Fundamentals of Materials Processing (Part–1)
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Lecture Number 18
Mixed Mode Solidification and Zone Refining

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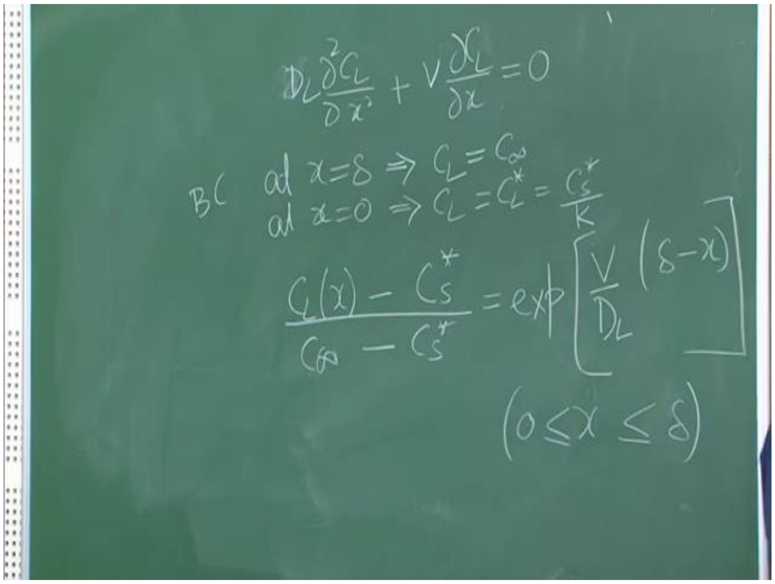

$$D_L \frac{\partial^2 C_L}{\partial x^2} + V \frac{\partial C_L}{\partial x} = 0$$

BC at $x = \delta \Rightarrow C_L = C_\infty$
at $x = 0 \Rightarrow C_L = C_L^* = \frac{C_S^*}{K}$

$$\frac{C_L(x) - C_S^*}{C_\infty - C_S^*} = \exp\left[\frac{V}{D_L}(\delta - x)\right]$$

$(0 \leq x \leq \delta)$

So let us get back to our equation that we were talking about. So this is for the mixed mode, this is the form of the equation, describes concentration of liquid ahead of the solid-liquid interface when we are using the mixed mode form of solidification. So here CL x is the variable, CS star is the constant value, which we said is the concentration of solid at the interface, and C infinity is the concentration of liquid at a distance very large or even you can say even at a distance greater than x equal to delta. V is the velocity, DL is the diffusivity of liquid, delta is the distance beyond which the concentration remains constant, and x is the variable x as a function of which we are trying to find the concentration of liquid.

So as we saw that this equation is valid only between this range x greater than equal to 0 and less than equal to delta. Now let us see how we can get a relation between K effective and K, which will be very meaningful when we put x equal to 0 over here; when you put x equal to 0, this becomes CL star. So, we will use this equation.

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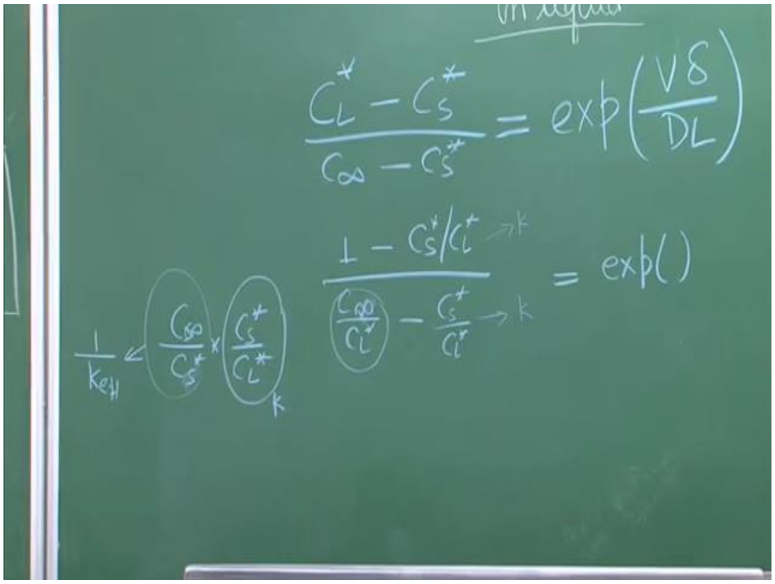

