Heat Treatment and Surface Hardening (Part–1)
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Lecture Number 15
Heterogeneous Nucleation

Hello everyone, let us start our 15th lecture.

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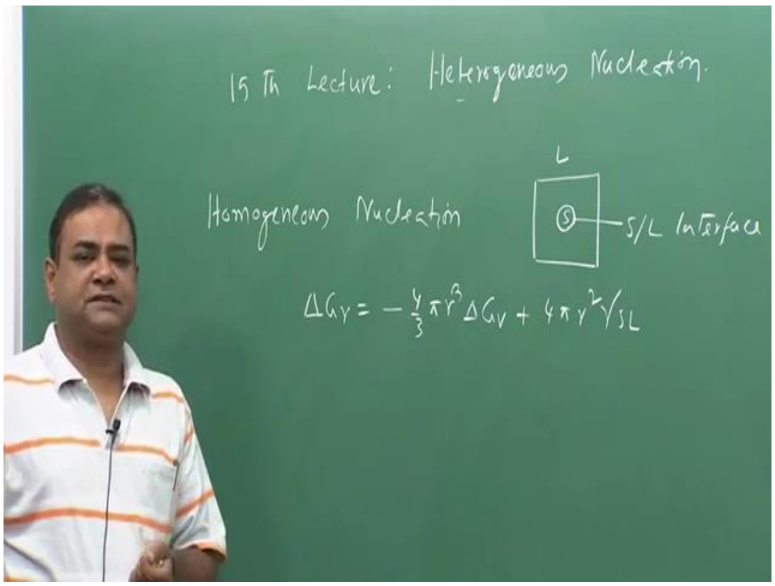

So in the last lecture we said that we will start with heterogeneous nucleation, which is very much practically observed. Now whenever we are talking about heterogeneous nucleation, it actually talks about transformation on some existing surface. And in the last instance, whenever we talk about heterogeneous nucleation, first we need to understand homogeneous nucleation.

So in case of homogeneous nucleation, the nucleation that means the phase formation from parent phase does not need to form on some surface rather when it forms it creates the interface between the parent and product phase and there are no more interfaces coming into picture during the transformation. So that makes it clear that whatever discussion we had, that means in case of liquid volume.

If we have a formation of a solid, ok. And that time, this solid liquid interface is the only interface. This is the only interface which is solid liquid interface. And the total energy requirement for this interface creation is coming from the volume free energy change which is the thermal factor. And that means the expression what we have received, what we have got del Gr is equal to -4 pi by r cube delta Gv +4 pi r square gamma SL.

So this expression, this is the energy supplied which is due to the thermal gradient thermal gradient means from Tm to a temperature where transformation is taking place. And this is the surface energy which is being created during the transformation. This is a classic example of homogeneous nucleation where it does not need to form on any surface. And it can be practically possible but though we need to do a very sophisticated experiment.

For example, let us say whenever you have solidification from a liquid, our common perception is we need to pour it in a molt, ok. For example if we would like to form let us say engine block, or engine head, or let us say manifold, exhaust manifold or clutch housing, so those are auto castings. So what we have to do you have to melt the metal, ok.

And then also you have to create a mould and inside that mould you have to also place core in order to make hollow parts in this casting and then you have to pour that liquid metal into the mould. So whenever liquid is poured into the mould, the liquid metal it starts solidifing. But the solidification is hassened or is does become easy because of the (already) ex already existing moulds surface.

So the solidification (is) is easy on the mould surface. So that there we have some sought of assistance from the mould, ok. But then how do we avoid thit that particular whenever we have that means it is also solidification the casting example. But in case of homogeneous nucleation of solid in a liquid, if we would like to do it we have to also avoid that mould surface. Now the mould can be acting as a container.

But here also somehow can we avoid the container, ok. If we avoid the container on mould I can create an instance where I do not be having any assistance from mould surface. So if we do not have any mould surface assistance the solidification mode would be a homogenous mode and people do levitation study. So the liquid metal droplet is created and that droplet does not have any surface, does not have any mould surface, it is a container less solidification, there we do exist, do experience homogenous nucleation.

So but as we have mentioned that the mould is required for any casting, ok. That particular mould surface would benefit casting, ok. Now we have to see whether it does benefit or not. Because we have seen that the mould surface does get the first solidification. We will now go into that part, where this solid will not form in the bulk of the liquid rather if this is a control volume we (is a) (is a) (is a) is a volume which is closed volume let us say.

