Steel Making

Prof. Deepak Muzumdar

Prof. S.C. Koria

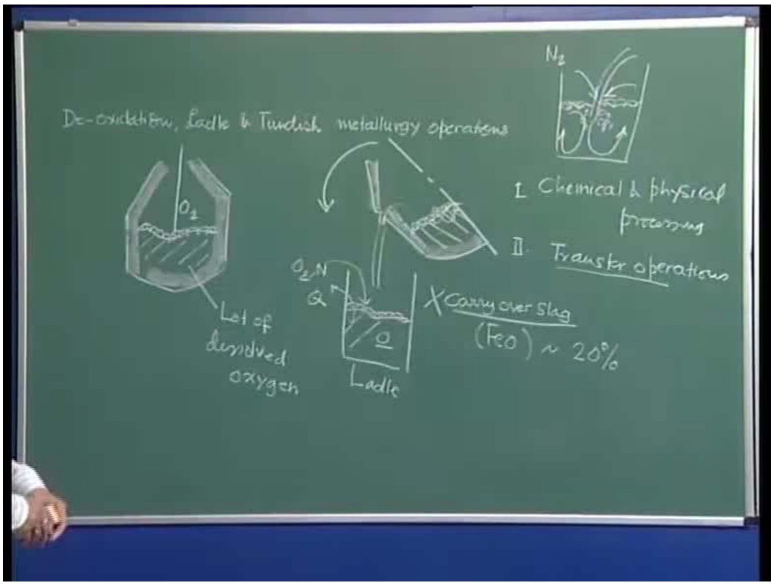
Department of Material Science and Engineering
Indian Institute of Technology, Kanpur

Module No. # 01

Lecture No. # 25

Deoxidation, Ladle and Tundish Metallurgy

(Refer Slide Time: 00:16)



We are going to now start talking about De-oxidation Ladle and Tundish metallurgy operations. However, before I start talking about these topics in details, let us quickly go through the section of primary steelmaking, and then, the relevance of secondary steel making or the De-oxidation Ladle and Tundish metallurgy will be clear to you.

Now, for example, you have this BOF vessel in which it is a refractory lined vessel with one lance and we have molten metal here, and after say about the duration of oxygen injection when the end blow period is over, what do we do? We typically - so, this is the half of the furnace and we have the tapping hole here and we have a ladle here, and tapping streams as this furnace is been tilted.

So, the metal builds up in this ladle. This is my BOF which is I am showing only one half of it with the line of symmetry here and this is again to show that the vessel is refractory lined. So, the inevitable consequence of primary steelmaking as this metal is going to be nearly saturated with oxygen.

We have lot of dissolved oxygen in the melt, and once decarburization is completed, we have to take it out in order to first remove the dissolved oxygen, because we know that oxygen dissolving steel is going to seriously impair the properties of steel when molten steel will be converted to solidified product such as bullet blooms and other shapes.

This is true not only of a BOF - basic oxygen furnace, BOF stands for basic oxygen furnace as you all known, but it is equally true for other oxygen steel making or electric arc furnace processes where we inject oxygen, and as a consequence of the refining reactions, we have lot of dissolved oxygen in the melt.

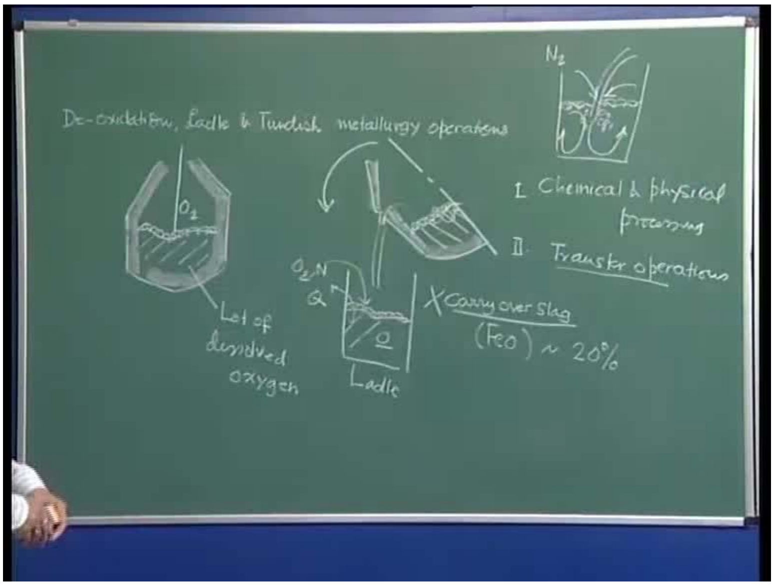
Now, at this particular point, I will try to classify steel making under 2 different processes and I will say chemical processing, chemical and physical processing, and number 2 is transfer operations.

So, the steps that we carryout in a BOF vessel or an electric arc furnace or an oxygen steel making converter such as an EOF energy optimizing furnace. We will classify those as chemical and physical processes where we change the composition. On the other hand, when oxygen steel making processes is over, we have to trap the molten metal into the ladle. This particular process, we are going to call it as a transfer operation.

As we will see in the secondary steel making, that transfer operations are also equally important as does the physical and chemical operations carried out in the primary steel making vessels. So, the objective of primary steelmaking as we have seen during earlier lectures is to primarily decarburize the, bath because once we wish to take out many other aspects of steel making, for example, composition adjustments, temperature adjustments, then the unnecessarily the duration of the blow is going to be substantially large.

So, today, the tendency in modern steel making companies is that use these vessels only for decarburization, and subsequent operations like may be desulphurization’s or composition adjustment or temperature adjustments can be carried out in the vessel which is beyond the primary steel making vessel, and there, we will see as we advance that the ladle will be involved into a very useful reactor which will call as the ladle furnace.

(Refer Slide Time: 04:32)



So, having made the steel of the correct composition, say we have, we started with pig iron which has 4 percentage or 4.3 percentage of carbon, and now, we have blown oxygen through the lance into steel. As a result of which, the steel which is coming into the ladle does not contain much of carbon, but as a consequence of this, this oxygen injection, it contains lot of dissolved oxygen.

And you got to remove this dissolved oxygen. We must remember that as we tilt the furnace, rotate the furnace to top the BOF, to tap the content of the BOF into the ladle, what is going to happened is that there will be a possibility to entrain the slag because we had generated lot of slags also here if we remember. So, this slags are also can be entrained as we tilt the furnace, you know, to drain out most of the material.

So, this slag which is going to come inevitably along with molten steel are going to be termed as the carry over slag. This slag is a highly basic slag contains silica and most importantly because of large amount of oxygen injection, these carry over slag is going to be reached in dissolved oxygen or it is iron oxide content is going to be very large. Depending on the process, we can have approximately 20 percent iron oxide in the slag itself, and mind it, this slag has a highly oxidizing is a highly oxidizing slag, its oxygen potential is very large. We are not going to entertain any amount of this slag coming here because we are now going to remove oxygen which essentially a deoxidization or reducing operation itself.

So, the carry over slag as we advanced we will see influences adversely the properties of the steel. So, as a result of which, all subsequent refining reactions beyond the primary steel making vessels which are going to be carried out in a ladle are actually going to be used in the presence of a new slag. We must remember that we would like to have some slag here, but this slag is not going to be the carry over slag. This slag is going to be a fresh slag which will be devoid of any iron oxide as such.

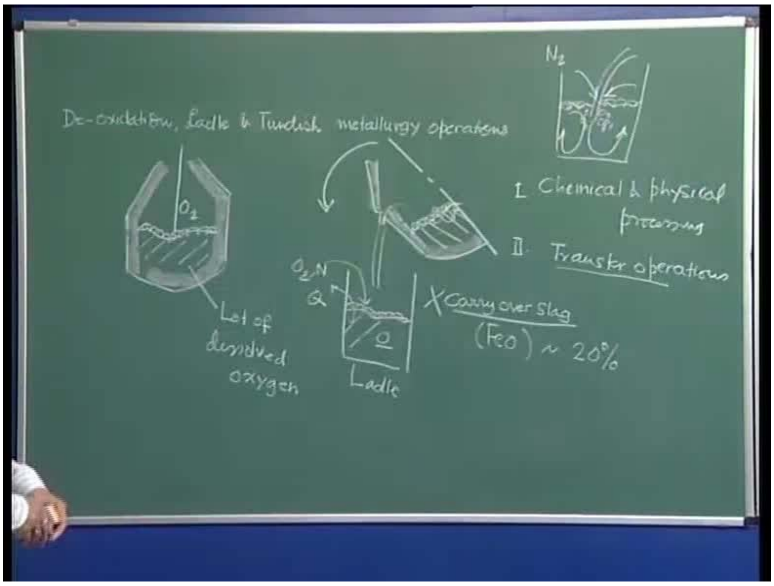
So, we may add some to start with when the ladle is empty. We can start some lime; we can, we can we can add some fluorspar or we can add some silica, and as a result of which, we can form a fresh slag which may float on top of steel because the slag as we all know is lighter than steel, and as this slag floats on top of steel, what happens is that it provides a protective cover over the steel, so, it is not going to be in contact with the atmospheric oxygen or nitrogen.

Similarly, the heat will not be able to escape, Q will not be able to escape through the slag layer because it is going to act as a, you know, thermal insulator over the bath itself, but this slag I would repeat again is not the carry over slag, not the slag from the basic oxygen furnace but it is the slag which is made a fresh in the ladle.

So, initially, we will have the ladle which is empty. The net steel is made or decarburization is completed. We will tilt the furnace or the basic oxygen furnace and then tap molten metal, and as molten metal comes into occupy the ladle, we are now going to see that there is going to be extremely large amount of recirculation which is going to be produced as a result of molten steel impinging. This is just like the way

For example, if you take a bucket in your bathroom, open the tap and then that is the kind of a filling operation that basically goes on here, and as you can see that our witness, you know, I would request you that you go to the bathroom, you know, take a bucket, open the tap and observe for yourself how the bucket gets filled up, and that is precisely the scenario that one would see in the case of the ladle filling operation.

(Refer Slide Time: 08:42)



If you take a plastic transparent bucket, you possibly see, can see in the bathroom air entrainment. So, you will see lot of oxygen, sorry, not oxygen but nitrogen because the material is already saturated with oxygen; there is not much concentration gradient between the dissolved oxygen or the oxygen potential in the atmosphere and here. So, as a result of which, there will be no oxygen transfer between the molten metal and the ambient. On the other hand, you know, you have lot of nitrogen gas here, we can have some nitrogen hydrogen which can be absorbed by the tapping stream and you will see or one can see really that there is lot of air impingement.

