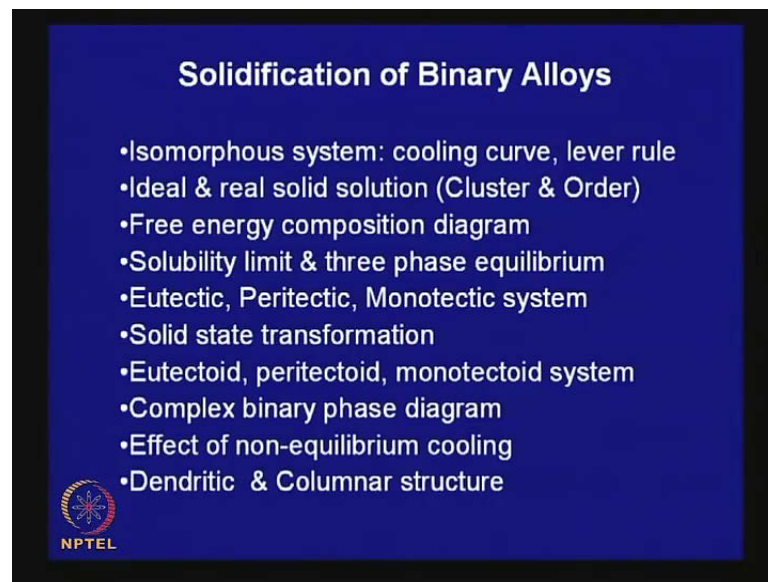


Principles of Physical Metallurgy
Prof. R. N. Ghosh
Department of Metallurgical and Materials Engineering
Indian Institute of Technology, Kharagpur

Lecture No. # 22
Solidification of Binary Alloys (Contd.)

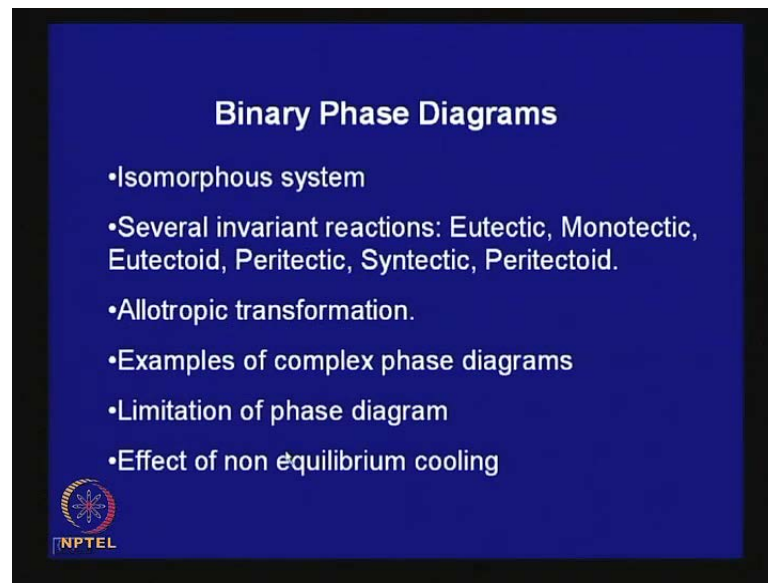
Good morning. We continue with our lecture on solidification of binary alloys. We already have 4 lectures on this topic, and this will be the last lecture on binary alloys.

(Refer Slide Time: 00:36)



And here we will be considering... See most of these items which were supposed to be covered in this topic have been covered, we looked at isomorphous system, we looked at free energy composition diagram, we looked up why do we have solubility limit, and how these are represented in phase diagram. We looked at reactions involving three phases in a binary system, we also looked at some solid state transformations; allotropic transformations, we looked at complex binary phase diagram. And the last class, I introduce the concept of non-equilibrium cooling.

(Refer Slide Time: 01:20)




We also and in fact solidification closes is the base A is represented in the form is graphically represented by phase diagrams, and these are the things we have looked at isomorphous system, several invariant reactions, allotropic transformations. We also had examples of complex phase diagram involving several of these features appearing in the diagram. We also looked at limitation of phase diagram. Say, one of the important limitations is it considered the case of equilibrium; but nevertheless assuming that there is a possibility that local equilibrium exist between the interfaces; that is, solid, liquid or one solid with another solid. It will also possible to explain evolution of microstructures during solidifications and subsequent transformation and some examples we saw in the last lecture and we will build up on this and look at it little more critically.

(Refer Slide Time: 02:32)

Effect of heat flow on interface movement

R = interface movement rate
 L = Latent heat
 ρ = density

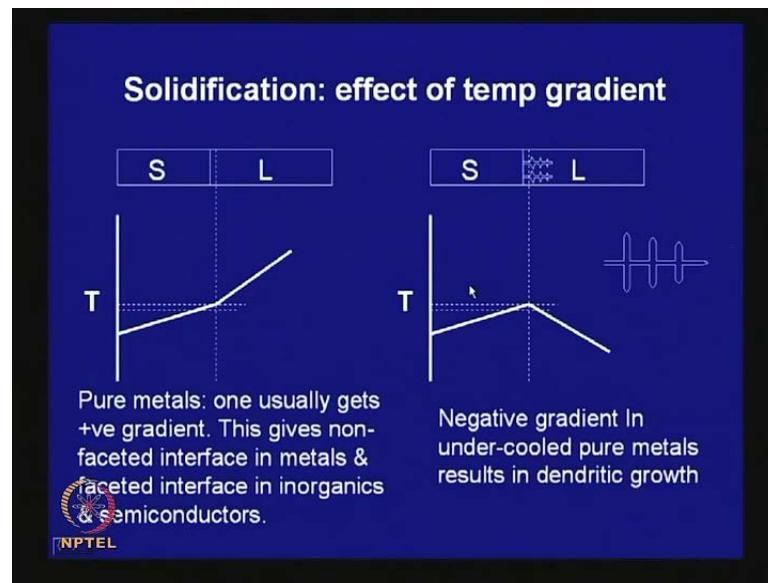
$$-k_s \left(\frac{dT}{dx} \right)_s = -k_l \left(\frac{dT}{dx} \right)_l - L\rho R$$
$$R = \frac{k_s \left(\frac{dT}{dx} \right)_s - k_l \left(\frac{dT}{dx} \right)_l}{L\rho}$$

 NPTEL

Now, here the evolution of structure depends primarily on how the heat is extracted from the system from the liquid metal, when it is poured in the mould. Let us take a simple case say which is listed here. Say, suppose this is the **the** portion of the liquid, which has been poured in the mould and the heat is extracted unidirectionally through these directions. Now, there can be now primarily this and when it is extracted, there will develop a solid liquid interface and this interface will progress as more and more heat is extracted. This interface will progress this side and then each evolution of structure depends primarily of the nature of this interface. Now, for many (()) some of the calculations will do assume that this interface is planar.

