Steel Quality Role of Secondary Refining and Continuous Casting
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Module - 06
Lecture - 30
Deleterious Effect of Phosphorus

Good morning. In the last lecture I have talked about this concept of segregation of alloying element. I had mention that this is very important, because steel is basically and alloy, it is not an single element like in steel, we have along with iron, we have alloying elements like carbon, we may have manganese, we may have silicon, we may have phosphorus, silicon, sulphur and similar other alloying element, maybe some amount of nitrogen. So what is important is, what are the role of this alloying elements in causing segregation we have to understand very clearly. It has you know impact on the quality of the final product, cast product as well as the posses product role product.

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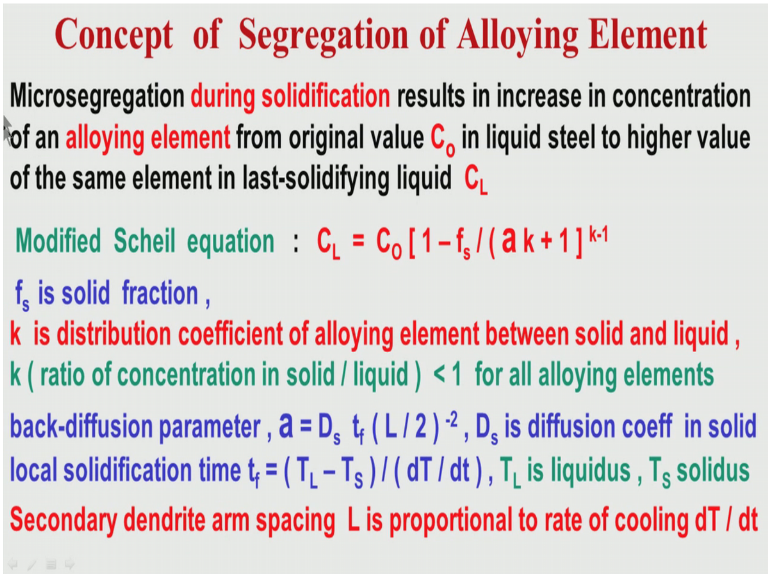

So, let us try to understand what do we mean by segregation. So, I have mentioned that micro segregation during solidification it is always bound to happen. When you have alloying elements you will have micro segregation. These results in increase in concentration of an alloying element, of a particular alloying element say we are talking of sulphur. So, initially whatever is the content of sulphur in the steel grid in the finally what we have get due to segregation is different it is going on increasing. So, what is important is- the increase in concentration of the alloying element from the original value if it is C 0 in the liquid steel; that means, when the solidification is starting in that liquid steel if the concentration of a particular alloying element say sulphur if it is 0 C 0.

Then due to segregation it increases; that means this to the concentration of sulphar in the last solidifying liquid. See if it is called C L, so C L is more than C 0 this is called segregation, because you know the solid will release the alloying elements, alloying element will be going to the liquid. So, the liquid becomes more and more rich in the alloying element, so the concentration of the particular element say sulphur for example in our example the last solidifying liquid if it has C L concentration then modified Scheil equation gives how these C L, to what extent it will increase from C 0 is given by this relationship. Here what are the factors? C L is the final you know concentration of a particular alloying element, say for example is a sulphur.

In the last solidifying liquid if this is C L then how is it related to the original concentration C 0. It is related to the solid fraction the more the solid fraction more will be the segregation and higher is the value of C L. So, there is no confusion regarding that. But what is that you know relationship of k? K is basically the distribution coefficient of alloying element between solid and liquid. So, k is always less than 1. So, lower is the value of k more is the segregation, higher will be the value of C L. So, k is important, f s- solid fraction is important solid fraction it is directly related, higher is the solid fraction that means more it is going towards the end of solidification C L also increases.

Small k is basically the distribution coefficient of that particular alloying element between solid and liquid. So, a concentration of that particular element in solid divided by the concentration of that particular element in liquid; this is the ratio k. And k as I have told you is always less than 1 because of the liquid we will always become rich in the solute alloying element. So, what is the value of k? Lower the value of k you can get from this figure. Lower the value of k higher will be the value of C L. So, this is important.

