Iron Making and Steelmaking
Prof. Gour Gopal Roy
Department of Metallurgical and Materials Engineering
Indian Institute of Technology, Kharagpur

Module – 08
Lecture – 36
Secondary Steel making: Introduction and de-oxidation

We are starting the Secondary Steel making and in this lecture, I will discuss introduction of secondary steel making and de-oxidation.

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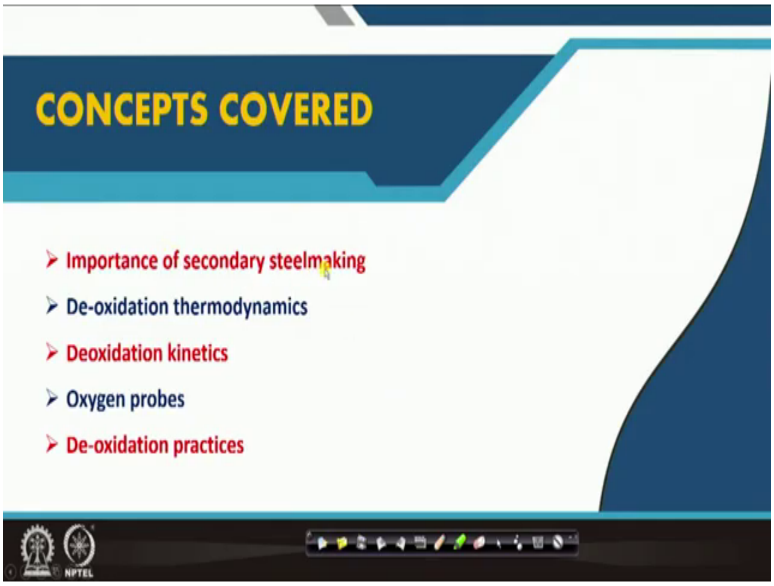

CONCEPTS COVERED

- Importance of secondary steelmaking
- De-oxidation thermodynamics
- Deoxidation kinetics
- Oxygen probes
- De-oxidation practices

Topics covered will include importance of secondary steelmaking, de-oxidation thermodynamics, de-oxidation kinetics and measurement of dissolve oxygen, oxygen probes and de-oxidation practices.

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Secondary steel making

- Higher productivity
- Special grade steels with ultra low impurity tolerance
- Clean steel
- Continuous casting requires stringent quality control

First, let us talk about significance or importance of secondary steelmaking. Stringent composition control, demand for ultra low impurity steel (say, 20 ppm interstitial free steel, 50 ppm sulphur steel are some of the examples of new steel specifications) has motivated secondary steel refining in ladle with advanced equipment, which is otherwise not achievable in primary steel making. The aim of primary steelmaking has been towards producing steel at rapid rate to keep productivity high. Special refining with special devices are left to ladle refining during transit from SMS (steel melting shop) to caster. Thus secondary steelmaking, or ladle refining helps to keep productivity high and at the same time fulfills the demand for stringent quality steel. Inclusion removal and its control is another major objective of secondary steelmaking. Use of vacuum allows preferential decarburization to lower carbon to a very low level; synthetic slag treatment lowers the sulphur to a very low level; Ca injection modify the inclusion to make those harmless and even helpful for further processing of steel.

Finally, due to rapid solidification rate, continuous casting cannot tolerate large amount of impurities in steel, which otherwise form inclusions, or precipitates undesirable compounds during solidification, causing cracks. Gaseous impurities produces void defects. So, vacumn treatment are used for removal of gaseous species. Gas stirring homogenize liquid steel bath and remove thermal and chemical stratification. Inclusion removal and its control helps to produce clean steel. Clean steel does not mean making steel completely impurity free, which is not possible. In a solidified steel large number of tiny inclusions (harmful product of reactions between impurities) exist, because it is not possible for all such tiny inclusions to float up and annihilate into the slag phase. So concept of inclusion modification appear. Inclusion modification means to modify the inclusions to desirable size and shape such that those does not interfere for subsequent steel processing. Usually calcium treatment for aluminum killed steel is done to form spherical liquid calcium aluminate and subsequently calcium oxy-sulphide which are harmless and sometimes even beneficial.