But planar interface is always not stable and it also depends on several factors; not only on the heat extraction, it also depends whether there is super cooling in the liquid or not. And infact, this expression gives you a heat balance means how the heat is extracted from this liquid; so that, it solidifies. And here, there will be some amount of latent heat which will come out and that latent heat also has to be extracted and this latent heat also **you know** if the only direction it can flow through is this. Now, there are two important things which are important. One of course is the **the** cooling rate or the rate of heat at extraction to conduction through solid through the liquid layer; the boundary layer that forms and it also depends on the rate at which, this interface moves. But often these two the heat extraction and the movement of this interface, they are often related; they are not independently controllable.

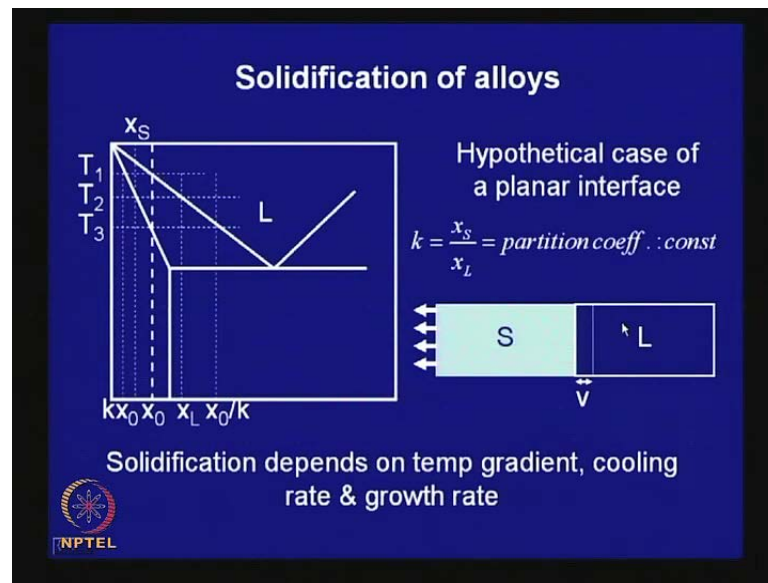
(Refer Slide Time: 04:52)



Now, in case of a simple as a pure metal where there is no transformation. We can think about two kind of a temperature gradient. This temperature gradient is important; because this determines the rate of heat flow or heat extraction through conduction. Now, in one case **the heat** this gradient is like this. So, that liquid is at higher temperature; higher than the freezing temperature particularly and solidification starts, when there is a little amount of super cooling. So, this is you can say this is that freezing temperature. Let us say there will be some amount of super cooling, which will be necessary. So, that will see this is the interface. So, here the temperature that solid interface is slightly lower than the freezing point and this is how, the gradient looks like.

Now, here that from the liquid if the heat has to be extracted, it can only direction; it can go along this. So, here if there is we talked about if there is a departure from the **primary** interface, a bulge develops. Automatically, when this bulge develops, heat will come out from these surfaces also; so, which will infact again... So, this will not be able to extract it. The only way it can be extracted is through direction. So, therefore any bulge formation here in this kind of gradient is impossible; whereas, if we pour in the mould super cool liquid; so that means, within the liquid this is the type of gradient you have. So, in that case this kind of bulge formation is stable; the bulge on that is stable and which is reflected here and this promotes dendritic growth.

(Refer Slide Time: 06:56)



Now, let us see what happens if there are or there is some solute present in the liquid. And one of the simple diagram that we talked about a simple let us look at the solidification behaviour of the terminal solid solution in a eutectic system and this can be applied anywhere. It can also be extended to isomorphous. Infact, this portion behaviour is like an isomorphous alloy and it can be extended to other complex diagram as well. Now, let us take a hypothetical case. We assume that for simplicity to do some calculation; often it is assumed we assume planar interface; this type of planar interface as formed. And infact, even though overall macroscopic scale, it may not be planar; but we can still on microscopic scale in limited region, it will still be valid.

And here, when solidification starts (()) such as say x_0 is the solid content of the alloy and here so this is at any temperature, this liquidus line will give you the composition of liquid and this will give you the composition of the solid. Let us say for a particular temperature in between here at T_2 , this is the composition of the liquid. x_L is the composition of the liquid, which is in equilibrium with solid with composition x_S . And then let us define this ratio is partition coefficient k ; this ratio x_{solid} , the composition of the solid to composition of the liquid we say that this is defined as partition coefficient. And let us take a case, where we assume that this is constant and let us see what happens and we assume that growth rate is constant that in rate at which, this interface moves is constant.

(Refer Slide Time: 09:13)

1. Equilibrium solidification: extremely slow cooling
2. No diffusion in solid & perfect mixing in liquid
3. No diffusion in solid & mixing by diffusion in liquid

Now, there are **there can be** several possibilities and three of these let us look at. One case we look at equilibrium solidification. Here, we allow enough time for the composition of the solid to change. The liquids and the mobility of atom here is much higher. Obviously, we can **we** expect that mixing will be quite fast and for the liquid composition to change in not need to allow long time. But **the** for the composition of the solid to change, we need extensive hold time; that means, let us take a case where the alloy is cooled very slowly and heat is extracted **(())** in unidirection will be like this.

And case two, let us take up a case where an extreme case; there is no diffusion in solid and here we say that there is unlimited diffusion; the diffusion is very fast. One example is either we cool it slowly or we are assume that solid also the movement of atom is very fast you reach equilibrium through and through as you cool. Now, second case we assume that movement of atom in solid is very slow and there is no diffusion taking place; but still there is perfect mixing in liquid. And a third case where we assume there is no diffusion in solid; but in liquid that is not perfect mixing; this mixing takes place by diffusion. So, let us look at these three cases one after the other.