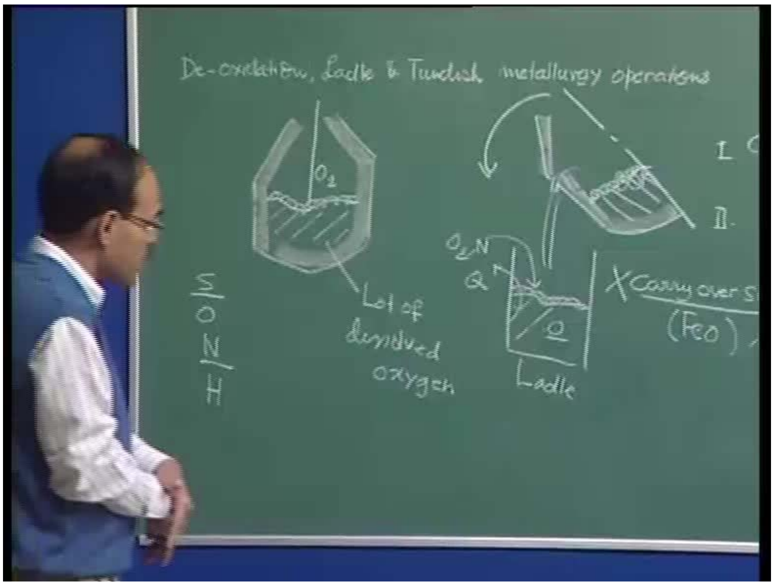
What happens is that when this jet which we say is an impinging jet on the surface of the ladle, it strikes the ladle, then it moves in a counter clock direction, and as a result of this rotation, it is a very extremely high speed of rotation. So, whatever you have added here to make the fresh slag, they get dissolved or melted very quickly and instantaneously, possibly, we are going to have.

So, we must understand that during the taping operation, an extremely intense hydrodynamic stirring is available in the bath itself. So, now, if I going to add some elements which are going to react with the oxygen, in order to take away the oxygen from the bath itself, those elements can melt and dissolve in steel, you know, very quickly.

For example, if you add a drop of potassium permanganate in a in that bucket, you know, on which you can do an experiment in a bathroom. You can see that the potassium permanganate will dissolve in the bath bucket of water very rapidly, and same happens in steel making ladle also during the furnace tapping operation.

So, refining is far from being complete in the primary steel making vessel and that is why there is a need for many subsequent operations or a entire ladle metallurgy treatment stations in steel plants to, you know, adjust the composition and temperature of steel, and I say repeatedly say temperature and composition, composition is for to meet the demand of the customer and temperature because there is, you know, there is a stringent requirement on the part of continuous casting that the metal be delivered into a continuous casting mill continuous casting mode at the right amount of superheat.

(Refer Slide Time: 10:56)



So, as primary steel making is offer over, we can assume that there is going to be may be sulphur which is more than the required specification, although we would like to have. Now, phosphorus absolutely, you know, in the right level, we must also, I must also mention here that there is an increasing trend that, you know, for high phosphorus steel, that we will going to have some kind of a pretreatment which you, of course, have done, you know, the between the blast furnace and primary steelmaking, we have pretreatments like disrecognition, desulphurization and we are building up gradually dephospherization as well.

So, we can have lot of sulphur in the basic oxygen furnace, and we know why sulphur is going to be there because the conditions in basic steel making furnace or BOF is not conducive for the removal of sulphur because removal of sulphur requires and basic reducing environment, and that is why in primary steel making which is an oxidizing process sulphur removal is not facilitated. We have to carry out sulphur removal under a reducing condition as we will see later on.

So, we can have lot of dissolved oxygen also and may be, you know, because of the transfer of nitrogen as I am saying that the material which comes may have lot of dissolved nitrogen and hydrogen also, and all these things must be adjusted the composition and also we may remember that the we may not always want a prime, you know, plane carbon steel there may be a demand for alloy steel, etcetera. So, we have to make some alloying additions into the ladle also in order to get to the final desired composition.

So, these are unwanted elements which are present beyond the primary steel making vessel, primary steel making reactor or vessel and these have to be eliminated in the secondary steel making process or in ladle metallurgy treatment. We must understand here that the capacity of a ladle is identical to the capacity of a BOF or an electric arc furnace. So, if it is a, we are talking of a 130 ton capacity, we are going to have 130 ton capacity for the ladle also.

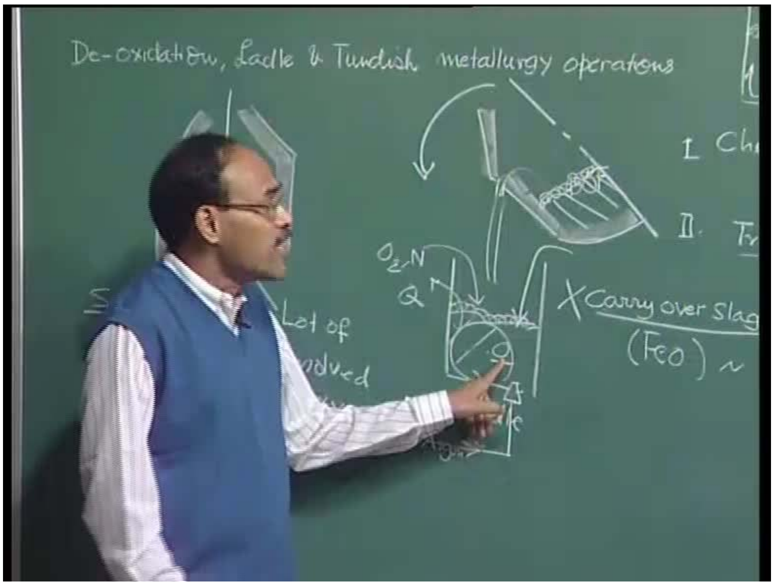
There are going to be innumerable number of ladles in the plants and the ladles are typically recycled because this ladle which is below the oxygen steel making furnace will be moved from the steel melt shock to the ladle metallurgy station where we may carry out a host of treatments or a variety of processes including tan degassing, ladle furnace to raise the temperature, composition adjustment, gas stirring, etcetera.

And finally, the ladle will be placed over the tarred in the continuous casting mill and where it is going to be casted, and as the ladle level over the continuous casting mold is going to be emptied, it is going to be recycled back and brought under the primary steel making furnace, and this is called the recycling of the ladle that from here, it goes to the continuous casting bay and from the continuous casting bay, an empty ladle comes and, you know, so, ladle is going to be used for a number of heats, you know, before relining is necessary.

But typically we must understand that the capacity of the ladle and the capacity of the furnace are going to be identical. One heat is going to be poured in one single ladle itself.

To summarize in this particular sections or before we proceed further, we must remember that we do not want oxidizing slag to be present in ladle, we want fresh slags, and to start with, we must remember that the metal which comes here contains lot of dissolved impurities and these have to be driven out, and also, we must remember that there is going to be an intense agitation which is going to be build up in the system because of the incoming jet of molten metal from the BOF.

(Refer Slide Time: 14:43)

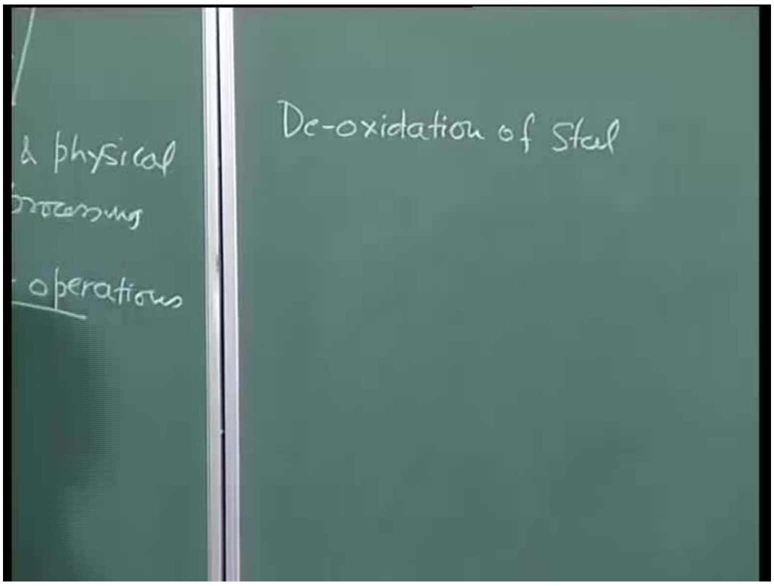


But we must also understand that as the metal is going to be emptied from the BOF, then eventually these intensity of motion here is going to die down, because at some point of time, this is completely emptied, so there is nothing is coming out, so, there is going to be not sufficient amount of stirring. So, that is why the moment we start to pour molten metal, we will see that we have a porous slag which is located here at the bottom, through which we are going to inject Argon. So, even when the intensity due to the impinging stream will die down, this gas or Argon which is being injected through the porous slag will gives rise to a reasonable amount of stirring in the system.

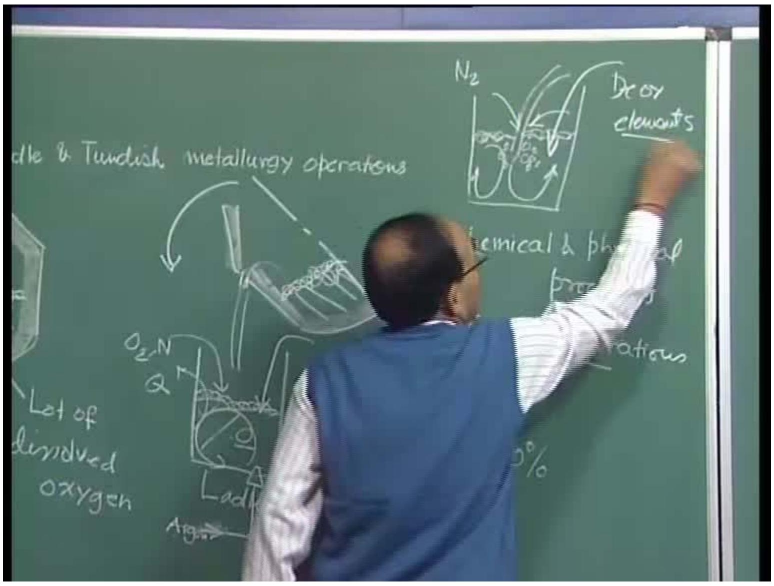
We want stirring in the system because as we know steel making reactions are basically mass transfer control. So, therefore, unless we have good amount of stirring, the mass transport of mass from one point to another point is not going to be needed. So, therefore, to facilitate various steel making reactions or, you know, moving of heat from one point to another, we have to have some amount of stirring present and gas stirring by the way is the cheapest mode of ensuring stirring in a high temperature system which is at 1600 degree centigrade.