So this is the left hand side, and this is the right hand side. Because we have put x equal to 0, therefore we have only V times delta times divided by DL. So this is the form of the equation. Now, if we divide it by CL star, then this becomes. Now what is this CS star by CL star? You remember that is the partition ratio. So this is very easy, this gets translated transformed to K, this gets transformed to K; but what about this one? If you look at this, this can be written as C infinity by CS star into CS star by CL star.

What is this? This is; you remember we defined something as K effective; so this is inverse of this K effective, and this is K. So this becomes, the whole equation on the left hand side; for the sake of simplicity let me just put this whole thing like this, we will, I will not write in what goes in there; we know it remains same, V delta by DL. And therefore this becomes we will put 1 minus K; this becomes K by K effective minus K equal to exponential term. So let me write it over here.

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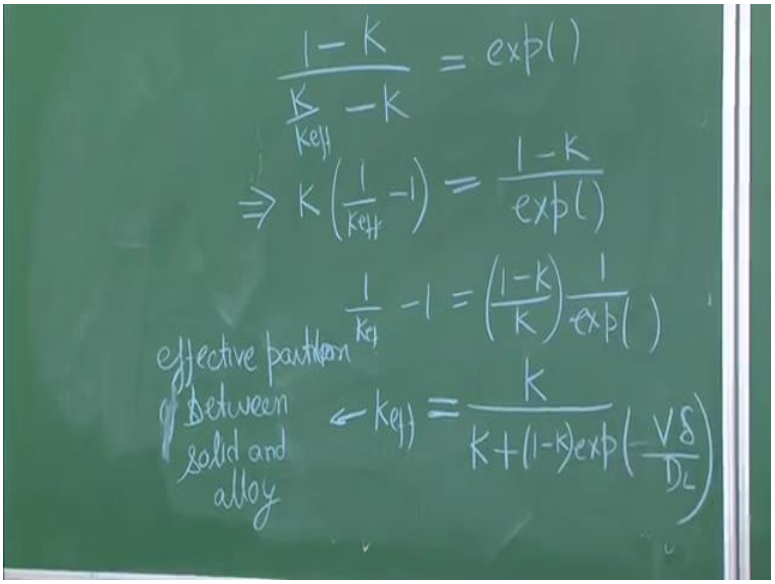

$$\frac{1-K}{\frac{K}{K_{eff}} - K} = \exp(\;)$$

$$\Rightarrow K\left(\frac{1}{K_{eff}} - 1\right) = \frac{1-K}{\exp(\;)}$$

$$\frac{1}{K_{eff}} - 1 = \left(\frac{1-K}{K}\right)\frac{1}{\exp(\;)}$$

effective partition
between
solid and
alloy

$$\leftarrow K_{eff} = \frac{K}{K+(1-K)\exp\left(-\frac{V\delta}{D_L}\right)}$$

So this is 1 minus K, this is K by K effective minus K, is equal to whatever this exponential term is, which is V delta by DL. Or we can write, this take it, take this whole thing over onto that side; and therefore this becomes K 1 over K effective minus 1 equal to 1 minus K divided by this term. Or, we can say 1 over K effective minus 1 is equal to 1 minus K divided by this K; so this we take this out, all these K terms together, and this becomes 1 over exp; exponential V delta by DL. And, if you put these things together, you will see that this becomes K effective equal to K by K plus 1 minus K.

So we can find this K effective if we know what is the slopes of the, of your liquidus and solidus, and from there we get K. If we know what is the velocity at which your solidification is taking place, and because of convection, if we know what is this delta and the diffusivity of liquid, so we can find a effective value for this term, or the effective partition ratio K effective; meaning what is actually the partition between the solid that is forming, and the overall alloy composition. So this is giving nothing but effective partition between solid and the alloy.

