

Theory of Production Processes
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Lecture - 03
Solidification of Pure Metals and Alloys

Welcome to the lecture on solidification of pure metals and alloys. So, in the last class, we had discussed about the concept of solidification, the principles behind solidification, why solidification occurs? How it occurs? How it progresses? So, through the mechanism of nucleation and growth, as we know that there will be birth of tiny grains, tiny nucleus, I mean nucleus and then that becomes stable under certain conditions of temperature, thermal conditions. And further depending upon further conditions of growth, the nuclei further get added, atoms are getting added to the first atom and then this is how you get the grains.

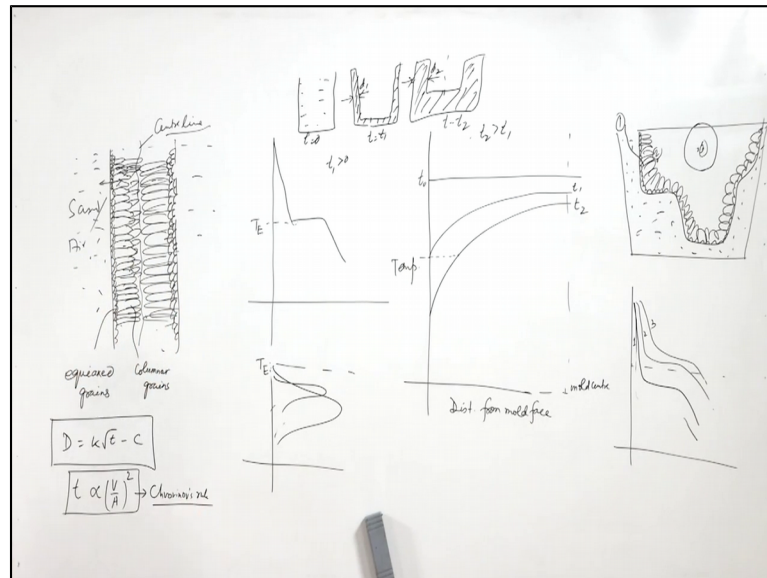
So, since you have the domain and you have the nucleus and at many points. So, anyway at every point, you have the nucleation of new grain and then that grain develops to its size and then from other sides also the grains are coming. So, anyway, they are basically approaching each other and then they will have one common surface, that is the grain boundary. So, this is how the grains are formed. So, you can refer to the books of phase transformation of materials. There are many standard books, which talks in deep about this nucleation and growth concept that how nucleus and what is the rate of nucleation? How the rate of growth varies? What are the concepts?

So, that you can study; let us discuss about its use and how we can further interpret it for the solidification of pure metals and alloys. So, as we discussed that in the case of pure metals. So, pure metals whenever we have purity, whenever the metal is pure, pure means most of the pure metals.

They will freeze at a common temperature, at a fixed temperature. So, that is how we define pure metals and if they are not solidifying at a fixed temperature then they are the example of alloys. Now in the case of pure metals what happens that, when the temperature at any point will basically come to the equilibrium temperature, when we pour, when we are pouring, basically the temperature is higher than the solidification temperature, or the temperature at which it freezes.

So, once it reaches there in that case with slight under cooling, there will be solidification and then there will be latent heat release. So, once you have latent heat release, then that will basically be transferred to both the sides and this is how the since it is transferring the heat to another side.

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So, as we see that once you have the liquid in this liquid touching this boundary and here everywhere is liquid basically; all is liquid. So, once it touches this boundary and in that case if it is there, is a heterogeneous nucleation condition and it is practically that, whenever we cast any material. So, in that case if this is the mold wall, it is at lower temperature and it has many sites, where the nucleation starts.

So, if the nucleation starts here and largest under cooling is felt here. So, you will have that we have discussed that, you have initial solidification happening here and since, because as we know that when we, if you look at the cooling curve of pure metals. So, once you have reached this temperature and there is slight decrease in temperature from this position then there will be formation of tiny grains and that is nucleus.