We can see that when the material is completely filled or before the material is completely filled actually, as the furnace here, the basic oxygen furnace is being emptied, we are going to continuously now add deoxidizer elements into the steel bath.

(Refer Slide Time: 16:22)

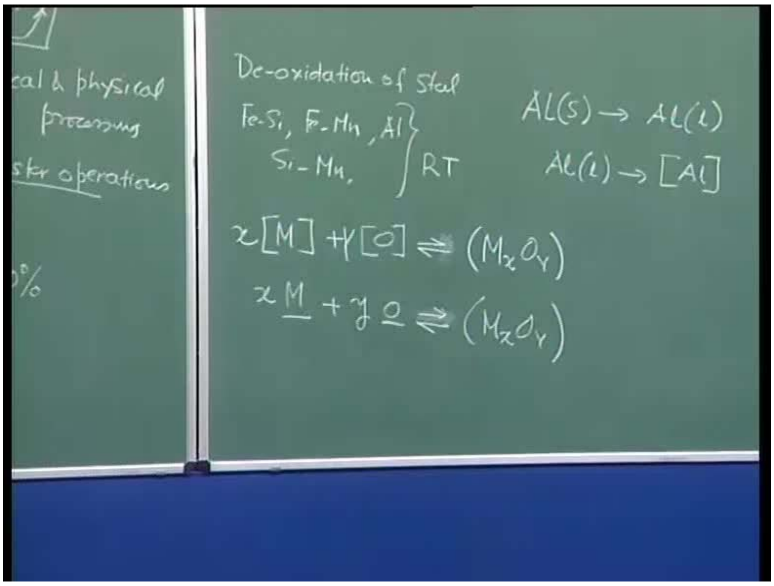


(Refer Slide Time: 16:48)



Now, we have to eliminate the first step is as I mentioned is to drive out this oxygen and this is called De-oxidation of steel bath, and to deoxidized the steel bath, we basically add elements which have greater affinity or a very high affinity for oxygen. So, what we can do basically? We can just as the ladle is being filled up with the stream, we can drop deoxidizer elements. In bulk form, and you can go to the steel plant and see that aluminum bars of these sizes are going to be poured into the molten steel.

(Refer Slide Time: 17:04)



And also I said that we can, you know, we can use other kinds of a deoxidizer elements also and commonly used elements in addition to aluminum are ferrosilicon, ferromanganese, silica-manganese, etcetera.

So, aluminum, ferrosilicon, ferromanganese, silica-manganese, these are commonly added deoxidizers in steel bath and these additions including aluminum can be made, you know, in long forms, we can take solids or in powdered forms again, if you take powdered forms or small particle sizes, we can understand that their melting and dissolution is going to be very rapid because of the larger surface area.

So, as the bath is being filled up we can keep on adding. Typically if you go to steel plant, you will see that gunny bags filled with ferrosilicon ferromanganese, etcetera, are been continuously done into the ladle and this have been does not have too large melting point. Therefore, they melt and dissolve very quickly into steel, and once they dissolve into steel, what happens is the reactions between the oxygen and the dissolution and that dissolved species set same.

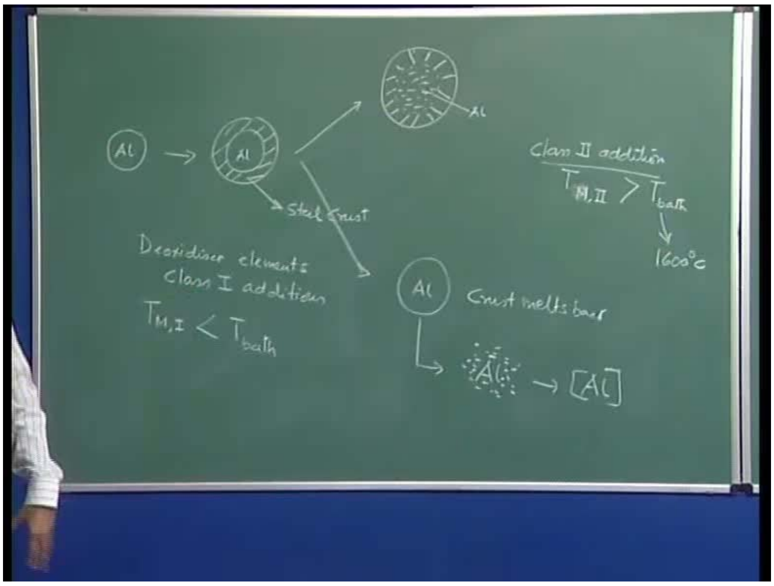
Now, we must understand before you proceed to discuss De-oxidation that these are cold elements, they are staying in the steel layer, steel company layered, at some places in some godowns, and these are basically at room temperatures. On the other hand, when you add them into the steel bath, what is going to happened? Their temperature is gradually go up, they have to melt because we have the dissolved oxygen in steel. So, these solids are will not be able to react with the oxygen present in steel unless this also dissolves. So, we have, for example, aluminum which is in solid form and then this aluminum becomes in liquid form; so, aluminum melts because of and this liquid aluminum basically, then what happens, it gets dissolved.

Once aluminum gets dissolved into steel, it can now see oxygen; as a result of which, aluminum and oxygen can react. So, before actually the De-oxidation reaction which is generally represented like, note that a third bracket essentially implies that it is dissolved in steel; a first bracket on the other hand, it takes of a different phase, and we say that is an oxide phase basically the slag phase.

It is also written like the, dissolutions, dissolved state is also written like, if you write the reaction, it essentially tells that it is a forward reaction, but if you wish to consider the reaction operating close equilibrium, in that case, we would say that, you know, we erase this, we write it like this which tells us that the reaction is operating under reversible condition. It is about to reach or operating close to equilibrium itself and these De-oxidation equilibrium, we are going to study in great detail.

But before this reaction as I have mentioned to you, can take place really we have to have, you know, M for example, here if its aluminum, then aluminum solid aluminum I have added. The solid aluminum has to melt, the solid aluminum has to dissolve, and then there can be reaction between dissolved aluminum and dissolved oxygen itself.

(Refer Slide Time: 20:40)



So, therefore, we must understand the interactions - thermal and physical interactions - between the solids, added solids as well as the oxygen itself. So, the solid initially at room temperature as it is projected into a liquid bath, typically what happens is that we have a solid shell which forms around the initial solid.

So, this is the crust. Therefore, if this is aluminum, we can expect that the crust material is essentially a bath material, so, this is going to be actually steel crust. Now, what sort of a thickness of crust is going to form that will basically depend on the bath temperature, depend on the size of the addition, depend on its specific heat, and there are lot of other physical properties on which the extent of the solid crust forms, but nevertheless, it is a, it is a well-known fact that when a cold solid is projecting into a hot bath, like aluminum projected into steel, we are going to have a steel crust around the solid.

Now, typically what happens is there are two possibilities. now that within the crust itself, we can have the aluminum already melted, this is one possibility, and this we say is aluminum and this is the solid crust, and the other possibility is that we can have that the solid aluminum is going to be released the crust melts that and the solid aluminum is, so, the crust melts back and the solid aluminum is released.

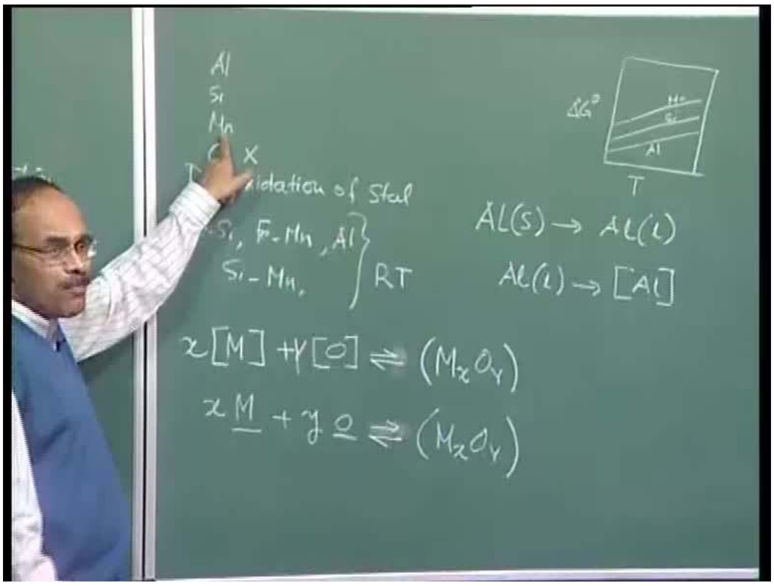
So, these two possibilities will again depend on the bath superheat, etcetera, but in any case, what happens is that from this, the aluminum, if it happens like this, then the aluminum will become again aluminum liquid which I say, and then, we can see that it is going to go to aluminum in the dissolve level. So, these are basically the way it look solid projected into steel is going to behave like.

Now, this particular step I would like to draw your attention to can only happen, provided the addition has a melting point which is lower than the bath temperature itself. For example, if I add a addition like ferroniobium, of course, I am not going to add ferroniobium to deoxidize the bath but just to mention in the, in this context that if I add ferroniobium which has a melting point greater than that of the bath temperature of steel, which is about 1600 degree centigrade. So, ferroniobium actually will never melt in steel, ferroniobium will dissolve in steel. For example, if you add sugar to a pot of tea or a cup of tea, the sugar does not melt in tea, the sugar dissolves in tea, and dissolution is a mass transport step melting is a heat transfer step.

So, those additions which has melting point greater than the bath temperature will not dissolve and they are typically said that these are class 2 additions, and the class 2 additions have T 2 T melting point 2 is greater than actually T bath, and this T bath is what we are talking about is 1600 degree centigrade.

On the other hand, deoxidizer elements, deoxidizer elements are called elements are basically class 1 type of additions, class 1 additions, and the feature of the class 1 additions is such that T melting of class 1 is less than T bath. So, therefore, we can understand that this class of additions or the deoxidizer additions are going to Melton steel ferrosilicon ferromanganese, etcetera, and we are going to you know aluminum. On the other hand, if you are talking about, for example, ferromolybdenum, then ferrovanadium, ferroniobium, etcetera, and these types of additions are going to really not melt but dissolve into steel because their melting points are greater than steel.