(Refer Slide Time: 11:03)

Equilibrium solidification

Allow sufficient time for solid state diffusion:
only way composition of a solid can change

Conservation criterion: shaded area = amount of solute crossing the boundary

NPTEL

Now, equilibrium solidification, which is shown here; See here when it has just begun, this portion is solid; this is liquid and **and** intermediate time, this is the situation. This interface has moved to this place and this is towards the end, where it has come up to here; the amount of liquid. So, this area you can say **this area you can say** this is the amount of solute. This area is the virtually you can say that is the amount of solute, which has moved in to solid. So, here we assume that interface is moving slowly.

(Refer Slide Time: 11:57)

Equilibrium solidification

Allow sufficient time for solid state diffusion:
only way composition of a solid can change

Conservation criterion: shaded area = amount of solute crossing the boundary

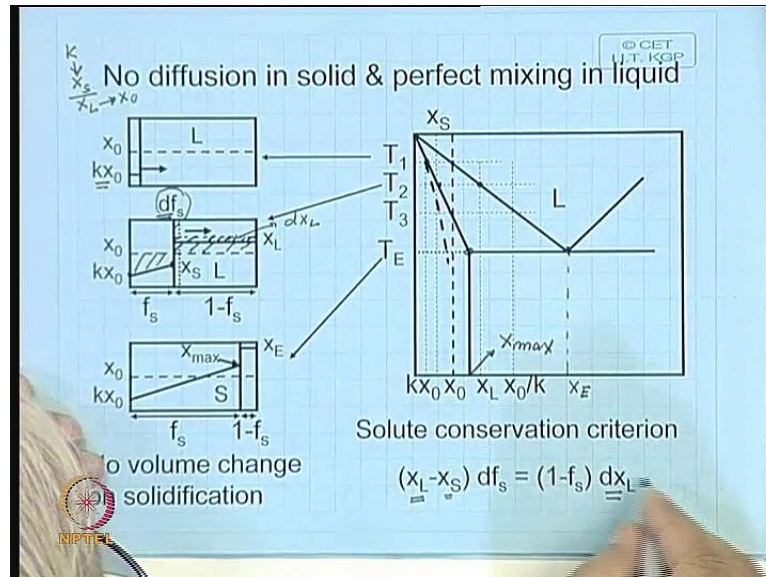
NPTEL

© CET
I.I.T. KGP

And this is the amount of solute from liquid is getting transferred in to solid. So, this area will be equal to this. So, intermediate stage here also; this area is equal to this and ultimately, when the solidification is above to be completed, the composition of solid

you know it comes; it starts here; it moves up; here it moves () for the... And ultimately, when it is totally solidified, here will be uniform composition through and through.

(Refer Slide Time: 12:42)



Now, let us take up a case where in there is no diffusion in solid; but there is diffusion that there is perfect mixing in liquid. Now, in this particular case let us say the first solid which solidifies will have this composition, which is shown here and k is this partition coefficient. So, if X 0 we have said that X solid over X liquid is defined as a partition coefficient. Partition coefficient is defined as this. So, in this case X solid is this. X 0 is the liquid composition; X L equal to X 0; this liquid composition is X 0. So, the first solid which precipitates out will have this composition and then the liquid, if this much amount is coming out over this way, that liquid will get ().

So, liquid composition will change along this line. Say at intermediate temperature somewhere here, this is the liquid composition and the solid composition as see initial first layer, which solidifies is this. But next one which is just solidifying now will have a composition, which is given by this point and which is x s and there will be a composition gradient like this. And the liquid composition will shift will be richer in solid; that means, its concentration will be higher than X naught; it comes here and this area be equal to this. So, this is the principle of conservation of the solute element.

And in extreme case as it goes down, ultimately you will find that you will reach a temperature here, where that liquid will attain the composition of eutectic. This is the

eutectic composition and then the solid will attain this composition, which we say this is X_{max} and which is represented graphically here. Now, if you write down try to balance; that means the solute transfer from liquid to solid. Now, if you assume that f_S represents fraction of solid; so this is the total structure; this is f_S represents fraction solid and which is... And now let us say this interface move slightly towards right. So, that means these changes there is an additional df_S ; amount of additional solid is forming.

So, in that case how much amount of solute has to be transferred to solid? So, this is obviously this will be the difference; the solid concentration difference between liquid and solid; this is X_L minus X_S . So, this is the amount has to be moved in to this. So, therefore do multiply by this fraction transform. So, this will be the total amount of solute, which will move from liquid to solid and this will be equal to the change in liquid composition. The change in liquid concentration, the X_L ; now X_L so there will be a dX_L . So, this will be the change in liquid concentration. So, what we are doing? So, this area and this area we are trying to balance. Now, so therefore this is the conservation; when we apply the conservation criteria, you get this equation.

(Refer Slide Time: 17:14)

No diffusion in solid & perfect mixing in liquid

$$-\ln(1-f_s) = \frac{\ln x_L}{(1-k)} + \text{const}$$

const

Initial condition: $f_s = 0$, $x_L = x_0$

$$\text{const} = -\frac{1}{1-k} \ln x_0$$

NPTEL

And if you try to solve it, which is shown here; this is the simple differential equation and which can be **which can be solved**.

(Refer Slide Time: 17:27)


No diffusion in solid & perfect mixing in liquid

$$(x_L - x_S) df_S = (1 - f_S) dx_L$$

$$\text{or } \int \frac{df_S}{(1 - f_S)} = \int \frac{dx_L}{(x_L - x_S)} + \text{const.} = \int \frac{dx_L}{(x_L - kx_L)} + \text{const.}$$

$$\text{or } -\ln(1 - f_S) = \frac{\ln x_L}{(1 - k)} + \text{const.}$$

Initial condition: $f_S = 0$ $x_L = x_0$

$$\text{const.} = -\frac{1}{1 - k} \ln x_0$$


And if you integrate it, there will be an integration constant and this is therefore the expression. After you integrate, what you get is $\ln(1 - f_S)$ equal to $\frac{1}{1 - k} \ln x_L$ plus constant. To evaluate this constant, you can substitute that initial condition that when there is just solidification just begins at that stage x_L equal to x_0 . So, if you substitute this over here, you get constant; this is 0. So, therefore the constant is equal to for which is given here; constant comes out to be this and if you substitute this constant $\left(-\frac{1}{1 - k} \ln x_0\right)$ and if you go to the screen.

