Heat Treatment and Surface Hardening (Part–1)
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Lecture Number 30

Interface controlled growth

So in the last several lectures I have devoted a lot of time on discussing the rate of nucleation. And now in any phase transformation first a nuclei forms and then a nuclei grows. So now what we are going to look from today onwards or from this lecture onwards is the rate at which an nuclei grows a stable nuclei grows or the growth kinetics of the stable nuclei.

It is together the rate of nucleation and the growth kinetics put together will give us quantitative idea of the rate of phase transformation. So now considering growth kinetics of a stable nucleus, there are several steps in which or couple of steps in which stable nuclei will grow, this may involve diffusion over large distance distances and atomic jump across the parent phase and the nucleus phase interface.

So in the case of liquid to solid it would be the liquid solid interface. In the case of solid to solid it would be a atom jumping from the parent solid phase to the product solid phase. So it is the rate of diffusion of atoms within the parent phase and then the rate of jump of atoms. Now the question is which of the two processes will control the rate of growth would be dependent on which process is slow and which process is fast.

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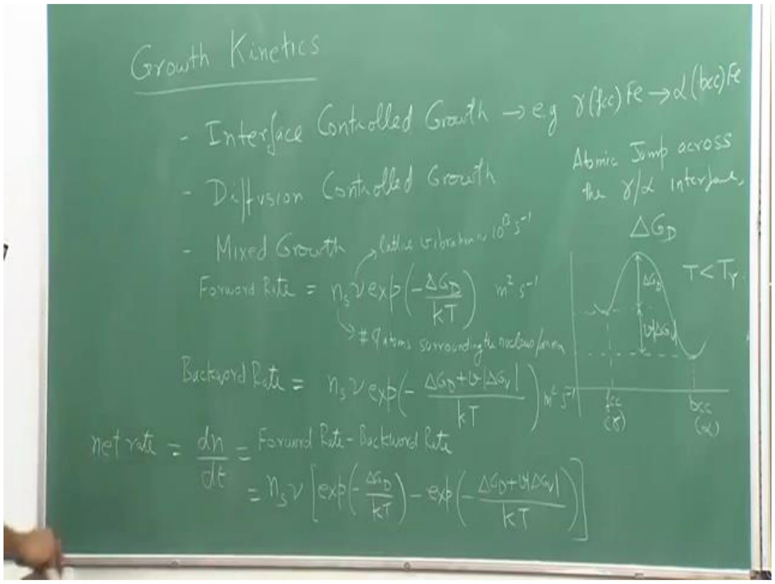

Growth Kinetics

- Interface Controlled Growth → e.g $\gamma(fcc)\,Fe \rightarrow \alpha(bcc)\,Fe$
- Diffusion Controlled Growth
- Mixed Growth

lattice vibration ~ $10^{13}\ s^{-1}$

$$\text{Forward Rate} = n_s \nu \exp\left(-\frac{\Delta G_D}{kT}\right)\ m^2 s^{-1}$$

→ # of atoms surrounding the nucleus/embryo

$$\text{Backward Rate} = n_s \nu \exp\left(-\frac{\Delta G_D + \upsilon|\Delta G_v|}{kT}\right)\ m^2 s^{-1}$$

$$\text{net rate} = \frac{dn}{dt} = \text{Forward Rate} - \text{Backward Rate}$$

$$= n_s \nu \left[\exp\left(-\frac{\Delta G_D}{kT}\right) - \exp\left(-\frac{\Delta G_D + \upsilon|\Delta G_v|}{kT}\right)\right]$$

Atomic Jump across the γ/α interface,

For example if there is no large distance diffusion involved and only jumping of atoms from a parent phase to the product phase is involved. Then in that case that is going to be the rate controlling step or what we call as an interface controlled growth. In a situation where there is diffusion involved and if the diffusion step is a slow step compared to the jump of atoms across the interface.

So the barrier for jumping across the interface must may be far smaller as compared to the barrier for the diffusion then what the kind of growth we mechanism that is going to control is called as diffusion controlled growth. And of course there can be a situation where both the processes may be contributing significantly to the growth in that case we would call that as mixed growth.

Now let us consider first growth kinetics where interface growth or the atomic jump across the interface is controlling the growth kinetics. And such a growth an example of that could for example occur in the example that we have been taking in the last few lectures of ice nucleating in water. It is a single component system where actually it is the water molecules jumping across the liquid to solid interface.

Or another example in the solid case could be gamma FCC iron transforming to alpha body centered cubic iron. Again a single component system where it is going to be an interface controlled growth because there is no diffusion involved but atoms have to jump from the parent phase centered cubic phase across the interface to the product phase which is alpha or the body centered cubic iron.