So, once they are transferring the heat, they are transferring the heat in this direction as well as in this direction. So, this side is the sand or air; so, this is your sand or you can have air or so, whatever it is; Now so heat will be transferred to this direction as well as in this direction. So, that heat is nothing, but the latent heat super heat has already been released up to this

point. So, this is the theory of super heat and this is already released up to this point. Now, once you come here, then in that case the latent heat, which is released.

Now, this latent heat once it goes to this direction, the immediate liquid which is there, it's under cooling is reduced. So, anyway because of these conditions there will be under cooling going on there will be basically drop of temperature going on; now in that case what happens? So, suppose nucleation will start in the whole domain if whole domain temperature is coming near to the equilibrium temperature, but that does not become the case. Basically wherever there is largest under cooling certainly the temperature will fall more rapidly at this place and the time will come first only at that place where that temperature comes equal to the equilibrium temperature.

So, this is your melting temperature or equilibrium temperature; now what we discussed, that from here, once the heat goes into this direction whatever under cooling, this reason might have experienced this under cooling, basically is reduced. Suppose, this temperature is 800 degree centigrade at which the solidification has to start, Now, let us say for copper, it is 1083 degree centigrade. So, suppose at 1083 degree centigrade the nucleation has started.

So, what happens? In this zone also here the probable temperature will be close to 1085 or maybe 1084, 1086 which will basically come towards 1083. So, that it will also start solidifying, but the thing is that when heat releases in that direction, then its temperature becomes smooth. So, that under cooling which it could have experienced that is reduced. So, nucleation is not promoted here; so, once you have nucleation here.

So, certainly up to certain distance, you can experience that, because of degree of depending on the degree of under cooling or depending upon the rate of heat extraction. You can see that there will be some formation of these small tiny grains, which are spherical or which have no directionality, they are known as acquiesced grains. Now, what happens? That the heat flow is primarily going in this direction.

So, and since the under cooling experienced or that temperature drop here that basically is delayed. So, and here in this case that since it is less. So, it will be closer to the equilibrium temperature, in that case what happens; the nucleation does not remain predominant. So, in the early stages of the solidification the nucleation is predominant, but as the time progresses, because of the heat release and because of the equalization of the temperature in the remaining area, what happens that the nucleation does not remain predominant and, in fact, in

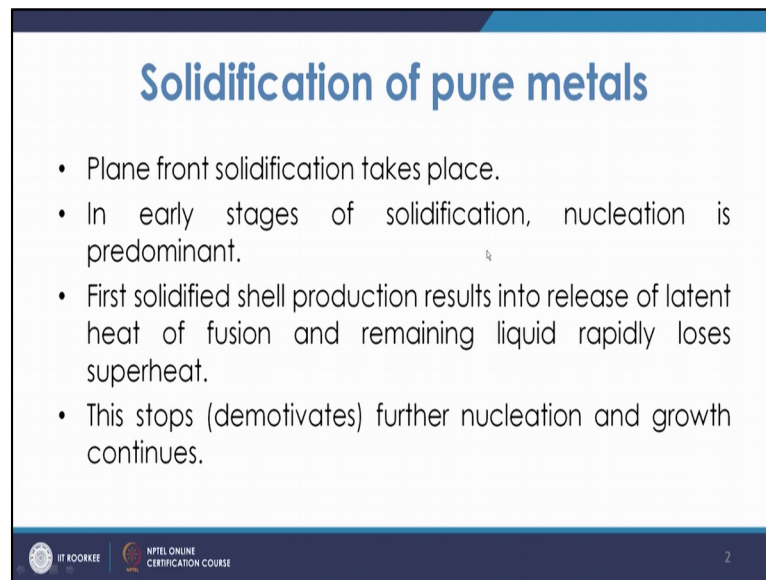
that temperature reason, the growth becomes predominant we have seen earlier by looking at; so, rate of nucleation and rate of growth was going like this. So, what we saw that if your rate of growth will be maximum towards this.

