Structure of Materials
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Lecture - 39
Chapter-08
Phase Transformations

Of course, one question we have not answered so far is that, why does heterogeneous nucleation dominate.

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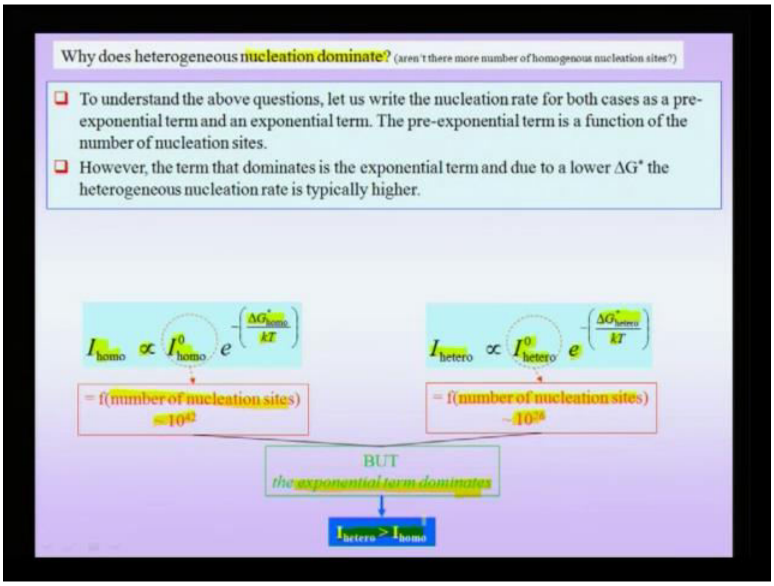

Why does heterogeneous nucleation dominate? (aren't there more number of homogenous nucleation sites?)

- ❑ To understand the above questions, let us write the nucleation rate for both cases as a pre-exponential term and an exponential term. The pre-exponential term is a function of the number of nucleation sites.
- ❑ However, the term that dominates is the exponential term and due to a lower ΔG^* the heterogeneous nucleation rate is typically higher.

$$I_{homo} \propto I^0_{homo}\, e^{-\left(\frac{\Delta G^*_{homo}}{kT}\right)}$$

$= f$(number of nucleation sites)

$\sim 10^{42}$

$$I_{hetero} \propto I^0_{hetero}\, e^{-\left(\frac{\Delta G^*_{hetero}}{kT}\right)}$$

$= f$(number of nucleation sites)

$\sim 10^{26}$

BUT

the exponential term dominates

$I_{hetero} > I_{homo}$

Because, we have noted that, in homogeneous nucleation, every point say for instance in the liquid melt, which is going to solidify is a potential nucleating site. On the other hand, when we are talking about heterogeneous nucleation say suppose, you could have even added a million particles so say for instance, zirconium in a magnesium melt, the number is considerably smaller in terms of, now even many, many orders of magnitude.

And therefore, we would expect that, even though heterogeneous nucleation is preferred in terms of energetic, it is homogenous nucleation should dominate because, the number of such potential sites are much, much more. Now therefore, we write down the nucleation write for both cases and we of course, write down the proportionality. That, in case of homogeneous nucleation, the nucleation rate is proportional to minus delta G star homogenous by k T and the pre-exponential term is a function of the number of nucleation sites.

Similarly, for heterogeneous nucleation rate, the pre-exponential term I 0 heterogeneous is a function of the number of nucleation sites and the exponential term is minus delta G star heterogeneous by k T. Now, in the case of homogeneous nucleation, you can clearly see that the pre-exponential term, which is 10 power 42 is much larger than the number of heterogeneous nucleation sites, which of course, could be even much lower than the number sited here.

But, what happens is that, it is the exponential term, which dominates because now, the delta G star is sitting in exponential. And we have seen that, even in the case of a wetting angle of 90 degrees, which could of course, be better considerably by use of an appropriate nucleating agent, in which case the nucleating agent may practically wet the heterogeneous nucleating agent.

That means, the product phase can wet the heterogeneous nucleating agent, in which case I would get a considerable benefit in terms of delta G star heterogeneous. Because of this dominance of this heterogeneous dominance in the exponential term, wherein the delta G's are heterogeneous sits, I find the heterogeneous nucleation rate is larger than the homogeneous nucleation rate. And therefore, when we are talking about phase transformations and especially nucleation, there is a benefit of adding heterogeneous nucleating agents.

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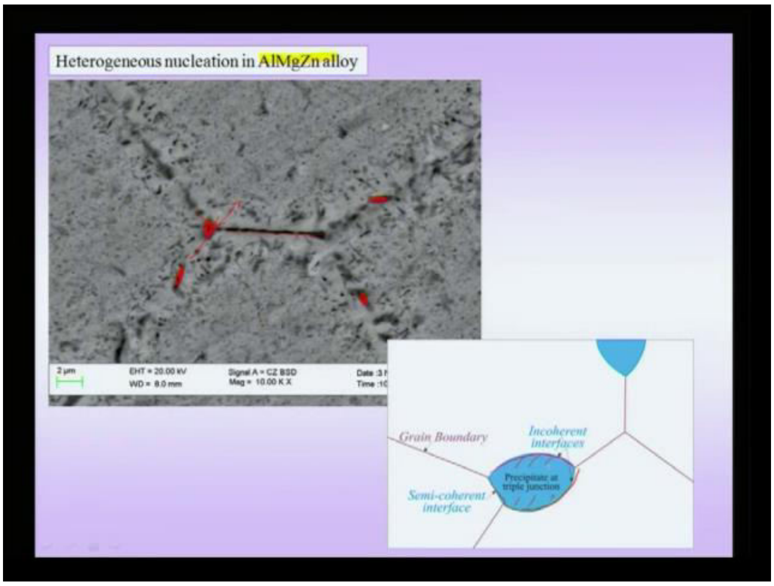

Heterogeneous nucleation in AlMgZn alloy

Now, here are there is a micrograph and a schematic which shows that, how heterogeneous nucleation is taken place. In this case of course, you can see that, in the solidification or the phase transformation of aluminum magnesium zinc alloy, this is a solid to solid phase transmission. There has been preferential nucleation of the second phase at triple junctions and at the grain boundaries, some of these has been etched away by the nucleating etching agent.

And therefore, you find that of course, there are other points within the medium, where also a homogeneous nucleation might have occurred. But, these heterogeneous nucleation sites like along the grain boundaries or the triple junctions so, this triple junctions play an important role in heterogeneous nucleation. And it may so happen that, of course, I may have a precipitate forming like in the schematic below, along the triple junction and this precipitate may have a semi-coherent and incoherent interfaces, which maybe present. And it is to be noted that, incoherent interfaces or semi-coherent interface are more glissile as compared to coherent interfaces.

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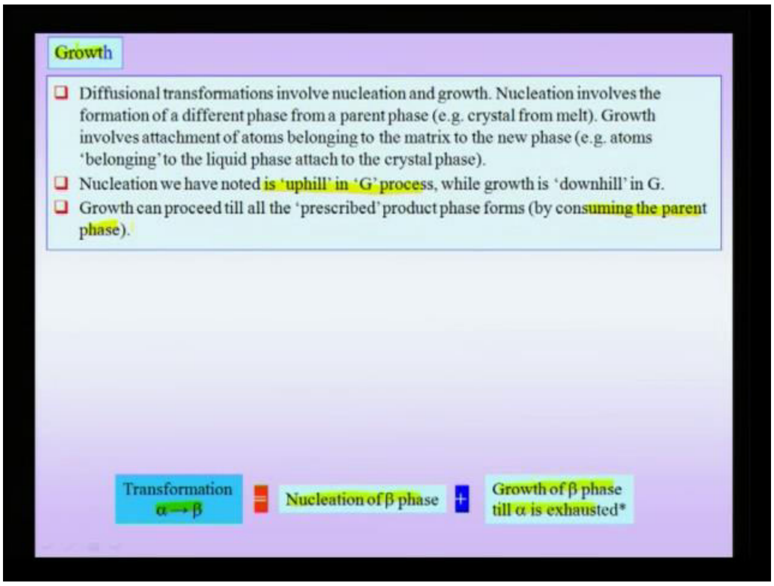

Growth

- ☐ Diffusional transformations involve nucleation and growth. Nucleation involves the formation of a different phase from a parent phase (e.g. crystal from melt). Growth involves attachment of atoms belonging to the matrix to the new phase (e.g. atoms 'belonging' to the liquid phase attach to the crystal phase).
- ☐ Nucleation we have noted is 'uphill' in 'G' process, while growth is 'downhill' in G.
- ☐ Growth can proceed till all the 'prescribed' product phase forms (by consuming the parent phase).

Transformation $\alpha \rightarrow \beta$ = Nucleation of β phase + Growth of β phase till α is exhausted*

Therefore, I need to worry about heterogeneous nucleation, whenever I am talking about phase transformation especially, solid to solid phase transformation. So, the second step in a nucleation growth or in a transformation involving nucleation growth is the stage called growth. So suppose, I may talking about alpha to beta phase transformation then, I need to understand the nucleation at the beta phase and the growth of beta phase till alpha is exhausted.

Now, the step growth we have already noted is actually downhill in Gibbs free energy, while the nucleation step is uphill in Gibbs free energy. And during growth, atoms belonging to the matrix jump on to the product phase so, they become part of the product phase and in this process, the whole of the parent phase is consumed during growth. And we have seen this nice example, even in the solidification of the melt where, there melt liquid is consumed and finally, we have a complete solid phase, which is present.

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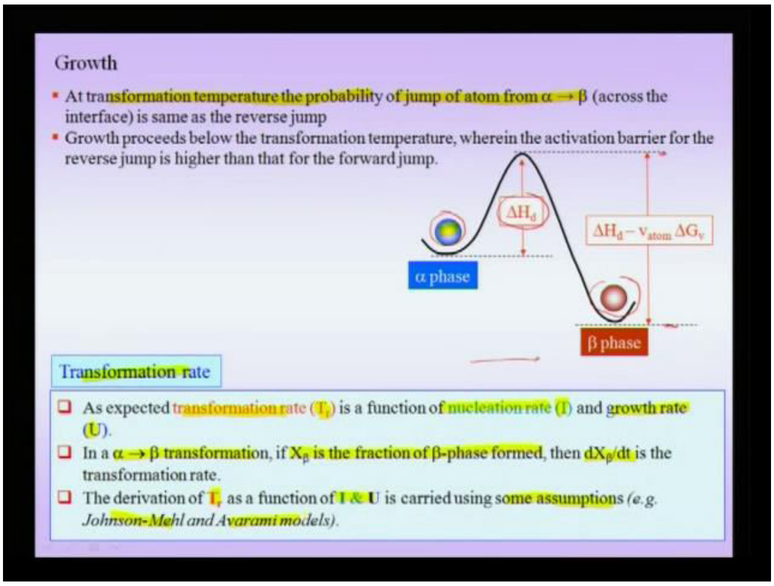

Growth

- At transformation temperature the probability of jump of atom from $\alpha \rightarrow \beta$ (across the interface) is same as the reverse jump
- Growth proceeds below the transformation temperature, wherein the activation barrier for the reverse jump is higher than that for the forward jump.