Another factor here is the a; a basically called back-diffusion parameter because what is happening you know the there is a difference between the two liquid and solid and also from that high level of concentration in the liquid when the particular alloying element will defuse towards the solid.

So, in the solid what is the diffusion parameter it is very important. So, this is back-diffusion parameter a is directly related to the diffusion coefficient of the particular alloying element in the solid. Solid means in the dendrite whichever is solidifying in the form of dendrites. How this particular alloying element we will diffuse, so it depends on that figure.And then it depends on the local solidification time T f it is basically the solidification temperature interval, you know difference between liquidus and solidus divided by this cooling rate d T; d capital T by d small t rate of change of temperature with time.

So, the dendrite arm spacing capital L is dendrite arm spacing capital L is basically here you will find there is a capital L figure. So, that is the dendrite arm spacing. So, here l is proportional to the rate of cooling and I have told earlier and the local solidification time is depends on the solidification interval temperature interval divided by the cooling rate.

So, higher this temperature interval the solidification time also increases and more the solidification time mode will be the segregation. So, this is important. So, T L is the liquidus T S is solidus. So, what is happening is the final concentration in the liquid last solidifying liquid is increasing from the original solidification by this relationship. This is dependent on the solid fraction higher is the solid fraction higher is the you know; concentration in the liquid that is more is the segregation lowered is the value of k mode is the segregation and then higher is the value of diffusion have been diffusion coefficient in solid you know. So, this is also we will change the C L value of C L.

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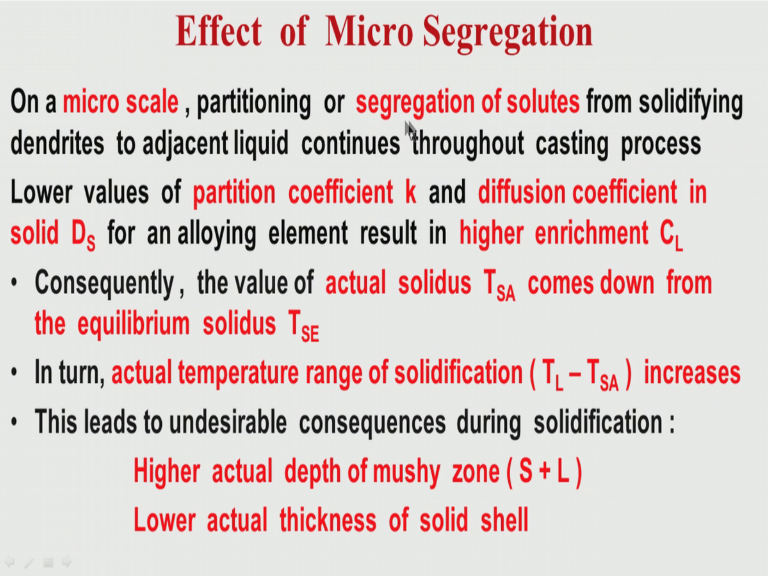

Now, let us see; how does it change on a micro scale partitioning of segregation of solids solutes from the solidifying dendrites to adjacent liquid is continues throughout the casting process; that means, throughout the process of solidification throughout the course of solidification. This partitioning of the segregation of solutes what is which is the cause of segregation, it is continues because the solidifying dendrites will become less rich in the particular element.

So, salute elements at that adjacent liquid we will become more rich. So, this difference in concentration is called the micro segregation now lower values of partition coefficient small k as I have was telling and lower values of diffusion coefficient in solid D S this 2 we will result in higher enrichment that is high values of C L. So, consequently the value of actual solidus T S A comes down from the equilibrium solidus. So, there are 2 impacts of segregation first the last solidifying liquid who is more rich in the solutes in all the alloying elements.

So, the last portion which is getting solidified is more reaching solutes. So, is concentration all the alloying elements in steel in the last portion which is getting solidified is much higher compute to the original you know concentration or the initial portion of the solid which is solidifying, it is with that is much linear and the last portion which is solidifying is having more concentration that is it is richer in all alloying elements.

