Iron Making and Steel Making
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Module - 08
Lecture – 40
Ladle de – sulphurization, alloying, stainless steel making

In this lecture we will discuss 3 topics in secondary steel making. The topics covered are ladle desulfurization using synthetic slag, effective deoxidation and alloying by CAS technique and stainless steel making using EAF-AOD method; that is the Electric Arc Furnace and Argon Oxygen De-carburization.

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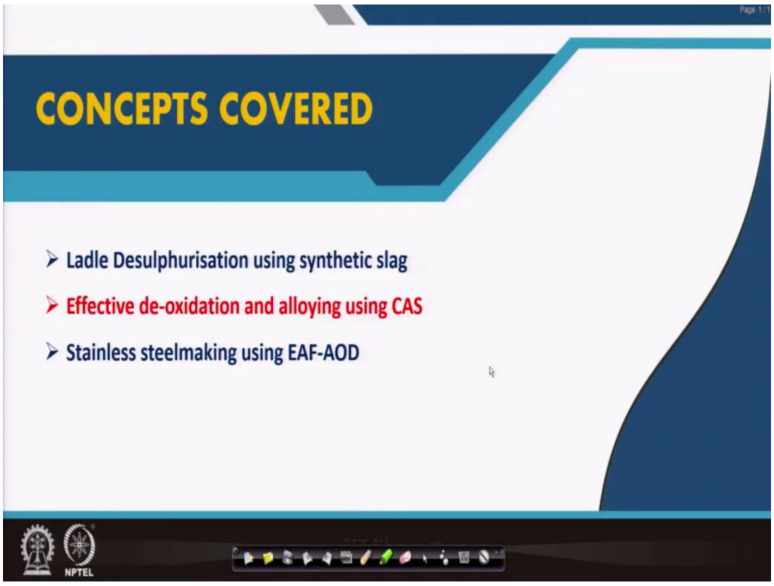

CONCEPTS COVERED

- Ladle Desulphurisation using synthetic slag
- Effective de-oxidation and alloying using CAS
- Stainless steelmaking using EAF-AOD

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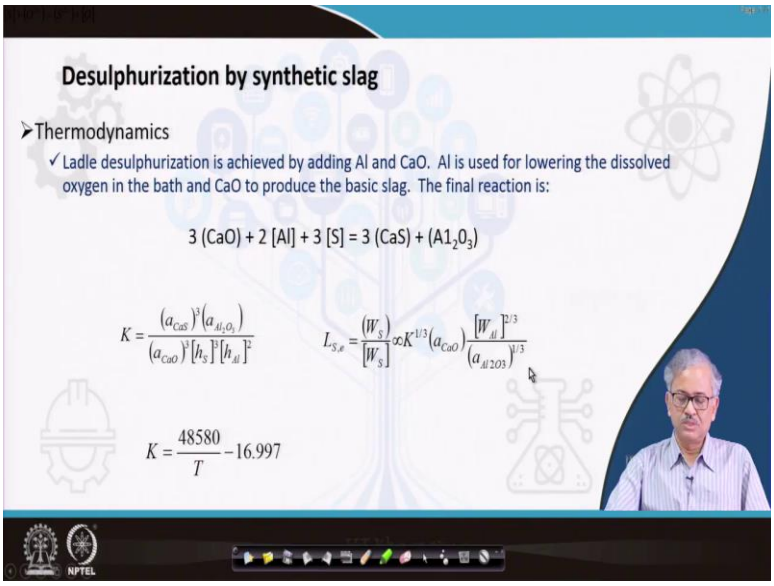

Desulphurization by synthetic slag

- Thermodynamics
  - ✓ Ladle desulphurization is achieved by adding Al and CaO. Al is used for lowering the dissolved oxygen in the bath and CaO to produce the basic slag. The final reaction is:

$$3\,(CaO) + 2\,[Al] + 3\,[S] = 3\,(CaS) + (A1_2 0_3)$$

$$K = \frac{(a_{CaS})^3 (a_{Al_2O_3})}{(a_{CaO})^3 [h_S]^3 [h_{Al}]^2}$$

$$L_{S,e} = \frac{(W_S)}{[W_S]} \propto K^{1/3} (a_{CaO}) \frac{[W_{Al}]^{2/3}}{(a_{Al2O3})^{1/3}}$$

$$K = \frac{48580}{T} - 16.997$$

As the name suggests in synthetic slag treatment, we artificially prepare the slag by adding the constituents like CaO and the aluminium in ladle, which makes the slag highly reducing and basic; and then gas stirring is used to increase the kinetics.

By this time we know that sulphur can only be controlled under the blast furnace operation; because there exists a basic slag and reducing slag. In BOF, we do not have much control and we cannot reduce any amount of sulphur. So, to reduce the load of the blast furnace, sometimes de-sulphurization is carried out in an intermediate rector in between the blast furnace and the LD process, that is called the external de-sulphurization.

