Materials Science and Engineering
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Lecture - 18
Solidification structure

Hello friends; we were discussing about the equilibrium transformations ok, we were seeing that in equilibrium condition under eutectic phase diagram also, that how the micro structures will come out. In that now today's lecture I will try to discuss about solidification structures, basically how the solidification structures are going to be present in a in a material and also we will see is the non equilibrium, how the non equilibrium transformation will takes place.

If I am doing under non equilibrium condition because, earlier we only discussed about the equilibrium condition in eutectic phase diagram this time we will discuss under non equilibrium condition and we would like to give a little bit of mathematical treatment to that ok. So, till now we were only discussing qualitatively that these micro structures will be there, now we will also try to give a mathematical treatment to that and from there we would like to bring a very important structure.

That I am I will tell you in the next slide.

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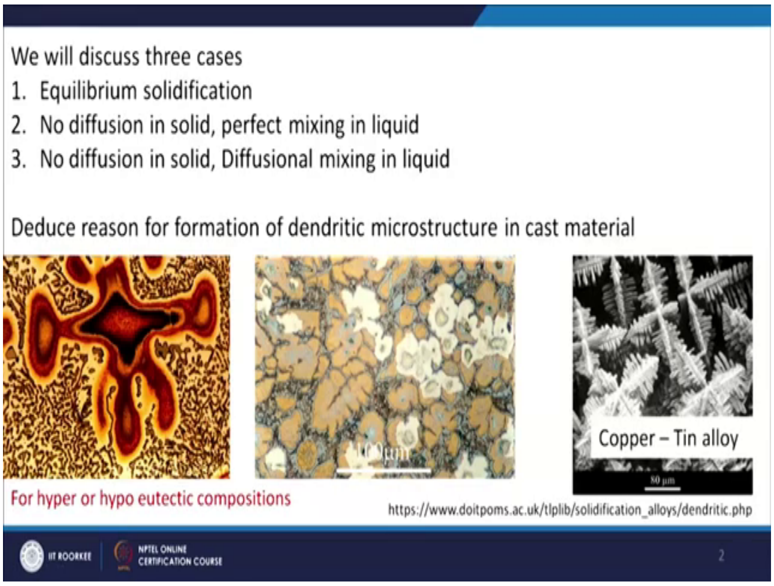

We will discuss three cases

1. Equilibrium solidification
2. No diffusion in solid, perfect mixing in liquid
3. No diffusion in solid, Diffusional mixing in liquid

Deduce reason for formation of dendritic microstructure in cast material

For hyper or hypo eutectic compositions

Copper – Tin alloy

https://www.doitpoms.ac.uk/tlplib/solidification_alloys/dendritic.php

So, basically we will discuss three cases here and these are equilibrium solidification, no diffusion in solid, but perfect mixing in liquid. So, in the liquid portion we will keep doing some through studying process some mixing and in the solid it will be there will not be any diffusion.

So, no diffusion means why we are saying no diffusion because, we are going to do cooling very fast. So, we are not giving enough time for solute atom to diffuse in the solid, the third case will be again no diffusion in solid and in the liquid also the mixing is diffusional ok. So, there these will be the 3 cases and you will see in the slide some very nice micro structures are there ok.

So, the first microstructure if you see this is a a pro eutectic phase. So, you can see this as a prophetic phase which is there and in between a pro eutectic phase these are the eutectic microstructure. So, you can see dark phase and the bright phase together and in the pro eutectic phase also you can see that effect of coring. If you remember we discussed about solidification coring ok.

So, you can see the gradient in the composition is starting from the where the first solid which has started forming and as it is going away from that centre. You can also see that this the eutectic- a pro eutectic phase which is formed, it has some nice shape here ; that shape you can see from another angle like you can see that there are some branches which are coming so there is a main branch and some other branches another 1 you can see here very nicely.

So, you have a main branch coming and then there are side branches which are coming. So, it looks like a dendrite, dendrite is a tree like let inward where when we say dendrite it looks like a tree. So, you have a main branch then you have other sub branches and thumbs up some more tertiary branches and so on ok. So, you have this primary branch then you are getting these secondary branches and there may be some tertiary branches also can be formed.

So, this type of structure is called dendritic structure or these are called dendrites and this is a very typical microstructure you will see in a in a cost material, where solidification is taking place under non equilibrium condition so and you can see that there is a large variation in the microstructure and of course, there will be compositional variation also.

So, you have all this dendrite, these are all pro eutectic phases and then between 2 dendrites you have a inter-dendritic region which is a eutectic phase. So, all these things we have to take care in the subsequent processing, so for any material the first condition is that you do melting, pour the molten metal into some ingots or cast whatever cast mould you have prepared and then in that it will do there will be a solidification, during solidification you may might have this kind of dendritic structure between dendrites, you will have inter dendritic structure and there will be large compositional variation and this kind of microstructure.

