Fundamentals of Materials Processing (Part–1)

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Lecture Number 20

Cellular Solidification of Single Phase Alloy(Continued)

So we were discussing about the critical thermal gradient and that is the relation we have for critical thermal gradient.

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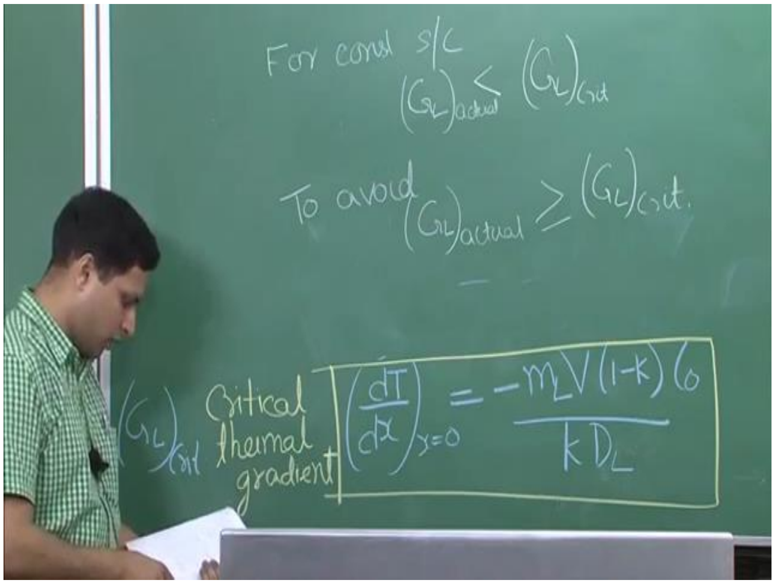

So let us say this is our GL critical. So this is the critical thermal gradient, and what do we know, or what did we say earlier? That if you want, for constitutional super-cooling, the actual thermal gradient in the liquid should be less than this. So GL should be less than GL critical. So this is your actual. To avoid, we should have GL actual greater than or even equal to GL critical. Now, people have done various experimental studies, and what they have tried to relate is they have tried to relate GL over V.

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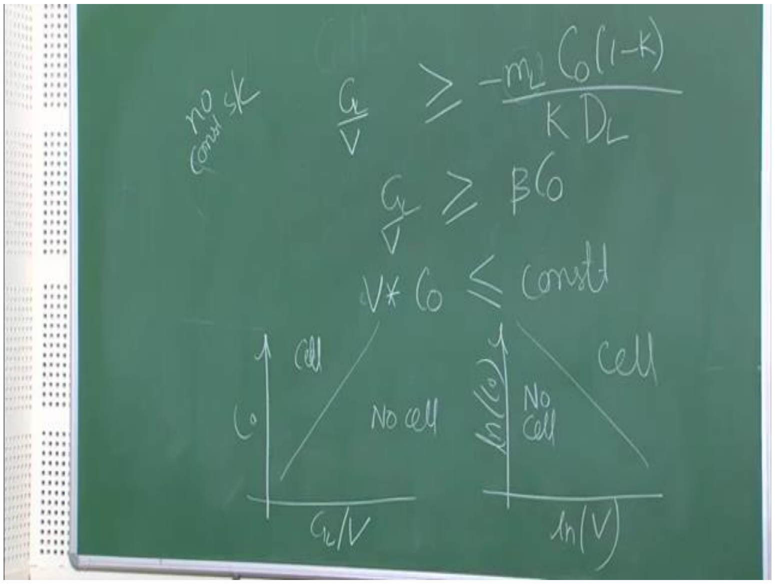

Now this becomes, this should be equal to, this is the condition for no constitutional super-cooling; so you can write it, we want GL actual (equal), greater than equal to GL critical; so GL by V should be greater than equal to this minus. Okay there is one thing that just you must realize at this point; we have a negative sign over here. So you, do you think that this will always be positive, this will or so, this is always negative; so our actual thermal gradient will always be bigger than this, higher than this; actually it is not, because here mL is a negative term, so minus times this negative term, it is a positive term.

