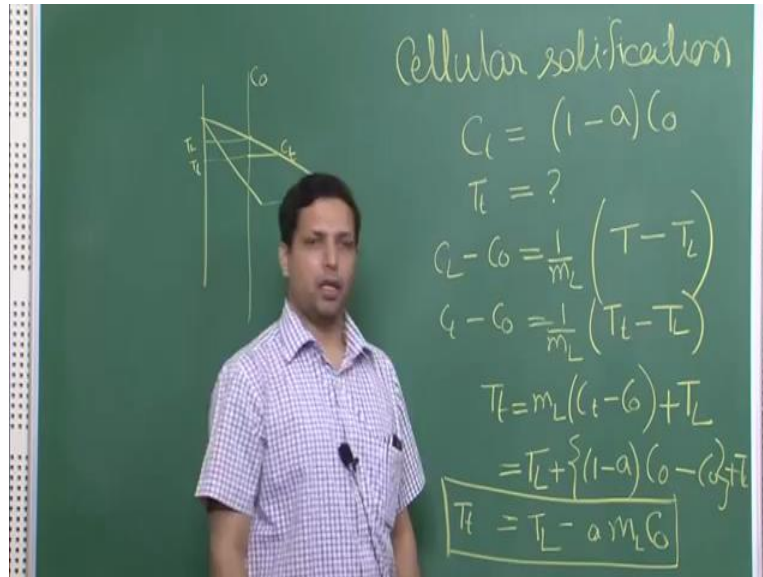


Fundamentals of Materials Processing (Part-1)
Professor Shashank Shekhar
Department of Materials Science and Engineering
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Lecture Number 22
Cellular Solidification of Single Phase Alloy (Continued)

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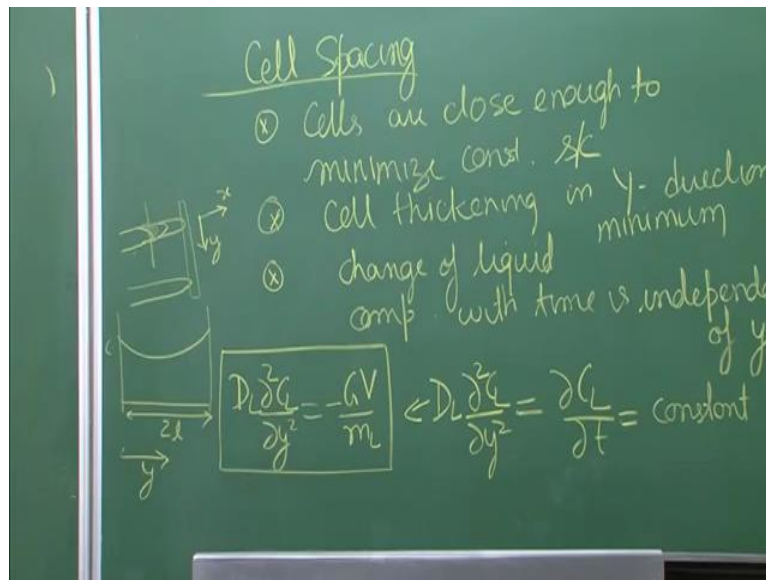
So we were looking at cellular solidification in single phase alloys. And in the previous lecture, we obtained the relation, what is the concentration at the tip of the cells that have formed, and we found it is of the form $1 - a C_0$. So this is one aspect of cellular solidification; another aspect we wanted to explore was cell spacing. But even before that, why not let us try to find out if we know the concentration of the tip, what is the concentration, composition concentration at the tip of the cell, why not also find the temperature corresponding to that? That is T_t . So how do we find?

So, before we get to cell spacing, let us try to find out what will be T_t . So how do we start with or how do we go about it? Well, it is not very difficult. We have the simple relation that we know. From the phase diagram, we can get a slope and we have already assumed a straight line so the slope is constant, and this is given by m_L ; so composition at any point given by C_L in the liquidus plot, and this is C_0 , which is the given composition, it will be related to T , which is the temperature at that particular composition, and T_L , which is the liquidus temperature corresponding to that.