Now this micro structure is not a good microstructure from material property for material properties mechanical properties basically. So, we have to get rid of this microstructure in the subsequent processing. So, if you remember for 1 processing already we have discussed which is called homogenization.

So, homogenization will with homogenization we will try to at least homogenize the composition throughout the ingot and with other processing for example, rolling or extrusion or forging we would like to break this dendritic structure and maybe try to get some fine recrystallize microstructure. So, these microstructure we will see subsequently. So, this is the idea. So, this we want to understand and for that this lecture is ok.

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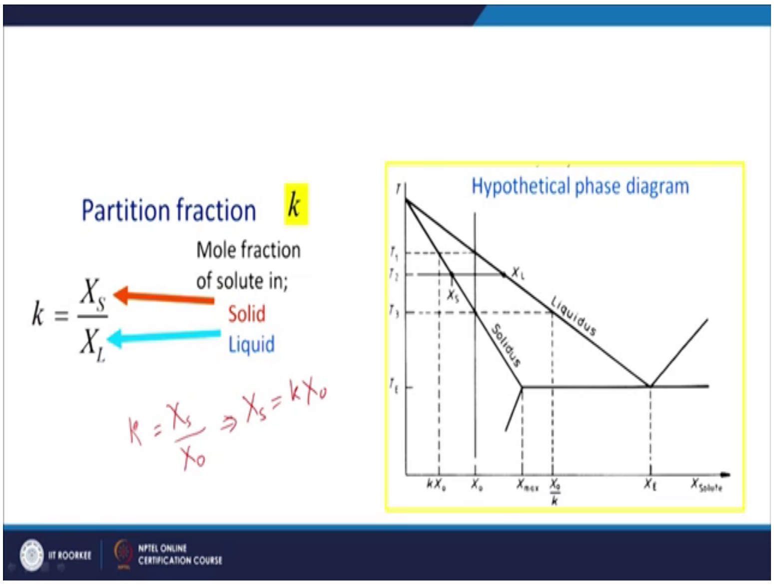

Partition fraction k

$$k = \frac{X_S}{X_L}$$

Mole fraction of solute in;

Solid

Liquid

$$k = \frac{X_s}{X_0} \Rightarrow X_s = kX_0$$

Hypothetical phase diagram

So, the to define variation in the solute content in the solid and the liquid ok, we will define a term called partition fraction ok; which is given by we are saying that is k the partition coefficient is k and which is the mole fraction of S, divided by mole fraction or weight fraction of L ok. So, if you are talking in terms of weight fraction it can be weight fraction so or if you are talking in terms of moles, it will be mole fraction of solute in solid XS and mole fraction of solute in liquid XL.

So, as you can see here in the in the diagram here ok. So, we have a material for which we have kept overall composition X as X naught and we are starting the solidification from some temperature in which it is fully liquid and when it crosses this temperature T1 here and when it crosses this liquidus line at T1 ok, the solidification will start ok.

So, the first solid which is going to form you already know we can plot a tie line, wherever it is cutting the solidus curve that will be the composition of the solid.

So, this is the first solid to form ok, so at this my liquid is it is totally liquid. So, my liquid has the composition of X naught. So, what will be the composition of solid at this point ok, so I can just say that the if this is k equal to XS and XL is the overall liquid which has a composition of X naught here.

So, I can put XL as a X naught here right now at this condition, which gives me the composition of XS as k into X naught. So, where what that is what is written here, then we will go to some temperature T2 at T2.

You have some solid which has composition of XS and some liquid which has composition of XL ok. So, you can see that as the solids are forming which much lower solute content, my solute content of liquid is increasing. I am actually rejecting this much solute in the liquid when solid is forming that is how I can form. So, my initial composition is X naught, so I have to reject this much solute content in the liquid.

So, that is why the composition or the solute content of liquid is increasing. So, you can see this graph is going like this. So, initially the liquid has the composition of X naught, but with the progress of solidification the solute content in liquid is increasing and at T3 temperature where the my composition is crossing the solidus line here.

I will have solid now the total solid is of X naught composition ok, this is this whole thing is going under equilibrium condition right now and my liquid will be having similar expression again because, my the total solid has composition of X naught.

So, my liquid will have composition of X naught by k, so at XS I will put X naught and this will be XL, so XL will go here k will come here. So, it will be X naught by k. So, last liquid which is going to be there in the or last droplets of liquid which is going to be there in the system ok.

It will have a composition of X naught by k, so that is I will represent here. So, this is a very kind of a nice experiment people have done ok.

