## Phase Transformation in Materials Prof. Krishanu Biswas Department of Material Science & Engineering Indian Institute of Technology, Kanpur

## Lecture - 30 Growth Rate for Dendrite Formation

(Refer Slide Time: 00:13)



Well let us now discuss on something about how we develop a mathematical expression first they heat transport in the solid liquid phase transformations.

As you see this is a interface which I have drawn between the solid and liquid and this is solid this is liquid temperature get in both on solid and liquid are positive because the slope of this curves are positive. So, therefore, as the latent heat is getting release at the interface during unit step of solidification as a one layer of liquid solidifies this and joins the solid the amount of heat which is generated will be evolved here. So, if I write the growth rate as V dot V dot means dx by dt right because that is what is the growth rate per unit time if it moves dx distance then it is dx by dt. Growth rate multiplied by the heat evolved per unit volume is what is the total heat generated because of the latent heat evolution that is must be equal to or that is this plus; obviously, this plus the temperature gradient in the liquid multiplied by thermal conductivity as you know this is the 4ier term this must be equal to the temperature gradient the solid multiplied by the conductivity of the solid.

So, K L and K S are thermal conductivities of the liquid in the solid. So, at a study state this must be satisfied the heat generated plus the heat transport heat generation rate actually you can see this is because this is dot plus the heat transport to the liquid it must be equal to the heat transport to the solid. So, this actually allows us to calculate what is the V dot. So, V dot is K S dT S dx minus K L dT L dx divided by minus delta H divided by L divided by V alpha.

So, as you clearly see if you want to have a very very high growth rate very high growth rate, here what you need? You need to have because this term is always positive delta H is the heat evolves that is why you put a negative sign here otherwise this is positive volume of solid this is volume of solid not alpha sorry volume of solid is also positive. So, K S dT dx is positive here right dT dx is positive K is positive similarly dT d L dT L by dx and K L is also positive.

So, therefore, this invert to maximize this I must make dT d L as negative because if that is the negative then this plus this become very high value in that case I can make the system grow very fast. That is the reason we better to have this situation which you have I have shown in the book in the slide this situation where temperature in the liquid is negative. So, the temperature in the liquid is negative dT L dx become negative. So, this negative sign and this negative sign become positive. So, this plus this become very high value and then growth rate is very high. That is the one important aspect you must understand that this thermal heat balance tells you that if I want to make that very high I must develop negative temperature gradient in the liquid. That is the first thing which you have understood.

Now, let us you know do a little bit of calculation of the dendrite growth which I have shown you, so that we can get into Maths. I erase this part and get back to you as you have seen the way I have drawn the dendrite are shown you basically looks like a this.

## (Refer Slide Time: 04:18)



This is on a surface and no protrusion has form this is solid this is liquid this quite. So, normally dendrites keep the shape same when they grow to the liquid they do not change the shape.

So, therefore, I can write down when the dendrites grow this growths actually happens in some crystal of directions I can write down that this the heat release at the and let us suppose this is this, this is the radius of the tip of the dendrites that is what is more important whether is in touch with the liquid. So, this is this total area multiplied by the; obviously, heat flux or rate that is must be equal to growth rate multiplied by phi R square correct multiplied by delta H L by V S this is the heat evolution correct. So, that is we can write down.

And here q dot is nothing, but K L T L minus T S divided by R that is the heat divided by the distance is what is your flux correct. So, finally, we can actually get the V dot growth rate of the dendrites as like this, this is the heat evolution. Remember this is half because half of this surfaces are only in touch with the liquid that is why and this is what is your flux this is given by this and this is growth rate multiplied by the area multiplied by the heat which is evolve because of the latent heat.

So, this gives you idea about growth rate that is equal to minus K L V S T L T S minus T L this is T S minus T L divided by R multiplied by delta H L that is what you get correct remember this V is the volume this V is not the growth rate V the V dot is what is the

growth rate. So, finally, you can convert because you are basically using this term of q and converting everything that is why the R comes into picture. So, this is what is the maximum growth where topic dendrite whose growth is basically depend on heat transport, heat is basically transported to the liquid because liquid is undercooled this situation is same like to this. So, liquid is under liquid has a negative temperature gradient. So, heat will be basically rejected at the interface and travelling into the liquid or basically transported to the liquid because of this negative temperature gradient develop.

Heat can also be transported to the solid, but you know transport to the liquid is faster than the solid that is what happens. And this is the kind of calculation one can do as you can clearly see if I know the temperature basically we know the liquid temperature very well, but the important point is knowing the temperature of the solid that is temperature this interface which is very difficult to measure; rest of the things are known K L is known V S is known and your delta H is known.

