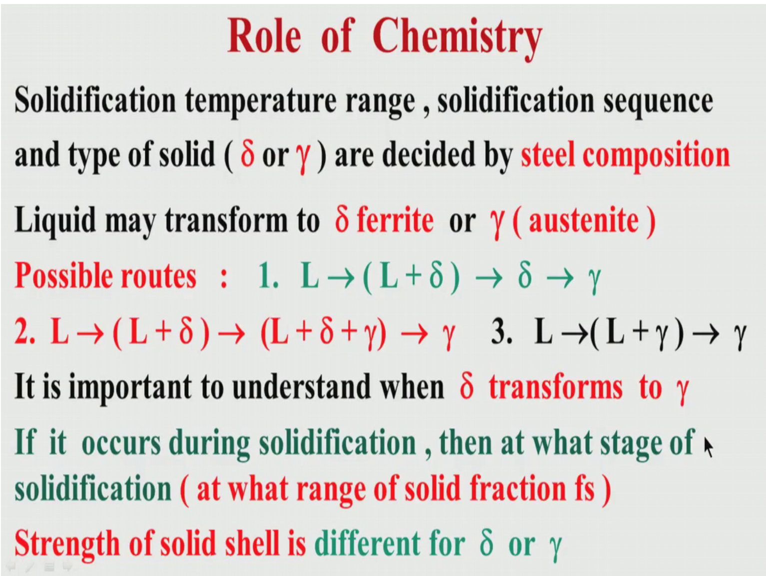
Steel Quality Role of Secondary Refining and Continuous Casting
Dr. Santanu Kr Ray
Department of Mechanical Engineering
Indian Institute of Technology, Madras

Module - 05
Lecture - 28
Role of Segregation: Part I

Good morning. Last session I talk about the role of chemistry of a steel grade, how does it affect quality? So, understand that I have talked about the mode of solidification, the sequence of solidification, which takes place when the particular steel grade comes during solidification comes from liquid to solid state. I have mentioned that you know the solidification sequence can be of 2 types, is a delta or gamma or something in between, this is decided by the steel composition.

(Refer Slide Time: 00:41)



Now, liquid may transform either to delta ferrite or to austenite gamma. So, the possible routes are liquid going through liquid plus delta to delta, and finally gamma. Another route may be liquid going to liquid plus delta, then liquid plus delta plus gamma; that means, in the liquid steel itself through peritective gamma transformation is starting, and then finally will become total solid austenite.

Another sequence may be liquid going to liquid plus gamma; that means, there is no delta. And finally, going to solid gamma. It is important to remember that finally, let us speak of the chemistry the solid this thing solid type is austenite. Whether we go through delta mode delta plus gamma mode or gamma mode of solidification finally, we have austenite, but how liquid to austenite transformation takes place to different stages that is what is important.

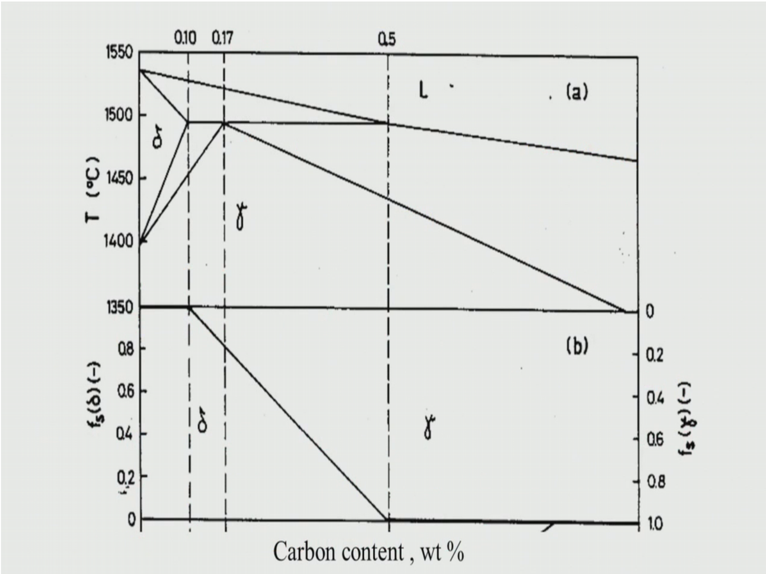
So, there are 3 possible routes depending on the carbon equivalent for you know, low alloy steels or plane carbon steels, and for you know stainless steels again the routes are similar, but the criteria there is nickel equivalent by chromium equivalent and not carbon equivalent.