So overall it is still a positive quantity. So do not get confused that it is a negative quantity and so your whatever whatever thermal gradient you, as long as it is positive would lead to no constitutional super-cooling. So that is not the case. So this can also be written as GL over V greater than equal to beta, C0 that is you have sed up or lumped up all the remaining parameters into one quantity which is beta; or you can also say V into C0 should be less than equal to constant. So these are the various ways to describe the condition for no constitutional super-cooling, and people have obtained experimental results where they have shown that if you plot C0 versus GL over V, then you get a sharp demarcation you see over here GL over V should be greater than certain value times certain parameter times C0 to avoid cell.

So here, you will see no cellular formation, in this condition you will see cellular formation, when you plot C0 versus GL over V. So these are some experimental findings; also people have plotted something like ln C0 and ln V; so you remember ln C V times C0 should be less than constant. So ln C0 times ln ln C0 versus ln V gives us straight line and below this, if you are there, then there are no cell; so this is for no constitutional super-cooling. So here, you have no cell; over here people have found that you get cellular formation in the (micro) in the during the solidification. So these relations that have been obtained have been shown to be experimentally true.

Now again coming back to this particular criterion, GL over V greater than equal to this particular condition, or this particular value, you see we have derived this considering only thermodynamics of the overall system. But, the kinetics also has a role to play, and some parameters get added onto it. And therefore, although this is on the right line, but this is not the very accurate relation and you may get some additional parameters to make it more accurate because of the kinetics term. Now that we have talked so much about cells, it is time that we look or try to understand a little bit about the cell structure.

So we have looked at the condition that will lead to cellular solidification leading to cellular structure, but what what are the other things that are important about cellular structure? So let us get to the slides to understand a little bit about the cell structure.

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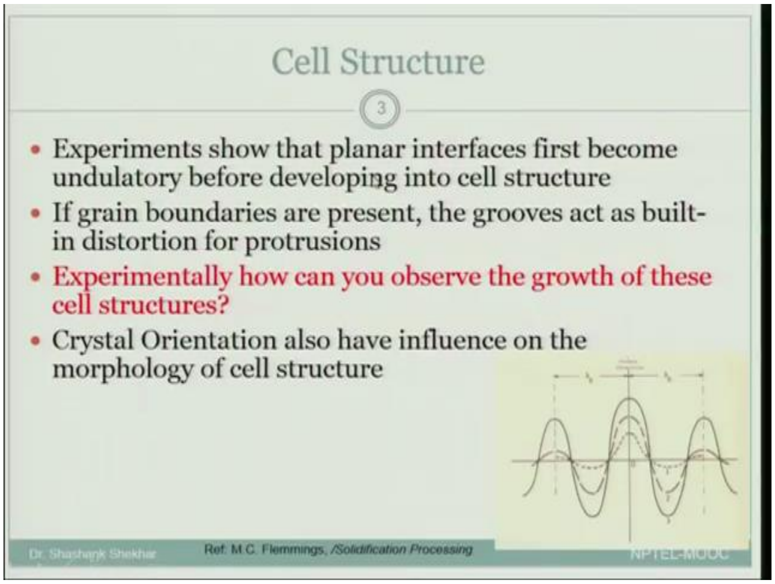

Cell Structure

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- Experiments show that planar interfaces first become undulatory before developing into cell structure
- If grain boundaries are present, the grooves act as built-in distortion for protrusions
- Experimentally how can you observe the growth of these cell structures?
- Crystal Orientation also have influence on the morphology of cell structure

Dr. Shashank Shekhar Ref: M.C. Flemmings, /Solidification Processing NPTEL-MOOC

Experiments have shown that planar interface that that is the other kind; planar interface first become undulatory, meaning small amount of protrusions first occur, and these protrusions then grow into larger cells. So it is not that the cells start to grow just like a, you can say a plant; it is not growing like that, but it is that there are small undulations onto the surface and these undulations become larger and larger, which is also depicted in the diagram over here, so you will first get some small undulations like this, then a larger undulation like this, and over course of time, it will become a cell like this. So this is how the cell (grows) growth takes place.

Other interesting aspect about cells is that if there are grain boundaries present in the material, then these grain boundaries act as grooves, and they act as built-in distortion for protrusions. So there may be grain boundary and over the near the grain boundaries, the protrusions may become much more easier to form and then grow further into the liquid. Another important thing that you should ask is experimentally how can you observe the growth of the structures?

