Fundamentals of Materials Processing (Part–1)

Professor Shashank Shekhar
Department of Materials Science and Engineering
Indian Institute of Technology, Kanpur

Lecture Number 07

Heat Flow

Okay so let us continue with where we left over in the previous class, which (was) we were talking about nucleation; so we had completed the homogeneous nucleation. Now we were looking at nucleation, the heterogeneous nucleation. And one more thing in the heterogeneous nucleation that we are still to discuss is the 'nucleation rate'.

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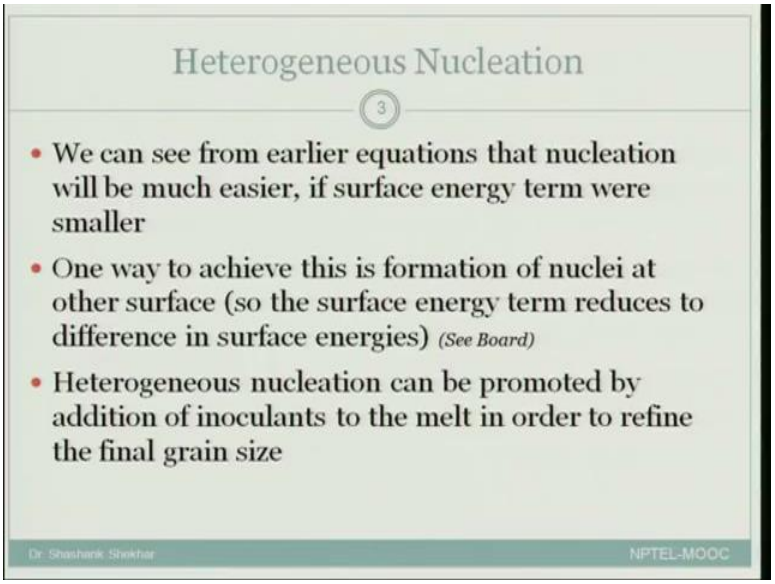

Heterogeneous Nucleation

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- We can see from earlier equations that nucleation will be much easier, if surface energy term were smaller
- One way to achieve this is formation of nuclei at other surface (so the surface energy term reduces to difference in surface energies) *(See Board)*
- Heterogeneous nucleation can be promoted by addition of inoculants to the melt in order to refine the final grain size

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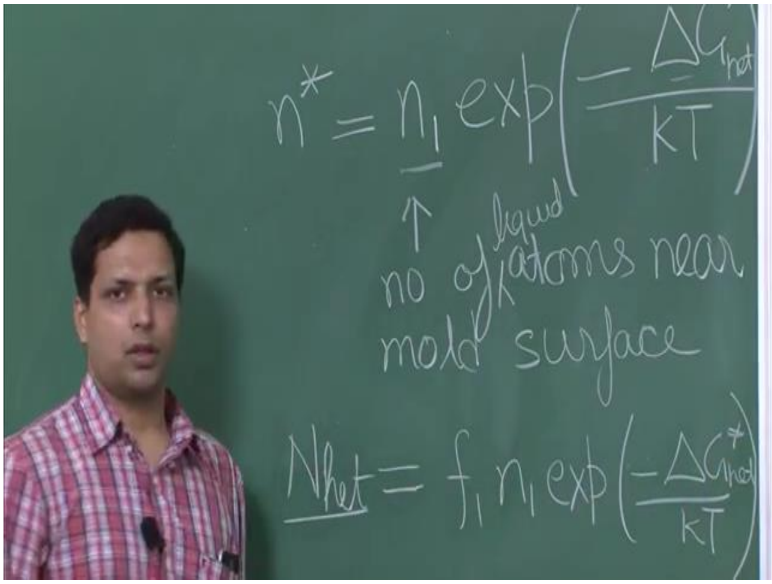

