Heat Treatment and Surface Hardening (Part–1)
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Lecture Number 16
Heterogenous Nucleation

Let us start our 16th lecture and in the 16th lecture we will continue on heterogeneous nucleation.

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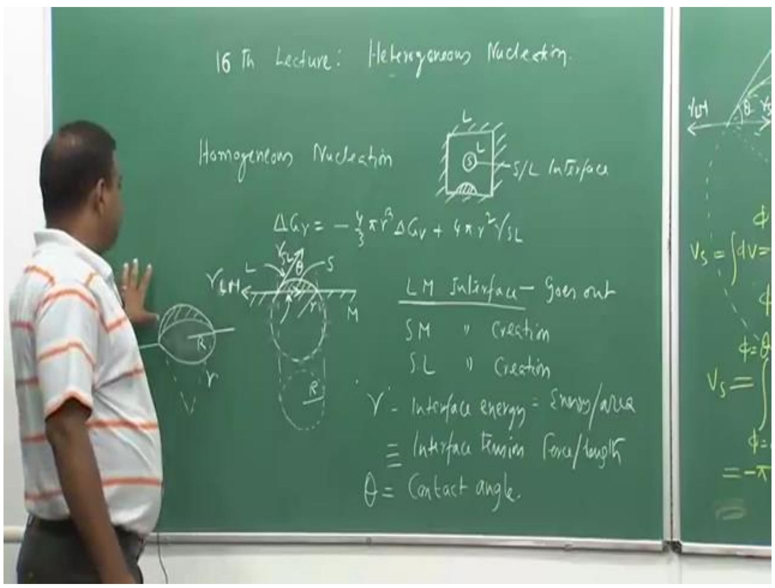

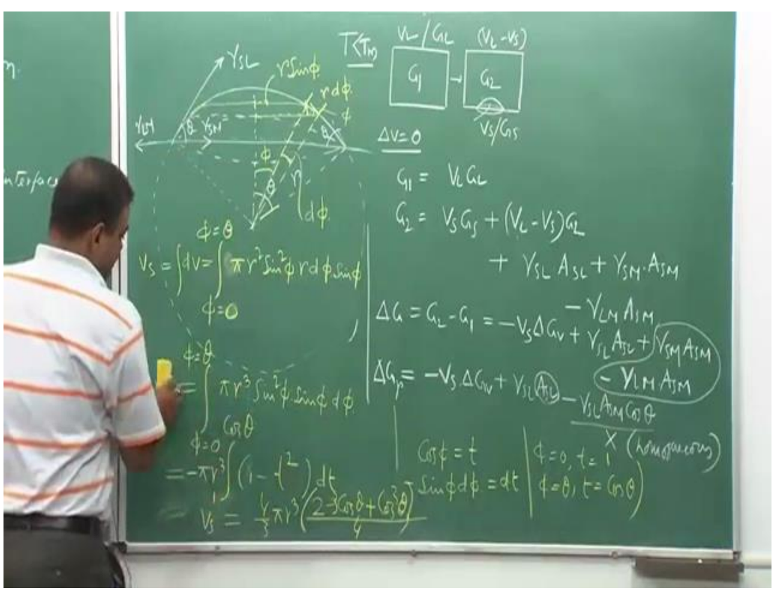

And in the 15th lecture the way we have moved is basically we tried to see what happens if solid forms on a mould world. And that time we have seen that it is forming a spherical cup and this is solid and then we try to find out what would be the expression for free energy change and expression will depend on volume free energy change as well as the surface free energy change.

And in case of surface free energy change, though there are two positive terms but there is also a negative term and finally we will got to this particular expression. And then we started calculating what would be the volume of this particular cup. So that means that volume is nothing but the VS. And we missed one negative sign here, you just have to put negative sign here because when we had taken this this particular thing was coming negative.

