the inclusions are less and smaller inclusions they will coagulate to form larger inclusions, fortunately larger inclusions are floating up at a higher velocity.

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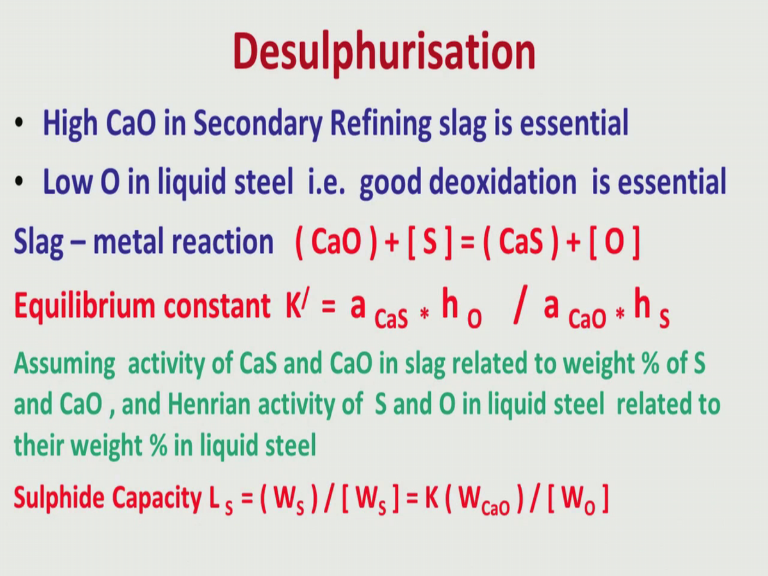

Desulphurisation

- High CaO in Secondary Refining slag is essential
- Low O in liquid steel i.e. good deoxidation is essential

Slag – metal reaction $(CaO) + [S] = (CaS) + [O]$

Equilibrium constant $K' = a_{CaS} * h_O \ / \ a_{CaO} * h_S$

Assuming activity of CaS and CaO in slag related to weight % of S and CaO , and Henrian activity of S and O in liquid steel related to their weight % in liquid steel

Sulphide Capacity $L_S = (W_S) / [W_S] = K (W_{CaO}) / [W_O]$

So, they will float up and get absorbed by at the basic slag. Then I talked about desulphurization and I have mentioned how CaO in slag is very important. So, we must have about 50 percent CaO in the slag in the secondary refining processes and the basicity; that means, the ratio of CaO and SiO2 in the slag should be at least 3 it should be preferably more than 3.

So, I have explained why more CaO is useful and less oxygen in liquid slag is important. You will see here yeah the sulphide capacity is proportional to the weight of CaO in the slag, and inversely proportional to oxygen content in liquid steel. So, oxygen content in liquid steel that it means the dissolved oxygen in liquid steel has to be low to get a good amount of desulphurization, that is why I have mentioned earlier and again I am repeating good deoxidation is a prerequisite is a necessity for getting good desulphurization.

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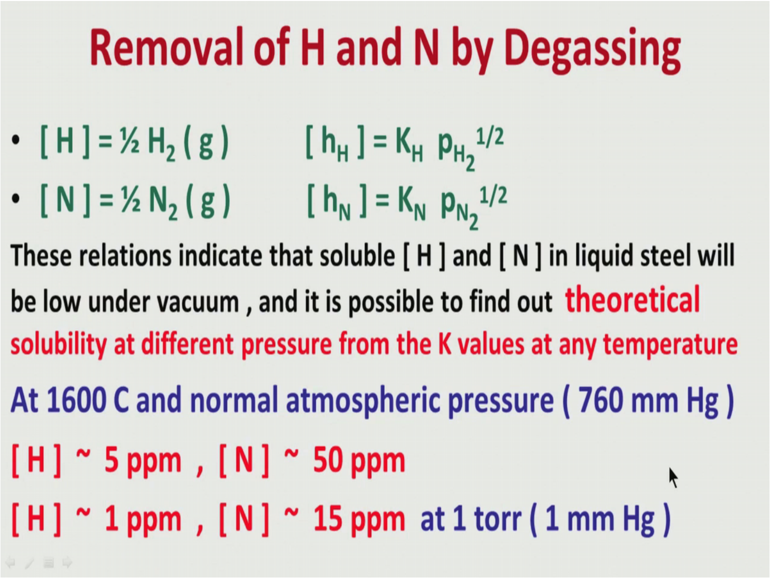