(Refer Slide Time: 25:02)



But, these features of formation of transfer you observe everywhere, and then, finally, the melting through melting dissolution, we are going to have the material in the dissolved state and it is under this dissolved state that an interaction with oxygen is going to take place, and as a result of which, the oxygen from the bath is going to be continuously take place.

As we see that more and more metal oxide is going to form or the oxide is going to form, the less and less oxygen is going to remain in the bath itself as the reaction is being driven forwardly. We also must realize that the solubility product principle tells us that if the activity of the oxide is going to be smaller and smaller, this reaction will have a tendency to be moved into the forward direction, and therefore, you know, if we have some kind of an oxide to stabilize the De-oxidation product, we can take this De-oxidation reaction in the forward direction in a much more efficient manner.

Now, what sort of an element? Why we add this kind of an element like aluminium ferrosilicon? One feature is that we must realize that silicon aluminum manganese, etcetera, have very high affinity towards oxygen.

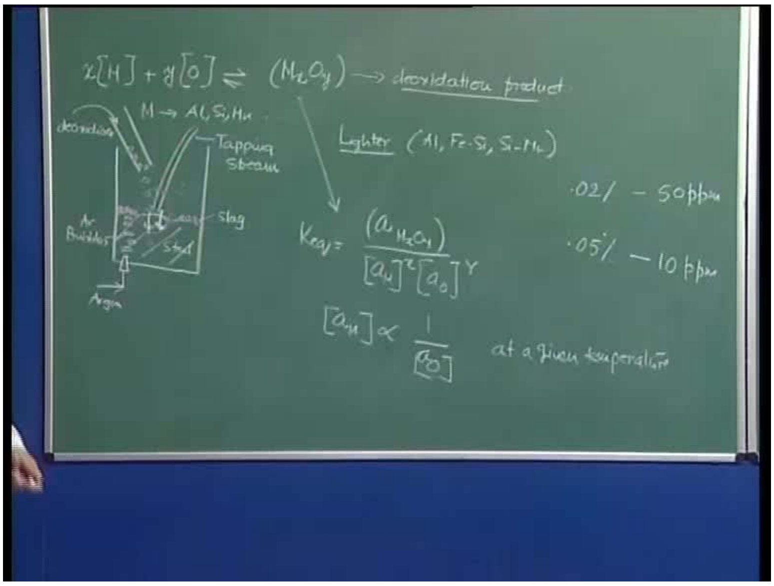
Now, in terms of, you know, their capability to remove oxygen, I would say in descending order it goes like - carbon also has some affinity towards oxygen. So, but, we do not want to add carbon to deoxidize the bath because we have already, you know, struggling hard to remove carbon during the oxygen steel making processes. So, this is, you know, not ruled out as a potential deoxidizer in the case of steel making.

Now, these elements have great affinity towards oxygen and perform, we know these things. You have done same the oxygen Ellingham diagram. In the Ellingham diagram which is the plot between delta G naught and temperature, and there we have seen that the aluminum, if line is here, and then, we see we have the silicon line here, and then, we see manganese line here and, you know, carbon line even above. Lower is the position of the line aluminum oxide Ellingham diagram, greater is the stability of the oxide or greater is the affinity of the element towards oxygen.

We can also say that if the affinity towards oxygen is higher, therefore, the residual level of aluminum for a given oxygen is going to be less in the bath. So, therefore, the contamination of the bath, as a result of De-oxidation, if I say that the final oxygen is fixed, then I can say that on the basis of this information I can conclude that the residual level of contamination with aluminum is going to be lesser in comparison to silicon, in comparison to manganese, and these we can immediately this conclusion, we can immediately draw from the oxide Ellingham diagram and that is why, you know, in the study of carbothermic reduction, in the study of De-oxidation Ellingham diagram, you know, occupies a preeminent position. We have to know this really well.

So, we would like to have a deoxidizer element, that element must have a great affinity towards oxygen, and then, we are going to add and then we find that the most commonly used deoxidizers which are also easily available. We must understand, we do not add pure manganese, we do not add pure silicon, they are added in the form of ferrosilicon ferromanganese, because technologically it is far more, you know, advantageous to make ferrosilicon than pure silicon as we all known or ferromanganese than pure manganese. Therefore, ferrosilicon, ferromanganese, silica-manganese aluminum are the potential deoxidizers because of their higher affinity towards oxygen.

(Refer Slide Time: 28:42)



Now, this shows the bulk addition of the deoxidizer elements like aluminum, etcetera, as we are talking about, and one property I think you should have been able to register by now is that these deoxidizer elements like ferrosilicon, silica-manganese aluminum, they are much lighter than steel; their density is much lighter than the bulk steel.

So, therefore, the deoxidizer elements when they are added and lighter includes aluminum ferrosilicon, ferromanganese has the same kind of silica-manganese. Ferromanganese nearly can depending on the grade of ferromanganese, how much percentage of manganese you have in that you can have, you know, almost neutrally waned; that means almost same density as that of steel manganese and iron f e, they are close in the periodic table. So, their properties are similar, they form ideal solutions, their densities are similar. So, ferromanganese also has you know depending on how much of manganese, you have, may have the same type of density as that of steel.

So, these deoxidizer elements are basically lighters, and when you are trying to pour them into the steel bath, it is understood that these deoxidizers will not penetrate much deeper into the bath. For example, go to a swimming pool, take a ball, you know, and you try to submerge the ball into water, under water, suppose you force the ball with extreme speed on the surface of water in the swimming pool, what did you see that the ball does not really penetrate much because the density of the ball is substantially larger, smaller than the density of the bulk water itself.

So, even though the deoxidizer element is falling from a height of 3 to 4 meters in a typical steel melt shop, these deoxidizer elements are going to hardly go subsurface. So, they are going to remain mostly near the free surface itself or free surface means the surface of the steel itself, and that is why if you visit a steel plant next time, take note of it that this lighter deoxidizer elements are going to be shown in the vicinity of the impinging spot for the impinging stream is actually entering, because it is in the vicinities of the impinging stream that we have an extremely large downward motion, and we want these additions to be captured by this downward motion and drawn inside the bath, because we do not want the deoxidizer elements to react with the environment.

Now, I do not want my aluminum to be reacting with the oxygen which is present in the atmosphere. I want my aluminum to react with oxygen which is present in the steel bath itself.

So, therefore, my objective would be that you take, you add the deoxidizer locations, deoxidizers in such a way that the deoxidizer has some potential to go below the surface of the steel where it can melt, it can dissolve, and then, it can react with oxygen which is present in the metal itself.

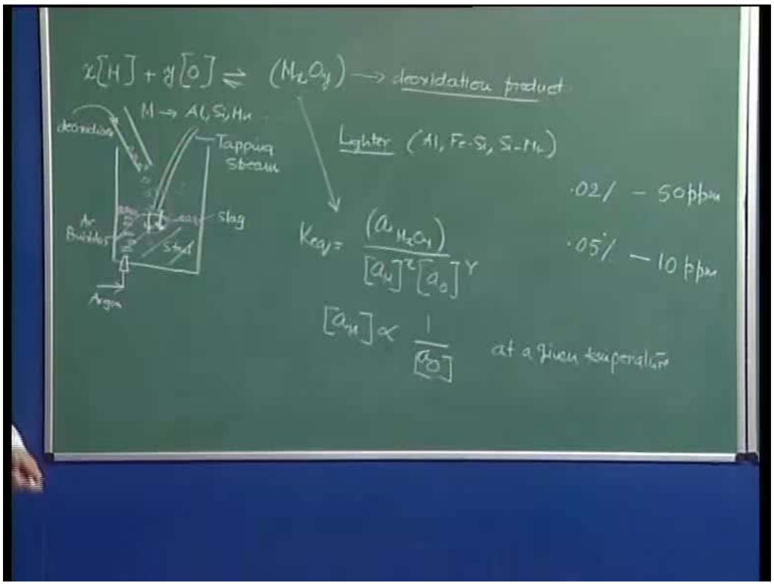
And the most important site as far as their entrainment or their motion in subsurface is concerned is the region, you know, which is close to the impinging jet region where you have a largest downward motion of liquid steel, and if this additions can be caught in this particular region, then they have a potential to spend substantially a longer time under the bath and their efficiency of utilization is going to be larger.

As the deoxidizer elements get inside the bath, they melt and dissolve react with oxygen, slags form, and I have shown with color chalk here that the formation of the slag. Simultaneously, the stirring goes on and, you know, because what we did the mass transfer reactions, we always want that the oxygen and metal must come in contact with each other and then only this product is going to form.

So, we want to create a kinetically favorable condition. We want to create some stirring all the time such that oxide is transported from one place to another place. From this part to this part, the oxides are always lighter. That is why the oxides and the slag is going to float up, and this the amount of slag is going to be progressively building during the process of ladle filling operation as well as deoxidizer element addition.

So, deoxidizers upon their entry into the bath will spend some time on the surface, and then, in the process of that, they are going to react, they are going to dissolve melt, and dissolve and react with the bulk steel oxygen in the bath steel. So, these we say is the deoxidation product, and if we assume that the deoxidation product is in pure state, so, that means there is no compound formation here.

(Refer Slide Time: 28:42)



If aluminum is projected, aluminum reacts with oxygen and pure homogeneous aluminum forms. There is no calcium aluminate or aluminum silicate, etcetera, no other phases are present. In that case, we can consider that this is going to be activities of the deoxidation product is going to be one, and if we write down under equilibrium, if we assume that the reaction is under equilibrium because we want to study the thermodynamics of the deoxidation process. First we can say at the k equilibrium is going to be equal to activity of the metal oxide M x O y in the slag, and then, activity of metal raise to the power x and activity of oxygen raise to the power y.

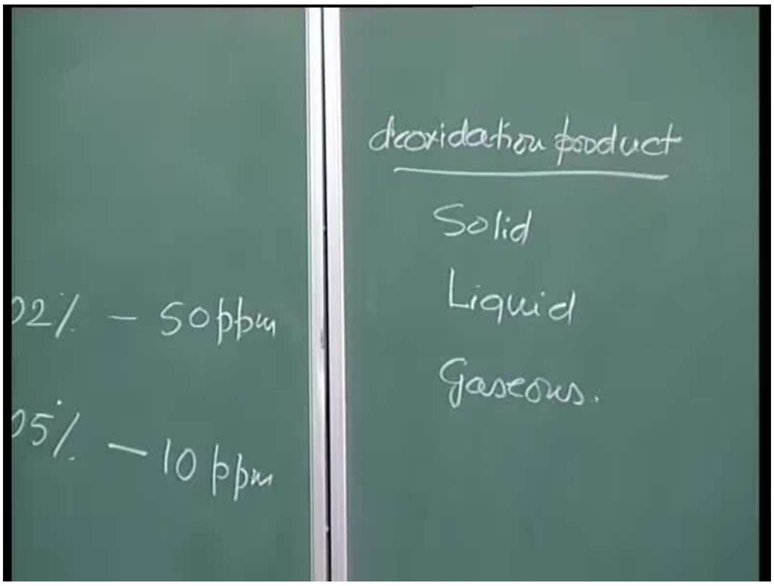
For the time being taking the case of a pure deoxidtion product, we can find out that activity of metal is going to be, in the bath is going to be inversely proportional. So, therefore, lower and lower oxygen, we wish to achieve greater and greater is going to be the activity of oxygen or the activity of metal or activity of concentration of metal in the bath itself.