So, first is this concentration of the last solid is very high quite rich the last portion of solid which is getting solidified number one number 2 the actual solidus which is known as T S A T S is solidus T S E is the equilibrium solidus T S A is the actual solidus. So, the actual solidus also comes down because of the segregation. So, higher is the segregation more will be the C l; that means, the last concentration in those liquid which is getting solidified similarly the solidus actual solidus is also decreasing. So, because of this; this range of solidification which is nothing, but the difference between the liquidus and the actual solidus this also is increases and if this decreases have told you what is going to happen the actual depth of mushy zone solid plus liquid is more and the actual thickness of the solid shell during solidification is less.

So, the actual thickness of solid shell is narrow and the depth of mushy zone is more. So, segregation is causing this 2 2 important you know consequences which you have impact on the which we will have impact on the quality of the cast first the last portion of the solid which is forming that is the last portion which is getting solidified is very rich in alloying elements compared to the earlier portion of the solid. So, the central portion of a cast material is always more rich in alloying elements more rich in solutes number one because of segregation which is a important consequence of you know solidification there will be segregation all alloying elements will segregate because all for alloying elements the partition coefficient k is less than 1.

Now it is a question of which value is lower the lower value of small k and lower value of diffusion coefficient in solid D S they will increase enrichment C L; that means, segregation more is the segregation lowered will be the actual solidus and lower is the actual solidus more will be the actual solidification range and because of this the depth of mushy zone increases at the cost of the solitary shell during solidification.

Depth of mushy zone is increasing solid shell is becoming less this is a consequence of segregation. So, whatever alloying elements cause more segregation which we I will come just subsequent to this which elements which alloying elements we will cause more segregation the results are you know the last portion of solid will be very rich in those elements number 1.

Now mushy zone will be quite broad actual solid shell will be quite narrow. So, these have lot of consequences on the quality of the cast product. Now why we tell that phosphorus and sulphur are very deleterious these are harmful for a cast product the reasons I have mentioned some of the factors which are responsible I have mentioned that partition coefficient partition coefficient between solid and liquid small k is always less than one for all alloying elements during solidification.

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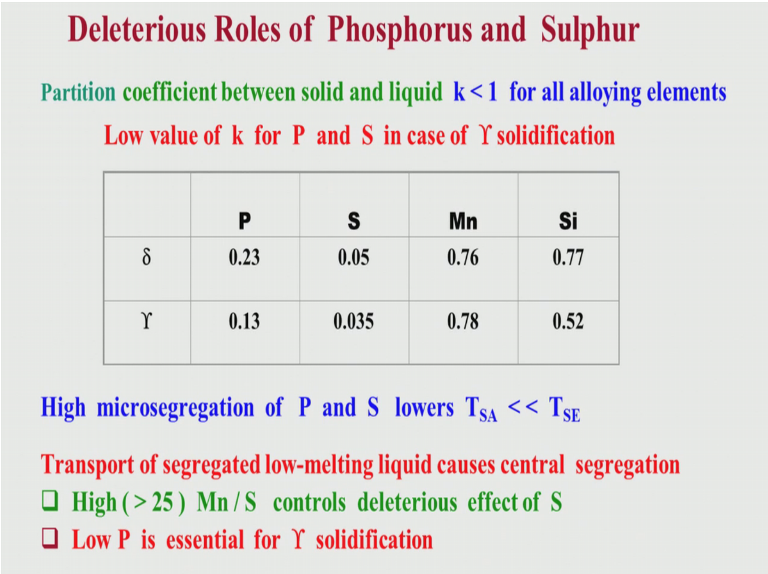

Now, this k values are not equal for all alloying elements different alloying elements have different k values number one number 2 k values are also different for the solid which is forming from liquid if it is delta ferrite you have some k values if it is austenite; that means, gamma you have some k value. Now wherever k values are smaller I have mentioned several times that is very small k. We will cause very high amount of segregation. So, look at the different values of k for different alloying elements a manganese silicon what are the values of k it is around 0.7 and look at the values of phosphorus and sulphur in delta and gamma in delta 0.22 phosphorous gamma solidification is 0.12 still lower sulphur 0.05 compared to phosphorus sulphur segregation is more gamma 0.025.

