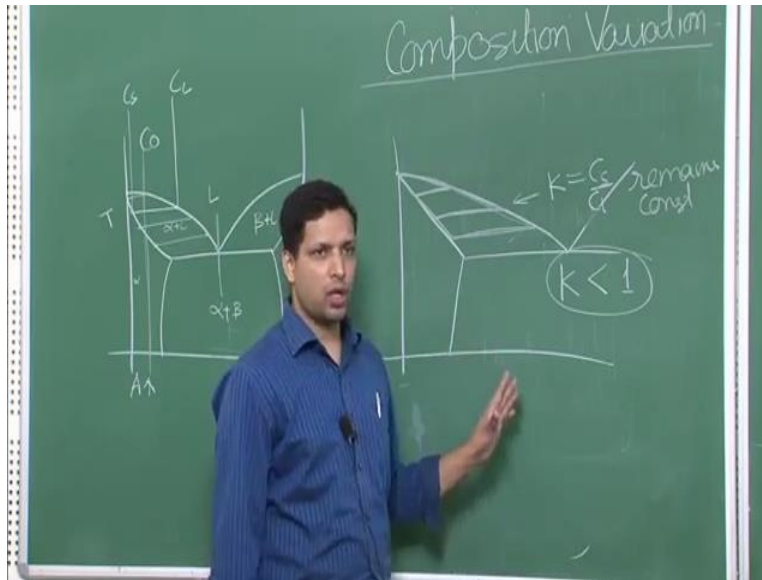


Fundamentals of Materials Processing (Part-1)
Professor Shashank Shekhar
Department of Materials Science and Engineering
Indian Institute of Technology, Kanpur
Lecture Number 15
Composition Variation (Continued)

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So last time, we asked a question that instead of taking this usual curved lines for the phase diagram, what will happen if you take the straight line for the curve, for this phase diagrams particularly for the solidus and the liquidus line. Well the, if you look at it closely, what you would see is that it makes the (most) biggest difference to or in fact, which is why we take this assumption is because this partition ratio K , if you take at any value now, any temperature value it remains constant, and you can easily prove this using similar triangle principle. So this is a similar triangle, this is a similar triangle, this is a similar triangle, and therefore K will equal to C_S by C_L remains constant.

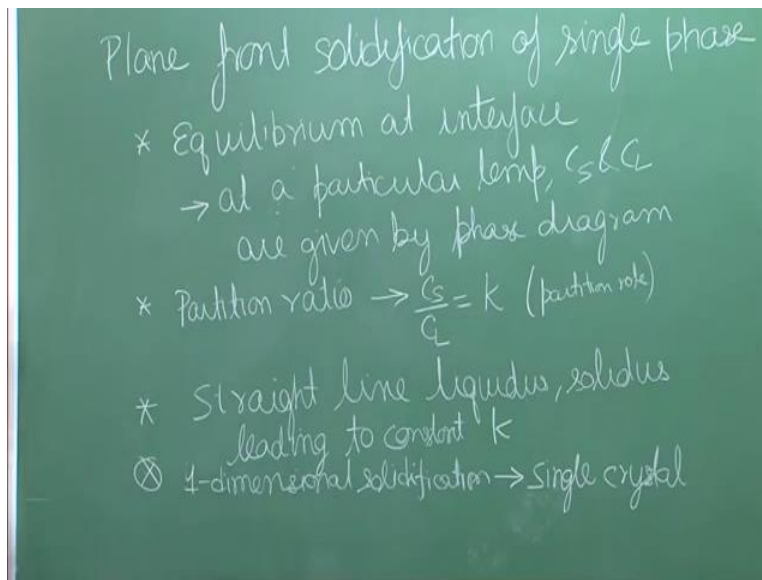
So that is why we have assumed or we assumed for our understanding and for formulating the relations that these solidus and liquidus are straight lines. So the straight line liquidus and solidus leading to constant K . So these are some of the assumptions that we make. But other than these assumptions, for the sake of simplicity, you would see what we will do is that we will always be assuming the left side of the phase diagram. If you want to talk about B in A, then you put A

over here and say B is the increasing fraction. If you want to understand about A in B, then you put B over here and say percentage fraction of A.

So, that does not take away the generality of this whatever we talk about later on; but what it does is that for the again, for our sake of simplicity, it ensures or it make sure that K is always less than 1. Because we are always on the left side, so this is CS, this is CL; so CS by CL will always be CL is less than CS, so therefore, CS is less than CL, so the K will always be less than 1.