So, for example, if we use aluminum and your final, suppose you decide that your final level of oxygen you want is 50 p p m, so then you got a residual amount of oxygen residual amount of aluminum, say of 0.02 percentages, I am just arbitrarily coating a figure for 50 p p m final oxygen.

Now, if I say that, if you want to go to 10 p p m, in that case, this value is going to be smaller or larger. These value is going to be substantially larger than this because of this particular relationship that the activity of oxygen, sorry, the activity of oxygen is inversely proportional to activity of metal in the bath. Lower and lower is the concentration of oxygen, you wish to achieve in the bath itself. So, maybe, you know, it will be consistent at least to show a realistic value. I would say that it will go up to this level, these are not exact values. We will have to calculate it out, I, but I just want to show the trend that, you know, if one goes down, the other goes up, and this is as the result of the consideration of the deoxidation equilibrium.

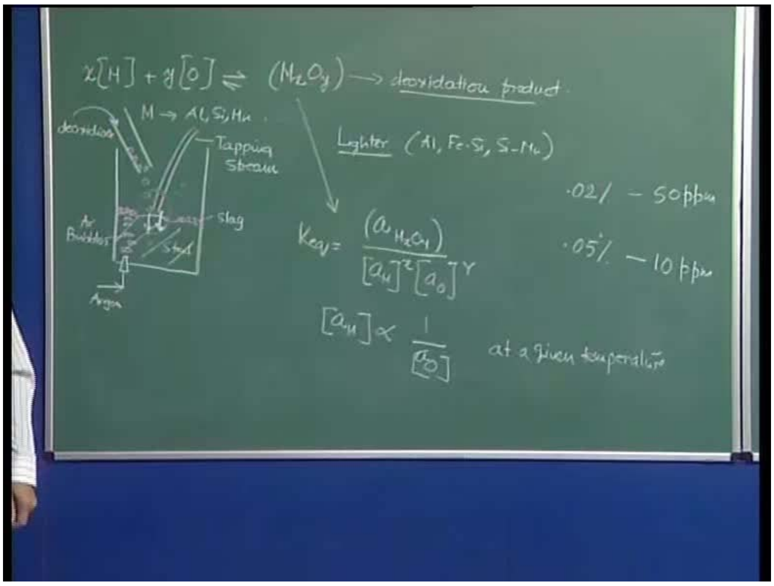
So, this is at a given temperature, when there is equilibrium. Now, these deoxidation product need not be solid all the time, a deoxidation product will be liquid also, and under extreme cases, if you are using carbon to deoxidize the bath, that is a hypothetical situation of course, in that case you have a deoxidation product which is the gaseous deoxidation product, carbon monoxide or carbon dioxide, depending on what condition an oxygen potential you have in the system.

(Refer Slide Time: 36:21)

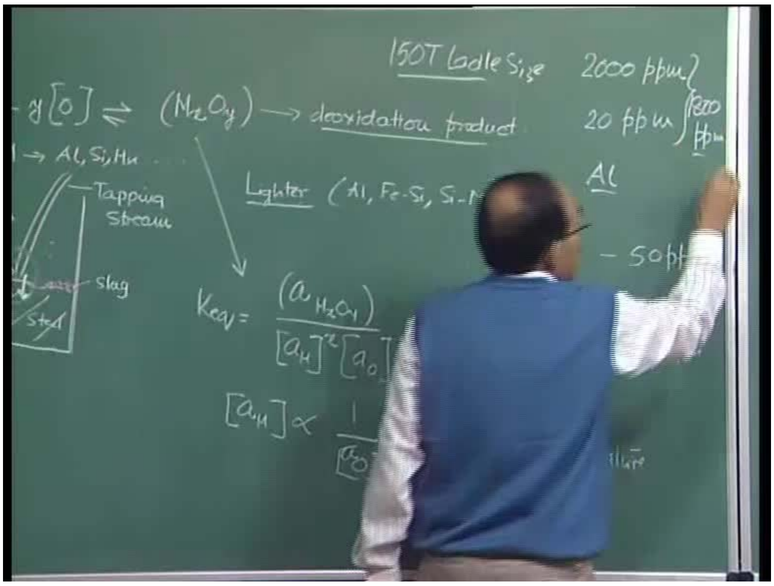


So, deoxidation products need not be solid all the time. We can write deoxidation product can be solid, liquid and gaseous, and we can have liquids liquid deoxidation products are basically, you know, compounds as we will see later on. Solid deoxidation products as I have mentioned aluminum, you can visualize in solid deoxidation product, and then, gaseous deoxidation product is in often you had carbon monoxide.

(Refer Slide Time: 37:03)



(Refer Slide Time: 37:14)

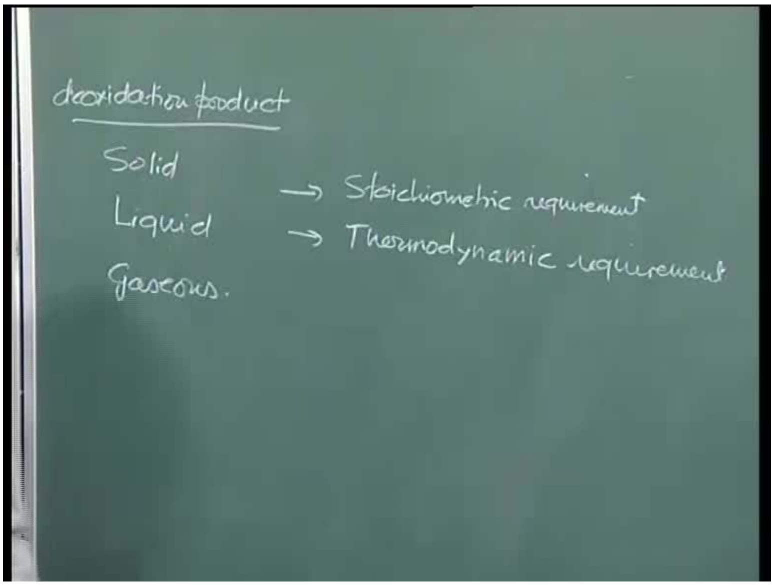


Now, the amount of deoxidizer required in steel melt shop is a very important, you know, information that one would like to say that, you know, I started, for example, with

2000 p p m of oxygen in the bath. Now, I want to get to 20 p p m of oxygen I want to add aluminum, and can you now tell me that how much of aluminum really I would be adding to the steel bath itself? I have a vessel size of, you know, 100 and 50 ton, for example, is the ladle size.

Initial oxygen from the basic oxygen furnace is 2000 p p m, final oxygen is 20 p p m, and then, I wish to, you know, add aluminum in that 150 ton ladle. Now, I want to know that how much of aluminum I should be adding in order to achieve a final level of oxygen or a net reduction of, you know, 1800 p p m of oxygen.

(Refer Slide Time: 38:03)



deoxidation product

Solid

Liquid

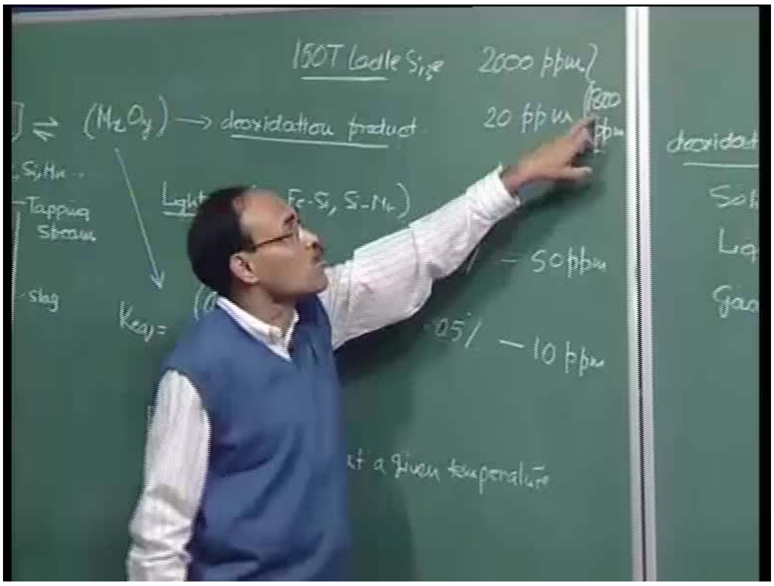
Gaseous.

→ Stoichiometric requirement

→ Thermodynamic requirement

So, how do you do this kind of a calculation? We must understand that there are 2 requirements which the deoxidizer has to fulfill, and one is called the stoichiometric requirement and the other is the thermodynamic requirement.

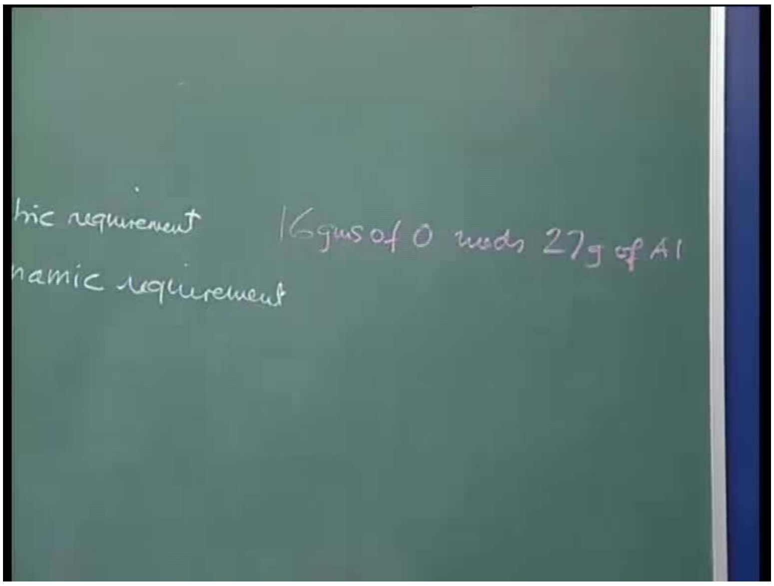
(Refer Slide Time: 38:35)



What do I mean by stoichiometric requirement that you have, if you did, you know, for every 16 grams of oxygen, you are going to need 27 grams of aluminum straight forward calculation. This is of this is the stoichiometric requirement. So, I know that 2000, 1800 p p m of oxygen is to be eliminated and this 1800 p p m oxygen with respect to the 150 ton ladle size can be translated to so many k g of oxygen.