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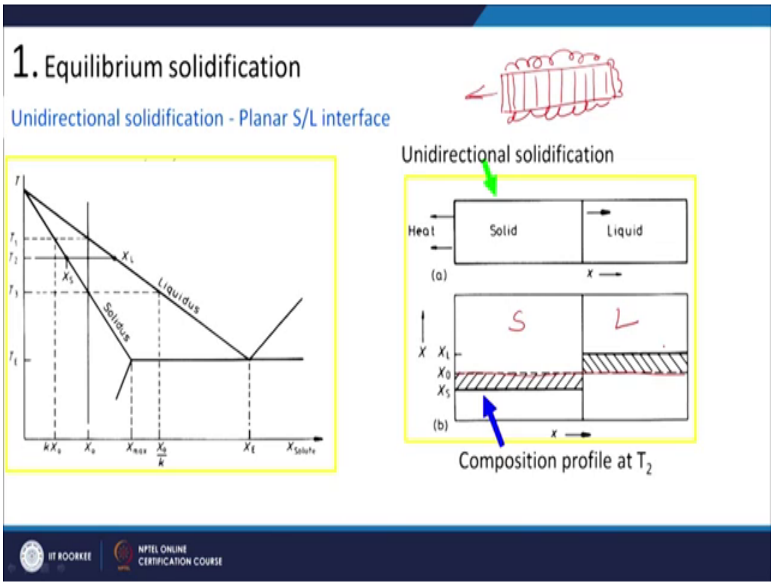

1. Equilibrium solidification

Unidirectional solidification - Planar S/L interface

Unidirectional solidification

Composition profile at T_2

So, you start with a with a bar like this and this you fill the liquid and you do you have a insulation around it ok. So, you have insulation around it and you are allowing heat to be extracted only from this end ok, so initially it is fully liquid. So, because I am allowing liquid to heat to be taken out only from one end, the solid will start forming from this end and it will keep on there is a progressive increase in the solid content and the whole liquid will transform to solid at some point ok.

So, we can now see because solid is growing only from 1 side I can see that how the composition is changing at different temperatures ok. So, initially at T1 temperature as I told you the composition of solid or solute content will be this, which is given by a kx naught and liquid will have X naught composition, let us see what happens at T2 temperature in this particular volume in terms of solute content.

So, on the X axis we have solute content and on y axis we have the distance from the the end from this so solidification has started ok. So, at t temperature the solid will have overall composition will be XS, which is given by this phase diagram.

The solute content in the liquid, so this is my solid this is my liquid. So, solute content in the liquid will be given by XL which is given here and the overall composition is X naught. So, at different temperature the solute content in liquid and solid will keep on changing ok, till at the end of it the whole solid will solidify with their composition of X naught throughout the volume of the this particular cast material ok.

So, this is under equilibrium condition, so you can see that in the overall solid the composition is same in the whole liquid the composition is same. So, there is not going to be any compositional variation, when you are doing under equilibrium condition.

Which is not the case in normal practice because, to do this I have to do this solidification very slowly. So, we will see what happens in the non equilibrium condition, so for this condition we are taking is non no diffusion in solid and perfect mixing in liquid.

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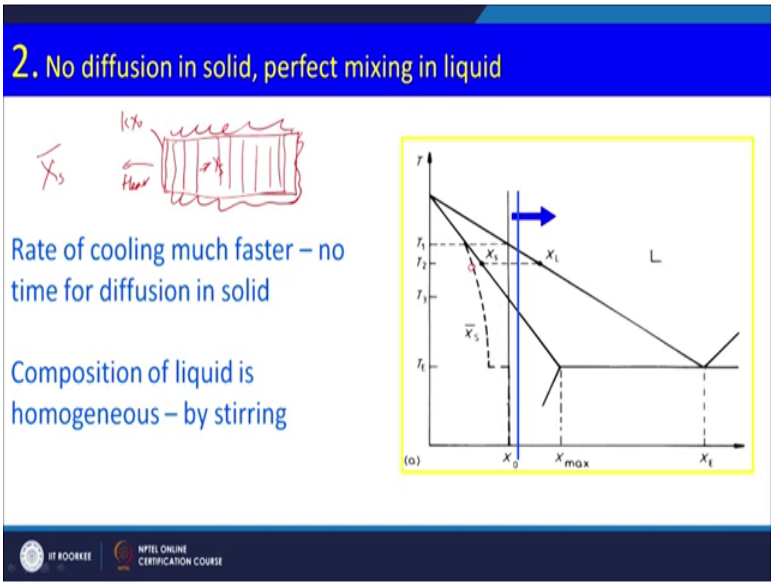

2. No diffusion in solid, perfect mixing in liquid

Rate of cooling much faster – no time for diffusion in solid

Composition of liquid is homogeneous – by stirring

So, rate of cooling has to be much faster because I am not allowing any diffusion to takes place and composition of liquid is homogeneous, that is why we are ensuring by a putting a stirrer in the liquid ok. So, whatever solute is rejected from the solid, it will be uniformly distributed throughout the liquid ok; now what will happen to my phase diagram if we do under non equilibrium condition ok.

