Welding Metallurgy

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Lecture – 06
Phase Transformations

Welcome to the lecture on phase transformations, so phase transformation is an important phenomena and we must know the basic principles which are involved during the phase transformation. So as we know that there will be phase changes even in case of welding where we call of normally about fusion welding processes. So there also there is a phenomena of phase change.

So you will have if you are trying to you know join two pieces so initially they are in solid state solid phase. Then once you heat them I mean a certain zone is heated then that you know converts to liquid phase and further as there is change in temperature drop in temperature after being exposed to surroundings. Then there will be further transformation from liquid phase to solid phase.

Now we all know that this is all governed by certain principles why certain material is in solid state or in liquid state at any temperature this is all the governed by you know the free energy concepts. And how there will be phase transfer what will be the mechanism of phase transformation with what you know way the phase transforms. So we will have certain discussions in this lecture about those points.

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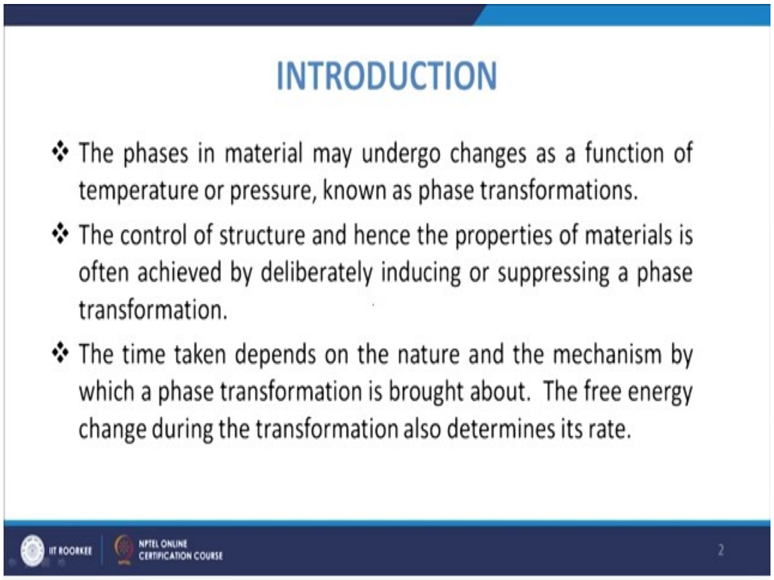

INTRODUCTION

- ❖ The phases in material may undergo changes as a function of temperature or pressure, known as phase transformations.
- ❖ The control of structure and hence the properties of materials is often achieved by deliberately inducing or suppressing a phase transformation.
- ❖ The time taken depends on the nature and the mechanism by which a phase transformation is brought about. The free energy change during the transformation also determines its rate.

So coming to the introduction about that so as we know that the phases in the material that may undergo changes as a function of temperature or pressure. So the change of that phase normally what the material is undergoing that will be known as the phase transformation. And the control of structure and hence the properties of material is often achieved by deliberately inducing or suppressing the phase transformation.

So as we know that when there will be liquid to solid suppose state transformation. Now in that case we will have the light later on in this lecture that often occurs by the process of nucleation and growth. So and basically that is what we call it, so the end result will be having certain structure and at microlevel that is known as microstructure. So now this type of microstructure which is achieved or you know the properties which are the result of the type of microstructure you get.

So that is basically you know achieved by deliberately inducing or suppressing the phase transformation. So phase transformation if you allow it to happen in normal manner then the structure may be something and then if you try to alter it you alter the rate of phase transformation, speed of transformation then the you know structure will be different and associated properties will be different.

So that is how so the time taken that will be depending upon the nature and the mechanism by which a phase transformation is brought about. So by what mechanism that phase transformation is brought about and the free energy change during the transformation also determines its rate. So basically we should know that the you know the free energy change which occurs that basically will be determining the rate of phase transformation.

So we might have the understanding about you know the free energies you know because at any you know temperature or so at you know any material is in solid state or in liquid state so that basically is governed by the free energy value. So if you talk about say free energy so what we might have this idea that if you talk about you know liquid to solid you know transformation liquid.

