Steel Quality Role of Secondary Refining and Continuous Casting

Dr. Santanu Kr Ray
Department of Mechanical Engineering
Indian Institute of Technology, Madras

Module – 05
Lecture – 29
Role of Segregation: Part II

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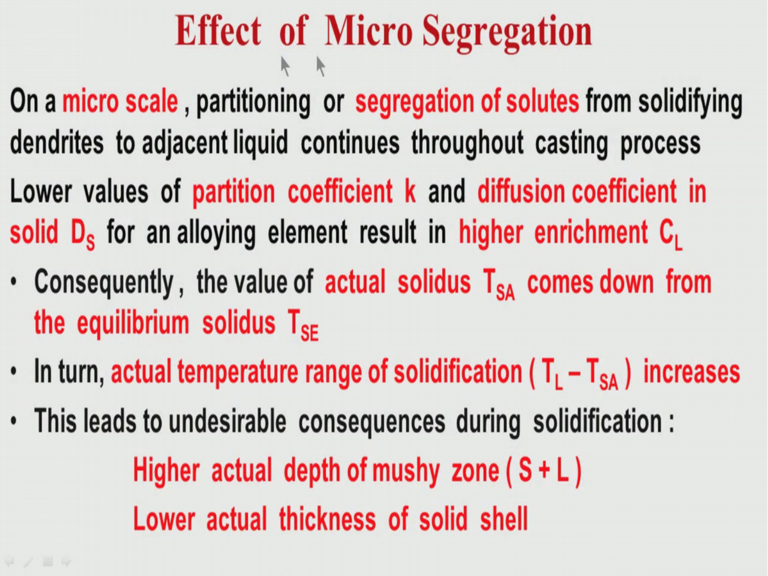

Effect of Micro Segregation

On a micro scale, partitioning or segregation of solutes from solidifying dendrites to adjacent liquid continues throughout casting process

Lower values of partition coefficient k and diffusion coefficient in solid D_S for an alloying element result in higher enrichment C_L

- Consequently, the value of actual solidus T_{SA} comes down from the equilibrium solidus T_{SE}
- In turn, actual temperature range of solidification ($T_L - T_{SA}$) increases
- This leads to undesirable consequences during solidification :
  - Higher actual depth of mushy zone (S + L)
  - Lower actual thickness of solid shell

So, I have mentioned here what is the effect of microsegregation? Why are we really So much concerned about microsegregation? During solidification, what are it is actual impact on quality? Let us try to understand. On a micro scale; that means, on a on a scale of say few microns when solidification is taking place; that means, there is I have told you the solidification is taking place 2 dendrites formation of dendrites.

So, what are the within a dendrite distance. So, it may be say 20 micron you know 30 micron, 40 micron, 50 micron. So, on a micro scale this partitioning of segregation of solutes, all solutes, all soluble elements or alloying elements from solidifying dendrites to adjacent liquid, it continues throughout the casting process. Please try to remember this.

Whenever there is a solidification there is a segregation. So, this is taking place throughout the solidification or casting process. So, the solutes they are segregating from the liquid to the solid, which was the reverse from the solid to the liquid; that means, they are becoming more and more rich in the liquid. The solids are becoming relatively less rich in this alloying elements, liquids are liquid is becoming more rich. So, the dendrites are relatively less in concentration of the alloying elements, the liquid which is a to be solidified is becoming more and more rich.

So, the adjacent liquid is becoming more rich. These continuous throughout the solidification process. So, we call it microsegregation of solutes from solidifying dendrites to adjacent liquid. Now as I was telling you lower values of this partition coefficient k, what implication does it have? And if the diffusion coefficient in solid is low, then what happens?