So, whatever is there under non equilibrium condition in the phase diagram are usually shown with a dashed line like is shown here and why we are going to get this let me explain you, you can see that at the first when the solid is forming it is forming with a composition which is given by kx naught X naught is my overall composition at temperature T2.

Now my again if I take the same experiment again I have done insulation here ok. So, there is no heat taking out from here the heat is only taking out from this end, so solid is forming. So, the first solid which is going to form let me show by a very thin layer here and plot it ok.

This will have a composition of k X naught now slowly it is progressing, now my the system is coming from T1 temperature to T2. So, what will happen now the and the same story will be repeated for every temperature in between T1 and T2 ok. So, at T2 temperature let say what will happen is that, my composition of the solid is XS which is more than the kx naught ok. So, let us plot some more lines here. So, at this point now my composition is XS and now it started from kx naught and I am not allowing any diffusion to takes place and the now the composition is XS.

That means, there is a composition gradient from this end to this end the solute content is increasing. So, if I want to give a an average composition for whole of this solid which I am going to call as XS bar, that will be much lower than what is given by the phase diagram under equilibrium condition. So, my this point is shifting from this XS to this this here, let me show it here.

So, the at temperature T2, now the composition is not XS of for the throughout the solid, the composition is some new composition which is an average composition which is XS bar same thing will keep on repeating and what will happen that my progressively my solid has a lower composition than given by the phase diagram and you can also understand that if in equilibrium condition it should have composition throughout composition should be XS, but it is much lower than that.

That means, I am enriching the liquid by that much amount of solute ok. So, liquid the concentration will keep on increasing. So, you can see that this graph instead of going like this it is continuously increasing and it is this the graph is coming like this and where the eutectic reaction or isotherm of the eutectic temperature is there, at that point it is the remaining liquid which is which is increasing the solute content of remaining liquid is continuously increasing and reaching the eutectic composition ok.

So, the remaining last part of the liquid, so my solid will keep on growing with a lower composition than what is given by that and the last part of the liquid will transform with a eutectic composition ok. So, always in a non equilibrium condition though my composition is not going to show under equilibrium condition is not going to show any eutectic because, it is in single phase ; but because of the non equilibrium cooling I am always going to get some eutectic mixture in the material ok, a very important thing is there to remember.

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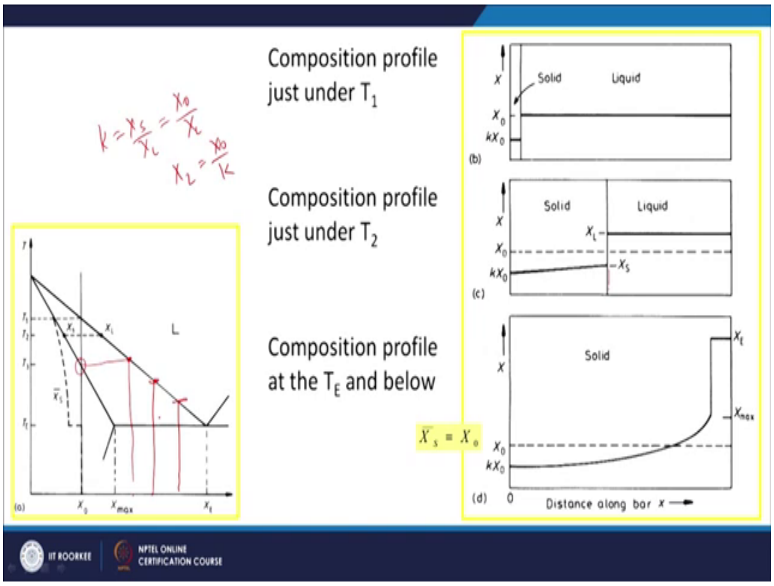

$k = \frac{X_S}{X_L} = \frac{X_0}{X_L}$

$X_L = \frac{X_0}{k}$

Composition profile just under T_1

Composition profile just under T_2

Composition profile at the T_E and below

$\bar{X}_s = X_0$

So, again composition profile if you want to see at different temperatures, so composition profile just under T1 just when the solidification has started.

So, my solid is composition of kx naught my liquid is composition of X naught, the overall composition at temperature T2 the first solid which has formed has composition of kx naught and now because I am not allowing any diffusion to takes place the composition is increasing and at T2, at the interface the composition is XS and the composition overall is given by XL ok.