So, in that case, in the larger; so, if this is the equilibrium temperature. So, rate growth basically is predominant when the temperature is a little higher, closer to the equilibrium temperature. So, that is why then what happens; the growth starts. So, the growth of the grain starts; now, the nucleation ceases and the growth of these grains start. Now, growth of grain basically will normally take place in all the directions, depending upon the. So, basically you have growth going on in all the directions, because heat transfer may take place in every direction, but then, because this being the primary direction of heat extraction. So, primary growth is taking place in this direction.

So, this way the growth which takes place here, these are the kind of grains, they are known as columnar grains. So, initial grains are equiaxed grains and these grains are known as columnar grains. This is the typical structure of pure metals and this growth continues till the center line of the casting. So, from this side also similarly, you have the fine equiaxed grains initially, and then, so after that you will have the columnar grains extending till the center of the casting like, that you will have the structure, microstructure in the case of pure metals.

So, pure metals show like this. So, what we see in our slide that you have in early stages of solidification, that nucleation will be predominant. And the first solidified cell production that results in to release of latent heat of fusion and remaining liquid rapidly loses the super heat.

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Solidification of pure metals

- Plane front solidification takes place.
- In early stages of solidification, nucleation is predominant.
- First solidified shell production results into release of latent heat of fusion and remaining liquid rapidly loses superheat.
- This stops (demotivates) further nucleation and growth continues.

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So, that is what we see here and that since it loses it is super heat. So, the chances of further nucleation stops and the chances of growth predominate over nucleation and that is how the solidification takes place. So, what happens if you look at the temperature at any point? When you pour the liquid metal in this, at that time the temperature is, suppose, you are giving the temperature like this then what happens? So, as you see that whenever you start pouring the liquid metal into it, the immediate solidification starts at basically the mold walls. And so, if this will be the distance from mold phase, so at zero time you have this temperature.

So, at that time distance from, so, everywhere you have at the mold phase and you go suppose, in the mold center, maybe this is the mold center suppose, this line is a mold center. So, what we see is initially your temperature is everywhere the same, but then quickly as a time progresses here, the temperature comes down. So, this way you will have the temperature line slowly, after some time again, maybe that you have your growth like this. So, suppose this is your equilibrium temperature. So, this is the equilibrium temperature, in that case what we see is that, at this mold phase what you see is slowly. So, this way that at the center, you have temperature at the mold phase, that temperature is becoming quite less.

So, solidification has started here itself, at this time itself or the phase the solidification has started whereas, here in this case that is not the case, here already it is solidified and at this point the temperature; so, here at this point the solidification will start. So, this way as a time progresses you see that there will be temperature more in the central region, you will have

more temperature in the central region. So, suppose you have a casting here, in that case if this is the central region, then in that case once you pour, suppose this is a casting and this is your sand.

So, once you pour the liquid metal into it then what will happen? The first solidification will start at these places, then after that you will have start forming the columnar grains. And so, this is how what we have understood is that your initial formation will be of the acicular grains and then further. Now, if you look at this temperature, the temperature drop will be quite fast at this points, if you take this point as 1, this point as 2, and this point as 3, what we see is that normally the temperature drop, if you look at the cooling curves. Now, at the first point it will quickly down.

So, it will come and then it will go like this and similar, suppose, this is the equilibrium temperature, second point will come and then it will go like this, third will come and then they may go like that. So, this way you have the delay these results, this is the second point, and this is the third point. So, this way you have, you see that the temperature in this region is more and more, it is solidifying in the end.

So, what we see now; this kind of solidification mechanism, where you will have initially the formation of certain small thickness and then this thickness further grows slowly and this grows in a very uniform way from both the sides, the growth of these cells goes on continuously and this growth continues till these grains meet at the center. So, in this way the solidification will cease at this point, because from both the sides the solidified cells are approaching each other and they are meeting there. So, this way your solidification is complete here.