Sulphur can be reduced to 0.05 level easily in blast furnace itself and then it could be further lowered to 0.01 level (or, 100 ppm) by external de-sulphurization. In order to lower Sulphur further down to 20 ppm, synthetic slag treatment in gas-stirred ladle during secondary processing of steel could be carried out. We might also use injection metallurgy, where calcium powder is injected into melt through submerged lance, for deep desulphurization –that will be discussed later. In this lecture, we will talk about the synthetic slag treatment of liquid steel in gas stirred ladle. So, let us first discuss the thermodynamics of desulphurization using synthetic slag. Ladle desulphurization is achieved by adding Al and CaO. Al is used for lowering the dissolved oxygen in the bath and CaO to make the basic slag. The final reaction using synthetic slag could be written as given by equation 40.1.

$$3(CaO) + 2[Al] + 3[S] = 3(CaS) + (Al_2O_3)$$

(40.1)

The equilibrium constant (K) for the reaction may be given as:

$$K = \frac{(a_{CaS})^3 (a_{Al_2O_3})}{(a_{CaO})^3 [h_S]^3 [h_{Al}]^2}$$

(40.2)

It may be noted that activities of all the constituents in slag phase are represented in terms of Raoultian standard state that is pure solid/liquid as the standard state and for all the dissolved constituents like aluminum and sulphur, activities are represented in Henrain standard state; that is with respect to one weight percent standard state. And accordingly K has been calculated and the relationship is given below:

$$K = \frac{48580}{T} - 16.997$$

(40.3)

The equilibrium sulphur partition coefficient $(L_{S,e})$ can be written as equation (40.4), by manipulating the equation (40.2):

$$L_{S,e} = \frac{(W_S)}{[W_S]} \infty K^{1/3} (a_{CaO}) \frac{[W_{Al}]^{2/3}}{(a_{Al2O3})^{1/3}}$$

(40.4)

Where, (W_S) and $[W_S]$ represent the weight percentage of Sulphur in the slag and metal phase respectively. $L_{S,e}$ is found to be directly proportional to K, or inversely proportional to temperature to the power one third. It is also directly proportional to the activity of a CaO and weight percent of aluminum to the power two third and inversely proportional to the activity of Al_2O_3 to the power one third. So, decrease in temperature, and increase in CaO in slag and increase in aluminum in the bath, favor the partitioning of sulphur in the slag.

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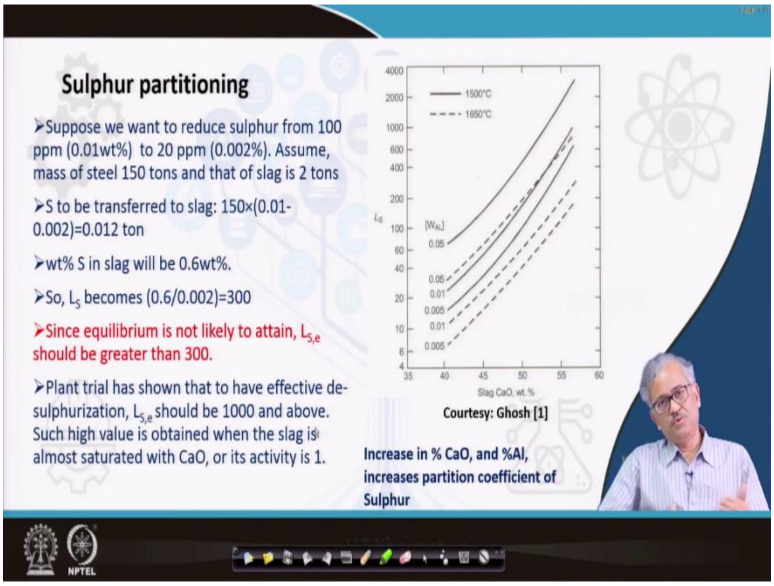

Sulphur partitioning

- ➢Suppose we want to reduce sulphur from 100 ppm (0.01wt%) to 20 ppm (0.002%). Assume, mass of steel 150 tons and that of slag is 2 tons
- ➢S to be transferred to slag: 150×(0.01-0.002)=0.012 ton
- ➢wt% S in slag will be 0.6wt%.
- ➢So, L_S becomes (0.6/0.002)=300
- ➢Since equilibrium is not likely to attain, $L_{S,e}$ should be greater than 300.
- ➢Plant trial has shown that to have effective de-sulphurization, $L_{S,e}$ should be 1000 and above. Such high value is obtained when the slag is almost saturated with CaO, or its activity is 1.

Courtesy: Ghosh [1]

Increase in % CaO, and %Al, increases partition coefficient of Sulphur

Figure 40.1 shows the inter-corelationship between equilibrium partition coefficient of Sulphur and temperature, CaO in slag and dissolved aluminum in the bath.

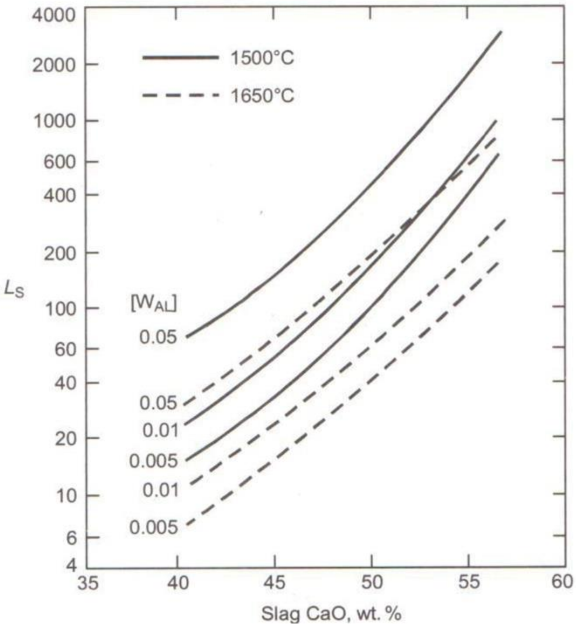

Figure 40.1 Variation in equilibrium partition coefficient with CaO percentage in slag at different bath aluminum and temperature[1].

