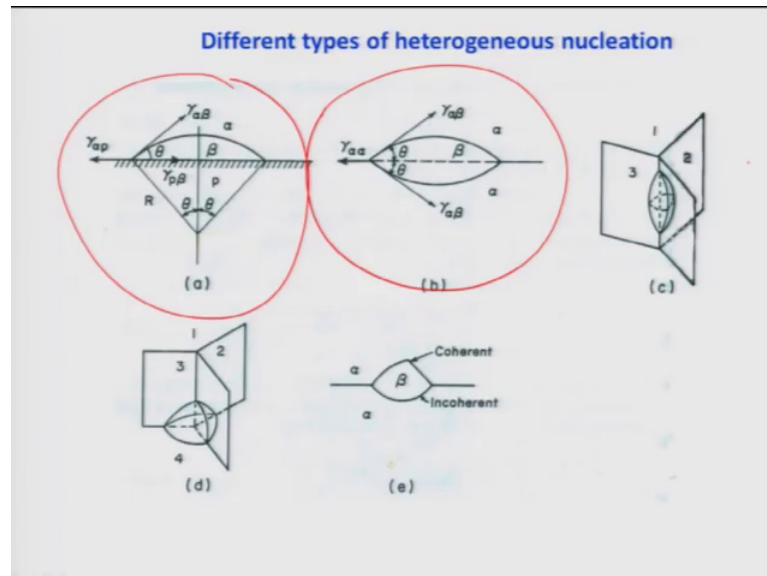**Phase Transformation in Materials**
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Lecture - 26
**Heterogeneous Nucleation (cont.)**

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So, after giving you a brief introduction and mathematical derivation of the heterogeneous nucleation for a solid on a substrate, let me just move on to the solid solid when we put that. Let me just tell you that this theory has been used extensively to make different type of heterogeneous nucleant for the industrial practices. To give you some example of aluminum alloys we used titanium diboride TiB2 as a nucleating agent and it is well proven that the aluminum nucleates nicely on these substrates.

Similarly, if that graphite in it, in a cast iron or ferrosilicon in a cast iron or zirconium in others carbon is used in magnesium alloys as one of the nucleating agents. So, there are such many nucleating agents which can be actually prepared or a designed using these theories. So, as I said I am going to take a few cases of solid nucleating agents and here are the few examples; first one which I already discussed with you that is some beta forming different alpha phase in such way that there is a such a phase precipitate on already present on the in the alpha and on which beta actually forms.

Mathematics will remain exactly same just like one I have derived for the liquid solid the next one is basically nucleation in the grain boundaries as you know the grain boundaries acts as an nucleating agent for the many precipitates, we will see in our phase transformation discussion later part the grain boundary actually can be considered as that. Now it is very simple compare to first one that is much simpler than this one in the sense that what we are going to happen the phase which is forming from the parent phase alpha on the grain boundary of the alpha will be forming like a double lens.

If this is the first lens of the top second lens of the bottom and at this corners, the interfacial energies are balanced, but the balancing is basically for the both parallel components and as well as perpendicular components. So, if you simply allow you simply do the maths because using 2 spherical caps it is basically done. So, how things are done again I will be doing you the little bit maths of that, but I am not going to discuss you in detail because details you need to do yourself.

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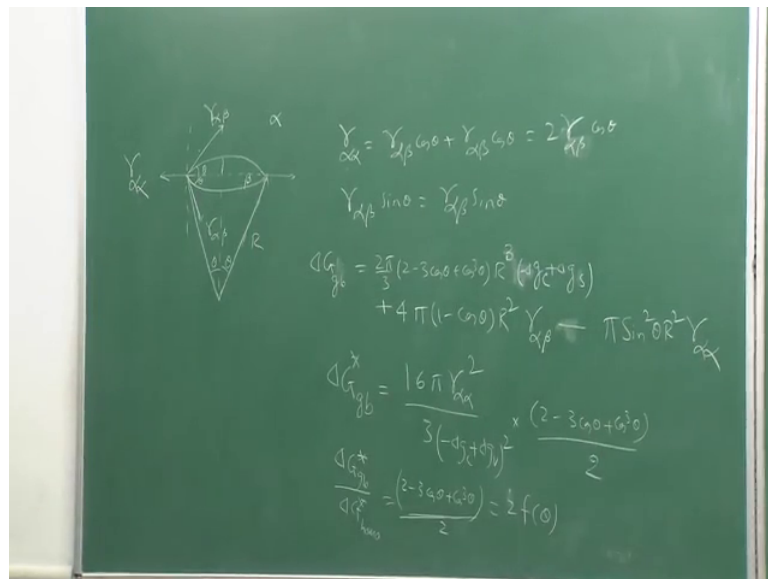
So, suppose I have a grain boundary and I form a new solid phase as a 2 caps on the grain boundary that is what you seen in some of the pictures, I will show you later also in the actual micro structure. Therefore, this is my alpha phase, this is my beta phase and this is a fire alpha grain boundary. So, therefore, this energy is basically alpha-alpha and other energy parts is basically gamma alpha beta. Similarly this is also; what this is not