So let us consider that kind of a situation now what is the so there is a for the atomic jump in this case across the gamma alpha interface. So alpha is a (nucl) stable nucleus that forms in the gamma FCC iron phase when the temperature is below the transformation temperature which is of the order of 910 degrees celcius. So considering this what is the barrier to this atomic jump and that also we have already encountered when we were talking about nucleation and that barrier is delta GD, the energy barrier across the interface.

So this is the term whose magnitude also we have we have some idea from our earlier lectures where essentially an atom would jump from the parent phase to the product phase. Let us look at this in this following representation so I have this is FCC gamma. So for an atom to jump to body centered cubic alpha it has to cross this barrier delta GD. And this is for temperature less than the transformation temperature Tr.

You would also know from this diagram that there is a reduction in the free energy as we transform from phase centered cubic to body centered cubic iron for temperatures less than the transformation temperature. And that reduction is is given by this level and what is that level well one atom jumps and if that atom has a volume of v than this barrier is of the order of v times delta GV, the volume free energy change per unit volume multiplied by the volume of the singe atom.

So delta GV also we have seen and of course this is going to be a function of temperature and hence this these levels will change for different temperatures. Now, I want to figure out from here what would be the rate or the net rate of atoms jumping from the gamma phase to the alpha phase, ok. So let us first look at what is the probability of a jump for an atom on the phase centered cubic side to jump across the solid interface to the body centered cubic phase. Well that also we have already seen and that probability is simply exponential minus delta GD divided by KT.

Now I want to find out the overall forward rate forward rate means atoms jumping from FCC side to the BCC side. So I will call that as the forward rate that would be a function of lattice vibration frequency which is we have already seen is of the order of 10 to power 13 per second multiplied by ns which is the number of atoms or molecules surrounding the nucleus per unit area.

Now just as the atoms can jump from FCC to BCC similarly an atom can also jump from BCC to FCC there is a finite probability for that as well. And what is that probability well that probability would be exponential but here you will have a bigger energy hill would be this would be much delta GD plus v delta GV. So if I add this up well let me put this delta GV in modulus sign to indicate that I am going to take the positive quantity here.

And let me write this as delta GD plus v delta GV divided by KT. So here we have a higher barrier in for an atom to jump from BCC to FCC for temperatures below the transformation temperatures. So the probability is less and in a similar manner I can express the backward rate of jumps as ns times new times the exponential. So obviously if I look at this these quantities the units are going to be meter square second inverse.

Now, I want to know what is the net rate that is the number of atoms jumping per unit area per unit time in the forward direction. For the net rate of jump, let me call that as dn by dt the net rate.

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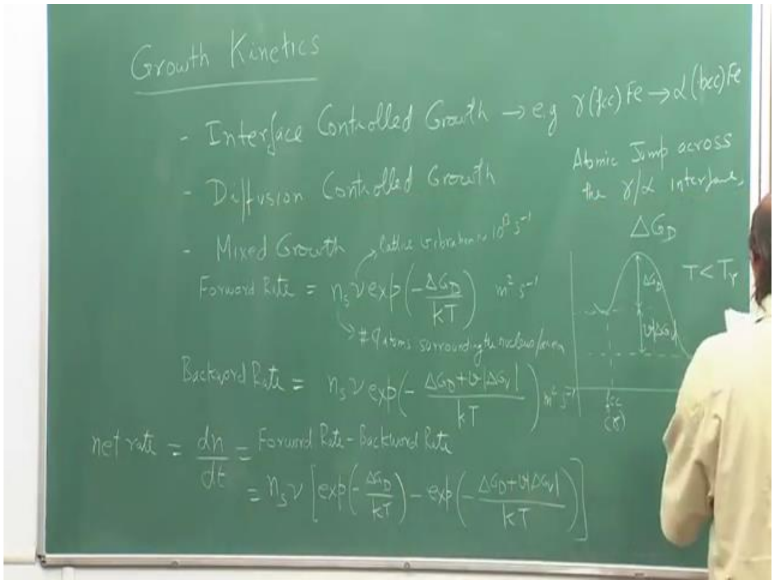

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Lattice vibration ~ $10^{13}\ s^{-1}$

Forward Rate = $n_s \nu \exp\left(-\frac{\Delta G_D}{kT}\right)\ m^2 s^{-1}$

→ # of atoms surrounding the nucleus/area

Backward Rate = $n_s \nu \exp\left(-\frac{\Delta G_D + \upsilon|\Delta G_v|}{kT}\right)\ m^2 s^{-1}$

net rate = $\frac{dn}{dt}$ = Forward Rate − Backward Rate

$= n_s \nu \left[\exp\left(-\frac{\Delta G_D}{kT}\right) - \exp\left(-\frac{\Delta G_D + \upsilon|\Delta G_v|}{kT}\right)\right]$

So dn by dt is simply the forward rate minus the backward rate. Now forward rate minus the backward rate I substitute this two expressions in this and I would get well I can take out ns mu times exponential minus delta GD by KT minus exponential minus delta GD plus v delta GV upon KT.

