Iron Making and Steel Making

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Module – 09
Lecture – 41
Inclusion and its control

In this lecture we talk about the inclusion and its control.

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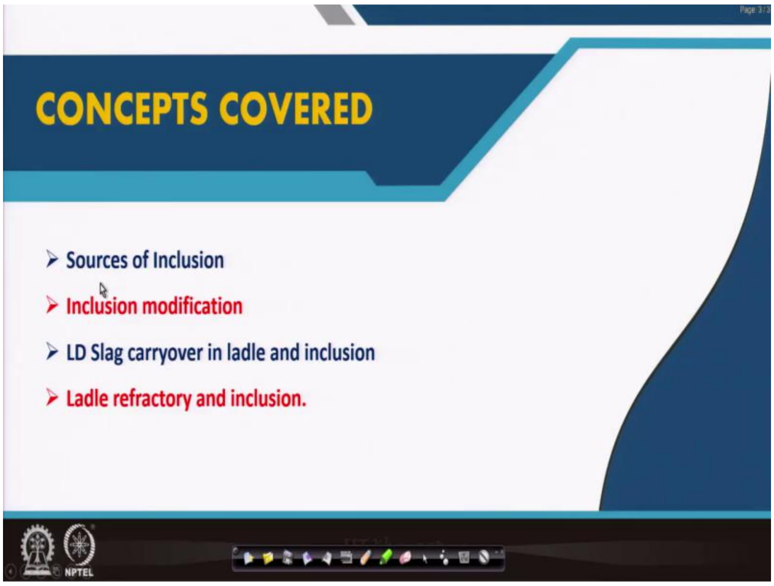

CONCEPTS COVERED

- Sources of Inclusion
- Inclusion modification
- LD Slag carryover in ladle and inclusion
- Ladle refractory and inclusion.

Topics covered will include sources of inclusions in steel, inclusion modification, LD slag carry over and its effect on inclusion, and quality of ladle refractory during secondary steelmaking.

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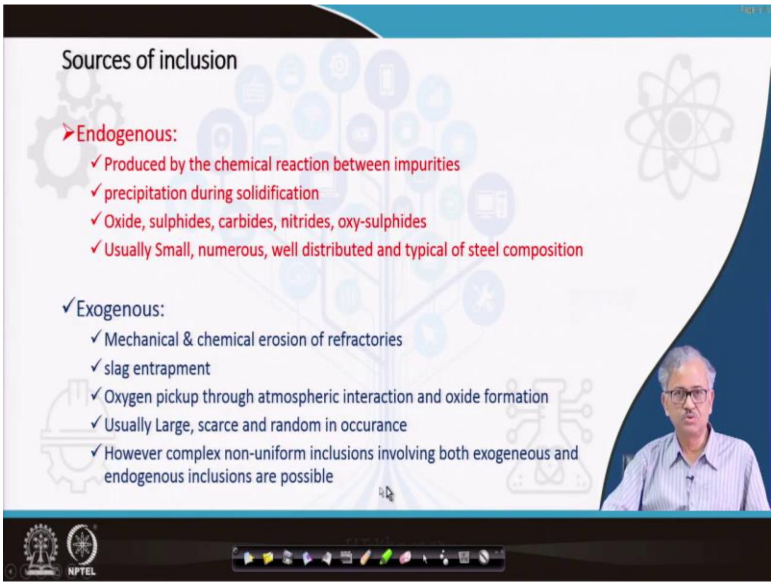

Sources of inclusion

- ➢Endogenous:
  - ✓ Produced by the chemical reaction between impurities
  - ✓ precipitation during solidification
  - ✓ Oxide, sulphides, carbides, nitrides, oxy-sulphides
  - ✓ Usually Small, numerous, well distributed and typical of steel composition
- ✓Exogenous:
  - ✓ Mechanical & chemical erosion of refractories
  - ✓ slag entrapment
  - ✓ Oxygen pickup through atmospheric interaction and oxide formation
  - ✓ Usually Large, scarce and random in occurance
  - ✓ However complex non-uniform inclusions involving both exogeneous and endogenous inclusions are possible

Generally two types of inclusions are observed; one is called the endogenous inclusion and the other is called the exogenous inclusion. Endogenous means the inclusions that evolved within the steel melt by in situ reactions between impurities. Endogenous inclusions may also form by precipitation during solidification. Solutes are rejected at the solid-liquid interface during solidification due to limited solute solubility in solid and when the concentration of such solutes exceeds the solubility product of certain compound, the compound inclusion is precipitated. The major inclusions are oxide inclusions; other inclusions include sulphide, carbide, nitrides, oxy-sulphides. Endogenous inclusions are usually small, because they grow by nucleation and growth process. Those are usually small, numerous, well-distributed, and they their composition are basically governed by the typical composition of the steel.

Exogenous inclusions, as the name suggests, are sourced outside the melt. Those can generate from mechanical and chemical erosion of the refractories. Shear stress at the refractory wall due to liquid motion could be high enough for mechanical erosion of refractories. Besides thermal shock could cause spalling of refractories. Refectory can also undergo chemical erosion where it reacts with the liquid metal, and slag, and dissolve in liquid metal, causing exogenous inclusion. Fine slag entrapment into liquid iron through emulsification of slag into metal under intense stirring could lead to physical slag particles incorporation in steel during solidification. And then oxygen, nitrogen pickup from atmosphere could also lead to oxide and nitride exogenous inclusions. Usually these exogenous inclusions are large, scarce, random and also very irregular in shape.

Differentiation between exogenous and endogenous inclusions are difficult sometimes; because sometimes exogenous inclusion can act as nucleation site over which the endogenous inclusion form, producing a complex inclusion with a large variation of composition from center to the periphery of inclusion.