So this is not really an assumption, but you can say, some certain kind of simplification, where we are not losing generalization. We still get all the things, we do not lose any of the information, we are just keeping it like this, so that it becomes simpler for us. Okay, so having said this, we are looking at certain conditions. Now the solidification that will take place, if you look at the phase diagram again, it will not be very simple.

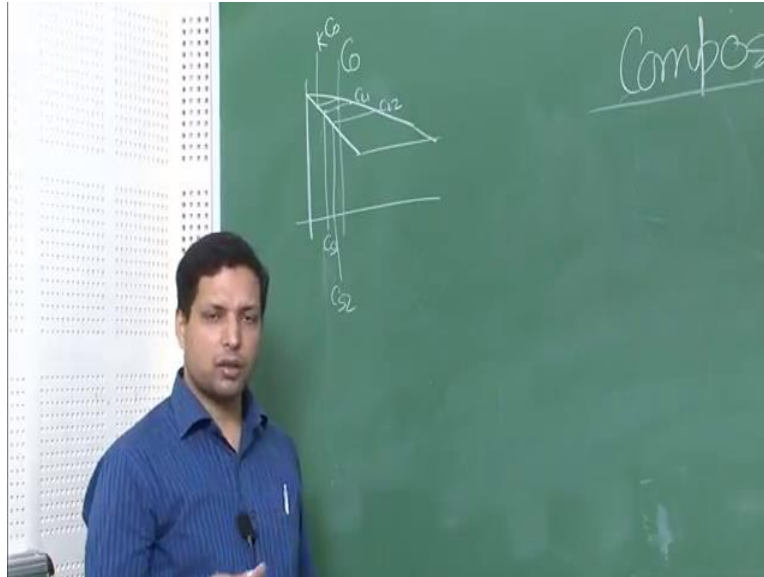
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Just as a simple example, look at this. So let us say this is our C_0 . This is the composition of the alloy that we want to solidify. At this particular point, when the first solid forms, the composition of that solid according to our first assumption of (03:28) interface will have a composition like this. And what will it be? It will actually be equal to KC_0 . So the first solid that forms will always have the composition KC_0 , because the liquid when it comes to this liquidus temperature,

at that point the solid will have the composition KC_0 . CS by CL is equal to K , so the solid composition is equal to KC_0 , which is the C_0 is a liquid composition.

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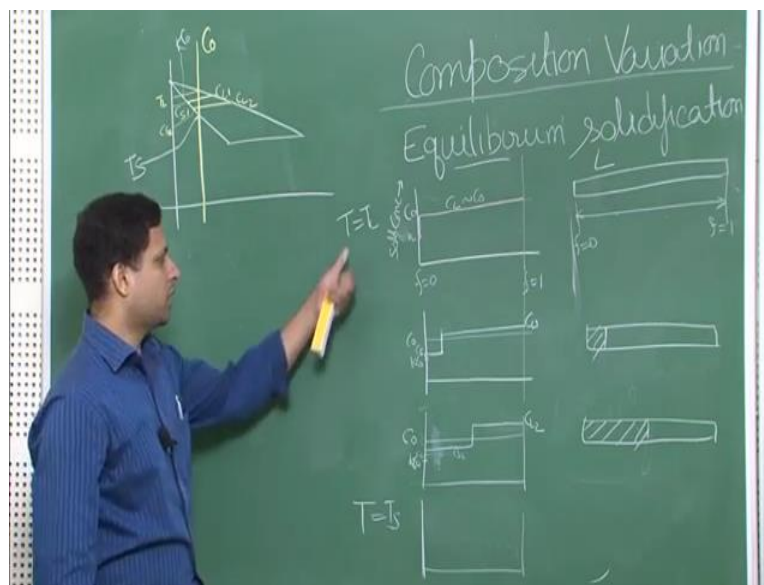
Now as you lower the temperature at this particular point, the liquid will have a composition like this, and the solid will have a composition like this. So the solid that forms at that particular temperature will have a composition like this. CS , let us say CS_1 , somewhere over here, it will have CS_2 and so on; this is. Now you can see that although the overall composition that we have talked about should have, the composition as C_0 , and we would have assumed that the solid and liquid would have (equilibrium) the overall solid will have that kind of composition in the single phase; but the way the solid is forming, it has changing composition at different point in temperature. And hence it leads us to ask question, "Is some kind of homogenization taking place in the solid?", "Is some kind of homogenization taking place in liquid?" Yes, then what kind of homogenization?