We are saying so many things about, people have found so many things but what is the, how can you experimentally see? You cannot be inside the liquid to see that, nor can you put anything inside the liquid; you cannot have a microscope inside it to see those growth. But what you can do is that at various stages of the cell growth, you can freeze the structure, you can cool it down at a very fast rate so that the structure is maintained; whatever structure was there at that particular point of time during solidification is retained.

So that is one technique that people that researchers apply to be able to see the evolution of the cells. Now these cell structures are also dependent on crystal orientation. So what is the crystal orientation of the grains that also influences the morphology of the cell structure, and we will see at one of the figures from the book Flemmings, which will be able to explain this in a better way. But before that, let us look at the effect of grain boundaries which we just described.

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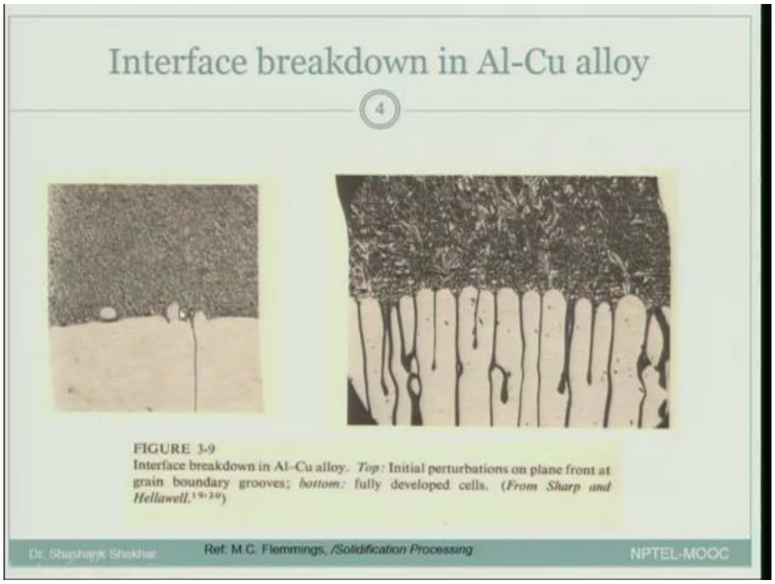

Interface breakdown in Al-Cu alloy

FIGURE 3-9
Interface breakdown in Al–Cu alloy. *Top:* Initial perturbations on plane front at grain boundary grooves; *bottom:* fully developed cells. (*From Sharp and Hellawell.*[19,20])

Ref: M.C. Flemmings, */Solidification Processing*

So let us say there is a grain boundary over here, it is at one stage and you can see that a small protrusion gets developed, so it acts as a depression, the grain boundary acts as a groove and a depression, and therefore cells were able to develop, and in later stages, a lot of cells get developed because of the presence of these grain boundaries. So grain boundary interface allows the breakdown of the interface and allows the formation of the cells.

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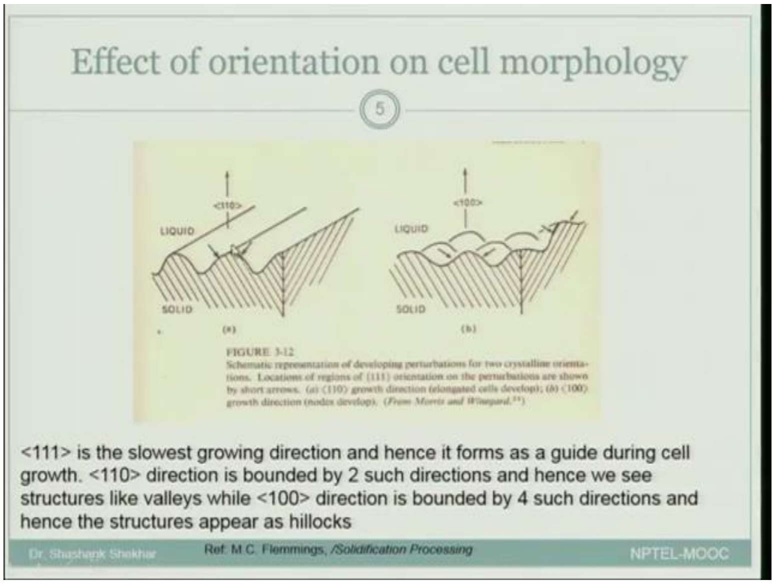