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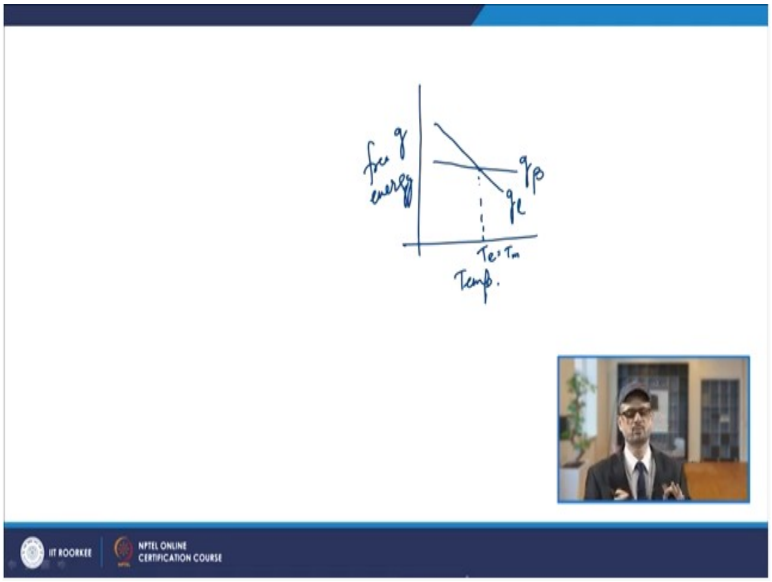

If the liquid is converting to crystal phase suppose β crystal is being I mean being formed. So we can see that you know if this is your free energy and so this is you know g and if you take this as temperature. So any material if it is in any phase of state at any temperature it is all governed by the you know phase free energy values. So the free energy values go like this you know this is your equilibrium temperature or you can have the so that is normally the melting temperature.

Now if you do know that so this is after a melting temperature so this is basically the free energy for the liquid phase and this is free energy for the solid phase suppose solid crystal is β. So in that case you are below the equilibrium temperature you see that this line is for the free energy of the solid phase β. So below the this equilibrium temperature this free energy value of β that is solid form is less so material exists in solid state.

And once you increase the temperature after this equilibrium temperature or melting temperature so in that case you know the liquid state or liquid phase has the higher you know lower free energy value. So it comes into liquid states that is how the material exists either in the form of liquid or solid phase and you know now we can say that whenever any transformation has to occur you know so what is being said so if you go to our next slide.

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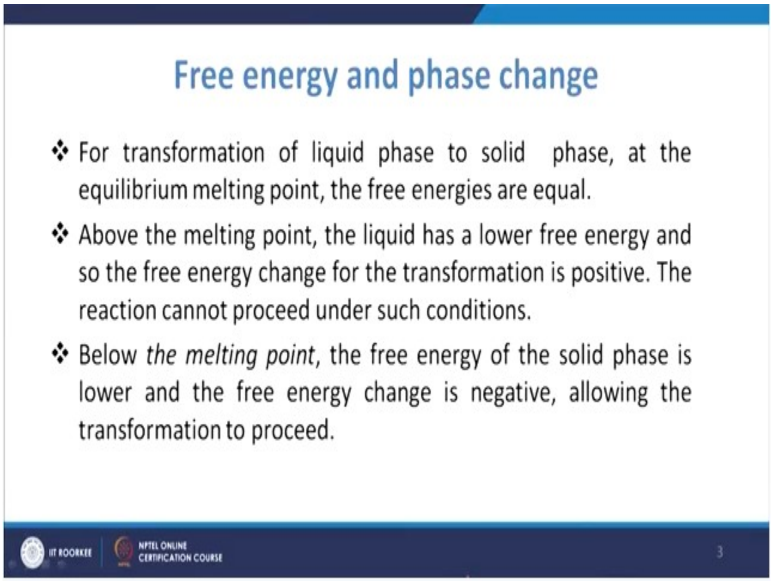

Free energy and phase change

- ❖ For transformation of liquid phase to solid phase, at the equilibrium melting point, the free energies are equal.
- ❖ Above the melting point, the liquid has a lower free energy and so the free energy change for the transformation is positive. The reaction cannot proceed under such conditions.
- ❖ Below *the melting point*, the free energy of the solid phase is lower and the free energy change is negative, allowing the transformation to proceed.