this one; this one is gamma, alpha, beta and these are actually angles will be of theta correct.

So, I can write down gamma alpha-alpha is equal to gamma alpha beta cos theta plus gamma alpha beta cos theta, if I consider only the parallel components so; that means, this is equal to twice gamma alpha beta cos theta. If I consider perpendicular components, it is very simpler perpendicular components will be all equal gamma alpha beta sin theta gamma alpha beta sin theta, you can do this very simple it is about that these energy balance is must be happening at this point.

So, now what are the; what is the delta G b equation delta G; actually, now let us write down this is delta G for grain boundary gb. So, that is obviously again volume and as you know volume will be double of the earlier volume which I have done. So, this is very simple twice pi by 3 that is equal to 2 minus 3 cos theta plus cos cube theta multiplied by R cube again R is you can actually draw that R like this. So, that is equal to r.

Same idea I can draw here sphere; correct. So, now, what is the laws of energy what is the gain of energy. Obviously, loss of energy is these 2 interfaces created between alpha and beta and gain is that earlier grain boundary is now recovered the earlier grain boundary between alpha-alpha is now recovered that is the gain. So, let us write down that. So, this obviously, will be multiplied by delta G c plus delta G v, sorry, delta G s right, it has to be because that is the volume that is the energy per volume plus the energy created because of these 2 interfaces new interfaces has formed that again double 4 pi 1 minus cos theta R square and this is into multiplied by the gamma alpha beta, right that is the interfacial energy between 2 alpha between alpha and beta.

Basically if you consider single lens, this is will be twice pi one minus cos theta R square that is very clear; why if you draw this one that is basically is equal to pi 1 minus R 1 minus cos theta basically so the moment you consider that as a basically part of the sphere. That means, become 2 pi 1 minus cos theta R square plus; sorry, this is the energy which has been which is basically required. So, what is the energy gain? Energy gain is because of this boundary which has got completely balanced that is equal to pi sin square that R square c R square multiplied by gamma alpha-alpha.

The sin square is basically coming because of this angle; these angles are also theta remember. So, now, we can actually do all the things you can plug in this from this equation you can change gamma alpha-alpha basically we can change we can make everything in terms of energy. So, therefore, this gamma alpha beta can be replaced the gamma alpha beta is equal to gamma alpha-alpha divided by 2 cos theta and one can simplify this equation and get something else.

So, what you get finally, I am not going to do everything the barrier for the grain boundary nucleation is again 16 pi gamma alpha-alpha square divided by 3 minus delta G c plus delta G v square multiplied by 2 minus 3 cos theta plus cos cube theta divided by 2. So, what you can see by making 2 double lengths, I reduce the barrier or rather I increase the barrier actually compared to the complete single lens systems which I shown you earlier that is compared to the first picture on this slide half. That means, what; that means, delta because we are going to compare everything with in terms of hetero homogeneous nucleation that is easy homo that is equal to 2 minus 3 cos theta plus cos q theta divided by 2 that is nothing, but 2 s theta, this f theta is basically 2 minus 3 cos theta plus cos q theta by 4. So, everything will be doubled basically all this theta everything I showed you the values will be doubled here.

So, that is for the grain boundaries and what will happen to the grain edges basically is very simple one if you look at very carefully otherwise it will be for you it will be look like very complex see grain edge is what a grain edge means 3 grains are meeting here I have shown you 1, 2, 3 grains are meeting you see here 1 2 2 and 3 3 grains are meeting at this edge. So, instead of 2 caps 2 caps here there will be 3 spherical caps or 3 basically 3 spherical caps. So, you can use this concept which just now I have done for both single cap and double cap you can extend that for 3 cap situation and do the maths basically it will be again factor 3 will come into picture what happen to the grain corner grain corner is again not extensively difficult why because at the grain corner 4 caps are meeting you see there are 4 grains 1, 2, 3, 4.