Effect of orientation on cell morphology

FIGURE 3-12
Schematic representation of developing perturbations for two crystalline orientations. Locations of regions of {111} orientation on the perturbations are shown by short arrows. (*a*) ⟨110⟩ growth direction (elongated cells develop); (*b*) ⟨100⟩ growth direction (nodes develop). (*From Morris and Winegard.*[21])

<111> is the slowest growing direction and hence it forms as a guide during cell growth. <110> direction is bounded by 2 such directions and hence we see structures like valleys while <100> direction is bounded by 4 such directions and hence the structures appear as hillocks

Ref: M.C. Flemmings, */Solidification Processing*

Next we said about the effect of orientation; so what happens is that one on one, the orientation is the slowest direction, and hence it is, it acts like a guide in giving the shape to the cellular structure. Now if you are looking at 110 orientation of the grains, then 111 is there only in in two directions. So these two will act as the guide, and you will see undulations onto the surface. But for the 100 orientation, what happens is that 111 is present in four directions, so you see small mounds, instead of undulations you see small mounds because the 111 is now is now holding or in a way guiding the cellular formation from all the four directions; and therefore, you see these kind of mounds that are shown over here. So orientation also has a important role to play on the cell morphology.

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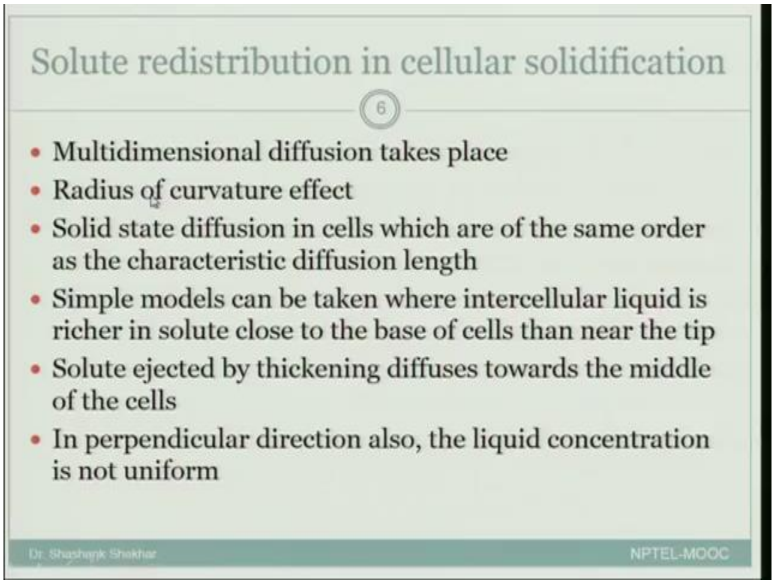

Solute redistribution in cellular solidification

- Multidimensional diffusion takes place
- Radius of curvature effect
- Solid state diffusion in cells which are of the same order as the characteristic diffusion length
- Simple models can be taken where intercellular liquid is richer in solute close to the base of cells than near the tip
- Solute ejected by thickening diffuses towards the middle of the cells
- In perpendicular direction also, the liquid concentration is not uniform

Now when we are talking about the condition for cellular solidification, we also need to take a look at how the solute gets distributed inside the cells. But this question is again not very easy to deal with because of various reasons; what are those reasons? There are multi-dimensional diffusions taking place. Diffusion is taking place not only along the growth of the cells, it is also taking place along the circumferential direction. So in all three directions, diffusion is taking place; that is one factor. There is radius of curvature because of which the melting point changes. So melting point is changing not only because of the composition in the liquid, but also because of the radius of curvature of the cells that are forming.

Solid state diffusion in the cells is also taking place. So far we have assumed that the solid state diffusion is negligible, but when we are talking about cells, the size of the cells is of the same length of the same order as the characteristic diffusion length, and therefore, solid state diffusion becomes a important parameter, a important consideration over here. However, just like in all other things, simple models can be taken where inter-cellular liquid is considered to be richer in solute close to the base. So, simple module can be taken; you take a simple assume that there are cells growing like fingers, and in between those fingers you have high concentration of the liquid which is slowly decreasing towards the bulk of the liquid.

