**Fundamentals of Materials Processing (Part–1)**
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Lecture Number 16
Complete and Limited Liquid Diffusion

Good morning friends. So we were discussing about the composition variation during solidification. We looked at one very simple case, which was of 'equilibrium condition', where everything is under equilibrium. And then we started looking at the other case where we have no solid diffusion, but still full homogenization of full mixing in the liquid. So we found that there is a equation which is called; so first let me write what is the title which is our no solid diffusion, complete homogenization in liquid.

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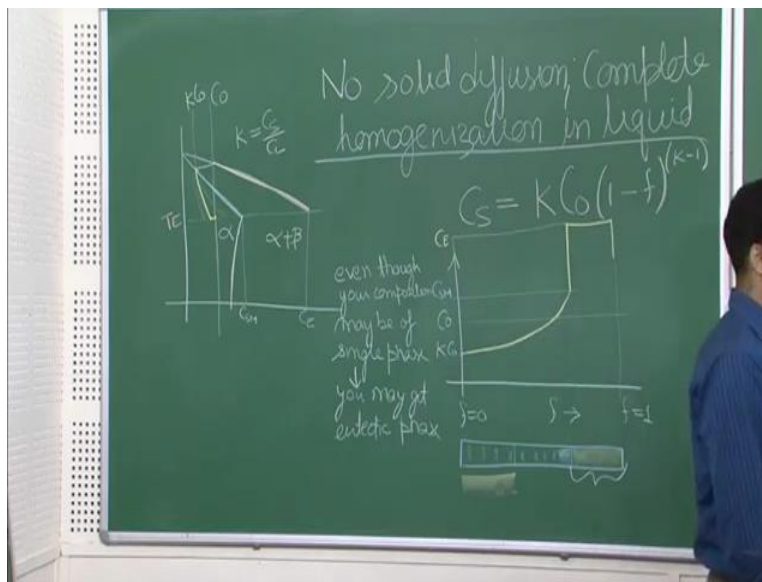
And we derived equation for this condition, which is called Shell's equation, which gives us the concentration of solid as a function of distance. Remember, we are talking about single crystals and one-directional objects; so you can think of a rod, a bar, where we are growing single crystals. So, when we are going from one direction to another direction, in that sense we are talking about concentration variation in the solid, in that particular component or rod. So this concentration CS is given by KC0, 1 minus f to the power K minus 1, where K is the partition ratio, C0 is the overall composition, and CS is the concentration as a function of f, where f will be 0 at the beginning, f will be equal to 1 at the end.

Now let us again look at the phase diagram that we were talking about. So it was straight lines like this, and we took a composition like this, C0; and in this respect we said we were also interested in some other compositions that we will discuss in a moment. So this is our C0, and, the first liquid that solidifies, that solid concentration will be equal to KC0, right? Where K is our equal to CS by CL in general, and since the first liquid has the concentration C0, so the solid has a concentration K times C0 is equal to KC0. So that is the first concentration of the solid that forms.

So now if you draw the plot over here like this; let us say this is our C0, this is our f, so this is f, and f is equal to 1 over here, f is equal to 0 over here. So if we want to depict the concentration of (solid) solid that is forming, the first, at the f equal to 0, what will be the concentration? I guess you must have guessed it; it is KC0. So it starts from this value KC0. And then, you can see that overall the concentration of solute of the solid will keep varying along this direction. So it will keep changing along this direction. It will keep increasing, the solid concentration keeps increasing. But it will not be a straight line, it will follow the equation like this, and so it will, at some point, it is crossing C0, it comes over to this point. But now, the question is, how long will this increase, can it keep increasing all the way upto upto the point that it reaches f equal to 1?

So in that case you will have to see what is actually happening over here. If this is the concentration of the solid, this solid is following a path like this; which means the liquid is following a path like this. Now if you look at this, can the liquid concentration go beyond this? If the liquid reaches this point, it means the temperature is this TE, and if you go below this temperature, the effective temperature, then the solidification takes place. So the answer is, that no, the solid concentration will not go beyond this, and the liquid concentration will not go beyond this.

So the outer layer, or the the last point that has formed, if I want to draw it like this; this is our single crystal rod that we are forming, and the concentration over here is increasing, upto this point, it has. So what I am trying to show is that the (concentration) solute concentration is increasing in the solid upto this point, and at this point; what is this point where beyond which it will not increase? It is this, CSM. So this concentration would be equal to CSM. What happens to the rest of the liquid? The liquid is at this concentration, CE, and if you lower the temperature any further, then all of that liquid will freeze simultaneously.

