

Steel Quality Role of Secondary Refining and Continuous Casting
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Module - 06
Lecture - 32
Brittle Zone Near Solidus

Good morning. In the last session I have been talking about the role of you know alloying elements on segregation and its consequences. I have mentioned that you know phosphorus and sulphur these are the two elements which we have to look into very carefully because their role is deleterious.

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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 γ solidification

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

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

Transport of segregated low-melting liquid causes central segregation

- High (>25) Mn/S controls deleterious effect of S
- Low P is essential for γ solidification

Why it is deleterious? I have mentioned that small k the value of partition coefficient between solid and liquid which is less than one for all alloying elements, but for phosphorus and sulphur there are very low, like mentioned phosphorus in delta solidification it is 0.23, sulphur is 0.05 you see these are very low compared to manganese and silicon. Manganese silicon is 0.76 0.77.

So, compared to normal alloying elements like manganese silicon, this table is just to give a relative you know relative values of small k for the different alloying elements. So, what we find here is that phosphorus and sulphur are very deleterious, because their values small k values partition coefficient values are quite low and between delta and

gamma, if the solidification is through delta or through gamma depending on that the values for small k with respect to gamma; that means, austenitic solidification are steel lowered compared to delta ferrite 0.23, in delta ferrite for phosphorus 0.13 for gamma. For sulphur it is 0.05, for delta ferrite it is 0.035 the value of k its quite small quite low for austenitic solidification.

So, what is the impact of this? Impact is this high micro segregation of phosphorus and sulphur they lowered, the actual solidus temperature compared to the equilibrium solidus. These I have been telling repeatedly that not only there is segregation, but the impact of segregation is the actual solidus is lowered compared to the equilibrium solidus. So, if the actual solidus is lowered the solidification range the temperature difference between the liquidus and the actual solidus also increases. If this is low liquidus is not much affected. So, the difference between TL and TSA; that means, the difference between the liquidus and the solidus is becoming large.

So, what is the consequence of that? Consequence of that is them as I have told you earlier now mushy zone, which is the zone of liquid plus solid that is that becomes quite wide and the actual thickness of solid shell during solidification is relatively narrow. So, what is the impact of micro segregation, heavy micro segregation, high micro segregation due to phosphorus and sulphur. Is that the actual solidus is coming down, from equilibrium solidus consequently the temperature interval for solidification. The temperature interval between liquidus and the actual solidus also is increasing f Ts at comes down means TL liquidus remaining modulus similar, the temp temperature interval for solidification. Solidification temperature is region or zone also increases and if this increases the mushy zone will be wider and the actual solid shell during solidification will be narrow.

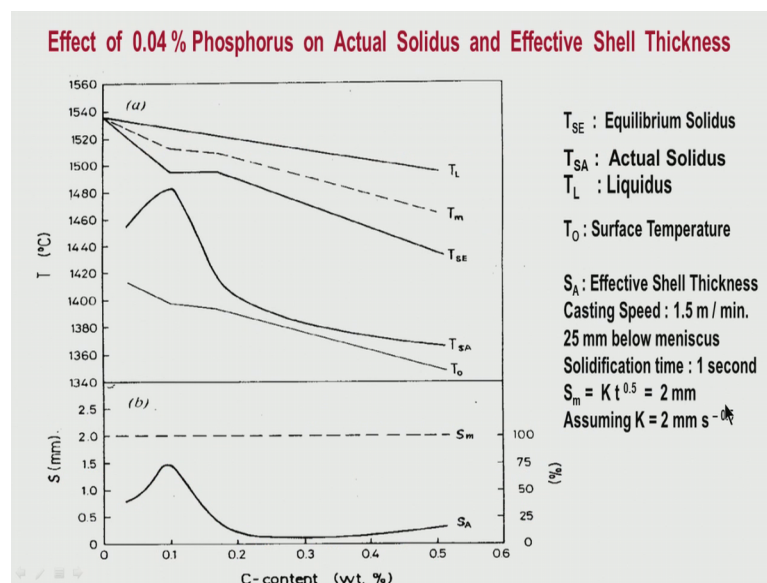
So, this has lot of implication on the solidifying strand, its strength its toughness everything we will depend on that. Now I have also mention that fortunately for silicon for the deleterious effect of silicon there is a severe like which is know which we know as manganese. So, manganese reacts with sulphur and forms manganese sulfide. So, the deleterious effect of sulphur is taken care of to certain extent because if manganese would not have been their then sulphur would have reacted with iron, forming iron sulfide and the melting point of iron sulfide is quite low. So, it causes lower del TSA because of that effect of sulphur is quite you know perceptible when it is present at such

