Phase Transformation in Materials

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Lecture - 31
Alloy Solidification

In the last few lectures, I have been discussing about the growth forms of solidification. And in the later part of the last lecture I told you how we can deal with alloys. So in fact, todays lectures we are going to describe how solid partitioning during solidification alloys takes important role in the siding even the growth forms. So, first let me tell you that whenever you discuss about alloys, we all need to know phase diagrams, because phase diagrams will tell about the equilibrium behavior of the alloys. So, we start with the equilibrium solidification, then slowly relax the equilibrium conditions and show you how actually actual condition. So, real conditions will affect different growth morphologies.

So, first let me discuss with you about the solidification of a bar under equilibrium condition.

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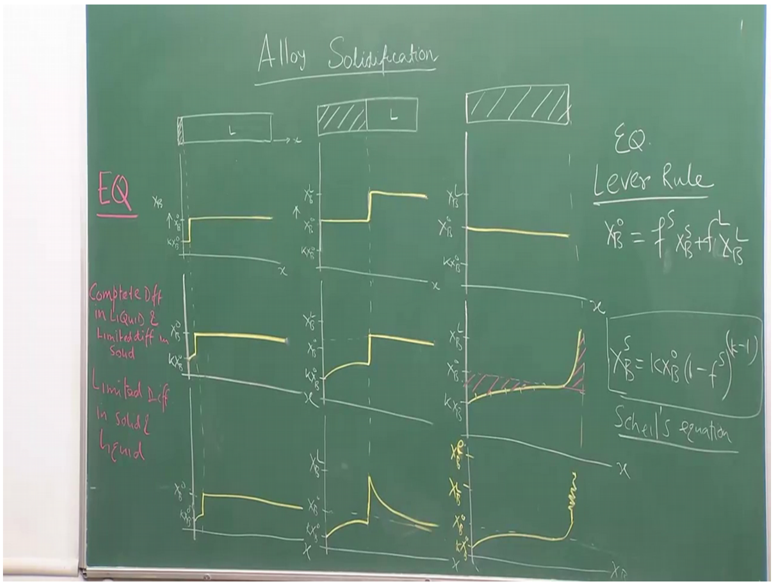

Suppose if I have a bar of this kind of shape and I want to solidify this bar contents in alloy with certain amounts of solid.

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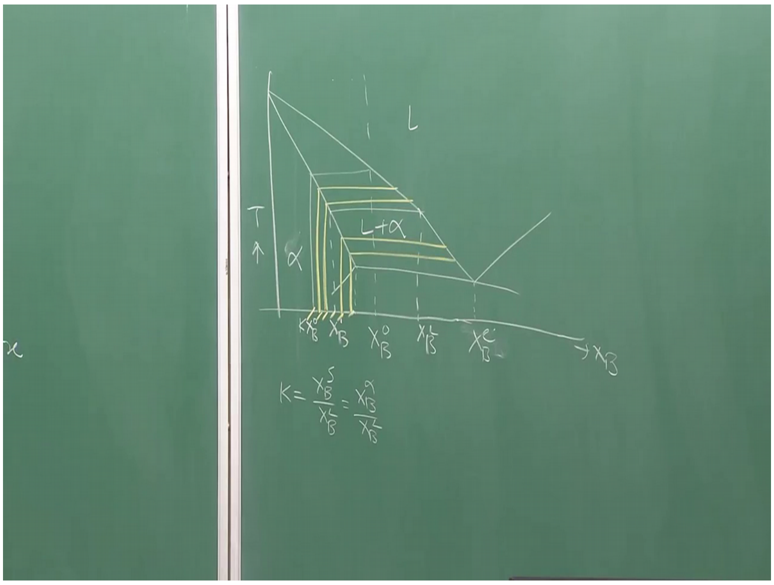

So, I just kept is phase diagram picture on the right side which I have drawn in the last class also to make you understand things very clearly. Little bit modification of these aspect as per the composition excess are concerned.

So, we are talking about solidification of the alloy with composition XB 0. That is in between the solid and liquid. So, this is alpha this is liquid plus alpha and there is a eutectic composition you see this eutectic composition XB e. And this is the maximum composition of the solid which can be there in the alpha phase. So, after knowing little bit of idea about the phase diagrams, let us now consider an alloy of composition XB 0, which we are solidifying from the left side. That is from this side to this side. What I am going to plot is basically composition that is XB as a function of distance x this is x.