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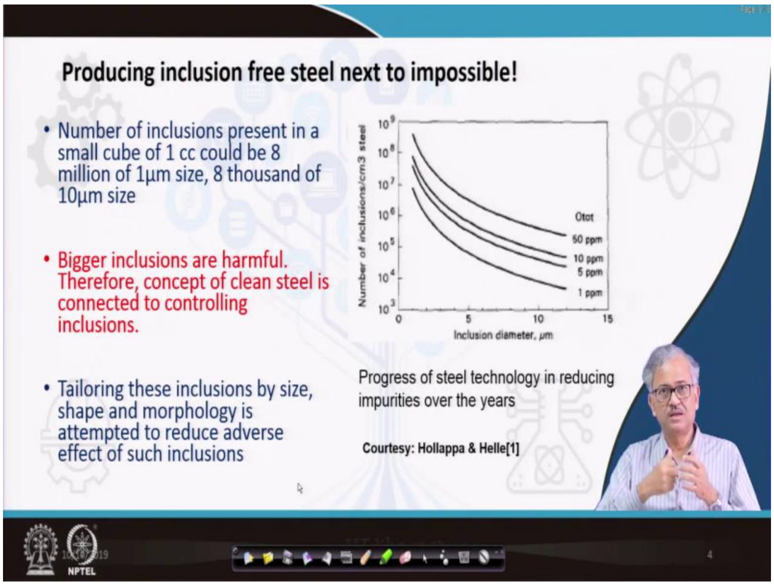

Producing inclusion free steel next to impossible!

- Number of inclusions present in a small cube of 1 cc could be 8 million of 1µm size, 8 thousand of 10µm size
- Bigger inclusions are harmful. Therefore, concept of clean steel is connected to controlling inclusions.
- Tailoring these inclusions by size, shape and morphology is attempted to reduce adverse effect of such inclusions

Progress of steel technology in reducing impurities over the years

Courtesy: Hollappa & Helle[1]

Producing inclusion free steel is next to impossible. Because numerous tiny inclusions that cannot float up to the overlayer slag during steel processing get entrapped in the steel. Millions of tiny inclusions exists in solid steel, but fortunately very tiny inclusion does not hamper the mechanical properties of the steel. But little bigger inclusions like 10 µm and above, can have harmful effect on downstream steel processing and on the mechanical properties of steel. Figure 41.1 shows the number density distribution of inclusions of various sizes entrapped in solid steel as a function of total oxygen.

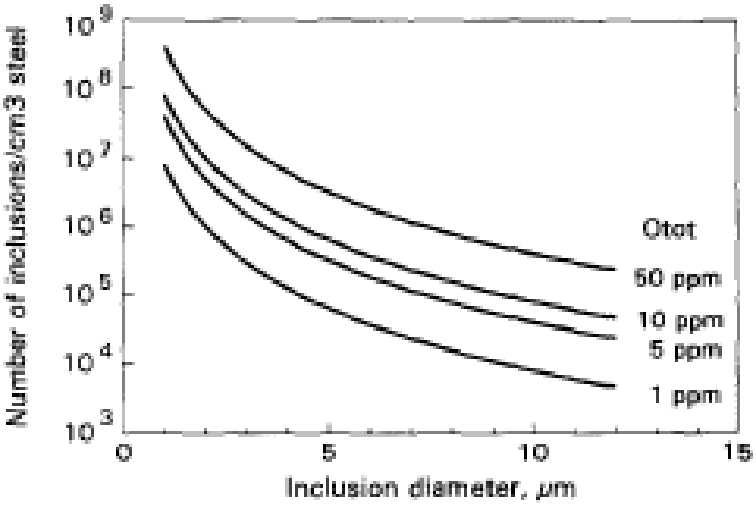

Figure 41.1: Variation of number density of inclusions as a function of their size for different total oxygen in steel [1].

It is observed that 1 µm inclusions could be several millions when total oxygen exceeds 5 ppm. Fortunately, tiny inclusions does not have harmful effect on steel processing or on steel in service. Comparatively bigger inclusions above 10 µm are, however, harmful and should be avoided. But, as seen from the figure 41.1, these inclusions are also present in significant amount of the order of several thousands. Therefore, concept of clean steel is connected with controlling the inclusion, which means reducing harmful effect of inclusions by tailoring their size, shape, morphology, and composition; this is also called inclusion modification.

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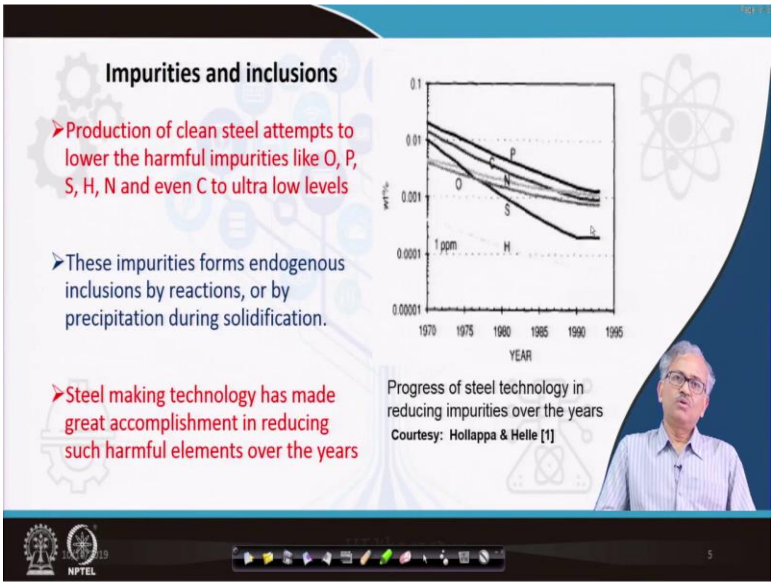

Impurities and inclusions

- Production of clean steel attempts to lower the harmful impurities like O, P, S, H, N and even C to ultra low levels
- These impurities forms endogenous inclusions by reactions, or by precipitation during solidification.
- Steel making technology has made great accomplishment in reducing such harmful elements over the years

Progress of steel technology in reducing impurities over the years

Courtesy: Hollappa & Helle [1]

Endogenous inclusions that form during solidification are sourced from impurities in liquid steel before casting. Therefore, efforts have been made over the years to reduce the impurity content in steel. Figure 41.2 shows the evolution of impurities in steel over the years. Higher the impurities in steel, higher is the numbers of inclusions in steel. So, control of impurity is very important.