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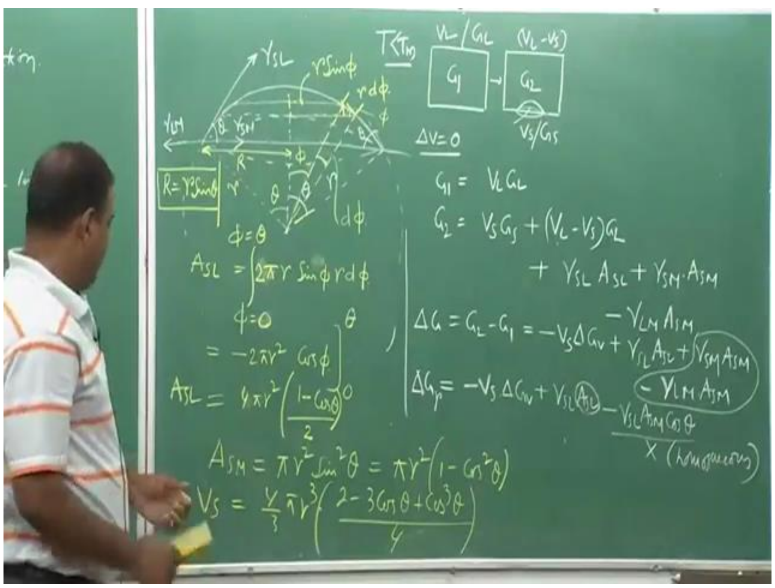

So that negative term will come here. And finally the expression of VS would be if we do that VS will be like this. Now similarly we can also calculate the area of this sphere spherical part this area we can calculate and that area calculation again it will be a small integration and at that time if we remove this, so that time it is basically so this perimeter multiplied by this particular curved length that become my ASL, ok.

And the limit would be same from this to this 0 to theta, ok. And now if we do this particular treatment so we do not have to do this particular adjustment. So we simply directly we can get to -2 pi r square, because this r and this r it will be Cos phi. And 0 to theta and then it becomes 2 pi r square. So this phi equal to 0 equal to 1, so then 1- Cos theta, I can make it 4 and then divide it by 2, yes.

So you will get this, now similarly I have to also calculate because there is a ASM term. Now, I can get to know this particular radius, this is capital R, so capital R is nothing but and if this is my r and this is my theta, the capital R is R equal to r Sin theta, ok. So this is my radius, now the area would be simply that area so that means ASM would be pi r square Sin square theta.

So it is simply pi r square, now we can also may convert it in terms of Cos Cos square theta. So now we have and then we have also calculate that this is ASL and then VS equal to 4 by 3 pi r cube, 2-3 Cos theta + Cos cube theta by 4. See if we simple replace this values here, ok you just replace that value. You will get to an expression which will be see if I try to do it here.

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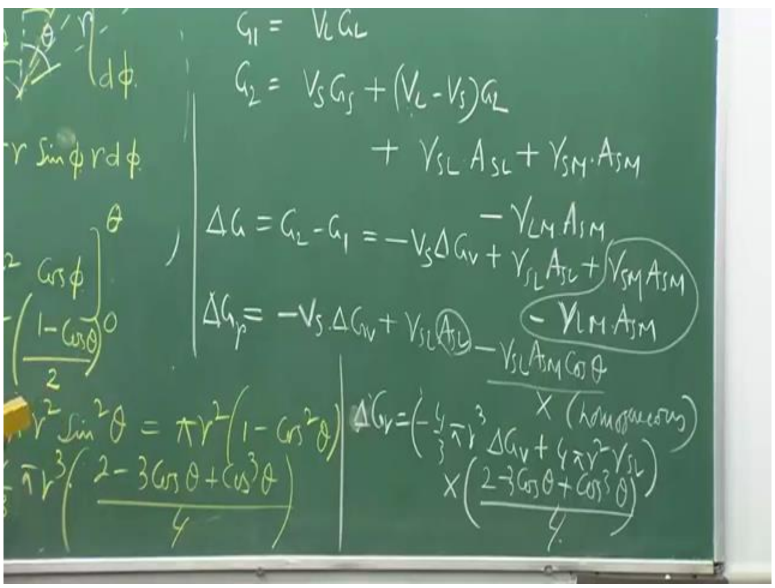

I am not getting into the details of this replacement and doing adjustments you will get V del V del Gr would be equal to -4 by 3 pi r cube delta Gv+4 pi r square gamma SL. This into there will be one more term which will be 2-3 Cos theta + Cos cube theta divided by 4. So this part multiplied by this, see if I take this thing if I remove this part, if I remove the top part.