Transformation rate

- ☐ As expected transformation rate (T_r) is a function of nucleation rate (I) and growth rate (U).
- ☐ In a $\alpha \rightarrow \beta$ transformation, if X_β is the fraction of β-phase formed, then dX_β/dt is the transformation rate.
- ☐ The derivation of T_r as a function of I & U is carried using some assumptions *(e.g. Johnson-Mehl and Avarami models).*

Now, this atomic jump, which I have talked about at the transformation temperature, the property of jump of an atom from alpha to beta phase that means, across interface is same as the reverse jump. But, typically when we are at an under cooling then, there is a benefit in, this is of course, the reaction coordinate along x axis so, this is my reaction coordinate.

And now, an atom belonging to the alpha phase, if it jumps to the beta phase, which is the product phase then, the forward jump the activation barrier is delta H d, which is smaller than the reverse jump, in which case my activation barrier is taller. Therefore, below at a, if I am below the transformation temperature that means, I am at an under cooling then, atoms would preferentially jump from the parent phase to the product phase in this process now, my growth can take place.

Now, my overall transformation rate, which I call T subscript r just to differentiate it from the capital T, which could be a symbol for temperature. The overall transformation rate is a function of the nucleation rate and which I use a symbol I and the growth rate, for which I use a symbol U. Therefore, this function is some important function, I need to locate this function in which case, I would note my transformation rate, as I go from the parent phase to the product phase.

Suppose, I am talking about an alpha to beta transformation, if X beta is a fraction of the beta phase formed then, d X beta by d t is the transformation rate that means, the fraction of the beta phase, as a function of time is the transformation rate. This T of r, which is now my transformation rate, which we already noted as a function of I and U can be carried out using some kind of assumptions and in later slides we will see, what are these assumptions briefly.

And based on these assumptions, we have various models to calculate this transformation rate like for instance, the Johnson-Mehl model or the Avarami model. So, if I know my transformation rate then, I know that, how my parent phase can transform into the product phase or as we shall see later, instead of working with rates we may also want to know, how long for phase transformation at a certain under cooling.

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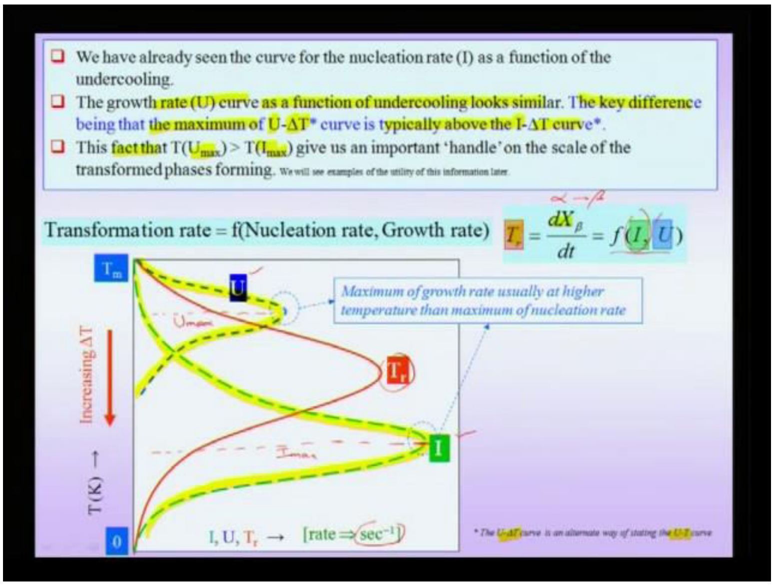

- ☐ We have already seen the curve for the nucleation rate (I) as a function of the undercooling.
- ☐ The growth rate (U) curve as a function of undercooling looks similar. The key difference being that the maximum of U-ΔT* curve is typically above the I-ΔT curve*.
- ☐ This fact that $T(U_{max}) > T(I_{max})$ give us an important 'handle' on the scale of the transformed phases forming. We will see examples of the utility of this information later.

Transformation rate = f(Nucleation rate, Growth rate) $T_r = \frac{dX_\beta}{dt} = f(I, U)$

Maximum of growth rate usually at higher temperature than maximum of nucleation rate

* The U-ΔT curve is an alternate way of stating the U-T curve

So, we will directly jump to the result, before we even consider the derivation of the function T subscript r, which is what we are interested in here and we will try to see the relative maxima of the nucleation rate versus the growth rate U. The growth rate curve U, which is now the result, we are jumping to the result, as a function of the under cooling it looks very similar to the nucleation rate curve. The key difference being that, the maxima of the growth versus under cooling curve is typically above the nucleation rate versus under cooling curve.

Of course, the under cooling, the nucleation rate or growth rate versus under cooling plot can alternate the rate of stating that, it is actually I am talking about the nucleation rate with temperature, this we already noted. Now, this fact that, the temperature at which the maxima of the growth rate lies, is above the maxima or above the temperature, at which the maxima of the nucleation rate lies gives us an important handle so that, we can control the transformation process.

That means, we can have a process, in which it is nucleation dominant or a process in which could be growth dominant. Suppose, I want to have a process, in which I want to produce very fine grain material then, I will work at a temperature wherein, the nucleation rate is more and the growth rate is small. So therefore, now I have the transformation rate T subscript r, which we stated is nothing but, for d X beta by d t that means, the rate at which the beta phase forms.

And now of course, I am referring to a phase transformation, in which I am going from the alpha phase, pure alpha phase to a pure beta phase. Like for instance, this could be a process of cooling of iron, in which I am having the FCC form forming into the BCC form. And this function we have already said, has this transformation function, has to be a function of both of the nucleation rate and the growth rate.

Of course, assuming that, both of these rates are finite numbers now, as I pointed out suppose, I have already noted how the nucleation rate curve looks with temperature, the green curve. Now, the maxima of this lies at a certain lower temperature as compared to the maxima of the growth rate versus under cooling curve so, this is my maxima of the so, this is I max and this is U max.

So, this is the typical scenario where, my transformation rate T r is a function of the nucleation rate and the growth rate, and the maxima of the growth rate is typically above in temperature that means, it is at a higher temperature compared to the maxima of the nucleation rate. So, the x axis units are in per seconds and I have finally, a master curve which is now my transformation rate curve. So, whenever we see a transformation rate curve, we have to understand at the underlie or at the bottom of these transformation rate are 2 important functions, a nucleation rate and the growth rate, which further depend on the under cooling.

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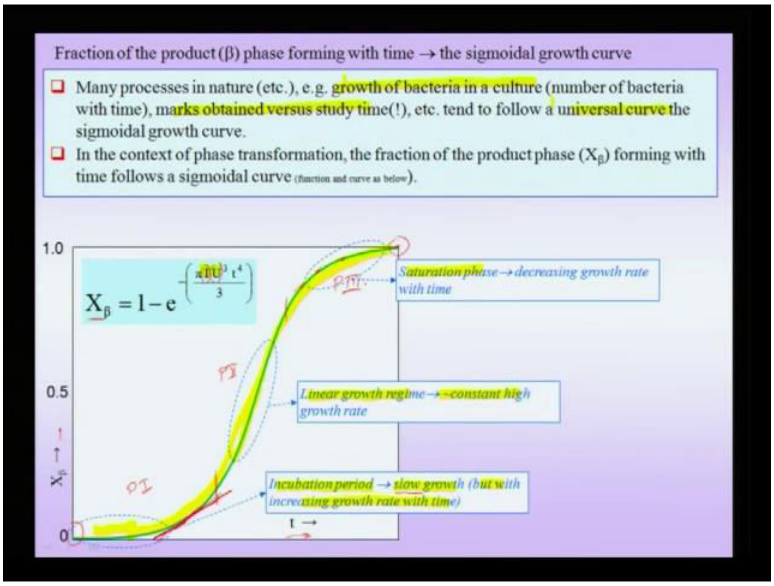

Fraction of the product (β) phase forming with time → the sigmoidal growth curve

- ☐ Many processes in nature (etc.), e.g. growth of bacteria in a culture (number of bacteria with time), marks obtained versus study time(!), etc. tend to follow a universal curve the sigmoidal growth curve.
- ☐ In the context of phase transformation, the fraction of the product phase (X_β) forming with time follows a sigmoidal curve (function and curve as below).

$$X_\beta = 1 - e^{-\left(\frac{\pi I U^3 t^4}{3}\right)}$$

Saturation phase → decreasing growth rate with time

Linear growth regime → constant high growth rate

Incubation period → slow growth (but with increasing growth rate with time)

Now suppose, I plot this X beta, which is the fraction of a beta, as a function of say, for instance the nucleation rate I and the growth rate U then, I would get a curve, which is typically is called a sigmoidal curve. So, you can see this now X beta, which is on the Y and time on the x axis and I would get the green curve as shown here. Important point to note is that, this kind of a sigmoidal curve is practically universal and this found in many scenarios.

For instance, growth of bacteria in a culture where, the number of bacteria with time can be plotted and such a similar kind of function would be obtained. You could even think of a marks obtained versus time of study for instance suppose initially, you put in lot of initial time you put in for study, your marks may not increase. Because, the time you are investing is actually going into understanding the basics, later on when you put in more time your marks would increase because, now you can able to translate more effectively your understanding into marks.

But, how much ever you study, trying to increase the marks from 95 to 100 may be a very difficult task. So, this universal curve is found in many many scenarios and in the current context, if you plot X beta, which is a function in the nucleation rate and the growth rate, you would find a similar sigmoidal curve. So, the sigmoidal curve can be understood in 3 phases, phase one which is called a incubation period where, the growth is slow but, the growth rate is increasing with time.

Of course, the growth rate in this curve is the slope of this curve at any point suppose, I am talking about the growth rate here, I am talking about the slope of this curve here. So, the slope of this curve at any point is my growth rate and this slope initially is increasing, though my overall growth rate is very very slow in the incubation period. Later on, we reach some kind of a steady state regime wherein, what we call the linear growth regime where, the growth return is high but, the slope is approximately constant.

So, if you draw a tangent at this stage, it is approximately constant that means, I have a high growth rate but, it is typically or approximately constant with time. Then, there comes what we call the saturation phase where, the growth rate is decreasing with time and therefore, if I plot the slope at various points so, I take a slope here then, a slope (Refer Slide Time: 13:21) here and a slope here, I would notice that the slope is actually decreasing. And slowly, I would tend to approach my completion of phase transformation wherein, X beta reaches 1.

