

**Steel Quality Role of Secondary Refining and Continuous Casting**  
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**Module - 02**  
**Lecture - 07**  
**Deoxidation**

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## Deoxidation

**Reaction represented as**  $x [ M ] + y [ O ] = ( M_x O_y )$

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

**M<sub>x</sub>O<sub>y</sub> is deoxidation product** : MnO , SiO<sub>2</sub> , Al<sub>2</sub>O<sub>3</sub> , 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** ,  $h = \text{weight } \%$

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

Let us go in to one by one details into the different processes; that means, different requirements different steps. As I told you earlier, deoxidation is the first and most important requirement in secondary refining.

Now let us try to understand how deoxidation takes place. Deoxidation; the name implies that oxygen has to be brought down. So, now, what is the reaction this is the basic M stands for the deoxidant, the metal, the element which is used as the oxidant and oxygen is dissolved oxygen in liquid steel. This third bracket in incidentally all of you possibly know means that this M and this O; that means, this deoxidant and the oxygen these are in liquid steel and the first bracket indicates this constituent will be generated first and then first bracket indicates it should go to the slag; that means, it is a slag constituent. So, the reaction is M x plus oxygen in to y will find get you deoxidant like M x O y. When we are deoxidizing with aluminum; that means, the product is Al<sub>2</sub>O<sub>3</sub>, so, x is 2 y is 3, so,

2 aluminum reacting with 3 atoms of that means, 2 atoms of aluminum reacting with 3 atoms of oxygen giving rise to  $Al_2O_3$ , the molecule  $Al_2O_3$ .

So, as I was telling you M can be any deoxidizer which can be manganese, it can be silicon, it can be aluminum, it can be calcium, these are the you know common deoxidizer which can be used in liquid steel for taking care of oxygen. So, what is the product, what is the deoxidization product? If we are using manganese it is manganese oxide, if you are doing using silicon it is  $SiO_2$ , if you are using aluminum I have told you  $Al_2O_3$ , if you are using calcium it is calcium oxide. Sometimes you know the 2 elements also can be used like manganese silicon if you do it can be manganese oxide and  $SiO_2$  combination if you are using aluminum and calcium which is a combination of alumina and  $CaO$ . So, depending upon what is M that is which deoxidizer we are using for killing the steel, we get the product which is known as deoxidation product.

Now, if you look at this reaction the deoxidation product if you assume that it is a pure oxide say alumina when it is forming it is not reacting with anything; that means, it is pure alumina either in liquid steel and finally, it will go to the slag. So, the activity of this oxide we can take it as one and since the element M and the oxygen in liquid steel is a very low in content we know from basic thermodynamics that if we assume Henry's law for dilute solution then this h is a activity which can be taken as equal to weight percent because it is very very low much less than 1 weight percent. So, the equilibrium constant for this reaction  $K_M$  dash what is it activity of the oxide divided by the activity of the metal multiplied by the activity of oxygen of course, depending on you know the reaction; that means, how many atoms are reacting with how many atoms of oxygen the x and y will depend.

So, now as I have told you this a M O can be assumed to be one and  $h_M$  and  $h_O$ ; that means, the activities of the particular deoxidant for example, aluminum let us take and the activity of oxygen in liquid steel since these are very present in very small amount assuming Henry's law for dilute solution these are activities of these elements can be taken as equal to their weight percent. So, finally, what this reaction finally, goes in to that the weight person of that metal to the power x in to weight percent of oxygen to the power y equal to one divided by  $K_M$  dash. So, if you this is taken as  $K_M$  this can be taken as the deoxidation constant. So, one important relationship is emerging from this that that weight percent of the deoxidant in liquid steel and the weight percentage of

oxygen in liquid steel after the deoxidation reaction when they are in equilibrium they are multiplication; that means, weight percentage of the deoxidant in liquid steel.