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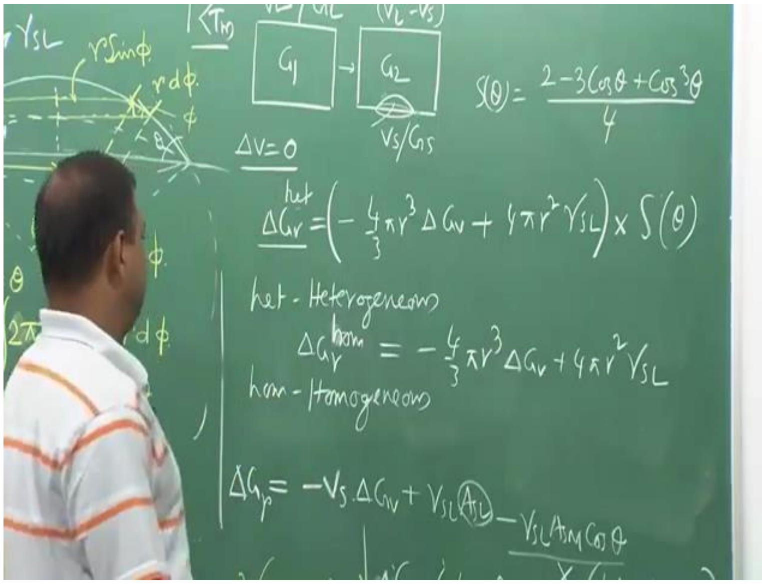

So this is delta Gr equal to -4 by 3 per I cube and where S theta equal to by 4. Now interestingly since this is forming on top of a mould world, let us put a name, let us give a name as het. So this het is coming heterogeneous from heterogeneous, so now in the beginning we have seen that when we first started attacking this nucleation process in solid liquid delta Gr homogeneous, this homo is basically homogeneous was simply gamma SL.

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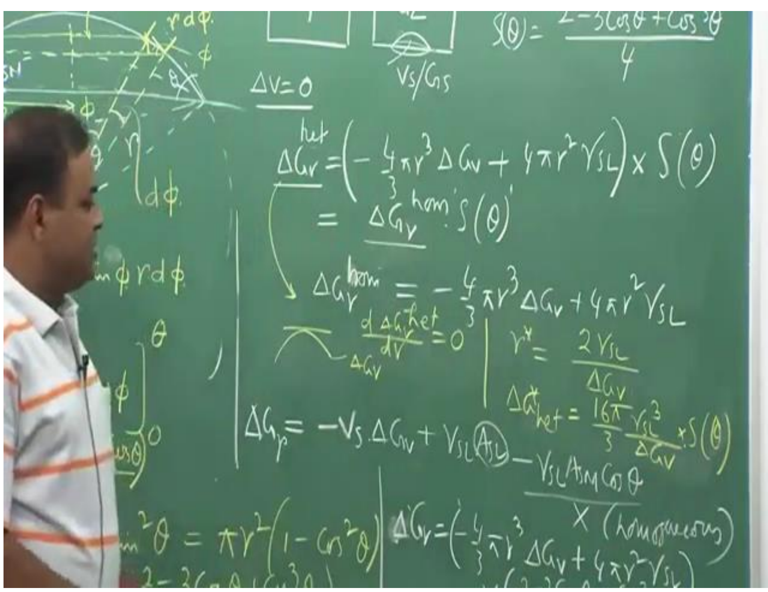

Now you can clearly see that S theta. So if we want to see the free energy change due to the formation of solid which is not forming in the bulk rather forming on the mould world. We are having an expression which is a similar expression like that but only difference is S theta. And this S theta factor is this. And in fact during heterogeneous nucleation this S theta is the factor which is extremely important factor which decides how easily that particular mould world will affect nucleation or will enhance nucleation.

Now in order to do that we just try to plot the del G, del Hr, del Gr heterogeneous and del Gr homogeneous on the same plot, ok the way we have done last time. Now if we have this expression, now at a particular contact angle, ok so now we can also see what would be the unstable criticality. So that means here also you will have a hump like this. And now this is the slope and this would be my delta Gr.

And then at slope, at slope delta Gr dr equal to 0, ok. See if you want to try, if you want to find out what would be the r value at which this particular thing would go to 0. We can also do that, since S theta is independent of r, ok so we will see that in this case if we see would be, would be equal to 0 and then we would get r* would be equal to similar like 2 gamma SL divided by delta GV.

And if we (repl) reintroduced this particular thing into this particular expression, ok. You will see that delta G* het would be equal to 16 pi 3 gamma SL cube by delta GV S theta, into S theta. The critical r would be same at a particular temperature, below Tm. But delta G star heterogeneous which is the activation barrier for nucleation (ener) nucleation formation, the stable nucleation formation that is influenced by S theta.