This statement will become much more clear when we look at the effective distribution of all the conditions that we have talked so far; so let me draw it and I will be using various colours for it, so that it becomes easy to distinguish, differentiate. So now what I am doing is I am trying to draw the concentration profile for all the cases that we have looked so far. So let me draw in white the access.

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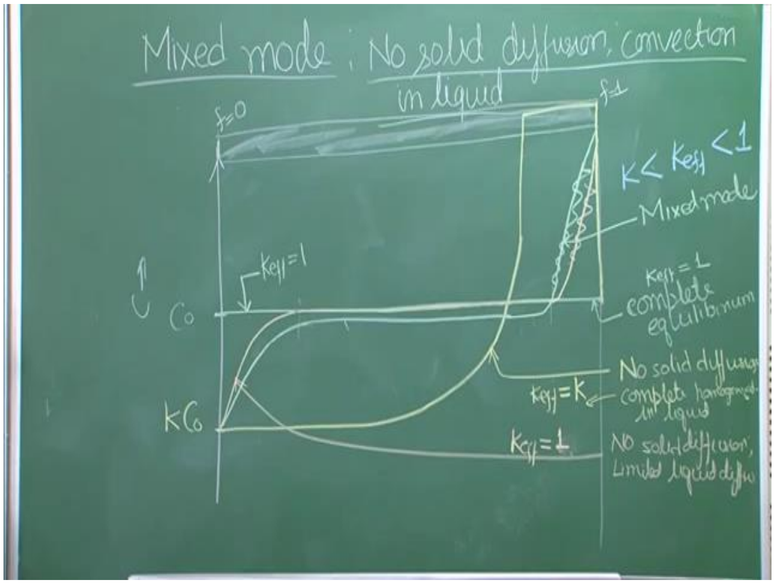

This is our C0, whatever alloy composition that we have taken; and we will put a line over here to describe this is the end of our crystal. So remember, everything we are talking is, so this on the x, y-axis we have concentration, and this particular concentration value is C0. Everything that we are talking is in terms of the crystal that, single crystal that we are trying to grow; so let us say this is the single crystal and we may describe it by some length, or we may describe it by fraction; so if we are describing by fraction this is f equal to 0, this is f equal to 1.

Now what was the simplest condition that we discussed in the first case? That was when we had complete equilibrium. So, the solid that formed was, had the same composition as the original liquid. Although it is very unrealistic, but let us say, that is the case. So, this is complete equilibrium. Next was the case when we discussed the Shell’s equation, that is when there is no diffusion solid, but complete mixing in the liquid.

So let me draw it with and then (again) in this respect, there will be a concentration which will become very important; whenever there is no diffusion in solid, the first solid that forms will have the concentration KC0; and therefore, let me write, let me put it very distinctly over here; and so this will have a concentration profile like this. So there is no solid diffusion and complete homogenization in liquid.

Next we describe the condition, where we had two different conditions; one was the steady state, one was the transient state which was when we have no diffusion in solid, and no forced convection in the liquid. So what we get is only diffusion controlled flow of solutes into the liquid, and there we obtained, again we started with KC0, there was a initial transient, and then over here, you had a steady state, then there was a final transient region. So this formed when there is no solid diffusion and limited liquid diffusion.

That is our third case, and next, next we discussed about the case where we had a mixed mode; meaning, although solid, there is no diffusion in the solid, but in the liquid part, we are saying that it is neither completely standstill, that is only diffusion control, nor is it complete mixing; there is some amount of stirring. But even that, after that some amount of stirring, there is a you can say a diffusion profile, very close to the interface. So that was the condition of mixed mode; and over there, what we obtained was something like this where there is a concentration gradient or initial transition, and in the steady state solute does form, but this solute is not exactly at the C0 concentration, and then, you had another transient condition.