$$n^* = \underline{n_1}\exp\left(-\frac{\Delta G_{het}}{KT}\right)$$

↑ no of liquid atoms near mould surface

$$\underline{N_{het}} = f_1 n_1 \exp\left(-\frac{\Delta G^*_{het}}{kT}\right)$$

So now let us take a look at the nucleation rate, and as you will see, the overall equation, the form of the equation for nucleation rate, for heterogeneous nucleation remains the same, which is, we can still say if n star is the number of clusters of critical radius, then n star is equal to n1. See we are not using the term n0 which was equal to the total number of atoms present in the liquid. Here we are using the term n1. n1 represents the number of atoms which are close to those heterogeneous sites, for example, in this case, if you are talking about the mould. So number of atoms close to the mould, and then we will have the exponential term minus delta G star, heterogeneous over KT.

So you see the form of the equation is same; what is what is different is n1, and what is different is delta G. Now n1, as you can, as like I said, is the number of atoms near mould. And if you are talking about some other kind of heterogeneous nucleation, then it will represent number of atoms in vicinity or which will contribute to those heterogeneous nucleation. So, number of atoms near mould surface.

Okay so to be specific, number of liquid atoms; so we are talking about the liquid material, the atoms of those material we are talking about the quantity of those which are present near the mould surface. Compare this with the, and not that we use in homogeneous nucleation, which is the total number of atoms in the liquid. So this n1 is a small quantity, and therefore, if you look at, if we set n n star by n0 is the probability, then over here, n star by n1 is the probability, which means this will be a smaller quantity.

But no; here delta G star heterogeneous is a very is a much smaller quantity. Remember there is a factor S theta, and which depends on this theta; the smaller the theta, smaller is the delta. S theta, and therefore smaller is delta G star heterogeneous. So this is a very small quantity and not only that, it is inside a exponential factor. Therefore a small drop over here means it will exponentially (())(03:04) is there is a minus sign over here, it will exponentially increase. And therefore n star will increase.

And therefore, what you see is that rate of nucleation for heterogeneous reactions or heterogeneous nucleation, the nucleation rate is much much higher, and therefore if we are to again form the equation similar to the earlier one, where we multiplied or where we are trying to get this is the number of nucleus of critical size, you have to just add one more atom to make it stable and solid; so the if the frequency is f1, nucleation rate will be given by f1n1 exponential minus delta G star heterogeneous by KT.

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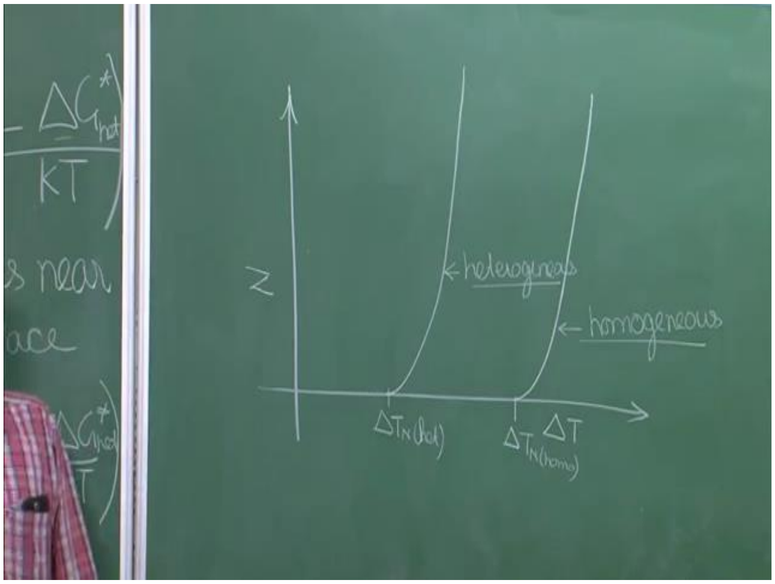

Okay, so you remember how this plot turned out to be, if we are looking at delta T and we are looking at N. So for the homogeneous, there was a delta T critical delta T beyond which this nucleation will explode; so this was for homogeneous nucleation. How will it be different for heterogeneous nucleation? In heterogeneous nucleation, this will happen at a much smaller under-cooling. So, this is for heterogeneous nucleation. So there is a delta, this is the delta TN; you can say this is for homogeneous. This is delta TN, for heterogeneous. Now imagine a liquid which has both possibility of homogeneous nucleation and heterogeneous nucleation. If you keep lowering the temperature, it will encounter this under-cooling first; meaning heterogeneous under-cooling delta, the critical under-cooling would be reached first, and exponential growth of nucleation will take place.