when manganese is not there, is manganese by sulfide issue is high like is more than 25, then this deleterious effect of sulphur is taken care of to some extent.

So, that is why we should always use manganese by sulfide issue of more than 25 to take care of the harmful effect of sulphur. But unfortunately unlike sulphur there is no alloying element which is used in steel which can take care of the deleterious effect of phosphorus. So, phosphorus as I have mentioned here that small k value is quite low, 0.23 for delta 0.123 for gamma; that means, for gamma solidification; that means, when the you know carbon or carbon equivalent is relatively high, the solidification will be through austenitic mode, in that case the segregation effect is relatively more compared to segregation happening when the solidification takes place through delta ferrite. So, in case of austenitic solidification effect of phosphorus and sulphur is more deleterious and since sulphur effect is taken care of partly by having manganese in steel.

So, we have to be careful about phosphorus because there is no other alloying element which can take care of the deleterious effect of phosphorus. So, low phosphorus is essential particularly for situation of austenitic solidification; that means, for carbon or carbon equivalent more than 0.25, 0.3, 0.4, and 0.5. So, these are the like chemistries of order you know steel compositions which we will have more amount of micro segmentation because of phosphorus.

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So, I have also mentioned the some values have been shown here some calculated values are shown here for a particular level of phosphorus is 0.4. So, if 0.4 percent phosphorus is present in steel, then how this amount of phosphorus effects the actual solidus and the effective shell thickness how is it reduced is shown in this figure.

As the carbon content increases you know as I have told you the liquidus temperature that is some decrease, you can get this from the normal phase diagram. So, this is the equilibrium solidus and this is the liquidus. Now what is the role of 0.4 percent phosphorus? At a I have mentioned here that this is at a depth of 25 millimeter from the meniscus.

So, if the casting speed is 1.5 meter per minute then at this depth; that means, corresponding to a solidification time of 1 second, this can be found out from this relationship what is the shell thickness at a time interval of 1 second. So, this value this means k value that mean solidification constant is 2 millimeter per second to the power 0.5. So, this 2 millimeter is a theoretical shell thickness this is the 2 millimeter S_m in this the theoretical shell thickness, but what is the actual shell thickness that is very important to understand.

So, that is why if you calculate what is the effect of segregation of 0.4 percent phosphorus, then we can calculate what is the c_l that remains the final concentration of phosphorus in the last liquid which is to solidify from the modified Scheil equation we can find out that, and from there we can find out what was the final you know final concentration of phosphorus in the last liquid to solidify, from there we can find out what is the actual solidus temperature. So, if you know the actual solidus temperature then we can know; what is the temperature interval. Now look at these figures at 0.1 percent carbon, you see the effect of segregation is relatively less is minimum why it is so? Because the actual segregation is less because the solidification is taking place through delta ferrite and only towards the end of you know solidification is delta ferrite to austenite transformation is taking place.