So this is our C_0 , this is what we are calling as T_L , and let us say this is some temperature T and this is the composition, this is the composition over here as C_L . So this is how C_L and T_L are related. C_L , T_L and T are related. Now what we need is we need the we know the composition; at the tip we want to know temperature at the tip. So, we will replace this C_L by T_t , C_t . So this becomes; so this is the temperature, so this becomes our; let us say this is the composition at the tip, so this becomes C_t and the corresponding temperature T_t that we are interested in finding, and so it now is just a matter of algebra; we can rearrange it to get the relation T_t equal to mL ; C_t is equal to 1 minus a C_0 , so we will put this over here, and therefore T in terms of a , this becomes $T_{liquidus}$ minus a $mL C_0$.

So, we can find out not only the composition at the tip, but also what will be the corresponding liquidus temperature at that particular point. So now we have a lot more information about the cell.

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Next thing that we are interested in looking at is 'cell spacing'. One important assumption that is always made and it is justified by experiments is that whenever you have a cell type of growth, cellular growth, then composition concentration in between the cells tries to minimize itself. Why is that? It does that so as to avoid dendritic growth. So the cells are themselves trying to adjust the distance which, minimize the distance so as to super-cooling as low as possible. So

that is one thing about the cellular growth that it tries to minimize the spacing and hence the constitutional super-cooling.

So let us write a few important facts about this. So cells are close enough for to adjust the distance to be close enough to minimize constitutional super-cooling. SC I mean I refer to as super-cooling. So they are trying to minimize the super-cooling. Another aspect is that when we are assuming the growth of cell, we are assuming that cells will be growing mostly along this longitudinal direction. So, whatever concentration difference you see, it is because of the growth of the tip along this direction; so if you look at the several layers that are over here, because of this there will be composition difference in the cell, but it is not because the cells are growing in this direction; no, that is not the case. Cells can be assumed to be growing only along the direction of solidification, and there is, you can assume minimal growth in the lateral directions. So that is how the cell growth is taking place.

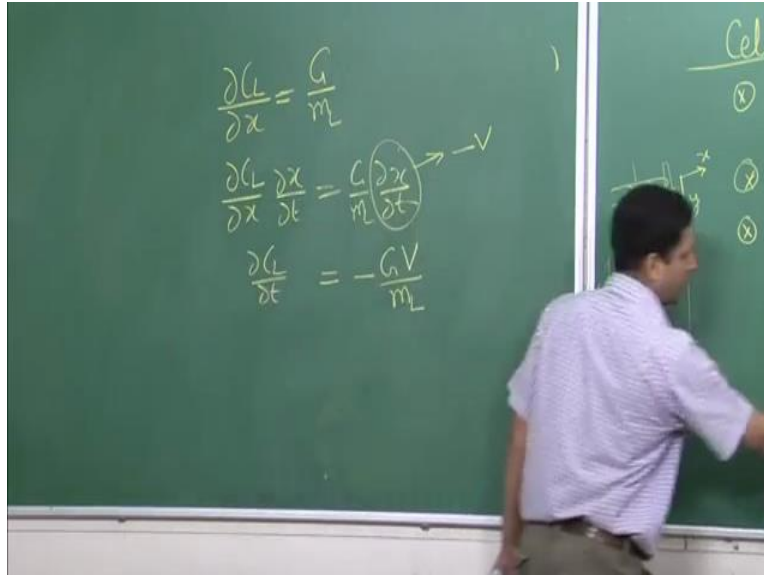
So we can say the cell thickening in y-direction is minimum. Another aspect about this; so if there are two cells like this, we have already seen if you look at the concentration distribution like in this, it is like this. So this is concentration, this is the $2l$ distance; so concentration drops a little bit somewhere in between, and then again picks up. So this is high over here at the ends and a little lower. And this is the composition difference which is what will determine, what will, how much will be the constitutional super-cooling.

So that part, it will try to minimize; we will see how when we get to the equation. But before that, what we need to understand is that the composition difference, the the composition variation with time can be assumed to be constant with y . So whether you are taking composition change at this point or this point or this point; this is y -direction by the way. So let us say this is y . So if we are looking in this schematic, this is y , this is x ; so x is the direction which the total solidification is taking place, and y is the direction transverse to it. So if we take the composition variation with respect to time in the liquid in between this inter-cellular region, then with time, the change at any particular point is independent of y . So that is how it is (())(08:00).

