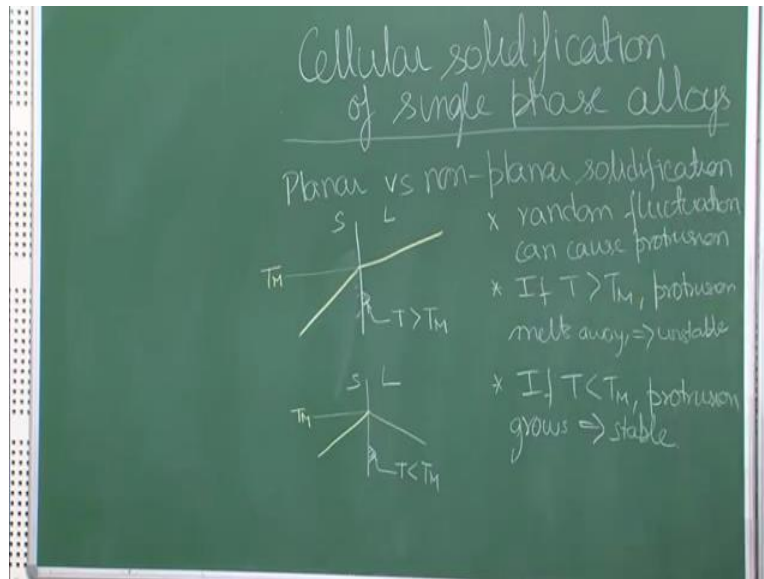


**Fundamentals of Materials Processing (Part-1)**  
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**Lecture Number 20**  
**Cellular Solidification of Single Phase Alloy**

Until last lecture we completed the planar solidification of single phase alloys; but the single phase alloys when you are trying to get planar solidification that is mainly for single crystal growth. But that need not always be the case, and planar solidification may also need not be the case; you may get non-planar or what is called as cellular solidification. So today we will look at 'Cellular solidification of single phase alloys'.

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So this is our topic for this and probably the next lecture. Now, first try, let us try to understand why should we get planar or in some cases non-planar solidification. So, let us try to understand planar versus non-planar solidification. Let us say this is the interface between solid and liquid, this side is solid, this side is liquid; and let us say this is the temperature profile and if we are talking about temperature profile, why not use a different colour? So let me; so this is the temperature profile in the solid, and this is let us say the temperature profile in the liquid and this is if this is the interface, this is somewhere very close to  $T_m$ , the melting point.

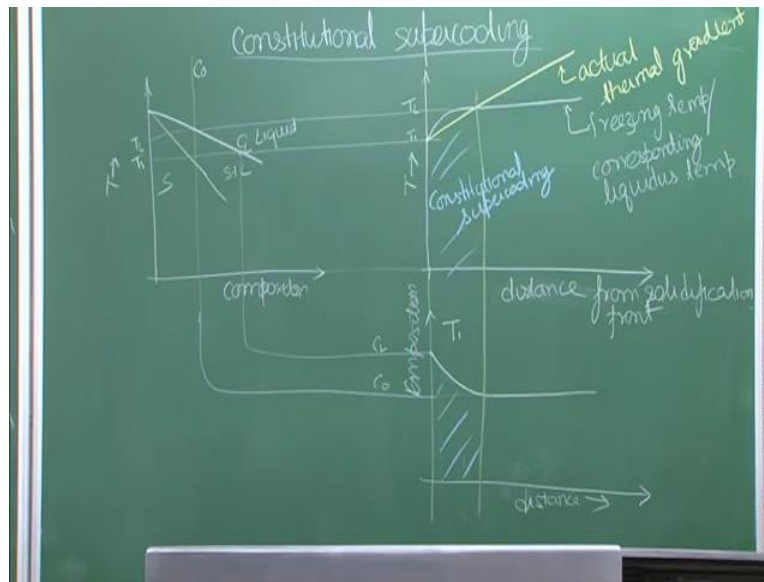
Now let us say that a protrusion of occurs onto the solid; so this is some solid because of some random fluctuation; a small protrusion grows. So this part is also solid, along with this all, but

rest of it is liquid and the liquid temperature is like this. So what happens to this solid that is, that grows like this? You would see that the temperature that it is exposed to is greater than  $T_M$ . So, although some random fluctuations may cause the growth of such kind of protrusions and cells, but these cells will not be stable; they will get melted away, they will vanish away.

So, what do we now understand that random fluctuations can cause protrusion. But if the thermal gradient, if  $T$  is greater than  $T_M$ , protrusion melts away, meaning it is unstable. Can you think of a condition where this protrusion would be stable? Let us draw this a little bit differently now this time. Let us say the temperature profile is like this; so like this means it is increasing, so this is the  $T_M$ , and this part is solid, this part is liquid; but, because it is not in condition, somewhere inside localized region, the temperature inside the liquid is the thermal gradient inside the liquid is like this. So the temperature inside the liquid is also dropping. So it is a super-cooled liquid, it has not solidified but it is still below the melting point.