So, if I have 2 grains 1 and 2, I have 2 caps we have 3 grains 3 caps 4, there are 4 caps. So, I can again calculate these very easily simply multiply the areas and the volumes volume will be 4 times area will be again 4 times. So, you can do that it is not very difficult task. So, once you do all this maths and get this delta G b; this is for the grain boundary delta g.

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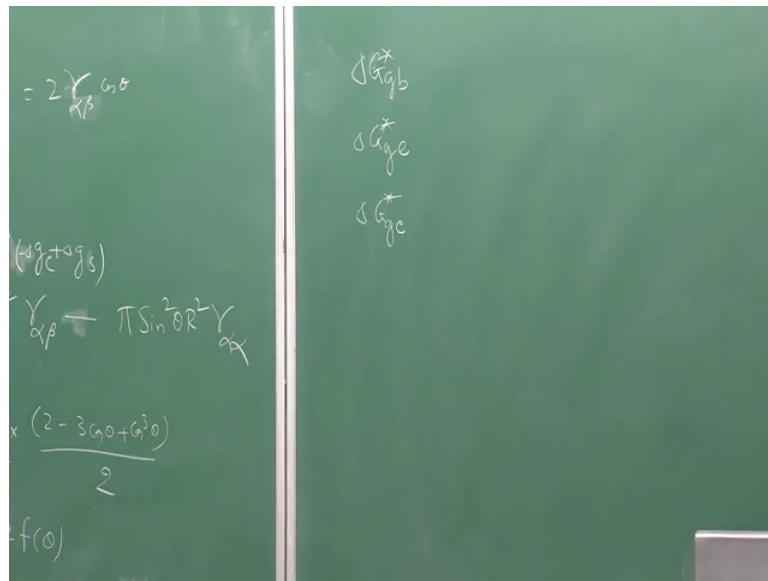
Basically you can get all these values you can get delta G b star you can get delta where edge G e star and delta G corner star 3 different 3 values for this critical barrier.

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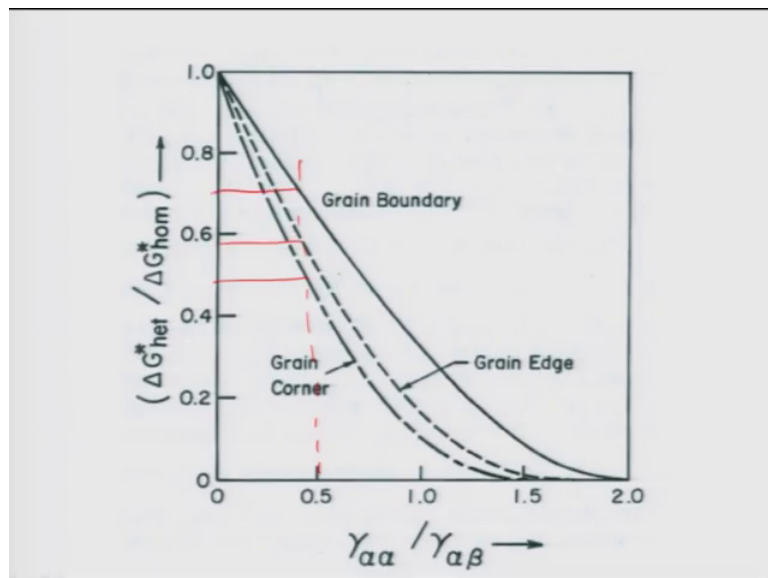
And then whatever you plot, it will look like; it will look like this as you see here, this is heterogeneous nucleation compared to delta G star homogeneous for these 3 situations grain boundary grain edge and grain corner. So, as if you clearly see grain corners are the most or the easiest nucleation sites they are the places where the new phase will form will be you know for the new phase, it is easier for you to nucleate followed by the grain

edges and grain boundaries that is what you see in the actual practice we always find at the grain corners more number of nucleation of the heterogeneous nucleation happens than at the grain boundaries.

