Steel Quality Role of Secondary Refining and Continuous Casting
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Module - 03
Lecture - 12
Injection of Calcium

Today will I talk about an important issue, which is I have discussed this earlier I had discussed that, injection metallurgy is very important for getting enhance quality. Now I try to explain, why it is so? How it helps?

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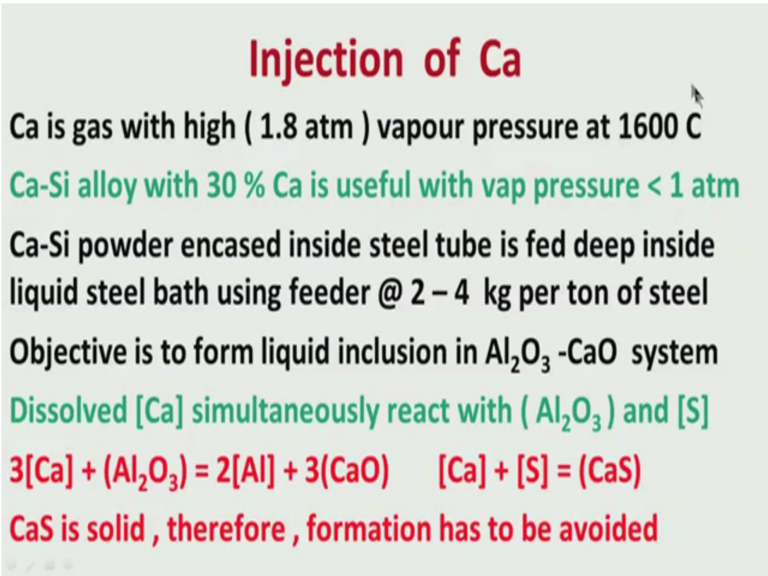

I am mentioning here the injection of calcium; that means if proper amount of calcium can be injected in liquid steel then it can help in different ways, I will try to explain.

Now first we should remember that calcium is gas at about 16000 centigrade of temperature in liquid; that means, whatever calcium we inject in liquid steel it becomes gas because the vapor pressure is relatively very high 1.8 atmosphere; that means, at one atmosphere hardly any calcium will remain in the liquid steel because the vapor pressure is high, So calcium will come out in the form of vapor.

So, hardly any calcium will be retained in liquid steel. So, what is the way out? Way out is instead of calcium we send calcium silicon alloy within the liquid steel. This calcium silicon alloy which is known as Ca-Si which has about 30 percent calcium. So, instead of 100 percent calcium if we send 30 percent calcium in the form of Ca-Si, so the vapor pressure will come down, because you know why the activity of calcium is coming down? Here it is pure calcium here it is 30 percent calcium only. So, in this process the vapor pressure of Ca-Si is much less compared to vapor pressure of calcium, which becomes a less than much less than one atmosphere.

So, it is possible to retain calcium though, some amount of calcium will be lost, because even if the vapor pressure is less than one atmosphere still some amount of vapor of calcium will come out, but if you use Ca-Si you know, the loss of calcium will be much less rather than if you calcium which cannot be used at all. Because, all the calcium will be lost because the vapor pressure of pure calcium is much higher 1.8 atmosphere compared to normal atmospheric pressure.

So, we use Ca-Si calcium silicon alloy with our 30 percent calcium and not pure calcium for injection. So, this is a first important issue which we have to remember. Now how is Ca-Si injected in steel, liquid steel? This Ca-Si powder is encased inside steel tube and then this tube is fed deep inside the liquid bath using feeder, we call it ware feeder. This you know Ca-Si powder encased in steel tube this is owned in the feeder as a spoon. So, this then where which is basically a steel tube inside which is calcium silicon powder has been put inside.

So, it is a Ca-Si powder encased in steel tube. It is in the form of it we call it a ware, which ware is fed through ware feeder deep inside the liquid steel you know. How much of Ca-Si is used? It is about 2 to 4 kg per ton of steel this is very important. In what rate this ware should be fed? This is very important. How deep should the ware go? Is also very important, because Ca-Si is the powder relatively you know, lighter it will try to come up moreover I have told you the Ca-Si has a calcium has a you know probability of you know getting coming out of liquid steel because of this low vapor pressure. So, at what speed things you know the spoon should rotate at what speed the ware should get inside the liquid bath these are all important issues, but the amount of Ca-Si which is required per ton of steel has been found to be about 2 to 4 kg.