Now let us say because of some random fluctuations, again a protrusion has grown. Now this time the temperature is less than  $T_M$ , so there is no reason that this protrusion will melt away. And therefore this protrusion is stable. So if  $T$  is less than  $T_M$ , protrusion stays; in fact it will grow, implies it is stable. Now this is what is called as thermal under-cooling; so there is a temperature lower than the melting point, the thermal gradient is basically negative, and because of which the protrusions are stable. But there is something similar that happens in alloys and it is called constitutional super-cooling. So let me take couple of colour chalks to draw this.

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Now let us say we have; let me draw three plots; this time, one is the phase diagram, so this is called a temperature, and this is, these are our liquidus and solidus, and let us say this is our  $C_0$ . So this is the liquidus temperature  $T_L$ , and somewhere, let us say we are at some temperature  $T_1$ ; and at this temperature this is the this is the temperature of the liquidus at this particular condition; and here we have the liquid. This is a solid plus liquid region, this is solid region, and on a different plot, what we will draw is temperature versus composition; so this time this is temperature, this is composition, and we will also draw a third plot which is sorry this was composition, this is distance; so we are talking about real crystal. And this is a composition, and this is distance.

Okay, so now let us say the liquid that is present is at the, at the interface at this particular concentration; but if we are solidifying, then in the overall pool, the liquid concentration should have this concentration, which is  $C_0$ . So this is the concentration let us say, we call this  $C_L$ , and this is our  $C_0$ ; and let us say this is this particular point we are looking at the distance; so this is the interface; and this side we have liquid, this side we have solid.

So at this particular point, just at the interface, what will be the concentration of liquid? It will be equal to  $C_L$ , because of the interface equilibrium, the concentration, we are at this particular temperature  $T_1$ . So the concentration of the liquid, just at the interface must be this, which is  $C_L$ .

So this is our concentration  $C_L$ ; and this is the concentration  $C_0$ . If we are assuming a diffusion controlled solidification, therefore the concentration of the liquid must follow like this.

So at very large distance, it is equal to  $C_0$ ; just at the interface, it is equal to  $C_L$ ; and this is the distance into the melt. So this, you can also call it distance from solidification front. Now if the composition is like this, at each, for each and every composition that you see over here, there is a liquidus. For a composition like  $C_0$ , the liquidus is higher, for a concentration like  $C_L$ , liquidus temperature is lower.

So if you were to project it onto this, this is how it will look like. So for this particular composition, this is your temperature, liquidus temperature; for this particular composition, this is the liquidus temperature. So somewhere over here, this is your  $T_L$ , this is  $T_1$ ; and therefore, corresponding to each and every composition, there will be a liquidus temperature and the temperature versus the liquidus temperature versus the composition plot would look like this.

Now, remember this is not the actual temperature of the melt; this is just the temperature, liquidus temperature for the corresponding composition. So you can even call it freezing temperature or you can say corresponding liquidus temperature. But this is something like a theoretical value, just like you talk about copper and the melting point is 1080 degree celsius; so we are just talking about the theoretical melting point for corresponding compositions, so and for the corresponding distance. For each particular distance, there is a particular composition as you can see, and for each particular composition, there is a corresponding liquidus temperature. We are not talking about what is the actual temperature.

Next we get to what is the actual temperature. So let us say this is the actual thermal gradient; something like this, what we were talking over here; so still we have a positive thermal gradient over there; something like this, and we have a positive thermal gradient over here. But now, this positive thermal gradient has different overall effect in the liquid in this particular case, just because the composition is changing. So because the composition is changing along with the distance, the liquidus temperature is changing; therefore the liquidus temperature at this particular point happens to be higher than the actual temperature that is present in the liquid.

Even though the thermal gradient is positive, the liquidus temperature is higher which means that the temperature, the actual temperature is lower than the freezing temperature of the material; all