So, it is important to understand when delta transforms to gamma, here you see particularly for this 2 and 3, delta rather in 2 delta liquid is becoming liquid plus delta, delta ferrite, and then liquid plus delta ferrite is partly getting transferred to gamma through the peritectic reaction.

Now, this is important I have mentioned, it is important to understand when delta transforms to gamma during solidification. This route there is no delta to gamma transformation during solidification. Here also there is no delta transformation only liquid going to liquid plus austenite and then finally, austenite. So, delta to gamma transformation in the course of solidification; that means, from liquid to delta and delta to gamma in liquid stage itself, to express only in the medium range of chemistry. So, there it is important to know when this delta is transforming to gamma, at what state of solidification this transformation is possible, this is very important.

So, then I have mentioned that what stage of solidification; that means, at what range of solid fraction fs this is very important, because why this is important? Because the strength of solid shell is different from delta to gamma. So, the sequence of solidification is important to understand what is the strength of the solid shell, what is the you know ductility of the percentage area reduction of the solid shell during solidification this is very important.

(Refer Slide Time: 03:58)



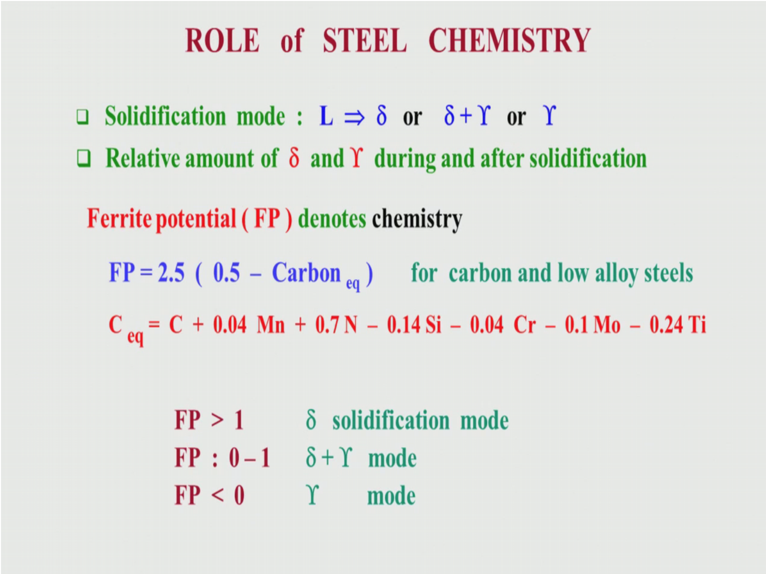
Then basically I talked about here from the iron carbon diagram high temperature portion, that when the carbon or carbon equivalent is less than 0.1 this is plane carbon iron carbon diagram or plane carbon steel. Here we have carbon content allowing the x axis, but if you have a you know low alloy steel where instead of carbon, carbon equivalent is important, which I have talked about I will discuss today also what is the formula for carbon equivalent, how it is determined from the chemistry; that means, from carbon from silicon manganese you know, other alloying elements. So, all this will finally, chromium this will finally, determine what is the carbon equivalently in low alloy steels.

So, if it is less than 0.1 the solidification takes place through delta only. If the you know carbon equivalent is between 0.1 to 0.5, this is the range it is delta plus gamma; that means, initially from liquid delta will form and then there is a peritectic transformation liquid plus delta giving rise to gamma; that means, in the stage in the sequence of solidification itself delta will transform to gamma.

Now, the question is depending on the chemistry it is important to know, at what stage this delta to gamma transformation is taking place. Whether at the early stage of solidification or towards the final stage of solidification, that is very important.

Now, when the you know carbon equivalent is more than 0.5, solidification takes place liquid to liquid plus gamma, and then to only gamma so; that means, there is no delta during any course of solidification, any stage of solidification. So, this is important that how chemistry is playing a role in identifying what are the solid phases, what are the sequence or formation of delta or gamma during the course of solidification.