So for a transformation of liquid phase to solid phase at the equilibrium melting point the free energies are equal so that is what it is clear. We have seen that when the curves are meeting at the equilibrium temperature or the melting point temperature. At that point the free energy value of the liquid as well as the solid phase they are equal and there will be no transformation occurring because the solid and liquid both are existing in the equilibrium there.

Now if you take the temperature above the you know melting point then what we have seen that there is liquid which has the lower free energy and so the free energy change for the transformation is positive certainly because that change will be positive and so there will be no transformation you know going on. Then if you take the you know if you take the temperature below the melting point in that case the free energy change will be lower.

Because the liquid will have to come to you know solid values if you take the free energy change values you know that in that case. So if you take this, this is your liquid value.

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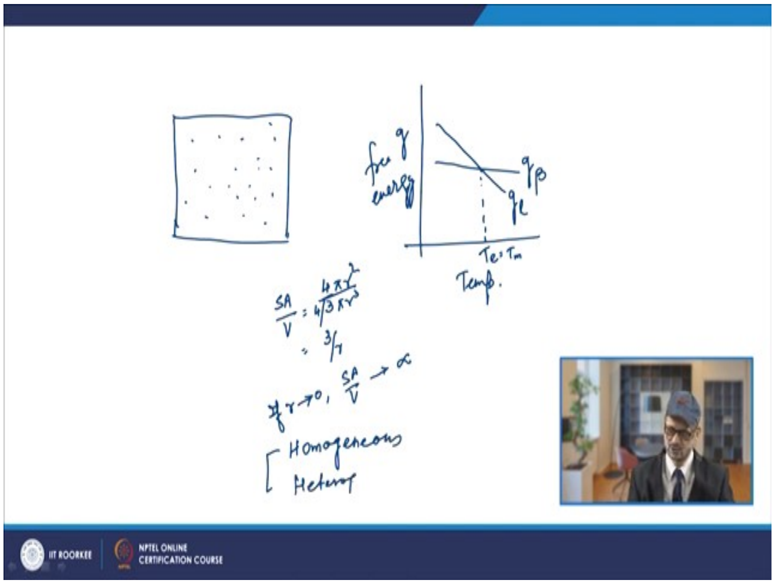

$$\frac{SA}{V} = \frac{4\pi r^2}{4/3\,\pi r^3} = 3/r$$

$$\text{If } r \to 0,\ \frac{SA}{V} \to \infty$$

So if you have to change from liquid to solid and if you take you know so that free energy change value will be positive. So there will be no transformation after this temperature. While if you take the temperature below since the free energy value of the you know solid phase is less than the liquid.

So the free energy change value is negative. So that is why once you have the temperature less than the melting temperature then there will be transformation proceeding from liquid state to solid state and you know that is the essential mechanism of having the phase at any temperature in what phase the material will exist. So now what we need to know that this mechanism by which you know this transformation has to occur.

So that is by the mechanism of nucleation and growth. So when the magnitude of this free energy change is very small the reaction proceeds very slowly if you talk about the scale of transforms and time scale changes of the transformation. So the magnitude of the free energy change what we have seen if this is very small then reaction will proceed very slowly and with a large super cooling below the equilibrium melting temperature, the magnitude of free energy change will be large.

If you take the equilibrium melting temperature and from there if you have the temperature quite less so if the degree of super cooling is more and under cooling is more, that is difference between that equilibrium melting temperature and the temperature which we are talking about. In that case you will have very fast you know transformation. So and if it is very small in that case the reaction will proceed very, very slowly.