You will find that that this is more than the theoretical level. Why it is So? Because, some amount of calcium will always be lost. So, the yield of calcium from this Ca-Si edition is not very high. So, therefore, we have to take in to account this therefore, it has been found out through trial and error, that about 2 to 4 kg per ton of steel is required for effective calcium injection. Now what is the purpose of adding Ca-Si in steel or calcium in steel? The basic idea is to form liquid inclusion in the form of alumina CaO we know that alumina has a very high melting point.

So, in normal liquid steel temperature of say 16000 1650, it is solid I have told you earlier also. This solid creates problem, this will create problem not only during steelmaking it might create problem when it is steel is solidified then if you have solid alumina inclusions it might create problem during informability when we are rolling the steel forging the steel. So, our aim is to convert this solid alumina inclusions to alumina, you know CaO alumina then calcium aluminate liquid inclusion. Will come to it how we can make it a liquid inclusion; that means, some amount of calcium is necessary. So, this calcium it will show the dissolved calcium, how it will react with alumina inclusion to give rise to generate you know CaO. So, this CaO will react with aluminum inclusions.

So, the inclusion will get converted to some combination of CaO and Al 2 O 3. So, that is again important what will form is CaO Al 2 O 3, what is their ratio that is going to dictate? You know, what it will be liquid or solid that the temperature of the liquid steel? Now please try to see remember that calcium is reacting with alumina, calcium will also react with sulphur because, it is a good deoxidizer also at a good desulphurizer; that means, these 2 reactions reaction of calcium with alumina in inclusions solid alumina inclusions as well as calcium reacting with sulphur in liquid steel both are occurring simultaneously.

Now it depends how much of sulphur is present, how much of aluminum is present, which will dictate how much of reaction will take place with alumina because, it that is in equilibrium with aluminum in solution is equal in equilibrium with alumina as deoxidant. So, the amount of sulphur aluminum and calcium in liquid steel, oxygen liquid steel all these will determine what will form whether it will be solid inclusion, whether to liquid inclusion, whether calcium sulfide which form to what extent, whether calcium aluminate which form what is the ratio of CaO Al 2 O 3 in that compound, whether it will be liquid all these things will be decided based on how much of calcium we are adding, how much of sulphur and aluminum is present in steel, these are very very important considerations.

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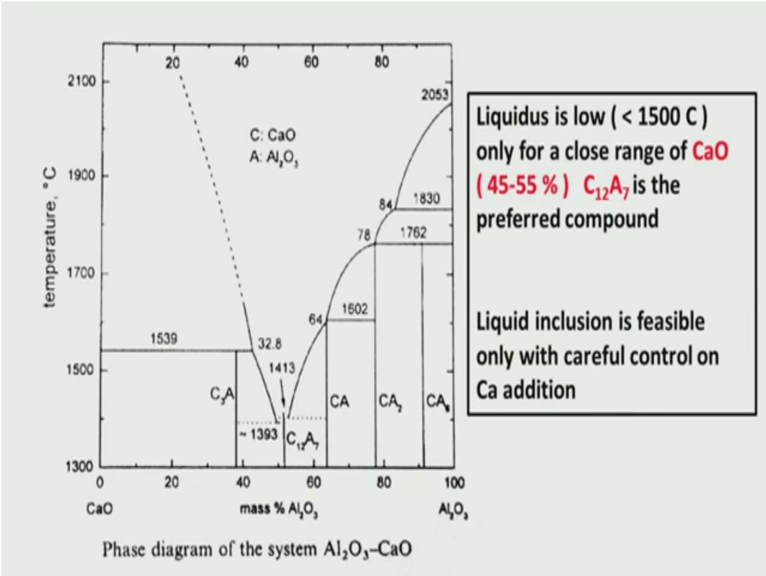

So, let us now look at the Al 2 O 3 CaO phase diagram. Alumina Al 2 O 3 you know, melting point is very high. So, our liquid steel temperature is around maybe say here, somewhere around here 15, 50, 16000 slightly it may be slightly more than 16000 not more than that; so in this temperature range if the inclusion has to be liquid. So, what should we it is constituent? This CaO is represented as capital C. Al 2 O 3 is represented aluminum for brevity. So, when we are talking of you know what are the constituents, you look at here look at here this is Ca; that means, one mole of one molecule of calcium oxide is combined with one molecule of Al 2 O 3, so calcium aluminate CaO Al 2 O 3 which has a melting point of somewhere here, so more than 16000 16, 50 or so.