So, at 0.1 percent carbon; that means, at the start of the peritectic temperature zone at peritectic temperature chemistry at the start of that at 0.1 percent carbon or carbon equivalent, the extent of micro segregation is less because of that the actual solidus also is depressed relatively less. So, the temperature interval for solidification is also

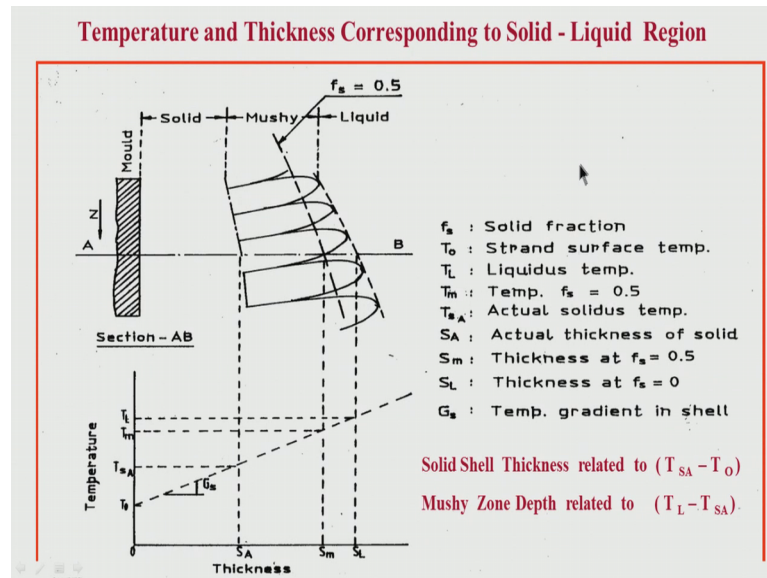
relatively less compared to a situation like say at 0.3 percent carbon when the level of segregation is more because of that actual solidus is suppressed to a large extent, and because of that the temperature interval for solidification the difference between TL and TSA this is quite wide quite large, because of this as I have mentioned the solid shell is decreasing in thickness and the mushy zone is increasing in thickness.

So, what is important is to understand here that, the solidus temperature actual solidus temperature is getting decrease due to segregation of phosphorus and the effect depends on the extent of this effect micro segregation, depends on what is the carbon or carbon equivalent in the particular steel grid. If you have a 0.1 percent carbon; that means, when we have just at the beginning of the peritectic zone if the chemistry is 0.1, if the carbon continuous 0.1 micro segregation is relatively less and the actual solidus is therefore, relatively less depressed the difference between liquidus and the actual solidus is relatively less.

So, the shell thickness is also relatively quite more, solid shell thickness. If the solid shell thickness is more the mushy zone is relatively narrow, but you look at 0.3 percent carbon, for the same amount of 0.04 percent phosphorous, here what is happening is because of austenitic solidification becoming more and more predominant has we are increasing the you know carbon content. So, segregation is also more, if the segregation is more the actual solidus also suppressed to a large extent, and because of that the temperature interval for solidification is more and consequence of this is the shell thickness is quite narrows. Actual shell thickness solid shell thickness is narrow and the mushy zone depth; that means, the thickness of the mushy zone is quite wide.

So, what is happening is with increasing carbon? Mushy zone is becoming wide and the actual solid shell thickness is becoming narrow. This has lot of implication on the strength of the solidifying strand because the strand consists of what? Strand consists of solid shell mushy zone and liquid. So, if the mushy zone is more wide during solidification, you are solid actual solid shell is narrow. So, the strength of the strand also we will be less this we have to keep in mind.

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This is what I was discussing about the thing about the relative thicknesses of the solid shell and the mushy zone, this the thicknesses depends on basically the temperature intervals. The temperature interval between the liquidus and the actual solidus; the solidification temperature range is proportional to the mushy zone depth. So, if T_{SA} that means, the actual solidus decreases due to micro segregation, then this temperature interval increases, because T_L is more or less constant, it does not vary with micro segregation, but actual solidus is varying that is what is important to remember.