(Refer Slide Time: 18:39)

No diffusion in solid & perfect mixing in liquid


$$x_S = kx_0 (1 - f_S)^{(k-1)}$$

$$x_L = x_0 f_L^{(k-1)}$$

Non-equilibrium lever rule
Scheil equation

$$f_L = \left(\frac{x_L}{x_0}\right)^{\frac{1}{k-1}}$$

There will always be some eutectic in the last drop of liquid on solidification.



You can simplify it and you will get this type of equation; that is, this gives the first equation gives the concentration of solute and solid as a function of fraction

transform. And this is for the liquid concentration of solute in the liquid as a function of f_L . This is the 1 minus f_S equal to the fraction; that is liquid. 1 minus f_S is actually is fraction liquid.

(Refer Slide Time: 19:39)

© CET
I.I.T., KGP

No diffusion in solid & perfect mixing in liquid

$$x_L = x_0 f_L^{(k-1)}$$

Non-equilibrium lever rule
Scheil equation

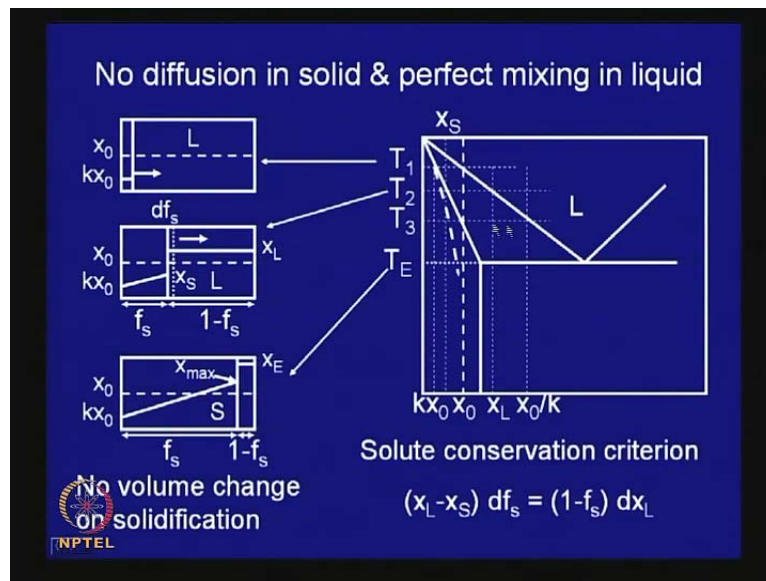
$k < 1$ $x_L = \frac{x_0}{f_L^{1-k}}$
 $x_L \rightarrow \infty$

There will always be some eutectic in the last drop of liquid on solidification.

NPTEL

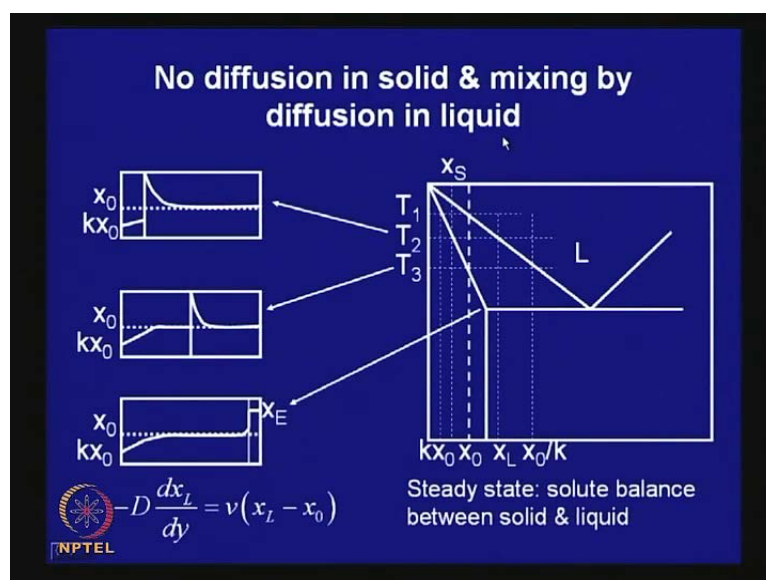
Now, it is interesting you look at it; this f_L say if you look at this expression that would critically what it shows that concentration x_L is equal to initial concentration times the fraction liquid to the power k minus 1. Now, k is less than 1. So, k is less than 1. What does this mean? So, x_L is equal to say suppose let us say k is 0.5. So, if this is equal to x_0 minus k is less than 1. So, this will have some power. So, suppose this is let us say 0.5. Now, suppose this fraction liquid if it becomes very small, in that case what is show that this increases; this is approaching infinity. So what does this mean?

(Refer Slide Time: 21:19)



This means, if we go back couple of slides back here; so that means as the solidification proceeds, x_L can easily reach this point. So, even before the (C) the solidification will not be complete, until this temperature the (C) composition of the liquid reaches this and once it reaches this point, then you have a eutectic. So, that last solid that will solidify in this case will always be (Refer Slide Time: 18:39) you will always have some eutectic in the last drop of liquid to solidify, even if the amount of solid in the alloy is very low.

(Refer Slide Time: 22:05)



Now, let us move on to a case where there is no diffusion in solid; but there is mixing by diffusion in liquid. In this case the few cases, which have been represented here. Let us consider the similar system exactly here. Say, suppose at this temperature say T_2

somewhere here, as we have seen the first solid that will solidify. We will have this composition k times; the partition coefficient times X_{naught} ; this is the initial solid. And final solid at the solid liquid interface will have the composition, which will be given by X_S . So, this temperature; it is given by at this point; any point on this solidus line. So which we shown over here and now what happens is what does this...

Since some solute there obviously will be some build up; because we are assuming that when this transfer is taking place, the composition of the liquid far away is X_{naught} . But when the solid is rejecting the solute, it is going into the solid liquid interface. So, the composition will build up over here and let us say this has gone up somewhere here and **and** after a certain distance, it becomes equal to the X_{naught} . So, because of this concentration gradient there will be some diffusional flow of solute from this higher concentration to lower concentration. So, in this case also therefore we can build up similar using conservation principle, we can build up a equation that will **that will** describe how the solute gets redistributed in the liquid.