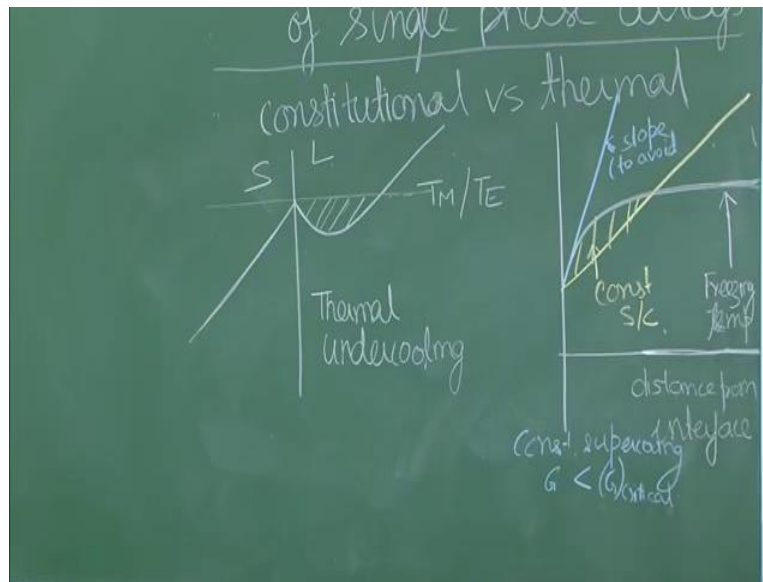
the way upto this point, meaning, upto this point you have what is called as 'constitutional super-cooling'. So again look at the plot carefully. This is the composition variation with distance; so this is how the composition will vary.

We are assuming a diffusion controlled liquid mixing. So this is what, how we know, at the at the solid liquid interface, the composition is governed by the phase rule, and if we say that this is the temperature, this should be the composition at the interface. And very far from the interface, the concentration of the liquid must be  $C_0$ ; so this is what we have shown, and this is the typical diffusion profile for the liquid concentration.

Now this is, this is the composition that is varying with distance. For each composition, there is a liquidus temperature which has been plotted or the freezing temperature. So now the freezing temperature looks like this; and when you draw the actual thermal gradient. So this is the actual thermal gradient inside the liquid. And this is the theoretical freezing temperature; and when you compare the two you see that upto a certain point, it may happen, it need not always be the case, but it may happen that even with a positive thermal gradient, a part of your liquid is below the freezing point, or below the liquidus temperature. So thermodynamically it should be in the solid state; and this part which is, although the thermal gradient is positive, which is, but it is still less than less than at it's freezing temperature, is called 'constitutional super-cooling'.

Now, we have looked at 'constitutional super-cooling'; so at this point it is a good idea to compare our to be able to differentiate between 'constitutional super-cooling' and 'thermal under-cooling'; both are different things, and in the in the liquid, you can have both 'constitutional super-cooling' as well as 'thermal under-cooling'. So let us look at 'constitutional' versus 'thermal'.

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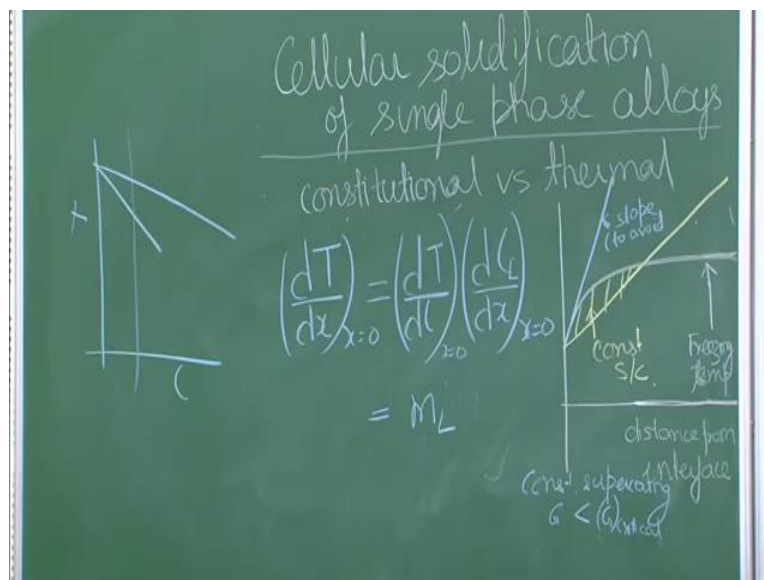
Let us say this what I have drawn here is the thermal gradient, and this happens to be the  $T_M$  or  $T$  eutectic, depending on whether you are talking about a pure material or a alloy eutectic composition. So this is the melting point; but the actual temperature, for whatever reason, may be in a localized pocket or something that actual temperature is, the temperature profile is like this. In the solid of course it is going down or basically increasing upto the interface; so the solid is stable. But in this part, as you can see, now this part is again because of the temperature presence, the temperature being lower than the  $T_M$ ; it is lower than the freezing point, and this is called thermal under-cooling, or super-cooling; you can use the term interchangeably, under-cooling and super-cooling.

While, as we described for our case of constitutional super-cooling, even if you have a positive thermal gradient; but because the liquidus is changing continuously, so this is distance from interface. So this is the liquidus, variation in the liquidus temperature or freezing temperature. And why is the freezing temperature changing? Usually you would expect for same material the freezing temperature to be constant; but here the material is same, but the composition is changing, which we saw over earlier, and because of that, you got this kind of a curve that freezing temperature is changing and your actual thermal gradient, like we drew over there; it may be like this; and therefore this part is, as we said, constitutional super-cooling.