So, the plot should look like, so this, at this point, rest of the liquid has concentration CE. So this will be the concentration, that was of liquid, but if you go just a delta below that temperature, then all of it freezes; and therefore this one is uniform concentration. So, now it is all solidified, but it has a increasing concentration of upto CSM, and beyond this, it suddenly reaches to CE, which is a eutectic composition, which is this one, and this is your final rod that you see over here.

Now, this is the, what this line I draw drew over here is depicting the delta length of solid that solidifies with this concentration. But if we want to look at the effective or the average concentration of the solid upto that point, which is what the phase diagram is supposed to depict, then what will that approximate average look like? So let me use another one, so let me use this one. Now, should I draw like this, should I draw like this, or like this; that is the question that you must ask.

Then, you would see that the average concentration of the solid upto this point cannot be more than C0, because rest of the liquid that is forming has a concentration higher than C0. That means that this plus this must balance, so that this final composition comes out to this. And therefore, your this plot that we are drawing, the effective solidus or the average concentration of the solid should be below or less than C0; and therefore the right plot would be something like this. It may even be a little to the left, but it cannot cross this line of C0.

So his is now, this is what becomes your effective solidus. And at this particular point, when this liquid also solidifies, then the average concentration suddenly changes to this value; and you will have; because in the end, overall composition is not what you are changing or the overall composition remains constant, and therefore this will be your overall composition. And this is what is represented over here; so this one that we are representing over here let us be clear about one thing; what we are representing over here is the incremental solid that has solidified the concentration for that, while what we are representing over here is the average concentration of the solid.

So if something, if you are looking at this particular point, then this plot represents the concentration at this point. But this plot represents the overall concentration upto this point because that is what the solidus is supposed to be, remember in the equilibrium, everything

becomes equilibrium at that point, and that is what the equilibrium phase diagram is lies. So this represents the overall average concentration, while this represents the incremental or the point concentration at the at that particular point.

Another interesting aspect is that what you see is that this was supposed to be a single phase alloy, right? Over here, you were supposed to get only single phase alloy. If I draw it to the bottom, let us say, this is the like this, and let us call this alpha; over here you had alpha, you were supposed to have alpha plus beta. So, the concentration was such that you should have gotten only alpha. But what is this region?

You see, the concentration over here has reached CE, the eutectic composition. So, even though your composition may be that of single phase, you may get eutectic phase. I am calling eutectic as a phase because usually it comes out as, the two different phases com out together as a lamella; so that, that is what I am calling as a eutectic phase. So, it is all the way upto this point, a single phase, over here it is two phase.

The length of this two phase will depend on where the composition is; as you go closer and closer to this point, that length will become larger; if you go to the left, then the length of the eutectic will over here reduce. So this is how your condition for no solid diffusion and complete homogenization in liquid will look like. Now having said that, let us move on to little bit different condition.

So here, we said complete homogenization in liquid; meaning, when you looked at over here, when the solid was forming, so if you solid was forming at this particular point; let us say the liquid had the concentration something like this; over there we assumed a flat line for liquid. So this was complete homogenization for liquid. But again, that may not always be the case. In fact, that is never the case. So, we will assume now some limitation in homogenization in the liquid part.

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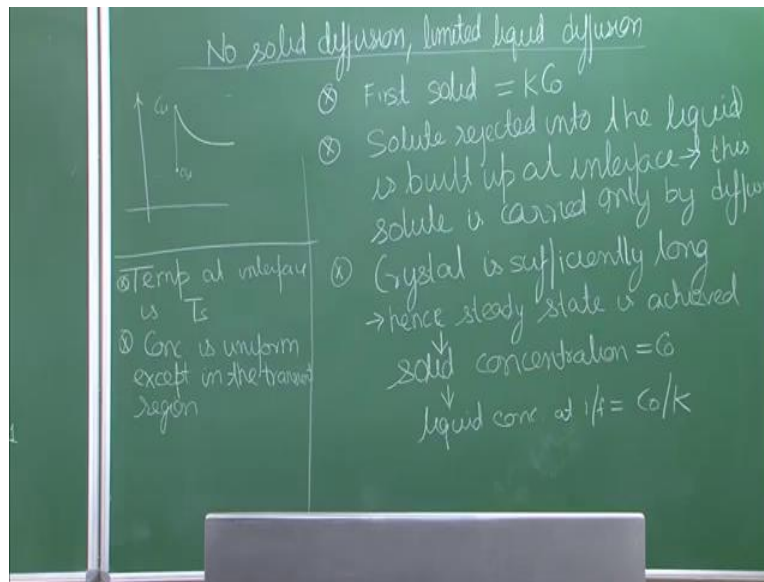
And now we have the condition where you have no solid diffusion as before, because this is a more, this is almost always the case; so no solid diffusion, and limited liquid diffusion. Limited homogenization by diffusion, or you can say limited liquid diffusion. So now, what we are trying to say is that, the concentration of liquid that you saw at some particular point, is not a flat line. So let us say this is the concentration of solid, CS1. Corresponding to that, there will be a CL1, which you can obtain from the phase diagram because we have equilibrium at the interface. Now beyond this, the liquid concentration if you look, it will not be flat line, but it will have a diffusion profile like this.