So we can say change of liquid composition. Now this fact can also be put in terms of equation, and how will that come out to be? This will come out like this. So $\frac{dC_L}{dt}$ is equal to constant, no matter what why you are looking at. So that is how we can put this. So this is our,

you can say starting equation, from here we will try to get some in-depth information about our cell spacing. So let us move onto trying to get to this solve this equation, and keeping in mind our geometry which is given over here.

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Now we know that $\frac{\partial CL}{\partial x}$ from the previous, if you look in the previous lecture or may perhaps previous to that, we found that $\frac{\partial CL}{\partial x}$ is equal to m_L . So now if we say $\frac{\partial CL}{\partial x}$ and multiply it by $\frac{\partial x}{\partial t}$; so this becomes $\frac{\partial CL}{\partial t}$, and $\frac{\partial x}{\partial t}$, if you are looking from the reference frame of the interface, then this quantity is actually minus V . Remember with respect to the reference frame, this is minus V . So, and you can see, this is a constant as we had said as we had written over there. So $\frac{\partial CL}{\partial t}$ comes out to be a constant minus $\frac{G V}{m_L}$, and therefore we can put it in this equation now.

So this equation turns to; I forgot to put that 2 over here. So we have an equation like this. Now, this is, so we have simplified this equation to this point; now let us solve this. Once we have this equation, let us. So how do we solve it? We will try to integrate it.

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$$|\Delta C_{\max}| = \frac{GVl^2}{2m_1D_L}$$

$$\Delta T_{\max} = \Delta C \times m_1$$

$$\frac{GVl^2}{2m_1D_L} = \text{const}$$

$$(GV)(l) = \text{const}$$

$$GV \Rightarrow l$$

$$D_L \frac{d^2C}{dy^2} = -\frac{GV}{m_2}$$

$$\frac{dC}{dy} = -\frac{GV}{Dm_2} + C$$

$$\frac{dC}{dy} = \frac{GV(l-y)}{m_2D_L}$$

Int. again

$$C = \frac{GV}{m_2D_L} (l-y)$$

$$\frac{dC}{dy} = 0 \text{ at } y=l$$

So we will integrate with respect to y ; and when you integrate with respect to y , what you get is a equation like this with a constant. So this D we can put over there, and we have a equation like this plus a constant. How do we obtain this constant? If we know the value of $\frac{dC}{dy}$ at any particular value, we can obtain this equation, obtain this value of constant. So where do we know the value of $\frac{dC}{dy}$? We know that $\frac{dC}{dy}$ at this particular point, which is equal to y equal to L ; what is it equal to, $\frac{dC}{dy}$ by $\frac{dC}{dy}$? It is minima, so it is equal to 0. So at y equal to L , $\frac{dC}{dy}$ is equal to 0. So when we put it over here, we get a equation like this.

Now we can further integrate this with respect to y , and this time it gets integrated to CL , and on this side we have l minus y . So now, let us say we are looking at some distance from 0 to l ; so over here, let us say we have this value 0, and this value is l . Basically what we are saying is we want the difference between the maximum and the minimum concentration. So if you look over here, then this is C , at 0 it is C highest; and here it is C lowest. So when you get C highest minus C lowest, what you will get is the maximum change in concentration. When we integrate it over here from y equal to 0 to l , and the equation that you will get after this.

And remember, we are interested in the magnitude; so what we will do is we will take the positive value. So we will do it like this, and we get; you can easily integrate and show that this comes out to. So this is the maximum concentration difference. This, this is the value that we

have. So now we have obtained the maximum composition difference. If you know the maximum composition difference, it means you can also find what is the maximum temperature difference that can exist.

So this gives you, in effect what is the maximum constitutional super cooling that you will get in between the region of two cells. So this is the centre of one cell, this is the centre of one cell, and in between these two, there is a maximum concentration difference, and when you multiply that with mL , you get what is the maximum temperature difference that can exist, or maximum constitutional super cooling that you can obtain.

Now let us look back again at this equation; this ΔC_{\max} equal to GVl^2 square by $2mLDL$. Now what did we say that cells are close enough or they adjust by themselves to minimize constitutional super cooling. Or in that case, if a cellular growth is preferred by the system, then what it will try is to keep this value constant. Therefore this whole thing will try to remain constant. So we can put it like this; so the system will try to keep this constant, or in other words, we can also put this as one quantity, and this as another quantity; this will try to be constant because these two are constants, so we put all the constants at one place, and we get this. These are some parameters, experimental parameters which can be changed or managed.