It may be observed at 1500°C, the partition coefficient could be 2000 at 55% CaO and 0.05% aluminum in the bath. The corresponding value at temperature 1650°C is only 600. The value would be lowered further to 30, if CaO is reduced to 40%. The value could be further lowered to only 6 when the aluminum percentage is reduced to 0.005%. So, it is obvious the effect of CaO in slag, temperature and dissolved aluminum in the bath plays a significant role controlling the value of equilibrium partition coefficient for Sulphur.

Now, let us calculate the actual partitioning of sulphur when sulphur is reduced from 100 ppm to 20 ppm in 150 ton ladle with 2 ton overlaying slag. Sulphur transferred to slag may be calculated as: $\frac{(100-20)}{10^6} \times 150 \times 10^3 = 12\ kg$. After sulphur transfer to slag, the weight percentage of Sulphur in slag becomes: $\frac{12}{2000} \times 100 = 0.6\ wt\%$. The weight percentage in the metal phase becomes: $= 20 \times 10^{-4} = 0.002$. So, the partition coefficient achieved is: $= \frac{0.6}{0.002} = 300$. But it does not represent the equilibrium partition coefficient because the process hardly achieve the equilibrium; and this achieved partition coefficient under actual practice may be termed as apparent partition coefficient. If the kinetics is poor, to achieve such high apparent partition coefficient at 300, the equilibrium partition coefficient is needed to be very high (say, 1000) to set up a large gradient for the transfer. Such high equilibrium partition coefficient may be assured by exploiting the thermodynamic conditions like the high activity CaO in the slag; highest activity value of 1 could be achieved when CaO in slag achieve its saturation level. Aluminum in the bath may be increased and temperature of operation could be lowered. However, by achieving higher kinetics the difference between the apparent and equilibrium partition coefficient could be reduced.

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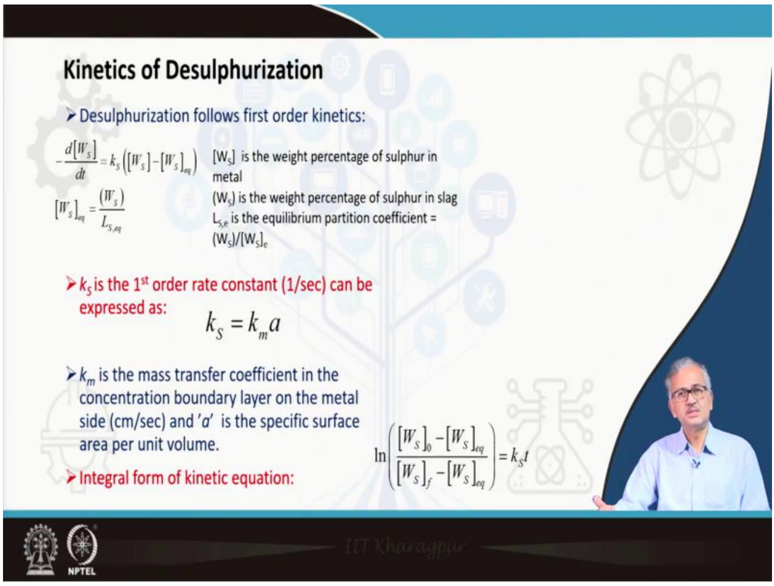

Kinetics of Desulphurization

- Desulphurization follows first order kinetics:

$$-\frac{d[W_S]}{dt} = k_S\left([W_S]-[W_S]_{eq}\right)$$

$$[W_S]_{eq} = \frac{(W_S)}{L_{S,eq}}$$

$[W_S]$ is the weight percentage of sulphur in metal

(W_S) is the weight percentage of sulphur in slag

$L_{S,e}$ is the equilibrium partition coefficient = $(W_S)/[W_S]_e$

- k_S is the 1st order rate constant (1/sec) can be expressed as:

$$k_S = k_m a$$

- k_m is the mass transfer coefficient in the concentration boundary layer on the metal side (cm/sec) and 'a' is the specific surface area per unit volume.
- Integral form of kinetic equation:

$$\ln\left(\frac{[W_S]_0-[W_S]_{eq}}{[W_S]_f-[W_S]_{eq}}\right) = k_S t$$

.

Let us now discuss the kinetics of desulfurization. The rate equation of desulphurization based on first order kinetics may be written as:

$$-\frac{d[W_S]}{dt} = k_S\left([W_S]-[W_S]_{eq}\right)$$

(40.5)

Where k_S (per second) is the first order mass transfer rate constant, which may be expressed in terms of mass transfer coefficient, k_m (cm/second) across the concentration boundary layer on the metal side as:

$$k_S = \frac{A \times k_m}{V}$$

(40.6)

Where A and V represents the slag metal surface area and volume of the metal, respectively.