The composition of the liquid and because we are doing a stirring the composition profile here is constant, the composition profile at the temperature TE eutectic and below TE is your eutectic temperature ok. So, what will happen the composition in the solid is increasing from k X naught and slowly it will cross the X naught composition and then suddenly it will increase and go up to kx max which is given by this is my X max and the remaining liquid last part of the liquid will transform with the composition of eutectic composition.

So, this is how the composition or the solute profile will be there in the solid at the end of the solidification. Now I can also give a mathematical kind of analysis for this problem here ok. So, what is the variation of XS along the bar.

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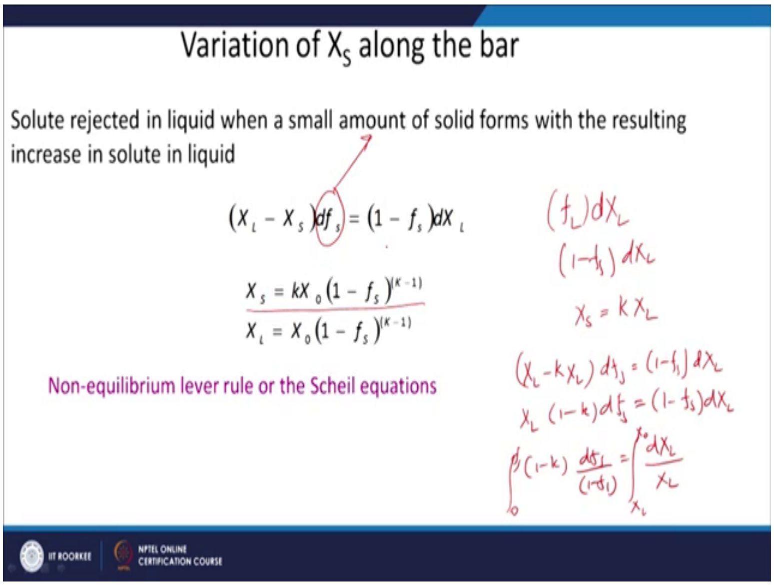

Variation of X_S along the bar

Solute rejected in liquid when a small amount of solid forms with the resulting increase in solute in liquid

$$(X_L - X_S)df_S = (1 - f_S)dX_L$$

$$X_S = kX_0(1 - f_S)^{(K-1)}$$

$$X_L = X_0(1 - f_S)^{(K-1)}$$

Non-equilibrium lever rule or the Scheil equations

$$(f_L)dX_L$$

$$(1-f_S)\,dX_L$$

$$X_S = kX_L$$

$$(X_L - kX_L)\,df_S = (1-f_S)\,dX_L$$

$$X_L\,(1-k)\,df_S = (1-f_S)\,dX_L$$

$$\int_0^{f_S}(1-k)\frac{df_S}{(1-f_S)} = \int_{X_L}^{X_0}\frac{dX_L}{X_L}$$

So, what we are saying is that solute rejected in liquid when a small amount of solid forms ok. So, when a small amount of solid forms which is given by dfs ok. So, this is my small amount of solid.

Which is forming and what will be the solute rejected there is always going to be some solid which is rejected when solid is forming and that will be equal to, this is the this composition of liquid from which I am forming this solid. So, this much amount of liquid has to be rejected in the liquid, then only I can form the solid of XS composition. So, I am so forming a solid of XS composition from a composition of liquid which is given by XL.

So, I have to reject this much solute whenever a small amount of solid is forming into liquid ok, so that is what we are saying here. So, XL minus XS amount of solute has to be rejected when I am forming a small amount of solid and with the resulting increase in solute in liquid ok.

So, the liquid fraction will be given by fl. So, then I am forming a small amount of solid the remaining fl the fraction of liquid will be enriched by that much amount of solute ok. So, the increase in solute in liquid will be this much. So, fl I can write as 1 minus fs dxl.

So, now if I if we do a little bit rearrangement here XL or XS I can replace again here as for example, XS I can replace is k XL or I can say it as k k XL I can say. So, this will become XL minus k XL into dfs is equal to 1 minus fs D XL the XL can be taken out here.

So, it will be XL 1 minus k dfs is equal to 1 minus fs dxl and I can do another rearrangement here. So, it will be 1 minus k dfs upon 1 minus fs is equal to dxl upon XL and now if we integrate on both the sides. So, I will integrate it from 0 to 1 or 0 to fs and this I have been integrating from XL to X naught.

So, when I integrate this and after doing the integration the solution will be like this ok. So, it will be XS equal to kx naught 1 minus fs to the power k minus 1 and this is actually what we call as non equilibrium non equilibrium lever rule or Scheil's equations.