Now, if I carefully write it down then it becomes V dot R basically the growth rate is V dot R is equal to minus twice K L V S T S minus T L divided by delta H L correct. So, this completely depends on basically temperature difference with solid and liquid; that means, the difference in the undercooling delta t. So, if I have any idea of measuring the undercooling then I can calculate the V multiplied by R that is the growth rate multiplied by tip radius, but remember both these 2 things are actually are known because I do not have any idea what is the tip radius is (Refer Time: 08:53), I do not I want to know what is V dot what is a growth rate basically I want to calculate. So, finally, I get downs on equation which tells me that these 2 are actually related to that by a function.

So, in order to obtain individual values of both these 2 I need another equation very clear because this are coupled together a growth rate and the tip radius R coupled together with a function and this function can be calculated by knowing the undercooling by knowing this volume of the solid K L and latent heat evolve. But I cannot determined independently V dot and R is not possible. So, that is why you need a second equation.

The second equation people normally use or normally people is to use is basically maximum growth rate criteria; that means, whatever the situations at the given condition exponential condition V dot will be maximum. So, therefore, you can differentiate V dot

with respect to temperature and find out what is the V dot values and then probably V dot we can calculate R, but you know most of the systems do not grow like that way most of the system do not grow at the estimum or at the maximum growth conditions.

So, that is why this show you which was develop much early 1940s elect, 1940s 1947 1948 was unsolved for long long time because this requires another equation to be developed. And then long after long time about thirty years some people have discovered some things which is a much some people have discovered that the second equation which is required to solve this R and couple problem is basically must come from the stability of the dendrites. That suppose I have a dendrite keep like this under what condition this tip will not become like that or under what condition this tip is tip will not become like that condition tip will remain stable.

So, therefore, people actually can use the stability conditions for the planar interface; that means, under what condition a planar interface this is a planar interface under what condition the planar interface will become like that and so, this condition was used to obtain the second equation for growth rate and problem are solved. So, let us now discuss much about that because that is basically requires very weaken part of discussion while in an actual this is what actually is leads to the phenomenal growth of the dendrite growth theory. Now, we will go back into the situation of alloys because that is also very interesting you know in case of alloys we need to discuss how not only the heat, but also solid transports to the solid and liquid basically liquid because solid transport to the liquid solid is very slow. Now I will just start the process I will just let me see how much I can discuss today for that correct let us do that let me see ok.

So, first let me draw a simple phase diagram this is temperature this is composition X B I am drawing part of it part of the diagram and let us suppose I have got solidus and liquidus. So, I draw solidus by green line and I draw liquidus by a red or pink basically pink is better this is my liquidus.

## (Refer Slide Time: 12:07)



Now, let us suppose that I want to solidify I want to solidify an alloy with a composition given X B 0 I have to solidify that this is my liquid, this is alpha, this is liquid plus alpha, this is basically part of the phase diagram like this. I am not drawing the part of that basically a (Refer Time: 13:16). So, what will happen if I start cooling it down from the liquid suppose if I have a temperature some are there I start with that this is my liquid temperature T. Let us suppose as you see if I cool it down till this temperature this what this liquid has curve is basically temperature line or liquid has curve cross over.

So, at temperature T one things will start happening at temperature T 1 a solid will form whose composition is basically given by this point let us suppose this is X B 1 a solid composition. So, as you cool it down little move on because solid and liquid compositions are widely different you can see the liquid composition X B 0 initially initially liquid has a composition X B 0 and the first part which is forming out of these as a composition of X B 1. So, therefore, solid you just form as a much lower B X B basically than the liquid which from which it has started to form.

So, there is a compositional difference; that means what? A solid forms because its composition is lower, so therefore, whatever (Refer Time: 14:41) solid which was present in the liquid because of solid formation will be reject in the liquid things will be much clear if I cool if I basically drop the temperature little more suppose if I drop the temperature from T 1 to T 2 this is my T 2 temperature this is my T 1. So, at T 2

temperature you can clearly see solid which will form as a composition X B 2. On the other hand liquid which is form which will form has a composition X B L 2 further suppose.

So, this was my first liquid composition X B L one you can write down this is equal to X B 0 because there is a starting composition of the alloy. So, therefore, I have again difference between the solid which was formed at the temperature T 2 at the liquid which is present at contact with that. And these difference is what is the solid rejected in the liquid because you cannot create mass you cannot destroy mass. So, whatever is basically present the system must be balance between the solid and liquid say therefore, solid has a lower composition then remaining solid will be rejected into the liquid. And this will keep on happening as you lower the temperature again further again further you see here things will happening.