So, basically impurities like oxygen, phosphorus, sulphur, hydrogen, nitrogen, and carbon should be in the ultralow level, such that inclusion formation will be the least.

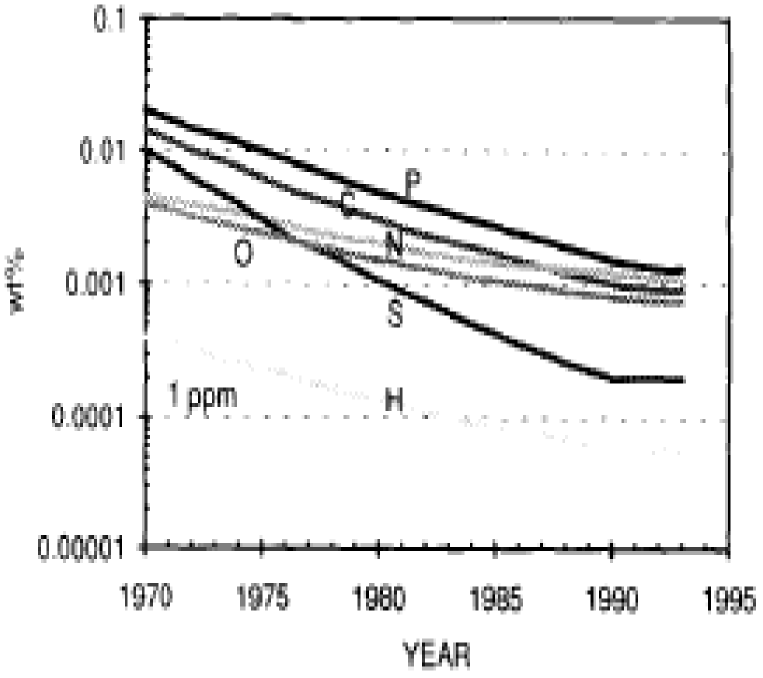

Figure 41.2: Progress of steel technology over the years in reducing impurities in steel [1]

Therefore, production of clean steel basically attempts to reduce these impurities to a very low level, such that inclusion formation becomes the least. And the steelmaking technologies over the years has make a great accomplishment in reducing such harmful elements over the years.

It may be noted that even by 1995, we have achieved a significant improvement in reducing sulphur to ultra low level below 10 ppm; other elements like C, P, N, O around 10 ppm level and hydrogen near 1 ppm level; and all these achievements by 2000.

However, several inclusions form during upstream processing of steel like deoxidation, desulphurization, refractory dissolution, and atmospheric interaction. Attempts are made to remove those inclusions by float up to the slag phase. Various efforts like bath stirring, making liquid product of deoxidation are adopted to remove the inclusion effectively. And those tiny inclusions that cannot be removed, are modified according to their size, shape, morphology and composition, such that they do not have adverse effect on the future processing, product in service.

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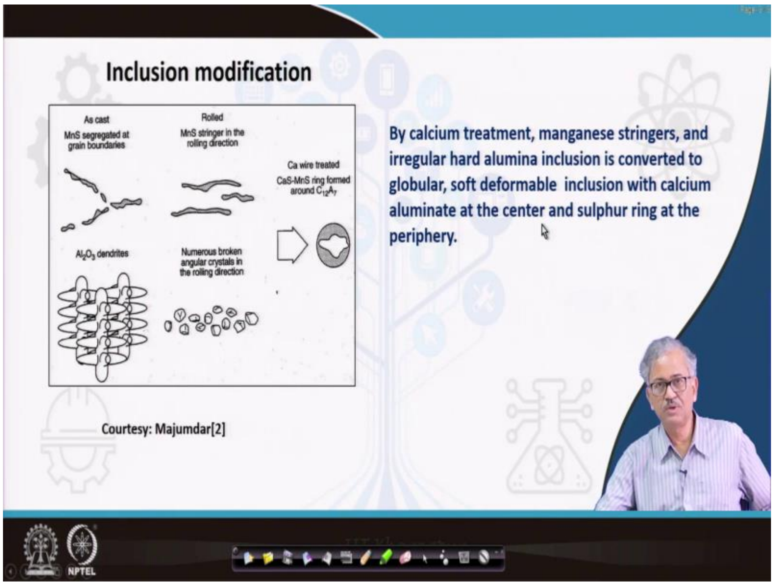

Inclusion modification

By calcium treatment, manganese stringers, and irregular hard alumina inclusion is converted to globular, soft deformable inclusion with calcium aluminate at the center and sulphur ring at the periphery.

Courtesy: Majumdar[2]

Now, let us discuss inclusion modification. Two major harmful inclusions in steel are MnS and Al_2O_3. MnS is a one of the deleterious inclusion in the steel and when steel is rolled, they become elongated, flat and long and called the stringers. They are very soft and deformable and are the point of weakness and allow propagation of cracks easily through them. In cast structure alumina inclusion remains in the form of alumina dendrites. Because alumina inclusion are hydrophobic; in other words they are unlikely to be wetted by liquid, but alumina inclusions try to combine together to reduce surface energy and form aggregate. Such alumina inclusions also causes difficulties during teeming operation by blocking nozzle. In rolled steel such aggregate disintegrate into numerous irregular, small and hard inclusions.