So, only this particular you know compound which is having low melting point which is around maybe 1350 or 400. So, it is very clear that liquidus if you want to bring down the liquidus we need a very close range of Cao; that means, about 45 to 55 percent. Then only we can get C 12 A 7 type of compound. So, basically it is 12 CaO 7 Al 2 O 3. So, this has very low melting point and this inclusion, if you have this chemistry this inclusion is liquid. So, our aim is to get liquid inclusion it should be liquid at steelmaking temperature.

So, the idea is to add CaO, but if you do not add the required amount of CaO it should not be very low if it is very low; that means, that alumina melting point is high if you go on adding some amount of small CaO the liquidus is coming down, but it is still higher.

Only at this particular CaO minus amount that this one is 45 to 55 percent, when c 12 a 7 type of inclusion is formed then only we have liquid inclusion.

So, it is very important that how much of calcium addition is necessary this is very important. Just like that we go around go on adding calcium oxide if it is very less it is solid if it is very high then also it is a problem you know, first here I am showing that it is that my melting point is going to be high. Another problem is if you have sulphur in liquid steel which is going to have going to be there it cannot be sulphur cannot be 0. If slump small number slightly larger amount of sulphur is present there is a formation of calcium sulfide I will come to it in the next subsequent slides. So, liquid inclusion is feasible only with careful control of calcium addition.

I have shown in this slide that calcium is reacting with alumina inclusion and generating CaO and this is reacting with alumina So, CaO alumina is forming. The amount of calcium we add how much of CaO will form in the inclusion it depends on that. It depends on how much of aluminum is present in liquid steel which will dictate how much of alumina inclusion will be present.

So, depending on how much calcium we are adding the ratio of aluminum to calcium will dictate what will be the formula CaO Al 2 O 3, this has to be as I have told you CaO 12 Al 2 O 3 7 then only we get liquid inclusions. Then only the melting point of this inclusion is quite low and then it becomes liquid. So, we also do not want calcium sulphide because calcium sulphide is solid therefore, if you have large amount of you know soluble sulphur in steel and we go on adding calcium. So, after formation of this is also going to happen. So, it is equilibrium, let us try to understand what is happening.

If you add calcium these reactions are happening to simultaneously. Now which one will form to what extent depends on how much calcium we are adding, how much aluminum and sulphur is there in steel, this will dictate whether there will be calcium sulphide in steel whether they will be calcium aluminate, and what is the formula of calcium aluminate the formula will dictate what is the melting point. So, all these are important issues. We want calcium oxide in the range of 45 to 55, which will react with alumina to give rise to 12 CaO and 7 Al 2 O 3, which has very low melting point and makes the inclusion liquid.

So, the amount of calcium addition I am again repeating is very very important. It is related to it is not independent of the chemistry of steel it is related to the amount of aluminum and sulphur in steel. Moreover I have told you earlier that calcium solubility in steel is not very high, because, it is very difficult to control calcium in liquid steel. That is why we are adding Ca-Si and we are not adding calcium, calcium addition just if you add calcium is almost impossible, because of vapor pressure of you know, calcium is very high.

So, all these calcium will be lost as vapor from liquid steel at maybe 16000 degree centigrade. So, we are adding Ca-Si which has only 30 percent calcium. Even with the addition of Ca-Si some amount of calcium is lost as vapor from liquid steel. So, the solubility of calcium at 16000 degree centigrade is only to the extent of 0 to 5; that means, we even if we want we cannot add more than 0.2 percent, 0.25 percent calcium in liquid steel.

So, how much calcium will add whether it is 01 whether it is 02, and what is the you know, amount of aluminum and sulphur in steel that is going to dictate whether we form liquid steel liquid inclusion or not in liquid steel. So, this is going to be very important issue.