So, what happens that which time suppose, you have, this is the section, which is to be solidified, what you see is initially all is liquid and with time, what will happen that your some portion will get solidified. So, this will be solidified at certain time. So, if T is 0, it will be T_1 , T_1 is more than 0. Similarly, after some time further you will have this much solidified. So, this will be T equal to T_2 . So, here there was at 0 time, there is no solidified cell, there is some thickness of the cell that is D_1 . So, and then after at time T_2 , the solidified cell is thickness is D_2 . So, T_2 is more than T_1 .

So, this way what happens that, as the time progresses the thickness of the solidified cell goes on increasing and it is increasing in a plane wave. So, the front is moving in a plane from

both the sides, the plane that the front is moving in a planar wave in a straight line wave as you see here, that they are moving on the inner size and it will go till it reaches in the central portion. So, at certain time, it will completely solidify. So, this is an example of plane front solidification. So, what we see is that, this is a case of plane front solidification and the thickness of skin solidified. This is known as instant skin.

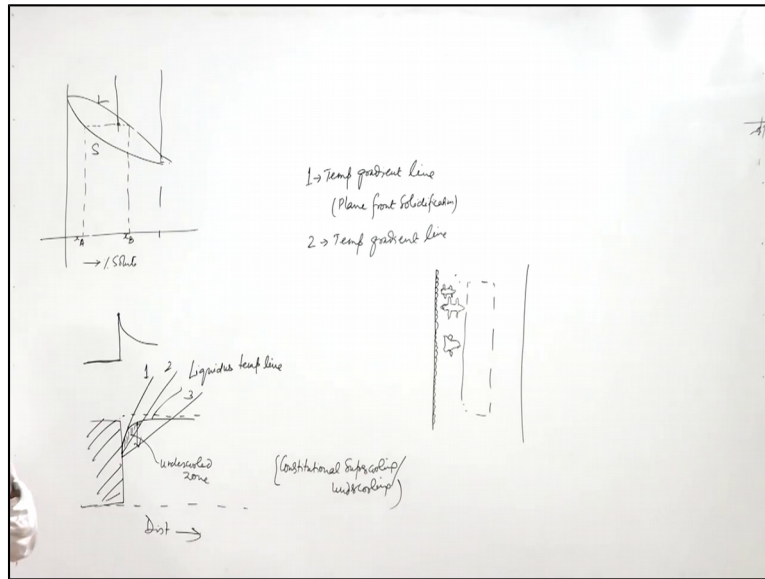
So, the skin which is from initially, you will have a very thin skin formed and slowly that thickness is basically increasing. So, the thickness of this skin solidified that will be basically depending upon the time and the formula $D = \sqrt{K(T - C)t}$, this formula tells that what will be the thickness of the cell formed at certain time.

So, K and C are constant and D is thickness of the skin. So, the K and C is magnitude, they are determined by the size of casting and how fast you are extracting the heat from the mold. So, that will be depending upon the type of the size of the casting, then type of the mold. What kind of mold material is there? So, the based on that the constant K will be depending upon and this C is largely determined by the degree of superheat.

So, this way you can find the value of the thickness, I mean thickness of the solidified cell further, if you do the analysis of the solidification time for a casting, then it has been found, you can study it and it is seen that the solidification time basically, is proportional to the square of the ratio of volume to surface area of the casting. So, that rule is known as the Chvorinov's rule. So, this is proportional to V/A^2 . So, in this case, this is known as Chvorinov's rule.

So, this is something about the solidification of pure metals, where the metal is expected that it will, it is freezing at a constant temperature or even it may apply, it will be applied in the case of eutectic materials, eutectic composition, where the freezing is carried out at a constant temperature now. So, we should discuss about what is the mechanism of solidification in case of alloys. So, as we know that in case of alloys, you have a freezing range. So, once you see the phase diagram of any binary alloy, you will have the phase diagram like this.

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So, what do you see? This is the solute percentage. So, what happens when the temperature drops the solid particle? So, any solid, which is precipitating out, this solid will have the. So, at any point you have solid as well as liquid. Now, what we see is that at this point, you will have the solid as well as the liquid. This is the concentration of the precipitating solid.