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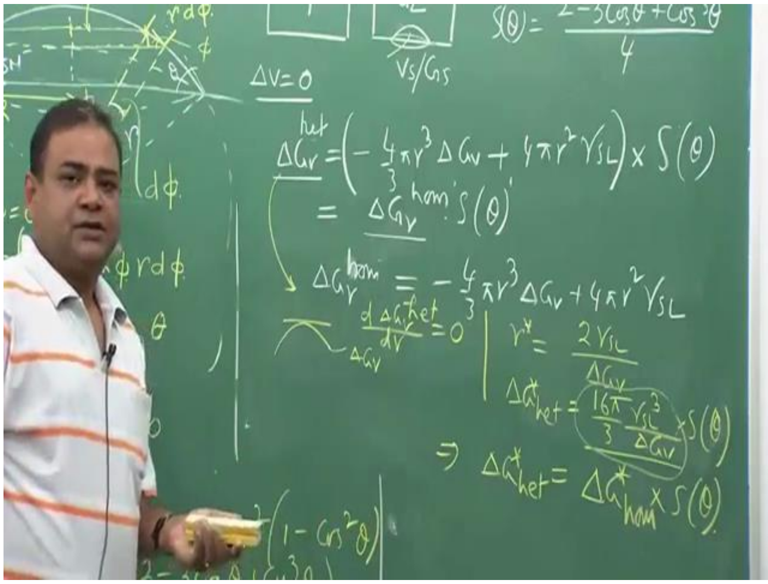

So now if I try to see, this delta G star het equal to this is the same as in our last analysis we have seen that this becomes my activation barrier for nucleation in case of situation in case where the solid is forming in the bulk liquid. And where it is not forming on any surface rather the only interface that is there, it is solid liquid interface. That time this is my activation energy into S theta.

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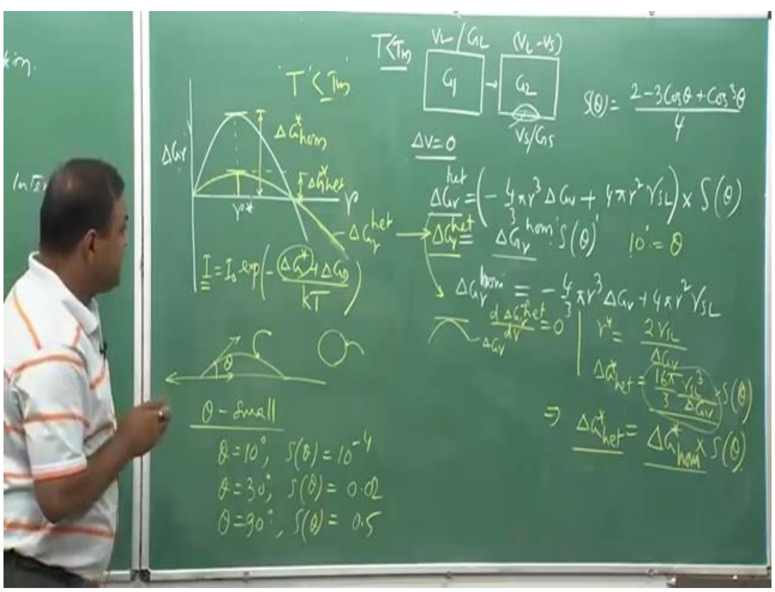

Now we let us see what does S theta do there, ok. If I try to plot a function of r. Last time we have plotted delta Gr for homogeneous, it is like this. And this was my r star and this is my delta G homo. So I do not do it as delta G homos it is only delta Gr. Now this is my delta Gr homo. Now if I try to see the variation of delta Gr heterogeneous, so that means this one. We have to see what is the value of S theta.

Now you will see that, if we see this theta which is the contact angle. If theta is small then this term would be very very small, because if we put theta value you just randomly put some theta value if you see theta equal to 10 degree you will see that S theta would be around 10 to the power -4, let me check the value. If theta equal to 30 degree S theta would be equal to 0.02 and theta equal to 90 degree, S theta would be equal to 0.5.

Now it is interesting that means if I consider these expression that means delta Gr het, this expression so that means if the contact angle is 10 degree that means theta is 10 degree then delta Gr heterogeneous at the same critical r would be very very long. Because as we have seen that r star does not change, r star in case of homogeneous or in case of heterogeneous in both the cases r star remain remains the same.