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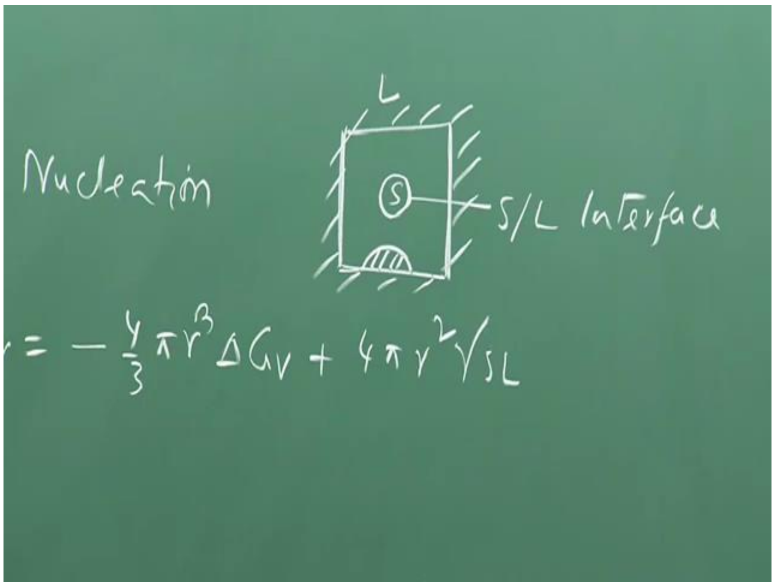

So this closed volume I can also make it like this are all my mould, ok. And there I can also have a situation where the solid is forming on top of this mould, ok. So this is my solid which is formed, now interestingly let us assume that the solid is basically a spherical cup, ok.

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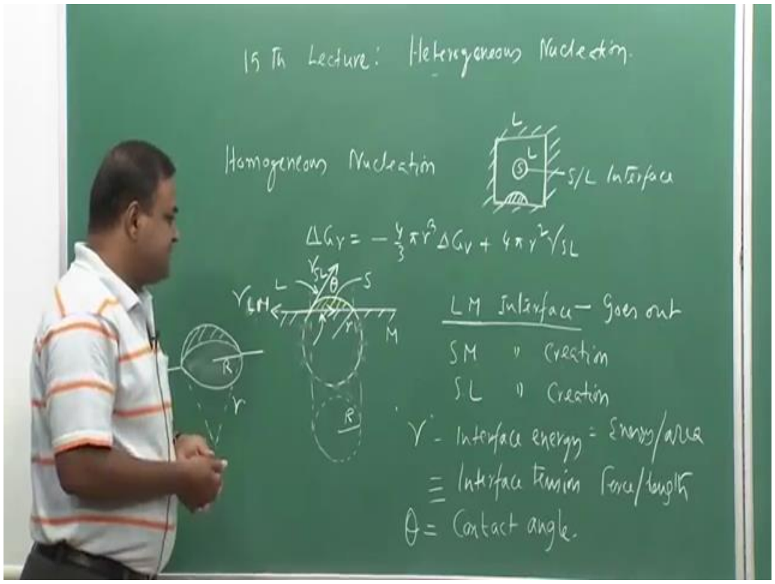

Now (if we have a sphere) if we have a sphere, ok. Now this sphere if you see that if we trunk it that sphere, ok. So then it would become a (so) spherical cup, ok.

And that cup will have radius of r, ok. So now if we consider that this cup is forming that means this is the part of solidified portion and this is the mould world this is the mould world. So this is exactly implicating this scenario where this this cup is forming on top of a mould. But if you connect that (cutticular) cup, if we complete that particular cup it will form a sphere. And that sphere radius is r.

Now if we have this situation, so now this is my mould let us say and this particular thing is invisible. This is invisible, so that means this part is not there, but if we complete this it will become a sphere. Now this is mould now, last time it was solid or liquid interface. Now we have mould, we have liquid and then we have solid. Now this situation is interesting situation, because before the solidified portion everything was liquid mould interface. So everything was liquid mould interface.

Now whenever this solid is forming on top of this, if we try to see in 3 dimension, it can look like this. So this is my, so this kind of stuff it will form. So this particular section that means if we try to see a projection on top of it, if we if I look from top, it will form a circle. This will form a circle of some radius r let us say. So this was r and this is capital R. So this is my capital R. And this is my small r.

So (this is that cup), this is that cup. So now before formation of this solid everthing was liquid metal interface. Now after the solid forms, this particular interface, this particular zone, that means this particular zone. We are forming a liquid not solid mould interface, so here we are replacing this particular interface with solid mould interface. And ofcourse we are creating another interface which is solid liquid interface, which is this one, which is this particular spherical cup.

So this is solid liquid interface is created, this is creation, this is creation. Now what happens to this interface within this zone, that is destruction that means it goes out, it is destroyed. So now whenever we have this kind of situation two interfaces are created one interface is out but there is one more interface which is this one at the at this particular junction we have another interface.