So you will have many kind of you know if you talk about the qualitatively the transformation scales, in that case if it may take time from milliseconds to years and that will be representing you know the also that what kind of transformation it is whether it is very fast whether it is fast moderately fast or whether it is slow or it is extremely slow and depending upon that you know you will have also the concept of suppressibilities of these you know transformations.

So when in the transformation is extremely fast it is occurring in the term of microseconds it cannot be you know suppressed so it is in-suppressible. Whereas below that you know if it is very fast if that takes time maybe from milliseconds to seconds in that case it may be suppressed by very, very large cooling and then it is suppressible in the normal case when you have slow transformations or you have fast transformation that way it can be suppressed.

And you know when it is extremely slow then in that case the suppressibility is normally not possible. So in that case basically transformation is virtually impossible because the you know that it is extremely slow in nature. So you have many you know methods to go you must have seen that in normal case you are cooling in the air or you can go to cooling in the water. You go further to increase that by cooling in the oil or brine solution or so you have splat cooling which is very extremely high cooling rate or so.

Now we will talk about you know the so the next point which is important is the transformation is divided into two discrete phases and these two discrete phases are that you have the formation of tiny stable particles that is known as nuclei. And then further you know the growth of these particles so that is known as growth. So with that mechanism basically your transformation is basically complete you have transformation is complete by the mechanism of you know nucleation and growth.

And we will have certain understanding about the concept of nucleation and growth. So as you know that if you have a liquid domain your domain filled with liquid. In that case you have already where you have liquid. Now when the temperature will come down in that case and it will come down below the equilibrium melting temperature then there will be transformation started from liquid to solid phase.

Now as we know that when the solid crystal has to come out of the liquid phase. So that will be by the birth of a new phase. Now any new phase if it is created you know it requires energy to be supplied. So that energy you know it has you know to be supplied during the transformation and if you talk about a very small tiny particle in that case the for and if you assume the particle to be spherical.

Then the surface area by volume ratio that becomes if you take the spherical particles so it will be $4\pi r^2$ basically $\frac{4}{3}\pi r^3$. So it will be coming as $3/r$. So basically when you have very, very small r, so if r will be approaching towards 0. So this ratio SA/V is moving towards infinity very, very large. So initialy it will be preventing the formation of new interface you know. So that is why but then as this r if you are at one point of time this r it is more in that case this you know as the r goes on increasing.

Then this certainly it will try to stabilize and that will lead to so I mean as long it is not able to sustain it is known as embryo and then when it sustains that is known as the you know nuclei. So and then after that there will be further addition of atoms and then it will be you know subsequent process of growth. So that is way, the way this nucleation and growth phenomena you know proceeds.

So if you talk about normal case if you say if you are talking about the nucleation. So in nucleation also you have two types of nucleation one is homogeneous nucleation and heterogeneous nucleation and this is heterogeneous nucleus. So the thing is that in the case of you know homogeneous nucleation your probability of nucleation at all these sites inside the domain is identical.

And in heterogeneous nucleation the probability of nucleation at preferred sites are more. So at certain sites they are more. So in normal case when you have a domain and you don't have any preferred you know nucleation sites so that will be homogeneous nucleation. If you assume that to be homogeneous for a homogeneous nucleation you know case. So if you take the Δf as the free energy change. So if Δf is the free energy change because of the formation of new spherical particle.