So; that means, if T_s is decreasing my actual solidus is decreasing, temperature interval of solidification is increasing. So, the mushy zone depth is also relatively more in this case. And if T_s is decreasing means the temperature interval between T_{SA} and the surface temperature of the solid shell this is more or less constant this is around the data of cooling secondary cooling. So, this temperature T_{SA} decreasing means this difference is also less. Here T_{SA} decreasing which is difference is more, here T_{SA} less means this difference is less.

So, difference is less means the solid shell is becoming more narrow the thickness is much less. So, what is happening is this solid shell this thickness S_A is becoming less s a is becoming less because T_s is decreasing. As T_{SA} decreases s a also we will decrease. So, the solid shell actual thickness will be less and consequently the mushy zone. T_{SA} decreasing means T_L minus T_{SA} that is interval is increasing solidification temperature

zone is increasing, the mushy zone is increasing in depth, s coming in down means that thickness of this; that means, S_L minus S_A is increasing.

Therefore, now mushy zone is increasing in thickness.

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Strength and Toughness of Solid Shell

Solidifying shell undergoes strain during and after solidification

- Ferrostatic force from liquid during solidification
- Shrinkage due to solidification and transformation from δ to γ
- Mechanical strain due to bending and unbending of strand
- Thermal strain during secondary cooling

Solid shell (δ or γ) must have adequate strength and toughness at high temperature to withstand the different strains

Understanding of strength and toughness at 1400 – 600 C is useful to control formation of crack in solid shell

Now, I have told that; what is the implication of these. The implication is the strength of the solidifying shell if it is less means the whole solidifying you know solidifying area; that means, the whole area of the strand solidifying strand stress during continuous casting the strand is continuously under moment. So, if the strand has less strand less toughness it has lot of problem, there is a chance of crack formation. So, this is important to remember. So, let me try to mention here the solidifying shell whatever shell is forming through solidification during casting, is undergoes lot of strain during and after solidification you know. Unlike continuous casting here the relatively mode of strain will be there because it is continuously under movement it is not static.

So, what are the different strains on the solid shell? First and foremost if the ferrostatic force from the liquid during solidification, when solidification is underway there is liquid in the strand. So, this liquid we will create ferrostatic pressure on the solid shell, this shall be pushed towards the mould when you know the strand you inside the mould. So, this ferrostatic force from liquid steel during solidification is one important reason for generating strain and force on the solid shell.

Next is the shrinkage due to solidification whenever there is solidification from liquid solid is forming; whether it is delta or gamma there will be shrinkage. The extent of shrinkage is less for delta or gamma whatever it is different for delta or gamma nevertheless there will be shrinkage. So, shrinkage due to solidification is one aspect which we will generate some strain and force on the solid shell.

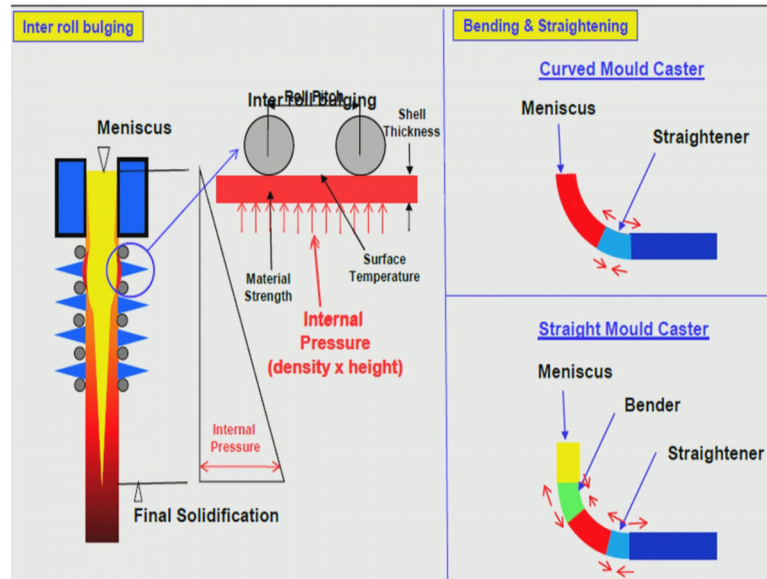
Now, I have mentioned this delta to gamma there is a possibility of transformation in for certain chemistry. Whenever initially delta is forming this delta is finally, transforming to gamma at low temperature. Now when this delta to gamma transformation takes place whether during solidification or it may be below solidification means lowered temperature than solidus or they are may not be delta to gamma transformation at all because you know there is a gamma transformation, gamma solidification.