So, under non equilibrium condition this you can consider as a lever rule, which tells me about the fractions and their compositions ok. So, using this you can be able to find out what will be the composition of solid for a given fraction of solid ; knowing the partition fraction ok. So, I can use this equation under non equilibrium condition. So, this is my now mathematical representation of a non equilibrium cooling ok.

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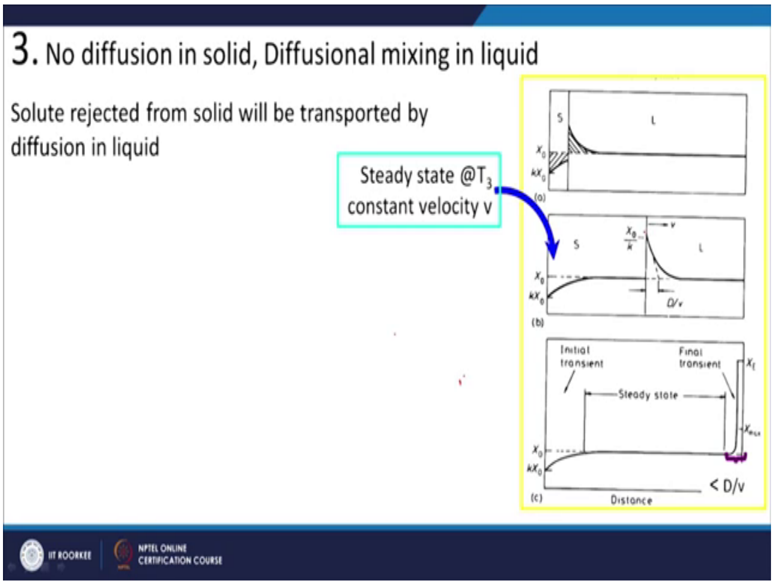

3. No diffusion in solid, Diffusional mixing in liquid

Solute rejected from solid will be transported by diffusion in liquid

Steady state @T_3 constant velocity v

Now, the third condition is no diffusion in solid and diffusional mixing in liquid, the solute rejected from solid will be transported by diffusion in liquid ok. So, you can see that in this case now my first solid is forming again with kx naught composition and the solute content is increasing and in the liquid now you can see the composition is not constant throughout ok, because the solute will build up at the interface and the solute is taken away from the interface by diffusion process. So, again in there is an exponential curve here through which that through diffusion it is taken out.

At T3 constant velocity at a constant velocity V a steady state will be reached at T3 temperature ok, the T3 temperature I can just show you which T3 temperature we are talking about. So, from here to here it will be an a non steady state condition at when the my the system reaches a temperature T3 you will reach the steady state condition. So, this will be an initial transient from when the composition in solid is increasing from kx naught to the composition X naught ok, which you can see from here.

So, now, my solid is forming at the composition of X naught ok, so starting from kx naught the solid has reached the composition of X naught here. So, solid is forming at kx naught composition the composition in the liquid at the interface is equal to X naught by k, so is that you can see here.

So, composition at the liquid will be equal to if I again draw a tie line here. So, this will be my composition and it will be equal to if this is X naught again if I use my partition fraction, so XS is at X naught. So, XL will become X naught by k that is what we are seeing here, at the interface X naught by k and away from the interface at some point the liquid will have the composition of X naught.

So, some solute is rejected that will that solute will diffuse in the liquid by in diffusion process and we can define this that what will be the slope of this curve ok, by a characteristic width here which is called which is equal to diffusion coefficient of solute in the liquid divided by V velocity, velocity with which my interface is moving.

So, at the end of the solidification you will see this kind of concentration gradient in the in the solid bar. So, at the from where the solidification is starting you will have kx naught composition, then the steady state will come where the whole solid will have a composition of X naught and then the final transient will be there where again whatever solute I am rejecting in the material that will build up and when this D by v reaches the last part of the bar the remaining liquid will the composition will rise suddenly to the eutectic composition and the remaining liquid will transform with a eutectic composition ok.

So, this is how the variation of solute content will be there in the solid. Now, we will do a further analysis that what is happening in the liquid, if you see in the liquid the solute content is varying like this in exponential curve.