And therefore, nucleation will be preferred or will take place by heterogeneous nucleation instead of the homogeneous nucleation. So whenever you will have a mould, a surface whichever can give it a preferred site, then homogeneous reaction, you can assume would be out of question. But then you may ask how are people able to achieve homogeneous nucleation if at all, what is what are the possible ways, the simplest answer is get rid of any surfaces that there may be.

One way could be magnetic (leti) levitation, magnetically levitated. Another method is floating zone method; we will discuss a little bit about in the next part when we talk about heat flow. So in that also, when the liquid is getting solidified, it is not in touch or contact with any surface, with any mould (inter) mould or interface, and therefore, whatever (homo) reaction will take place, would be homogeneous in nature. So that is all we had to talk about nucleation; so let us just summarize the heterogeneous nucleation, let us get to the slide.

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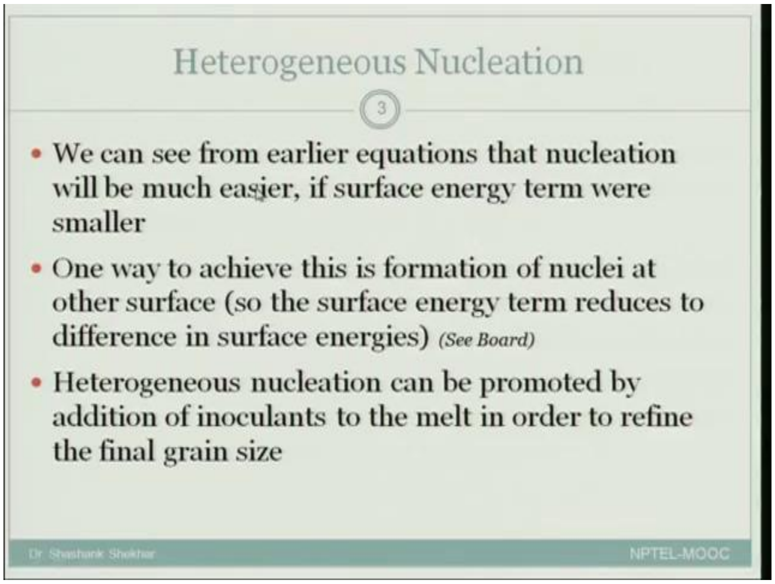

Heterogeneous Nucleation

- We can see from earlier equations that nucleation will be much easier, if surface energy term were smaller
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So we saw, when we talk about talking about the heterogeneous nucleation, that from the homogeneous nucleation itself we can see surface energy has a great role to play; whenever the surface energy term increases, the homogeneous nucleation used to become improbable. So if, in heterogeneous nucleation, that is what makes the big difference. Here the surface energy term becomes very small because you are nucleating the small clusters at the surface thereby changing the surface energy or what what you get is difference in the surface energy, and therefore the total surface energy term is smaller. So one way to achieve this is formation of nuclei at the other surface meaning that mould liquid interface which we discussed in detail.

Heterogeneous nucleation can be promoted, for example if some time you are not able to get heterogeneous nucleation as you can say in a preferred way as you would like, then you can still do if you think that can make sure that heterogeneous nucleation is preferred or it is promoted. One way is to introduce or add some inoculants. Now these inoculants inside the liquid will be homogeneously distributed, but they will also act like a heterogeneous site where the surface, the surface where the liquid will like to get solidified. So this will become your new surface where particles or the nuclei will form, and therefore it will be promote heterogeneous nucleation. Okay so that is like I said, that is all we wanted to talk about nucleation, so we have covered two important fundamentals about solidification already; one was the thermodynamics in brief although, and then similarly in brief the nucleation or the kinetics.