So, there is no delta formation. That means, for carbon content or carbon equivalent more than 0.5, there will be no delta ferrite formation during solidification. So, therefore, there is initially austenite and finally, solidification takes place entirely through austenite. So, there is only austenite. So, there is no delta to gamma transformation.

So, but for certain get sub chemistry certain grids I mean chemistry where the carbon is less than 0.5. We have carbon is less than 0.1, total solidification we will take place through delta and delta to gamma transformation takes place at lower temperature; that means, lower than the solidus temperatures. So, after solidification that is transformation nevertheless there is transformation. So, this delta to gamma transformation we will also create a shrinkage and therefore, a strain because the density of delta and gamma different. So, delta to gamma transformation also creates some shrinkage and strain.

Now I have mentioned that there may be mechanical strain due to bending and unbending of strand, I think these I have mentioned earlier let me just go back to their.

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This is the curved mould caster; that means, the mould itself is curved this mould this is the mould, here the mould is indicated as a vertical you know mould.

So, the strand which is coming out from the mould is also vertical like here, is a straight mould caster like this vertical mould caster. So, the strand which is coming out of it is vertical finally, this has to be made horizontal, you know then only it is possible to cut the solid strand you know to get the different cast product of different length. So, first it has to be bend and then after sometime it has to be straightener or unbend; that means, the strand of a straight mould caster, vertical mould caster initially it has to be bend and then it has to be made straightened; that means, there has been straightener. So, during bending what is happening you look at here? This is the inner radius this portion is the called inner radius there is a inner radius of the casted, though there is a shell solid shell which has formed near the inner radius, this is subjected to some kind of stress this is the direction of the stress, ok.

So, and the solid shell which is present at the outer you know radius, it is just the reverse it is here some you know direction of the stress is here this way and the outer shell it is something just the reverse. Now what is happening during straightening? Straightening this portion of the shell is inner shell it is something it just the reverse. So, what I am trying to under tell you is that during bending and straightening the solid shell if is at inner radius it is undergoing certain strain, if it is outer radius it is going some strain of

other direction; that means, of different direction. So, both during bending and straightening there is strain on the solid shell, but if you have a curved mould; that means, the mould itself is curved that the strand is coming out in curved fashion. So, it is not necessary through bend it any longer, what is necessary after sometime is to straightened it so that it is made horizontal.

So, in case of a curved mould we have a only straightener only straightening of the strand is necessary, but in case of a straight mould we initially must have bending and then straightening. So, this is what is important to understand. So, here you just look at here, here it is a compressive force look at the direction of the arrows, here it is a tensile force here. During straightening just the reverse is happening at the internal, you know shell at the internal radius it is becoming tensile and it is the outer radius it becoming compressive straightening for curved mould only straightening no bending is there. So, the solid shell at inner radius is tensile undergoing tensile strain and solid shell at the outer radius is undergoing compressive stress or strain.

So, this is important to remember like the shell solid shell is undergoing different type of strain, you see here this is the internal pressure you have liquid here within the strand. So, this liquid is creating you know internal pressure this is called Ferrostatic pressure. So, this pressure is always coming to the solid shell which is forming. So, this is the first source of pressure or tension on the solid shell what force on the solid shell is the ferrostatic pressure. Then we have at the bender we have internal stress at the surface we have the shell at max, and this is maxima of the surface inner and outer, and as you go inside it is slightly going down.