Now, here if you progress if you cool it further, it will come down somewhere here. Let us see at this particular temperature and **it is** it has been found an experimentally also; that after certain time, what happens? When you reach this temperature, you get a situation like this; that solid composition becomes equal to the composition of the original the alloy; that X_{naught} . And we assume that half **(())** the solid composition does not change and the solidification is completed at temperature T_3 . In that case, we have some kind of a steady state situation. It comes here and it comes, you get a steady state situation and this composition of solid there after does not change.

But at the interface there is that build up is still there and this is the build up. This is the concentration in the liquid and it proceeds further and towards the end, there will be some amount of eutectic; towards the end there again will be some **(())** towards the end of the solidification again there will be some **(())**. So, that means there will be a stage somewhere here, where there will be a balance and there will be a steady state and after it reaches the end, then again that liquid will try and get **(())**. So, this is **this is** something like this; that means towards the end, **this** there will be a large difference in composition in the liquid. A liquid will have a build up and here it may reach that eutectic composition.

And now, let us see that what this equation if you balance the solute movement, what type of equation do you get. Now, if we say that x_L is the liquid concentration and x_0 is the solid concentration. When the solidification starts and we have shown that this interface moves with a velocity v . So, in unit time what we have is amount of solid transfer will be v times x_L minus x_0 . And here, so therefore there will be some amount of that solute has to move through the liquid. And let us say that liquid, there is a concentration gradient setup and this distance we represent by this direction we represent by y and then this is the diffusivity D in liquid. And then this is the equation, which describes the solute balance between solid and liquid at this interface.

(Refer Slide Time: 27:28)

**No diffusion in solid & mixing by
diffusion in liquid**

$$-D \frac{dx_L}{dy} = v(x_L - x_0)$$

$$\frac{dx_L}{(x_L - x_0)} = -\frac{v}{D} dy$$

$$\ln(x_L - x_0) = -\frac{v}{D} y + \text{const}$$

initial condition: $y = 0 \quad x_L = \frac{x_0}{k}$

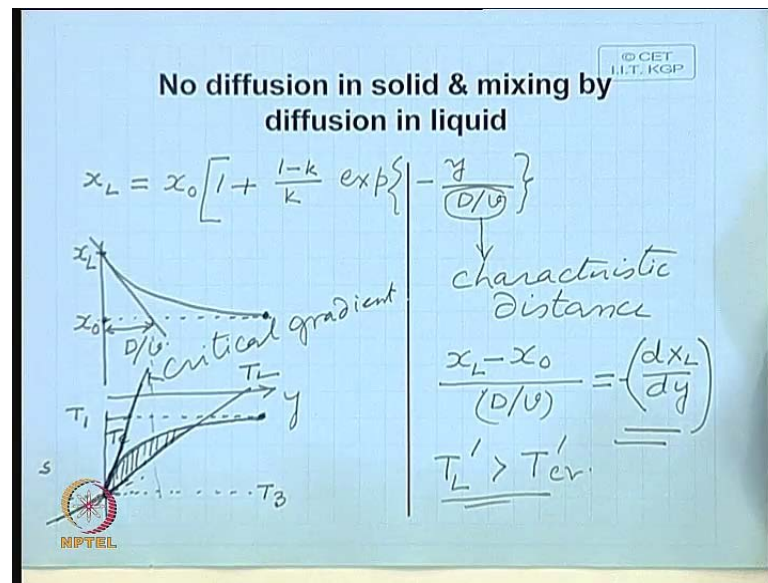
$$\text{const} = \ln\left(\frac{x_0(1-k)}{k}\right)$$

$$x_L = x_0 \left[1 + \frac{1-k}{k} \exp\left(-\frac{y}{(D/v)}\right) \right]$$

NPTEL

And once you solve this; this also is a very simple equation, which can be solved and the solution, which is shown over here. And when you integrate, there will be an integration constant, which you can evaluate by this initial condition. And once you evaluate this by that initial condition and substitute the constant back, what you get is the concentration profile and you see that this profile has an exponential character.

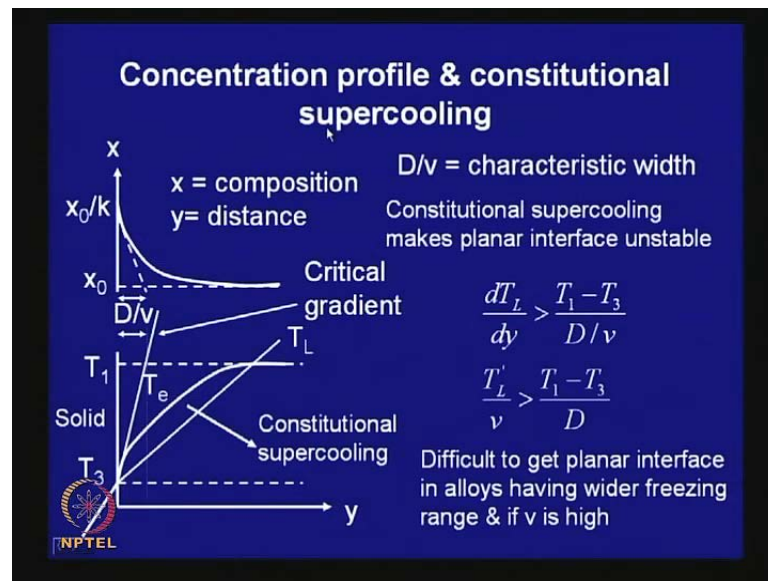
(Refer Slide Time: 28:08)



So, that means and if you try and plot; that means the concentration in the liquid will be equal to x_L minus then an exponential term minus this is the distance over D minus v . Now, here look at this dimension. This dimension of this is also that of a distance and this is called a characteristic distance **characteristic distance** for the concentration profile. So, that means from that interface, say suppose this is the interface and here your concentration at the interface is x_L .

And as you go in this direction y , your concentration is changing like this and at a large distance, it becomes equal to x_L . So, this is x_L ; this is x_L . Now, if you go back to the previous expression what we said that; so this is x_L minus x_L is this; this if we divide by D by v , this is equal to dx_L/dy ; this is negative. This is the expression; that means solute balance gives this. So, that means if you draw a line here the tangent, then this distance is equal to D by v and this is and it is quite important to see look at what is the effect of this magnitude of this characteristic distance of the concentration profile and this is shown in this diagram.