So, when a small amount of liquid solidifies and major part of the liquid has not at solidified, it how the composition profile will look like. How the compositions of the solid b will if the solid and the liquid will vary? Let us see that. As you know I have already defined a term called partition coefficient that is equal to K, K is nothing but XB s divided by XB L that is the compositions of the solid divided by the composition of liquid. Sometime this can be also written as XB alpha by XB L even alpha is a solid phase. So, this is the fraction in this phase diagram is always less than equal to 1. Maximum value can be 0.99, but mostly this fraction. Now the first solid which will form as you see here, is basically having a composition given by this which I have discussed in the last class will not go back again.

So, therefore, if I draw and if I write this is K XB 0 K XB 0 is the solid composition. As you known if XB 0 is the liquid composition, then if I put it XB 0 here solid composition will be K XB 0. And this is suppose my XB 0, point this point. So, what will happen it will it will solid will have because equilibrium case where discussing equilibrium of solidification. Solid will have uniform compositions then it will rise and it will become remain XB 0 all throughout the liquid right, is better actually plot be seen color chock. This is what is happening under equilibrium condition am I right. So, solid which will form as a weakening first will have a composition of K XB 0, where the liquid has a composition of XB 0 all throughout.

Now if I solidify little more what will happen? Suppose if I solidify same bar half the h side is solid and this one is liquid. So, again let us plot the composition bar says distance this is XB passes distance. And this is my solid liquid interface. So, I made a dotted line here. So, what will happen is very simple. And this is again K b 0 because equilibrium case means this is XB 0, again XB 0 and this is XB L right. XB L is the any compositions in the liquid. Obviously, this will go and increase as you look at it this will go and increase to XB 0 here.

And then it will remain x XB L because a liquid will have more compositions as per as these solid partitioning concern. As you see here if I have some are there. So, this is my XB L this is XB 0 and this is my XB 1. Suppose, but initial solid has K x b0, but because we are doing an equilibrium conditions, this compositional difference will be completely any loud.

So, initially although there will be little bit of problem, but it will go back and may like this slow little catch up. So; that means, what solid will have always uniform composition of XB 0, always. Now let us do it for the completely solidify block. Again this is distance x this is x b. So, K XB 0 XB 0 and XB L, because is completely solidify the technique about equilibrium situation. So, it will be flat line with the composition XB 0. That is what will happen in the equilibrium under equilibrium conditions. So, let me write down. This is equilibrium that is better to write. Now as you know equilibrium condition is like an ideal condition never prevails in the actual experimental conditions.

So, we have to think how far we can go away from the equilibrium. So, one such situation is that complete diffusion in liquid, but limited diffusion in solid. We are going to delete that what does that mean; that means, that because liquid has diffusivity (Refer Time: 08:28) had than the solid. So, anything which is getting reject in the liquid will uniformly adjusted right. On the other hand, in the solid there is a problem of diffusion because diffusivity in solid is very low. And because of this low diffusivity in the solid we are going to have a situation where diffusion will be very limited.

If that is what happens when how things will look like? It will let me tell you the things will be completely you know distinctly different. So, I am going to draw it for you purpose; obviously, first thing the beginning of solidification will be similar as compared to as same as the equilibrium. So, remember this is K b 0, x K b K XB 0 this is x b0. So, and; that means, what this will be almost similar it will not change much this is my interface. Let me draw it on color chock little bit slope will develop here. Then this will remain like this. Things will start changing that is mainly because diffusion in the liquid is uniform that is why the liquid composition is same all throughout, but diffusion in the solid is not uniform. That is why you see the solid composition of the beginning it was K XB 0. Then slowly rises there is a small you know rise because of these limited diffusion in the liquid solid.

So, once you do that for the next thing that is half solidified again K XB 0 XB 0 and XB L suppose here. So, this is my interface. So, what how things were happen things will be happen like this. I am sorry let us use a chock things will happen like this. As very clear again there is liquid has uniform composition because liquid has no diffusion problem is complete diffusion is possible, but solid has a compositional difference that is what is a coring we discussed in the last lecture. That different paths were solid has different compositions and that is mainly following the phase diagram.