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Operations in secondary steel making

- De-oxidation
- Degassing
- Decarburization
- Desulphurization
- Inclusion removal and modification
- Temperature and compositional homogenization
- Temperature compensation

The following operations are carried out in the ladle after tapping liquid steel from LD vessel to the ladle onwards. Deoxidation, Degassing, deep decarburization, deep desulphurization, Inclusion removal and modification, temperature and compositional homogenization, and temperature compensation. Compositional homogenization of the liquid bath in the ladle after making alloying addition, is also an important objective to avoid elemental segregation, precipitation during solidification. Elimination of temperature stratification in ladle is also an important activity to pour liquid at constant superheat in concast (continuous casting) mould to avoid skin rupture at mould exit. Temperature compensation is also an important activity in secondary steel making; because significant amount of heat is lost during secondary processing and heat compensation is required to meetup the particular superheat for concast. Usually electric arcing is used for heat compensation. Chemical heating using aluminum is also done some times but unless precautions are taken chemical heating may lead to unclean steel with Al_2O_3 inclusions.

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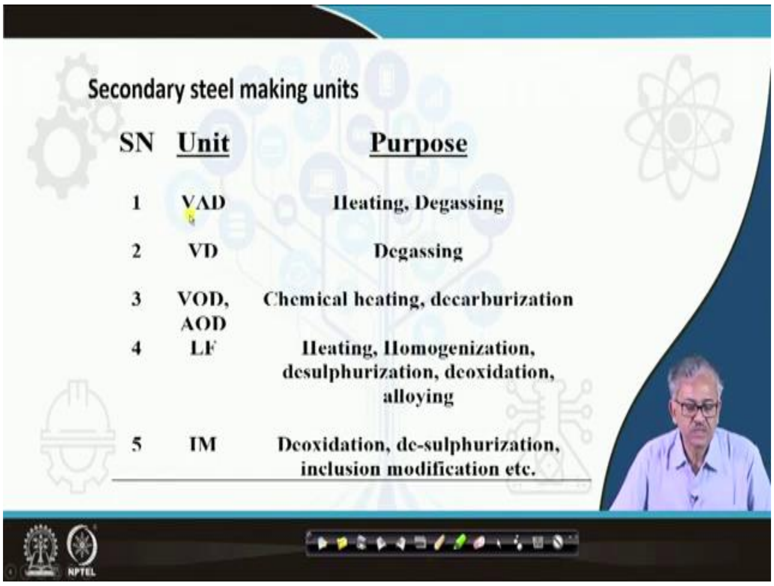

Secondary steel making units

SN	Unit	Purpose
1	VAD	Heating, Degassing
2	VD	Degassing
3	VOD, AOD	Chemical heating, decarburization
4	LF	Heating, Homogenization, desulphurization, deoxidation, alloying
5	IM	Deoxidation, de-sulphurization, inclusion modification etc.

Some of the secondary steel making units with their function are shown in the slide above. VAD (vacuum arc degassing) is used for degassing and temperature compensation; electric arcing is used for heat compensation and vacuum for degassing.

While VD (Vacuum degassing) is used only for degassing. VOD (vacuum oxygen decarburization) is used to decarburize the bath at a very low level of carbon. Oxygen is used to oxidize carbon and vacuum reduces partial pressure of CO making preferential decarburization of the bath. AOD (Argon oxygen Decarburization) does the same purpose as VOD but it does not require vacuum and argon serves the purpose of vacuum, i.e. to reduce the partial pressure of CO. It is more widely used for stainless steel production.

LF (ladle furnace), as the name suggests, it acts as a furnace for the ladle for doing heat compensation using electric arc (Figure 36.1). Besides it does several other functions, namely homogenization by bottom gas stirring, desulphurization by using basic and reducing synthetic slag. So, LF is very versatile. For desulphurization it uses a basic and reducing synthetic slag. Besides the bath is vigorously stirred by bottom argon purging that emulsify salg droplets in the metal bath, enhancing the kinetics of desulphurization by manifold.