(Refer Slide Time: 30:44)



This concentration profile has been plotted here and this is the tangent at that interface and this side is solid; this portion is the liquid and here is the build up of concentration in liquid; that it is much higher than the concentration of liquid far away. So, there will be a diffusional mass transfer along this and we are considering the steady state diffusion only. And now and let us look at side by side the temperature gradient or how does this temperature plot would look like? Now, here the temperature if you plot here; the temperature (Refer Slide Time: 28:08) just down below; this side is solid and the solid is cooler. So, this is the temperature of the solid.

So, this is the temperature of the solid liquid interface under the steady state growth or **movement of this interface** steady state movement of this interface. So, this is we have seen that if you refer back to the phase diagram, where these temperatures **are** have been marked. So, this is the T_3 temperature and now here what happens is **and** the temperature far away in the liquid; this; this and far away in the liquid; it is a composition is x_0 . So, T_1 you can say the liquidus temperature far away and now you look at this concentration profile **look at this concentration profile**. With this profile, if you go and with this profile you refer back to the phase diagram that liquidus point.

Say, suppose here this is the concentration in the liquid that is x_0 . So, therefore here its melting point or liquidus point will be here and here is the liquidus point and in between that liquidus temperature, profile will be like this. So, this we say that this is **the temperature** that equilibrium temperature of the liquid, which is existing in front of the just near this solid liquid interface. So, far away its temperature is same as T_1 . But in

between the **transient** zone, it has this; this is the temperature of the liquidus. Now, let us look at what is the temperature gradient that we are maintaining and this is the **the** cooling condition that mould condition is such that we are able to maintain.

This is the gradient; this is the temperature of the liquid. So, we maintain a gradient and the liquid temperature gradient. So, as you move in other mould, the temperature is higher and this is the solid temperature. Now, in that case what we have? We have a region here, where there is super cooling. So, even though the gradient is positive; so refer back to the **(())** situation. Unlike that, here even though you have a positive temperature gradient, there is super cooling. So, here you can say that this is where your planar front will be unstable. Look at this case. If you are able to **(())** gradient, that means this distance; this is the distance. So, at this distance if you are able to maintain the tangent, you draw this tangent to this.

So, if this gradient it matches this; in that case, what we can say if this gradient try and find out what is this gradient? This is the **composition** temperature profile and let us try and find out this temperature gradient. And if this temperature gradient is greater than a critical value or you can say that this temperature is you can say this is the critical gradient; temperature gradient. So, if this temperature gradient that means first differential of this with y ; so if this is greater than that critical gradient, in that case we say that one can infer there is no constitutional super cooling. Therefore, planar interface will be stable and otherwise there will be deviation from planar interface.


(Refer Slide Time: 36:38)


Evolution of cellular structure

Alloys rarely solidify with planar interface. Temp gradient & growth rate can not independently controlled. They depend on heat transfer rate.

Cellular structure develops if temp gradient of initially planar interface is gradually reduced below its critical value.

$T_L' > \text{Critical}$

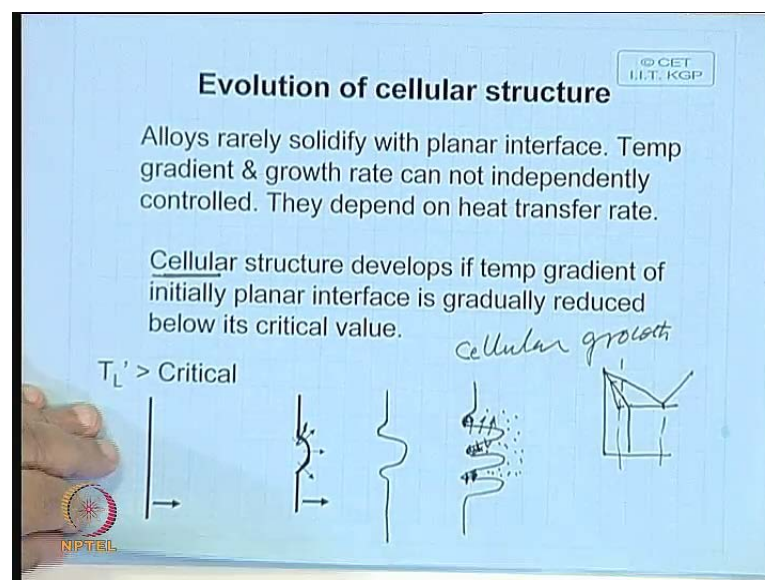


 NPTEL

And so this is the... So, therefore in this particular case, you will try and **it** you will tend to get... If you go back (Refer Slide Time: 30:44) and this condition which is listed here, look at this. If that means, this is the critical gradient, and if the actual gradient which you are maintaining that this T_L gives the actual gradient. The differential of this line with respect tangent of this, the dT_L over dy , if this is greater than this gradient, that is T_1 minus T_3 over this distance; that this is the **distance** characteristic distance. In that case, you will have constitutional super cooling, if this is greater than this, then the planar interface will be stable. If that means, if this slope the gradient is on this side, you will have planar interface, if the gradient on this side, you will have dendritic growth.

So, this side you have planar and this side you have dendritic growth. So, looking at this diagram you can say or this type of relationship you can see that it would be difficult to get planar interface in alloys, where this temperature is very high and also if the cooling rate is very high. The v , that rate at which that interface moves; if this is either cooling rate is very high, it will be extremely difficult to get planar interface and having and also if the alloy has wider freezing range, then also it will be very difficult to get **get get** a planar interface and now, let us look at say little departure.