And the weight percentage of oxygen in liquid steel equal to a constant we have to keep in mind; that means, whenever we are increasing the amount of deoxidant in liquid steel we are decreasing the amount of oxygen in liquid steel so; that means, for good deoxidation we have to add some larger amount of this M. Now this  $W_M$  and  $W_O$  the multiplication of this is constant I have told you.

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**Relative Deoxidation Ability**

$(\text{wt \% M})^x (\text{wt \% O})^y = K_M$ , constant for a temperature

At 1600 C, values of K for common deoxidisers

Mn : 0.2 – 0.3 , Si :  $2 \times 10^{-5}$  , Al :  $3 \times 10^{-14}$  , 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

Now, if you want to look in to what is this constant what are the values of this constant that will give an indication how good is the deoxidant. So, let us go in to the concept called relative deoxidation ability why do we tell that aluminum is a good oxidant manganese is not a good oxidant silicon is a moderate deoxidant calcium is oxide good these deoxidant why do we tell what are the quantitative figures how can we be sure yes let us go in to this aspect.

Now, I have told you that weight percent of the metal to the power x in to weight percentage of oxygen this metal M is a deoxidant and oxygen is oxygen present as element dissolve oxygen in liquid steel. So,  $x M$  to the power x and O to the power y is constant. So, at and this constant of course, since this is an equilibrium term is dependent on the free energy of the reaction this is dependent on the temperature. So, let us assume the temperature of liquid steel is 1600 centigrade which is a quite a reasonable

assumption. So, at 1600 degree centigrade we can find out the values of K from the oxidation reactions and the K for the different oxidizers I am giving you some rough estimate of the scale for different deoxidizers for manganese it is 0.2 to 0.3 for silicon it is  $2 \times 10^{-5}$  for aluminum it is much lower you just look at the value approximately I will give you the approximate  $3 \times 10^{-14}$  some people call it  $2 \times 10^{-14}$  some people call them give it the value of  $5 \times 10^{-14}$ .

Look at calcium  $10^{-12}$ . So, can you make out that manganese the value is high silicon value is lower than that aluminum and calcium much lower than these values. So, what does it signify if you look at what is  $K \cdot M$  weight percent of M in to weight percent of O; that means, if these values  $K \cdot M$  values are low; that means, this multiplication also will be low. That means, to get the same level of weight percent oxygen in liquid steel say we want 5 ppm in liquid steel 10 ppm in liquid steel the weight percentage of the deoxidant will be much more for manganese; manganese slightly less in silicon and much less for aluminum and calcium.

Please try to remember that this equation this reaction from the oxidation reaction we can come out with this understanding that K value; that means, the deoxidation constant for the common deoxidizers at reasonable temperatures say 1600 degree centigrade if the temperature changes values will also change. But let us talk about say any particular temperature say 1600 degree centigrade the values are given like this manganese around 0.25 say silicon  $2 \times 10^{-5}$  aluminum  $2 \times 10^{-14}$  calcium around  $10^{-12}$  so that means, using the same amount of deoxidizer; that means, if the amount of M is fixed if the value of  $K \cdot M$  is low; that means, soluble oxygen also will be low.

So, from this relation we can tell that soluble oxygen will be very low for calcium and aluminum will be moderate for silicon, but high for manganese. So, we can tell that calcium and aluminum are very potent deoxidizers very good deoxidizers they will bring down the equilibrium oxygen content in liquid steel to very low level unlike manganese; manganese you cannot get very low amount of liquid a low amount of dissolved oxygen in liquid steel it will be very high maybe more than 100 ppm maybe 150 ppm. So, manganese deoxidation is not very effective will silicon it is better than manganese maybe you can get 40 ppm, but for aluminum and calcium you can get value of less than

5 ppm this all can be calculated using this particular relationship at a particular temperature. So, we know that what is the criteria for using deoxidation which deoxidant is better it depends on the reaction of deoxidation reaction as I have told you this is deoxidation reaction M is the deoxidant oxygen reacting with oxygen finally, giving rise to the M K O y type of oxide depending on the deoxidant it will the deoxidation product is decided if it is aluminum it is  $Al_2O_3$  if it is silicon it is  $SiO_2$  it is calcium it is  $CO_2$ . So, from this equilibrium constants I have shown that weight percentage of the metal to the power x in to weight percentage of oxygen in equilibrium in liquid steel to the power y is a constant and this constant depends only on the temperature and nothing else. So, at a particular temperature using this relationship we can find out what amount of particular deoxidant will give rise to what amount of oxygen after deoxidation at equilibrium.