Such inclusions acts as stress concentrator under pressure, because they cannot absorb energy by deformation.

When these inclusions are treated by calcium they form an altogether different inclusion with modified size, shape and morphology, which are not harmful for subsequent steel processing or, product in service like fatigue property. Figure 41.3 shows the change in inclusion morphology after calcium treatment.

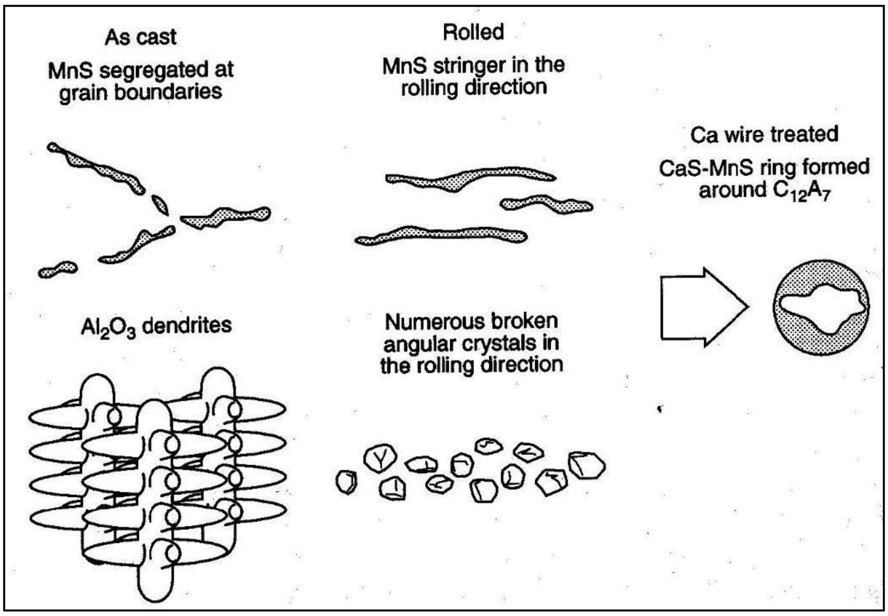

Figure 41.3: Evolution of inclusion morphology by calcium treatment[2]

It is seen from the figure that after calcium treatment, alumina is converted to the calcium aluminate and form the core of the modified spherical inclusion. And the sulphide stringers accumulates on the surface of the inclusion forming oxy-sulphide. So, manganese sulphide, calcium sulphide, appear on the surface of calcium aluminate, as a ring. Thus the formation of spherical inclusion eliminate the manganese stringers as well as rough, hard and randomly distributed alumina inclusions. Calcium aluminate formed are liquid at steel making temperature, thus the modified inclusions become soft and deformable. Thus calcium modify this deleterious inclusion to a soft deformable spherical inclusion; that is interesting.

Figure 41.3 shows the elemental mapping of such inclusion, showing a clear sulphur ring around the calcium aluminate core.

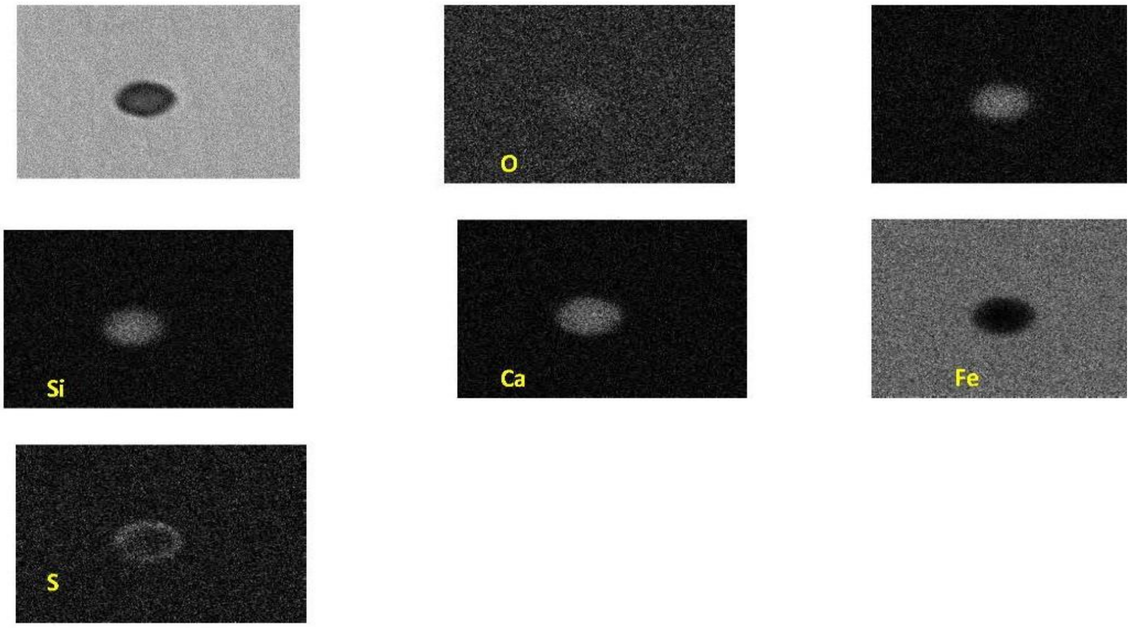

Figure 41.3 Elemental mapping of modified inclusion showing a clear sulphur ring around the calcium aluminate core[3].