(Refer Slide Time: 06:05)



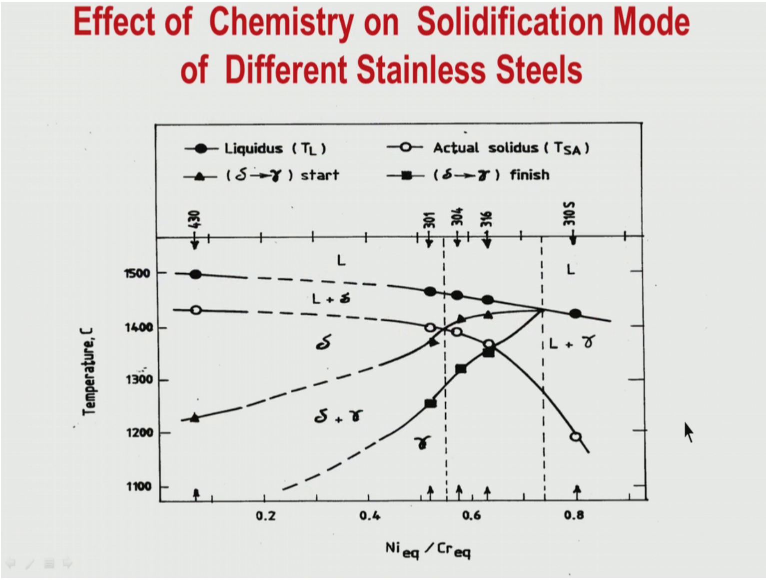
Ah then I have talked about the modes whether liquid to delta or liquid to delta plus gamma or liquid to gamma there can be 3 possibilities, it depends on the carbon equivalent. And the relative amount of delta and gamma during and after solidification this is also determined by the chemistry; that means, carbon equivalent.

And I have talked about the concept called ferrite potential which is given by this formula 2.5 into 0.5 minus carbon equivalent, for carbon and low alloy steels the carbon equivalent can be found out empirically through relationship, this has emerged after lot of experimentation done by many metallurgists.

So, from the chemistry one can understand whether it will be delta solidification mode, delta plus gamma or gamma mode. When the carbon equivalent is less than 0.1 you see no gamma formation takes place it is only liquid plus delta and delta to, after solidification only delta to gamma takes place. So, during solidification only liquid to delta.

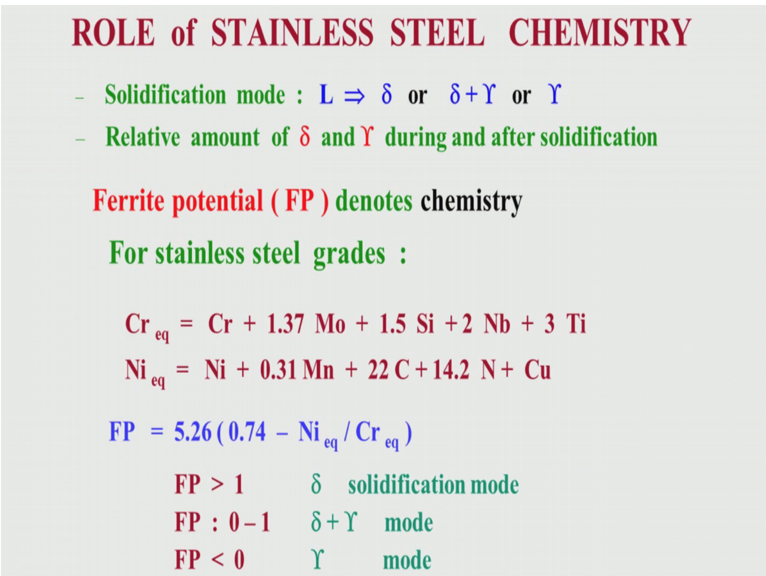
When carbon equivalent is between 0.1 to 0.5. So, ferrite potential is between 0 to 1, for this ranges of chemistry the solidification mode is delta plus gamma; that means, initially delta is forming and then finally, delta plus gamma is forming and finally, during solidification finally, only gamma solid gamma is here. So, if the chemistry or the carbon equivalent is more than 0.5, look at this more than 0.5 means this becomes negative, ferrite potential is less than 0. Then the solidification sequence or mode is only austenite, there is no delta formation.

(Refer Slide Time: 08:03)



Then I talked about that in stainless steel, this carbon equivalent is of no consequence. This cannot determine you know, what is the mode of solidification.

(Refer Slide Time: 08:19)



So, there what is important is the ratio of chromium equivalent sorry, ratio of nickel equivalent by chromium. Equivalent nickel equivalent is basically all alloying elements which are similar to nickel in you know making the stainless steel austenitic; that means, austenite stabilizer these elements like nickel, manganese, carbon, nitrogen, copper these stabilizes the gamma austenite phase. So, we can find out nickel equivalent from this empirical relation, where all these manganese, carbon, nitrogen, copper are austenite stabilizers. So, they are club together along with nickel in determining the nickel equivalent.