Okay, so this is one thing that we understand about this condition. Let us look at some other condition that we, that is implied when we talk about no solid diffusion and limited liquid diffusion. Now here, again the first solid that forms has a concentration equal to KC0, just like others, because the first solid will form where, when the temperature reaches liquidus; and at that particular point the concentration is equal to KC0; so this is still true for this case. The solute which is rejected into the liquid, builds up. So solute is getting rejected from the solid, and it is getting post into the liquid, so it gets built up at the interface. And, this solute is carried only by diffusion; carried away from interface only by by diffusion.

Okay? So this is another fact about this particular condition. Next, we will also make an assumption here, that crystal that we are growing, this length that you see over here, is

sufficiently long. But this is again a condition or assumption that is not going to make a large difference. Overall you would see that we can still find out what will happen when the crystal were not long. This particular assumption of crystal being long is taken only because later on we will need two we will see according to the equation, there will be two different cases, one for steady state, another for transient state.

So in the steady state condition, we (assume) we need the assumption that the crystal is long. So to derive that particular condition, we are assuming that the crystal is sufficiently long. And hence, steady state is achieved. Steady state, when I say, when we say steady state is achieved, meaning with time the concentration profile is not changing; but we are talking about concentration profile with respect to the interface; with the lab reference frame, the whole interface is moving, so yes, that can never be a in steady state.

But with respect to the interface, you would see that the concentration profile remains constant. And since it is in steady state, it means that the concentration of the liquid and the solid at far; so the concentration of liquid at far, and the concentration of solid that is forming is not changing, which means the only composition which the solid can form is C0. So the solid concentration is equal to C0.

And if the solid concentration is C0, then the liquid concentration at the interface is equal to C0 by K. You remember the concentration of liquid is always higher than the solid, and since K is small, so C0 by K; so and when we are talking from liquid to solid, that was, we multiply by small factor, which is K. When we are going from solid to liquid, we will divide. So this is the concentration of liquid at the interface, and this also implies that the temperature let me write it over here; at interface is TS, that is the solidus temperature, and you will see we will just plot the phase diagram, then it will become even more clear what we want to say.

And this will lead to, since we are assuming that the crystal is sufficiently long, and the concentration of the liquid, hence the concentration of the liquid that is forming in C0. So the concentration is uniform, except in the transient conditions, or the, in the transient regions. So these are some facts that that is true for this particular condition.

Okay so now let us try to draw a phase diagram. We already have a phase diagram, but we will now be looking at it from a little bit different model where the solid diffusion is as always not

there, but the liquid is also not completely homogenized, but there is a diffusion that is being carried out, and (there) and hence there is a concentration profile.