So, there are 2 observations from here fast phosphorus and sulphur we will segregate more compared to alloying elements manganese and silicon why because k values are smaller I have mentioned here that smaller value of partition coefficient k. We will give rise to higher enrichment; that means, C L from this modified shell equation you can see C L will be higher once this k becomes lower k to the minus 1. So, this is negative to the power. So, k smaller the value of k higher is the value of C L higher is the value of enrichment then another factor back diffusion parameter a it is consists of diffusion parameter in the solid DS. So, lower is the value of D S lower is the value of A and C L also we will increase.

So, 2 lower values of k small k and D S we will increase C L that is the enrichment lower values of partition coefficient small k and lower value of diffusion coefficient in solid D S for an alloying element result in higher enrichment C L higher is the enrichment I have told you actual solidus comes down from the equilibrium solidus because of this the actual temperature range of solidification; what is that the temperature difference between liquidus and the actual solidus this temperature interval the range of solidification also increases because of segregation. So, lower is the value of k lower is the value of D S higher is this French higher is the segregation. So, the depth of mushy zone will. So, also will be more actual thickness of solid shell also will be less.

So, now if you look at the values of phosphorus and sulphur these values are much less compared to manganese silicon number one number 2 in gamma solidification this values are still less. So, this partition coefficient between solid and liquid k is less than one for all alloying elements, but for alloying elements like phosphorus and sulphur these values are much lower compared to those for manganese and silicon the common alloying elements in steel number one number 2 this lower values of k for phosphorus sulphur in case of gamma solidification; you look at this values is still lower compared to delta values. So, phosphorus and sulphur k values in case of gamma solidification are relatively much lower. So, what is going to happen what are the consequences these 2 elements will give rise to high level of micro segregation and consequently the actual solidus becomes much lower compared to the equilibrium solidus.

So, what are the consequences the consequences are the micro segregation level caused by phosphorus sulphur when in case of gamma solidification is much more. So, high manganese by sulphur is necessary you know otherwise what is going to happen if you have sulphur it will react with r n. So, it will call formation of iron sulfide which has low alloying element that is the reason why you know sulphur segregation is bad for quality of steel because you know the actual solidus becomes much lower. Now if you have high amount of manganese in the steel if the ratio of manganese by sulphur is more than 25 then; what is going to happened there will be formation of manganese sulfide and not iron sulfide manganese sulfide you know temperature melting temperature is more compared to iron sulfide.

So, the deleterious effect of sulphur like why it is deleterious because it forms low melting iron sulfide; so, if you have higher amount of manganese by sulfide ratio then manganese sulfide we will form and not iron sulfide and in this process the deleterious effective of sulfide we will be taken care of to a large extent, but unfortunately for phosphorus there is no such element which can take care of this element phosphorus. So, what happens in presence of phosphorus iron phosphate forms f a 2 p? This is iron phosphate has low melting point. So, it causes in C p and fusion it causes the actual sorry just temperature to get down. So, that is the reason for phosphorus to behave in this fashion. So, the deleterious effects of sulphur can be taken care of by using manganese, but the effect of phosphorus the deleterious effect of phosphorous the harmful effect of phosphorus cannot be taken care of by any other alloying element in liquid in steel.

So, phosphorus has to be kept under control. So, that it is deleterious effect is not much now and other important thing is this low melting liquid which causes central segregation; that means, at the last stage whatever liquid remains during solidification as I have told you, it is very rich in allowing elements all alloying elements relatively, it is very rich in all alloying elements in steel because of segregation now some alloying elements we will segregate more like phosphorous sulphur some alloying elements manganese silicon they will segregate less.

So, we have to be more careful about phosphorous and sulphur and steel and I have also mentioned that the deleterious effect the harmful effect of sulphur can be taken care of to certain extent by using higher manganese in steel. So, say if you have 0 2 sulphur you know in steel what should be the minimum manganese percentage 0 2 into 25; that means, 0.5. So, normally we must have 0.5 percent manganese. So, that the deleterious effect 0 2 percent 0.02 percent sulphur is taken care of to a large extent by manganese. So, this is the role of manganese this is very important here, but since there is no such element which can take care of the; you know harmful effect of phosphorus. So, phosphorus has to be controlled to very low level.

o, that this harmful effect of segregation effect of phosphorous is taken care of by keeping the value of phosphorus to lower level this is very important.