Removal of H and N by Degassing

- $[H] = \frac{1}{2} H_2(g)$ $[h_H] = K_H \, p_{H_2}^{1/2}$
- $[N] = \frac{1}{2} N_2(g)$ $[h_N] = K_N \, p_{N_2}^{1/2}$

These relations indicate that soluble [H] and [N] in liquid steel will be low under vacuum , and it is possible to find out theoretical solubility at different pressure from the K values at any temperature

At 1600 C and normal atmospheric pressure (760 mm Hg)

[H] ~ 5 ppm , [N] ~ 50 ppm

[H] ~ 1 ppm , [N] ~ 15 ppm at 1 torr (1 mm Hg)

Then I have talked about the importance of degassing, how hydrogen and nitrogen which are gaseous elements present in liquid steel, how they can be removed by degassing. This hydrogen present in atomic form in liquid steel, nitrogen present in atomic form as soluble nitrogen in liquid steel, they get transferred to the surface of the steel gas surface and in that process the hydrogen gas the nitrogen gas is taken out. So, the partial pressure of hydrogen or partial pressure of nitrogen is going to play an important role, lowered the partial pressure better will be the degassing. So, lower will be the you know this h small h small is the henrian activity of h and nitrogen; that means, hydrogen and nitrogen activity and likewise the content in liquid steel will go down if I can maintain lower partial pressure of hydrogen or nitrogen. So, this is the way vacuum helps.

Vacuum reduces the partial pressure of whatever gases are present, and in the process this gaseous elements in liquid steel can be brought down and it can be shown that at about 1600 degree centigrade, and at normal atmospheric pressure the hydrogen and nitrogen soluble you know limits are about 5 ppm and 50 ppm, but at about one millimeter mercury which is called one torr it can be calculated from this relations relationships, that hydrogen can be brought down to 1 ppm nitrogen theoretical we brought down to 15 ppm.

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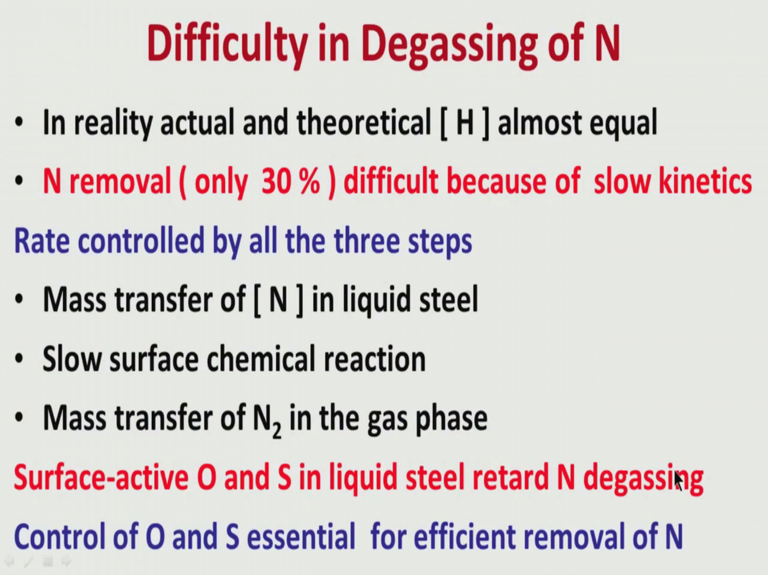