As you see here if I draw this straight line this is what going to happen? If I draw this vertical lines; so you have 1 2 3 4 5 6 different compositions and that is what we plot is looks like this. So, it goes at the interface; obviously, there has to be jump because solid and liquid compositions are distinctly different liquid compositions followed by the liquid as. So, these are the ones. So, at the interface there is a huge jump as compared to the solid compositions. So, that is understandable.

Now, let us look at what happens when is completely solidified when it is completely solidified again K XB 0, point XB 0 XB L. And I am just drawing a dotted line across the x b0. So, what will happen this will be like this, is very clear solid will have different compositional space function of positions do you see here. And finally, it reaches XB 0 at later end later part of these you can see here later part of that and it is compositions suits up. Because see the area under this curve whatever is lost here, solid in the solid must be same as whatever is area under this curve because we cannot destroy solids that is why it is.

Therefore, there will be huge composition spike at the end of the sample. So, let me just do a third situation, which is very important we will discuss each of this case today and that is the part of the 2 lectures. So, if I have another situation where I have complete. So, I have limited diffusion in both solid and liquid what does it mean; that means, that; obviously, limited diffusion solid is acceptable in the sense that solid has a very low diffusivity. Diffusivity of the solid in the solid is slow compare to the liquid it (Refer Time: 13:06) difference.

But suppose in the liquid also we have problem of diffusion; that means, there is no convection present or there is basically diffusivity of this pieces which is moving in the solid basically is also low compare to normally what we get. So, because of that we can have a situation that both diffusion in a solid and liquid will be limited. Then how things will look like things will be completely different as you have seen here. The major difference will be in the in the sense of you know mostly in the second or third part. So, first part it will be almost similar, there will not much change XB K XB 0 x b0. So, this is my interface I am drawing this thing.

So, this is what it will look like and not much difference, but things will be different here in the intermediate state. So, XB 0, K XB 0 XB L this is XB L. Please always refer the phase diagram as you see the compositions these are relative values. So, how it will look like it will be like this. Then there will be a spike because in the liquid there is a there is a limited diffusion in the liquid. So, whatever solid is getting reject in the liquid only piled up at the interface that is what oh sorry we have done the interface little it should be little ahead interface is here right. So, curve nature of the curve will remain same.

So, in the solid because of limited diffusion a composition will be looking like exactly same as that, but in the liquid it will no longer even flat it will be like a piled up at the interface there is a solid pile up. Because and the reason is very simple liquid has limited diffusion there is no convection. So, because of that there is a pile up. And this pile up is basically the reason for criticizes the spike of the solid profile at the interface.

Now, what will happen when you are at the end of the solidification that is not very difficult to understand of there will be huge spike at the end. So, this this is K b K x b0. So, it will be going like this. And at the end it will reach to XB e, that is the XB e XB e is here. You see that XB e is at the in a phase diagram it is almost at the end here this is the XB e this is XB l. So, we are much higher than the XB l. So, that is what is going to happen, but remember this is the more generalistic situation, which you observe in the real materials when you solidify.

So now, question is this for solid distribution of such a kind of stuff, we can easily use lever rule. The equilibrium situation lever rule can be applied what is a lever rule, lever rule says XB 0 is the best composition that is multiplied by suppose fraction of the solid fraction of solid multiplied by solid composition plus fraction of liquid multiplied by composition of the liquid. Mass balance must be retained correct this is the original like compositions that is must be equal to mass or the total composition of the solid total composition of the liquid. The how you get total composition of the solid fraction of the part which is solidified at each cases multiplied by the composition of solid plus fraction of the liquid in cases multiply the fraction of the solid. That is a compositional liquid in each cases that is how it is this is called equilibrium lever rule in the literature.

Now, for second situation we need to derive the rule. As you see clearly for the second situations at any time what is happening. At any type because of limited diffusion the solid there is a difference of compositions leads to change in the material change in the balance. So, let me do it for you. So, very simple let us suppose we have what shall I do let us we have to go to that side of the board. That is the problem remove this phase diagram. So, suppose I have d f s is the fraction of the solid formed. This because of formation of this there is a difference there is a solid change and solid composition differences is basically in the liquid minus solid. That is my difference of the solid multiplied by the fraction solid which is formed that is the d f s must be equal to the rise of the solid.