The equilibrium concentration of Sulphur in the metal phase corresponding to an instantaneous Sulphur composition in the slag can be expressed in terms of equilibrium sulpher partition coefficient, $L_{S,eq}$ as follows:

$$[W_S]_{eq} = \frac{(W_S)}{L_{S,eq}}$$

(40.7)

The integral form of the equation (40.5) can be written as:

$$\ln\left(\frac{[W_S]_0-[W_S]_{eq}}{[W_S]_f-[W_S]_{eq}}\right) = k_S t$$

(40.8)

Where *0* and *f* represents the initial and final value after time *t*, respectively.

So, using this equation we can calculate the final concentration of sulphur in the bath or you can calculate the time to achieve certain sulphur concentration in the bath.

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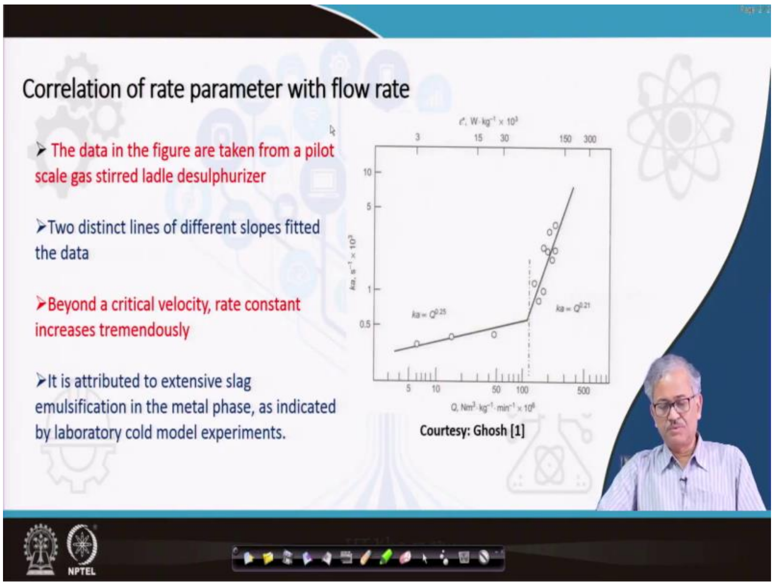

Correlation of rate parameter with flow rate

- The data in the figure are taken from a pilot scale gas stirred ladle desulphurizer
- Two distinct lines of different slopes fitted the data
- Beyond a critical velocity, rate constant increases tremendously
- It is attributed to extensive slag emulsification in the metal phase, as indicated by laboratory cold model experiments.

Courtesy: Ghosh [1]

Next, let us understand the correlation of rate parameters with the flow rates. Figure 40.2 shows the variation of mass transfer rate constant with the specific gas flow rate. The mass transfer rate constant is a product of mass transfer coefficient (cm/sec) and specific surface area (/cm) between slag and metal. So increase in mass transfer rate constant not only depends on the mass transfer coefficient, or, hydrodynamic conditions in the concentration boundary layer; it also depends on the specific surface area.

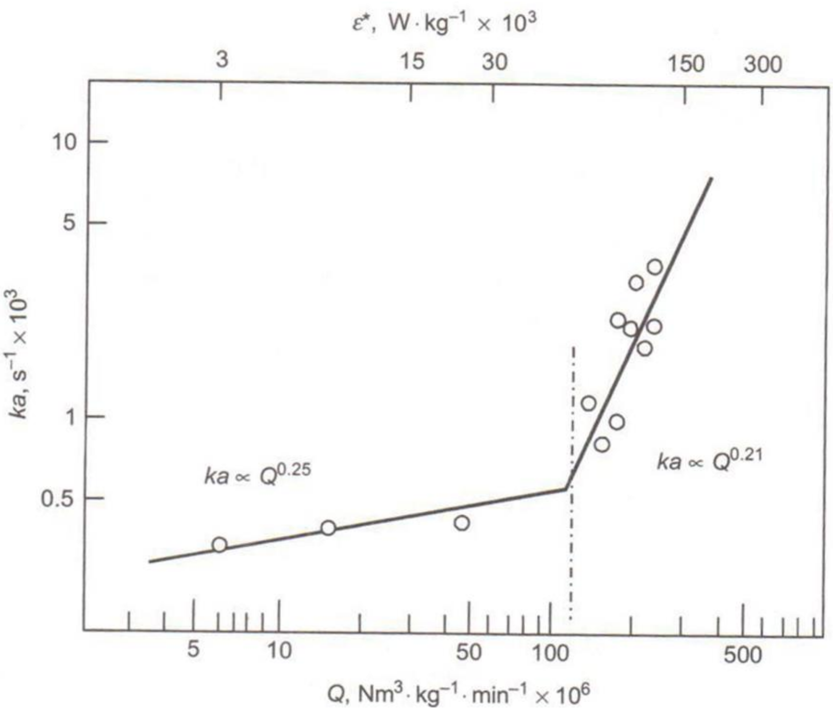

Figure 40.2: Variation of mass transfer rate constant (/sec) with specific gas flow rate[1]

It may be observed that there exists two distinct straight line relationships, when the gas flow rate is plotted on logarithmic scale. At comparatively lower gas flow rate, rate constant varies at a moderate rate following a straight line; in other words it is proportional to Q to the power of 0.25. But beyond a certain gas velocity, as indicated by 100 Nm^3/kg-m, completely different relationship with a much steeper straight line is followed. The rate constant suddenly starts increasing at a much faster rate with gas flow rate. Obviously the mass transfer coefficient can increase in the concentration boundary layer depending on the hydrodynamic condition, which was responsible for increase in rate with gas velocity in the first regime. But, this phenomenal increase can not be due to mass transfer coefficient; it is primarily due to sudden increase in specific surface area in a completely different regime. The nominal slag metal interfacial area over the metal phase is completely changed to a regime of emulsified slag droplets in the metal phase, which increase the slag-metal interfacial by many folds. The mass transfer in the new regime of emulsion give rise to phenomenal increase in mass transfer.