So, we can know that what are the deoxidants and how much do you get after deoxidation what is the amount of oxygen.

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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

Now, I have talked about the deoxidation process how deoxidation takes place now let us know in reality what are the stages how does deoxidation take place what are the steps.

We talked about deoxidation there are different stages we should know all the stages then only we should understand what are the implications how it can be facilitated how it can be enhanced how it can be more effective. So, as I have told you; however, how what we do deoxidation doing we are adding the deoxidizer in liquid steel for example, let us tell

we are adding aluminum in liquid steel how do we add aluminum we are adding; adding aluminum element we are adding silicon or Ferro silicon in liquid steel. So, faster that has to be added in the form of small particles small meeting the smaller it is better it is it will be faster going in to that solution.

So, after we added there is dissolution of the deoxidizer in the liquid steel. So, first we add then this gets in to solution in the liquid steel. So, this silicon or say aluminum or calcium when you are adding it is going in to solubility of liquid steel. So, oxygen is there in liquid steel that particular deoxidizer also goes in to liquid steel. So, then the chemical reaction which takes place between dissolve oxygen and dissolve aluminum what is all silicon what is all calcium the reaction what how the reaction takes place I have already mentioned to you in earlier slides. So, after adding and dissolution next stage is chemical reaction between dissolve oxygen and dissolves aluminum. So, finally, what happens what is the reaction product if it is aluminum it is alumina. So, alumina will be nucleated and there is an inclusion growth of this alumina particles initial growth of these alumina particles the first is an equation of alumina and there is initial growth of these alumina particles. So, these 3 steps takes place very fast may be within 2 or 3 minutes all these stages are over. So, you want to at this stage what is the situation

We have added aluminum; aluminum has you know got in to solution of liquid steel this aluminum in liquid steel is reacting with aluminum in oxygen producing alumina. So, in the process what is happening the d dot dissolve oxygen and dissolved aluminum have come down because of the reaction, but the product alumina they are in initially there in the liquid steel they are nucleated they have slightly grown to some extent, but this amount is very high alumina. So, from the cleanliness point of view we have taken care of dissolved oxygen by using aluminum dissolve aluminum, but there is alumina steel in liquid steel which is the alumina particles which is a deoxidation product this has to be removed. So, removal of alumina from liquid steel is necessary to enhance oxide cleanliness and then thereby reducing total oxygen what is total oxygen I have told you total oxygen is a combination of dissolved oxygen and oxygen present as oxide inclusion. So, by deoxidation by the process of deoxidation we have taken care of we have reduced dissolve oxygen, but the deoxidation product which is alumina it has aluminum as combined oxygen. So, the total oxygen is still high. So, this alumina now has to be removed from liquid steel to the slag.

So, then only we can enhance the inclusion enhance that cleanliness by removing the inclusion alumina. So, in the process reducing total oxygen, so, how it can be done this further growth of alumina by agglomeration it now is whatever alumina particles have formed we will try to agglomerate they to float up and subsequently they will be absorbed by the basic slag, but this takes time as I was telling you addition of aluminum soluble solubility of that aluminum getting in to solution and then reaction of soluble aluminum and soluble oxygen is very fast, but growth of alumina they are floating up their subsequent absorption by basic slag they all these stages are time taking and these are the rate controlling steps. So, we have to be careful how we have to get or how we have to enhance these stages.