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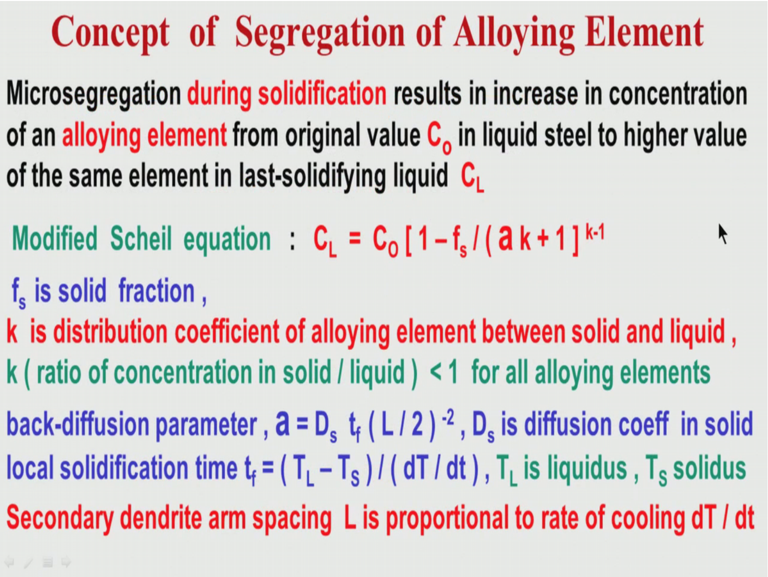

Concept of Segregation of Alloying Element

Microsegregation during solidification results in increase in concentration of an alloying element from original value C_0 in liquid steel to higher value of the same element in last-solidifying liquid C_L

Modified Scheil equation : $C_L = C_0 [1 - f_s / (a k + 1]^{k-1}$

f_s is solid fraction ,

k is distribution coefficient of alloying element between solid and liquid ,

k (ratio of concentration in solid / liquid) < 1 for all alloying elements

back-diffusion parameter , $a = D_s \; t_f (L / 2)^{-2}$, D_s is diffusion coeff in solid

local solidification time $t_f = (T_L - T_S) / (dT / dt)$, T_L is liquidus , T_S solidus

Secondary dendrite arm spacing L is proportional to rate of cooling dT / dt

Then as I was discussing from this relation, look at the figures, if you have small k; that means, k almost coming towards zero; that means, less than 1, k is always less than 1 I have told you, but lower the value of k, you have more of segregation. Again here you know this a this a means back diffusion parameter it directly dependent on the diffusion coefficient D s in the solid for a particular element.

So, if a and D as they are low then C L is also relatively high. So, please try to remember what is happening, small k means high C L small a small a means small D. So, D smaller the D value hard will lower will be the a value. So, smaller a value because of the smaller D value again will increase C L. So, segregation if the amount of alloying elements in the liquid, finer liquid which is getting solidified, is becoming more high, more rich value k is very low and the diffusivity of that particular element is relatively low in solid.

So, these are the 2 important things again. So, what I have told lower values of this partition coefficient k and lower value of the diffusion coefficient in solid D s, for an alloying element result in higher enrichment of that particular element, alloying element. Consequently what is happening? The value of actual solidus because this actual solidus depends on what? What will solidify? The last liquid which will remain that is solidifying finally and so, concentration of that liquid is become which is becoming more and more rich in the all alloying elements.

So, more is the enrichment more is the segregation more is the enrichment, lower will be the T SA because of the enrichment. So, this T SA; that means, the actual solidus comes down from the equilibrium solidus T SE. So, what we find trough iodine carbon diagram, or any space diagram In fact, iron silicon or iron manganese any space diagram what we get is T SE temperature equilibrium solidus, but what is important is the actual solidus.

So, you try to understand what is happening, microsegregation is resulting in higher enrichment compared to the c 0 value C L is increasing the concentration, of all alloying elements in that last liquid which is solidifying is more compared to the original you know concentration in the particular grain. So, the final liquid which is solidifying as a much lower temperature. So, thee solidus is increasing that particular solid which is solidifying is more rich in that alloying element. So, the last solidification last area which is solidifying which is heavily segregated; that means, the concentration of all alloying elements in that area is relatively more compared to a area which has solidified in the early stage of solidification.