So based on those homogenization, we will get very different solutions for different conditions. So we will begin with a condition of what is called as 'Equilibrium Solidification'. Okay one more assumption that we will be talking about in most of these cases; again those are not explicit assumptions is that it is you can say a 1-dimensional solidification. Why I just introduced it, because we (have) the way we will draw the composition profile, you would see that it is a 1-dimensional solidification, and this particularly for plane front solidification, this 1-dimensional

solidification would usually be done for growth of single crystals; because plane front solidification is very very slow process, and it is done only to achieve single crystal, single crystalline samples.

So, again, that is what we are doing is solidification of a single crystal and for that, we are taking different different assumptions regarding what kind of homogenization you will take see in solid, what kind of homogenization you will see in liquid. And we are here at 'equilibrium solidification'. Now what does this 'equilibrium solidification' mean?

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So let us say, this is the kind of a rod that you want to solidify. This will be single crystal in the end, but at some stage it will be all liquid, then it will become solid, and so on. So let us say, at the beginning it is all liquid. And therefore, at this particular point, we are somewhere; so let me draw this now with respect to our equilibrium concentration. So if our temperature is above this point, this whole thing is liquid. Now just at this particular temperature, which is your T solidus, sorry T liquidus; at this particular temperature, what will be the composition that you would see for this? Okay let me draw it over here.

This is the composition, this is let us say we call it in fraction; whatever length it is, we will, this f will be equal to 1 over here, and f will be equal to 0 over here. So this is the equilibrium, this is the composition we have taken, C, and on the y-axis, this is concentration. And we have, what we are trying to draw is solid concentration. How the concentration of solid will look like. So the

first solid that forms, what is the composition? We said earlier, it has to be KC_0 . So this is the first solid that forms, KC_0 , but it is only with a very small length, over here, and this is the rest of it is still liquid. So this part is the solid, a very very thin region, and rest of it is approximately equal to liquid. So we will say this is CL is approximately equal to C_0 .

Now let us decrease the temperature a little bit. So we are at this temperature; at this temperature, let us say this is our composition, which is equal to we said earlier; let us say this is CS_1 , this is CL_1 . So we will keep the process similar to earlier. And now over here, this was your C_0 , this was your KC_0 , and somewhere in between C_0 and KC_0 , you see this is the CS_1 ; this is somewhere between C_0 and KC_0 . So somewhere over here you have the solid concentration which is CS_1 . And this is, your liquid has also composition has also raised. You see gone above C_0 , it has become CL_1 . So this is CL_1 , the liquid concentration.

Now it is very easy to understand that the overall liquid concentration increased because diffusion in liquid is very fast. But what we are also assuming when we say this 'equilibrium solidification', is that the concentration of the solid part also gets very fast homogenized. This part, the original solid that formed was at KC_0 , but by the time the solidification reached to this stage, we are assuming that the overall concentration has also reached this stage. A liquid that formed at that particular temperature should be of this concentration, but we are assuming that the inside, the inside the solid the diffusion is taking so fast, but this point inside, any point beyond this inside the solid is also at this concentration.

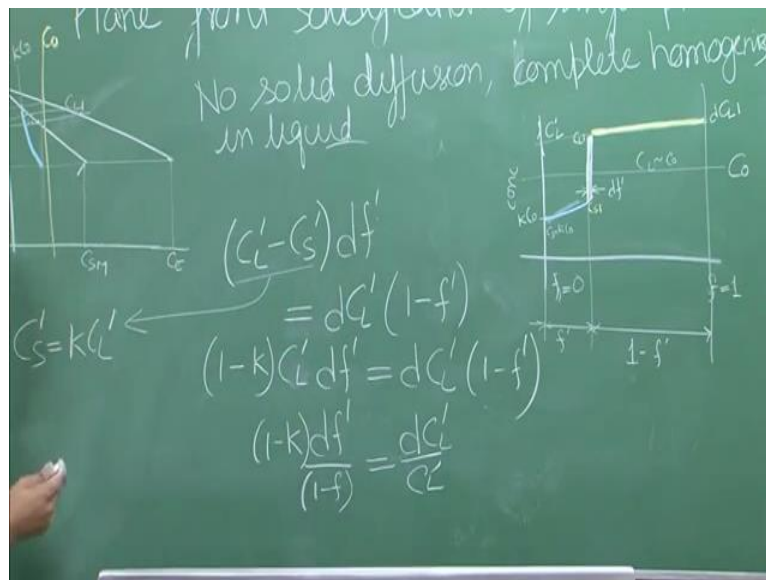
Similarly if you keep going further inside the solid, or further solidifying it; so now let us say we are at still lower temperature, so we are at CL_2 , and this is CS_2 . So this was C_0 , we started with KC_0 , we reached CS_1 ; and then even higher than CS_1 is some composition CS_2 , and this has, this extends for a longer region, so somewhere like this; and the composition of CL liquid has increased even further, CL_2 .