So, at the straightener also there is again you know mechanical strain here also mechanical. So, here it is in the directions indicates whether it is compressive or tensile. So, what is important to remember, the solid shell is under continuously under different strains for different sources, ferrostatic force is one then mechanical strain from bender at the straightener. Another source, another it is due to solidification there is a strain then ΔT to γ there will be a strain. So, there are different you know possibilities of strain at different locations to we have to understand that, what are the sources of strain at what temperatures these are you know actually happening, what are the what are the implications of that, what are the causes or the consequences of that. So, we have to

remember all these aspects to finally, arrive at what is their impact on the quality of the cast that is very important.

So, while discussing the quality of the cast, that is why we have come to the role of chemistry the role of segregation because the role of segregation finally, you know impacts on the shell thickness solid shell thickness. So, that is important now as I was discussing the different you know strains I have mentioned ferrostatic force from the liquid during solidification after solidification there is no ferrostatic force. So, it is during solidification only this happens then shrinkage due to solidification this also happens during solidification.

Then shrinkage due to transformation from delta to gamma it can happen during solidification or even after solidification it may not happen at all, for certain chemistries when there is no delta formation. Then I have mentioned mechanical strain due to bending and unbending of strand unbending means straightening of strand I have given shown you the examples whether it will be tensile or you know it will be compressive, it depends on whether is the inner radius or the outer radius whether it is bending or it is straightening unbending.

Again after solidification is complete or odd even before that when the you know strand is coming out of the mould, just it has come up the mould then what is happening, there is secondary cooling. So, secondary cooling means, cooling by water on the surface of the strand or by missed cooling. So, because of that there is a thermal strain because of temperature difference because of water or now what is that called air mist; that means, the combination of air and water that is called mist this mist is impacting on the surface, though the surface has maximum cooling the inside is relatively hot. So, there is a thermal strain because of this temperature difference. So, the solid shell is also undergoing thermal strain because of this temperature differential. So, these are the difference strains which are impacting on the solid shell.

So, the shell must withstand strains then only the quality we will be if it cannot withstand strand then there will be a formation of crack, and if there is a formation of crack, then in the final solidification product, also it might be having crack at different depth at may be at the surface may be sub surface may be internal. So, these are the problems of quality these are the issues of quality we have to keep in mind. So, that is why strength and

toughness of solid shell is very important. So, solid shell whether it is delta or gamma when the solidification is through delta you have delta finally, it will transform to gamma. So, the during solidification where is delta or gamma must have adequate strength and toughness, at high temperature to withstand the different strains as I have mentioned you.

After (Refer Time: 28:05) temperature; that means, after solidification you know for all types of chemistry of steel it is austenite only, but before that high at relatively higher temperature you may have delta ferrite depending on certain chemistry. So, whether the solid shell is delta or gamma, they must have adequate strength and toughness at high temperature to which stand the difference strains why high temperature I mean these temperature range, 1400 to 600 degree, centigrade why this is important? Because you know solidification is starting maybe at temperature of slightly above 1400 degree centigrade, but solidification is complete maybe around 1400 for very low carbon grids, but at higher carbon grids solidification is complete at relatively low temperature may be 1300 may be 1250 may even come down to 1200.

But even after solidification is over the shell the solid; that means, the whole solidification is completed you have only solid shell, the solid shell is now coming down the caster the temperature is also coming down, but there is certain temperature zones I will come to it later which is relatively brittle. That means, it cannot withstand stresses or strains in those temperature regions.

So, that is why we have to be careful not only during solidification, but even at temperature lower than solidification, that is why I have mentioned this temperature range of 1400 to 600 centigrade. In these temperature ranges we have to be careful we should know what is the strength and toughness of the solid shell whether it can withstand the stress or strain which is continuously forming during solidification and event subsequent to solidification during secondary cooling.

So, we have to be careful about that. So, these issues are important for controlling formation of crack in solid shell. If you can control formation of crack we will have a relatively good quality of solid shell the cast product we will be relatively good. We need not worry about it during subsequent processing of it.