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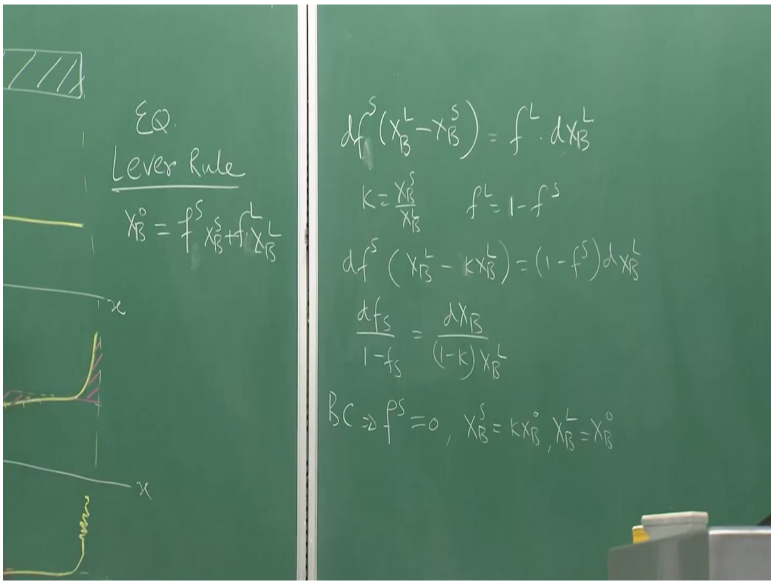

$$X_B^0 = f^S X_B^S + f^L X_B^L$$

$$df^S\left(X_B^L - X_B^S\right) = f^L \cdot dX_B^L$$

$$K = \frac{X_B^S}{X_B^L} \qquad f^L = 1 - f^S$$

$$df^S\left(X_B^L - KX_B^L\right) = \left(1 - f^S\right) dX_B^L$$

$$\frac{df_S}{1 - f_S} = \frac{dX_B}{(1-K)X_B^L}$$

$$BC \Rightarrow f^S = 0,\ X_B^S = KX_B^0,\ X_B^L = X_B^0$$

Let us write down s of the f s of superscript multiplied by change in the composition of solid in the liquid. Because whatever has been rejected by the solid because of these composition this (Refer Time: 19:25) things happening here because of that there is a rejection in the solid.

So, remember this composition is higher than the x XB 0. Because there is a buildup or there is a increase in the in the liquid. So, this is the increase this is the delta this is the delta d x L. And the fraction of the liquid how much liquid is left over that must be multiplied with that. So, this is this solid rejected into the liquid. And this rejection is equal to the change in the solid concentration in the liquid. Now we can we know that K is equal to XB s divided by XB L. This is the partition coefficient right. So, therefore, we can modify this and we also know that f L is equal to 1 minus f s, very clearly we know that. So, let us make change over d f s; so XB L XB s.

So, we will change XB s. So, XB L minus K XB L XB s you can do K XB L equal to 1 minus f s into d XB L right. So, you get a very nice differential equation. So, now, we can differentiate we can integrate as d f s 1 minus f sagain take out f s there and d XB L is equal to 1 minus K XB L that is my differential equation solid balance basically. So, if I integrate that I will do it full you should do it yourself I will simply write down the condition the boundary condition.

The boundary condition here is this that when f s equal to 0; that means, when there was no solid f s equal to 0; that means, this one solid balance is remember XB s is equal to K XB 0 right. Very simple when there is starting of solidification at the beginning of solidification solid fraction is very small. So, therefore, it is equal to 0 the compositions of the solid will be K XB 0, that is the first solid which forms will be equal to K XB 0. And these all XB L is; obviously, not require that is equal to XB 0 that will be also equal (Refer Time: 21: 48). So, if you plug in all this things final equation will write down here is will be XB s equal to K XB 0 1 minus f s to the par K minus 1.

And this one is known as equilibrium lever rule or non equilibrium lever rule or scheils equation. Many people say scheils equation. Is it clear? This is very easy actually anybody can do only thing were doing is this solid balance both in the solid and in the liquid. Because of the limited diffusion in the solid we need to take care of the balance. Now this problem thus this when you have a limited diffusion in the solid and liquid is very long thing to solve and I will not solve within detail because that will take lot of time of mine. So, but I will urge you to look at the book basically this is nothing but a diffusion problem.