So this term times this term will try to remain constant; that in other words means that when you increase this, this will try to decrease when the system prefers to have cellular solidification or when you try to increase this, this term will try to decrease or the system will reduce this term. And this is what has been experimentally verified. So yes indeed, the system always tries to maintain minimum constitutional super cooling when cellular solidification is preferred and that is done by maintaining the product of these quantities.

If you increase the l , or you increase the GV , l^2 square basically decreases. We cannot directly change l ; what we can change is velocity, velocity of solidification. So when you increase this, it will decrease; when you decrease this, l will increase. So when you increase GV , it implies l decrease, or the other way round. Now here there is, this is again two quantities; you can either increase V or you can increase G . So, depending on whatever you increase, you can still see a decrease in l .

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Example Problem

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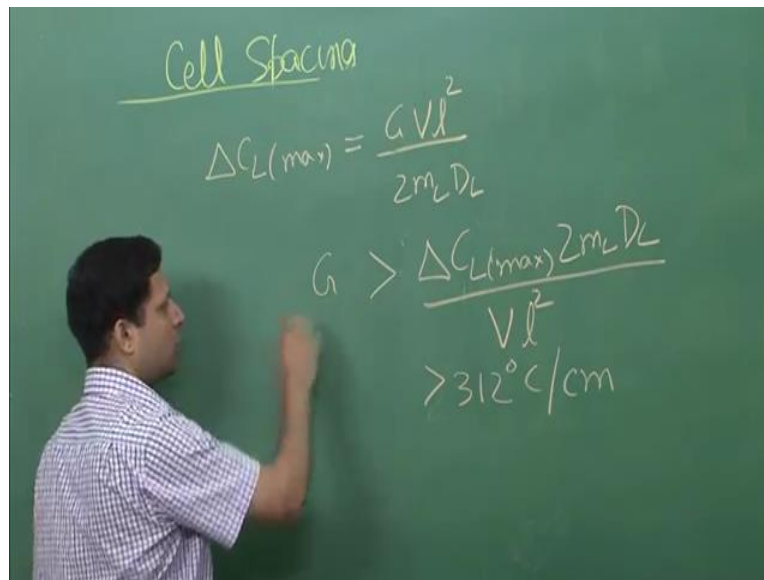
- A Sn-Pb alloy is solidifying by single phase cellular growth. The maximum concentration distribution in the intercellular region, which can keep dendritic growth suppressed, is $0.1\%Pb$. Growth rate is $8 \times 10^{-3} \text{ cm/s}$. Assume $l=40\text{micron}$, $m_L = -4^\circ\text{C}/\%$, $D_L = 5 \times 10^{-5} \text{ cm}^2/\text{s}$. What thermal gradient is required to maintain cellular growth, without forming dendrites?
- If the growth rate suddenly changes such that the equilibrium cell spacing required to suppress dendritic growth is 30 microns , how will the solidifying system make the transition from 40 microns to 30 microns ?

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So now, with this, it is time for us to take an example based on this. So let us look at the slide now and see what is the example problem over there. So now it says that a fine lead alloy is solidifying by single phase cellular growth. Okay; so, it is a single phase cellular growth. So we know the condition or what particular equations we have to deal with. Now the maximum concentration distribution in the inter-cellular region which can keep dendritic growth suppressed; you remember the concentration distribution or the constitutional super cooling has to do with dendritic growth. When it becomes very large, dendritic growth will be promoted.

So, if the system is such that the dendritic cellular growth can be subdued or can be kept away only by only when you have a maximum concentration distribution of point 1 percent lead; if the concentration distribution becomes larger than this, then what will happen? Constitutional super cooling will take place in the inter-cellular region, and the dendritic growth, or cells on the cells will start to grow; we will see about that in a moment, but let us focus on the question right now. So growth rate is given, you are given l for which the cellular growth is taking place; so also note what is the order of the length or the distance between the cells; it is of the order of few tens of microns. m_L is given, D_L is given. What thermal gradient is required to maintain cellular growth without forming dendrites? All we need to do is use our this equation; so our GV must be larger than this value.