Similarly, chromium equivalent consists of chromium this is the ferrite stabilizer, delta ferrite stabilizer or moly, silicon, niobium, titanium. All these elements are ferrite stabilizers. So, these are been clubbed together along with chromium and finally, chromium equivalent we can determine by this empirical formula.

So, if you know nickel equivalent by chromium equivalent, from this relationship you can determine what is the ferrite potential you know, unlike for plane carbon and look low alloy steels their carbon equivalent is a criteria in determining the solidification mode. Here since you have lot of chromium, lot of nickel, lot of other alloying elements so, carbon equivalent is of no consequence.

In stainless steel, here the ratio of nickel equivalent by chromium equivalent is important, that determines what will be the solidification mode. Whether it is delta, delta plus gamma, or gamma. So, the ranges are basically 0.55 to 0.74 these are the ranges. As you can see from this figure, if nickel equivalent by chromium equivalent is less than point, look at here is 0.5. So, this is around yeah 0.55 around that yeah. So, if it is less than 0.55 look at that transformation liquid to liquid plus delta then delta. And delta to gamma is basically a solid state transformation. So, during solidification there is no gamma.

Now, when we go to a nickel equivalent by chromium equivalent or more than 0.74, this dotted line 0.74. From liquid it goes to liquid plus gamma; that means, austenite and then finally, solid austenite there is no delta ferrite for this range of chemistry that have done 0.74 nickel equivalent by chromium equivalent.

When nickel equivalent by chromium equivalent ratio is between 0.55 and 0.74, then look at what is happening. Initially liquid comes to liquid plus delta ferrite, and then these temperature this triangles not that is triangle delta to gamma transformation taking place at this points.

So, as the nickel equivalent by chromium equivalent is increasing, the delta to you know austenite transformation is the temperature is also increasing, and they are taking place at a relatively lower solid fraction; that means, from delta austenite is becoming more and more stable. So, delta to gamma transformation is taking place relatively, all in the solidification stage.

So, if you look at the figure of say 304, you know stainless steel is a very common stainless steel. Here what is happening? Initially liquid then liquid plus delta and this delta to gamma transformation is taking place quiet at advance stage of solidification; that means, when say delta to gamma; that means, the solid fraction is around say 0.5 or 0.9, then only this gamma transformation is starting. This has lot of implication on the toughness of the you know strand. So, this is this will come to discuss subsequently. So, what is important to understand, is at what solid fraction delta to gamma is taking place. At what stage of solidification delta to gamma is taking place.

Now, you look at the you know 301 stainless steel, where nickel equivalent chromium equivalent is less than 0.55 may be it is 0.5, 2.53. So, here what is happening? Look at here, initially liquid then liquid plus delta and then solidification is complete then also it is just delta. So, gamma has not started solidifying, started forming during solidification, which has started you know forming only after solidification is complete.

So, delta to gamma transformation is a solid state transformation here and not during solidification. So, 301 here again 430, these are equivalent as far as the solidification sequence is concerned. Liquid to liquid plus delta and then solidification is complete there is no gamma.

Here gamma since it is very you know low in nickel equivalent chromium equivalent; that means, chromium equivalent is very high, nickel equivalent is low 430 that delta to gamma solid state transformation takes place at you know quite low temperature is around may be 1220 or 1230 here. And the solidification is complete at say 1420.

So, for quiet sometime. So, for our 200 degree centigrade, only delta is present at solid phase, delta to gamma takes place on the below this temperature; that means, during cooling of the strand, you know at the time of continuous casting and after solidification we have only delta, and gamma is taking place at quiet low temperature; that means, delta will be grains are available dendrites are available and it is possible that they will be some grain growth because, you know when austenite forms at the grain boundaries of the delta then only there is a illuviation of the grain growth in solid state.

So, this is very important to understand, at what stage delta gamma is taking place. Whether during solidification if during solidification at what stage like 304 at the final stage almost at the final stage of the solidification. But if you look at 316, it takes place when the solid fraction is maybe it is a 0.3, 0.3, 5.4. So, it is called early during solidification delta to gamma is transformation is taking place.