Next we need to go to the another important topic which is heat flow. Now heat flow would be important in all the cases, for example, single crystal growth or mould and you are doing poly crystal growth or (sand) sand cast moulding or investment (cast) casting, and therefore it is you will see that it will be treated in a separate sections for each of these conditions because heat flow will be very different in a single crystal versus say in a sand mould casting. So let us start with single crystal. Now in a single crystal, how will you have the growth, or what will be the heat flow that will promote the growth of single crystals?

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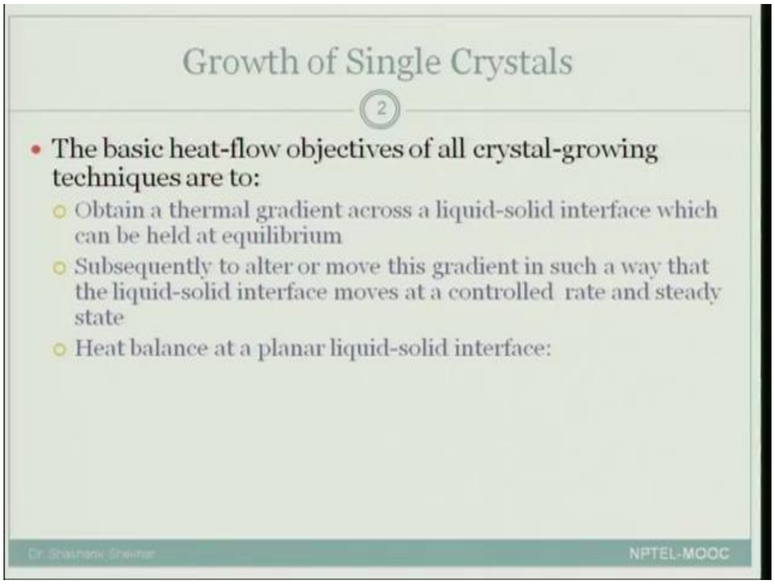

Growth of Single Crystals

- **The basic heat-flow objectives of all crystal-growing techniques are to:**
  - Obtain a thermal gradient across a liquid-solid interface which can be held at equilibrium
  - Subsequently to alter or move this gradient in such a way that the liquid-solid interface moves at a controlled rate and steady state
  - Heat balance at a planar liquid-solid interface:

Now when you are trying to grow a single crystal, the basic heat flow objectives in such cases is first to obtain a thermal gradient across a solid liquid interface. Now you remember, when you are growing a (si) single crystal, there will be a interface where there, at the interface you will have solid, and on the other side you will have liquid. Now, at the interface, the first thing that you want is to have a thermal gradient which is in equilibrium; meaning it does not, it is not continuously changing with time, so it should be in equilibrium. Second, once you are in a equilibrium condition, what you need or what you want is to be able to alter or move this gradient in such a way; now that there is a gradient, you want to move the gradient. The gradient itself will move and therefore the interface between liquid and solid will move, and therefore you can increase the solid length or that is the solidification would start to take place.

Now since the heat flow rate is same as the as the speed of the interface, therefore the solidification will take place only at that layer, a layer by layer solidification will take place. Now because of this layer by layer solidification, the new incoming atoms will take the same structure in terms of orientation that the previous layer had, and therefore, what you obtain is a single crystal and not a polycrystal. If instead assume that the cooling rate were not uniform and that there were some other pockets inside the liquid where you had lower temperature, lower than the TM. Therefore solidification would start to take place over there, nucleation will take place over there, so there will be lots of nucleation points, and therefore all of them will eventually grow and form a polycrystal. But that is not what we want in single crystal. In single crystal what we want is that solidification is taking place only at the liquid solid interface.