So this was mixed mode. Now you see these are the different types of concentration profile that you will obtain depending on what is the condition inside it. And at this point before I get to the more important point, let me tell you we were talking about the fact that we are taking a very long crystal for this particular case, where we have no solidification and limited liquid diffusion so that we get a steady state. What if you took a small sample where you do not get a steady state. What will happen? What will happen is that this region will get, will shrink, it will shrink and shrink and shrink until the point that your crystal becomes so small, that this region does not exist.

If you reduce the crystal even smaller than this, then these two these two parts of the equation will start to overlap and you may have to find a different equation for that. So this particular condition that we took where we said that there is a steady state; so steady state and that was obtained only for long crystal does not take away any information from us; it is just telling us for a particular case where we have a very long crystal. If you can always reduce that crystal and then this region will get reduced and you will have, you will still be able to get the solution. So that is why I said that it is not taking away any information away from us.

Now another thing is we looked at this K effective; K effective is the equilibrium or the effective partition ratio. Now if you look over here, what can you say is the effective partition ratio for this particular conditions. This is where the concentration of the overall alloy was C0, and the overall concentration of the solid was also C0. Therefore you can say K effective is equal to 1. Now let us look at the second condition; so for the complete equilibrium, let me write it over here itself, it will be better, K effective is equal to 1; meaning CS star by C infinity or which is C0, is equal to 1.

When we have no solid diffusion and complete homogenization in liquid, we see that there is a very wide variation of the solid. So the solid does not follow or does not get very close to the CS the concentration of the alloy. And therefore here, the K effective is actually equal to the K; whatever K that we obtained is what describes the solute concentration. Now in the next condition, which is the solidification limited but limited diffusion in the liquid, we see that the for the steady state, if we are looking only at the steady state, then the overall concentration is still equal to that of the C0 or the alloy composition. Therefore for this also, we can say that K effective is equal to K.

For the last K, which was the mixed mode, over here, we see that this K effective, here the concentration is constant, it is in steady state, but it is still less than the value, less than the original or the whole value. So it is less than 1, that is for sure; but we also see that it is higher than the concentration for that for that we obtained from Shell’s equation. So this must have this particular one for this, it must be that K effective is greater than K, but it is less than 1. If it were 1, then it would be like this, okay so I mixed up a little bit; this should have been 1. I am saying 1, but I somehow wrote K equal to K.

So this one is, because CS CS concentration of solid is same as the concentration of the liquid at par, so the effective distribution is equal to 1. So this is 1, and this is less than this, so it must be less than 1, but it is higher than that for Shell’s equation; so K effective is greater than K, and therefore this equation that we obtained, the K effective, in a way you can say that it describes a much more general condition. So whatever be the condition, you will be able to find the K effective for it and hence describe what is the real distribution of the solid.

So now with that, we have described the solute distribution in all the different possible cases, possible in the sense of which are well modeled, we have described all those. But what is still remaining is another aspect of solidification of single crystal, which is zone refining. So all this was, remember single crystal. So we were talking about single crystal. So for single crystal, these are the kinds of concentration distribution; but single crystals are also grown, or this method is also used, ‘plane front solidification’ is also used for zone refining. So that is one aspect that we are yet to discuss.

So now let us look at zone refining. As the name suggests, there must be some kind of refining taking place. But what is that refining that is taking place, or why do we want to refine? The answer is, when you will get to that plot again for this purpose.

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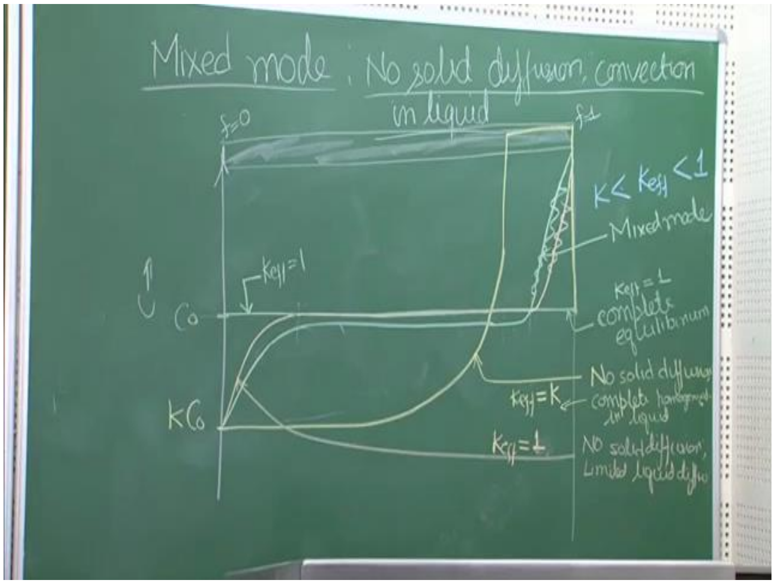