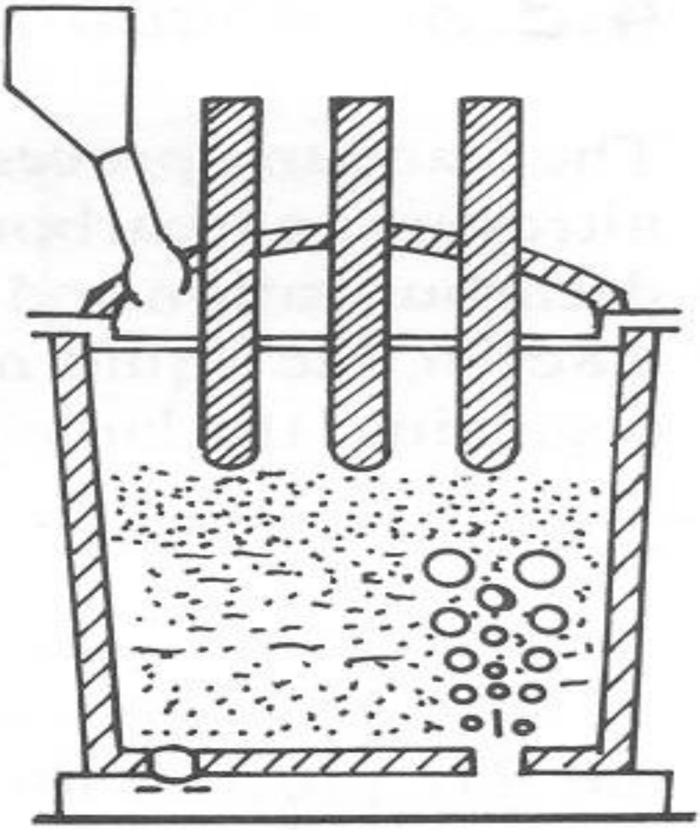

Figure 36.1 Schematics of Ladle Furnace [1]

IM (injection metallurgy), where reactive and volatile additives like calcium powder are injected either through submerged lance or cored wire injection (cored wire represents a hollow mild steel tube packed with calcium powder). Cored wire is charged in LF also along with bottom purging.

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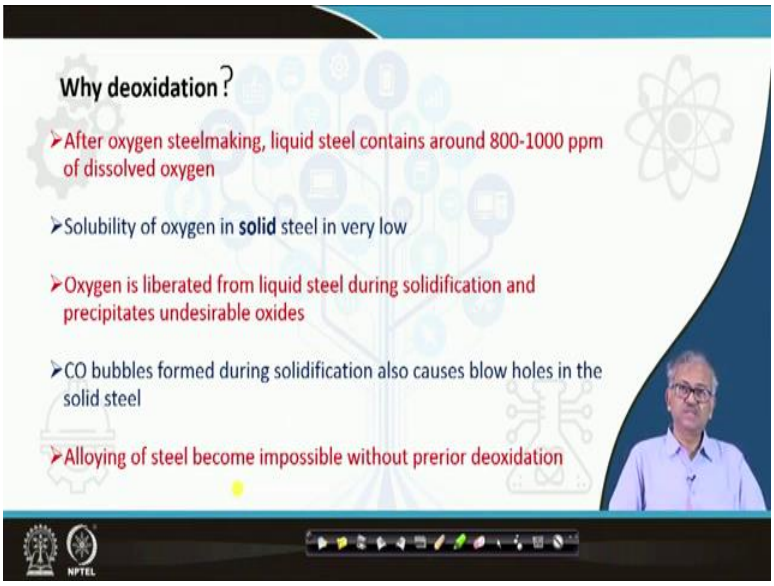

Why deoxidation?

- After oxygen steelmaking, liquid steel contains around 800-1000 ppm of dissolved oxygen
- Solubility of oxygen in **solid** steel in very low
- Oxygen is liberated from liquid steel during solidification and precipitates undesirable oxides
- CO bubbles formed during solidification also causes blow holes in the solid steel
- Alloying of steel become impossible without prerior deoxidation

Now, first operation in the secondary steelmaking is called the de-oxidation. After oxygen steelmaking residual oxygen in the turndown sample is estimated around 800 to 1000 ppm. This is large amount of oxygen which has to be removed before any alloying and solidification. Yield for alloying will decrease significantly as alloying element will get oxidized and join slag in presence such high level of oxygen in liquid bath. Besides during solidification these oxygen will evolve in the form of bubble and large amount of which will be entrapped into steel causing void defects. For these reason, you need to do deoxidation of liquid steel before you proceed to any further processing of steel.