So now let us look at what will the heat balance equation look like when we are talking about growth of single crystals. So like I said, there what you need is first, establish the thermal gradient at the interface; so you will have the thermal gradient inside the solid, and thermal gradient inside the liquid at the interface.

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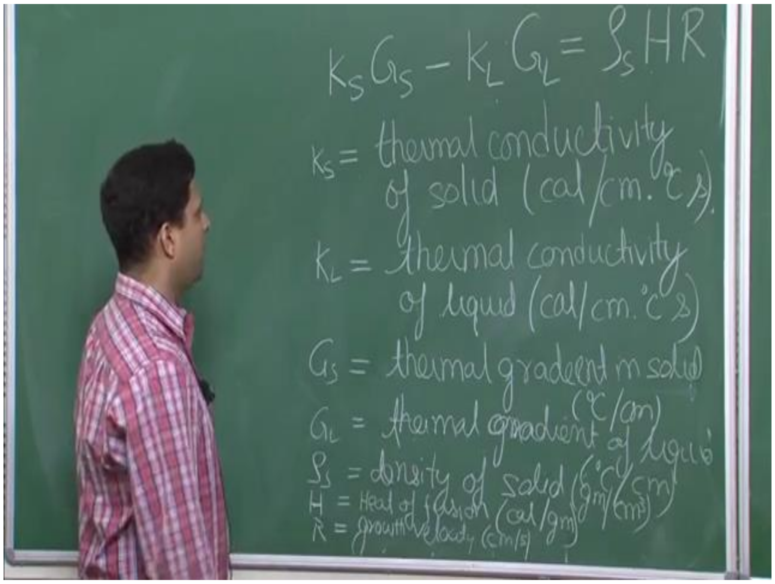

$$K_S G_S - K_L G_L = \rho_S H R$$

K_S = thermal conductivity of solid (cal/cm.°C s)

K_L = thermal conductivity of liquid (cal/cm.°C s)

G_S = thermal gradient in solid (°C/cm)

G_L = thermal gradient of liquid (°C/cm)

ρ_S = density of solid (gm/cm³)

H = Heat of fusion (cal/gm)

R = growth velocity (cm/s)

Now if those are, let us say GS and GL, meaning thermal gradient in solid and thermal gradient in liquid, then the heat flow condition requires; okay so first let me explain what are these terms. KS is simply the thermal conductivity of the solid, and I will give you the usual unit that this equation is valid for. So this is thermal conductivity of solid. I am giving the units here in calories but you may as well use Joules. So it is calorie per centimeter per degree per second. So that is your KS. Similarly, KL is nothing but thermal conductivity of liquid; and then since it is the same thing, its unit will also be same, which is calorie per centimeter per degree C per second. So that is your KS and KL.

GS, like I said is the thermal gradient in solid. Now if it is thermal gradient, then the unit as you can imagine will be degree C per centimeter. And similarly GL, which is thermal gradient in liquid. So the S denotes the (subs) subscript S is for solid, the subscript L is for liquid; so GL is thermal conductivity of liquid, sorry thermal gradient of liquid; and again the unit is degree C per centimeter. And we have three other (uni) quantities, rho S H R. So rho S is nothing but density of the solid. So this unit will be gram per centimeter cube. And we have H, which is nothing but heat of fusion. So this will be in units of calorie per gram. And R here is the rate of growth, or the rate at which the interface is moving. So R is growth velocity; centimeter per second.

You can very easily cross check that the overall units for KS (K) GS, or KLGL, or rho S HR would come out to be the same thing, because obviously we are talking about the calorie per centimeter square per second; that is the total amount of heat flowing through the interface per unit area per unit time. So what this equation is in effect saying is that heat is going from liquid into the solid and the difference of it is nothing but the heat of fusion. So the rate at which so it is not just heat but heat per unit area per unit time, that is going from liquid to solid, and the difference is the amount that has solidified, and therefore the heat of fusion that has being generated. So this is the condition that you require for growth of single crystals.