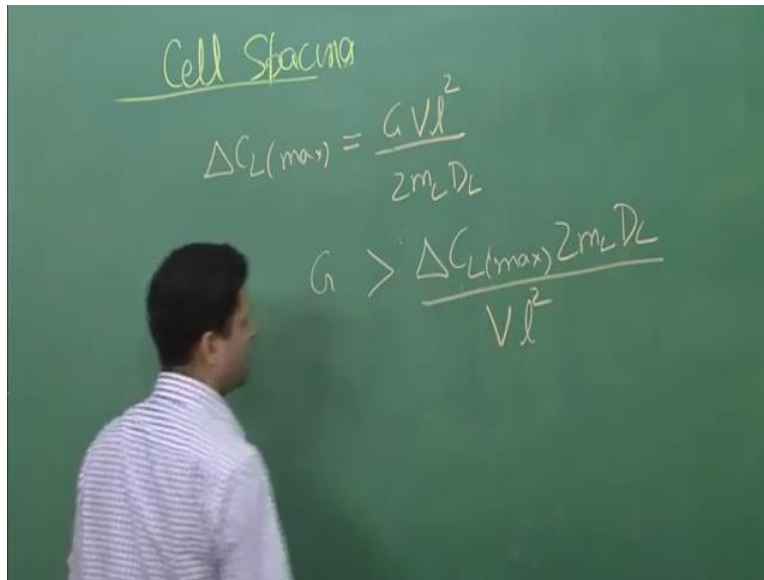
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Okay let us start with our delta CL max. So this is the maximum concentration distribution which we already know. What we need to find is this G. So this G should be greater than. So if the G is less than this; you remember what happens when the G, the thermal gradient is less than this; a larger amount of constitutional super cooling takes place. So the G must be greater than this; if it is lower than this, then constitutional super cooling will take place, which will lead to dendritic growth. So the minimum G or the G must be atleast this value, and if you put in all the values, you will see that it should be greater than 312 degree celsius per centimeter; so that is the kind of thermal gradient that must exist in the liquid to avoid constitutional super cooling. So that is the first part.

Now the second part says that the if the growth rate suddenly changes; you remember GL and l are related right. So now it says that the if growth rate suddenly changes such that the equilibrium spacing required to suppress dendritic growth is 30 microns. Remember if the V increases then l decreases. So V has increased in such way that the dendritic growth or dendritic spacing should be 30 microns, instead of 40 microns. But initially it was 40 microns. So what kind of structure would you expect, that you have initially 40 and then 30; what kind of thing will take place in the cell so that it can reduce the spacing? Well the answer to that is in the next slide which is this.

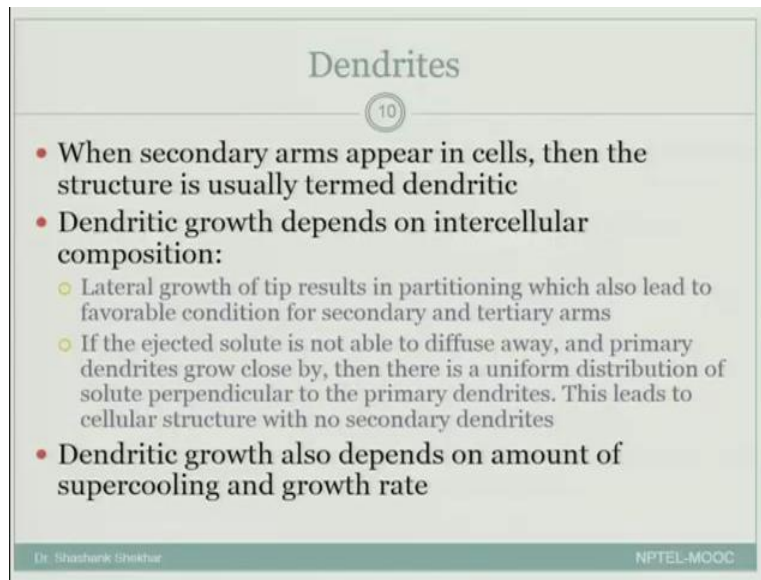
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So you have cell branching taking place, so you can start with a larger or basically if the conditions prevail, such the spacing has to be larger, and the spacing would be like this, and after a certain point of time, if you have changed the velocity, or say increased the velocity, the distance must increase; so the cell branching will take place. So it means the effective distance between the cells will be smaller; now it will be something smaller and for this case, it reduces from 40 microns to 30 microns. So that is how it is able to maintain cellular solidification, even if the cell the equilibrium cell spacing has to be changed.