So, please try to remember the 2 important implications. First during solidification segregation is taking place. So, in a on a micro scale this partitioning of segregation of solutes segregating from where from the solidifying dendrites to adjacent liquid. So, this takes place throughout the solidification process. So, because of that what is happening lower is the value of k and lower is the diffusion coefficient of that particular element in the solid which is we call it back diffusion because of that because of these 2 lower values C L is increasing; that means, segregation is more and more is the segregation the actual solidus becomes low because of this segregation.

So, the difference between T SE and T SA; that means, equilibrium solidus and the actual solidus becomes more actual solidus means much lower compared to the equilibrium solidus. So, what is happening? This is decreasing this is more or less constant. So, the actual temperature range of solidification which is supposed to be T L minus T SE theoretically, but actually it is T L; that means, liquidus minus actual solidus. So, this temperature differential is also increasing because of micro segregation.

So, 2 things are happening, the last solid which is solidifying towards the end of solidification is more rich in all the alloying elements. So, we call it central segregation any central area of any casting has to be rich, in all alloying elements what about alloying elements are present in the particular steel grain. So, all are causing micro segregate it is the question of degree some are causing more micro segregate some are causing less if this value of k that means distribution coefficient is relatively less all are less than 1, but for certain alloying elements I will come to it like phosphorous sulphur for this element this k values are relatively low, much low compared to say manganese silicon all these alloying elements.

So, what happens is more segregation is created by phosphorous and sulphur, and what is the other issue? Thus solidus is suppressed from the equilibrium solidus. So, the temperature range of solidification T L minus actual solidus this difference is also increasing. So, because of that temperature interval is increasing. So, temperature interval increasing means, what happens? Actual depth of mushy zone is increasing the actual thickness of the solid shell during solidification is relatively low and the mushy zone is more.

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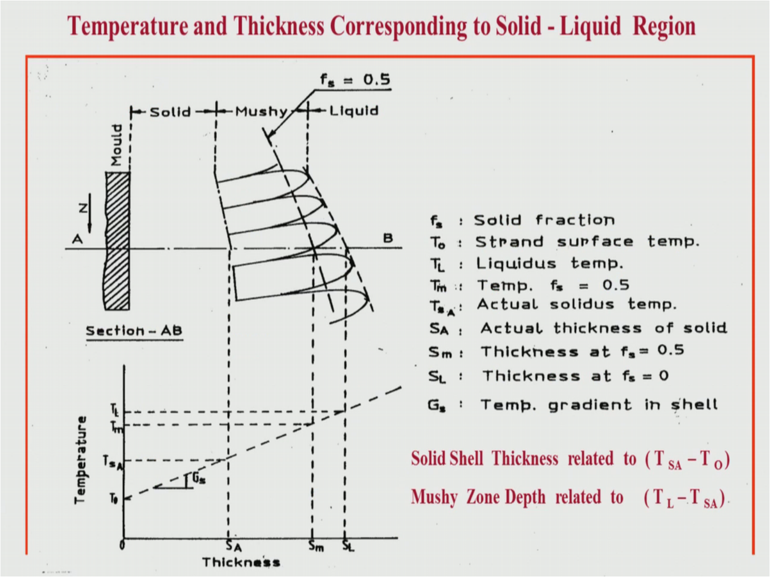

Temperature and Thickness Corresponding to Solid - Liquid Region

f_s : Solid fraction
T_o : Strand surface temp.
T_L : Liquidus temp.
T_m : Temp. f_s = 0.5
T_{sA} : Actual solidus temp.
S_A : Actual thickness of solid
S_m : Thickness at f_s = 0.5
S_L : Thickness at f_s = 0
G_s : Temp. gradient in shell

Solid Shell Thickness related to $(T_{SA} - T_O)$

Mushy Zone Depth related to $(T_L - T_{SA})$

Yeah look at this figure here, this I have discussed earlier. During the stage of solidification; that means, when solidification is you know under way it is not complete what we have we have a portion of the solid which has already become solid; that means, you know solidification there is of course, liquid because solidification is not yet complete and in between in between the liquid and the solid shell there is a mushy zone which is a combination of dendrites and liquid.

So, this area is solidified totally solidified. So, the solid fraction here is one mushy zone start; that means, the liquid at the interface between the liquid and the mushy zone you know solid fraction is 0. So, here solid fraction is increasing from 0 it is increasing towards 1 as we are going to the solid you know totally solidified area zone.