310 as initially liquid, liquid plus gamma and then solid gamma. So, no trace of delta ferrite, as I have told you beyond ratio of nickel equivalent or chromium equivalent of 0.74, it is this only gamma transformation during solidification liquid to gamma only, no austenite. So, every grade if you know the chemistry you can find out, what is the solidification sequence so, this is very important.

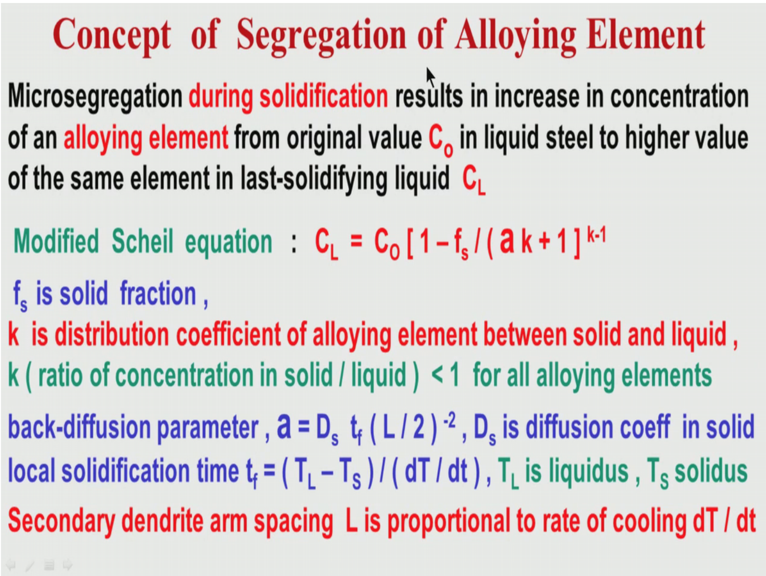
So, as I mentioned that you know depending on the chemistry you can find out nickel equivalent by chromium equivalent. More is high is the nickel equivalent, let it to chromium equivalent. So, more will be the gamma solidification tendency. Less is the nickel equivalent it will be delta solidification more; that means, more ferritic solidification. And higher the nickel equivalent by chromium equivalent more than 0.74 it will be austenitic solidification, gamma solidification.

So, this is important to remember that chemistry plays a very play an very important role in identifying the solidification sequence, whether it takes place through delta or delta plus gamma or gamma that is austenite. So, this is very important to remember.

Now, let me talk about the concept of segregation of alloying element. This you know in every preliminary fashion I have discussed earlier, that during solidification all alloying elements steel is basically an alloy of iron and other elements other alloying elements like carbon, 3 may be 3 may be silicon there may be manganese, there may be you know, chromium there may be nickel, phosphorous, sulphur all sorts of alloying element; that means, solids are there you know in the solution. So, it depends what are the alloying elements are there? You know, but one thing is common that during solidification the solid has less amount of these alloying elements. The liquid becomes slowly more rich and more rich in the solute elements this is called segregation.

Segregation means the solute alloying elements are segregating; that means, they are preferentially moving from solid to liquid, they are segregating they are preferentially going from solid to liquid. So, this is called segregation, there is a partition, there is a diffusion, there is a you know, movement of alloying elements from liquid to solid. Just the reverse from solid to liquid, the liquid is more rich in the aluminum yes it becomes more and more rich.

(Refer Slide Time: 19:13)



So, micro segregation during solidification they results in increase in concentration of an alloying element. Except iron all other alloying elements will undergo this you know segregation. So, all alloying elements from the if the original value is C 0 in liquid steel.

Suppose say we are taking we have taken a steel, where the carbon concentration is say 0.1. Now during the original value; that means, C 0 for any alloying elements say carbon further, let us assume this 0.1. So, initially the liquid has after solidification the liquid after liquid you know, after it has become liquid; that means, when you heat it up it becomes liquid. So, liquid steel the concentration of initial concentration C 0 of that particular alloying element, say carbon it can be silicon, manganese, phosphorous anything, sulphur. So, that is C 0. So, during solidification the value of you know carbon in the liquid increases, and the value of carbon in solid decreases.

So, the last solidifying liquid if it becomes if we denote it as C l, it is much higher compare to C 0, and this is can be formed out from the modified shell equation. Shell was the first who try to find out how you know the concentration will increase during micro segregation, during the course of solidification.