Now if we; this is constitutional super-cooling; at this point now we are in a position to ask, “what is the criterion to avoid or, under the circumstances you would start to see constitutional super-cooling”? So for that what you would need is the critical thermal gradient. You see this is the TL, or the T liquidus variation as a function of distance. What you want is what is this critical value. So we have drawn a tangent just at x equal to 0 of this plot. If your thermal gradient was like this, then you would not see any constitutional super-cooling. As soon as it goes below this, goes below the slope that you have at x equal to 0, small fraction, a small region of the liquid will start to fall inside this or below the freezing temperature; below the theoretical liquidus or freezing temperature, and then you will start to see constitutional super-cooling.

So if you want to avoid it, you want to have greater than or equal to this slope. If you want to have super-cooling, then G which is the thermal gradient should be less than this critical, G critical. So, from this formulation, it is clear that you need to find what is this G critical value; either way, to understand, or to predict when the cellular solidification will take place, or to avoid when you do not want cellular solidification, when you want only , when you want only the planar solidification. So let us look at the criterion or criterion to describe this critical gradient; not the criterion, but the formulation to describe this. So overall we can say, we are looking at.

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Criterion for Constitutional supercooling

$$G = G_0 \left\{ 1 + \frac{1-k}{K} \exp\left(\frac{-Vx}{D_L}\right) \right\} G_0$$

$$\frac{dG}{dx} = \frac{C_0(1-k)}{K} \left(\frac{-V}{D_L}\right) \exp\left(\frac{-Vx}{D_L}\right)$$

at  $x=0$

$$\left(\frac{dG}{dx}\right)_{x=0} = -\frac{V}{D_L} \frac{(1-k)}{K} C_0$$

Critical thermal gradient

$$\left(\frac{dT}{dx}\right)_{x=0} = \frac{-m_L V (1-k) C_0}{k D_L}$$

So now we are looking at criterion for constitutional super-cooling. Let us start from the liquid plot liquid profile; how the liquid concentration varies, and if you are taking just the liquid diffusion as the way of mixing in the liquid, then we can, we know from the previous, that the concentration of the solid looks, sorry the concentration of the liquid is given by this equation. If we know the concentration of the liquid, we can find  $dC_L$  by  $dx$ ; you will see in a moment why we are interested in  $dC_L$  by  $dx$ . So let me, at this point, say why we are looking at  $dC_L$  by  $dx$ . We said that we are interested in  $dT$  by  $dx$ , at  $x$  equal to 0. But this  $dT$  by  $dx$  can also be written as  $dT$  by  $dC$  at  $x$  equal to 0 times  $dC$  by  $dx$  at  $x$  equal to 0.

Now this  $dT$  by  $dC$  is nothing but  $m_L$ , which is, which comes from your phase diagram. So we are looking at  $dT$  by  $dC$ , this is  $T$ , this is  $C$ ; when we say  $dT$  by  $dC$ , we are only saying what is the slope, and you remember we have already taken it as a straight line. So this is a constant value. If we are not taking it as a straight line, then this  $dT$  by  $dC$  value would also be a function of  $x$ . But fortunately for us, we have taken the assumption that this is a straight line; so no matter what composition you take, this  $dT$  by  $dC$  value would remain constant which is equal to  $m_L$ .

Next we want  $dC$  by  $dx$  at  $x$  equal to 0. So this is the  $dC$  by  $dx$ ,  $C$  is our concentration of liquid, so here we have the subscript  $CL$ . So let let me put  $L$  over here to be consistent. Now, what we want is; if you put  $x$  equal to 0, what you are left with is minus  $V$  over  $D_L$ , 1 minus  $K$  by  $K$  times  $C_0$ . So this is your  $dC_L$  by  $dx$  at  $x$  equal to 0. Now you multiply it by this, and you get  $dT$  by  $dx$ . Now this is your  $dT$  by  $dx$  at  $x$  equal to 0. This is a critical thermal gradient. Now this thermal,



critical thermal gradient we have already said, if you want to have super-cooling, then your actual thermal gradient should be lower than this critical thermal gradient.

So, let us write it here; this is critical. So this is the critical thermal gradient. If you want super-cooling, your actual thermal gradient should be lower than this critical thermal gradient. If you want to avoid super-cooling, then your actual thermal gradient should be greater than or even equal to this critical thermal gradient. Even if it is equal to, it will have no liquid which is below the freezing point, and then you will not get any constitutional super-cooling. So we will leave it at this point and we will come back to our cellular solidification and look at it in more detail in the next lecture. Thanks.