So, for desulphurization you require a very strong stirring of the bath beyond a certain critical gas velocity or volumetric flow rate of the gas that carries the desulphurization rate at a super fast rate and bring the process very close to the equilibrium such that sufficient desulphurization to a very low value like 20 ppm can be carried out in a reasonable amount of time.

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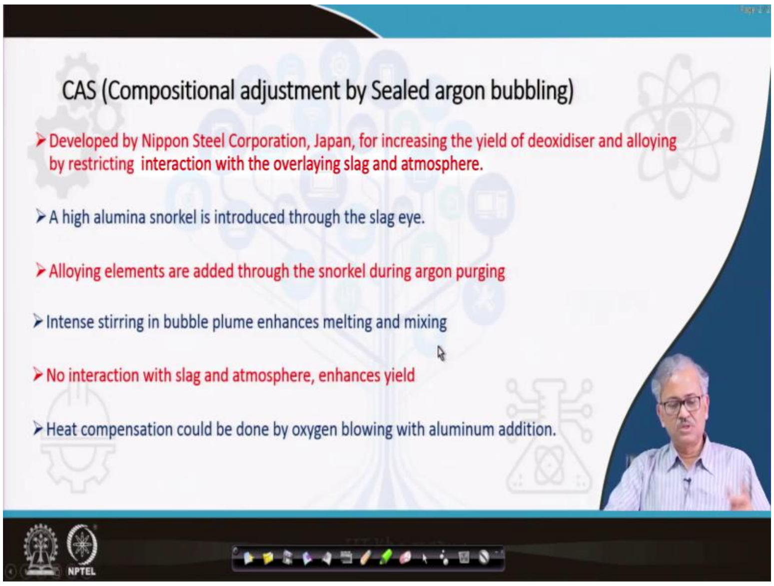

CAS (Compositional adjustment by Sealed argon bubbling)

- Developed by Nippon Steel Corporation, Japan, for increasing the yield of deoxidiser and alloying by restricting interaction with the overlaying slag and atmosphere.
- A high alumina snorkel is introduced through the slag eye.
- Alloying elements are added through the snorkel during argon purging
- Intense stirring in bubble plume enhances melting and mixing
- No interaction with slag and atmosphere, enhances yield
- Heat compensation could be done by oxygen blowing with aluminum addition.

We will go to the next topic; that is the CAS. CAS is called the Compositional Adjustment by Sealed argon bubbling and it was invented by Nippon Steel Corporation in Japan for increasing the yield of deoxidizer and the alloying by restricting interaction with the overlapping slag and the atmosphere.

In this process a snorkel lined with high alumina refectory is inserted into the slag eye of the melt from top and thus the liquid inside the snorkel get detached with the over laying slag and the atmosphere. Figure 40.3 shows the schematics of a CAS process.

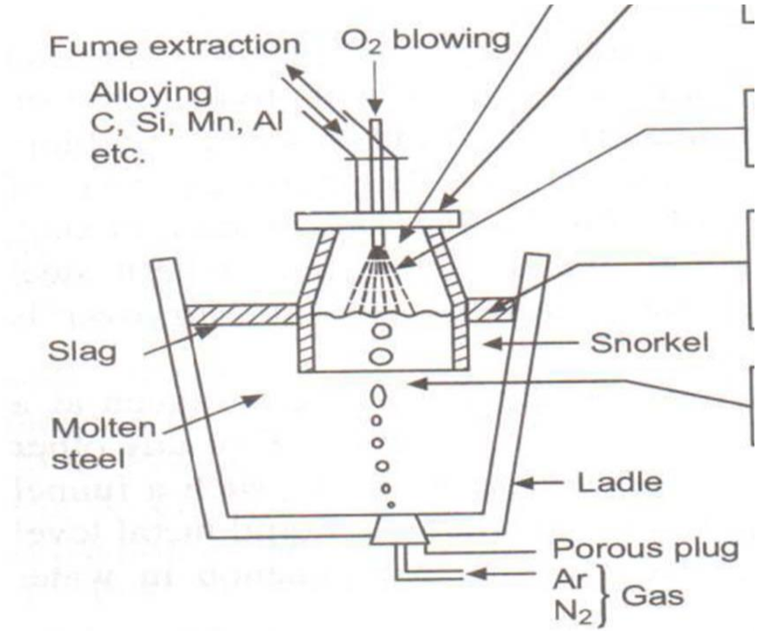

Figure 40.3: The schematics of a CAS process [1]

In such system when deoxidizer or the alloying elements are added, their undesirable interaction with overlaying slag and atmosphere is minimized and therefore yield of deoxidation and alloying becomes high. Because, liquid metal get protected from oxygen, nitrogen in the atmosphere and reducible oxides in the slag. This simple yet very effective technology. Since the process is confined in a small volume in an isolated chamber the temperature loss is also minimal. Since the eye is protected, intensity of stirring could be high that enhances the kinetics of the process. And heat compensation could be done by the oxygen blowing from top and aluminum addition. This is called the CAS-OB process. Aluminum oxidation generates heat and alumina inclusion can be separated in the slag under stirring effectively.