So, and finally, original shell equation was modified and that (Refer Time: 20:55) and then it becomes a modified shell equation, here just look at what are the factors, C 0 is the initial concentration of the alloying element. C L is the concentration of that particular element in the last solidifying liquid C l. So, if there is a increase from C 0 to C l, now C L it has increased from C 0 how it is related it is related by the solid fraction fs small case, the distribution coefficient of alloying elements between solid and liquid. This k is a thermo dynamic entity it depends on the you know particular phase diagram any phase say iron carbon if you look at plane iron and carbon you can find out what is the what is the value of k at different temperature; that means, the ratio of solubility of carbon in liquid in solid divided by liquid; that means, k is always since the solubility in solid it is less than the solubility liquid. So, k is always less than 1.

So, this k distribution coefficient of alloying element if it is solid and liquid is the ratio of concentration in solid divided by liquid it is always less than 1, for all alloying elements. Now this small a these are back diffusion parameter; that means, whatever alloying element is there in the solid you know. So, it will try to be with the solid which is forming later on during solidification it is rich in relatively rich in the alloying element compared to the solid which has formed earlier. And moreover the liquid is also having more of that alloying element. So, there is a possibility of you know back diffusion in the solid.

So, this is determined by this back diffusion a is determined by the D as their diffusion coefficient in solid t f is the local solidification time; that means, time taken for local solidification. So, it again depends on you know the temperature difference between the liquidus and solidus and the rate of solidification T L is the liquidus T S is the solidus; that means, the temperature difference between liquidus and solidus, divided by the rate of cooling local rate of cooling at the particular you know particular distance particular time of solidification.

So, this given gives the local solidification time, and L, you know is the secondary dendrite arm spacing. This L is again proportional to the rate of cooling, because this secondary dendrites arm spacing gives the size or indicate the size of the solid dendrite. So, thicker the dendrites are the diffusion will take more time. So, it becomes it takes long time for diffusion to take place. So, that is why secondary dendrite arm spacing L is important you know, diffusivity D s is important, diffusion coefficient you know local solidification time is important because mode is this difference mode will be the solidification time it of course, depends on the rate of solidification.

So, with all this factors it is possible to find out C L with respect to C 0. C L is always more than C 0; that means, due to the small value of k C L becomes more and more rich in that particular solute. So, please try to understand the segregation of alloying elements will make the concentration of that particular element in the last you know, liquid which is solidifying more rich compare to the original value, and because of this we call it segregation.

So, the last liquid which is which will finally, solidify it is relatively more rich in the solutes this is this is 2 for all solutes carbon, manganese, silicon, phosphorous, sulphur. Now to what extent, you know, the segregation will take place depend on this value of k will come to it more is the segregation means lower is the small k, because k is basically the ratio of solid by liquid ratio of concentration in solid by liquid for a particular element, it is always less than 1.

So, suppose small k is 0.1 for particular element; that means, the liquid is becoming more and more rich in that particular element. Compare to the original concentration and take another element where k is a 0.8. So, it is relatively les segregation, you will have less segregation of that particular element. So, lower is the value of k more is the segregation, then liquid will become more rich in that particular element. So, the final solidus temperature will become more suppressed. So, the difference between liquidus and solid become more wide. So, this has segregation has lot of implications during solidifications.

What are the implications? As I have told you lower the value of k more is the segregation. So, those element alloying elements whose small k; that means, the segregation ratio or the you know distribution coefficient is quiet low, those elements will create more segregation, more segregation means the concentration is of the final liquid which is solidifying is quiet rich much more rich compare to the original value. So, what is going to happen more amount of segregation, and the because of the segregation the solidus temperature is getting more and more low. So, the temperature interval for solidification, temperature interval between liquidus and solidus, this solidus is becoming more and more low as you know k is low. More low is k T S will become more low, this I will discuss in details subsequently. So, we will come to know what are the implications of segregation. So, please try to remember segregation is a factor for all alloying elements. It is a question of whether it is relatively more or less.

Now, another important thing is segregation is not equal, when solidification is taking place between delta and gamma or gamma. If it is through delta segregation amount of segregation is something, if the solidification mode is through gamma for that particular element alloying element you know, the k value; that means, the extent of segregation may be different. So, we have to know what is the k value for delta segregation delta solidification, what is the k value of that particular element alloying element for gamma solidification. So, lower is the k value, more is the problem of segregation, more is the suppression of liquidus temperature. So, you have to keep in mind what are the implications of these. So, this will be becoming more and more clear as I go ahead with this concept.