Now, over here, in general what you want is that, if you want a very good quality single crystal, then what you want is that these quantities, GS and GL, they should be as large as possible. However the growth velocity when you have, in basically in terms of the technique when you have a, when you are actually using some technique and it is here again, what I told you earlier, which is the floating zone technique, I will talk to you about floating zone technique; so in the floating zone technique I will tell you in more particular that what you want is GS and GL to be large. But the growth velocity should be as small as possible and basically as small as possible meaning, it should be equal to the theoretical velocity. So this is the theoretical velocity. Whatever thermal gradient of solid you have, whatever is the thermal gradient you have of the liquid, so based on that you get a value of R.

Now you when you are actually doing the experiment, when you are actually trying to grow the crystal, you can actually move things at a very fast rate and start to get very high growth velocity. But, if you have a very, if you do it at a very high growth velocity, higher than what is recommended by this equation, then what you get is not single crystal. So, in order to get single crystal, you must, your growth velocity must be small and match with the theoretical growth velocity. Now, when we say small but still we do not ideally want to be very small. So what is the maximum growth velocity that we can go.

So for that, just look at that equation. How do you maximize R? If you want to maximize R, what do you want? You want to reduce this term as small as possible. And how do you reduce this term? You can make this GL equal to 0; so if you reduce this GL to 0, so GS rho S HR, which is this quantity minus this quantity, this will be the maximum that you can obtain, and that will give you the maximum R value; and therefore Rmax can be given by KSGS by rho S H.

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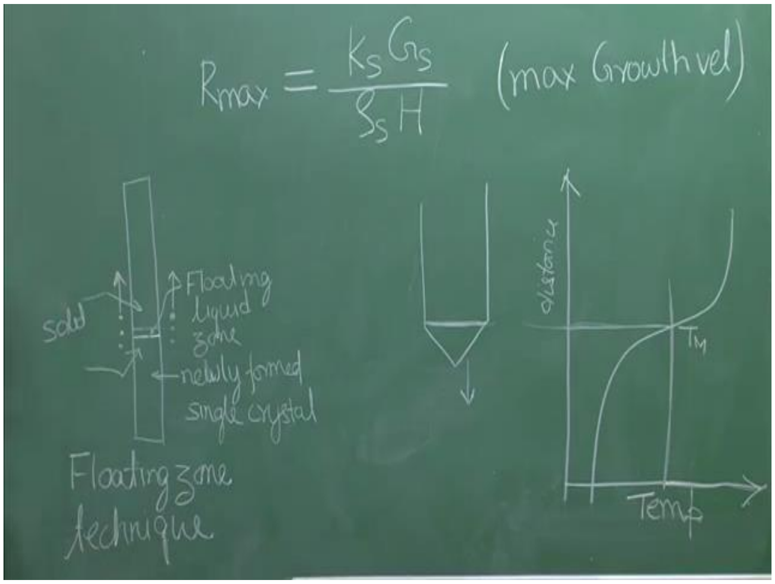

So this gives you the maximum growth rate velocity that can be obtained under given conditions; so if you so, you must not move your system at a speed higher than this. Now let us, at this point let me invoke the growth the mechanism that I was talking about which is our floating zone technique. So let us say, this is a rod that we want to grow into a single crystal, or from which we want a single crystal. So what you do over here, I will show you a intermediate step somewhere over here, there is a heater around this rod and this is what you can call as floating (liquid) liquid zone; and these are the solid zone.

Now this liquid, you would think that this is liquid, how come it is in its place; it is in its place because of the surface tension. Another way to make sure that the liquid stays in its place is by, you can apply some magnetic field to ensure that the liquid does not come out of its place. So that is what and that is what gives it the (name) name ‘floating zone technique’. And here, you will keep moving your coil in one direction so that this is your this is the interface where you have formed a new solid and once you keep moving this coil in this direction, a new layer will start to form of solid over here, and so on.