So we are talking about zone refining. The purpose is purification of metals. See here; the, it is different from others; in the earlier the purpose was to grow single crystals; that is why we were using ‘plane front solidification’, but here the purpose is purification of metals. For example, now let us come and take a look at this plot. This is the alloy composition, C0; let us say you are looking at pure (copper) not pure copper, copper with some amount of impurity; just 1 percent of impurity, the C0 represents that 1 percent of impurity that could be several elements or may be just one element; so for sake of simplicity, let us say we are talking about 1 percent silicon.

So this is the concentration of silicon 1 percent silicon. Now when you do this ‘plane front solidification’, you bring, let us say mixed mode, or may be this no solid diffusion and limited liquid diffusion, then what you are getting is this particular range, the transient region; over there, the concentration has dropped, the concentration of the solute has dropped. It is now less than C0; it has become KC0. Therefore this region has become purified, and this particular concept can be extended to get a much more long region of purification or purified material, which is what we will see over here.

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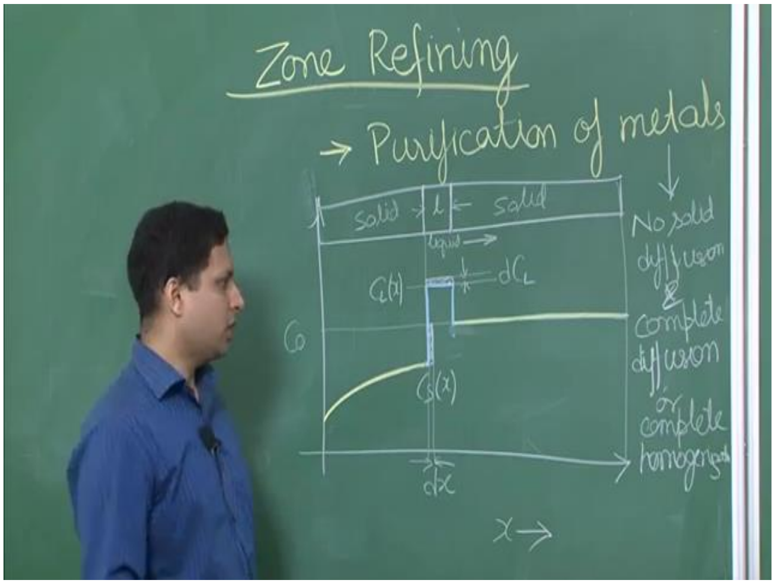

So C0 here is not a intended composition addition, but you can say this is something like a impurity in this material. Now let us say to begin with, this was the concentration overall. Now, if your solid bar was like this, and in the zone refining what you do is that you melt only a small region of that. Let us say this region, the length of this region is L; this L is also the length; do not get confused with also the fact that it is also in liquid state. So this part is liquid, and this part is again solid.

So here you have solid, here you have solid, and this is the liquid region, which is actually moving in this direction. If you look at only the small region, it can be compared with this particular case where we had no solid no solid diffusion and limited liquid diffusion. So for most of this purification of metal, this is the condition which is maintained, which is; and complete diffusion or may be sometimes even complete homogenization. So this or complete homogenization; because as you can see I went for this complete homogenization in the liquid, you get a very long range of purification.