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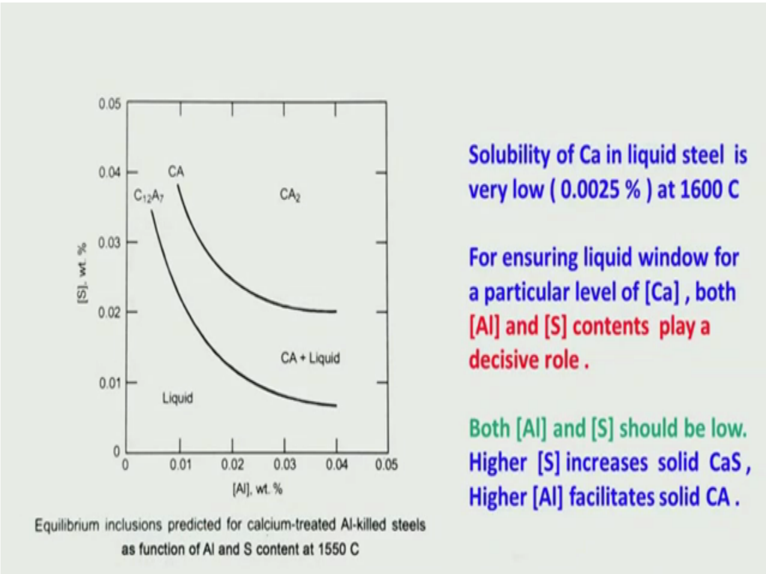

Now, this particular figure shows what I was telling that the calcium and sulphur, aluminum all why this all 3 are important. This particular figure shows for a particular level of calcium layer. Let us say assume it is 02 percent. We cannot add more than 025 percents. Calcium even if you add it is going to be lost; that means, the this liquid slag cannot contain liquid; sorry, liquid steel cannot contain more than 025 percent calcium at 16000 degree centigrade. So, how much calcium we will add whether it is 01, 015 or 02 that is going to play an important role depending on how much of, aluminum and sulphur is present in liquid steel.

So, for a particular amount of calcium, let us assume that it is 02 in this particular figure. So, what is going to happen where is the liquids window is here; that means, if percentage of aluminum is more the possibility of going to a solid inclusion is increasing. Similarly if the amount of dissolved sulphur is more possibility of going to a solid inclusion is increasing. Only way if the aluminum and sulphur solubility or the soluble in liquid steel what is their content in liquid steel they are less then only we are getting a liquid inclusions for a particular level of calcium. So, this is please try to remember for ensuring liquid window for a particular level of calcium, both aluminum and sulphur dissolve aluminum dissolve sulphur in liquid steel they are important. They should not be very high neither sulphur nor aluminum should be very high. If the aluminum is very high you know Ca type of inclusions which are solid will form; that means, the solubility the melting point of the inclusion is going to be high. As I have shown as I have shown in this particular you know figure which depicts alumina CaO system phase diagram.

If you have very high amount of alumina you know the melting point is high. As you are increasing the CaO melting point is coming down, and at about 45 to 55 percent CaO the melting point is relatively less, and at liquid steel temperature the inclusion will be liquid. So, if we have high you know, high amount of aluminum liquid steel; that means, the inclusion will be more reach in alumina and the inclusion will be solid like CA and CA 3 CA 2 CA 6 compounds like this will form, but at the other end if you have more amount of sulphur what is going to happen we have solid calcium sulfide.

So, that is why both sulphur and aluminum present in liquid steel has to be within limits, and then only we have liquid inclusion. This in this is very important we have to keep in mind to get the desired amount of liquid inclusions calcium sulphide has to be low, and preferably you know CaO should be around 45 to 55 percent.

Then only you have a combination of alumina CaO which is you know which is having a formula of CaO 12 alumina 7 and on this level of; that means, around 45 to 55 percent CaO then only we have a liquid inclusion in liquid steel. So, the importance of aluminum and sulphur for getting this liquid window I am again highlighting this is very very important. So, amount of calcium will depend on how much of aluminum how much of sulphur is there in liquid steel to ensure we get liquid steel and not solid steel.