But the only difference would come in case delta Gr heterogeneous. So there that means it is very clear that delta G heterogeneous at all the r since theta is right 10 degree would be very very long. So the peak would appear on the same r, because at the same time delta G star heterogeneous is also equal to delta G star homogeneous into S theta. Here also that similar reduction effect would come.

You will see that the this particular plot will be like this. So this is my delta Gr het. So now r star appears on the same line even this point would appear on the same line, same point. Now you see interesting thing, so that means my activation barrier. So if this is my activation barrier for homogeneous nucleation at the same r my activation in a barrier for heterogeneous nucleation would be very very long.

Now if I try to find out what could be my nucleation rate, then at that particular temperature this is at a particular temperature Tm. So that time I can express that I in the form of similar expression, which is I0 exponential minus delta G star plus delta GD KT. So there only thing would be in case of homogeneous it would be delta G star homo and in case of heterogeneous it will be delta G star heterogeneous.

But this term will not change, because liquid atom has to jump and come to this surface of the solid (ass) solid surface. In case of homogeneous the liquid item was also travelling through the liquid, in case of heterogeneous it is also through the liquid. So this would remain same we can assume that this term remains same. So that means if this term reduces what happens to I. This is exponential factor, this is the minus term, so the I would increase, ok.

So that means at the same r star value, in case of heterogeneous nucleation I would experience more number of nucleation per unit volume per unit time. So that means if I have a surface where contact area is very very small, it gives me a very good influence for the enhancement of nucleation rate. That means I would have easy nucleation, ok. So now what does this easy nucleation means.

The easy nucleation means that means I will not be needing much of energy for the transformation of solid from liquid, ok. So now when this surface would become very activated surface, ok. Activated surface means it will help heterogeneous nucleation. So that means if I try to see the effect of this surface we can have a plot where S theta can be plotted as a function of theta.

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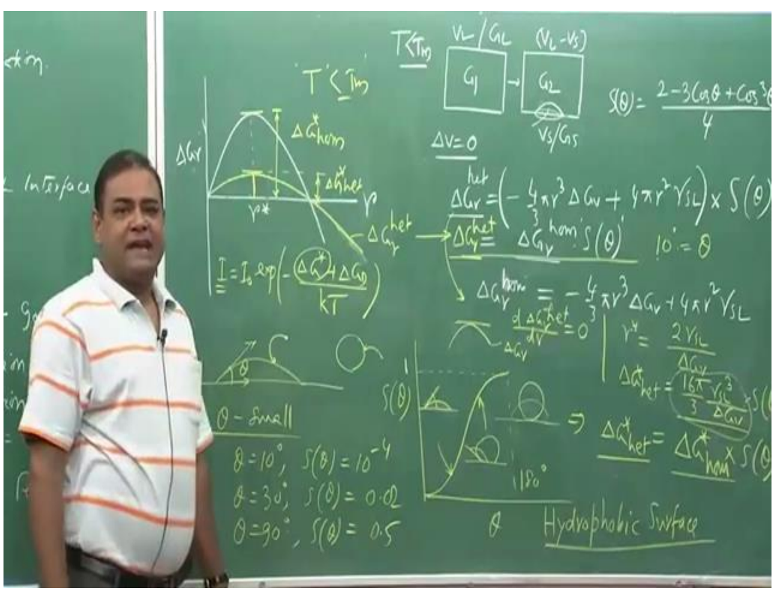

You will see that the plot would be like this, this is one and that time it would be 180 degree. And if I try to see what is the shape at this two points, the shape would be in this case, shape would be like this, in this case shape would be like this. So that means here the contact angle is very large and here the contact angle is very small. And in at 180 degree interesting thing happen is basically is this.

Now this has been observed in nature for example lotus leaf you might have seen a lotus leaf if you put a (dr) water droplet, water it forms a small small sphere and that sphere does not wet the surface. It remains as a sphere so that there I have a very very large contact angle and it does not wet the surface. And the lotus leaf you just tilt it that water droplet will fall off and your surface will be absolutely dry no water, ok.

So that means it has non wetting nature and that non wetting surface we also call it as hydrophobic surface. This hydrophobic surface is (ex) is is very very interesting surface where water does not stick. Now on the other hand that means if water does not stick, so that means I do not have any influence from the surface. If you see this particular thing, so that means if we do this particular thing S theta becomes 1, when theta equal to 180 degree and that time del Gr heterogeneous equal to del Gr homogeneous.