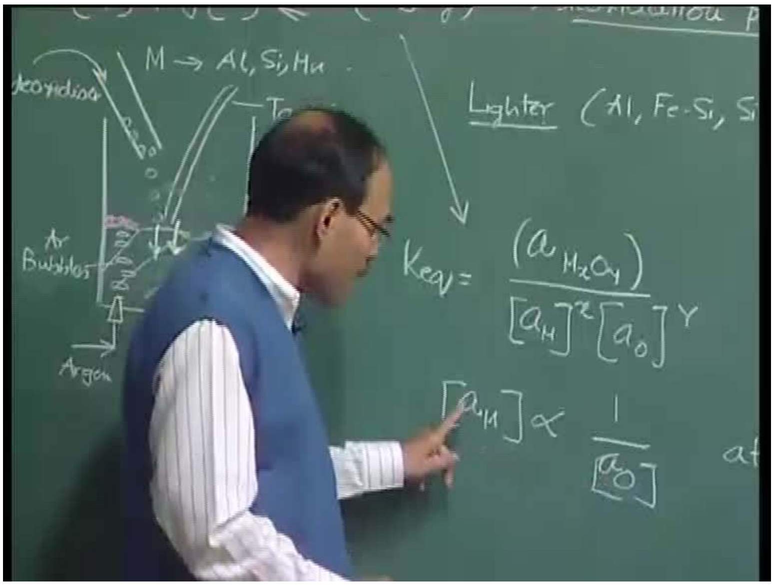
Then, by using this relationship that 16 k g of oxygen will require 27 k g of oxygen, I will be able to immediately calculate that how much of oxygen is going to be required in order to reduce the total amount of oxygen which is present, you know, oxygen is present in the bath corresponding to 1800 p p m.

(Refer Slide Time: 39:28)



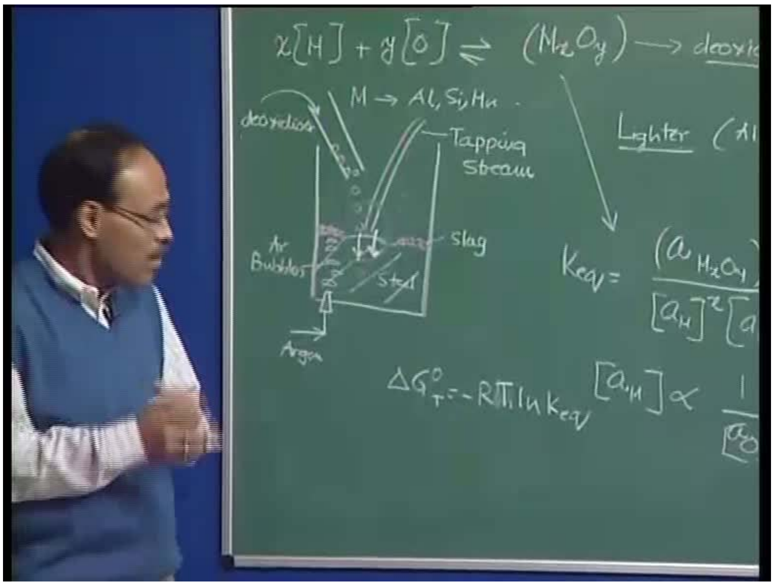
And this I say as a stoichiometric requirement 16 grams, I will write it for you 16 grams of oxygen needs 27 grams of aluminum, and on the basis of this, you will be able to carry out.

(Refer Slide Time: 39:46)



So, beyond this stoichiometric requirement, we have another requirement to fulfill and that is the thermodynamic requirement because I mentioned to you that for a given level of final oxygen, there is going to be some equilibrium aluminum content or deoxidation content in the bath itself. So, we have to find out that well one part of aluminum which has reacted with oxygen and has gone into the slag phase. The other part of the oxygen is which is lying in equilibrium and which is which remains in the dissolved state, which has to be calculated on the basis of this particular expression.

(Refer Slide Time: 40:13)

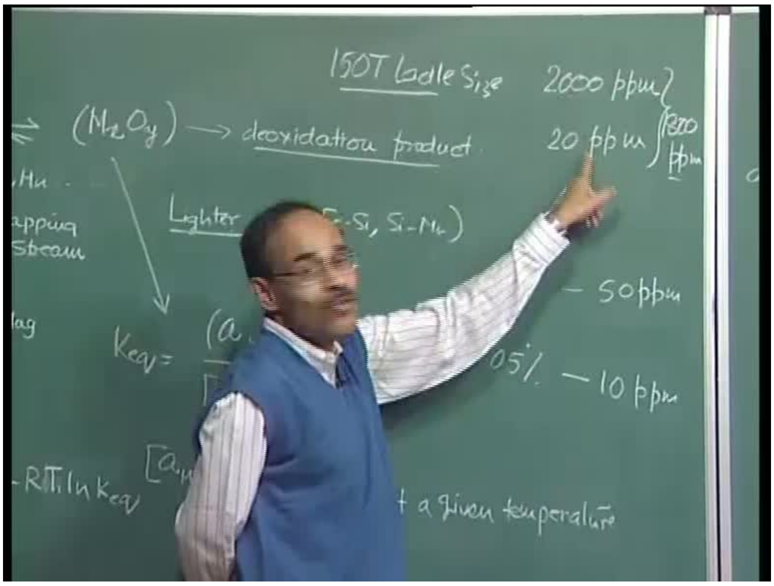


Now, as I said, if I assume for the sake of simplicity that the metal oxide is in pure form or alumina is in pure form; there is no other oxide present. I can set that activity of this is approximately is equal to 1. I can obtain the value of the k equilibrium because I know that delta G naught is equal to minus R T l n k equilibrium, and therefore, using the value of the gas constant, the right temperature and because I know the value of delta G naught at various temperatures, and how do I know because this is tabulated in thermodynamic data books.

Many people have done experiments and have determined this data. So, therefore, determination of data is very important step for us particularly when it you evolve new systems. So, knowing the value of delta g naught, I should be able to calculate that what is the value of k equilibrium. So, if I know the final level of oxygen in the bath, and that final level of oxygen is 20 p p m.

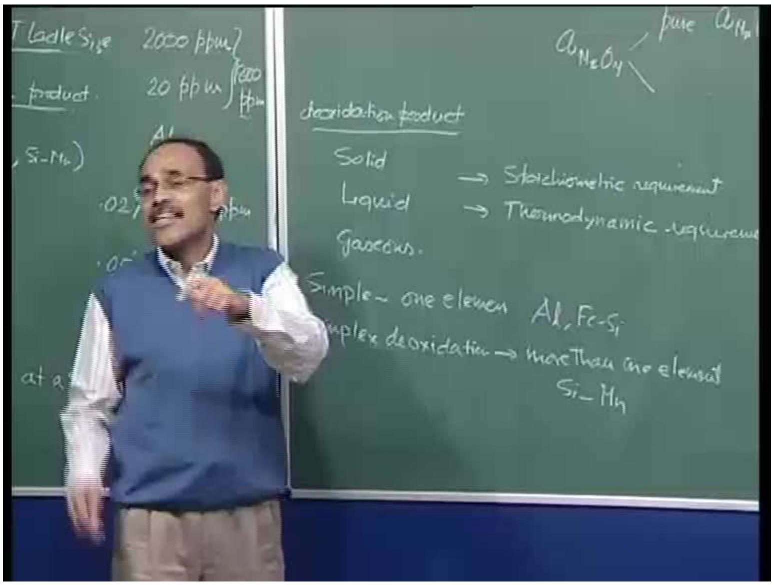
Of course, this has to be written in appropriate scale here. I can use a hernia activity weight percentage scale or whatever comes out to be convenient. Typically the weight percentage scale suffices here. So, if k equilibrium is known, this is equal to 1 for the given value of activity of concentration of oxygen. I will be able to find out that how much aluminum is there in equilibrium and I can translate that much aluminum with reference to 150 ton bath and say that, well 4 k g of aluminum is there, you know, in the dissolved state.

(Refer Slide Time: 42:43)



So, if I say that 10 k g is required as far as this stoichiometric, you know, stoichiometric of the reaction, stoichiometry of the reaction. In that case I can say that add this with the thermodynamic requirement and that is going to be your total requirement. So, you have to add that much of aluminum into the bath in order to reduce the initial 2000 p p m oxygen to the 20 p p m. So, this is a very important calculation which the melt shop people as well as you all should be able to carry out, you know, without much hiccups.

(Refer Slide Time: 42:18)



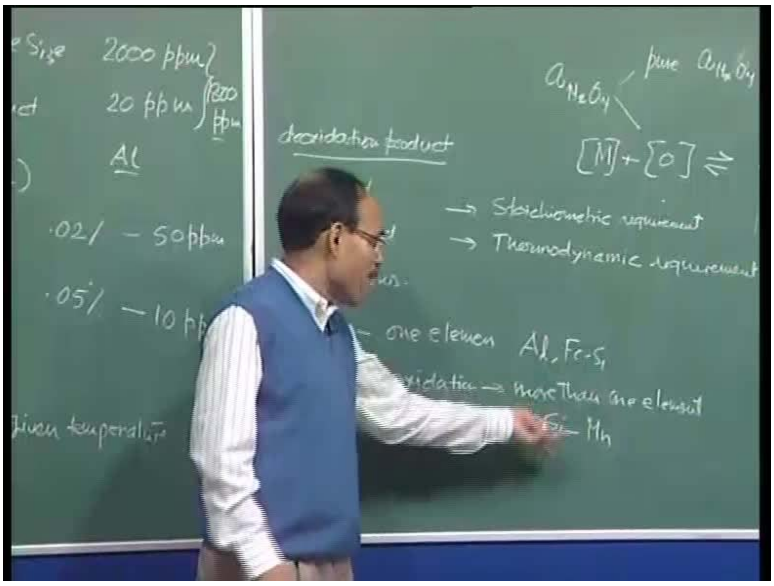
De-oxidations basically are two types - one is called the simple de-oxidation and the other is called complex de-oxidation. Now, what are the, what does this imply? The simple de-oxidation means that you have only one element and complex de-oxidation means we have more than one element.