So, as you clearly see here the solid which is forming here T 3 this is a T 3 suppose T 3 or at T 4 solid which has form has compositions given by this points and liquid which is touch with the solid has a composition given by this points. So, therefore, as this solid solidification happens as the system is getting cooled continuously from the higher temperature to lower temperature solidification will happen and this solidification will lead to solved getting need to the liquid because of that liquid composition will further increase as you see here liquid composition in case of X B 0 to X B 2 to further and solid composition also has increased from X B 1 to X B 2 to and further, but important aspect is that there is a difference between the solid and liquid compositions.

And this happens in equilibrium situations; that means, when you are cooling slowly this will happen because this is a phase diagram which is basically based equilibrium calculations thermodynamic calculations you see equilibrium, so this happens. Now, that means, if I want to create a solid whose composition is exactly same as the liquid starting with X B 0 I have to basically keep at every temperature at a very long time for the adjustment of the compositions because the solid and liquid which is forming at every temperature has different compositions at this different compositions will lead to innovative in the solid.

To give an idea suppose let us suppose T 1 I have a solid which is from the solid as a composition of X B 1 at T 2 this another solid form it will; obviously, forming on the

surface of the X B 1 of this first one this is composition of X B 2 at T 3 there is a composition of X B 3 suppose, X B 3 is here X B 3 is here and this is X B 4. So, X B 3 and then the last X B 4 I have shown you what is happening here. Because of the solidification is have solidification if we do not allow sufficient time to system the compositions of these solids will be varying X B 1 is different from X B 2 then X B 3 then X B 4. So, if I draw a line from the center to the periphery, periphery will be having higher solid than the center periphery will have higher solid X B 4 than the center which is X B 1. So, there is a compositional gradient created from the center to the periphery and this is widely known as coring in the literature. Because you are creating a structure which is shell like the inside one has a lower solid then the outside shell and that is why it is call a coring.

This is widely observed in the real situation because real situations of the once in which diffusion is very very slow and we do not have sufficient time on a cooling down from the liquid to the solid. So, therefore, if you want to stop this if you want to stop this and have a uniform composition of solid X B 0 you need to keep this solidification you know keep the system at T 1 T 2 T 3 T 4 further long time sufficiently long time. If I keep it then what will happen these 2 layers will get homogenized the composition of X B 1 and X B 2 will become homogenize, either will composition of X B 1 and X B 2 X B 3 will be homogenize at T 3 if I keep it long time. So, on and this is known as equilibrium solidification in equilibrium there is what is done it is done at a slow rate the sample is kept at the temperature T 1 T 2 T 3 4 for long time sufficient long time these compositional differences are any loud, these compositional differences are basically completely taken care of.

But actual situation normal solidification we cannot do that we cannot actually keep the system sufficiently long time because in industry or even research laboratories experiment will have a time scale and that time scale cannot be infinity because there is a production loss many other things can happen because of that actually temperature is dropped from the liquid to the solid continuously and because of this drop this is very common the situation of like this where a compositional gradient develop from the center to the periphery is very very common and it has been observed that this situation are actually there in the actual practice.

So, therefore, the solid will form will have a coring structure at core structure. And because of this the proprieties of solid from the composition variation is so much that will vary from one place to other place and this is not desirable and that is why this kind of solids actually are later on heated at high temperatures close to solidous temperature to make this systems homogenized that is done at real practice. So, that is one part of it.

Now question is this how I can scientifically analyze this problem knowing this aspect this is solid partitioning from the liquid to the solid how we can analyze that. Well, I will do that, but let me first define we will continue doing that let me first define a parameter known as partitioning coefficient K. Partitioning coefficient K is basically define as composition of solid divided by composition of the liquid that is what it is.

And because liquid composition is always have the solid this is the fraction in such a kind of phase diagram while it is going down this is the fraction basically. So, because of that K normally is less than one as you see that in a phase diagram is little bit other way that is the phase diagram is like that then K can be more than one also here liquid has higher composition than the solid.

So, therefore, it is always possible that sorry solid has higher composition than liquid because this is solidous, this is liquidous, this at higher than this one. So, therefore, K can be more than 1, but normally we can convert such a kind of phase diagrams more. So, therefore, we will be assuming all our calculations K is less than equal to 1, less than 1 actually, so how this situation will lead to a dendrite growth. And other things will discuss in the next class in detail manner and show you that we can use this phase diagram data to formulate a new theory.