So, I am starting with X beta equal to 0, which is the start of the phase transformation, in which case of course, I have the incubation period, which I can approximately call this the phase 1 here somewhere here then, I have the phase 2. So, I have phase 1 in this boundary then, I have the phase 2 in this region and of course, I have the phase 3, which is my saturation phase.

So, this also tells you something that suppose, I want a phase transformation alpha to beta and suppose, this phase transformation is sluggish, I can of course, accelerated by using heterogeneous nucleating agents. But, I may typically not want to wait very long because, to get to full beta, the times involved may be prohibited.

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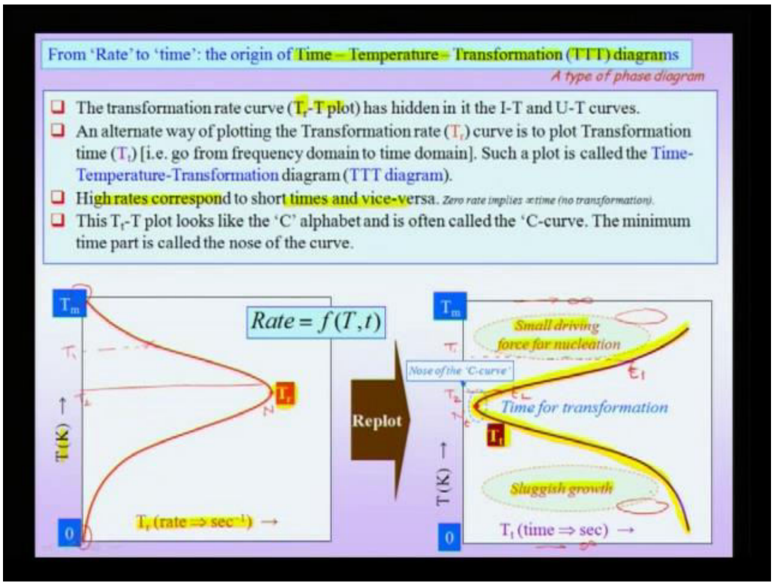

From 'Rate' to 'time': the origin of Time – Temperature – Transformation (TTT) diagrams

A type of phase diagram

- ❑ The transformation rate curve (T_r-T plot) has hidden in it the I-T and U-T curves.
- ❑ An alternate way of plotting the Transformation rate (T_r) curve is to plot Transformation time (T_t) [i.e. go from frequency domain to time domain]. Such a plot is called the Time-Temperature-Transformation diagram (TTT diagram).
- ❑ High rates correspond to short times and vice-versa. *Zero rate implies ∞ time (no transformation).*
- ❑ This T_t-T plot looks like the 'C' alphabet and is often called the 'C-curve. The minimum time part is called the nose of the curve.

$Rate = f(T,t)$

Now, the way we have plotted the transformation rate, we have used rates along the x axis, which is per second and we have plotted as a function of the under cooling or the temperature. Now, in typical scenarios, when suppose for instance, I am actually doing a phase transformation and I want to cause a phase transformation in the certain under cooling, I need to know, how long do I have to wait for this phase transformation to take place.

In other words, it is inconvenient to work with a rate domain on the x axis, I would rather prefer to plot along the x axis, the time which is nothing but, the inverse of the rate. So, I go from a frequency domain, which is in the left hand side for the transformation rate to a time domain, again the same thing the transformation is being plotted not in the frequency domain but in time domain, again the curve representing the transformation time.

Now, such a diagram, which shows the transformation time as a function of the temperature is called a time temperature transformation diagram or in short, known as the TTT diagram. So, TTT diagram is nothing but, just a replot of the transformation rate curve but, locating the time it takes for transformation at each under cooling and therefore, I have the time temperature transformation diagram. So, this simply a replot of the transformation rate curve with temperature.

Now, the plot is can be understood as follows, high rates of transformation correspond to short times for transformation and vice versa. And suppose, I have a transformation rate, which is 0 like for the points, which are close, which is here. So, I have a 0 transformation rate here or a 0 transformation rate at the transformation temperature then this implies, the times here involved are infinite that means, I have to wait infinite time for transformation to take place.

And if I now, have a rate somewhere in between here so, I have a rate here at this under or a temperature t 1. Then, correspondingly I can take it and find out that, how long does it take at this temperature or how much time does it take for transformation to take place at this temperature, I can locate point t 1. Now, if the rate increases like closer to the maxima here and I go to a temperature t 2 then, I find that, my transformation time actually is smaller.

So, t 2 at temperature 2 is smaller than t 1 therefore, at the maximum transformation rate, I have the minimum. So, the maximum transformation suppose, I label as N so now, I can label this N t, which is in the time domain is the minimum time for transformation. Of course therefore, the overall shape of the curve in time domain, the same transformation curve looks like the one, which is shown in the purple color, which is like this. Therefore, I take long times at high under coolings and very small under coolings but, some intermediate under cooling, my transformation time is smaller.

Of course, we have already noted that, this transformation rate function is already a function of the nucleation rate and growth rate. Therefore, the reason it takes very long time for transformation at small under coolings is because, there is small driving force for nucleation. And at very large under coolings, again the transformation time is much larger because, the growth is sluggish. So, I have a nucleation porosity domain here, at the small under coolings and on the other hand, I have a growth sluggish domain at very large under coolings.

So, where both my nucleation rate and growth rate are helping me in the intermediate times, intermediate under coolings then, I have a short time for the transformation. So, to summarize this diagram, I note that, I can plot my transformation rate function in time domain that means, I grow from a frequency domain to a time domain. And in the process, I can generate what is known as a time temperature transformation diagram where, for each under cooling, I find out how much time do I have to wait for the transformation to take place. Again, we have also noted that, at the heart of this transformation time function is also the nucleation time and the growth time. Now, let us spend a little more time trying to understand this TTT diagram, which we have generated.

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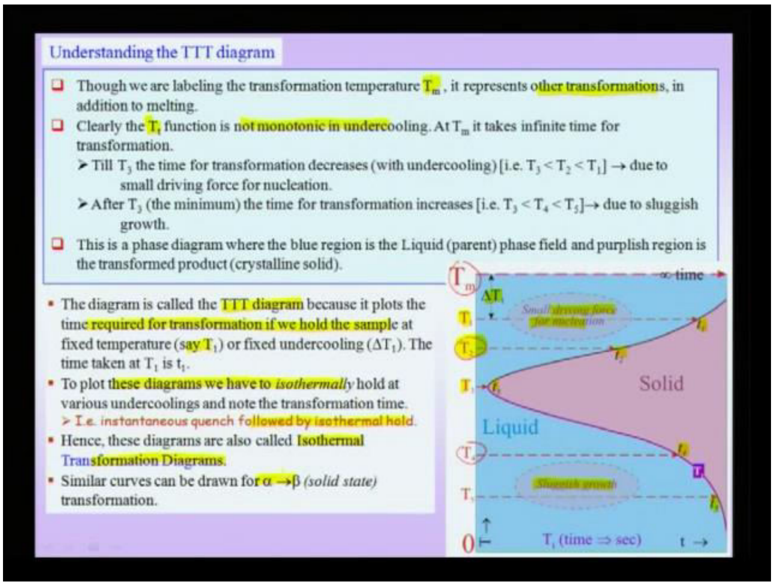

Understanding the TTT diagram

- ☐ Though we are labeling the transformation temperature T_m, it represents other transformations, in addition to melting.
- ☐ Clearly the T_t function is not monotonic in undercooling. At T_m it takes infinite time for transformation.
  - ➢ Till T_3 the time for transformation decreases (with undercooling) [i.e. $T_3 < T_2 < T_1$] → due to small driving force for nucleation.
  - ➢ After T_3 (the minimum) the time for transformation increases [i.e. $T_3 < T_4 < T_5$]→ due to sluggish growth.
- ☐ This is a phase diagram where the blue region is the Liquid (parent) phase field and purplish region is the transformed product (crystalline solid).

- The diagram is called the TTT diagram because it plots the time required for transformation if we hold the sample at fixed temperature (say T_1) or fixed undercooling (ΔT_1). The time taken at T_1 is t_1.
- To plot these diagrams we have to *isothermally* hold at various undercoolings and note the transformation time.
  - ➢ I.e. instantaneous quench followed by isothermal hold.
- Hence, these diagrams are also called Isothermal Transformation Diagrams.
- Similar curves can be drawn for $\alpha \rightarrow \beta$ *(solid state)* transformation.

First thing of course is that, often we have used a solidification as an example and sometimes, we had also used the phase transformation is alpha to beta. But, this general kind of a scenario represents other kind of transformation as well in addition to melting. We also noted that, the transformation time at any under cooling is not monotonic with under cooling.

That implies, that suppose, I take 3 under coolings say, delta T 1 at temperature T 1 or T 2 or T 3 I would notice that, my transformation times t 1, t 2 and t 3 keep on decreasing till I reach the nose of the curve. If I cool down even further then, again my transformation times increase, which is like labeled as t 4 and t 5 and we have noted that, these behaviors can be understood in terms of the small driving force for nucleation or a sluggish growth at large under coolings.

Now, we have also noted, which is needs to be emphasized, is the fact that in the TTT diagram, we plot the time required for transformation, if you hold a sample at a fixed temperature T 1 that means, we are at a fixed under cooling delta T 1. That implies, that to plot these diagrams, we have to isothermally hold samples at various under coolings and this automatically implies that, how do I reach my temperature say for instance T 2, like in this diagram below or a temperature T 4.

The assumption involved is that, I am above my transformation temperature T m, for instance here and I instantaneously quench my sample to whatever a temperature of design like T 2 and then, I isothermally hold. So, at the heart of these TTT diagram is the assumption that, I am instantaneously quenching to T 2 or whatever temperature or whatever under cooling, I am interested in but then, after that I isothermally hold my sample.

So, 2 key words here are, instantaneous quench and isothermal hold and therefore, in this context, TTT diagrams are also called isothermal transformation diagrams. Because, this is important because, later on we would be constructing what are known as CCT diagrams or continuous cooling transformation diagrams, which are closely related to TTT diagrams but, not the same. Now, of course, for each transformation like for instance, the alpha to beta transformation or some other transformation, I need to draw separate TTT diagram to understand the transformation times.