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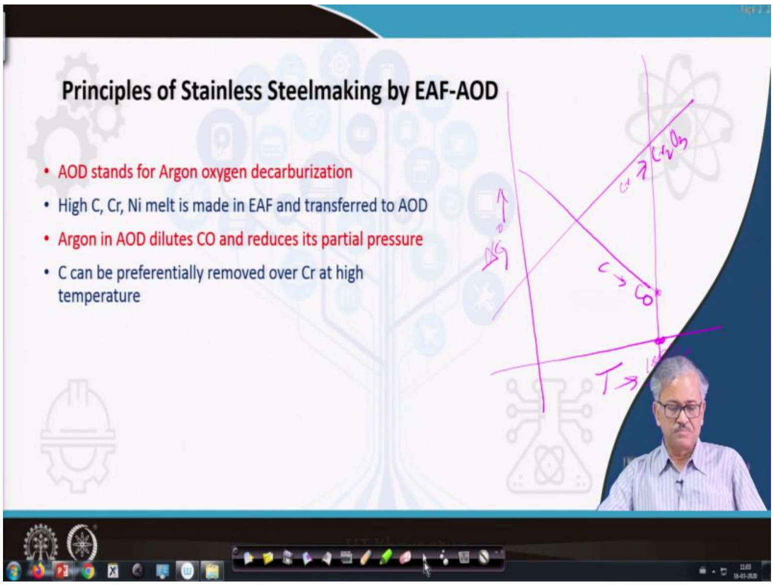

Principles of Stainless Steelmaking by EAF-AOD

- AOD stands for Argon oxygen decarburization
- High C, Cr, Ni melt is made in EAF and transferred to AOD
- Argon in AOD dilutes CO and reduces its partial pressure
- C can be preferentially removed over Cr at high temperature

Here is the last topic of the lecture - the principles of stainless steel making by EAF-AOD process (electric arc furnace and argon oxygen decarburization). In this method first a melt with high carbon, chromium, nickel is made in an electric arc furnace by melting scrap, high carbon ferrochrome, chromite ore. Then the melt is transferred to AOD converter.

In AOD, oxygen is lanced from the top and argon from the bottom. Argon basically dilutes the CO gas reducing its partial pressure that moves the reaction in forward direction. From that point of view the argon serves the purpose of a vacuum. Since chromium and nickel oxides are solid/liquid and entrained in the slag, and consequently carbon can be preferentially oxidized by reducing its partial pressure in argon atmosphere and could be removed preferentially over chromium and nickel. This is what we want; we want to keep Cr in the melt and remove the carbon from the melt; such that finally we can make high alloy (Cr) and low carbon stainless steel. It is to be mentioned that in stainless steel carbon should be low to avoid sensitization and intergranular corrosion during heating.

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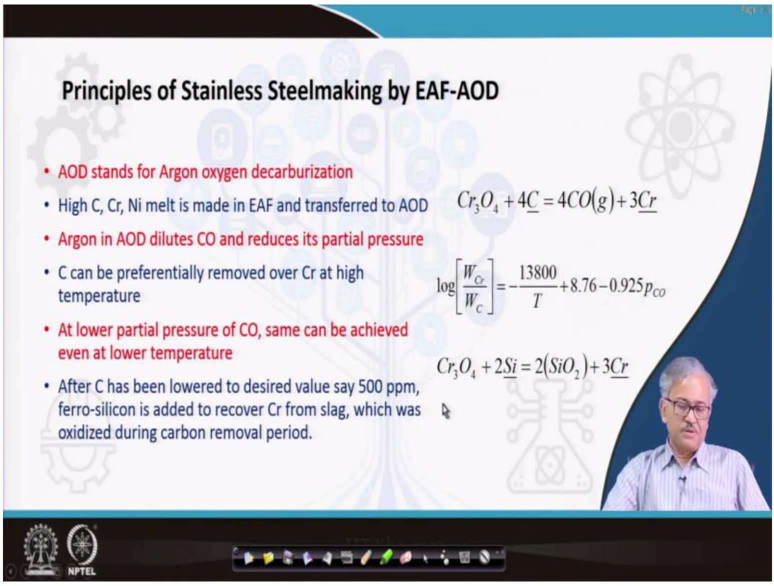

Principles of Stainless Steelmaking by EAF-AOD

- AOD stands for Argon oxygen decarburization
- High C, Cr, Ni melt is made in EAF and transferred to AOD
- Argon in AOD dilutes CO and reduces its partial pressure
- C can be preferentially removed over Cr at high temperature
- At lower partial pressure of CO, same can be achieved even at lower temperature
- After C has been lowered to desired value say 500 ppm, ferro-silicon is added to recover Cr from slag, which was oxidized during carbon removal period.

$$Cr_3O_4 + 4\underline{C} = 4CO(g) + 3\underline{Cr}$$

$$\log\left[\frac{W_{Cr}}{W_C}\right] = -\frac{13800}{T} + 8.76 - 0.925 p_{CO}$$

$$Cr_3O_4 + 2\underline{Si} = 2(SiO_2) + 3\underline{Cr}$$

.