So, it is the solid zone, it is the mushy zone, this is liquid plus solid and this is liquid. So, the solid fraction is 0 here it is solid fraction is 1 here it is 0 percent it is 100 percent in between we have a mixture of solid and liquid. So, the mushy zone is determined by how much will be the width depth of mushy zone, what will be the depth of solid space during solidification depends on? If you look at this figure this is the thickness. So, the actual solid the depth of solid it depends on what depends on look at here what is the temperature here corresponding temperature, look at the temperature here this is depends on here this is the temperature. So, this is depends on the actual this is the actual corresponds to the actual solidus temperature.

So, the thickness depends on the actual solidus temperature which is T SA. The liquidus point corresponds to this is the liquidus points. For any section a b I am talking about this is the liquidus; that means, the depth of mushy zone depth depends on this and this is equivalent to proportional to the temperature range of solidification; that means, the difference between T L liquidus and T SA in the actual solidus.

So, the more is segregation means the actual solidus is suppressed. So, T SA is suppressed. So, if T SA is suppressed means this temperature becomes lower. So, T L is more or less fixed more the segregation means T SA is coming down if T SA coming down means T 0 is the temperature surface temperature of the solid.

So, let us assume during cooling it is more or less constant. So, if T SA is suppressed means S A the thickness of the solid shell also comes down if the solid shell thickness is proportional to the temperature difference between the actual solidus and the surface temperature of the solid. And thee mushy zone depth is proportional to the temperature of you know solidification the temperature difference of solidification; that means, the difference between the liquidus and the actual solidus.

Since segregation is suppressing this is bringing down this actual solidus T L; that means, the liquidus more or less constant, T 0 is more or less constant. So, what is happening during segregation if T SA is suppressed T SA comes down. So, difference between liquidus and actual solidus increases this difference increases. This difference increases means, the mushy zone depth S A, S L minus S A this depth also will increase.

So, the mushy zone will depth will increase, and the solid shell thickness you know this is coming down where T 0 is constant T SA is coming down means it is becoming near and almost near to T zero; that means, this difference is also coming down this difference is increasing T L minus T SA is increasing.

So, solidification temperature range is increasing. So, the mushy zone depth is increasing, but you see here T SA coming down means T SA minus T 0, this difference temperature difference is decreasing this temperature difference decreases means, this at S A will also decrease. So, what are the implications of segregation, one is the last solidification, which is taking place the last area of the solid is definitely more rich in all alloying elements. It is a question of relatively whether how low is the k value. How low is the diffusivity in solid? And both these 2 are very low; that means, you know it will increase the segregation will increase segregation increases means you know, the particular area which is solidified at the last is more rich.

Number one from the chemistry point of from the you know temperature point of view the actual solidus, because of more segregation is suppressed from the equilibrium solidus. So, the actual solidus comes down. So, the temperature difference between the liquidus and the actual solidus increases. So, the mushy zone becomes quite void, and the actual solid depth becomes less narrow.

So, during solidification when there is too much of segregation what is evident is the mushy zone there is a big mushy zone, deep mushy zone and the actual solid shell is narrow. So, this has implication on the strength of the you know strand, because the strand consists of solid and liquid during solidification.

So, during solidification the strength of the strand is determined by how much of solid is there how much of liquid is there. So, if the solid shell is relatively thin and the mushy zone is relatively more the strength of the shell also will be relatively less. So, this will be discussing later on.

But what is important to know that, because of the suppression of the actual solidus going to segregation the depth of mushy zone increases, and the thickness of solid shell decreases. This is important to remember. Now as I was telling you because of the microsegregation what is happening, higher actual depth of mushy zone solid plus liquid zone is more actual thickness of solid shell is less. This is a consequence of segregation, which is contributed by all alloying elements question of more or less. Depending on what is the k value will smaller is the k value more is the segregation. This please try to remember this will be of you know immense consequence in you know identifying what are the factors causing crack formation at different stage of solidification different stage of you know cooling.