So, therefore, if I say that I have added aluminum or ferrosilicon, I will say that well aluminum is deoxidizing the bath or silicon is deoxidizing the bath. I am not adding them together, I am adding just one of this for example, so, if I add one element to deoxidize the bath, I am going to say it is a simple de-oxidation. If I add more than one element, for example, what is this? Silica-manganese, so, some oxygen is going to be eaten up by silicon, some oxygen is going to be eaten up by manganese. So, I am adding silicon and manganese simultaneously into the bath in the form of silica-manganese. I am going to say that this is a complex de-oxidation.

Typically, the efficiency of complex de-oxidation is far more than simple de-oxidation, and why it is so? You should be able to understand. For example, if I, if you look at the product of de-oxidation as I mentioned to you, it is and I mentioned to you that smaller is the activity of this product of de-oxidation, better will be the possibility of the deoxidizer reaction to go from the left to right.

So, metal will combine more efficiency with the oxygen itself. Now, in the pure form, if the oxide is pure, then activity of M x O y is going to be is equal to 1. On the another hand, suppose the de-oxidation product is silica, and then, I am adding some lime into it, so, the lime and silica are going to combine with each other. So, in a pure silica melt, silica reach melt, the activity of silica is going to be equal to 1. On the other hand, if I have calcium silicate, there the activity of silica is going to be substantially smaller because the silica is in a bound state.

(Refer Slide Time: 44:37)

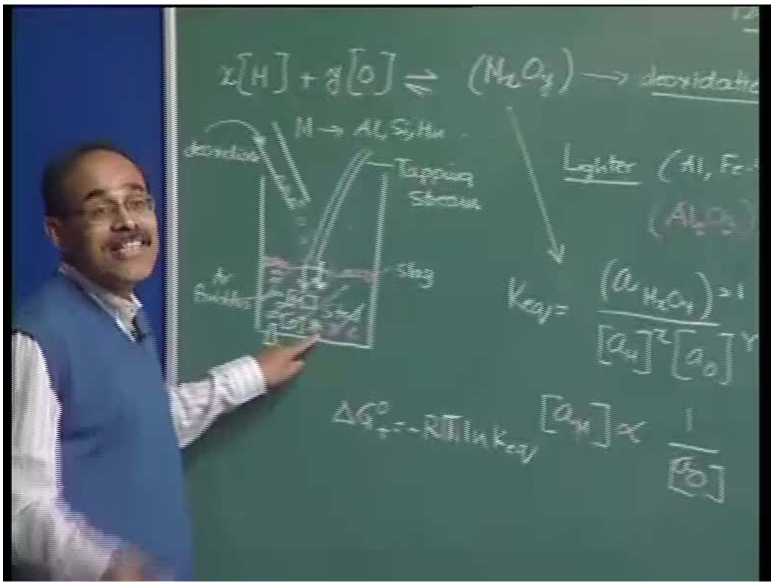


So, therefore, the activity of silica is going to be substantially less in the presence of a calcium silicate slag, and in that case, if you look at the de-oxidation reaction, we can say that well lesser is the activity. Now, I am writing it in simple form, M O, I can say that the lesser is the activity of M O, more is going to be the efficiency of de-oxidation reaction or lesser is this reaction will be moving. The lesser activity means as if we are continuously removing the product from the side, and as a result of which, the reaction will have more spontaneously proceeding towards the forward direction itself.

So, therefore, we understand that simple de-oxidations are less efficient than complex de-oxidation, and as a result, as a matter of fact in steel plants if you go, you will see that, you know, you there the de-oxidation is taking place, not only by aluminum but we are adding some silicon also, some ferromanganese also, some aluminum also, and aluminum by far is the most powerful deoxidizer.

So, a substantial amount of de-oxidation will be carried out by the aluminum itself but not necessarily all de-oxidation will be carried out by entire de-oxidation will be carried out or facilitated by aluminum. We will be adding some silicon ferrosilicon or ferromanganese also along with aluminum.

(Refer Slide Time: 45:53)



Now, coming back to the de-oxidation product again, as I have mentioned that the de-oxidation products are forming where? The de-oxidation products are forming be it liquid, solid or gas, it is going to be forming in the bulk of the liquid because it is here that the metal is going to come in contact with oxygen, and it is here the de-oxidation product is going to be formed.

So, we do not want this de-oxidation products to be you know interrupted in the molten steel itself. There is a necessity that these de-oxidation products actually go out of the melt and float in the slag, you know, which can be, you know, eliminated suitably during the following process itself.

So, we want steel which is free from contamination by the de-oxidation products. That is an essential requirement at no stage, and particularly in the final stage, we must not have even a little bit of the de-oxidation product which is there in the steel, because it is well known that de-oxidation products are going to hamper the mechanical properties of steel.

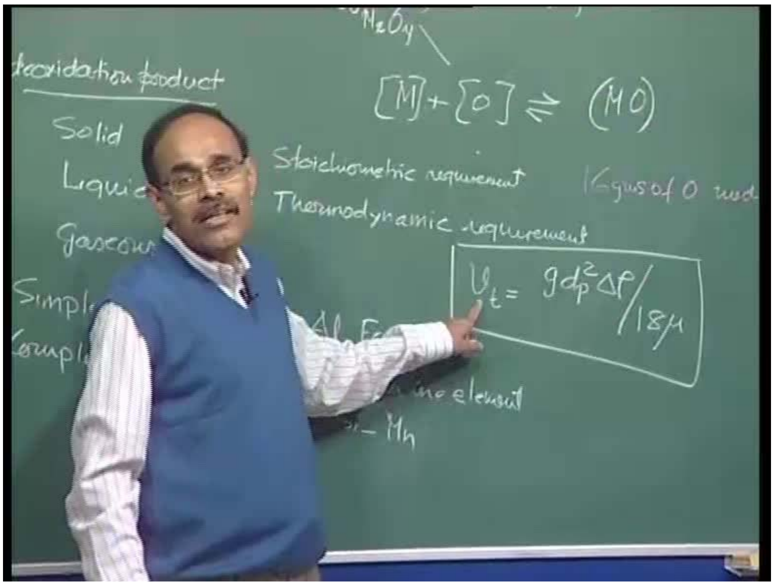
So, if you have solid de-oxidation products, for example, the solid de-oxidation products, they do not the one solid de-oxidation product can form here, the other can form here, but the solids do not collide, and this de-oxidation products are basically lighter particles.

So, they naturally have a tendency to float up through the melt, but one important thing is that these de-oxidation products if they are solids, in that case they do not tend to form their masses.

On the other hand, if we have liquid de-oxidation products, in that case the liquid de-oxidation products, if they come together, then immediately they form a bigger particle, and as you all know that a smaller particle will have a smaller rise velocity and a bigger particle will have a lot of rise velocity.

So, the bigger we would like to have bigger particles, and therefore, if you trace back, you would say that a liquid de-oxidation product is perhaps more desirable to us than a solid de-oxidation product. Interestingly aluminum has the largest affinity towards oxygen, most powerful deoxidizer, you know, the least level of contamination but this aluminum is going to give us a de-oxidation product. That is essentially solid in nature. So, there, you know, the contamination of steel with Al 2 O 3 is a major issue. Lot of alumina particles can be interrupt and this tends to make what is known as a dirty steel.

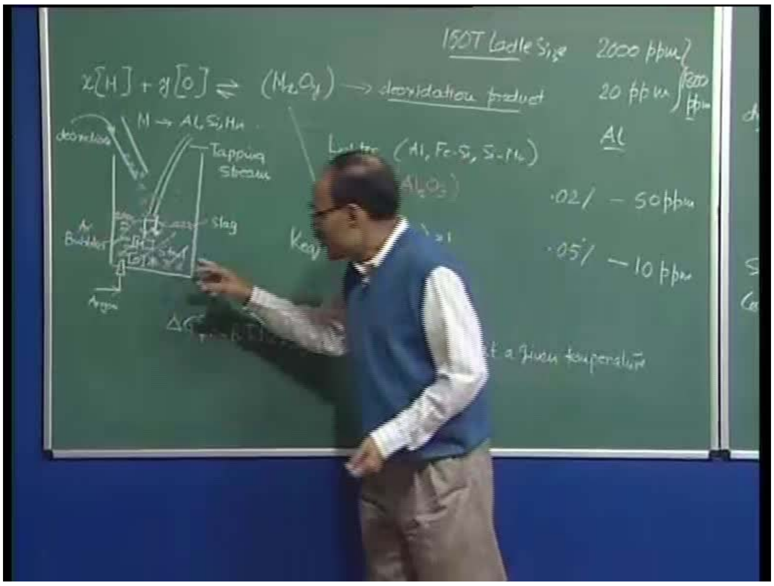
(Refer Slide Time: 48:20)



So, in this particular case, we can have, you know, the point that I have made that aluminium, alumina particles or the solid particles smaller particles will rise slowly and bigger particles are going to rise faster. We can use the stokes settling velocity or settle rising velocity, and we can say that the terminal rise velocity is actually g diameter particle square into delta rho divided by 18 into mu.

So, I am not saying that this equation does hold good all the time, for all size ranges, but it gives us some idea and tells us that the rise velocity is going to be directly proportional to the square of the diameter. If you increase the diameter by factor of 2, the rise velocity is going to be increased by a factor of 4.

(Refer Slide Time: 49:08)



So, therefore, you know, once the ladle is filled up here and you are taking it to subsequent stations, you get some time, and in that particular time, what happens? The de-oxidation products which have formed deep inside the system. They have a chance to float up. So, you have to give sufficient time also for these conclusions to float up to the free surface or the surface where we have slags already forming and, you know, these slags can capture the de-oxidation products.