So, at this point A and this point is B, A is the point which talks about the concentration of the solid, I mean solute in the solid whereas, in the B part the concentration of the solute is different that is more. So, the liquid which is there in the adjacent region at the same time, you will have solid as well as liquid. The solid is having lower solute concentration and the liquid which is adjacent to it. It has the higher solute concentration. Now, as you see that since with the increasing concentration of the solute percentage, the liquidus line is basically what we see, this is liquidus line and this is the solidus line.

So, with the increase of the solute concentration, the liquidus line is basically going down the liquidus temperature line will be less. Now, what happens; because of that now, what we see is that if you talk about this instant, you will have solid of this solute concentration. And so, this suppose you take X A and X B solid of X A solid concentration liquid of X B solute concentration now, this sets up a temper a concentration gradient; so because of this concentration gradient, at this interface, if you take this point. So, if you have, this is the solute, solute concentration in the solid.

Now, at this point you will have this way your concentration will vary this is the concentration on this side. So, this at this point at the interface what you see that there is large.

So, at this point you have this is the concentration of solute in the solid and this is the concentration at the interface or the solute in the liquid. So, what happens because of this very high value of solute concentration in the adjacent liquid if you already you have this much of solidified layer and it has to move further in that case what happens since the solute concentration here is quite high the liquidus line or liquidus temperature will be quite low. So, this liquidus temperature will have a gradient it go like this, this is the equilibrium temperature. So, this may be the equilibrium temperature.

So, basically because of this solute concentration difference there will be another new this liquidus temperature line which is defined liquidus temperature line this liquidus temperature line is because of this is the earlier liquidus temperature line which has gone modified in this shape and because of that what happens what you see is that in this reason that this temperature is quite. So, here the liquidus temperature line has come down quite considerably.

So, this is so because now this is basically, now we let us see how the solidification will proceed in that case now if your cooling conditions are so, that you have the temperature gradient line one if you have one as the temperature gradient line if your temperature gradient goes like this because this is your solidified you know you have the distance from the mold wall and this is basically the temperature now in that case what happens if this is. So, if you have this is as the temperature gradient line and if it does not it goes past this liquidus this gradient line is concentration gradient line in that case you will have a plane front solidification.

So, what you see is that the temperature is near the liquidus at this solid cell and that is why slowly the temperature will I mean through d the temperature will come down and the nucleation will start and there will be plane front solidification. Now this is a very high kind of heat extract some rate. So, normally that is not achieved. So, what happens you are practically you suppose get this number 2 if 2 is the temperature gradient line what you see that in the case of two you will have this reason which has the temperature lower than the liquidus temperature and this zone is said to be under cool zone and this zone has become

under cooled, because of the change in the solute concentration. So, that is why and that is why this phenomena is known as constitutional super cooling or under cooling.

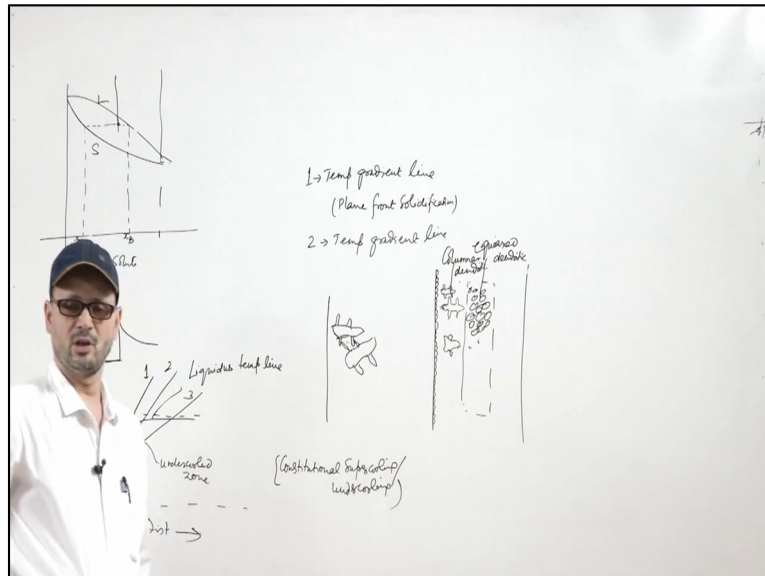
So, since this under cooling is experienced, because of the change in the concentration. So, that is why constituents percentage or so, or concentration of the solute. So, that is why this is known as the constitutional under cooling and this is prevalent, whenever we talk about the solidification of alloys. Now, if we see that if the solidification, I mean temperature gradient line goes like this even 3.