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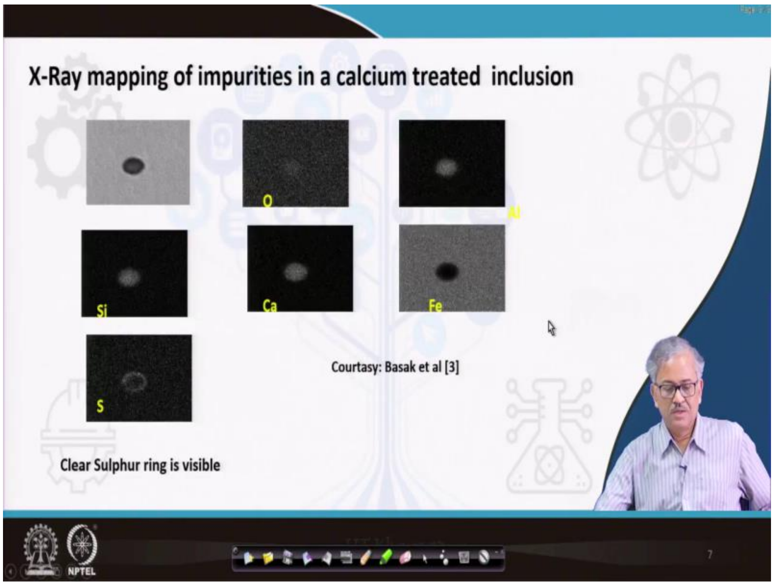
X-Ray mapping of impurities in a calcium treated inclusion

Courtasy: Basak et al [3]

Clear Sulphur ring is visible

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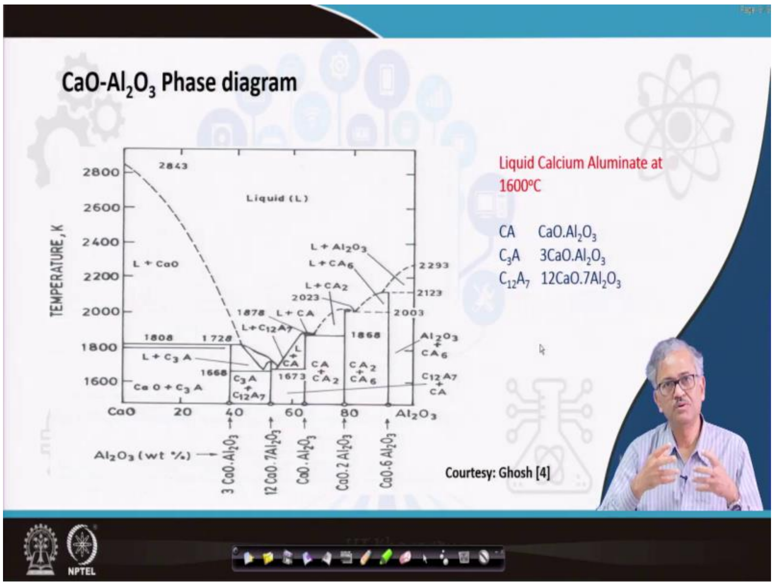

CaO-Al_2O_3 Phase diagram

Liquid Calcium Aluminate at 1600°C

CA	$CaO.Al_2O_3$
C_3A	$3CaO.Al_2O_3$
$C_{12}A_7$	$12CaO.7Al_2O_3$

Courtesy: Ghosh [4]

Figure 41.4 shows the binary phase diagram of CaO and Al_2O_3 system.

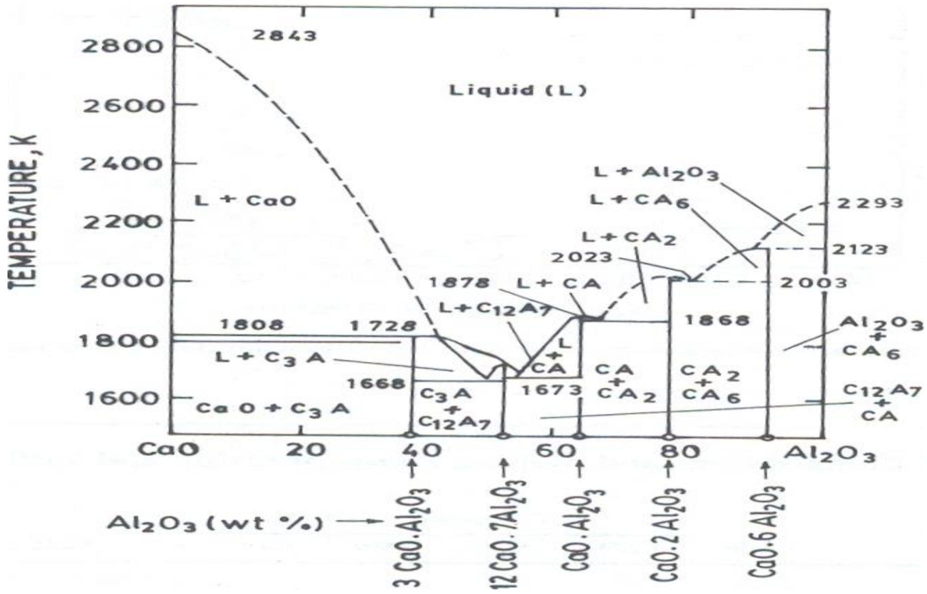

Figure 41.4: Binary phase diagram of CaO and Al_2O_3[4]

In the figure 41.4 calcium aluminate are represented as C_xA_y, where C represents CaO and A represents Al_2O_3, and x,y represents the number of moles of CaO and Al_2O_3, respectively. From the figure 41.4, it is seen that several calcium aluminates can form; but only 2/3 calcium aluminates are liquid at steel making temperature. For example, $C_{12}A_7$, C_3A and CA are liquid with melting temperatures below the steel melting temperature (1900K). So, only these liquid CxAy are will be soft and deformable. And are desired in the modified inclusion and can be obtained by maintaining Ca/Al ratio in liquid iron in certain range only. Forming liquid calcium aluminate during upstream processing also help in removing nozzle clogging during teeming. So, calcium treatment serves two purposes: it produces a liquid calcium aluminate and avoids nozzle clogging by solid alumina network in the nozzle. Besides, those inclusions that cannot be removed from the system, could be modified to a soft deformable inclusion, which are not harmful for subsequent downstream steel processing and product in service.