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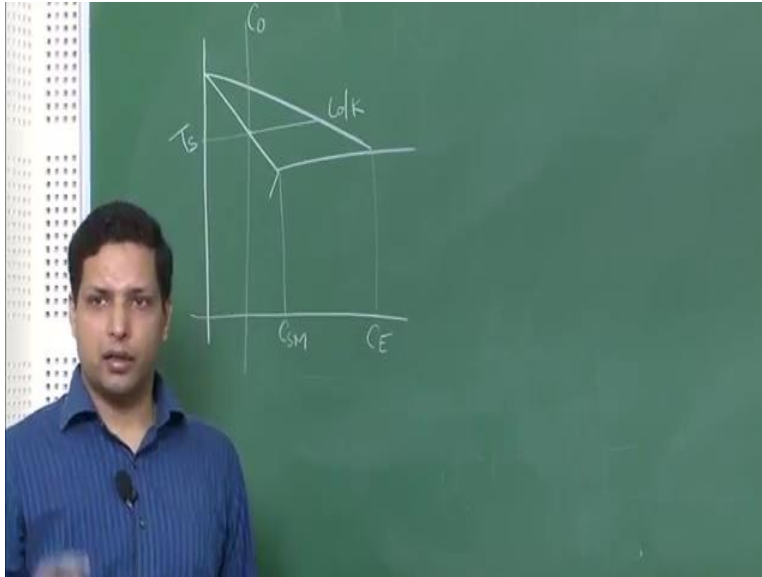
So, let us look at again, you see this is our straight lines for liquidus and solidus; this will be your C eutectic, this is CS, and, and let us say this is C0, concentration of the overall alloy. So, whenever we remember, whenever we say C0, the overall concentration, when you take the overall average, it must come out to be C0; it cannot be different from C0, although at, at a particular point in the solid or in the liquid it may be different, but when you complete thing has solidified, the average concentration must be C0.

Now, when we were talking about the C0, the steady state, we said that the solid must have a concentration of (C) C0, which means, this is the temperature we are talking about; so this is the concentration of solid which is C0, and this is the concentration of liquid, which is C0 by K, and this is the temperature, the solidus temperature. So you see, we have said that temperature at interface is TS, and that is what it will be, for the steady state. Remember, it will be there for the steady state, but not for the transient state. Now, that we have so many times talked about transient state and steady state, let us look at where are we getting that from.
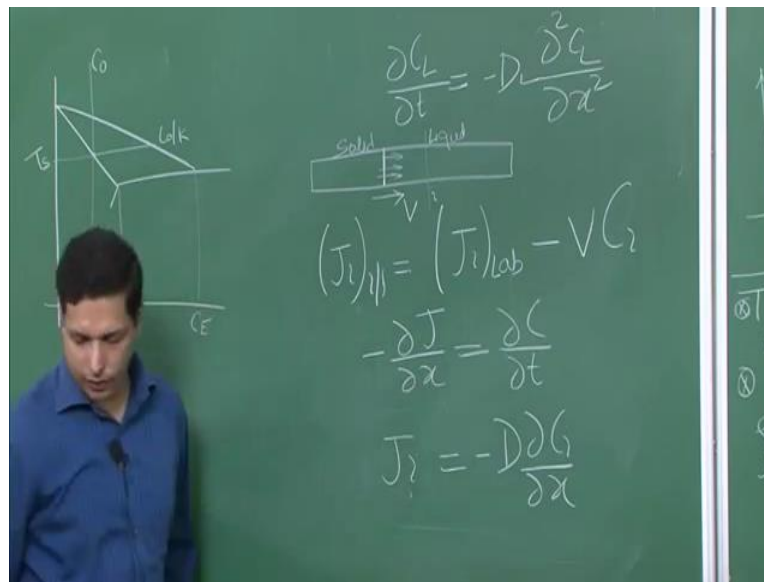
So you see, we have, if you remember, we have, we have said that the concentration profile would be like this, and usually the concentration profile as a function of time is given like this. However, in our case, the interface is also moving. So if we look at the interface; so let us say, this is the crystal that was growing, this is the solid part, from here the liquid is the solute is getting ejected; see this is the solid part, this is the liquid part; and this interface itself is moving at some velocity V. Now since this is also moving, if you look from the interface, from the lab reference frame, at any particular plane, let us say ith plane; if you look at the change in the concentration, del C over del t, that or the flux, basically the flux, that flux would be higher when it is in the lab reference frame.

But when you are looking at the interface reference frame, that is, let us say you are moving along with the interface, then that velocity is not there; and therefore there is no additional flux because of that; which means that the lab reference frame will give you a higher flux than the interface reference frame. So, to derive a equation, which will be valid for this moving frame moving reference frame. Let us look at some basic basic equation. Ji is the the flux at some particular plane i in the reference frame if; if is the interface reference frame.

Now we said that lab, reference frame also there is flux; so let us say this is this. Then, the this, these two are related by this quantity V, where Ci is the (inter) concentration at this plane i. So now you can see that the interface flux would be smaller than the (inter) the flux in the interface

reference plane would be smaller than the flux in the lab by this quantity, VCi. Now from continuity equation, we know that del J by del x is equal to del C by del t.