So now we have talked about so much about the cellular solidification and we have said cellular solidification constitutional super cooling should be minimum, otherwise dendritic growth should take place. So it is at this point it is important for us to take a little bit of look at dendrites; how and we will not get into very detailed study of this but atleast we should understand what the dendrites are and what are the conditions atleast qualitatively that will lead to dendritic growth.

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Dendrites

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- When secondary arms appear in cells, then the structure is usually termed dendritic
- Dendritic growth depends on intercellular composition:
 - Lateral growth of tip results in partitioning which also lead to favorable condition for secondary and tertiary arms
 - If the ejected solute is not able to diffuse away, and primary dendrites grow close by, then there is a uniform distribution of solute perpendicular to the primary dendrites. This leads to cellular structure with no secondary dendrites
- Dendritic growth also depends on amount of supercooling and growth rate

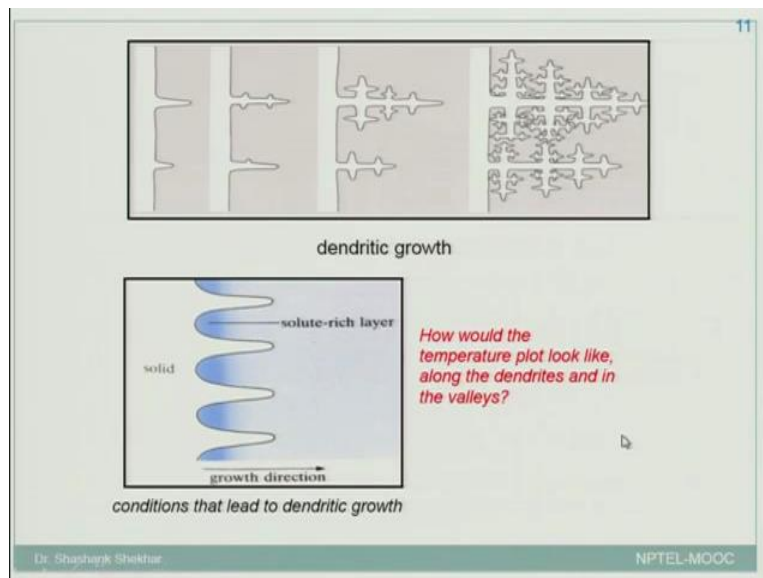
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So what are dendrites? When secondary arms appeared in cells, then the structure is usually termed dendrite. So you remember we have one cell; if it is one dimensional, then it is called cell, but if on those cell there are secondary arms, let us say the perpendicular direction and then tertiary arms; even yes, that is true, even tertiary arms can grow. So if those tertiary arms grow, then that is called a dendritic growth. So it has, you can say cells on the cells kind of structure. Dendritic growth depends on inter-cellular composition, like we have already said, if the inter-cellular composition is very large, or difference, there is a large difference between the maximum composition and the lowest composition, then you can get constitutional super cooling, and if constitutional super cooling exists, then cell on cell will be also be preferred and then you will start to see dendritic growth.

So lateral growth of tip results in partitioning which also leads to favourable conditions for secondary and tertiary arms. If the injected solute is not able to diffuse away and primary dendrites grow close by, then there is a uniform distribution of solute perpendicular to the primary dendrites; this leads to cellular structure with no secondary dendrites. So what it is saying is that if the spacing between the cells is so close that there is a uniform distribution of solute, perpendicular to the primary dendrites, then this leads to cellular growth; it means in those conditions, the dendritic growths or subdued or they can be avoided.

So basically dendrite growth depends on the amount of super cooling and the growth rate, which we have already seen what are the conditions if your growth rate or the G_V , it becomes very large, then l has to be very small. If the G_V is very small then what will happen is that ΔC_{max} will become very large; sorry not the ΔC_{max} , but the l will become very large, and in those conditions, there is possibility of getting constitutional super cooling, and therefore dendrite may grow; or the other condition is when your G , which is the thermal gradient, if that becomes smaller than a critical value which we have seen there is a critical value; if it becomes smaller than that critical value, then again the dendritic growth may take place.