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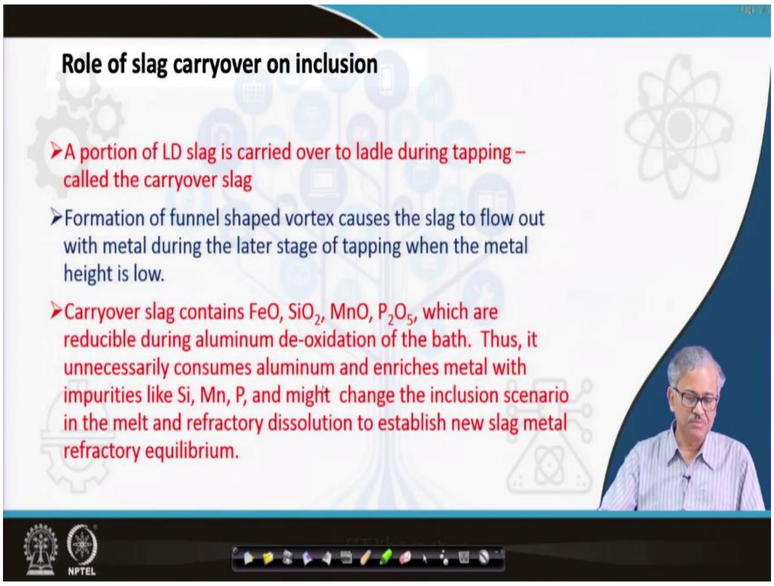

Role of slag carryover on inclusion

- A portion of LD slag is carried over to ladle during tapping – called the carryover slag
- Formation of funnel shaped vortex causes the slag to flow out with metal during the later stage of tapping when the metal height is low.
- Carryover slag contains FeO, SiO_2, MnO, P_2O_5, which are reducible during aluminum de-oxidation of the bath. Thus, it unnecessarily consumes aluminum and enriches metal with impurities like Si, Mn, P, and might change the inclusion scenario in the melt and refractory dissolution to establish new slag metal refractory equilibrium.

Now, I will talk about the carry over slag and its effect on the inclusions. During tapping of liquid steel from LD to the ladle, invariably some of the LD slag passed to the liquid metal into the ladle, that is called the carryover slag. The constituents in carry over slag like FeO, SiO_2, MnO, P_2O_5 are reducible oxides. In aluminium deoxidised bath where oxygen level become very low, such oxides are likely to decompose to oxygen and corresponding elements and thus increasing the impurity level in the liquid iron.

FeO having highest oxygen potential is likely to decompose first, followed by P_2O_5, MnO, SiO_2. Subsequently, when the bath oxygen increases it will consume more aluminium, decreasing the yield of aluminium for deoxidation. So, that is why the carryover slag is not good. Besides they may change the inclusion scenario by setting a new equilibrium between refractory, metal and slag. So, in that case some refractory dissolution also can take place.

At the end of tapping, slag passes to the ladle along with metal through vortex and drain sink formation. Dart and electromagnetic sensors are usually applied to minimize the slag carryover to the ladle. Dart has a density between that of metal and slag, such that it seats on the nozzle mouth when slag appear in the nozzle and close the metal tapping. But, operating dart or plug depends on lot of experience. Therefore, to avoid such human expertise, electromagnetic sensor became popular, which alerts at the first appearance of slag in the nozzle exit. Although it may be little more accurate to indicate the time of stopping metal tapping operation, but stopping slag carryover without sacrifice of iron yield becomes an issue for both the techniques. Therefore, although slag carry over could be minimized it could not be stopped altogether considering the metal yield. Typically, carryover slag could be of the order of 10 to 15 kg per ton of steel, while using dart, which could be further reduced to 4 to 5 kg per ton of steel using electromagnetic sensor, without sacrificing much of metal yield.

Ashok et al recently reported a cold model simulation and dimensional analysis of the drain sink formation during the tapping process.

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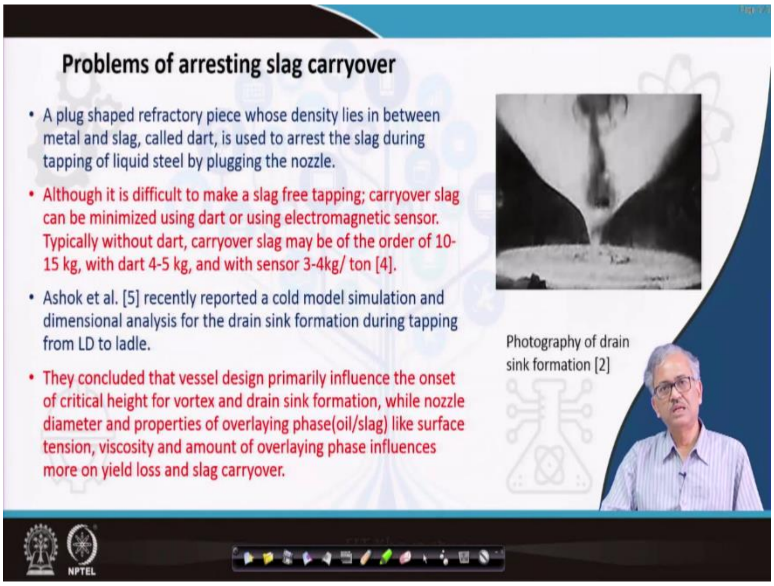