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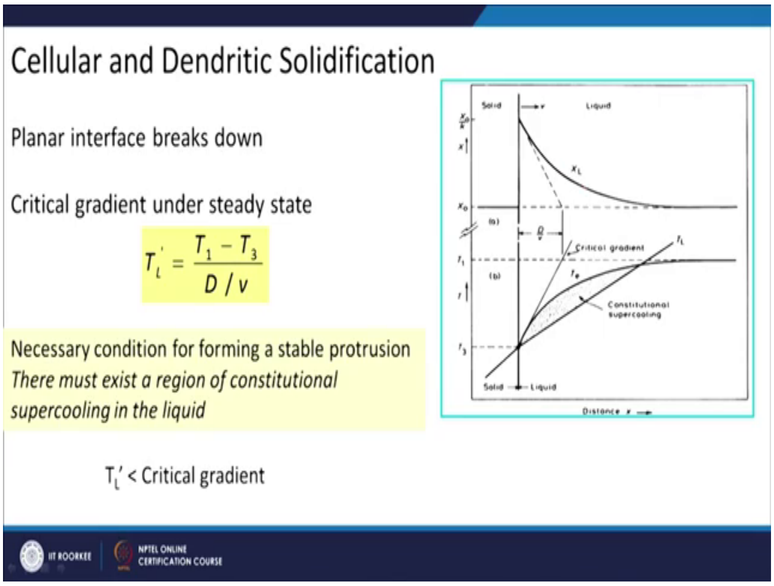

Cellular and Dendritic Solidification

Planar interface breaks down

Critical gradient under steady state

$$T_L' = \frac{T_1 - T_3}{D / v}$$

Necessary condition for forming a stable protrusion

There must exist a region of constitutional supercooling in the liquid

$T_L' <$ Critical gradient

Now if the solute content is varying like this, you can see that as the solute content varies in the phase diagram ok. See you can understand it like this if my solute overall solute content of a alloy is this, then the a melting point is given by this if my solute content is this then melting point is given at a lower melting point ; if solute content is this then my melting point will be this. So, my melting point of my alloy keeps changing with the solute content in the liquid ok, that much we can understand from this graph that if my solute content is more the liquid the melting point will be lower.

As I am going toward the pure material my liquid or melting point will keep on increasing. So, this is the effect of the solute content on the melting point. So, that we will use here to understand that my solute content in the liquid is changing like this. So, at this my solute content is equal to X naught by k, away from the interface the solute content is decreasing and it becoming X X naught at some distance away from the interface.

Now if this is the variation in the solute content there will be variation in the melting point of the material. So, my melting point of the material will vary like this, at in the interface the melting point is equal to the T3 temperature away from the interface the melting point is T1. So, solute content is more the melting point is less, as the solute content is coming down my melting point is increasing.

So, this can be a curve to show you the melting point of my solid my alloy of different solute content at different positions. Now when I am taking out the heat from this bar, I am actually superimposing a temperature gradient on that.

So, you can see that there is a temperature gradient given by TL that temperature from where I am taking out heat the temperature will be lower, inside the temperature is more ok. So, now, if that temperature is lower than the melting point here what I am doing basically is I am doing under cooling of the alloy, if my imposed temperature is lower than the melting point; that means, I am doing an under cooling.

So, you can say that some portion of my liquid is under cooled and if you are doing an under cooling ok; that means, there will be a driving force for phase transformation.

So, the critical gradient will be given by as you can see you if I plot a tangent for the solute curve here it will be equal to D by V. So, my critical gradient will also be defined by that I will plot a straight line from here which will be D by V distance away from the interface. So, this is my critical gradient, if my critical gradient is more is lower than this then you will have constitutional super cooling ok, because it is because of the solute content and if the critical gradient is more than that then of course, there is no harm and you won't have any problem in the solidification. So, when you have constitutional super cooling, we will see that what happens in the solidification structure.

So, the critical gradient will be given by T1 minus T3 basically y 2 minus y 1 divided by X 2 minus X 1. So, it will be T1 minus T3 divided by this distance which is given by D by y D by v. So, the necessary condition for forming a stable protrusion there must exist a region of constitutional super cooling in the liquid and my superimposed temperature gradient should be less than critical gradient if I am not able to maintain.

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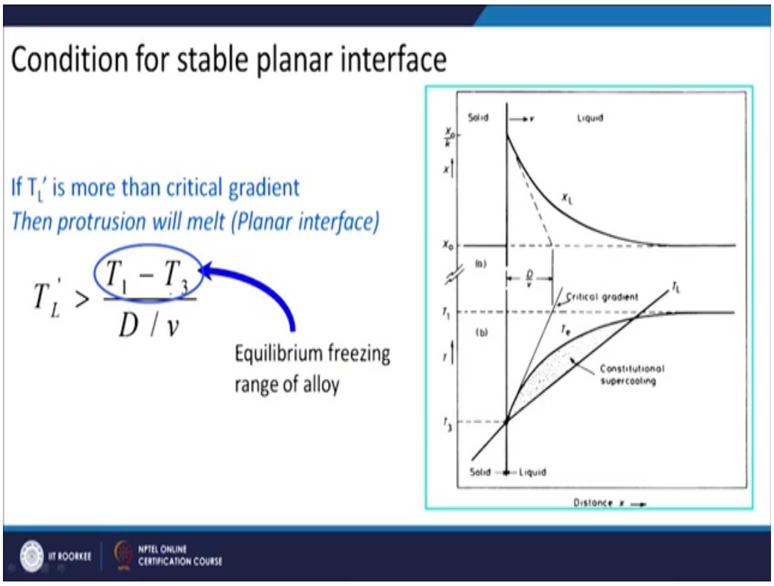
Condition for stable planar interface