So there is still a concentration gradient, although not, it will be a little bit different than what you saw for planar solidification, but you can still assume that there is a solute region at the base of the cells which gradually decreases and at very far lengths again assume it to be C0. Solute ejected by thickening diffuses toward the middle of the cells, so we can another assumption, which is of course not assumption but very valid that when the cells thicken, which is also not always the case but whenever the cells will thicken, it will eject the solute and it will get inside the liquid.

In perpendicular direction also, the liquid because of this the, in the perpendicular direction also the liquid concentration is not uniform but very soon we will see that we make a assumption which is a reasonable assumption that this variation in concentration is very very small; it is it is very small compared to the concentration gradient that you see along the direction of the growth. Now if we want to look at solute redistribution in cellular solidification, then we need to make some additional assumptions; and we will look at it in more graphic or visual way when we (look) get to the board but let us look at those assumptions in words.

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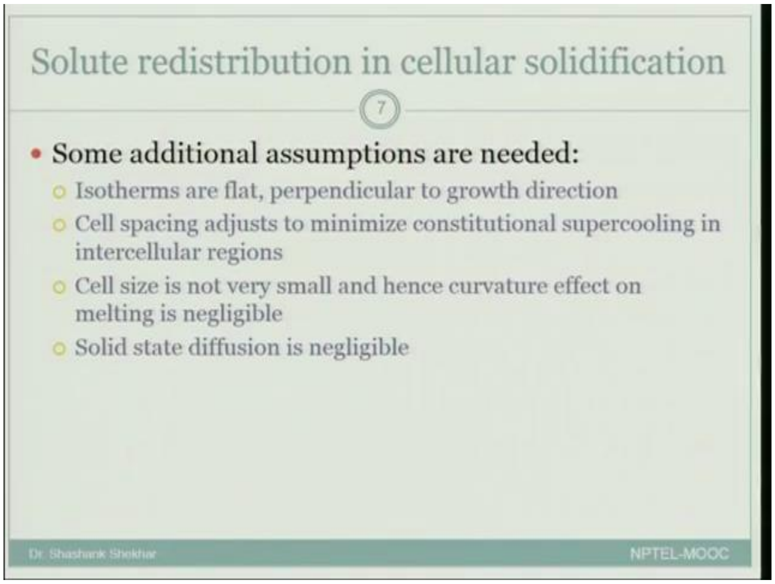

Solute redistribution in cellular solidification

- **Some additional assumptions are needed:**
  - Isotherms are flat, perpendicular to growth direction
  - Cell spacing adjusts to minimize constitutional supercooling in intercellular regions
  - Cell size is not very small and hence curvature effect on melting is negligible
  - Solid state diffusion is negligible

Isotherms are flat; we are assuming that the isotherms are flat, perpendicular to the growth direction; so they are straight lines. Cell spacing adjusts to minimize constitutional super-cooling in inter-cellular region. So this was the assumption that I was talking about which has been found experimentally true that cell-spacing adjusts so that the constitutional super-cooling, meaning the amount of, which also leads to the fact that the amount of composition variation in between the cells is not very large. Third is cell size is not very small and hence curvature effect on melting can be neglected.

Now this is assumption we have to make to make the keep the problem tractable is that cell sizes are assumed that they are not too small, otherwise the radius of curvature will start to play a role in the melting of the material, melting of the liquid, melting of the solid; and solid state diffusion is negligible. Now, we are also saying that the cell size is not small and hence solid state diffusion is negligible. If the cell sizes were very small, then we could not have neglected the solid state diffusion. So now let us with these assumptions and understanding, let us look at the cell (structure) the cell distribution, the solute redistribution in the cellular solidification. So, what does those assumption mean; let us look at it in a more graphic way.

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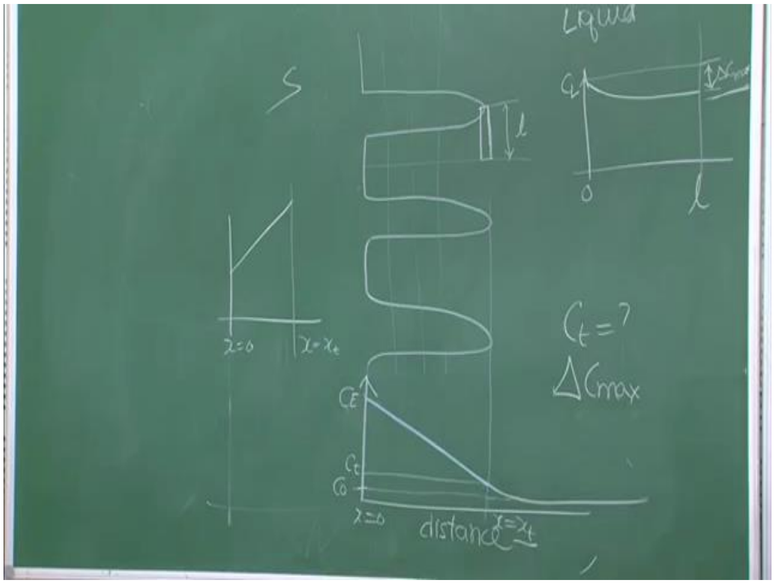