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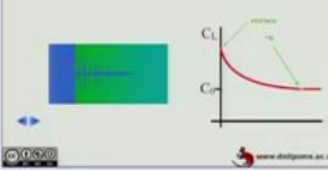
So here is again another schematic to show this. So here is how it grows; let us say this is initially cells growing, and then if the conditions are suitable then cells on the cells have grown up or secondary arms. So this is of the primary arm, these are the secondary arms, and even on the secondary arm there can be tertiary arms growing, and then secondary arms on those tertiary arms can be growing like this and this will be called a dendritic structure, dendritic growth. And what is the condition that leads to dendritic growth? As you can see, if the composition is very different between the cellular region and near the interface, then you can get dendritic growth because that will lead to constitutional super cooling. And we already know what the temperature plot would look like because you know what will the composition difference look like.

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Cellular vs Dendritic growth

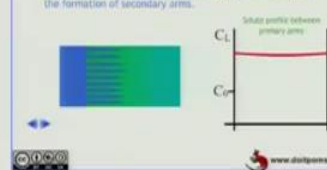
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Lateral growth of the tip results in partitioning of β perpendicular to the primary dendrite arms, so that secondary dendrite arms can form in the same way, resulting in a dendritic interface.



The diagram shows a blue rectangular tip moving to the left, indicated by a blue arrow. To its right is a green region. A graph plots concentration C against distance. The concentration is high at the tip (C_L) and drops sharply to a lower level (C_0) in the inter-cellular region. A red curve represents this concentration profile.

As the cells grow, they partition solute laterally, which can cause secondary arms to form. However, if the β that is ejected cannot diffuse away from between the arms, there will be an approximately uniform distribution of β perpendicular to the main growth direction. This disfavors the formation of secondary arms.



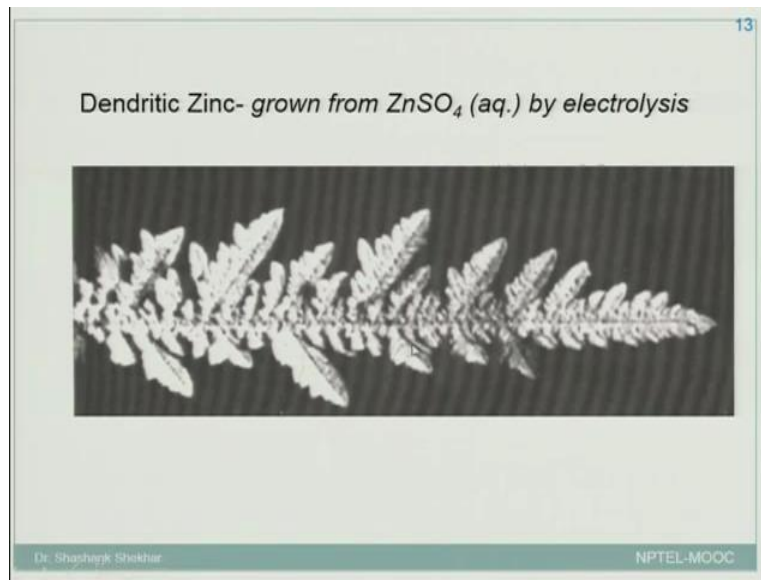
The diagram shows a blue rectangular block of cells moving to the left, indicated by a blue arrow. To its right is a green region. A graph plots concentration C against distance. The concentration is high at the tip (C_L) and remains relatively uniform (C_0) in the inter-cellular region. A red curve represents this concentration profile.

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So here is again another schematic and this is a very nice website, you can visit this for a little bit of animation to understand these concepts, and there you can see what the difference would be between this is your cellular growth and this is your dendritic growth. So when the cellular growth is taking place or is preferred, you can see that the concentration difference is very small. So all the concentration difference that we are looking at is a very small value. In fact it will be worthwhile to point out that for a typical ΔT values, would be of the order of point 01 degree celsius.