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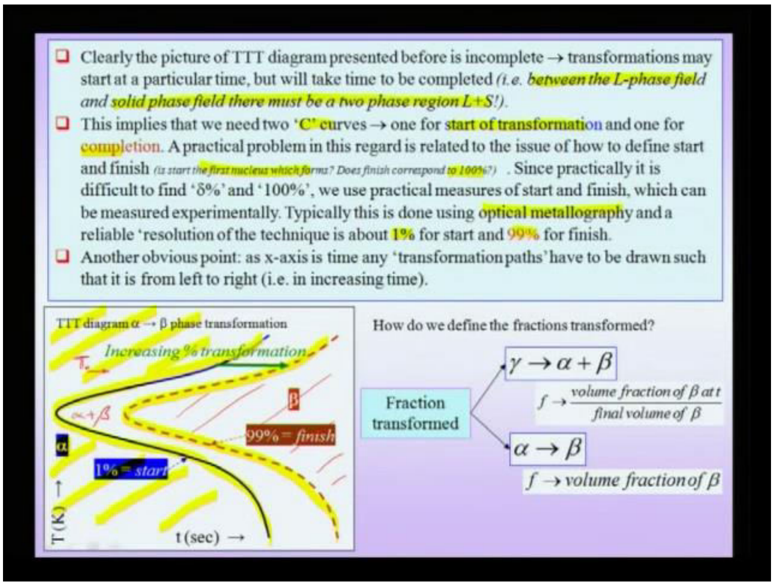

❑ Clearly the picture of TTT diagram presented before is incomplete → transformations may start at a particular time, but will take time to be completed *(i.e. between the L-phase field and solid phase field there must be a two phase region L+S!)*.

❑ This implies that we need two 'C' curves → one for start of transformation and one for completion. A practical problem in this regard is related to the issue of how to define start and finish *(is start the first nucleus which forms? Does finish correspond to 100%?)* . Since practically it is difficult to find 'δ%' and '100%', we use practical measures of start and finish, which can be measured experimentally. Typically this is done using optical metallography and a reliable 'resolution of the technique is about 1% for start and 99% for finish.

❑ Another obvious point: as x-axis is time any 'transformation paths' have to be drawn such that it is from left to right (i.e. in increasing time).

TTT diagram α → β phase transformation

How do we define the fractions transformed?

Fraction transformed

$\gamma \rightarrow \alpha + \beta$

$f \rightarrow \frac{\text{volume fraction of } \beta \text{ at } t}{\text{final volume of } \beta}$

$\alpha \rightarrow \beta$

$f \rightarrow \text{volume fraction of } \beta$

Now, a further point, which is noteworthy is that, the picture of a TTT diagram represented before is incomplete because, transformations as we have pointed out, take time to start. But then, it does not mean, that a transformation is instantaneously complete, it takes certain time to complete the transformation also. Therefore, I actually need 2 lines, one line to designate the start of the transformation as shown in the diagram below with the blue curve, another line which needs to say, that the transformation has been completed.

So, this simplification, as we did before to draw a single curve for transformation like the brown curve here, is only an schematic illustration and in reality, we should have 2 curves, one curve to say that, the transformation has started and one curve to say that, the transformation has being completed. Of course, all this we are doing at a certain under cooling for instance of delta T 1 or at a certain temperature T 1. So, I am isothermally holding at T 1 and noticing that, how long do I have to wait to cause my transformation to take place.

This also make sense because, we already noted while we studied phase diagrams and TTT diagram is a special kind of a phase diagram where, time is involved that, between two single phase regions, I need to have a 2 phase region. Like for instance, in this phase transformation from alpha to beta as shown in the diagram below, the alpha phase is to the left, the whole phase field to the left is an alpha phase field and the whole phase field to the right is my beta phase field.

And between the alpha phase field and the beta phase field, we need to have a 2 phase region, which is now my alpha plus beta. So, I have a two phase field as expected between the alpha phase and the beta phase and suppose, I am talking about a liquid to solid phase transformation, that between the liquid phase field and the solid phase field, there must be a 2 phase field, which is the liquid plus solid phase field. And as we already seen, there are 2 C curves involved, one to start the transformation and one for the completion.

One important issue in this regard is that, how do I define my start or how do I define my finish because, typically if I want to be very very pedantic, the start means, that the very first nucleus which forms and finish should typically correspond to complete 100 percent finish. But, practically locating the first nucleus is very very difficult so, we use and similarly, finding out when exactly the last little volume of alpha finally transforms to beta or the last liquid transforms to solid is very difficult to locate.

So, we use more practical measures, which are accessible by optical metallography techniques or even for instance suppose, I am using x-ray diffractions or x-ray diffraction techniques. But, classically it has been the optical metallography, which is useful in studying TTT diagrams is that, we use a practical measure of start and a practical measure of finish, which typically could be 1 percent and 99 percent. So, when 1 percent of phase transformation is completed, what will I do of course is that, I will do a metallography, which I will show on the board here, that I will take a sample.

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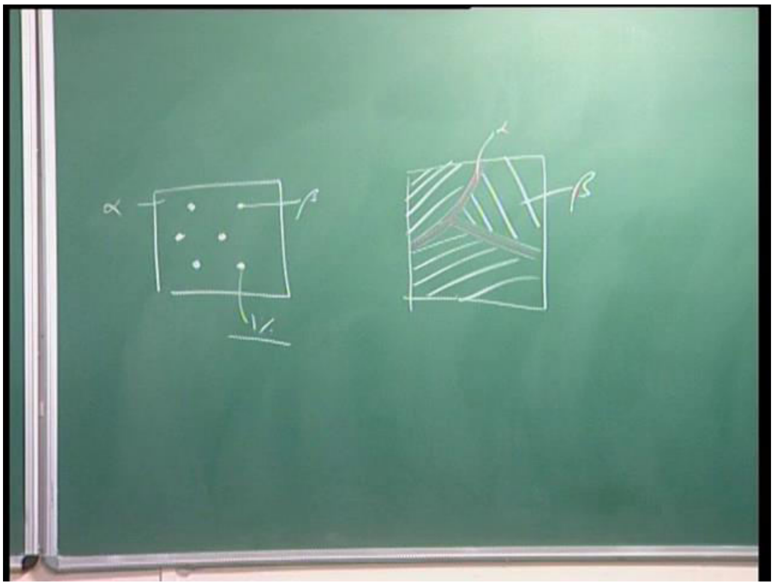

And so, I am starting with pure alpha so, this is my pure alpha, in which I notice that, beta is forming and I would notice that, if 1 area percent which of course, can be equated to volume percent of beta phase forms of course, you may be interested in weight percent then, I will have to convert it. Then, if my 1 percent of beta forms then, I would say the nucleation or the phase transformation is started and when this beta occupies 99 percent of my area for instance, and say a little bit of alpha is left at the boundaries say for instance, this is now my alpha, which is left and this all is beta.

So, most of the alpha phase is been consumed and only a little bit of the alpha phase is remaining then, in that case for instance, this is alpha phase which is remaining here then, I can assume that, my phase transformation is complete. So, I use optical metallography to practically locate the start and the finish, which can be of course, called 1 percent and 99 percent based on convenience. Now, another obvious point of course, is since these are special kind of diagrams involving time, I have to note that any transformation path has to be drawn such that, it is left to right, we cannot draw opposite direction paths on this.

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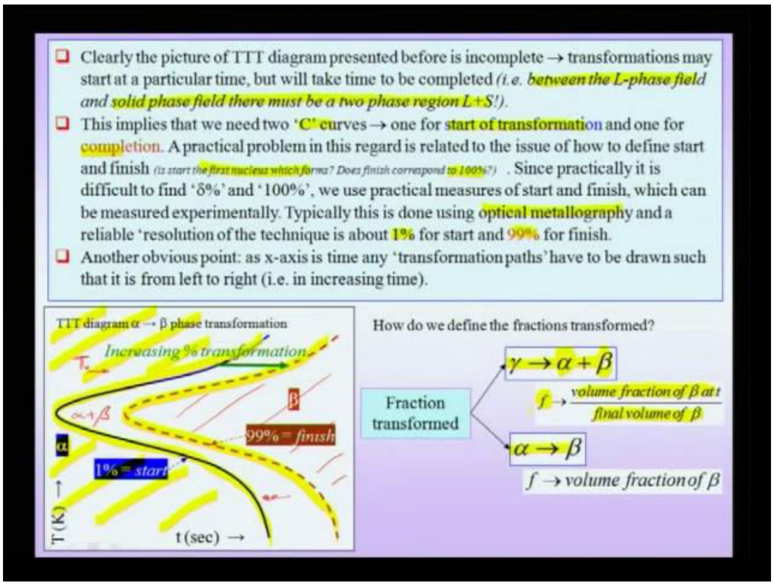

- ☐ Clearly the picture of TTT diagram presented before is incomplete → transformations may start at a particular time, but will take time to be completed *(i.e. between the L-phase field and solid phase field there must be a two phase region L+S!)*.
- ☐ This implies that we need two 'C' curves → one for start of transformation and one for completion. A practical problem in this regard is related to the issue of how to define start and finish *(is start the first nucleus which forms? Does finish correspond to 100%?)* . Since practically it is difficult to find 'δ%' and '100%', we use practical measures of start and finish, which can be measured experimentally. Typically this is done using optical metallography and a reliable 'resolution of the technique is about 1% for start and 99% for finish.
- ☐ Another obvious point: as x-axis is time any 'transformation paths' have to be drawn such that it is from left to right (i.e. in increasing time).

How do we define the fractions transformed?

Fraction transformed

$\gamma \rightarrow \alpha + \beta$

$f \rightarrow \frac{\text{volume fraction of } \beta \text{ at } t}{\text{final volume of } \beta}$

$\alpha \rightarrow \beta$

$f \rightarrow \text{volume fraction of } \beta$

Though it is isothermally of course, even a line going from left right to left is an isothermal line but, such kind of lines are not allowed on this diagrams because, as you know, time is decreasing for such lines. And therefore, only horizontal lines going from left to right can be drawn on such TTT diagrams now further, suppose, I am talking about not an pure alpha to beta transformation but, a gamma phase giving alpha plus beta in such a case, the fraction X beta, I can define as the volume fraction of beta at any temperature divided by the final volume fraction of beta, which I expect.

Because, the final volume fraction of beta in this case is not 100 percent because, there is also an alpha phase, which is present in the final product. That means, I know my final volume fraction of beta, which I need to form because, this is now based on the composition and the phase diagram. And if I note, how much of volume fraction of that, what is expected is forming at a time t then, I take the ratio with respect to, what I expect finally.

Then, I would note that, I have the fraction of beta, which is forming and this is so, Ii can use this function of beta for my calculation of this phase transformation lines. Now, (Refer Slide Time: 27:47) the next topic we will consider of course would be, how do I compute the transformation time for various under coolings. And that will be very important to consider hence, the nucleation rate I, which is d m by d t can be written as a product of the 2 terms in the equation below.