So again like I said, it is very easy to understand the homogenization in the liquid part; so the liquid has become homogenized, it has concentration CL_2 , but what is interesting or what is inherent or what is the assumption in this particular case of equilibrium solidification is that the whole solid also gets homogenized, meaning diffusion is so fast for one way; we are not

talking about how and why, but diffusion is so fast inside a solid, that the whole solid also gets homogenized and has same composition as predicted by the phase diagram.

So everything is going as per phase diagram; there is no change or deviation from the phase diagram. And if you keep going, so here, this is the length that has solidified, let us say, some amount of this; over here, some close to 50 percent schematically, we are not giving it a number yet, or we are not doing it in quantitative way. Now let us say, at the final temperature, which is T equal to TS. So this is T equal to TS, solidus temperature; over here we were at T equal to TL, liquidus temperature, and in between we were at some between temperature, so we are decreasing temperatures.

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And at this liquidus, the solid that forms has the concentration equal to C_S . So the beginning structure would be very same; this is our f equal to 1, this is f equal to 0; we are looking at the length in terms of fraction, so this is the total fraction, the whole fraction has solidified; over here, 0 fraction has solidified; here this is the concentration, this is the C_0 . Now the first solid that solidifies; yes you would have realized by now, it should have concentration of C_S , because C_S by C_L is equal to K , and C_L is approximately C_0 ; so $C_S = KC_0$, and therefore this is C_S . C_S equal to $K C_0$, and C_L approximately equal to C_0 , that is the composition of the solid (15:03).

Now what happens next is very different, from what we discussed earlier. Over here, when the solidification starts to take place, the next solid that forms is over here; but, this is only the outer

layer of the solid which has this concentration. So the solidification of the outer layer goes like this, like this, like this; but not the overall concentration. When we are looking at the phase diagram, in equilibrium condition, what it says is that, at this particular temperature, all of solid should have this concentration, not just the outer layer. At this particular temperature, and for this concentration, all of liquid should have this concentration. So if we are saying CL_1 , this is CS_1 ; so at this particular temperature T_1 , all of solid should have concentration CS_1 , and all of liquid should have concentration CL_1 . But what is happening is that only the outer layer of the solid that solidifies has this concentration, the inside has still concentration like this.

So what will it mean? It will mean that the average concentration would be somewhere below this. If you look at the average concentration plot of the solid, it will be like this. Now there are various things that we will need to understand when we look at this. But first I have one of those things is, for example that I have drawn it only up to T_M , another is that I have not crossed the C_0 concentration line; we will look at those reasons very soon.

But for now, look at this plot. So this is a continuously varying concentration, and therefore, if we draw a similar concentration over here, you will see; okay let me a little bit, draw it a little bit better. So let us say, at some particular temperature we have reached a concentration like this, and at this particular temperature, the liquid will have a different concentration corresponding to equilibrium at interface; at interface it is still equilibrium.

We are not losing the assumption of (inter) equilibrium at interface; we are only saying overall equilibrium inside the solid is not at equilibrium. So this is, if this is any particular concentration CS , then corresponding to this, this will be CL . So the, this is CS_1 , this is CL_1 ; and, since there is complete diffusion in the liquid, or homogenization in the liquid, the liquid will have uniform concentration. Now once this new layer of solid forms, what happens, when we go from over here, this temperature to let us say even next temperature just a little below it. The solid concentration that forms at the outside has higher amount of solute. So this is the (con), this is the concentration of the solute that has, that forms over here; and this is the concentration of the liquid.