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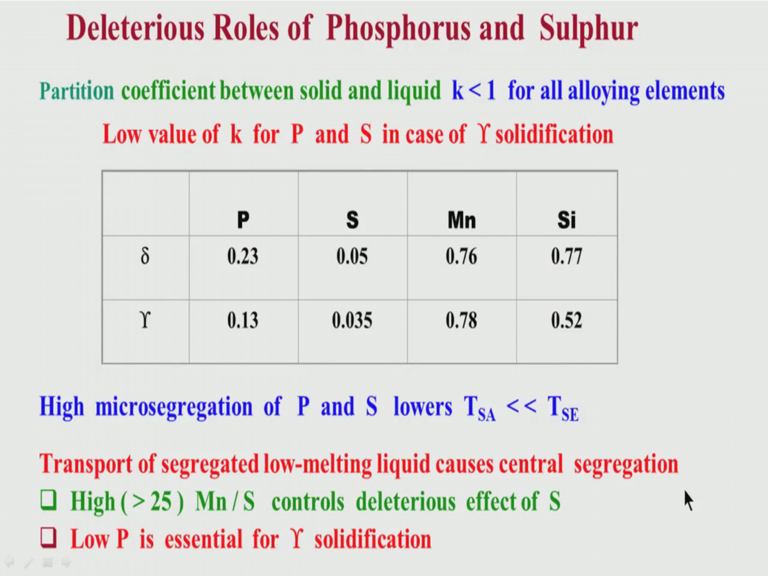

Deleterious Roles of Phosphorus and Sulphur

Partition coefficient between solid and liquid $k < 1$ for all alloying elements

Low value of k for P and S in case of ϒ solidification

	P	S	Mn	Si
δ	0.23	0.05	0.76	0.77
ϒ	0.13	0.035	0.78	0.52

High microsegregation of P and S lowers $T_{SA} << T_{SE}$

Transport of segregated low-melting liquid causes central segregation

☐ High (> 25) Mn / S controls deleterious effect of S

☐ Low P is essential for ϒ solidification

Now, as I was telling you partition coefficient between solid and liquid; that means, this k value which is less than 1 for all alloying elements. It is a question of how low is k, but k is always less than 1. Now look at the k values for you know for common alloying elements. So, manganese, silicon when solidification is taking place through delta for a initial solid it is 0.76, 0.7, 0.76, 0.77 for silicon. Look at the you know value of for gamma when solidification takes place through gamma. This 0.78 0.52 silicon. You know so, look at now the values for phosphorous and sulphur. 0.23 this delta sulphur point 0, 0.05 gamma for gamma solidification you know all value of this value of small k is very low, 0.13 the sulphide is much still lower 035

So, what is important to understand is between alloying elements, if you compare alloying elements say manganese silicon and phosphorous sulphur, phosphorous sulphur has much less value of k, more low value of k compared to manganese silicon. This is first point to remember. So, phosphorous and sulphur are more potent for causing microsegregation this is first thing to remember, compared to manganese silicon these values are not very low. But phosphorous sulphur the value k values are quite low and number 1.

Number 2 between delta and gamma the phosphorous and sulphur they segregate more when solidification mould is austenite; that means, gamma; that means, when carbon equivalent is more than 0.52; that means, when solidification is taking place through austenite, then you have relatively more segregation then for a you know very low carbon steel. But carbon is less than 0.1 say 0.07, 0.05 carbon any steel which is having very low carbon segregation the solidification is through delta, and relatively between delta and gamma. You know gamma is less in sorry, the k value small k value the partition coefficient for phosphorous sulphur this is for gamma it is relatively more. So, here you know for delta it is relatively high; that means, segregation is very high in gamma solidification. As such for phosphorous sulphur it is high compared to manganese silicon, but between delta and gamma solidification for gamma solidification; that means, austenite solidification phosphorous where is a steel lower.

So, what is important is, phosphorous and sulphur for phosphorous and sulphur microsegregation is very high. So, the actual solidus is much lower compared to the equilibrium solidus. So, more is the microsegregation as I have told you lower will be the value of actual solidus because it is suppressed, more it comes down relatively more compared to the equilibrium value because of microsegregation.