So interface energy if we consider this is interface energy. So we can also relate it to interface tension. So which is nothing but force per unit length. And here it is energy per unit area. So if you do the conversion you will get it surface tension. Now that means it has a directional nature, so now if I do that particular operation, so this is this particular force which is gamma SL is towards this. This is gamma (Sm) Lm, so because though this zone, this particular interface is out but this zone we have that interface.

And another interface which is Sm, which will be acting this way. So now we have situation like this and then this angle we call it as theta. Now this theta is called as contact angle, ok. So this contact angle will decide what would be the effectiveness of this mould world for the precipitation, ok. So now let us do this analysis then you will see that yes this mould world (alwa) tries to bring down the total energy requirement for solidification or phase transformation.

This will be valid though we will do it for solid liquid but this will be also valid for solid solid transformation, ok. So first do this , do this particular treatment in case of solid liquid.

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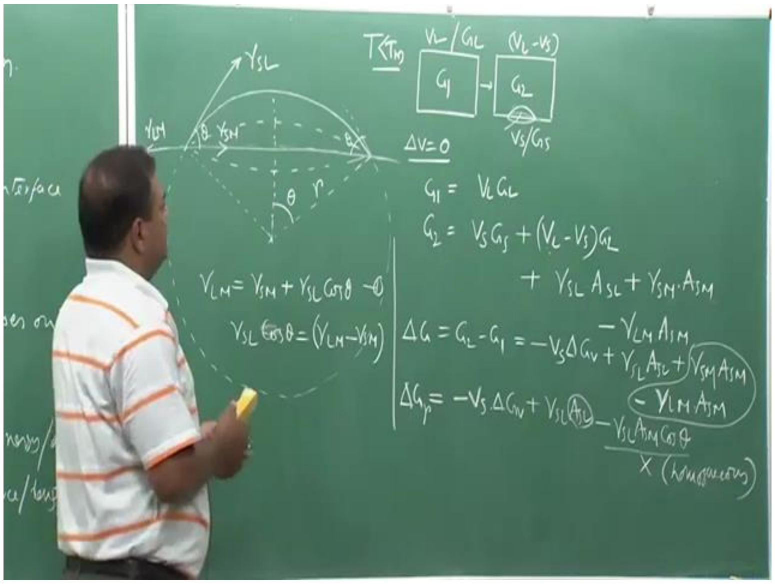

So now if we try to do the relation between if I try to plot it again, so this is solid liquid. If we have this arrangement, now this is also theta, now if we do a solid geometry, so then you will see that this also becomes theta.

Now in order to if we try to find out what could be the relation of the the balance between this three forces we can have a simple relation which is gamma Lm equal to gamma Sm + gamma Sl cos theta. So this is relation number 1, this will be very vital and if you see this doted portion, this is the bigger sphere, ok. And this sphere if you cut it, it will form a lens kind of thing, ok.

Now, this will be used for our treatment. Now second case if we try to understand the similar relation what we have got in, in case of homogenous solid liquid reaction, we have solid liquid transformation. So if that is the volume, Vl and if this is Vl and if Gl is the free energy per unit volume of that liquid and this is a temperature T which is less than Tm. So then we can get to another instance where solid will form.

But that case solid will form on top of that mould world. And then the volume of this solid would be Vs and the liquid volume would be Vl-Vs and here the assumption is there is no volume change during this transformation, ok. So that means the del V equal to 0, this is an assumption ok, though it does not happen.

There will be whenever solid to liquid or liquid to solid transformation happens there would be a definite volume change for example in case of water, volume increases during solidification that means liquid water to solid ice, the volume increase happens but in case of liquid metal for example aluminum or iron, ok the solid when solid forms the volume decreases that is what you have shrinkage problem in casting.

Now if we have this assumption but we are taking this assumption to have a a very easy treatment to this problem. Now this is G1 and this is G2, so that means G1 to G2 the transformation is taking place. Whenever I am trying to calculate G1 is the same calculation mode VlGl. And similarly G2 would be VsGs and Gs is the free energy per unit volume of that solid plus Vl-Vs, this is the remaining liquid Gl.

Now it does not stop here, we have we have already created interfaces. And the interface the relation is, this interface initially was liquid mould which is getting replaced with the solid mould interface. That means one part would be negative and we are creating one more interface which is this one, ok. So that means there would be two interface contribution one is gamma SL into ASL, ok. So the surface area of this alliance, ok.

Plus you are creating this interface also, so this is gamma SM and ASM. Now this interface is replacing the previous which was liquid metal, so that means the area would be same as this but the interface energy would change so minus gamma LM ASM. Now finally if I try to see what would be the free energy change the way we have calculated. It is G2-G1 equal to –V if you do that you will see this is plus, this is Vs plus gamma SL ASL plus gamma SM ASM minus gamma LM ASM.