If T_L' is more than critical gradient

Then protrusion will melt (Planar interface)

$$T_L' > \frac{\boxed{T_1 - T_3}}{D / v}$$

Equilibrium freezing range of alloy

This then what will happen is that I will have condition, where some material will be transforming at much faster rate, where the under cooling is taking place. So, this is what we call as the condition for the stable planar interface that my critical gradient should be more than this. If it is lower than that then I will have what we call is this kind of breakdown in the planar interface ok.

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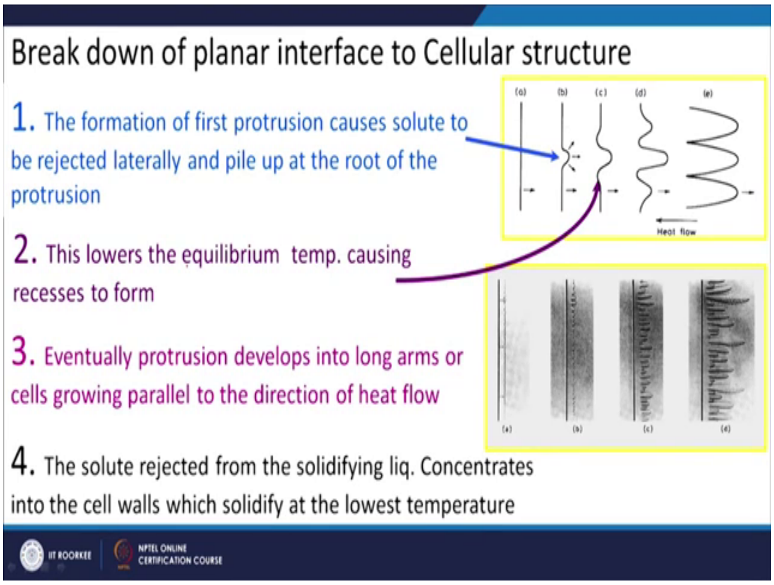

Break down of planar interface to Cellular structure

1. The formation of first protrusion causes solute to be rejected laterally and pile up at the root of the protrusion

2. This lowers the equilibrium temp. causing recesses to form

3. Eventually protrusion develops into long arms or cells growing parallel to the direction of heat flow

4. The solute rejected from the solidifying liq. Concentrates into the cell walls which solidify at the lowest temperature

So, if the temperature gradient is more, then you will have a planar interface like this. If the temperature gradient is less than the critical gradient then what will happen you will start getting this kind of unstable region and I will call it as a protrusion a protruding part is there and when protrusion is formed.

What it does it because my solid will always have a lower solute content ok. So, it will eject the solute. So, all these arrows are showing that I am ejecting solute in the liquid, so this is my liquid this is my solid. So, I am ejecting solute here and this solid will come and get deposited at the root of the protrusion and thereby when the as I told you when solute content is increasing my liquid melting point will decrease. So, again you will see that this may this temperature is higher than the melting point.

So, again some solid will again go into the liquid phase and by that what will happen is there will be kind of a depression here on both the side and that will trigger another protrusion ok. So, now, a planar interfaces become interface which is like this it is called a cellular structure, which is shown in this micrographs also here and the steps are shown here.

So, first step is the formation of first protrusion causes solute to be rejected laterally and pile up at the root of the protrusion, this lowers the equilibrium temperature causing recess to form eventually protrusion develops into long arms or cell growing parallel to the direction of heat flow. The solute rejected from the solidifying liquid concentrates in the cell wall which solute defy at the lowest temperature. So, when you have this condition then sometime what will happen that the these will become planar interface and this will also start developing protrusions like this.

This will also start developing protrusion like this and which will give you a dendritic microstructure. So, to get the dendritic microstructure I have to have a non equilibrium cooling and I have to have a condition where the solute is rejected in the liquid under diffusional process and there has to be a constitutional super cooling or under cooling in the liquid phase ok.

To have this kind of a unstable formation of the protrusion or unstable planar interface and then you will have secondary arms coming and then you start getting the dendritic structure and the liquid in between will get enriched in the solute content and at the end of it the whole thing will transform by a eutectic composition.

So, you can understand that though we took a composition which is much lower which is in the single phase of the eutectic also, ultimately I am going to get some liquid which is transforming under eutectic composition. So, with this I thank you and we will this is a very important topic of understanding the structures which form under during solidification.

Thank you.