Similarly if S theta equal to 1, then del t G star heterogeneous is equal to delta G star homogeneous. So that means everything become very difficult for the nucleation, because it has to cross higher energy barrier. Now in case of this situation, where the contact angle is small. That means the surface we say that once we put (a) any for example is a water surface where is a paper, you take a rough paper. If we put water we will say that the water is gradually trying to wet the surface.

Initially it will form a water droplet but gradually it will (cre) it will try to get absorbed in within the surface. And the water layer initially it will be like this, it will be like like this and then gradually it spread, ok. So that particular factor we call it wetting, ok. So this wetting is very important, whenever I have influence of heterogeneous nucleation from mould world, the liquid must wet the surface as quick as possible, ok.

And whenever we the liquid metal wets the surface, that time contact angle would become low. And if contact angle becomes low, S theta would be very low and S theta very low means delta

G heterogeneous would be also very low and it will enhance the nucleation, ok. So that means whenever we have a surface, it has to have very very high wettability.

And when I can have very high wettability, if we try to see the expression whatever we have on this on this particular section for example we I we del we remove that particular expression. We can get it back that expression, ok.

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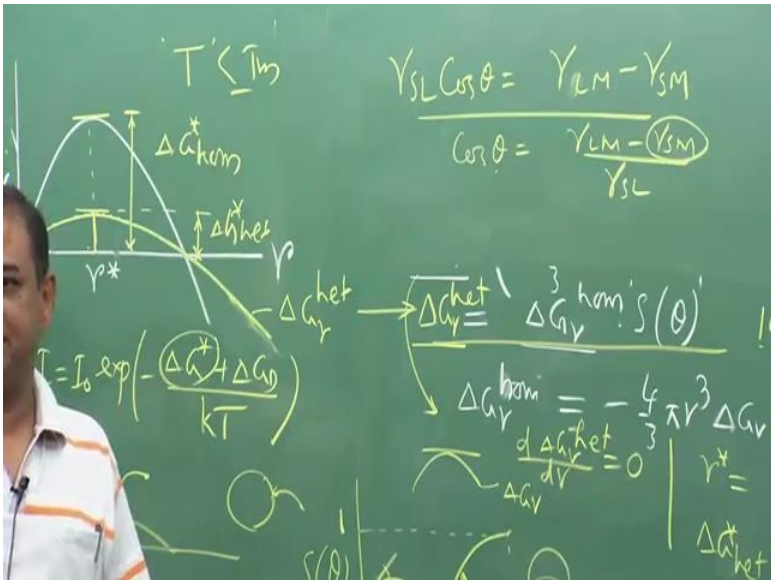

So let us get that expression, so if we see if we recollect our expression that expression was this expression. Now we can do it like this SL.

Now if it has to, if theta has to go down then Cos would be if theta is low. Then in order to that case this has to be low, ok. If this becomes low then S theta, theta would be low and S theta also would be low, ok. So that means the surface must have very low surface energy that means the mould world. The mould world would have a very low surface energy. So if the mould world has a low surface energy then it has a very good wettability too, ok.

Now what is it is application ok, now we are thinking from all sought of (ex) expression point of view. The application is inoculation, now you might have come across this particular word called inoculants. And in the casting process we many a times we add inoculants in the metal, ok. And those inoculants act as a nucleating sight. And those inoculant on those surface of the inoculant the liquid wets that surface and the solid starts forming on that inoculant.

And if you add a many many inoculant and at every inoculant you will have a crystal or the solid formation. And that means you have a very large number of crystals or solids and gradually this is used while making a very very fine structure or the grains in case of metals during casting, ok so this inoculation is decided by the wettability of that inoculant and finally it has to reduce this term or this term, ok.

So this inoculation there would be many factors, so one major factor is wettability also there are factors like slow surface energy as we have explained and then also we have to have very good (save) for example surface roughness is one factor, if we have then, this the compositional variation sometimes we add inoculants which has to react with the metal and to have a chemical bonding and those information would be very critical but we will not get into those information.

But at least from these expressions it is very clear that we do add inoculants to make it very very fine structures, ok so let us stop here. Now in the next lectures will go to the solid solid transformation and once we have learned this liquid solid transformation understanding solid solid transformation would be very easy, ok. And then finally we will go to the alloy systems because most of the engineering metals will be alloy (met) alloyed, ok. So that case how to we quantify this delta GV that would be an important aspects, ok. So let us stop here and we will continue in our next lecture, thank you.