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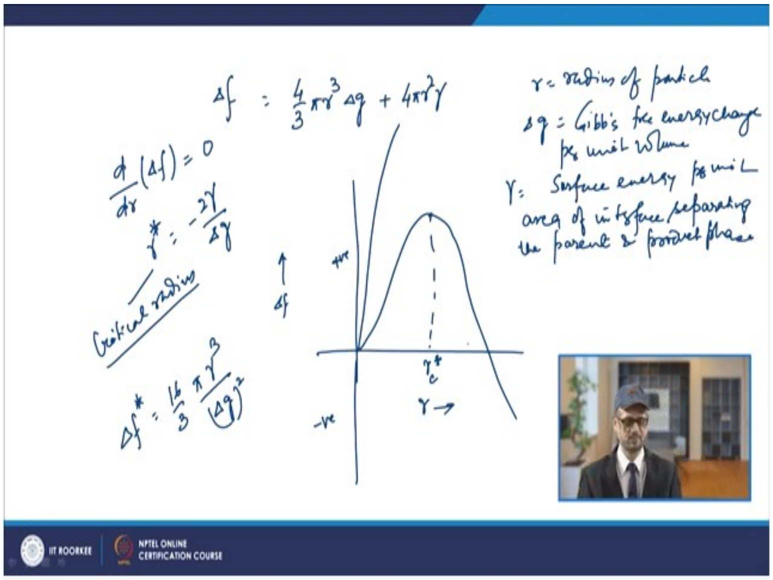

$$\Delta f = \frac{4}{3}\pi r^3 \Delta g + 4\pi r^2 \gamma$$

r = radius of particle

Δg = Gibb's free energy change per unit volume

γ = Surface energy per unit area of interface separating the parent & product phase

$$\frac{d}{dr}(\Delta f) = 0$$

$$r^* = -\frac{2\gamma}{\Delta g}$$

Critical radius

$$\Delta f^* = \frac{16}{3}\frac{\pi\gamma^3}{(\Delta g)^2}$$

So it will be $\frac{4}{3}\pi r^3 \Delta g + 4\pi r^2 \gamma$. So basically one will be positive term another will be negative terms so that is your volume free energy and we know that it has to be negative you know for the transformation to proceed. So where this so that is why you have r as the radius of particle and you have Δg as the Gibbs free energy change per unit volume.

And if you talk about the γ so it is surface energy per unit area of interface separating the parent and product phase. So you know that this will be positive you know of term and this will be negative term and you will have free energy you know curve and that curve basically what happens that initially when it is very small value of *r*. Then this value will have very large value and positive value.

And when as the r you know as the radius of that nuclei increases in that case you will have so ultimately as the r increases this term will starts dominating and then your resultant Δf curve will go on decreasing. So you will have a point at which after which it starts decreasing and that is the point from where the transformation is supposed to start. Now so for getting that point so what happens that if you talk about the you know free energy those values.

So if you take this as the you know positive and this as the negative values. So what happens initially when you are you know very for a small very small value this is going towards very high infinity. But then once you and if you take this value normally it goes like this so this will be $\frac{4}{3}\pi r^3 \Delta g + 4\pi r^2 \gamma$ for this side. Now this is the point you know from where it starts going on decreasing.

So for getting this point what we do is $d/dr(\Delta f)=0$ for getting this value of r. So this is r basically and this is Δf . So if you do that we get basically the so for that we are calling it as $r^{¿}$ and this will be $\frac{-2\gamma}{\Delta g}$. So this is known as the critical radius in this case and of the nuclei and for this the d$\Delta f^{¿}$ also it is critical value if you put these values into this expression.

So it will be $\frac{16}{3}\left(\frac{\pi \gamma^3}{\Delta g^2}\right)$. So this is what the value you are getting you know for the $\Delta f^{¿}$ you know values. Now you can have another also you know expressions for these $\Delta f^{¿}$ or for the transformation also. Now if the radius so this will be your critical radius and that will be known as $r_C^{¿}$. Now if the radius of the particle is below this line I mean towards the left in that case it is known as embryo and if it is after that it is said to be nucleated.

So then that is basically the nuclei. There are another also expressions for liquid to suppose the β transformation.