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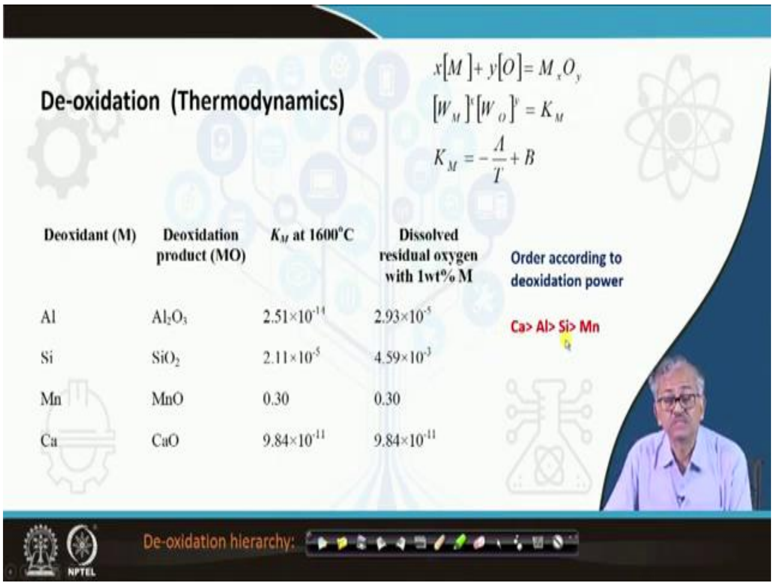

De-oxidation (Thermodynamics)

$$x[M]+y[O]=M_xO_y$$

$$[W_M]^x[W_O]^y=K_M$$

$$K_M=-\frac{A}{T}+B$$

Deoxidant (M)	Deoxidation product (MO)	K_M at 1600°C	Dissolved residual oxygen with 1wt% M
Al	Al_2O_3	2.51×10^{-14}	2.93×10^{-5}
Si	SiO_2	2.11×10^{-5}	4.59×10^{-3}
Mn	MnO	0.30	0.30
Ca	CaO	9.84×10^{-11}	9.84×10^{-11}

Order according to deoxidation power

Ca> Al> Si> Mn

De-oxidation hierarchy:

Now, let us talk about thermodynamics of de-oxidation. The general reaction for de-oxidation is given by equation 36.1. For pure metal oxide, the solubility product of dissolved oxygen and metal species can be represented by equation (36.2). Solubility product can be expressed in terms of temperature, given by equation (36.3).

$$x[M]+y[O]=M_xO_y \tag{36.1}$$

$$[W_M]^x[W_O]^y=K_M \tag{36.2}$$

$$K_M=-\frac{A}{T}+B \tag{36.3}$$

Table 36.1 depicts the calculated data based on the above equations and show the residual oxygen in equilibrium with 1wt% metal in the liquid bath at 1600°C.

Table 36.1 Showing the calculated residual oxygen in equilibrium with 1 wt% metal in the liquid bath at 1600°C.

Deoxidant (M)	**Deoxidation product (MO)**	**K_M at 1600°C**	**Dissolved residual oxygen with 1wt% M**
Al	Al_2O_3	2.51×10^{-14}	2.93×10^{-5}
Si	SiO_2	2.11×10^{-5}	4.59×10^{-3}
Mn	MnO	0.30	0.30
Ca	CaO	9.84×10^{-11}	9.84×10^{-11}

It is seen that residual oxygen that will coexist with 1 wt% aluminum in the bath at 1600°C is 2.93×10^{-5}. The corresponding value of residual oxygen with 1 wt% silicon in the bath is 4.59×10^{-3} and that for 1wt% Manganese is 0.3 and it is minimum with 1 wt% Ca in the bath at a value 9.84×10^{-11}. So Calcium is the strongest deoxidizer followed by Al and then Si and Mn is the weakest as deoxidizer.

But calcium is very reactive and volatile and therefore it cannot be dumped at the top. It has to be injected either through submerged lance or through cored wire. Inspite of injection its recovery is very low and could be maximum at 30%. Besides, calcium is very corrosive. So, next strongest deoxidizer, Al is preferred as de-oxidizer. Silico-mangaese is also used as deoxidizer because it yields liquid product of de-oxidation (MnO.SiO2), which is kinetical favoured for inclusion removal.