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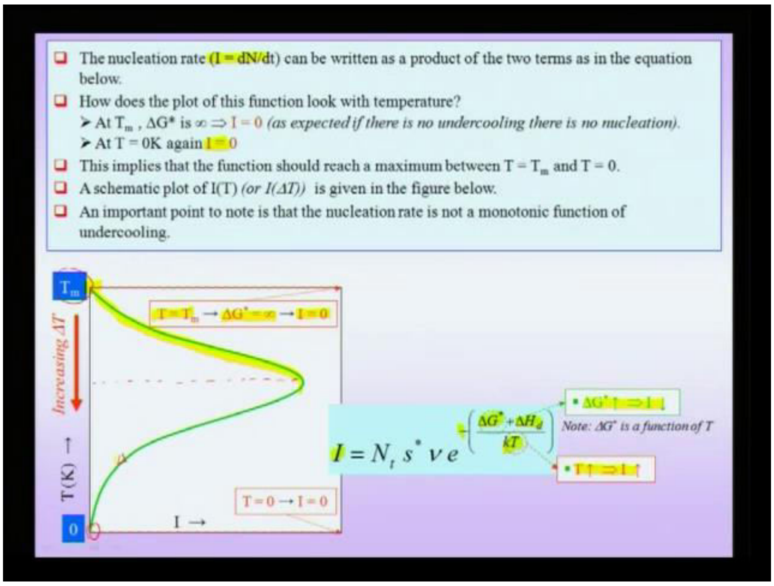

- ☐ The nucleation rate ($I = dN/dt$) can be written as a product of the two terms as in the equation below.
- ☐ How does the plot of this function look with temperature?
  - ➢ At T_m , ΔG^* is $\infty \Rightarrow I = 0$ *(as expected if there is no undercooling there is no nucleation).*
  - ➢ At $T = 0K$ again $I = 0$
- ☐ This implies that the function should reach a maximum between $T = T_m$ and $T = 0$.
- ☐ A schematic plot of $I(T)$ *(or $I(\Delta T)$)* is given in the figure below.
- ☐ An important point to note is that the nucleation rate is not a monotonic function of undercooling.

$$I = N_t\, s^*\, \nu\, e^{-\left(\frac{\Delta G^* + \Delta H_d}{kT}\right)}$$

- $\Delta G^* \uparrow \Rightarrow I \downarrow$
- $T \uparrow \Rightarrow I \uparrow$

Note: ΔG^* is a function of T

So, I finally turns out to be a product of the exponential of delta G star and delta H d with temperature residing in the denominator of course, the negative sign in front of it has to be noted. Now, we have to note, how does the plot of this function look with temperature, this variation will form the basis of, what we will see later is called the TTT diagram.

And therefore, let us see what happens to this function, which is the nucleation rate with temperature. At the transformation temperature we note that, delta G star is infinity that means, that there is no propensity for nucleation and nucleation rate is 0 so, the function is 0 at the transformation temperature. On the other end of the spectrum, is T equal to 0 Kelvin, which is here and when we substitute T equal to 0 Kelvin, we note again that the nucleation rate is 0.

So, substituting T equal to 0 here, gives that the nucleation rate is 0, further we note that, there are 2 competing factors, which come into play in determining the form of this function. One is that, as temperature increases the nucleation rate increases but, as delta G star increases, the nucleation rate decreases. Therefore, in the numerator and denominator, there are 2 competing terms and the final plot of the function look something like this, as shown in the green curve below.

That means, it goes through a maxima at some intermediate temperature below so, there is a maxima here at some intermediate temperature, below the transformation temperature and 0 Kelvin. And after reaching a maxima, again the nucleation rate reduces to 0 at 0 Kelvin. So, we have to note that, this function is not monotonic with temperature or is not monotonic with under cooling.

And this feature, we shall try to understand, that implies that unlike normal processes, in which if you talk about temperature dependence, it normally increases monotonically with temperature. But here, we are talking in effect not just temperature but, under cooling and therefore we note that, the function is not monotonic and goes through a maximum with temperature.

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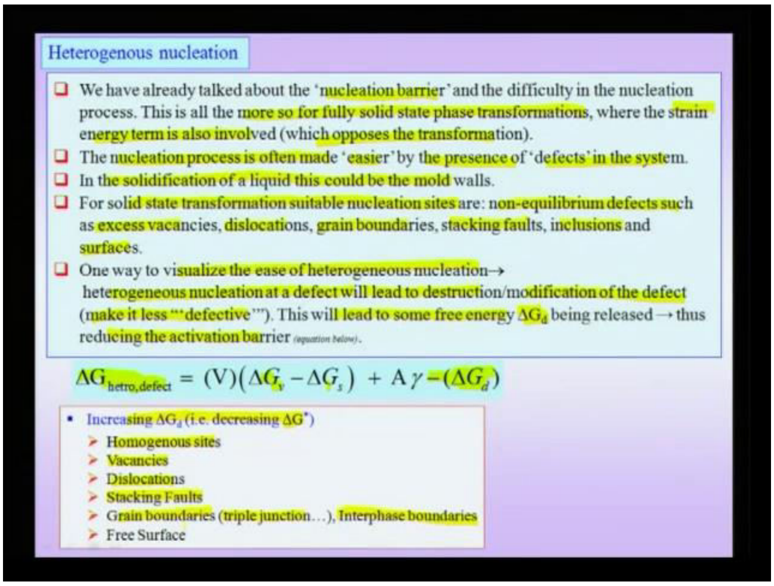

Heterogenous nucleation

- ❑ We have already talked about the 'nucleation barrier' and the difficulty in the nucleation process. This is all the more so for fully solid state phase transformations, where the strain energy term is also involved (which opposes the transformation).
- ❑ The nucleation process is often made 'easier' by the presence of 'defects' in the system.
- ❑ In the solidification of a liquid this could be the mold walls.
- ❑ For solid state transformation suitable nucleation sites are: non-equilibrium defects such as excess vacancies, dislocations, grain boundaries, stacking faults, inclusions and surfaces.
- ❑ One way to visualize the ease of heterogeneous nucleation→ heterogeneous nucleation at a defect will lead to destruction/modification of the defect (make it less "'defective'"). This will lead to some free energy ΔG_d being released → thus reducing the activation barrier (equation below).

$$\Delta G_{\text{hetro,defect}} = (V)(\Delta G_v - \Delta G_s) + A\gamma - (\Delta G_d)$$

- Increasing ΔG_d (i.e. decreasing ΔG^*)
  - Homogenous sites
  - Vacancies
  - Dislocations
  - Stacking Faults
  - Grain boundaries (triple junction…), Interphase boundaries
  - Free Surface

Next, we take up the topic of not homogeneous nucleation but, heterogeneous nucleation in this context, let me go back to the experiment which I had conducted, in which we had taken an aerated drink. We had opened the bottle of the aerated drink and then, poured the aerated drink into a glass we had noted that, when I do this there are bubbles forming typically at the glass walls. Further I showed that, if we put salt into this aerated drink then, lot of bubble evolution takes place.

The first question of course, we have to ask is that, when I am opening the coca cola bottle why is that, that all the gas does not escape because, the gas was put into this solution or put into the aerated drink at a higher pressure. And therefore, when I open the bottle, all the gas bubbles does not escape and we understood that, in terms of the term known as the nucleation barrier and we had even gain more than one perspective of the nucleation barrier.

In the of course, in the context of solidification, the relevant thermodynamic variable is temperature, under we are under cooling the system. But, in the context of this aerated drink, we are actually under pressurizing the system, when we open the coca cola bottle or the aerated drink bottle. So, what is happening, we under pressure of the system but, because of the nucleation barrier, even this though the solution is super saturated with respect to carbon dioxide or the atmospheric pressure, all the carbon dioxide cannot escape because of the nucleation barrier.

But, when I add this salt, I find that lot of these bubbles are evolved, this is typically a case of heterogeneous nucleation. That means, some selective regions are there in this case, of course the salt, which we had put into the solution wherein, gas bubbles can preferentially form. And this aspect of nucleation, is even more so or the problem with nucleation or the nucleation barrier is even more severe in the case of solid state solid state transformations wherein, strain energy term is also involved, which opposes the transformation.

Now, the nucleation process is made easier by the presence of defects in the system like of course, in the solution the defect is the salt and in the case of solidification therefore liquid, this could be the mold walls or certain other particles, which you may add intentionally. For a solid state transformation, suitable nucleation sites are non equilibrium defects such as excess vacancies, dislocations, grain boundaries, stacking faults, inclusions and surfaces.

Free surface also can play an important role in nucleation and whenever these secondary entities are involved in nucleation, we call them that means, there are preferential sites and this case is referred to as heterogeneous nucleation. And one way to visualize heterogeneous nucleation is to understand that, in heterogeneous nucleation at a defect will lead to destruction or modification of the defect. That means, that the defect will be made less defective and this will give us some free energy benefit, which I can call delta H d and thus, reducing the activation barrier.

So therefore, suppose I can write down my delta G heterogeneous at a defect, as in the equation here then of course, we have the usual term, which is the delta G v and delta G s. But, additionally we have here a minus delta G d term, which is now of course, helping us in the nucleation process. Therefore, we can understand heterogeneous nucleation as, when the nucleation takes place, the defectiveness of a defect in some ways modified or reduced and this helps us in easy nucleation at these secondary entities.

Now, the increasing delta H d, which also means that there is a decreasing delta H G star heterogeneous or of course, homogenous sites of course the simple case, which we have seen excess vacancies, further more dislocations, lot of work has been done on heterogeneous nucleation on dislocations. Then of course, there can be stacking faults, there can be interfaces like grain boundaries and special entities within grain boundaries, which are like triple lines, interface boundaries and finally of course, the free surface. Therefore, we can have all these entities in solid state phase transformations, which can play an important role in heterogeneous nucleation.

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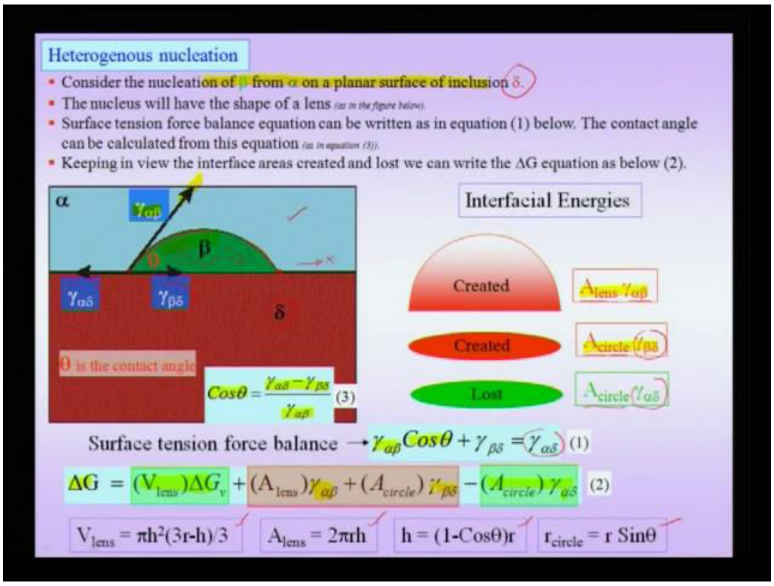

Heterogenous nucleation

- Consider the nucleation of β from α on a planar surface of inclusion δ.
- The nucleus will have the shape of a lens (as in the figure below).
- Surface tension force balance equation can be written as in equation (1) below. The contact angle can be calculated from this equation (as in equation (3)).
- Keeping in view the interface areas created and lost we can write the ΔG equation as below (2).