So this is all newly formed single crystal. Okay so this is the interface that we are talking about; it is at this interface everything is taking place where you need all the control. Now you could have (())(20:47) this for this (heater) heater which is over here, which I have shown as dots, at a very fast rate, much faster than what is recommended by the R value over here. But, then you will not be able to get single crystal over here. If you want to get a single crystal, then the rate at which you need to move this heater or the heating zone, must be less than equal to this Rmax, and governed according to the value of GS and GL. So you cannot move this at a very high rate; you have to make sure that it moves at a controlled rate and that controlled rate is given by this equation.

And not only for this, even if you assume if you remember we were talking about the Bridgman furnace earlier, over there also the temperature. So on the x, so let me redraw it so that it remains visible. So on the x-axis, I have the temperature, and on the y-axis I have the distance. So somewhere over here, you have the melting point TM. So everything below his line is in solid state, everything over it is in liquid state, and you slowly move the furnace or the whole ampule of the material that you are trying to solidify at a (very) at a slow rate; again the rate are governed by this equation, so that solidification takes place over here. So this is the layer over which everything is taking place, and like I said, here the rate at which the heat is coming out is the same at which your interface or you are ensuring that the interface moves at that rate, and that is why you are able to get single crystal.

So now let us get back to the maximum velocity that we are talking about, the maximum growth velocity. So this is our. Over here, KS is a material property, rho S is a material property, H is a material property. The only thing that can be controlled or can be influenced is GS. So let us try to find out what are the factors that will affect GS; GS again is nothing but the gradient in the solid. Okay and since we have drawn the diagram over here, so let me again just show you what exactly do you mean by gradient in solid and liquid. So, we are talking about gradients over here; so let me draw it in a different colour.

So we are talking about the gradient at the interface in liquid, so this is GL, and gradient at the interface in the solid, so this is GS. Notice the way I have drawn it will look like these are two similar quantities, but it need not be. It it could have been very different, like I said, you may maintain GL equal to 0, and you can have very high GS. Now what we want is to see what are the factors that actually make a difference to GS. So for that, we will again, look at the temperature profile of single crystal growth in a little bit different way, and, put together the heat flow conditions in the solid to see if we can find what are the factors that will affect GS.

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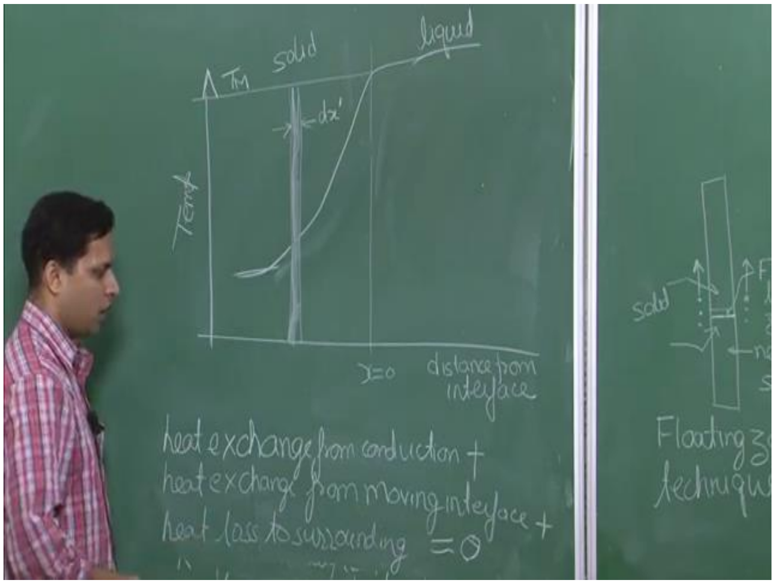

So let us say, this is the interface, we will say this interface is x equal to 0, and therefore this x-axis is nothing but distance from interface, interface of solid and liquid. So on one side we have solid and on the other side we have liquid. And; okay I have drawn it a little bit; my mistake, it should be like this because at the interface, the temperature must be TM, so this is your, on the y-axis if we have temperature, this is equal to TM. This is x equal to 0, this is solid region, and this is liquid region.