So, microsegregation results in a b first microsegregation of phosphorous and sulphur, causes very high level of you know partition. Because the k values are relatively low when solidification take place through austenite mould. And because of this high segregation high amount of segregation it is more amount of segregation you know, for phosphorous and sulphur in austenite mould. The value of solidus actual value of solidus is much lower compared to the equilibrium solidus. And what is happening is when the last solid which is you know solidifying; that means, the central area of the cast structure is having high level of segregation. Now this is called central segregation. This segregated low melting liquid they gets transferred during the stage of solidification mould towards the centre. And the central segregation is more rich with alloying elements. So, this is called central segregation.

If you measure the concentration of the alloying elements at the centre and at the areas which have solidified earlier, we will find always the central portion of the cast is having more of this alloying elements. So, this segregated low melting liquid causes central segregation and the actual solidus is also suppressed much becomes much lower.

Now, what is important to understand is that, all of us know that we want to add some amount of manganese in steel, to take care of the deleterious effect of sulphur. So, when the ratio of manganese by sulphur is more than 25 we find that this deleterious effect of sulphur in causing microsegregation is relatively less. Why is it So? If you do not have sufficient manganese, then what happens? Sulphur will combine with iron to form iron sulphide, whose melting point is relatively lower. So, to take care of that if you have some manganese in steel. So, preferentially sulphur with combine with manganese, rather than iron and the manganese sulphide you know temperature of that melting point of that is relatively higher compared to iron sulphide.

So, we do not have iron sulphide in steel. So, the relative if relatively bad effect of sulphur is taken care of if you have high manganese by sulphur ratio in steel; that means, we must have manganese by sulphur ratio more than 25; that means, if you have say 0 1 sulphur in steel are manganese has to be minimum 0.25. If you have 0 to sulphur manganese has to be more than 0.52 in the steel this is from the point of view of taking care of the deleterious effect of sulphur in causing you know, high level of segregation in causing in causing low melting constituent of iron sulphide this have to be taken care of by giving by photon more amount of manganese in the relatively more amount of manganese in steel.

But for sulphur there is a saviour called manganese, but for phosphorous there is no saviour. We do not know any alloying element which will combine with phosphorous and we will not create iron phosphide. So, manganese forms manganese sulphide it does not allow sulphur to form iron sulphide, but there is no alloying element which can prevent phosphorous from forming iron phosphide, which like iron sulphide is also low melting constituent and is the cause of concerned for segregation and suppression of actual solidus.

So, what is important to remember is that, phosphorous sulphur they are more photon for causing microsegregation, more photon for suppression of actual solidus, compared to the liquidus. So, the difference between liquidus and actual solidus increases. So, what is the consequence of this the relative depth on mushy zone is more. And the thickness of solid shell is less during solidification the process of solidification. So, strength of the strand will be less because we have more of liquid and less of solid.

So, the consequence of microsegregation is too fast, that is last area which is solidifying is heavily segregated that area has more of the segregating elements. So, relatively impure that is one we call it central segregation. Second the actual solidus is much less compared to the equilibrium solidus because of segregation.

And I have also mentioned the phosphorous and sulphur are more photon segregating solutes segregating elements compare to other alloying elements like manganese, silicon, chromium, nickel. So, this phosphorous and sulphur we have to very careful So that they do not create you know, segregation So, we have to very, very careful.

So, carbon also you know this k values are also less in for carbon, but for the carbon. What happens is back diffusivity D s for carbon for nitrogen all these interfacial element it is much higher they diffuse fast. So, even if there is a you know segregation during the stage of solidification because of diffusion the level of segregation comes down which does not happened for phosphorous sulphur. Here the k values are low diffusivity also relatively low.

Since I have discussed you know beforehand that when, k value are low and the diffusivity are low diffusivity of that particular element in solid is low, we have high amount of segregation. So, phosphorous and sulphur are 2 elements which are small k, and also small diffusivity, and that creates very high amount of segregation.

Thank you very much.