Interfacial Energies

θ is the contact angle

$Cos\theta = \frac{\gamma_{\alpha\delta} - \gamma_{\beta\delta}}{\gamma_{\alpha\beta}}$ (3)

Surface tension force balance $\rightarrow \gamma_{\alpha\beta} Cos\theta + \gamma_{\beta\delta} = \gamma_{\alpha\delta}$ (1)

$\Delta G = (V_{lens})\Delta G_v + (A_{lens})\gamma_{\alpha\beta} + (A_{circle})\gamma_{\beta\delta} - (A_{circle})\gamma_{\alpha\delta}$ (2)

$V_{lens} = \pi h^2(3r-h)/3$

$A_{lens} = 2\pi rh$

$h = (1-Cos\theta)r$

$r_{circle} = r\,Sin\theta$

Now, to understand heterogeneous nucleation, let us see again like in the case of homogenous nucleations, what are the energies involved, what are the relevant geometrical parameters involved. We will go through this briefly just to understand that, how heterogeneous nucleation can give us a benefit, more details the students can refer to standard text books.

Now, let us assume that, nucleation of beta is taking place with alpha that means, I have a beta phase, which is marked here and I should share the beta phase here. The beta phase shown in green, this beta phase is coming out from an alpha phase, which is the parent phase. Now, I add a heterogeneous nucleating agent, which is the delta phase, which is suppose to aid us in this nucleation process. When the nucleus forms, it forms in the form of a lens, as shown in the diagram that means, that it is typically taking a particular shape, the shape of a lens.

Now, once this lens is formed, I can write down my surface tension balance equation like as shown here. That gamma alpha beta, which is now my interfacial energy between the alpha phase and the beta phase into cos theta, which I have resolved this vector term, gamma alpha beta term along this direction and do an force balance along the x direction, the x direction being the direction here.

And therefore, I can write down gamma alpha beta cos theta plus gamma beta delta, which is the second force acting in the same direction, which is being opposed of course, or in the opposite direction is gamma alpha delta. So, therefore, I have an equation, that gamma alpha beta cos theta plus gamma beta delta is equal to gamma alpha delta. From this, I can find out the contact angle cos theta where, the cosine or the contact angle to be gamma alpha delta minus gamma beta delta by gamma alpha beta.

Now, in the process of this nucleation, what are the interfacial energies involved, one interface which is destroyed, is a interface originally present between my alpha phase and the delta phase, which extends from here to here, and which has the shape of a lens. So, this interfacial energy is of recovered and therefore, if gamma alpha delta scale by the area of that circle, gives us a benefit.

On the other hand, 2 new interfaces are created, a beta delta interface and an alpha beta interface so, both these interfacial energies add on to the delta G term. And therefore, the beta delta interface again is in the form of a circle and I can multiply that by the gamma beta delta term, to find out the interfacial energy, which needs to be supplied by the reduction in the volume free energy of the nucleation. Then the other interface, the beta alpha interface is in the form of a lens in three dimensions, of course and therefore, I can write down that as, an area of lens multiplied by gamma alpha beta.

The various areas can be written down as shown in the equations at the bottom of this slide but at this stage, we will not worry too much about the actual form of these equations. But, we will worry about the overall concepts involved in this heterogeneous nucleation and how, we can engineer an heterogeneous nucleating agent such that, I can have an easy heterogeneous nucleation.

So, number 1 what I do, I will identify that certain interfaces are created, one interface is lost then, I can do a force balance based on the surface tensions, interfacial tensions and I can use a contact angle, find the contact angle from those interface tension balance equation. Now, the technology for this nucleation process is consisting of 2 positive terms or 2 terms, which give introduction to delta G v, which are marked in green. One is the area of the circle into alpha beta delta, other is the volume term, which is actually helping with the nucleation.

The two red areas, which I marked above, they multiply with the respective interfacial energies that means, a lens into a gamma alpha beta and a circle into gamma beta delta, which tend to oppose this process. Therefore, I can now write based on of course, simplifying all the, putting in all these area terms.

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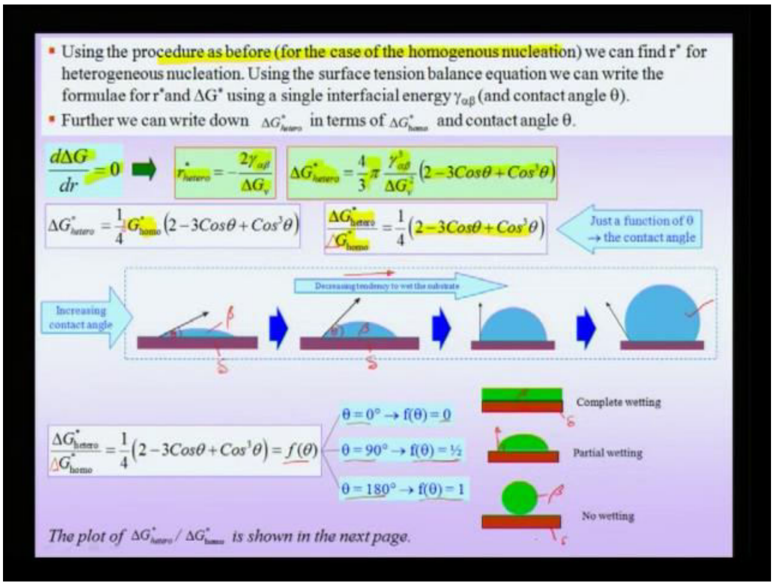

- Using the procedure as before (for the case of the homogenous nucleation) we can find r^* for heterogeneous nucleation. Using the surface tension balance equation we can write the formulae for r^* and ΔG^* using a single interfacial energy $\gamma_{\alpha\beta}$ (and contact angle θ).
- Further we can write down ΔG^*_{hetero} in terms of ΔG^*_{homo} and contact angle θ.

$$\frac{d\Delta G}{dr} = 0 \Rightarrow r^*_{hetero} = -\frac{2\gamma_{\alpha\beta}}{\Delta G_v} \qquad \Delta G^*_{hetero} = \frac{4}{3}\pi\frac{\gamma^3_{\alpha\beta}}{\Delta G^2_v}(2 - 3Cos\theta + Cos^3\theta)$$

$$\Delta G^*_{hetero} = \frac{1}{4}G^*_{homo}(2 - 3Cos\theta + Cos^3\theta) \qquad \frac{\Delta G^*_{hetero}}{\Delta G^*_{homo}} = \frac{1}{4}(2 - 3Cos\theta + Cos^3\theta)$$

Just a function of θ → the contact angle

$$\frac{\Delta G^*_{hetero}}{\Delta G^*_{homo}} = \frac{1}{4}(2 - 3Cos\theta + Cos^3\theta) = f(\theta)$$

$\theta = 0° \rightarrow f(\theta) = 0$

$\theta = 90° \rightarrow f(\theta) = ½$

$\theta = 180° \rightarrow f(\theta) = 1$

The plot of $\Delta G^*_{hetero} / \Delta G^*_{homo}$ is shown in the next page.

And then, simplifying all the terms, I can write and find out as before, the criteria for the extremum in this case. Of course, we know that, when in the case of heterogeneous nucleation the critical criteria, the maximum is found by writing d delta G by d r equal to 0. From that, I can find out the heterogeneous nucleation r star and the delta G star, and I find that, r star is equal to minus 2 gamma alpha beta by delta G v. And delta G star heterogeneous is 4 by 3 pi gamma alpha beta cube by delta G v square into a term involving cosines of the contact angle.

We have noted that, this procedure is very very similar to the case of homogeneous nucleation and we just find the extremum of this or the maximum of this function. And the important thing of course is that, when you note these functions like r star heterogeneous, we find that there is only one interfacial energy, which is coming out of these equations. The reason is that, we have used the force balance equations to eliminate the other equations and we are writing now, in terms of one interfacial energy and one contact angle or more to be more precise, one cosine of the contact angle.

Now further, what we can do, we can write down this delta G star heterogeneous not in terms of the interfacial energies but in terms of, the delta G star homogeneous. That means, now I can relatively compare, what is delta G star heterogeneous by delta G star homogeneous, in which case I can find out, what is the benefit of having an heterogeneous nucleation. Of course, this term in the bottom is an heterogeneous, this delta is the homogeneous nucleation and this delta G star is my homogeneous nucleation.

So, we note that, delta G star by delta G star homo, hetero by homo is one forth of 2 minus 3 cos theta by cos cube theta that implies, this is just a function of theta, the contact angle. And let us see some schematics of, what happens when the contact angle increases now, this is of course my delta phase, on which my nucleation is taking place and this is my phase product phase, which is beta. So, this is my nucleating agent delta and the above one is my product phase.

And I am noting that, I am going slowly increasing in terms of the contact angle theta, this is my contact angle theta, which is increasing from left to right. So, these are schematics to get give you a feel, of how the contact angle, what happens to the shape of the nucleus or the shape of the lens, when the contact angle increases. For small contact angles, it is looks like a thin lens and it gets thicker lens then, it becomes like almost like a semi circle.

And then finally, it looks like a droplet typically, you would observe like for instance, a water droplet on a non-wetting surface like for instance, glass or a lotus leaf. Now, this function delta G star heterogeneous by delta G star homogeneous, which is now a function of theta, becomes 0 for theta equal to 0. For theta equal to 90 degrees, this function is half and theta equal to 180 degrees, this function is 1. Now, what is theta equal to 0 means, that the beta phase is completely wetting my delta phase, which is here.

The theta equal to 0 case means, that this complete wetting and which means, that there is no barrier to nucleation. Suppose, I have a partial wetting case, which is means that theta is somewhere between 0 and 180 degrees, and one of those cases is the 90 degree case that is, my 90 degree case. And for this, f of theta turns out to be half now, for theta equal to 180 degrees, it is as if the droplet is completely beaded in the form of a sphere on the…

So, this is my beta phase, which is nucleating on the delta phase, which is completely beta which means that, there is no wetting and f of theta becomes 1.