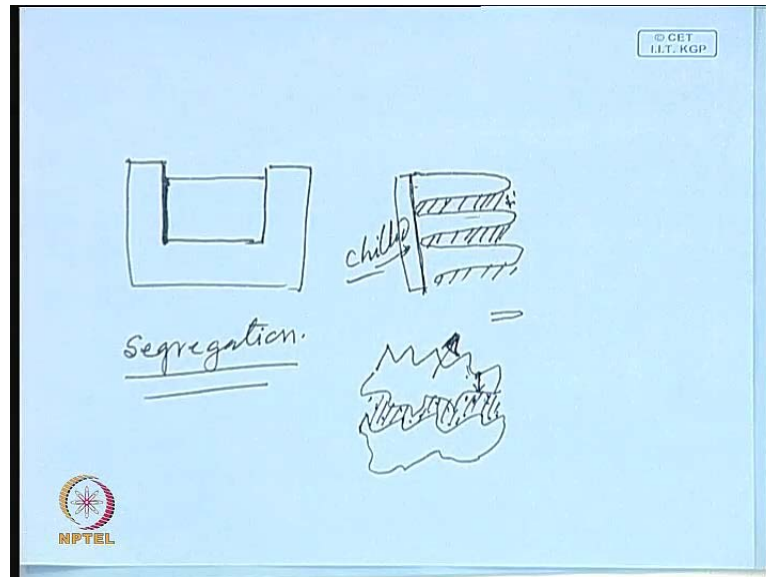
(Refer Slide Time: 38:59)



Let us case; but in reality if you look at alloy system, the alloy they rarely solidify with planar interface. And the temperature gradient and growth rate; they cannot be independently controlled **often** and they dependent on heat transfer rate. Now, let us take up a case and see, when cellular structure develops; we will come to know what is cellular structure. Now, suppose if the temperature gradient is initially favours planar

interface and in gradually. So, initially (Refer Slide Time: 30:44) you are able to maintain say a gradient on very high gradient and later on, it moves this side and which is in reality, it is possible. In alloy, it is possible in reality.

(Refer Slide Time: 40:02)



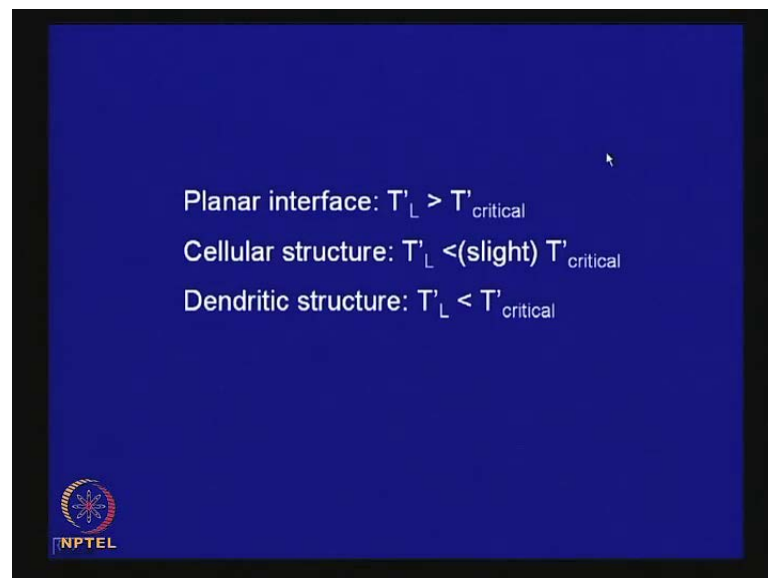
The reason is, if you look at you have mould and you pour a metal. So, initially that liquid here, you have a very high gradient. The mould is the temperature will be much lower and when you poured the metal initially here, the gradient is very high. So, on the surface, the initial gradient is very high and then let us says in that case, the interface is planar and after that the gradient when the solidification proceeds, this thickness grows. So, heat has to be move through this. So, the gradient decreases. So, later on say it comes to (Refer Slide Time: 30:44) this side. So, that means there is a departure from (Refer Slide Time: 38:59) the planar interface is gradually it is reduced.

In that case, what happens? This kind of bulge will now be stable and in this case, there is a constitutional super cooling. So, even if that there is some amount of heat can be accommodated this side. So, what happens when this heat is accommodated in this side? It will also go there. So, what happens? Later stage, it develops this side. There may be some amount of melting again and this type of this is how it starts growing. And you **you** grow further time, then you will find this type of structure develops and this is called cellular growth. And here, **you know** you have the liquid; the solute is also get in rejected here **rejected here**.

Now, clearly and when (()) and it is quite likely. So, here if you have an eutectic type of alloy, what happens? When it starts cooling down, towards the end there will be some eutectic solidification here. So, here you have liquid; here it is very rich in solute in this end very rich in solute; here it is linear in solute; this portion it is linear. And here, when it reaches that eutectic composition this composition, it will get converted in to an eutectic structure. So, what you will have is (Refer Slide Time: 40:02) here once the solidification is completed, you will get this type of a structure here and here you have eutectic.

So, that means in these channels, here you will have eutectic structure. So, this is what type of structure which will develop in a mould. Initially, because of high gradient, you may have a planar interface; this will be the change zone. Then you have this kind of a cellular type of structure. So, this in reality, you do get it. So, that means, we have made lot of assumptions and based on that, we have tried to understand the how the solutes get distributed in the liquid during the process of solidification and it results in structure, which are which can be explained.

(Refer Slide Time: 44:12)



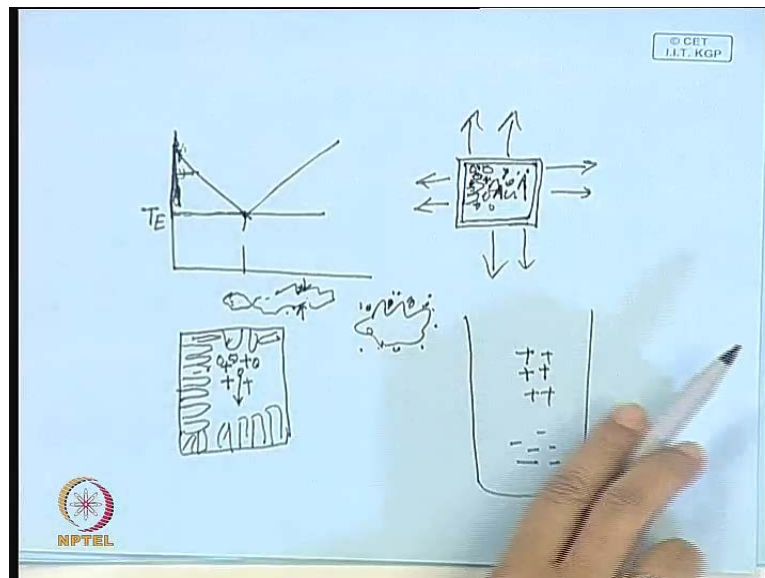
And the criterion of the type of structure that you get is if you have a planar interface, in that case the gradient should be greater than the critical. In case of a cellular structure, the gradient is slightly lower than the critical; then you get a cellular structure. And when it is much less than significantly less than the critical, in that case you will have (Refer Slide Time: 40:02) dendritic type of structure that this will... So, these will be dendritic type of structure will develop and here also this liquid, which is present here; they will

convert in to eutectic. So, you do get this type of structure in alloys and here **you know** and this redistribution of the solute; infact this is there is a general term we see that this is called segregation.