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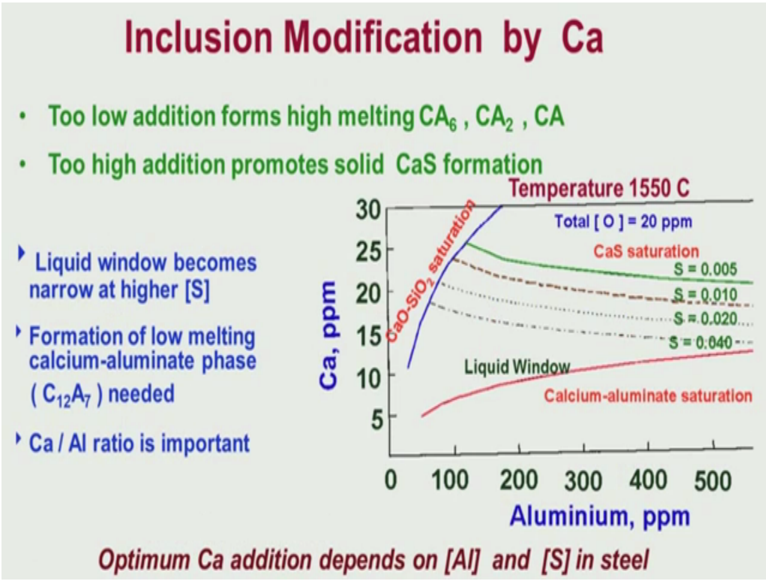

Now, again this figure will show similar thing, but in a more relatively quantitative terms. I have mentioned here the inclusion modification by calcium is possible or feasible, when if too low addition if we do if you add less amount of calcium what is going to happen you know this type of compounds are forming CA6; that means, CaO 6 Al 2 O 3, CaO 3 Al 2 O 3, 2 Al 2 O 3, CaO Al 2 O 3.

This type of you know compounds are forming at the for this you know the calcium addition is the lowest and as you are increasing calcium these are the compounds which are forming, but we do not want this we want 7 CaO or 12 CaO 7 Al 2 O 3; that means, calcium oxide around, around 45 to 55 percent. So, this is possible only for a particular level of addition of calcium. Moreover, if you go on adding calcium; that means, we going to higher level or in the solubility limit; that means, maybe we go to around 0 to 5 or so which is a higher limit we might form why might we I will actually form CA s also depending on there is some sulphur in the steel.

So, there is a possibility of forming calcium sulfide which is again solid. So, just look at this figure. This aluminum is ppm, 200 ppm means 02 percent. So, if you have 02 percent aluminum in steel, what is going to happen? Liquid window is here. So, calcium has to be accordingly somewhere here. If you have low calcium at 02 what is going to happen we have calcium aluminate saturation; that means, we have solid calcium aluminate. CaO Al 2 O 3 solid we do not have a liquid. You know inclusion; that means, we are having maybe CA 6 CA this type of combinations which are having solid. So, we have to have some amount of good amount of relatively more amount of calcium maybe somewhere here. Maybe somewhere, 15 amount of ppm is necessary then only we have good amount of liquid you know inclusions. Now look at the sulphur level. This figure has been you know drawn on the basis of calculations done for liquid steel temperature of 1550 which is quite reasonable and a total oxygen of 20 ppm; that means, oxygen here also is playing an important role.

Because this dictates, how much of oxygen is present? How much of dissolved aluminum will be present to get that much of dissolved oxygen? What will be the sulphur level? This is also important. Now if we have very low amount of sulphur say 005, you see the liquid window is quite large so; that means, the amount of calcium the window of calcium is slightly more; that means, it can be from 10 to 25 any amount of calcium is good enough beyond 25 is not possible to retain because it will come out of calcium. So, 25 if you take 25 is the maximum amount; so minimum say let us assume has to be 10. So, the liquid window is indicating you know for this amount of aluminum. So, 02 or 025 we are getting about say 10 to say 20 or 25, 22 this amount of calcium is good enough. Now if we increase the sulphur level in the steel.

Say if we have 0 somewhere here, so 020 somewhere here. So, what is going to happen? The amount of calcium has to be restricted to may be around fifteen. So, it is very close 10 to 15, if you have less than 10 ppm calcium aluminate; whatever calcium aluminate is forming, this type of calcium aluminates which is solid. If you have more calcium more than 15, for this amount of sulphur we have calcium sulfide, beyond this calcium sulphide is forming. So, as sulphar is coming down our liquid window is becoming very narrow.

So, we have to operate in a very close range of calcium look at this figure, 040 if you have such high level of sulphur and if you are not careful about adding calcium, what is going to happen? Even 15 percent you know 15 rather 15 ppm calcium will generate calcium sulphide which is solid. So, our liquid window is becoming very very narrow it is very difficult to actually operate; because you know when you are doing calcium addition I have told you is very tricky if you add more of calcium more of why it will be lost. So, control of calcium is very difficult.