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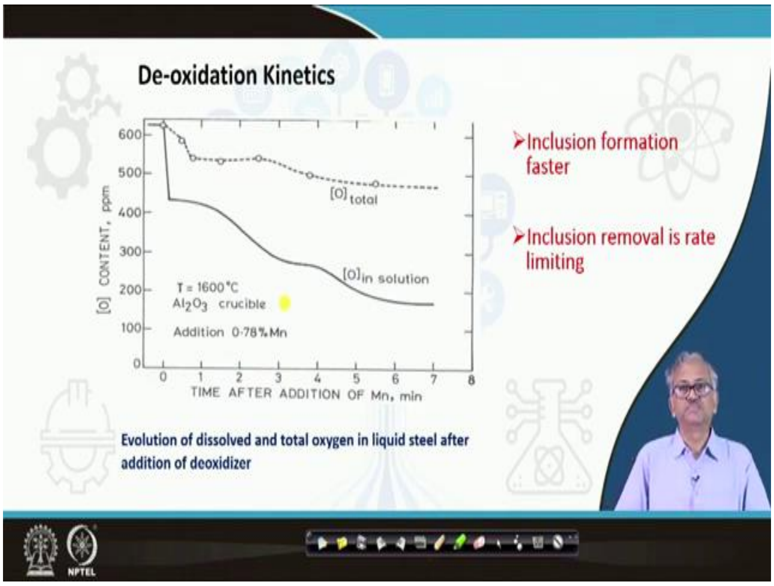

De-oxidation Kinetics

Evolution of dissolved and total oxygen in liquid steel after addition of deoxidizer

- ➢Inclusion formation faster
- ➢Inclusion removal is rate limiting

Now, let us discuss the de-oxidation kinetics. Figure 36.2 shows the evolution of dissolved and the total oxygen in liquid steel after addition of manganese as de-oxidizer in a laboratory scale experiments.

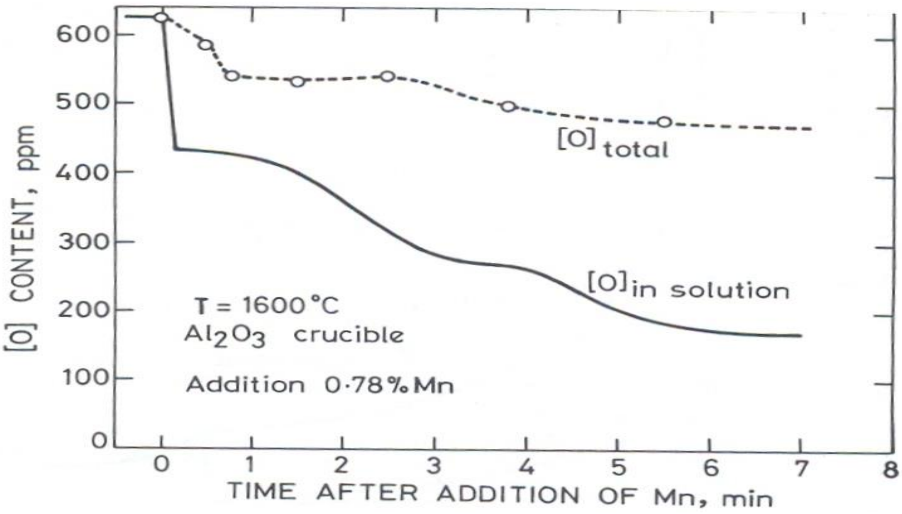

Figure 36.2: Evolution of dissolved and total oxygen in liquid steel after addition of manganese as deoxidizer[1]

It is seen that dissolved oxygen sharply drops from 600 to 400 in fraction of second, and then it progressively drops to less than 200 ppm after 6 minutes of addition of manganese. But if you see the total oxygen; it has dropped to only 500 ppm after 6 minutes of addition of manganese. Total oxygen represents the dissolved oxygen plus oxygen that remains in the liquid bath in the form of MnO. And total oxygen can be measured by chemical analysis. However, to measure the dissolved oxygen a special probe called the cellox probe (a solid electrolyte cell) is required.

From Figure 36.1, it is seen that although the dissolved oxygen drops to quite small value (by 83% of original value), the drop in total oxygen is not remarkable (by 17% only). What does it mean? It shows that oxide inclusions are forming very fast, but their removal from the bath is not significant. Although dissolved oxygen has reduced significantly, but majorly this oxygen has remained in the system in the form of MnO. Only a small fraction of MnO has joined the slag. Therefore, MnO removal from the liquid bath is rate controlling for deoxidation kinetics of the bath.