So, as a result of this non-equilibrium cooling, solute is not uniformly distributed and this is called a solute is segregated and that solute segregation is called this is one type of segregation. It is a micro segregation and if this dendrite if you want to make them a uniform composition, you have to heat it. And if this dendritic structure is very coarse, in that case it will take very long time. You may have to heat it for very long time to make this composition uniform. But in this dendrite, they are smaller; they are thinner. If the cells are thinner or if this dendritic arms, they are thin.

In that case, that time which is required for homogenization is small. (Refer Slide Time: 44:12) And now let **us let** me give a couple of example of segregation. Say, **one you have** all of you **have** must have seen ice cubes and the ice cubes actually **its** which you grow in home say in a chilled tray. If you are **are you** try to grow the ice in the freezer and you look at the ice; take out a cube; look at it. You will find that the edges they are transparent; whereas, at the centre it is foggy; this is actually a clear case of segregation and why does this take place?

(Refer Slide Time: 47:05)



Now, water actually has dissolved gas; that means air is dissolved in water. And air and water, it forms some kind of a eutectic phase diagram. So, let us assume that water this is pure; eutectic temperature is this; this is the eutectic composition. So, the first that ice

that will form; say this is let us say this is the container and the heat is extracted from all sides, let us say. In that case, the first layer that ice will form will form a planar and this will go on rejecting the air to that water. So, this becomes richer in air; air concentration increases here. And ultimately, when it reaches **this composition** this particular temperature that is eutectic temperature, then both solidify to get; that means ice will form.

But in the mean time, a crust will form on the top of the ice; because heat will be extracted from the top as well and the ice is lighter. So, therefore I **put** puts a cover and this air, which is trapped is also not able to come out. So, once these ice crystals form here; so the air bubbles will also get interrupt between you can see the dendrites of ice is the crystals of ice and in the channels say crystals of channel. There will be air bubble and this is what you see. So, in reality here you can say this is the defect free, segregation free region and air has segregated in the central portion and this is what you get, when you solidify alloys as well.

When you solidify steel also in a large mould, here also the steel will have dissolved gases. These gases will go to the centre and the mean time if the top has solidified, the gas cannot come out. So, in the central portion, you will get gas porosity as you and infact, these porosities will be present in the intra dendritic that crystal this channels and this is the type of segregation. The solute elements also do get segregated and amount of segregation will be moved to the centre of the mould. If you go from the mould wall, here a purer material and segregations, solute concentration in the centre portion will be more. And also **in the solid** in the liquid, there are other movements are also possible.

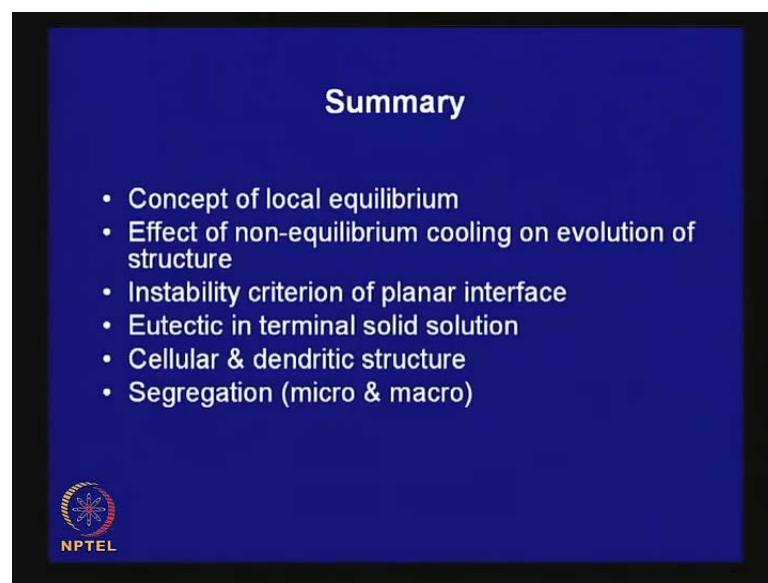
The movement due to convection; there will be temperature difference in the liquid; the lighter liquid, which has lower density. When it cools the liquid cools that the density increases. So, that therefore the cooler liquid will move down and this kind of convection current will be set up. Similarly, the solids which form the crystals which form and towards the end; say if this is the mould, you have this type of cellular structure. This is forming from the wall side. Crystals form and these are the **(())** grains, which are forming and towards the end, **you know** the super cooling here becomes so large; you will get crystals here also.

If these crystals which are heavier than the liquid, they settle down and so towards the bottom of that **(())** also, sometime you **you** get negative segregation. The first solid

which that precipitates out; they are purer; so you get negative segregation here. And positive segregation at these parts and this segregation you will always get in alloys and by controlling and one way you can control is control the processing that nature of segregation, the extent of segregation. And if you have to get, if some of this segregation which are macroscopic, there will be very difficult to remove by any subsequent heat treatment you have took.

So, one way will be that is types of segregation which you get which are very large, which you can see by naked eye which will be very difficult to remove. But if you have microscopic segregation, say small crystals have formed and there is difference in compositions are small these dendrites have formed. The dendrites armed they are finer; in that case, the width is less. So, here if you heat it, that composition uniformity may be possible to achieve. But if you have macroscopic segregation, then you have to do subsequent downstream processing may be large deformation to make it uniform.

(Refer Slide Time: 52:59)



So, with this we finish our lectures on solidification of binary alloys, and later on we will build up on it and look up more complex systems. And what we have looked today is we use the concept of local equilibrium to this to reason out to find out the type of structure that we develop in alloys during solidification. And we also looked at the instability criteria for planar interface, and why you get and we also found out why we get eutectic in terminal solid solution. And we also looked at the cellular difference between cellular and dendritic structure, and when do they form. We also talked about segregation with

micro and macro segregations .And later on a subsequent lecture may be we will using some of this concept, and apply them. **Thank you.**