The final reaction of preferential removal of carbon can be written as:

$$Cr_3O_4 + 4\underline{C} = 4CO(g) + 3\underline{Cr}$$

(40.9)

The equilibrium chromium to carbon ratio in the liquid bath can be expressed as:

$$\log\left[\frac{W_{Cr}}{W_C}\right] = -\frac{13800}{T} + 8.76 - 0.925 p_{CO}$$

(40.10)

So it is seen that chromium can be retained in the melt in preference to carbon either at higher temperature, or at lower partial pressure of CO, or both.

In rustless process, chromium is preferentially retained in the melt by utilizing the thermodynamic parameter - the temperature. So, in EAF itself the stainless steel could be made at elevated temperature using rustless process, as we have already discussed earlier. But at high temperature, the refractory lining get affected severely. Besides, toxic gas generation also becomes high. In AOD converter carbon is preferentially removed by utilizing the thermodynamic parameter – the partial pressure of CO. Therefore, carbon oxidation and removal is carried out using argon that dilutes CO and reduce partial pressure of CO and remove carbon preferentially over chromium and that too at comparatively lower temperature.

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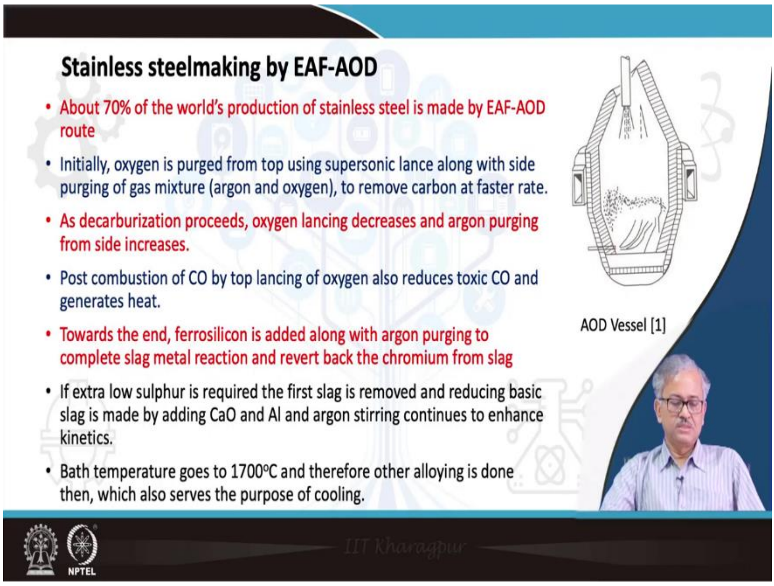

Stainless steelmaking by EAF-AOD

- About 70% of the world's production of stainless steel is made by EAF-AOD route
- Initially, oxygen is purged from top using supersonic lance along with side purging of gas mixture (argon and oxygen), to remove carbon at faster rate.
- As decarburization proceeds, oxygen lancing decreases and argon purging from side increases.
- Post combustion of CO by top lancing of oxygen also reduces toxic CO and generates heat.
- Towards the end, ferrosilicon is added along with argon purging to complete slag metal reaction and revert back the chromium from slag
- If extra low sulphur is required the first slag is removed and reducing basic slag is made by adding CaO and Al and argon stirring continues to enhance kinetics.
- Bath temperature goes to 1700°C and therefore other alloying is done then, which also serves the purpose of cooling.

AOD Vessel [1]

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Now, let us see the industrial process. Figure 40.4 shows the schematics of AOD reactor.

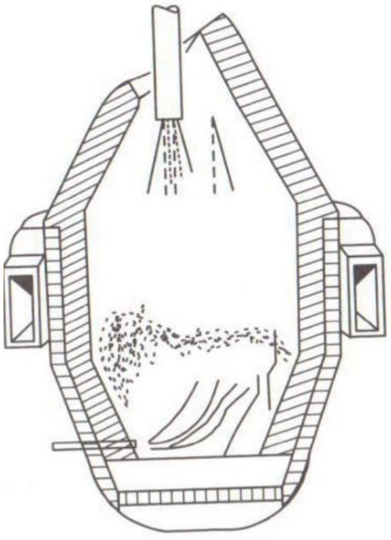

Figure 40.4 The schematics of AOD reactor[1]

Oxygen is injected from the top using supersonic lance; just like in the oxygen steel making in the LD process. A side lance is also seen at the bottom of the furnace through which argon along with oxygen is purged. Initially oxygen is purged from the top and carbon is oxidized at a faster rate in the emulsion formed by top oxygen lancing. Argon also purged from the bottom that dilutes the CO gas generated. As decarburization proceeds significantly, oxygen purging from the top is decreased and argon purging from the side lance at the bottom is intensified to mix the bath effectively to enhance mass transfer of dissolved carbon from the bath. Because at a later stage of refining when the carbon in the bath decreases significantly, the kinetics is controlled by mass transfer of carbon from the bath to the heterogeneous interface where CO bubble forms.