Now since we have this expression, we can replace gamma LM as well as SM with SL. So we can gamma SL would be equal to we can do it like this Cos theta would be, so I can replace this term with Cos theta because if you take the minus out the for gamma gamma LM minus gamma SM whole the bracket and then this would be the common factor. So it will come like this if you do this little calculation, you will get this.

So this is my final expression, so it is on the basis of this r, so I can also put it as r, ok. So in case of homogeneous nucleation the only difference was this was not there, this was not there in case of homogeneous. Homogeneous nucleation it was not there but in case of heterogeneous nucleation that means when we have a mouled surface where the solid is forming, so we have this creation but this particular area is also not the total surface area of a sphere rather part of that surface area and at the same time this VS is not 4 by 3 pi r cube, rather this is the volume only of this particular portion not the entire portion.

So the entire problem lies in the calculation of this volume and the surface area of this as well as the surface area of this particular portion, particular region, ok. So if we do that calculation we can definitely get the expression for del G and this del Gr would be expressed in the form of theta, ok. And theta we have seen is the contact angle.

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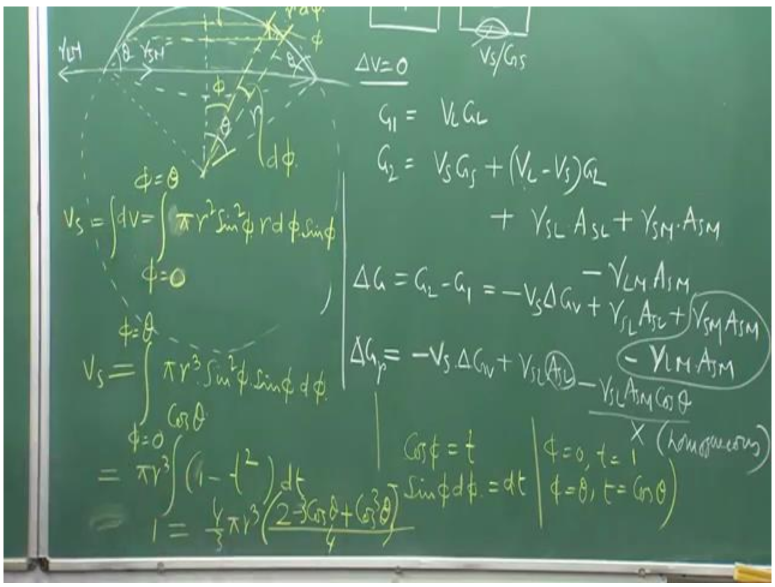

Now if we do that particular treatment it will be not that complicated only thing is you have to do little small integration and that time for example if I try to see for example if I try to take a small segment, let us say I take a small segment, if I take this particular, this is to be d phi and this is angle phi.

Then I will just do the integration and then we will get the value for example if I try to do the length calculation of this particular length, you will see that this particular term would come r, because this is r Sin phi. So this particular length becomes Sin phi, r Sin phi. So this is r d phi. And if I try to see this particular segment and this is a small portion.

So this becomes if we can assume it to be cylinder small desk. And the volume the desk could be, would be and the height and this radius this becomes my radius so 4, so pi r square Sin square phi. And this height if I try to find, so if I take if I draw a perpendicular to this line so then you would see that this angle becomes phi again, phi again. So then this length would be r d phi Sin phi again.

So then if I this is the volume of this small desk and in order to find the total volume of this particular section I will just have to integrate over phi equal to 0 that means from here to this portion. So then phi equal to 0 to phi equal to theta. See if we solve this we would get expression should I leave it for you to do the calculation or ok let me do this particular calculation.

And if we do that then I will take this out, this is VS now Pi r cube. Now I can take, I can make adjustment which is pi r cube d phi. And then if I assume that Cos phi equal to t, then then I can write Sin phi d phi equal to dt. So I can replace this one with dt and this one as t, so I, if I do this particular adjustment. So this becomes much simpler, so if we solve this and that time when phi equal to 0, t equal to Cos phi, Cos 0 equal to 1 and phi equal to theta, t equal to Cos theta. These are the limits.

And then the expression would change to 1 to Cos theta. See if we solve this we will get then adjustment, readjustment 4 by, 4 by 3 pi r cube 2-Cos phi -, + Cos cube (phi), theta sorry, it is theta divided by 4. So this expression just a minute let me have a look at this expression, sorry there will be three term here. So this is the expression you would get, ok if you do the integration, this is the final expression.

And this 4 will come because this 3 will come from this after integration and this 4 you have to take it outside and then also divide it by 4. So now this is the volume of this particular portion and we have to find out the area of this particular spherical cup and that we will do in our next class. I think let us stop here, thank you very much.