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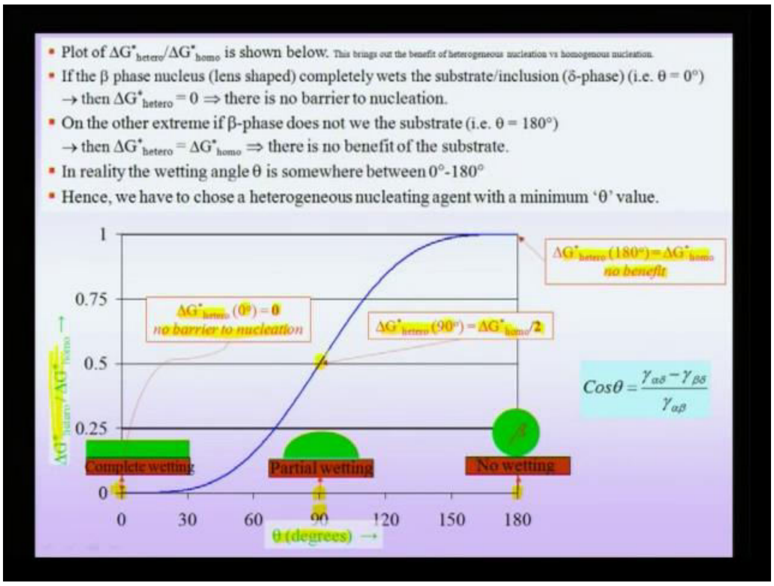

- Plot of $\Delta G^*_{hetero}/\Delta G^*_{homo}$ is shown below. This brings out the benefit of heterogeneous nucleation vs homogenous nucleation.
- If the β phase nucleus (lens shaped) completely wets the substrate/inclusion (δ-phase) (i.e. θ = 0°) → then $\Delta G^*_{hetero} = 0 \Rightarrow$ there is no barrier to nucleation.
- On the other extreme if β-phase does not we the substrate (i.e. θ = 180°) → then $\Delta G^*_{hetero} = \Delta G^*_{homo} \Rightarrow$ there is no benefit of the substrate.
- In reality the wetting angle θ is somewhere between 0°-180°
- Hence, we have to chose a heterogeneous nucleating agent with a minimum 'θ' value.

The important thing I need to track is, this delta G star heterogeneous by delta G star homogenous, which is shown here in this plot, as a function of the contact angle. Now, we have seen there are 3 cases we have considered in the previous equation, theta equal to 0 case which is here, theta equal to 90 degrees case and the theta equal to 180 degrees case. Now, when theta equal to 0 we have noted that, f of theta equal to 0 and that means, that delta G star heterogeneous at 0 degrees is 0 which means that, there is no barrier to nucleation that means, nucleation can take place readily.

Of course in reality, you never have 0 degrees or 180 degrees contact angle, you have something in between and let us see a example of 90 degrees where, there is partial wetting. In this case, delta G star heterogeneous at 90 degrees is delta G star homogeneous by 2 because, this f of theta we calculated, was half here in this previous slide. This f of theta of course, is a function of the cosines of the contact angle that means that, by heterogeneous nucleation I get a benefit of factor of 2.

Now suppose, on the other hand suppose, the product phase beta does not wet the second phase added or the heterogeneous nucleating agent, which I shown in red color. Then what happens is that, delta G star homogeneous turns out to be equal to delta G star heterogeneous which means that, there is no benefit as expected. Because now, the product phase does not interact with the heterogeneous nucleating agent and therefore, there is no benefit.

So, there are 3 cases, one where there is complete wetting in which case there is no barrier to nucleation, one case the other extreme where, the product phase does not wet the substrate in which case there is no benefit of adding the heterogeneous nucleating agent but, anywhere in between we get a certain benefit from heterogeneous nucleation. And this benefit for instance, for a case of 90 degree wetting angle is about half that means, that by adding a heterogeneous nucleating agent, I get some kind of a benefit, by in terms of the nucleation. And the I can reduce my nucleation barrier appropriately by adding a heterogeneous nucleating agent.

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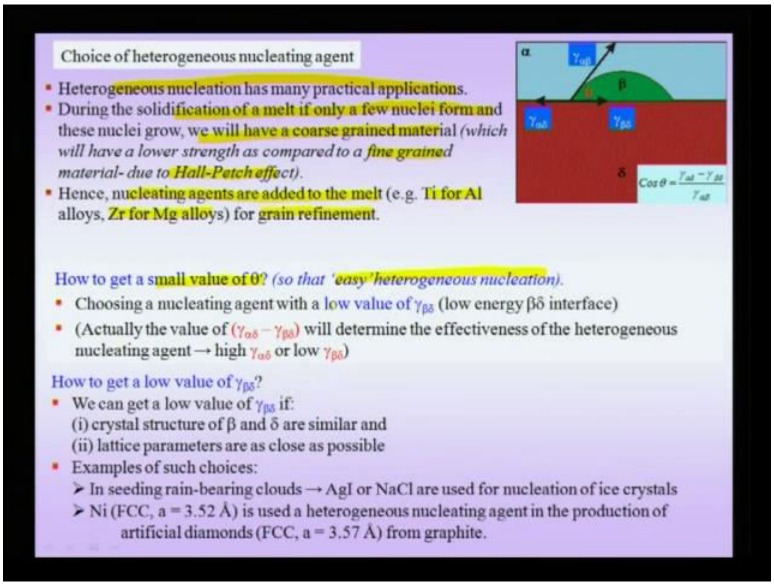

$Cos\,\theta = \frac{\gamma_{\alpha\delta} - \gamma_{\beta\delta}}{\gamma_{\alpha\beta}}$

Choice of heterogeneous nucleating agent

- Heterogeneous nucleation has many practical applications.
- During the solidification of a melt if only a few nuclei form and these nuclei grow, we will have a coarse grained material *(which will have a lower strength as compared to a fine grained material- due to Hall-Petch effect).*
- Hence, nucleating agents are added to the melt (e.g. Ti for Al alloys, Zr for Mg alloys) for grain refinement.

How to get a small value of θ? *(so that 'easy' heterogeneous nucleation).*

- Choosing a nucleating agent with a low value of $\gamma_{\beta\delta}$ (low energy βδ interface)
- (Actually the value of $(\gamma_{\alpha\delta} - \gamma_{\beta\delta})$ will determine the effectiveness of the heterogeneous nucleating agent → high $\gamma_{\alpha\delta}$ or low $\gamma_{\beta\delta}$)

How to get a low value of $\gamma_{\beta\delta}$?

- We can get a low value of $\gamma_{\beta\delta}$ if:
  (i) crystal structure of β and δ are similar and
  (ii) lattice parameters are as close as possible
- Examples of such choices:
  - In seeding rain-bearing clouds → AgI or NaCl are used for nucleation of ice crystals
  - Ni (FCC, a = 3.52 Å) is used a heterogeneous nucleating agent in the production of artificial diamonds (FCC, a = 3.57 Å) from graphite.

Now, what kind of an heterogeneous nucleating agent would I choose so that, I get a maximum benefit. Now, why we need to consider this heterogeneous nucleation is because, heterogeneous nucleation has many practical applications. During solidification of a melt, if only a few nuclei form that means, you have under cooled a melt and you are holding it and only a few nuclei form, and these nuclei grow then, we will have a coarse gain material.

Such a coarse gain material will have lower strength as compared to a fine grain material due to the hall-petch effect. We know that, the yield strength depends on the grain size via the hall-petch relation, as 1 by d power half. Therefore, I would prefer a fine grain material to get a higher strength and this is not happening, if I have only a few nuclei nucleation sites, which grow on to give you a large grain size material.

So typically, what happens is that, we want to add some nucleating agent to the melt like for instance, titanium is added into aluminum or zirconium for magnesium alloys, for grain refinement so that, I can get a fine grain product, which is stronger. Now, what kind of a nuclei, what criteria would I use to choose a nucleating agent so that, I can have easy heterogeneous nucleation.

And this implies, I want to have a nucleating agent, which has a small value of theta that means, the products phase tends to wet the nucleating agent more. And for choosing this, we need to have a low value of gamma beta delta.

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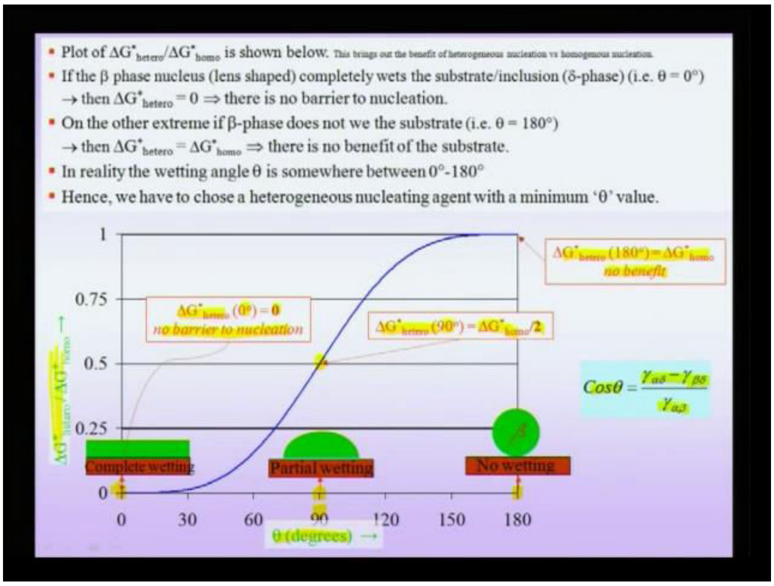

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- In reality the wetting angle θ is somewhere between 0°-180°
- Hence, we have to chose a heterogeneous nucleating agent with a minimum 'θ' value.

$$Cos\theta = \frac{\gamma_{\alpha\delta} - \gamma_{\beta\delta}}{\gamma_{\alpha\beta}}$$

So, if you look at the cos theta function written here, you know that cos theta is gamma alpha delta minus gamma beta delta by gamma alpha beta. Now, the gamma alpha beta energy cannot be changed because, that is basically the energy, which is natural to the product when it comes out from the parent phase, alpha beta and we have no control over that. What we have control over, are the 2 interfacial energies or perhaps, what we would like to control are the 2 interfacial energies involving the delta phase, which is the gamma beta delta and the gamma alpha delta terms.