The CO generated by carbon oxidation is burned at the top of the furnace in oxygen atmosphere. Such post combustion of CO increases temperature, reduces toxic CO emission and also decrease of CO concentration at the top, helps in decarburization. At the end of the process, the temperature of the melt increases to 1700°C and coolant like ferrosilicon is added effectively. Ferro-silicon also does its important job of reverting back some chromium oxide in the slag, which was generated during preferential carbon oxidation process due to kinetics reason. Silicon reduce the less stable chromium oxides, as par the equation (40.11).

$$Cr_3O_4 + 2\underline{Si} = 2(SiO_2) + 3\underline{Cr} \tag{40.11}$$

So ferro-silicon does both the purpose of coolant and reverting back the chromium from slag to metal by reduction.

Around 70% of the worldwide stainless steel production is carried out by EAF-AOD process.

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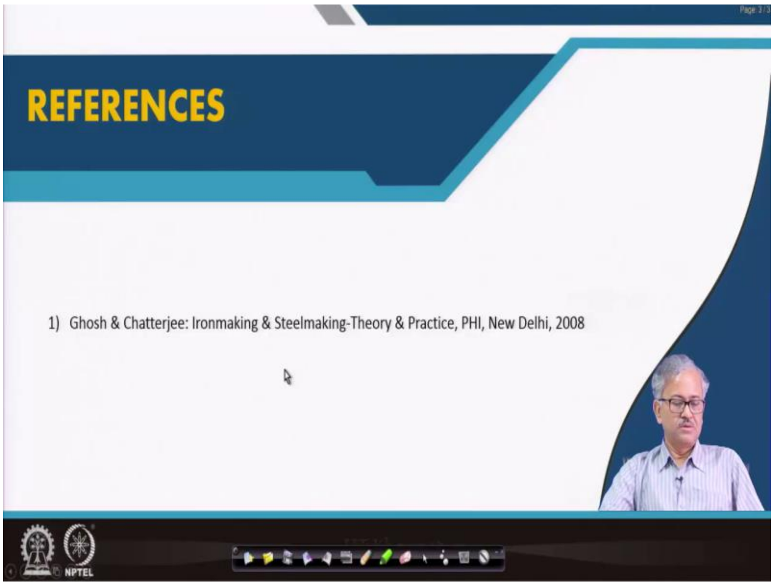

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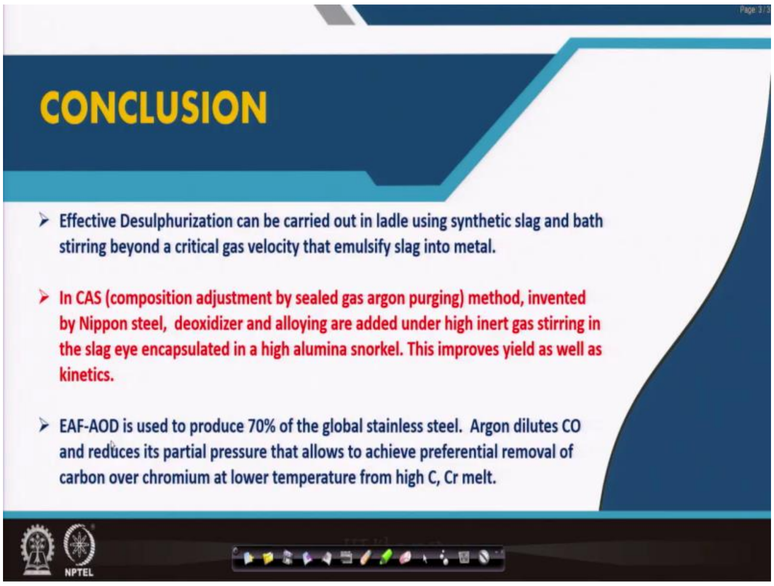

CONCLUSION

- Effective Desulphurization can be carried out in ladle using synthetic slag and bath stirring beyond a critical gas velocity that emulsify slag into metal.
- In CAS (composition adjustment by sealed gas argon purging) method, invented by Nippon steel, deoxidizer and alloying are added under high inert gas stirring in the slag eye encapsulated in a high alumina snorkel. This improves yield as well as kinetics.
- EAF-AOD is used to produce 70% of the global stainless steel. Argon dilutes CO and reduces its partial pressure that allows to achieve preferential removal of carbon over chromium at lower temperature from high C, Cr melt.

Conclusion: Deep desulphurization can be carried out in gas stirred ladle ladle using synthetic slag. Thermodynamically, lower temperature, high lime in slag and high dissolved aluminum in the bath favour desulphurization and a high equilibrium partition coefficient of the order of 1000 could be achieved.

Gas stirring beyond a certain velocity, emulsify the slag in metal that facilitate the superfast removal of sulphur for deep desulphurization. A very high apparent partition coefficient of sulphur could be realized in actual practice.

In CAS (composition adjustment by sealed gas argon purging) practice where metallurgical operations are carried out in an enclosed chamber by putting a snorkel over the slag eye that minimize the interaction of overlaying slag and atmosphere, alloying and deoxidation could be done effectively with high yield and less time under high inert gas stirring.

Around 70% of the global stainless production is done through EAF-AOD process, where a high carbon high alloy (Cr) liquid iron is melted in EAF first and then it is transferred to AOD reactor, for preferential oxidation and removal of carbon over Cr and Ni at comparatively lower temperature. In AOD vessel oxygen is lanced from top using a supersonic jet that remove carbon at a faster rate in the emulsion produced. Argon is purged from a side lance at the bottom of the furnace, which does the dual purpose of bath stirring and diluting the CO gas, reducing its partial pressure of CO.