Difficulty in Degassing of N

- In reality actual and theoretical [H] almost equal
- N removal (only 30 %) difficult because of slow kinetics

Rate controlled by all the three steps

- Mass transfer of [N] in liquid steel
- Slow surface chemical reaction
- Mass transfer of N_2 in the gas phase

Surface-active O and S in liquid steel retard N degassing

Control of O and S essential for efficient removal of N

But I have mentioned that what is the difficulty of degassing the nitrogen I have mentioned whatever I am told you in a earlier slide that is the theoretical consideration. Thermo dynamics, but if you look in to the kinetics which is associated with thermo dynamics; that means, in reality kinetics will play a very important role.

Now, if we look in to how nitrogen is getting transformed first the dissolved nitrogen which is present in liquid steel has to be transferred from the bulk of the steel to the surface of the liquid steel, then only it is possible to get transferred then at the surface this chemical reaction will take place between atomic nitrogen to gaseous hydrogen or atomic nitrogen to gaseous nitrogen or atomic hydrogen to gaseous hydrogen. So, first the mass transfer of nitrogen in liquid steel, then the reaction surface reaction from atomic to molecular or gaseous hydrogen and nitrogen and then this gaseous nitrogen and hydrogen it has to again get transferred in a gaseous phase if it remains at the interface the reaction is hindered.

Now all these three steps you know mass transfer of nitrogen in liquid steel slow surface chemical reaction and mass transfer of nitrogen gaseous nitrogen in the gas phase. These three steps are relatively slower from nitrogen compared to hydrogen. Hydrogen mobility is very fast because it is a very small constituents small element. So, it is diffusivity is very fast whether in liquid steel or in gaseous phase. So, instead of you know hydrogen which is very fast nitrogen removal is relatively slow moreover oxygen nitrogen if they are present in liquid steel they have surface active. So, they can create problem in this the nitrogen slag.

Why? Because you know this surface at the surface of the liquid steel and the gas there is a competition within nitrogen and surface active well it was like oxygen in sulphur if oxygen and sulphur are present in more you know the quantity is high that present in more or higher amount in liquid steel they will try to be accumulating more at the interface of liquid steel and gas and then the probability of nitrogen occupying the size will be less. So, this reaction surface chemical reaction will be slow.

So, therefore, I am mentioned earlier the control of oxygen and sphered is essential in liquid steel before we can get a removal of nitrogen. So, theoretically though we know the nitrogen removal is possible to a great extent, but in reality because of this kinetics we get that about 30 to 40percent only removal is possible, and this can be enhanced when we have very low amount of dissolved oxygen in sulphur and liquid steel.

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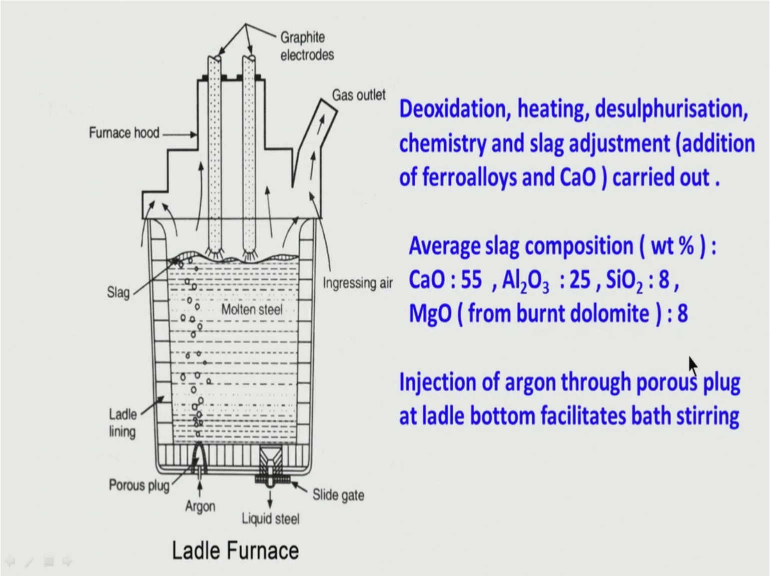

Ladle Furnace

Deoxidation, heating, desulphurisation, chemistry and slag adjustment (addition of ferroalloys and CaO) carried out .