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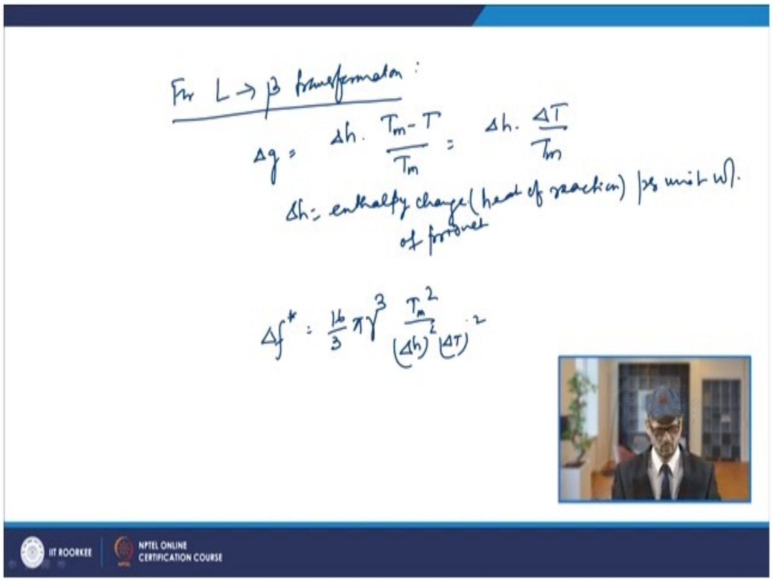

For L → β transformation:

$\Delta g = \Delta h \cdot \frac{T_m - T}{T_m} = \Delta h \cdot \frac{\Delta T}{T_m}$

Δh = enthalpy change (heat of reaction) per unit vol. of product

$\Delta f^* = \frac{16}{3}\pi\gamma^3 \frac{T_m^2}{(\Delta h)^2(\Delta T)^2}$

So if you talk about for liquid to β transformation so you have another you know simplified relationship that is that holds good that is $\Delta g = \Delta \frac{h * Tm - T}{Tm}$. So basically it will be $\Delta h \left(\frac{\Delta T}{Tm} \right)$. So basically Δh is you know that it is enthalpy change or we also could known as know unit of reaction per unit volume of the product heat of reaction so that is per unit volume of the product.

And it is independent of temperature and T_m is the equilibrium melting point and at T_m basically this Δg certainly if you talk about T_m so it will be ΔT_0 so Δg becomes 0. Now if you use this formula so you get the expression for $\Delta f^{¿} = \frac{16}{3} \pi \gamma^3 \frac{T_m^2}{(\Delta h)^2 (\Delta T)^2}$. So this is another expression you know by which you can get the value of $\Delta f^{¿}$ that is your this barrier now you know.

And that will basically be affecting your nucleation process. Now further so that will be just you know this gives you the concept of $\Delta f^{¿}$. Now the thing is that when you have you know the number of critical sized particles that basically can be estimated using the Max Boltzmann statistics. So that statistics concept is used and for from that Max Boltzmann statistics if you try to find the you know the number of these particles.

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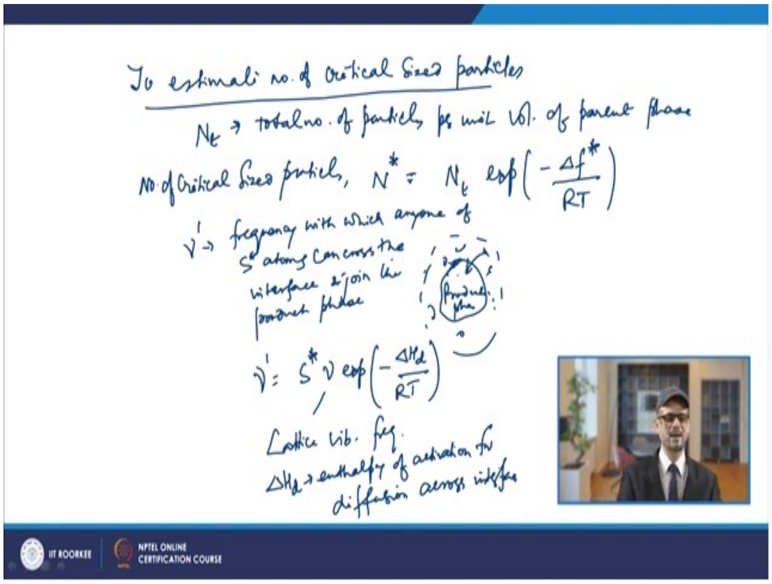

To estimate no. of critical sized particles

$N_t \rightarrow$ total no. of particles per unit vol. of parent phase

No. of critical sized particles, $N^* = N_t \exp\left(-\frac{\Delta f^*}{RT}\right)$

$\nu' \rightarrow$ frequency with which anyone of S^* atoms can cross the interface & join the product phase

$\nu' = S^* \nu \exp\left(-\frac{\Delta H_d}{RT}\right)$

Lattice vib. freq.