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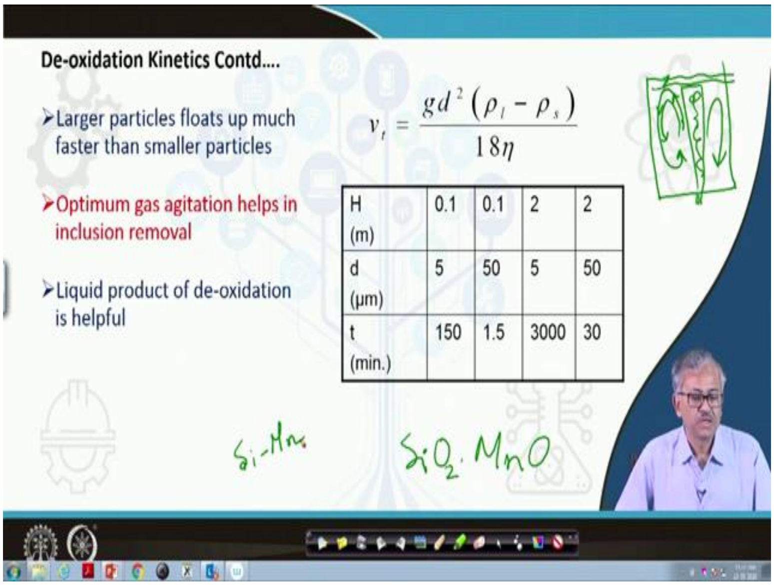

De-oxidation Kinetics Contd….

- ➤Larger particles floats up much faster than smaller particles
- ➤Optimum gas agitation helps in inclusion removal
- ➤Liquid product of de-oxidation is helpful

$$v_t = \frac{gd^2(\rho_l - \rho_s)}{18\eta}$$

H (m)	0.1	0.1	2	2
d (μm)	5	50	5	50
t (min.)	150	1.5	3000	30

Si-Mn

$SiO_2 \cdot MnO$

Let us see some factors on which deoxidation kinetics depends. First is the size of the deoxidized particles. According to Stoke's law,the velocity at which the oxide particles will rise up is directly proportional to the diameter square (Equation 36.4).

$$v_t = \frac{gd^2(\rho_l - \rho_s)}{18\eta}$$

(36.4)

So, large particles will float up much faster compared to the smaller particles. Table 36.2 shows some calculation indicating time required for float up of inclusion through the stagnant liquid bath as a function of their size and depth of the liquid bath.

Table 36.2: Time required for float up of deoxidation product as a function of size and depth of the liquid bath.

H(m)	0.1	0.1	2	2
d(μm)	5	50	5	50
t(min.)	150	1.5	3000	30

It is seen that an oxide particle of 5 µm diameter will take 150 minute, compared to only 1.5 minutes taken by an oxide particle of 50 µm diameter to rise a same liquid depth of 0.1 m. Similar values for a liquid depth of 2m are 3000 minutes and 30 minutes, respectively. 150 and 3000 minutes may be considered infinite time compared to the processing time in the bath and as a results oxide particles of 5µm diameter are unlikely be able to float up the bath and will be arrested in the solidified structure; unless some appropriate stirring arrangement is done to carry the tiny particles using liquid convection.

Stirring is another factor that facilitates the oxide float up but stirring has to be optimum. Bulk motion of the liquid is likely to entrain the smaller oxide particles and carry them to slag level for disposal. But if the stirring is very strong and the strength of recirculation is quite high, the entrained particles might not detach at the slag metal interface and might be dragged inside the bath again. So, starring helps in improving deoxidation kinetics but when it is done in optimum speed, it is only helpful.

Liquid product of de-oxidation is also helpful to improve deoxidation kinetics. Liquid products of de-oxidation are more likely to coalesce and as a result, they can form a bigger inclusion. Combined deoxidation by silicon and manganese, has been found to yield deoxidation product (SiO_2-MnO) that is liquid at steelmaking temperature. That is why sometimes silico-manganese (Si-Mn) are used us deoxidant to improve de-oxidation kinetics.

This is up to this lecture and it remains incomplete with respect to deoxidation and I will complete in the next lecture; where I will summarize the lecture 36 and 37 together.