Okay so, I have drawn just a few of the cells that are growing; so this is solid and over here you have complete liquid, and in this region you have both solid and liquid. So here you have the cells, and in between them there is liquid. One of the assumptions we said is that the isotherms are flat perpendicular to the growth direction. So the isotherms, meaning the temperature are constant. If you take any one line in this direction, the temperature, the T equivalent would be constant. Another assumption is that the whatever is the temperature, if you look at the liquidus at that particular point, the liquidus would not be very much higher than the actual temperature, because the cells would adjust in such a way that the composition remains composition remains below the liquidus temperature, and therefore there is minimum constitutional super-cooling.

So the cells themselves adjust to avoid constitutional super-cooling, that is the another assumption which has been experimentally validated. Now another assumption that we talked about is that concentration over here we have richer in solute and as you go away from it, the concentration reduces and at some particular point very far away, you will get C0. So if we, so now, if we are talking about concentration, so let me, it will be appropriate to draw a concentration profile like this. So it will go something like this. Near the base, solute is being continuously ejected or getting rejected and getting accumulated in the liquid. So it's concentration will reach very high values. What is the highest value that it can reach in liquid? It is CE.

So the concentration here will most likely be of the order of CE. Now just at the tip, we can say, let us, there is some concentration of the liquid; so we are looking at the concentration of the liquid, and not the solid. So remember that part; we are talking about the liquid but with respect to the length of the cells. So we are looking at the concentration; so this is C, and let us say this is Ct, or the concentration of the tip; and at very large distances, you would have concentration back to what is the overall composition which is C0. And if you look at, let us say this is approximately l, which is half the spacing between the two cells; then if you were to look at the concentration over here, there will still be some amount of variation in the concentration, but that is something we will assume is very small.

So this is the (con), we are taking a small element over here, very close to the tip, all the way to the centre of the two cells and we are looking at the concentration of the liquid and this is, let us say the concentration of the liquid here is CL; so it drops to some value delta Cmax at the centre, and then beyond this, it will again come back to this original value CL. So this is symmetric from the way we have drawn, from the way we have configured our problem, and this delta C value would be is very small; this is what is one of the assumptions that we have taken that this value will be very small.

Now next, what we aim to find is one; what is this concentration of t, tip? Another thing that we are interested in is to get a relation for delta Cmax and since we have said that the ohms, sorry the cells try to space themselves in such a way, so as to minimize constitutional super-cooling. So if we look at delta Cmax, we would be able to say or we will be able to predict something about the spacing between the cells. So these are the two things that we are interested in; so we will start with what is the value of Ct. So how do we get to the value of Ct?

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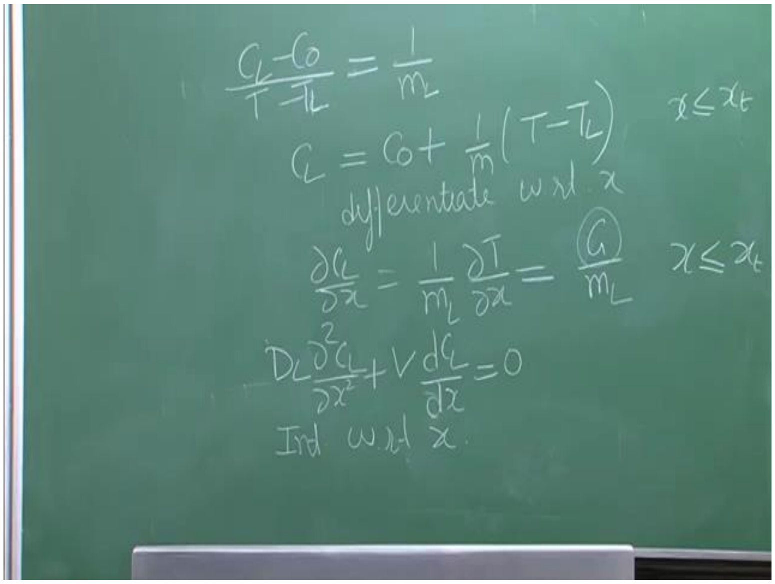