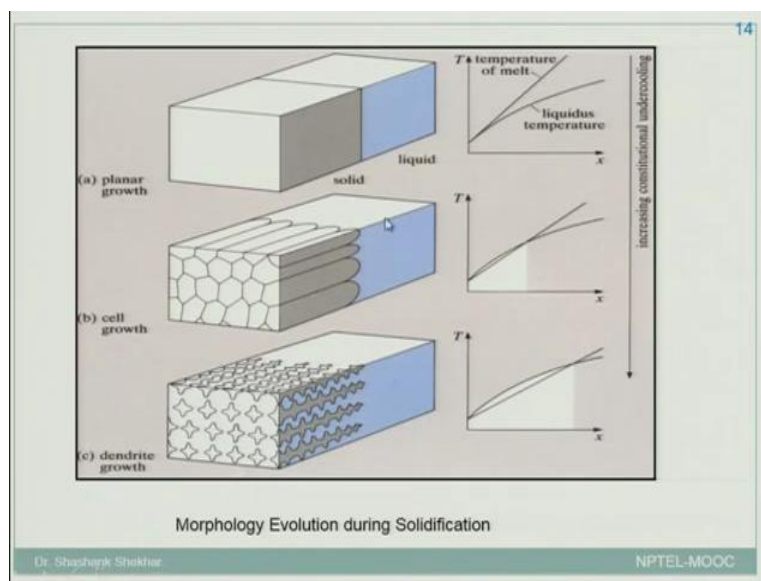
So, if you have cellular growth taking place, this is the kind of ΔT that is present in the system. And this explains in what condition you will have low ΔT and here high ΔT ; so when you have low composition difference between the tip and the inter-cellular region, then you do not get high ΔT ; here you may get very high ΔT . So here you can see, that when C_L is difference very large, so ΔT is large and therefore dendritic growth will take place.

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And this is an example of a dendritic growth; so here is the zinc, grown from zinc sulphate and you can see their primary arms, secondary arms and then even tertiary arms. So this is a dendrite that has been grown. This was grown using electrolysis.

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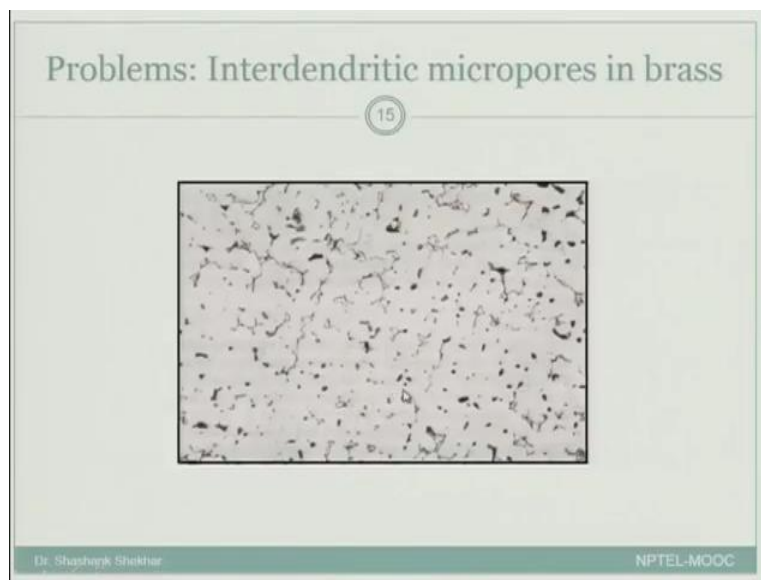


And to finish with the dendrites and cell, we just take a final look at what will be the role of thermal gradient? So here is a liquidus temperature or the freezing temperature. So if your actual thermal gradient is larger than what is the liquidus, or there is no zone no zone which is below this liquidus temperature, then you would not have any constitutional super cooling and you will

get planar growth. If you have a small amount of a region or a very small amount of ΔT , then you may get cellular growth, because this small amount of constitutional super cooling and small ΔT will ensure that there is not enough ΔT in between the cells, and therefore you will get only cellular growth and no dendritic growth.

But when the composition difference becomes very large and therefore the temperature difference becomes very large, so even between the cells, you can get composition difference and therefore, you can get dendritic growth. So this is how the plot, the thermal gradient will look like and their corresponding microstructure will look like; and we will end this with the fact that it is a dendritic microstructures have their own problem.

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What is it? The dendritic microstructures all often have pores in between them, because you can see that the solidification will take place in the solids you are growing, like those arms, and secondary arms and tertiary arms. So in between those there will be some liquid, but when those liquid solidifies, there will be shrinkage, and therefore, those shrinkage will be left as micropores in the solidified materials. So solidification of dendritic microstructure has its own problems and which is evident over here. So we will finish with this and next time what we will do, what we will do is we will be dealing with the planar front solidification of poly phase alloys. Thank you.