If we are using this one, so it is for this very large length that you are actually getting less solute concentration. So that is the overall concept that is being extended over here; but here instead of doing solidification from one side to another side by melting the whole thing, you are just keeping one particular zone of length L in liquid state, and you are doing the solidification. So, if this were the concentration, original concentration, then you would see that at this particular, let us say, we have reached upto this concentration of solid; so this represents the concentration of solid; so let me draw this by yellow and just in this particular region, this is a very small region; so the liquid concentration is almost constant, and beyond this this is how the liquid concentration; it is not the liquid, again this is a solid, liquid is only this part.

So this is the newly formed solid, and this is the original solid, and in between you have liquid. And why this concentration higher? Because of purification, the liquid, the solute has been thrown into the liquid; so the concentration of the liquid has increased over here. Now if you want to find a equation, then again we can set up a equation. Let us say that we have a small region dx, so this let us present this in x. So there is a small dx that solidifies. Now when this small x solidifies, it will throw out the solute; now that solute, where will that solute go? This solute must go into the liquid, and therefore if the liquid concentration over here was CL, which was a variable, and the concentration of solid over here was x CS, which is again a variable.

And again remember, because of the interface equilibrium, CL and CS are related; CS over CL will equal to be, will equal to K. So this is the concentration, this is the solute that has been thrown out, and this is the solute that has been adjusted or accommodated in the liquid. So what will be the relation? We can say; okay another thing is, so this is a small; since we are talking about x, so this region is dx, and therefore this will become dCL.

So now we can set up a equation to describe this is the solute ejected, this is the solute accumulated; so this should be equal to this. And when we set up this equation, we will be able to find a relation for the solute concentration after one pass. Remember we are still looking only at one pass. So here, the concentration of the liquid has been , the original concentration was C0, and we are doing one pass of refinement.

So this is going from, over here to over here, the liquid that we have liquefied, or the solid has been liquefied from here, and this is moving all the way upto here, and that constitutes one pass. You will do it in several passes when you want to purify it further and further. So, the equation that I am describing right now, over there we have assumed this is a concentration C0, which is the, which is constant and from there, we obtain the concentration of solid that will be there after one pass.

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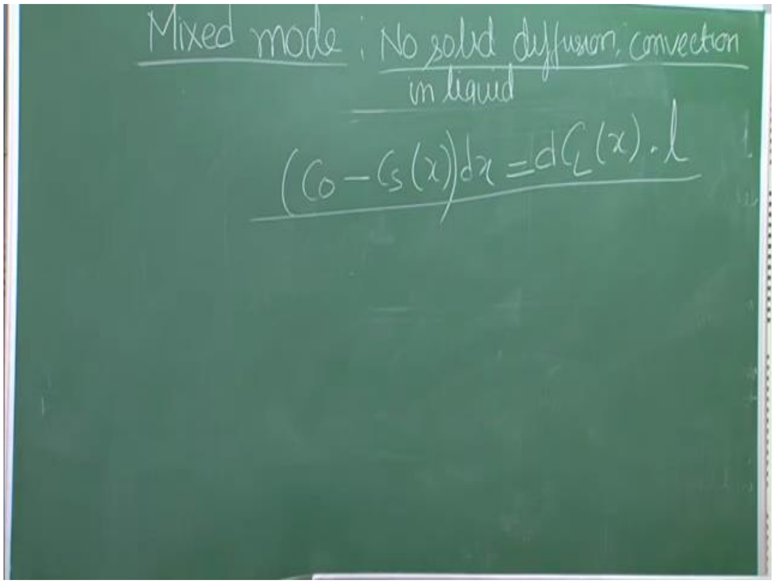

Mixed mode : No solid diffusion; convection in liquid

$$(C_0 - C_S(x))dx = dC_L(x) \cdot l$$

So, let us look at; so C0 minus CS, this is the distance, y-axis, this is the x-axis, which is dx; so this is the total solute that has been ejected. Now on the right hand side we have dCL x, which is this length, and the width is L, the total width of the liquid. So these two have to be equal; and once we solve this equation, we will get the concentration of solute over here. So we will come back to this in the next class, and we will derive the whole equation, and then after that we will also be solving some examples. So see you in the next class.