So, control of calcium within this narrow range will be very difficult that is why, we need some lower sulphur for getting a good amount of good rather a large amount of liquid window where we can have slightly more broader range of calcium where we can get liquid calcium. So, it is important to know that aluminum content calcium content oxygen and sulphur these are all very important parameters for getting inclusion modification because as I am again and again repeating, you see the interesting thing here if you add or do not add or add less amount of calcium, we are getting either alumina or this type of inclusions CA 6, CA 2, CA this type of inclusions as alumina as CaO is increasing we are going from CA 6 to CA 2 to CA final will go to maybe c 12 a 7 type of inclusion which is the desirable at around combination of say around 45 to 55 percent CaO.

So, as we are increasing CA, CaO in CaO alumina type of inclusion is increasing. And only at a particular level of CA we are getting a liquid you know inclusion, but if you go beyond that; that means, if we increase CA if the sulphur is more we are going to form calcium sulphide more and more of calcium sulphide which is solid. So, our liquid window becomes more narrow more restricted if we have more aluminum if we have more sulphur this is a problem. Then the calcium has to be within a very small range. So, this is the problem for calcium addition, we have to be very careful how much of calcium we are adding what is the sulphur content sulphur should not be more then with we are forming solid calcium sulphide.

So, the inclusion if solid is not liquid anymore. If you have very small amount of calcium addition we are getting this type of inclusion CA 6, CA 2, CA the melting points are relatively high. So, again we are getting solid. So, if you have less calcium solid inclusions if you are more calcium solid inclusions. The reason here is calcium sulphide reason here is inclusions of this constituents, CA 6, CA 2. So, the reason might be different, but we are getting solid inclusions. So, to get a liquid window we have to operate at low sulphur level, low aluminum level relatively and calcium in the range of say about 15 to 20.

If we can control calcium which is very difficult again and again I am telling within this frame, we will definitely get liquid inclusions in steel. So, please if we summarize here too low addition forms high melting constituents too high addition promotes solid CaS formation. So, calcium has to be optimum. Depending on what is the aluminum what is the sulphur liquid window becomes narrow at higher sulphur, as I am telling you, as the sulphare is increasing this way the liquid window is become initial liquid window has the whole thing, liquid window has become narrow, more narrow as sulphur is increasing that is coming down the window is becoming more and more narrow.

So, formations of low melting calcium aluminate phase C 12 A 7 which is the desired constituent which should form. So, the ratio of calcium aluminum is important what is the aluminum in steel? Calcium should depend on that what was the sulphur in steel you know calcium also should depend on that, but we have not much leeway here sulphur should be low, then only we have suddenly way then only we have slightly higher range of calcium optimum calcium. If the sulphur is more the optimum calcium is very narrow which is very difficult to actually get. So, optimum calcium addition depends on what is aluminum and sulphur in liquid steel.

And as I am again and again mentioning soluble sulphur should be low. To get relatively large liquid window where we can operate where the calcium will be calcium range will be reasonable more practical to get more realistic to get. I think I have try to highlight, that inclusion modification by calcium is theoretically possible, but it have will be careful about amount of sulphur amount of aluminum in liquid steel. So, this will dictate how much of calcium you know range will be there optimum range will be there for getting liquid window. Less is the sulphur the optimum calcium range becomes more narrow.

So, it is more difficult to obtain more difficult to obtain you know operate at that narrow level of calcium. So, even if you try we may not get liquid steel liquid inclusion. So, this is the problem with inclusion modification by calcium. We have to be very careful about sulphur desulphurization should be proper the sulphur level must be brought down earlier through desulphurization then only we are adding calcium, this is very important.

Deoxidation is fast, desulphurization is next then I have talked about degassing to take care of oxygen nitrogen which is useful or which is effective only when oxygen is less liquid steel sulphur is less in liquid steel.

Now, I am talking about inclusion modification, where again sulphur has to be less. Then only inclusion modification by calcium is possible in reality otherwise it is going to be a theoretical proposition only, as I am trying to heart fear heart pop on here that to get a realistic calcium range, slightly you know bigger calcium range say 10 to 20 if you take this is the realistic calcium range which will give liquid window, the sulphur has to be less than 01. 01 you see it cannot exceed 01. Aluminum has to be less than 025, it cannot be more than. That otherwise you know this liquid window is becoming more and more narrow. So, that is the requirement that is the essential requirement for getting inclusion modification by using calcium.