Now it is still lower than C_0 , it means it is ejecting some of that solute into the liquid. So once that (eject), once it ejects that liquid, sorry that solute, it forms, it gets into the liquid. And

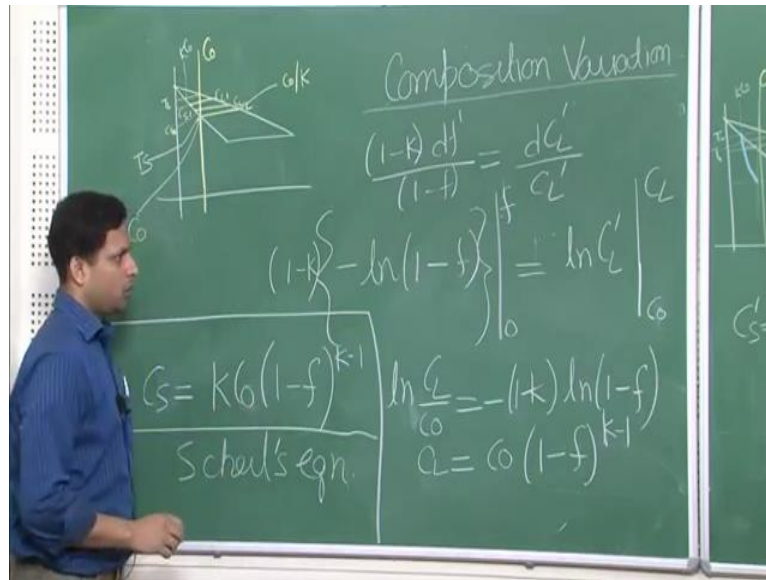
therefore the concentration of the solute in the liquid increases further. So this is the new layer of solid that has formed, which has concentration higher than what it (was) what the original layer had; but still, it is lower than C_0 , so some amount of solute is getting rejected. And this is the increase in the concentration of the solute in the liquid. Now if we equate these two, we will be in a position to get a relation of solute concentration as a function of distance.

So what is this; so let us say, we are looking at a distance f prime; therefore this becomes 1 minus f prime; and a small thickness has grown, so let us call it df prime. The concentration of liquid over here was CL ; instead of CL_1 , we will call it prime because we are putting all the variables; for now it is prime. So CL_1 is equal to CL prime basically. So here it was CL_1 , and it has increased by a small amount dCL_1 . Now the amount of solute that has been rejected from this, this formation of new layer, gets into the liquid. So, this amount of solute can be equated. The, whatever amount has been ejected from solute must be getting into the liquid part.

So let us see, let us try to formulate the equation for that. First let us try to find out what is the area of this, because this area represents the volume of solute that has been ejected. So this is CL prime minus CS prime into df prime. So this length CL prime minus CS prime, and this thickness is df prime; and this is equal to this area. What is this area? This area is equal to dCL prime into 1 minus f prime. So this is the length 1 minus f , and this thickness is dCL prime. So we have setup a differential equation.

Now, let us try to solve it and when we solve it, we will again invoke our equilibrium at interface; so CL prime is equal to KCS prime. Therefore this becomes 1 minus KCS prime df prime equal to dCL ; sorry CS is equal to KCL . Therefore, this is CL . So now, we will put the CL terms together, and we have. So let me take it to this board.

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So we know the form. If you want to get the integrate it, then df prime by 1 minus f , or dC_L prime by C_L prime, will get integrated into a log form, so this equation will become. And this has to be integrated from 0 to 1 ; not 0 sorry, not 0 to 1 , but 0 to some value of f , and this one will become $\ln C_L$ prime, which has to be integrated from 0 to some value of C_L ; and from here, you can easily come to. So this is equation and you can further reduce it to. Okay I missed something here; this is not 0 actually, this is C_0 . So this is the equation that you get C_L equal to C_0 times 1 minus f to the power K minus 1 .

Now let me put it in a form that you already know, which is in the shell equation form. So this will become C_S we will mix; we will again invoke the relation that C_S is equal to $K C_L$, so this becomes C_S equal to $K C_0$ 1 minus f to the power K minus 1 , which is called. So, this is the equation which describes how the solute concentration in the solid will vary, starting from the point where the solidification start to take place, and all the way up to the point, what up to what point; that is a question that again we should ponder over, and we will come back to it in the next class.

So there is lot of more, lot more things that you need to think in the meantime; for example I said that this does not cross the C_0 concentration, and plus this stops at C_0 , and then I am also saying that there is only up to a particular value that you can use this. So all these are related, and we will come back to this in the next class. Thanks.