Okay so, what we will do is, and we also know that Ji is equal to minus D del Ci by del x. So first we will put this over here, and over here, and than differentiate with respect to x. So we will see how to get to a diffusion equation which is valid in a moving reference frame; and we have already seen that why it is different, because the flux is different in the moving interface reference, the flux is usually smaller, which is what is given over here.

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So, now first, let us say that Ji interface; we will put this equation over here, so we have; this is again in the lab reference frame minus VCi. See for the concentration or the change in concentration as a function of x, we do not need a reference frame; it will be same, whichever reference frame you look at. Now, differentiate this with respect to x. So, we have, and using the equation like this, where we have del C over del t, so del J over del x becomes del C over del x, del J over del x becomes del C over del t.

And there is a minus sign; so this is in the interface reference frame, and we bring it over here. For sake of uniformity, since we are talking about diffusion, and for this is for a general system; so we will keep it D, and we will not use any subscript like DL, which we will later on use, because we are talking about diffusivity of liquid; but for now we are letting it be just D.

This is in lab reference frame plus V; this is i for the ith plane. So this is how it looks like. Now here, from this particular, this is the you can say the diffusion equation that is valid when your reference frame is itself moving. So del C over del t in the interface plane is equal to D, del 2 Ci by del x square in the lab reference frame times V del Ci by del x square; Ci is the concentration in any particular plane, in the ith plane. From here we can get two different conditions; one is steady state, which means this is, so we have; remember we already said that there will be two different conditions that we have always been talking about; one is the steady state, and the other is the transient state.

What is steady state? When nothing is changing with respect to time. So this becomes 0. What is transient state? When this is not equal to 0. So now, you would see this, when this is equal to 0, we have only two terms and it becomes very tractable problem, it is, it has a very simple solution. So we will try to solve the problem for, for this particular condition. However, for the transient state, the equation is not so (easy) so very tractable, but we will still give you the final solution for this particular condition. So we will just look at the solution for the steady state condition.

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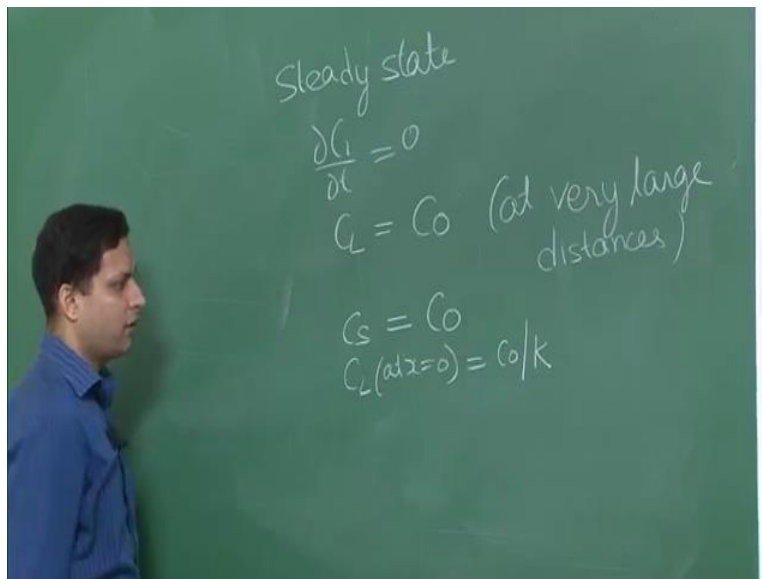
So like I said, we are looking at steady state, and you remember when do you get steady state? When you have del Ci over del t equal to 0. Another thing is that in the steady state, your concentration of liquid must be equal to, at must be equal to C0, at very the large distances. CL

must be equal to C0 at very large distances, because only, because we have already considered that the crystal is very long, and when the crystal is very long, the overall concentration of the liquid cannot be changed. It is so large that the small amount of solute addition is not changing it, and we are looking in the steady state region. And, the (liquid) the concentration of solid that is forming, is also equal to C0, which means, that the concentration of liquid at x equal to 0 is equal to C0 by K.

So these are some of the conditions or the boundary conditions you can say that we need to solve that equation. So we will come back to solve this equation in the next lecture; and we will use the equation that we have already derived for the diffusion condition with moving reference frame; and now we have two (conditions) two states; steady state and transient state. So for the steady state, these are the conditions, and we will solve the equation for it in the next class.