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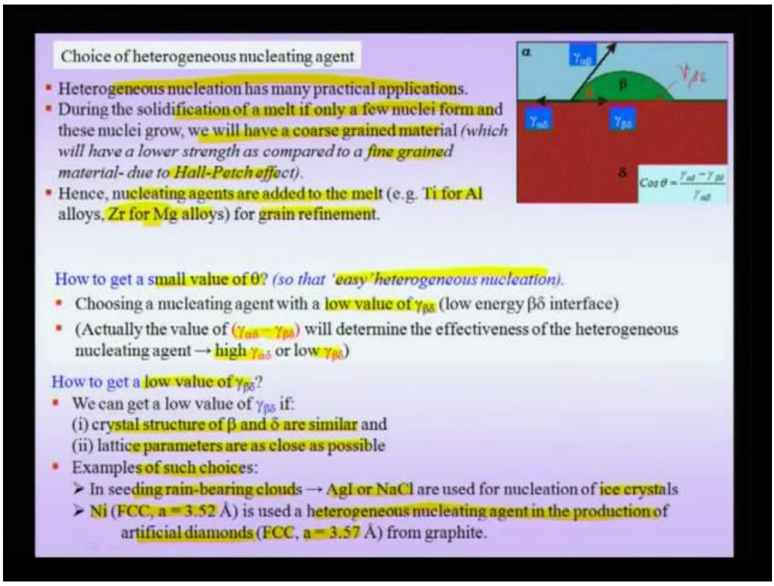

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$$Cos\theta = \frac{\gamma_{\alpha\delta} - \gamma_{\beta\delta}}{\gamma_{\alpha\beta}}$$

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- Choosing a nucleating agent with a low value of $\gamma_{\beta\delta}$ (low energy $\beta\delta$ interface)
- (Actually the value of ($\gamma_{\alpha\delta} - \gamma_{\beta\delta}$) will determine the effectiveness of the heterogeneous nucleating agent $\rightarrow$ high $\gamma_{\alpha\delta}$ or low $\gamma_{\beta\delta}$)

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- Examples of such choices:
  - In seeding rain-bearing clouds $\rightarrow$ AgI or NaCl are used for nucleation of ice crystals
  - Ni (FCC, a = 3.52 Å) is used a heterogeneous nucleating agent in the production of artificial diamonds (FCC, a = 3.57 Å) from graphite.

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So now, I would like to choose a low gamma beta delta so that, I can get a small value of theta that means, the product phase wets the nucleating agent more. Actually speaking, since it is not the gamma beta delta, which sits on the numerator we note here, it is actually the difference between gamma alpha delta and gamma beta delta, which sits on the interface. This implies that, if I want an actually a good heterogeneous nucleation then, I would typically want the value of gamma alpha delta minus gamma beta delta to be low or high which implies that, I would like an high alpha delta and a low beta delta.

But typically, we do not work with this difference but we say that, a low value of gamma beta delta is good enough, as a measure of the nucleation property. Now, how do I go about and getting a low value of gamma beta delta, which is now the interfacial energy between the, this is now the interface we are talking about, which is in the form of a circle, which is the gamma beta delta.

So, this energy we want to have low value and we can have a low value, if the crystal structure of beta and delta similar and lattice parameters are as close to each other as possible. So, the 2 criteria, which are commonly used for reducing the gamma beta delta interfacial energy, one is that we try to choose a nucleating agent such that, the beta and delta are similar in crystal structures and have a lattice parameter, which is very close.

Like in the example of zirconium and magnesium, both of them have an HCP structure, which helps us in the heterogeneous nucleation. If however, we have do not have the same crystal structure, still we may get lower interfacial energy if say, there is a certain plane, along which you have a atomic spacing matching like for instance, the 1 1 1plane in an FCC could match with an 0 0 0 1 plane of an HCP.

Examples of such heterogeneous nucleating agents, which are typically used in some important applications are in seeding of rain bearing clouds. So, in certain circumstances, what might happen is that, there is moisture in the atmosphere but, this moisture is non precipitating in the form of a rain because of, what you might say as the nucleation barrier. So, we can actually seed clouds that means, what we are doing is that, we are adding heterogeneous nucleation agent to the atmosphere and this will help in heterogeneous nucleation of water droplets.

And some of these water droplets of course, at higher atmospheres could be frozen and then of course, when they fall down in the form of a rain. So, for the silver iodide or sodium chloride are added as heterogeneous nucleation agents for ice crystals. And of course as I pointed out, we have to consider ice crystals because, in an upper atmosphere the temperatures are so low that, water is in the form of ice and we would like to nucleate ice on these heterogeneous nucleating agents.

So typically, what they do is that, they take planes and take these nucleating agents and seed the clouds at higher atmosphere where, clouds can form. The other nice example is the use of nickel as an heterogeneous nucleating agent in the production of artificial diamonds. Now, we know that, diamonds are nothing but, graphite but, we need to put high pressure in temperature on to graphite to form diamond.

But, this phase transformation can be what are accelerated or made faster by using a nucleating agent and nickel, which is an FCC structure and lattice parameter 3.52 angstrom, which is very close to that of a diamond. Diamond is also as we know an FCC lattice and the lattice parameters 3.57 angstrom therefore, if I want to form diamond from graphite, what I can do is that, I can use a nickel. And of course, I will have to use the appropriate thermodynamic conditions like pressure and temperature to form diamond from graphite.

Therefore, we have seen in this example that, we have a certain benefit of having a heterogeneous nucleating agent in case we want to accelerate the phase transformation or we want to produce for instance, a fine grain material then, there is a need for using heterogeneous nucleating agent. And most often actually, we cannot avoid heterogeneous nucleation like we saw in the case as suppose, I take an aluminum and pour it into a mold then, even though homogeneous nucleation of aluminum crystals can take place within the melt.

But, more often than not we notice that, the nucleation or the solidification starts from the mold walls and this kind of a solidification actually, may give us certain kind of you know columnar growth or a large grain size with certain kind of a properties, which may be undesirable. Therefore, what we do is that, we apart from this heterogeneous nucleation in the mold walls, we would like to add heterogeneous nucleating agent within the melt, which can now give us a fine grain material. Therefore, we have seen that, nucleation is an important step in phase transformation.

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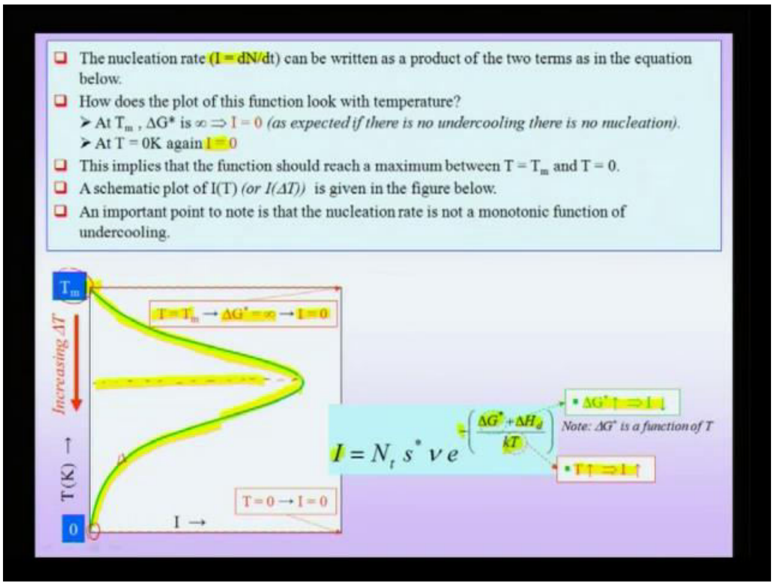

- ☐ The nucleation rate (I = dN/dt) can be written as a product of the two terms as in the equation below.
- ☐ How does the plot of this function look with temperature?
  - ➢ At T_m , ΔG^* is $\infty \Rightarrow I = 0$ *(as expected if there is no undercooling there is no nucleation).*
  - ➢ At T = 0K again I = 0
- ☐ This implies that the function should reach a maximum between $T = T_m$ and $T = 0$.
- ☐ A schematic plot of I(T) *(or I(ΔT))* is given in the figure below.
- ☐ An important point to note is that the nucleation rate is not a monotonic function of undercooling.

$$I = N_t\, s^*\, \nu\, e^{-\left(\frac{\Delta G^* + \Delta H_d}{kT}\right)}$$

There are 2 kinds of nucleation, one is a homogeneous nucleation wherein, there are preferred sites, other is heterogeneous nucleation where, there are certain preferred sites. And more so, this heterogeneous nucleation plays an important role in solid to solid phase transformations wherein, the strain energy term tends to oppose the phase transformation.

The second important thing we have noted so far, is the form of the function of nucleation rate with temperature we notice that, it is not a monotonic function, it follows the green curve as shown, as we saw before. That means, that there is the maximum of the nucleation rate is somewhere at some under cooling and, above and below this under cooling typically, the nucleation rate falls off.

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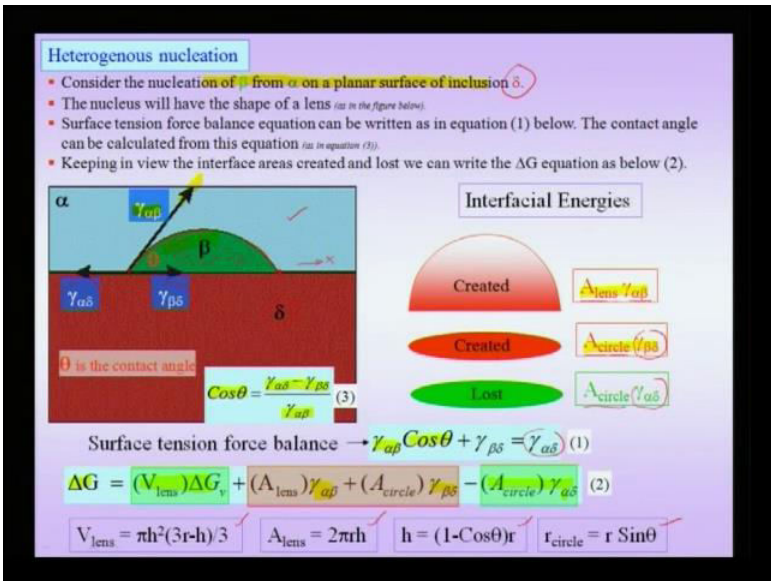

Heterogenous nucleation

- Consider the nucleation of β from α on a planar surface of inclusion δ.
- The nucleus will have the shape of a lens (as in the figure below).
- Surface tension force balance equation can be written as in equation (1) below. The contact angle can be calculated from this equation (as in equation (3)).
- Keeping in view the interface areas created and lost we can write the ΔG equation as below (2).

$$Cos\theta = \frac{\gamma_{\alpha\delta} - \gamma_{\beta\delta}}{\gamma_{\alpha\beta}} \quad (3)$$

$A_{lens}\gamma_{\alpha\beta}$

$A_{circle}\gamma_{\beta\delta}$

$A_{circle}\gamma_{\alpha\delta}$

Surface tension force balance $\rightarrow \gamma_{\alpha\beta} Cos\theta + \gamma_{\beta\delta} = \gamma_{\alpha\delta}$ (1)

$$\Delta G = (V_{lens})\Delta G_v + (A_{lens})\gamma_{\alpha\beta} + (A_{circle})\gamma_{\beta\delta} - (A_{circle})\gamma_{\alpha\delta} \quad (2)$$

$V_{lens} = \pi h^2(3r-h)/3$ $A_{lens} = 2\pi rh$ $h = (1-Cos\theta)r$ $r_{circle} = r\,Sin\theta$

Now, we are left with one more step in this to understand phase transformation, which is the growth rate. So that, we can now understand transformations, which involve nucleation and growth.