$\Delta H_d \rightarrow$ enthalpy of activation for diffusion across interface

So if so you have to estimate number of you know critical sized particles. So for that the Max Boltzmann statistics is used. So how what will be the number of critical sized particles in the apparent phase. So if N_t is the you know total number of particles per unit volume of parent phase. In that case if you have to find the number of critical sized particles. So number of critical sized particles that if you know denote by N*. So it will be denoted by $N_t \exp\left(\frac{-\Delta f^{¿}}{RT}\right)$. So this will be the value of the number of critical size particles and the process of nucleation is that you know is that step of process when this critical size you know particle becomes supercritical. So that will be by jumping off one of atom the atom from the parent phase to the product phase. So that basically will be make it super critical.

You have a critical size particle and then you have adjoining atoms on that interface and from that you know parent phase or the liquid phase one of the atom will jump into that critical size particle and that will make it super critical and then it is said to be a nucleated. So if suppose in that case if suppose you this is your product phase and this your parent phase so if this is your product phase and this is your parent phase where you have atoms and this atom has to jump from there to make it you know super you know critical.

So if suppose you have S* atoms which are you know which are facing that interface and if one of these S* atoms is basically jumping into the product phase then it is said to be nucleated and for that again you are using again this statistical concept and the frequency with which these any one of these S* atom that will be crossing that interface. So this v' so if you take nu dash as the frequency with which any one of S* atoms.

S* atoms are the number of atoms which are basically facing this interface in that parent phase towards the product phase. So if they are you know in the atoms can cross the interface and join the product phase. So if that is your $v' = S^{¿} v . \exp\left(\frac{-\Delta H_d}{RT}\right)$. So v is the lattice vibration frequency so nu is lattice vibration frequency.

And S* is the number of atoms which are basically across the interface which are touching you know on that surface and ΔH_d the enthalpy of activation. So ΔH_d will be enthalpy of activation for diffusion across the interface. So if you look at this v term a prime value now that will be $S^{¿} v . \exp\left(\frac{-\Delta H_d}{RT}\right)$. Now the thing is that if you talk about the rate of nucleation.

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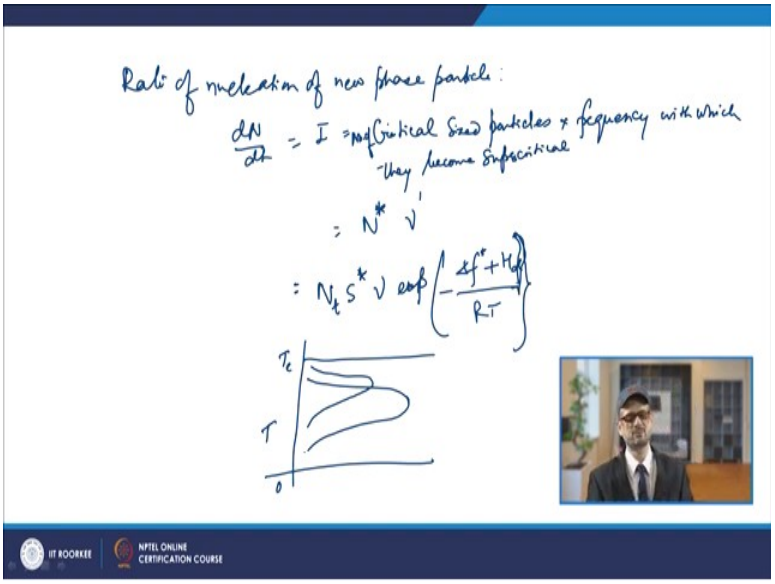