Problems of arresting slag carryover

- A plug shaped refractory piece whose density lies in between metal and slag, called dart, is used to arrest the slag during tapping of liquid steel by plugging the nozzle.
- Although it is difficult to make a slag free tapping; carryover slag can be minimized using dart or using electromagnetic sensor. Typically without dart, carryover slag may be of the order of 10-15 kg, with dart 4-5 kg, and with sensor 3-4kg/ ton [4].
- Ashok et al. [5] recently reported a cold model simulation and dimensional analysis for the drain sink formation during tapping from LD to ladle.
- They concluded that vessel design primarily influence the onset of critical height for vortex and drain sink formation, while nozzle diameter and properties of overlaying phase(oil/slag) like surface tension, viscosity and amount of overlaying phase influences more on yield loss and slag carryover.

Photography of drain sink formation [2]

Figure 41.5 shows the photography of the drain sink formation.

Figure 41.5: Photography of drain sink formation[5]

The figure 41.5 is captured by using a video camera; the white portion represents the metal-slag mixture (in cold model simulation it is the mixture of water and mineral oil, used as low temperature analogues for metal and slag, respectively) that leaves through the drain sink and the vortex could be seen in the center. Vortex column forms much before the drain sink formation when slag drains along with metal. Ashok et al. measured the critical liquid heights for the formation of vortex column as well as drain sink formation and reported that design parameters (like nozzle diameter) has a great role to play in deciding the critical heights of formation of vortex column and drain sink formation.

But as far as the yield of the liquid steel or the carryover slag is concerned, they observed that physicochemical properties of the slag like surface tension, viscosity, also amount of the carryover slag at the top.

And they also and also make some hypothesis, based on theoretical calculation, that the vortex could be dislodged from the nozzle by tilting the vessel. But they could not demonstrate through cold model simulation because of logestic problem.

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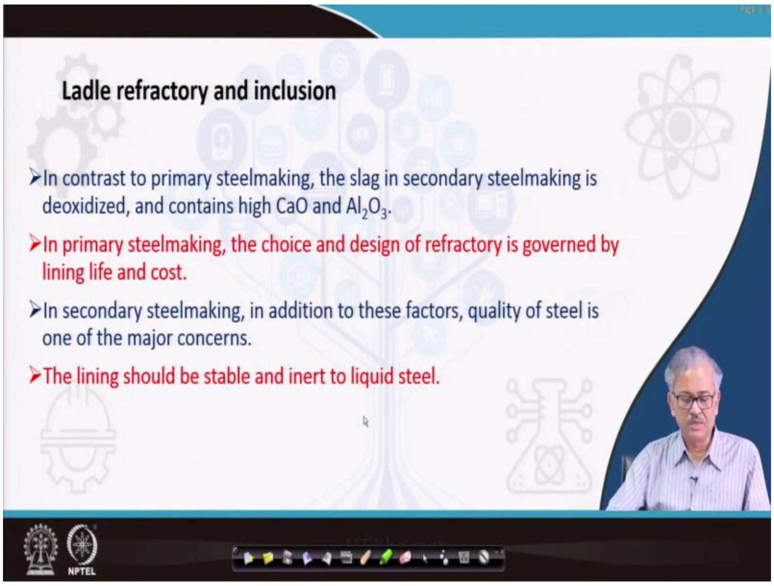

Ladle refractory and inclusion

- In contrast to primary steelmaking, the slag in secondary steelmaking is deoxidized, and contains high CaO and Al_2O_3.
- In primary steelmaking, the choice and design of refractory is governed by lining life and cost.
- In secondary steelmaking, in addition to these factors, quality of steel is one of the major concerns.
- The lining should be stable and inert to liquid steel.

Now, I will talk about the requisite quality for ladle refractory.. In the secondary steelmaking the liquid bath contains very low dissolved oxygen and slag contains high amount of CaO and Al_2O_3. The slag composition is totally different from that in primary steelmaking , which is mostly FeO, SiO_2 and CaO and FeO has significant amount, around 20%.

But in ladle slag, FeO is not there. So, refractory should be made of very stable oxide whose oxidation potential is lower than that of liquid iron under aluminium deoxidized state. Otherwise, oxides with higher oxidation potential like SiO_2 may decompose. The refractory could be made of calcia, magnesia, alumina etc. Second thing is that in the primary steelmaking the choice and design of the refractory is governed by the lining life and the cost of the process. In addition to that, in case of the secondary steelmaking, attention has to be given on the quality of steel. Consequently, mechanical and chemical erosion of refractory should be low. Mechanical erosion arises due to shear stress of the liquid acting on refractory wall and if the refractory does have very good wear resistance they are likely contaminate the liquid by spalling. Spalling may also occur due to chemical erosion and the situation can worsen, if the material does not have good thermal shock resistance and develops cracks that subsequently wetted by liquid.

Therefore, lining should be stable and inert to the liquid steel such that it does not contaminate the liquid iron; and it is very important because secondary steelmaking is the final stage where you can control the inclusion, beyond that it is not possible.