Average slag composition (wt %) :
CaO : 55 , Al_2O_3 : 25 , SiO_2 : 8 ,
MgO (from burnt dolomite) : 8

Injection of argon through porous plug at ladle bottom facilitates bath stirring

So, therefore, deoxidation and desulphurization which are essential steps for having good quality or prerequisites for degassing particularly for nitrogen. Then I have talked about ladle furnace how deoxidation, heating, desulphurization and adjustment of slag and chemistry of the you know steel all these are possible what is the average slag composition about approximately 55 percent CaO, SiO2 is much less. So, the ratio is quite high, some injurious coming from the you know burnt dolomite of the in the refractory lining, an intentional argon gas through porous plug at the bottom here there is a porous plug at the bottom.

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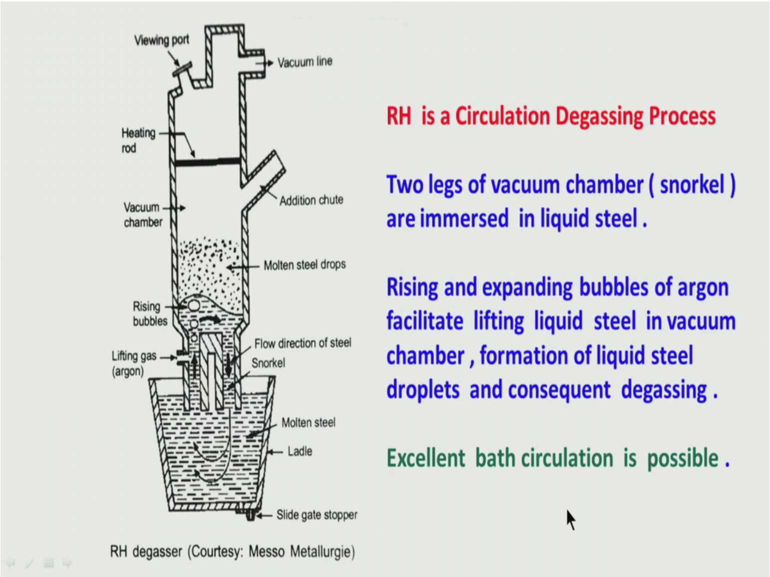

RH degasser (Courtesy: Messo Metallurgie)

RH is a Circulation Degassing Process

Two legs of vacuum chamber (snorkel) are immersed in liquid steel .

Rising and expanding bubbles of argon facilitate lifting liquid steel in vacuum chamber , formation of liquid steel droplets and consequent degassing .

Excellent bath circulation is possible .

So, through which argon is fast. So, this helps in bath stirring this helps in faster removal of the inclusions from the bulk of the liquid steel to the surface and get absorbed by the slag. Then I have talked about how circulation degassing process like RH is a very popular circulation degassing process in which way it can help degassing.

So, here rising and expanding bubbles of argon and here the argon is being send which forces which pumps up the liquid steel from the ladle to this vacuum chamber and droplets of liquid steel are formed this droplets because if the droplets are small it will be easier for the nitrogen and hydrogen present in liquid steel to go to the surface, and get converted to nitrogen hydrogen gas in the vacuum chamber and vacuum helps in their faster removal. So, this RH degassing which is a circulation degassing process is a very useful process for bath circulation and this you know argon which is being sent through one snorkel is helps the liquid steel go up get in to small droplets you know that come down again this will go up. So, in this process of circulation the degassing of hydrogen and nitrogen from the liquid steel is taken care off.