$$\frac{C_L - C_0}{T - T_L} = \frac{1}{m_L}$$

$$C_L = C_0 + \frac{1}{m}(T - T_L) \qquad x \leq x_t$$

differentiate w.r.t. x

$$\frac{\partial C_L}{\partial x} = \frac{1}{m_L}\frac{\partial T}{\partial x} = \frac{\textcircled{G}}{m_L} \qquad x \leq x_t$$

$$D_L\frac{\partial^2 C_L}{\partial x^2} + V\frac{dC_L}{dx} = 0$$

Ind w.r.t x.

For that, we know from the phase diagram, that CL minus C0 by T minus TL is equal to 1 over mL, that is the gradient of T del T over del C; so this is the way we can write it, or we can write CL equal to C0 plus 1 over m; where CL is some concentration of liquid for x less than xt. So this is your , so let me define x equal to xt over here; this is x equal to 0. So this is the total length of the cell, xt is the overall length of the of the cell, and xt also denotes the point, the tip point of this cell. So this is valid for x less than equal to xt.

Now, we can differentiate this with respect to x to get del CL by del x. And you can see this will come out to 1 over mL times del T over del x. Now del T over del x is thermal gradient which is G over mL for x less than equal to xt. So we are only we are able to derive this or we are deriving it only for the relation, for the distance x less than xt. So del CL over del x is 1 over L times del T over del x, where del T over del x is equal to G; so this becomes G over mL. Now, if G is constant, what does that mean? Meaning, del T over del x is constant.

So this overall if you go from x equal to 0 to x equal to xt, if the thermal gradient in this (particular) in the liquid between the cells is constant or basically it rises or slope remains constant something like this, then what it means is that del CL over del x also remains constant, because this quantity is constant, and if this quantity also becomes constant, then del CL over del x, which is the slope of this line remains constant for upto x less than xt.

So this becomes a straight line, under the assumption that G is a constant. So we have the relation or we have described the value of del CL over del x and fortunately for us, under certain assumption we get that it is a constant or basically it is a straight line, the slope is constant, so therefore it comes out to be a straight line. Next what we do is we will take our original equation of diffusion for moving interface and we will integrate this with respect to x. So let me put this on this part of the board. We will keep this plot still over here; so what we get is.

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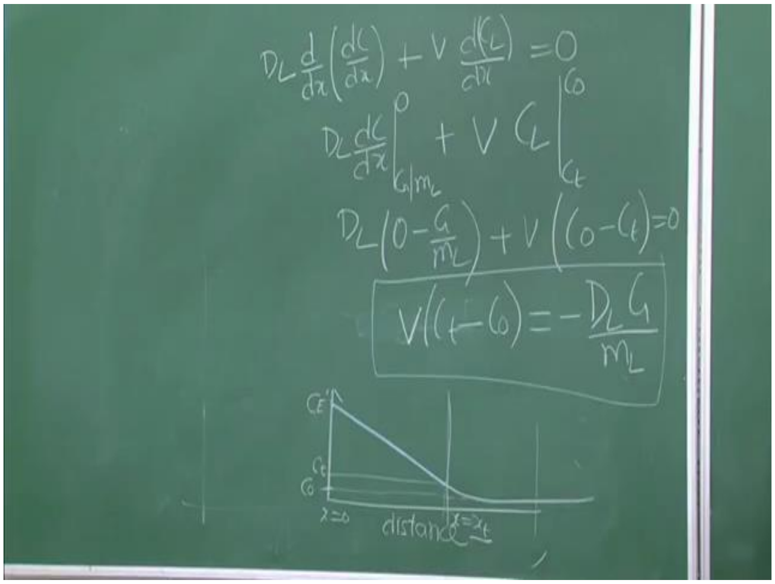

Now when you integrate with respect to x, you get; and what does the dC over dx value vary from? We will see in a moment. This becomes VCL, and what does the CL value vary from. Now this dC over dx, now we are looking at the concentration of the liquid away from this point now; from the point x equal to xt, we are, we want to this equation is basically describing the carried, the carrying away of solute away from this point x equal to xt into the bulk of the liquid. So this is the starting point is x equal to xt, and the end point is somewhere where C is equal to C0. And we are looking at dC over dx value; so what is the dC over dx value? At x equal to xt, we know that it is equal to G over mL.