This precipitation based alloys, aluminum, copper aluminum, copper silicon aluminum, magnesium silicon, all this alloys; these precipitates nucleation actually governed by these aspects remember this is nothing, but a gamma alpha-alpha by gamma alpha beta so; that means, what when the gamma alpha-alpha receive to gamma alpha beta becomes 1.5 every nucleation is the both can edge grain corner nucleation is similar and, but as you decrease this values; that means, when it become 0.5 if you look at 0.5 the values are much widely different. So, smaller the ratio of gamma alpha-alpha by gamma alpha beta what is the ratio tells you that is the contact angle basically that ratio the gamma alpha alpha by gamma alpha beta they are in the board you see on the first equation is basically 2 cos theta for the grain boundary.

So; that means, basically it depends on the cos theta. So, that ratio if you change if you become a smaller values that then the nucleation grain corner is much easy easiest one followed by grain edge and grain boundaries, but as this ratio becomes higher; that means, the energy is differences between alpha-alpha grain boundary and alpha beta interfacial energy difference as very you know widely differed. Then these the nucleation on the grain edge and grain corner will not very much and when it become very high, it is close to double then what will happen. That means, when theta is very high actually then what will happen these nucleation can happen anywhere there is no not much reference between boundary edge and the corner possible.

So, that is the one important aspect which comes early from this equation second important thing which I will discuss about is the nucleation on the sorry nucleation on the dislocations as you know dislocations are presence inside a crystal that is inside a grain and many times, they are actually help in nucleating certain phase; how does it do basically dislocation has a distorter zone dislocation has a distorter zone means there is a dislocation core and the dislocation core. Actually dislocation core, actually helps us to nucleate why because dislocation core has a lot of distortion energy; if a new phase nucleates on that the distortion energy can be relived and that is the reason, we can gain actually system can gain lot of energy, if it allows to nucleate some phase in the dislocation.

Mathematically how it will look like; it is very simple, again not very difficult gain, we can actually comes in a such a kind of model, but we do not need to do much like that it is much easy what we need to know is the strain energy it will because of the dislocation and that equation is available in the books in the mechanical metallurgy books its available.

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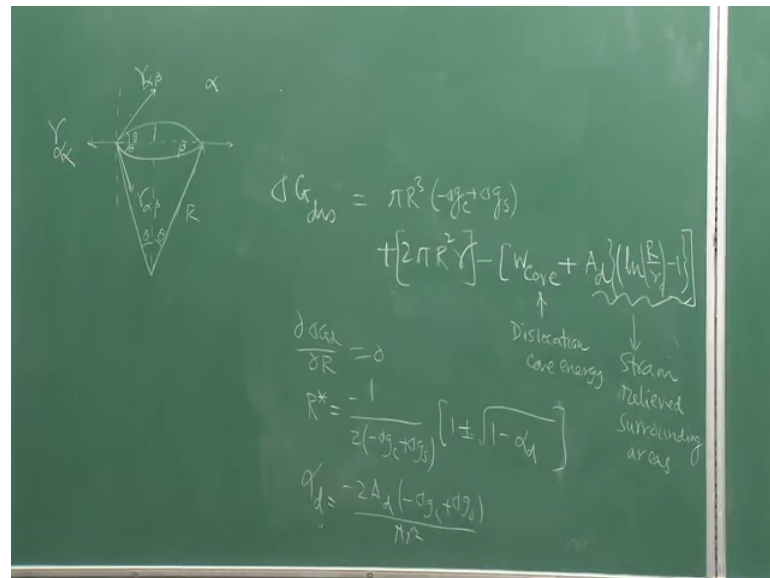
So, what is done is that. So, delta G dislocation where heterogeneous nucleation is nothing, but you know again pi R cube; this is the volume term minus g c plus delta G c plus delta G s that is basically the volume term plus twice pi R gamma minus, this is basically your pi square R square this is basically your because of the interfacial energy gamma between dislocation core dislocation and this crystal that this is the energy grain remember and what is the energy loss.

Energy loss is basically related to w core; core energy dislocations multiplied by a d is the surface area of this dislocation core log of R by R 0 minus sorry R by R 0 minus 1; this part is what is new this is core dislocation core energy. And this is basically because of the strain relived surrounding areas. And this equation is familiar to many of you if you have looked at any mechanical metrology book. So, that is the total energy of the system. Therefore, if I do the analysis that is if I make delta G by dell R 0, I get R star that is what R star is basically very complex equation it is not a.