The equation which we can be we can use to solve this thing the reason I am giving you the mathematical part is that you can practice yourself from the book as well. Also you can actually solve problems which will be part of your assignments in the books. So, for this situation the equation which is basically can be used is very diffusion equation which is already used.

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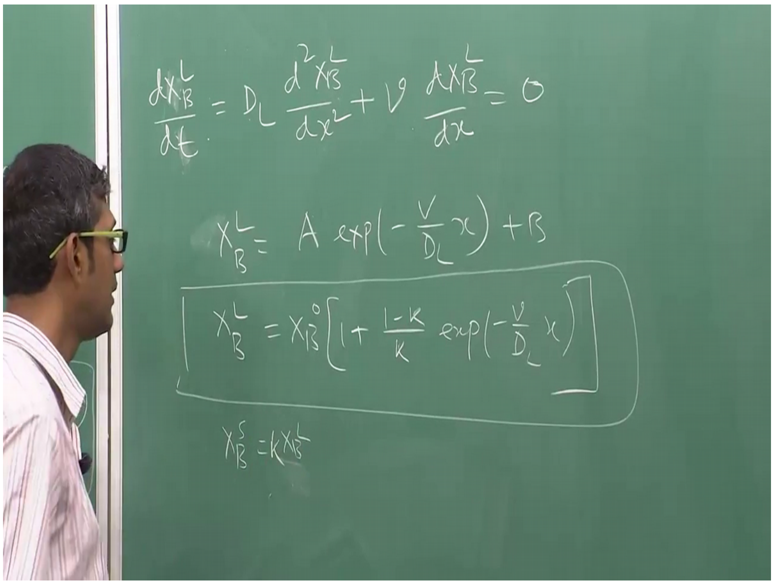

Let me write down that in the liquid, we can write down because things were happening the liquid remember things were happening in the liquid you can see here this is spike formation of the liquid then things happen. So, this is what the most generalistic picture the spike the built up in the liquid. So, this is we can write down a time dependent diffusion equation that is very easy d L in the space and time the small xs are space capital X when you have superscript subscript that is (Refer Time: 24:01) to the composition the small t is the time plus v is the velocity of the interface this will be remember this is my diffusion equation. We do not have this term third term on the right side of the diffusion equation. That is has to be built in here because interface is moving is not as (Refer Time: 24:15) interface as you see here, as you start solidifying this interfaces slowly moving from left to right. So, this interface moment will also change the solid balance that is taken care here in this part.

So first thing one can do is that we can assume study state. We can write down d b d x L b t 0 and then the solution of this equation is very easy that is what now is done in the book. If you want to take the solution of the time dependence of the equation that is the basically very cumbersome is there in the books in in many of the books, but that is very cumbersome that is not require we can always assume the studies is arrive here also because these profiles are drawn ones study states has been reached.

Finally, if I do that solve that equation what I can get, I can get XB L right. I can get XB L basically it will be solution will be very simple very easy it will be a exponential minus v by d L x plus b where b a and b are constant. We can see that the second order differential equations. So, d x 2 by this equal to this equal to minus v by d L v by d L multiplied by that. So, that there you can assume the solution of this equation is exponential kind of a solution and you can do is there in the standard mathematic books.

So, to find you can find out this conditions a and b using proper boundary conditions then it will be become XB 0 1 plus 1 minus K divided by K exponential minus v by d L x. That is what will be the actual solutions for this third case. And estimately you can write down XB s also XB is will be multiplied by basically divided by XB s is what XB s is equal to XB L divided by K no K multiplied by XB l. So, these will K will go down and it will be there.

So, that is basically very important aspect. So, as you see here these 3 situations which I have done I have discussed as a part of this discussion is growth and solidification for alloys is; what is generic very generic situations this will be thought in the solidification of different alloys also. So, we can logically understands this this aspects as I discussed with you we can also do mathematical equation formulation to understand that.

So, finally, this third situation is most common in the alloy solidification. We will we normally do not have sufficient convection the liquid to have uniform composition of the solids in the liquid. We are will have always such a kind of spike in the compositional profile. And this spike is very important for the formation of dendrites in the alloy cases.

So, in the next lecture which I will discuss how the dendrites will form and how we can actually use a novel theory to explain the dendritic formations in the alloys.