Now let us look at a particular point, a distance from the interface, somewhere inside the solid, over here. Let us say it is a small element of thickness dx prime. Okay. Now, if you look at this small element dx prime, what you will see is that the temperature of this particular element dx prime should remain constant. Why? Because we are talking in terms of distance from interface. So, when we are doing the solidification, this will be in steady state, and therefore the overall plot or the overall temperature profile all, near the interface would always look same. So some distance which let whatever the distance is, let us say x distance; at x distance away, the temperature would always be this value, and that means that whatever the heat flow is going into it, it is the same amount of heat that is going out from it.

And therefore, we can write something like this, which says that, heat exchange from conduction, plus heat exchange from moving interface, plus heat lost to surrounding is equal to 0. Now what is heat exchange from conduction? There is heat flowing into this element and then going out of it, that is the heat exchange from conduction. Heat exchange from moving interface. Now this interface moves from here to here, because of that, this this element also moves from here to here, and therefore the heat has gotten exchanged. Some of the heat has gone in, some heat has gone out. There is heat lost to the surrounding, this element, this particular element is also you know furnace environment, so some amount of heat is also being lost into that atmosphere, into that environment; so if you take all those heat exchanges, then the total sum of it should remain 0. Why? Because we said the temperature is constant.

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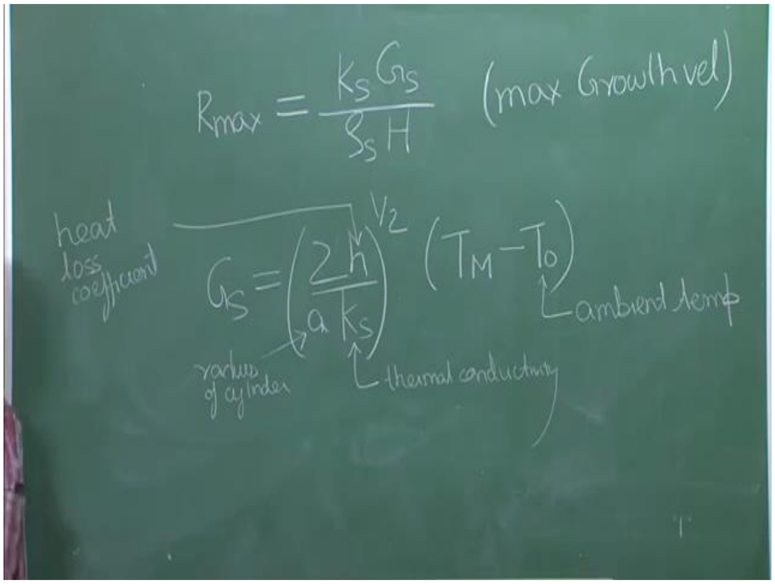

$$R_{max} = \frac{K_S G_S}{\rho_S H} \quad \text{(max Growth vel)}$$

$$G_S = \left(\frac{2h}{a K_S}\right)^{1/2} (T_M - T_0)$$

And, when we invoke these conditions, I am not again getting into the mathematics because this is beyond the scope of this, then it can be shown that GS that we were talking about can be written as. So just quickly, let us take a look at what are these different values. A is the radius; we have assumed that the in for derivation of this particular GS equation, assume that the crystal that is going is in cylindrical shape and A is the radius of cylinder. KS is the thermal conductivity. This H is the heat loss co-efficient, TM is the melting temperature, and T0 is the ambient temperature.

So these are the various factors that actually influence GS. Now you see, if you want to increase GS, you can say you want to increase this value, you want to increase this factor, or you can say you want to decrease these, and hence you will be able to get higher GS which is how you can increase the rate of crystal growth. So we will start from this equation in the next lecture. So we will leave it here, and we will come back to it in the next class. Thanks.