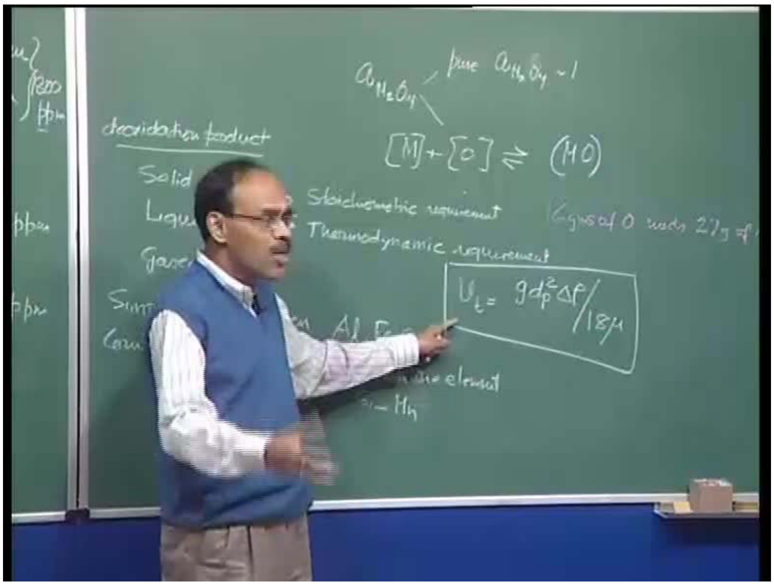
We must also, I must also tell you one important aspect that because there is going to be some stirring, so, the de-oxidation products can rise to the slag metal interface, but at the same time, because of the stirring present, these de-oxidation product can be re-entrained back into the steel also, and typically, the de-oxidation products rise to the slag metal interface, and the harm will harm, the slag captures the inclusion. The slag removes this nonmetallic inclusions or harmful inclusions, but the inclusions really stay for some amount of time in the vicinity of the slag before they are going to be completely captured by the slag itself.

And this is basically referred to in steel making reactor as the duel time of the inclusions or the duel time of the de-oxidations products, they have to duel in the vicinity of the slag for some amount of time before being continuously, before being completely captured by the slag there itself.

It is important for us that the metal be free of molten steel is free of such de-oxidation products. We must and the secondary steel making or ladle metallurgy steelmaking as you will see, you know, as the process go on and you generate more and more de-oxidation products as a function of time, you know, our one of the major thrust would be that if there are inclusions particles present in the melt, how to drive them out, how to produce scale steel, which is the very important issue, pertinent issue.

We do not want dissolving to reduce; we do not want much sulphur; we do not want oxygen; we do not want nitrogen; we do not want hydrogen. At the same time, we do not want these unwanted nonmetallic inclusions as well in the steel bath itself.

(Refer Slide Time: 51:10)



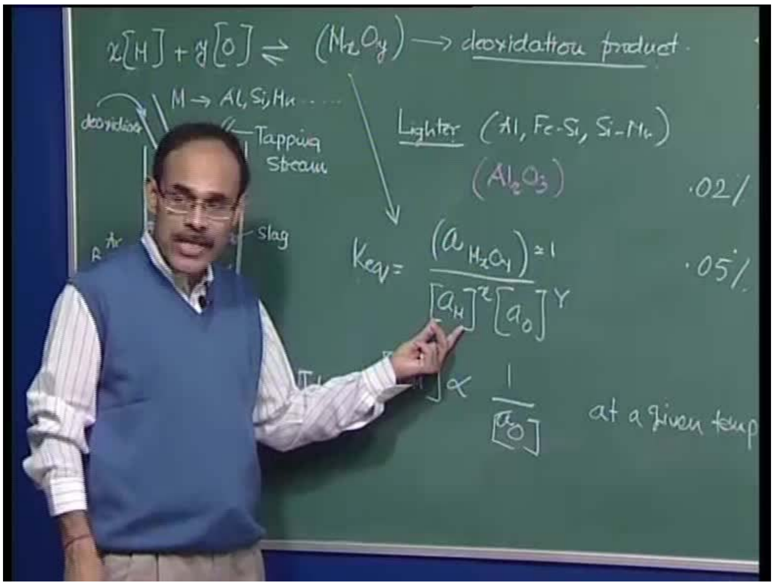
So, therefore, as I coming back to the stokes law of settling, I would say, you know, given the size range, and if I know the bath height, I should be able to find out, you know, what is the possibility of inclusion floatation, you know, we can calculate and show that if the inclusions are of the order of 40 50 microns size, they virtually have no possibility to rise up and, you know, float to the free surface.

On the other hand, if the inclusion size is, you know, 200 or 500 microns for example, in that case, their rise velocity is going to be so large that in 1 to 2 minutes of time, they should be able to cover the entire depth of liquid and come up with the slag metal interface; so, they can get absorbed.

Of course, stokes law is a very simple law we all know that it is valid for laminar flow. Even Reynolds numbers of the order of one very coquette kind of a flow, well, which is typically very weak coquette flow, and in this particular system, we know that it is a, you know, this is fluid motion also. It is not the particle rising through the stagnant bath also, you know, the surface tension in high temperature systems are different the particles may completely wet may not wet.

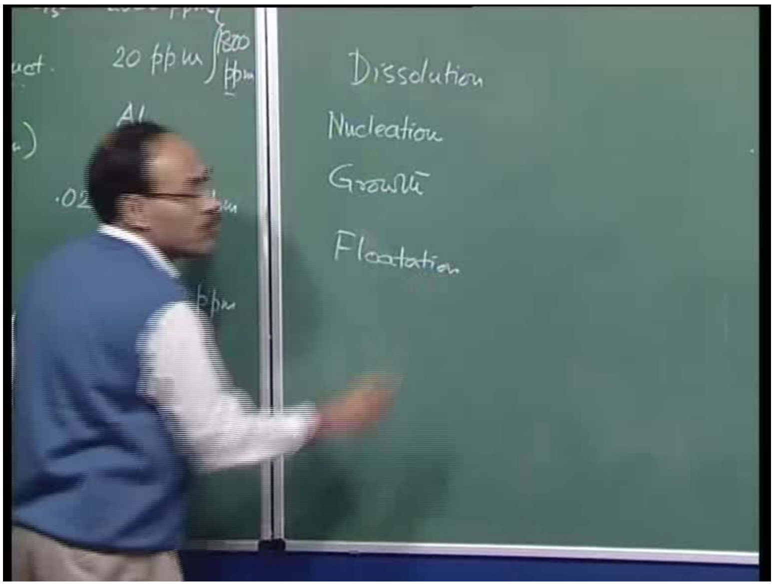
So, this is an approximate order of magnitude calculation these that need not be taken too seriously. We just get some idea that what size of inclusion can float on, what size of inclusion cannot float, and nothing beyond that. No serious process, design calculations or inferences should be drawn on the basis of the stokes law as far as the inclusion floatation is concerned.

(Refer Slide Time: 52:40)



So, before you proceed further, I also want to say that or draw your attention to one fact that if you have noted so far that, this is a, you know, the solid has added solid dissolve has dissolved into steel or oxygen is already dissolved in molten metal. They collide with each other; they come together react with each other because of their affinity, and now, this is a product which is all together new phase, for example, you have steel and then you can visually distinguish, you know, that alumina particles have formed.

(Refer Slide Time: 53:14)



So, a new phase is formed, and therefore, if you apply our knowledge that we must understand that the formation of a new phase is always accompanied by what is known as nucleation and growth. So, in de-oxidation, various complex phenomena are involved and I can tabulate them, you know, as a diverse kind of a, so, dissolution, and then, following by that the new phase is nucleated, the new phase is grown, and then, subsequently the new phase is floated and this totally constitutes the kinetics, various kinetic aspects of the de-oxidation process itself.

Now, I do not want to talk anything beyond this as far as de-oxidation is concerned. I think in the next lecture, I am going to show you a de-oxidation calculation, but to sum up today's lecture and give you a sum an overview of the de-oxidation process, well must say that we have primary steel making, the bath is rich in oxygen, we got to remove oxygen from the bath, and because we know that oxygen is going to… If it remains, you know, there is so much of oxygen during the solidification oxygen is going to be evolved because solid has less solubility than liquid. So, the oxygen present in steel is going to impact the mechanical properties. So, before we process steel further we would like to take out oxygen first.

There are other impurities also in present in metal but we are going to talk, you know, little bit later about them, and one you, we want to take that oxygen remove that oxygen from the bath, we realize that we have to now add an element which has a greater affinity towards oxygen and that we wish to remove oxygen from the bath. We make it sure that the oxidizing slag from the BOF and the carry over slag does not come to the ladle at all.

Most commonly used deoxidizers are aluminum silicon ferrosilicon ferromanganese silica-manganese, etcetera. If you use one single element to deoxidize the bath, it is the simple de-oxidation. If you use two elements or more than 2 elements simultaneously, it is the complex de-oxidation, and I have shown you that the efficiency of the complex de-oxidation is going to be greater than that of the simple de-oxidation.

Aluminum by far is the most commonly used deoxidizer element in steel. Deoxidizer elements are basically lighter than that of steel. Therefore, when you make bite addition into the ladle, you will try to target them near the falling stream where the velocities are extremely downward or highly downward, and this downward flow of steel can really take the deoxidizer elements along with it a subsurface where subsurface melting in dissolution can take place.

Now, once the deoxidizer element gets into the bath, it melts and dissolves. Once it dissolves, it reacts with oxygen; so, it is a mass transfer process, because oxygen has to go and find out a metal dissolve the deoxidizer element. Dissolved deoxidizer element has to find an oxygen atom and that is how they can collide and form a new phase.

So, therefore, this is a mass transport step, and therefore, we need some kind of a stirring. That stirring is initially provided by the convection generated by the falling stream or alternatively when the intensity dies, we have gas injection which is always being used and thus that gas injection gives rise to stirring and which basically aid in the de-oxidation process itself.

We have solid de-oxidation product, liquid de-oxidation product, gaseous de-oxidation product. Solid is not wanted, you know, as for as possible but we see that aluminum which is such a powerful deoxidizer, which gives low residuals, you know, can bring down oxygen to a very low level with little bit of contamination only unfortunately forms a solid de-oxidation product, and we want that final steel has to be devoid of this de-oxidation products which we call later on as we will know is inclusions, you know, and contamination of steel with de-oxidation product is basically, you know, referred to as dirty steel on subject associated subject is the cleanliness control and so on.

So, kinetically, we can assess the process of floatation of inclusion by adopting stokes law, and as I said that once you dissolves, then the nucleation because new de-oxidation phases occurred and that nuclei has to grow, and once it grows it, then floats, and floatation of the inclusion is a very important aspect, and as I have also finally, you know, towards the end I have mentioned that the inclusions will float, you know, collide first. They can collide with each other. If they are liquid gases, no problem, gas is very light, so, immediately they will move out.

So, once, you know, they come to the slag metal interface, we can say that they can duel for some time to be ultimately captured by the slag itself. So, I conclude here today’s lecture and I in the next, tomorrow I think I am going to show you, or in the next lecture, I am going to show you how to perform a de-oxidation calculation, you know, with exact data.