So, basically here, it becomes even large enough. In this case, this is the degree of under cooling, that it experiences. So in fact, in that case the temperature differential is low enough to promote the random nucleus. Now, what happens, because of this how the structure develops? So, in the case of alloys what happens? Now, in the case of alloys as we see that whenever the liquid metal will be poured, then the first certainly, because there is large under cooling here. So, you can have this very small equiaxed grains here, but the thing is that slowly. Now, in that case you develop, now in this case what happens, because of this under cooling, what we see is that in the zone, somewhere you have the formation of a spike and also there will be growth even in lateral directions.

So, what happens from that solidified cell itself in the near zone, in the liquid zone itself? You will have the formation of such spikes type of structure or arm type of structure tree, like structure. So, this type of structure, which is formed, they are known as dendritic structure. This is all happening, because of this under cooled zone. So, in this case, you will have many places, you will have these kind of spikes or tree like structure.

So, this way it goes; so, you will have this is known as and you will have the growth columnar grains, but then you will have the formation of these spikes or dendrites. So, that is known as columnar dendritic structure. Now, what happens in the middle zone? Now, in the middle zone, where it becomes the under cooling is, because the cooling rate becomes even slow as we know that as we go towards the center portion, the cooling rate becomes even slow. So, this differential becomes even more. So, that is why here you get again the equiaxed type of structure.

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So, this will be the equiaxed dendritic and this is columnar dendritic. So, what happens? So, if you have the wall here, you will have this kind of; so this is a primary dendrite and these are the secondary arms, what happens? The situation, this is very much deleterious, because when you have such dendrites suppose, you have another dendrite, whose arm has gone like this or so.

Now, what happens if the liquid is entrapped in between these arms, then this liquid is basically the source of shrinkage defect, because there is no plane front solidification. It is a case of the tree like structure formation and in between the arms, there may be trap meant of liquid steel, liquid material and that may be the source of some defect. So, that is a case of dendritic type of solidification. So, what we see here is that, when there is freezing range of solidification, precipitating solid differs in composition from liquid.

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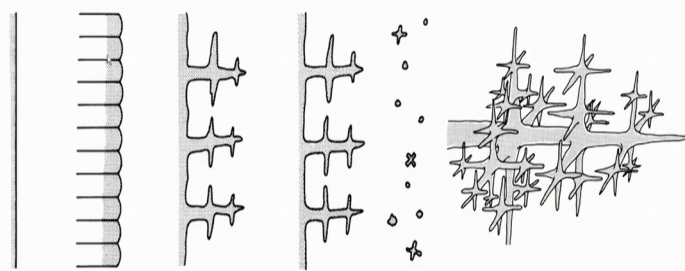
Solidification of alloys

- When there is freezing range of solidification, precipitating solid differs in composition from liquid.
- A concentration gradient is set up immediately ahead of the solid liquid interface.
- Depending upon the steepness of temperature gradient line (with respect to the liquidus temperature line),
 - There may be plane front solidification or
 - There may be undercooling ahead of advancing front, known as constitutional supercooling/undercooling.

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And then concentration gradient is set up and depending upon that you may have plane front solidification. When you have this condition, you will have under cooling ahead of the advancing front and that will be constitutional super cooling and then that promotes the promotion of growth, of a sort of spikes extending into the liquid and in the central zone basically, you will have the formation of the equiaxed type of structures and what you see here, this is how the dendrites move. And then you will have formation of the dendritic structure in case of alloys.

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Dendritic growth

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