Rate of nucleation of new phase particle:

$\frac{dN}{dt} = I$ = no. of Critical Sized particles × frequency with which they become Supercritical

$= N^* v'$

$= N_t S^* v \exp\left(-\frac{\Delta f^* + H_d}{RT}\right)$

So the rate of nucleation of the new phase particle, rate of nucleation of new phase particle so if you talk about it, it will be now you know so that will be dN/dt and this we also call it as the I and it is nothing but the product of the number of critical sized particles. So it will be a number of critical sized particles and multiplied by the frequency with which they try to become supercritical.

So you have we have got the expression for that and it will be N*ν'. So it will be $N_t S^{¿} v . \exp\left(\frac{-\Delta f^{¿} + H_d}{RT}\right)$. So that basically is talking about you know the expression for the rate of nucleation and what we see that in this basically this pre-exponential term value it is coming in the range of 10^{42} m^{-3}/sec.

And then depending upon these values your nucleation rate will be defined. So basically if you talk about the conditions like if you are talking about the equilibrium melting temperature in that case you know at that point you will have this value as. So depending upon that this Δf^* or H_d so depending upon these values at different temperatures so what is seen in that when you are at a temperature near the equilibrium temperature.

At that point also if you see the rate of nucleation. This rate of nucleation is basically 0 and if you go to the absolute 0 value here. In that case also it will be this value will come out to be 0. So what is seen is that if it is temperature and if it is 0 Kelvin and if it is your equilibrium temperature then what is seen is that your nucleation will proceed from here and then after certain time basically when these are T term starts dominating.

In that case then it starts decreasing further so and then it will come to 0 at the 0 term. So this is how the rate of nucleation will be you know curve will be shown. Similarly, will be the curve for the growth and for growth basically it will be similar but it starts you know this becomes predominant when you have you know the temperature in the upper zone. So your growth also has a similar curve but it will be more when it is near to the equilibrium temperature.

And depending upon these two you will have the transformation curve. So you will have the transformation curve dx/dt which will be in between the two. So this is the concept of transformation in between in the case of you know the materials. Now so this was the concept of transformation in the case of homogeneous nucleation. When we talk about the heterogeneous nucleation.

The heterogeneous nucleation at preferred places you will have the chances of nucleation will be more and that is basically governed based on the you know the particle which is nucleated and the interfaces which is created. So taking upon the surface tension you know forces also into account and other factors so summation of forces if you do if you read them from some standard books.

So the thing is that the energy which you have to supply for creating the surface in the case of homogeneous nucleation that basically is less in the case of heterogeneous nucleation. Because here you have certain surfaces present. Now that may be in the form of inclusions or that may be the wall of the container which is basically the sand basically sand moulding material you have inclusions.

So basically in that case that becomes your source and from there the nucleation is basically assisted. So the Δf^* value which you are getting in the case of homogeneous nucleation, in the case of heterogeneous nucleation it may be so maximum it will be there and the same as homogeneous nucleation for certain cases. However, depending upon the characteristics of the product particle and interface or so.

You will have the Δf^* requirement will be lesser and that will basically giving you know the easy nucleation and that is why that is the concept of heterogeneous nucleation. So we will be whenever we will be talking about the transformation of the you know from one phase to other all these things must be in our mind. So that we can correlate that what might have happened. This is from the liquid to solid state.

Similar thing happened in the case of solid to solid state transformation. Now in those cases you have other strain energy factor is coming into picture. So basically there also you will have nucleation and you may have nucleation at certain points many a times what we see that you have certain preferred places where the nucleation starts and that will be at those higher energy places like you have grain boundaries or the dislocation sites or so.

So that will so basically depending upon that free energy value is concept and also you know other whatever we have understood we must have the clarity of these concepts in mind. So that it will assist us in the understanding of other you know metallurgical processes or the welding processes in a better manner. Thank you very much.