What is dC over dx value? When concentration becomes C0, it is equal to 0. What is the concentration of liquid, at this point it is Ct. What is the concentration of liquid at this point? It is equal to C0. So we have the equation setup to describe the carrying away of solute from the tip of, from this tip away into the liquid. And when we combine these two, the we have combined the equation from this part upto this part to get G over mL, and used it into the diffusion equation to where we described how the solid gets carried away from the tip into the liquid. We are in a position to get the concentration of tip; so we can write, or we can say Ct is equal to okay even before that, let me write it in a one more step which is.

So now here we have Ct in terms of C0, which is known, DL which is known, G which is known, mL which is known and velocity which is being controlled during the experiment. So once we have these values, we will now be able to get the concentration of Ct. So we can write Ct now like this.

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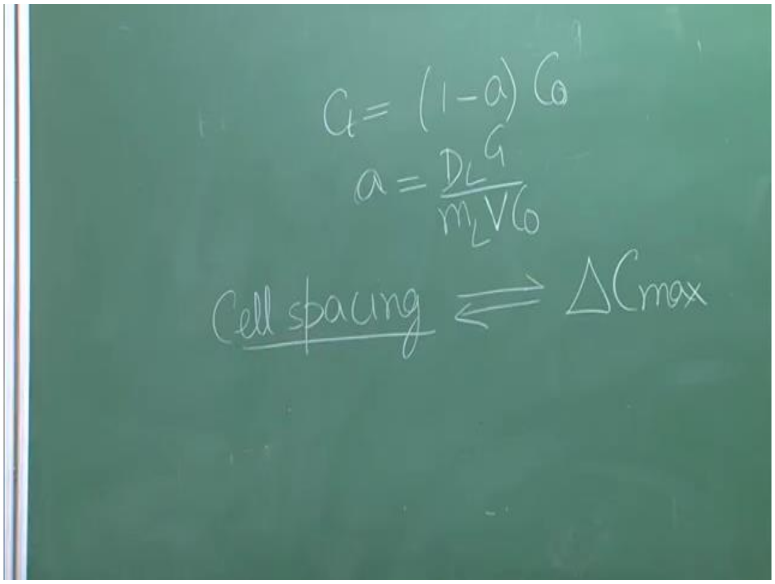

You can rearrange it and you can say that Ct is equal to 1 minus a C0, where a is equal to. So now we have, we have been able to describe the relation for Ct in terms of other parameters and we have Ct equal to 1 minus a C0. So that gives us the equation for Ct. now this is over here, you can see that a is a constant again because D we know, G is what we know, m is a (constant) m is what we know, C0 is what we know, that is the composition of the alloy, and V is being imposed during the solidification process, we have a velocity, so from there, that velocity we have the value of a. So the concentration of the tip gets fixed; so there is a particular value of concentration for a particular configuration or a particular alloy composition with where you are doing the solidification at a given velocity V.

So this helps us to get the concentration of Ct which is the first thing that we wanted to know. the second thing that we want to know that we wanted to find out was the cell spacing; actually we wanted to find delta T, but delta C, but we will relate that to cell spacing. So we will in the next class, we will go ahead with cell spacing and relate it with delta Cmax; this time we have looked at the cellular solidification in a single phase alloy and we have looked at the concentration at the tip, the solute distribution.

We have looked at the cell structure and the one more thing regarding this cellular solidification that remains is to relate this delta Cmax, which is the maximum concentration, that can take place between the two cells, and relate it with cell spacing because we have made an assumption that the cells tried to space themselves in such a way so as to minimize constitutional super-cooling.

So in order to minimize constitutional super-cooling, it will also have to have a maximum delta Cmax. So these two things will be related and we will look at it in the next lecture. So we will see you in the next lecture. Thanks.