Simple equation any more g c plus g s 1 minus alpha d what do you see here basically you see 2 roots of this equation, this is no longer; this will be equation related to R square that is the problem and because of the because log and other things there. So, this R star has 2 roots one plus minus this term will give you plus one root and minus one root and alpha d is ledge taken all this equations minus 2 a d delta G c plus delta G s; G s 9 divide by pi R square small R; so that means what? That means, I can actually have 2 sets of values of this nucleation for nucleation and this is what is shown here.

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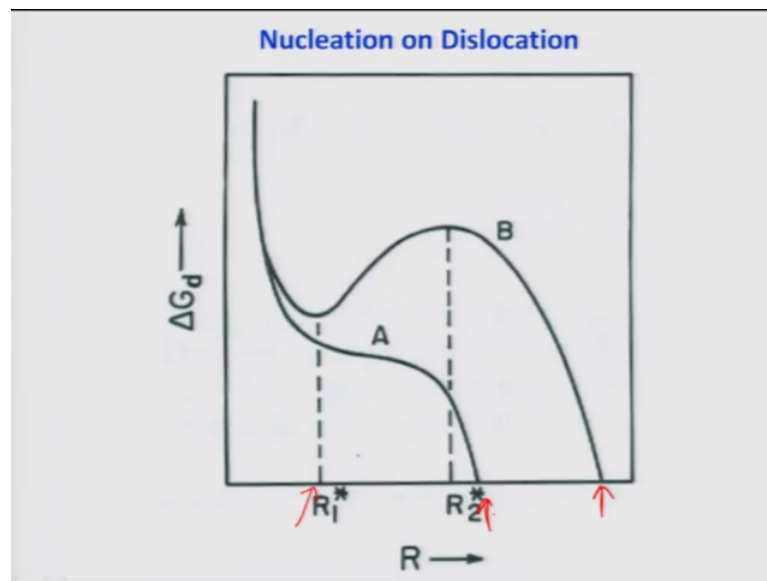
When alpha if you consider as plus value then a which situation will happen that it delta G will reduce as a function very connotocally will reduce you see a monotonically get reduced and final value will be R star 2 star, but when it is basically minus, then you have situation like B. So, it goes to A 1 minima and then another. Therefore, you have 2 different values of 1 R star 1 here another R star 1 there. So, if you clearly see that when the B is there, there is one value there another value there when A is there, there is only one value. So, that this is has been seen actually depending on the type of dislocation energies and basically if alpha d is very small, then does not matter, but alpha d is substantially high.

Its compared to the other parameters then this becomes this becomes very strong and in that case you can have 2 different values of R star actually, what does it means that you can you can actually 1 system can select 2 different R star 1 small value one high value.

So, you can have 2 sets of 2 precipitation dislocation when alpha d is very large one will start with the bigger size much bigger size almost 3 times bigger than these the other one. And then if the size the there will be distribution of these different phases the precipitates of different size that is what people have seen actually. So, mathematically one can actually show that it is possible basically what you need to do as a part of your home assignment is that you can take this equation and solve it. So, that you can get R star different values of R stars; so, you will get A; you know equation in terms of R square and solving that equation basically it is a quadratic equation.

So, that solving the equation will give you 2 roots any way you do that. So, that is basically for the nucleation only thing which I probably had to talk would have talked it that nucleation rate, but you know nucleation rate for homogeneous heterogeneous equation will remain same only thing which will change if you nucleation is that delta G star in the equation of homogeneous nucleation rate will replace by delta G star heterogeneous that is the only difference everything else will remains same F C 0 will remains same exponential minus delta G star heterogeneous pi divided by K T will be used in case of heterogeneous nucleation. So, the other than that everything is will be remaining same. So, I simply complete almost all the introductions of different things although it looks like introduction, but it is quite a beet of it a phase transformation because I have talked about thermo dynamics then I talked about.

Diffusion and then interfaces and followed by nucleation and I use different aspects now it is become very easy for me to talk growth because that is what is left growth of phases then phase transformations. What I am going to do is the next class onwards I am going to certification as a first thing although I have talked about certification quite a bit where we will take about certification morphologies certification and then followed by morphologies and what actually happens in the real cast structures.

And then I will move on to the solid to solid phase transformations there are many many solid to solid phase transformation to be covered. So, we will spent for each of them depending on the type of phase transformations we will spend about 2 to 3 lectures each and then complete.