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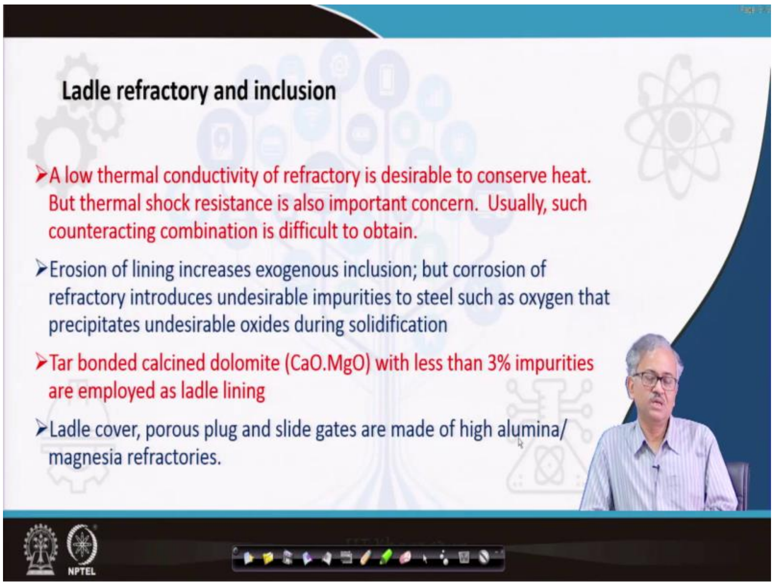

Ladle refractory and inclusion

- A low thermal conductivity of refractory is desirable to conserve heat. But thermal shock resistance is also important concern. Usually, such counteracting combination is difficult to obtain.
- Erosion of lining increases exogenous inclusion; but corrosion of refractory introduces undesirable impurities to steel such as oxygen that precipitates undesirable oxides during solidification
- Tar bonded calcined dolomite (CaO.MgO) with less than 3% impurities are employed as ladle lining
- Ladle cover, porous plug and slide gates are made of high alumina/ magnesia refractories.

Usually, tar bonded calcined dolomite is used as CaO-MgO lining with less than 3 percent impurities. Tar bonded refractory form a decarburized layer ahead of liquid melt, which restricts its penetration. Impurities like silica is not desirable that is like to decompose, and even volatilize in presence of sulphur as SiS gas.

Ladle cover, porous plug and slide gates are usually made of the high alumina or magnesia refractories.

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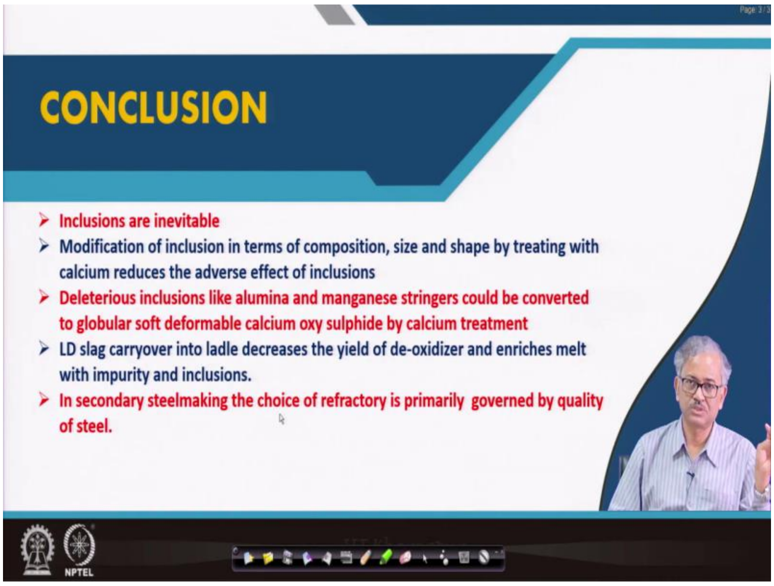

CONCLUSION

- Inclusions are inevitable
- Modification of inclusion in terms of composition, size and shape by treating with calcium reduces the adverse effect of inclusions
- Deleterious inclusions like alumina and manganese stringers could be converted to globular soft deformable calcium oxy sulphide by calcium treatment
- LD slag carryover into ladle decreases the yield of de-oxidizer and enriches melt with impurity and inclusions.
- In secondary steelmaking the choice of refractory is primarily governed by quality of steel.

Conclusion: Formation of inclusions isinevitable and making steel free of inclusions is also practically not possible. There could be millions of tiny inclusions in steel per cubic cm. Smaller inclusions like 1µm are harmless but inclusions greater than 10 µm could be quite harmful for further processing of steel and steel product in service, especially the fatigue properties. Modification of inclusion in terms of composition, size, shape, and morphologies by calcium treatment, reduces the adverse effect of the inclusion; in other words, deleterious inclusions like alumina, manganese stringers could be converted to globular soft deformable calcium oxy sulphide by calcium treatment, which does not hamper further processing as well as service life of the product.

LD slag carryover into the ladle decreases the yield of deoxidizer and enriches the melt with impurity and inclusions. LD slag contains lot of reducible oxide like FeO, MnO, SiO_2,, P_2O_5, which are likely to decompose in an aluminium deoxidized liquid bath with very low oxidation potential. Besides refractory might also dissolve in liquid melt.

So, that is why slag carryover is not a good thing and it has to be reduced significantly. Attempts are made to restrict the slag carryover by using dart, or electromagnetic sensor, but it could not stopped altogether with reasonable yield of iron. Carryover slag is entrained in liquid iron at the end of tapping by drain sink formation and research are going on to dislodge the vortex from the nozzle to restrict the slag entrainment. In secondary steelmaking, the choice of refractory is primarily governed by the quality of the steel, unlike in the primary steelmaking where main aim is to increase the life of refractory lining only. The criteria of choosing the refractory are stable, inert oxides with excellent wear, thermal shock resistance. Tar bonded calcined dolomite is used as refractory, which are stable even in deoxidized liquid bath. High alumina, magnesia refractory are used in slide gate, porous plug and ladle cover.