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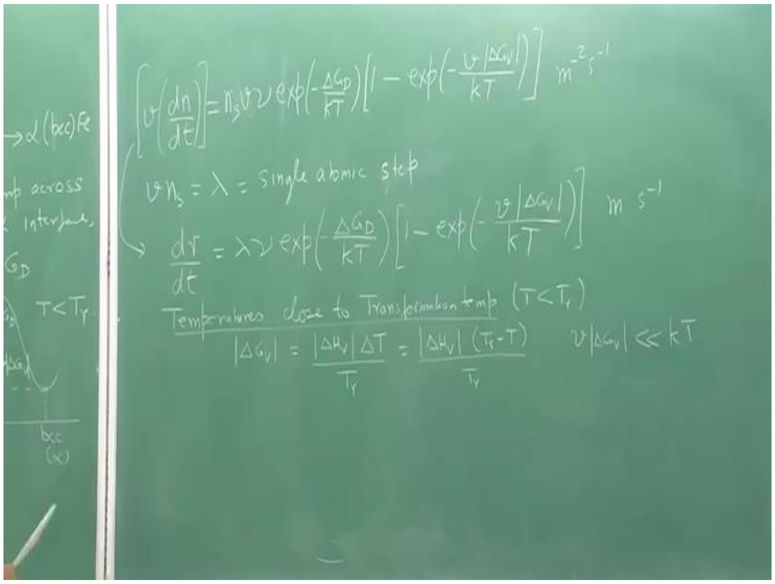

$$\left[v\left(\frac{dn}{dt}\right)\right] = n_s v \nu \exp\left(-\frac{\Delta G_D}{kT}\right)\left[1 - \exp\left(-\frac{v|\Delta G_v|}{kT}\right)\right] \quad m^{-2}s^{-1}$$

$v n_s = \lambda$ = single atomic step

$$\frac{dr}{dt} = \lambda \nu \exp\left(-\frac{\Delta G_D}{kT}\right)\left[1 - \exp\left(-\frac{v|\Delta G_v|}{kT}\right)\right] \quad m\ s^{-1}$$

Temperatures close to Transformation temp ($T < T_\gamma$)

$$|\Delta G_v| = \frac{|\Delta H_v|\,\Delta T}{T_\gamma} = \frac{|\Delta H_v|\,(T_\gamma - T)}{T_\gamma} \qquad v|\Delta G_v| \ll kT$$

So this gives me the net jump rate. Let me just rearrange some of the terms to write the net rate dn by dt as ns mu and I take out exponential minus delta GD upon KT common out of the brackets. And I will get inside the square brackets [1 – exponential (-v delta GV divided by KT)]. So this is the net jump rate per meter square per second. Out here this should also be per meter square per second, ok.

If I look at this I multiply both sides by volume of an atom, so I can write this as nsv instead of ns mu. Now this gives me the growth rate. So if I basically I am adding a for basically I can put v times ns equal to lambda which is equal to a single atomic growth. Or a single atomic step I should say that is added per meter infact single atomic step that is added.

So this term here actually I can then write it as a one dimensional growth rate as dr by dt which is equal to lambda mu exponential – delta GD by KT times [1-exponential (-v delta GV upon KT)]. And this essentially gives me growth as meters per second. So let us try to analyze this growth rate (equat). Let us consider a situation or let us consider temperatures close to the transformation temperature, ok.

But keeping (T<Tr) but close to Tr. And if we look at what is the growth kinetics at this temperature. So let us try to see this what is delta GV at temperatures, at any temperature T below Tr. Well that is simply delta HV change in enthalpy per unit volume multiplied by the undercooling upon Tr, the transformation temperature. Or I can simply write this as delta HV times (Tr-T) upon Tr.

So for small undercooling essentially temperatures close to the transformation temperature means we are talking about small undercooling. So for small undercooling the term v times delta GV could be much smaller than KT. If this is the case then I can make the following approximation using Taylor Expansion and how do we do Taylor Expansion very quickly.

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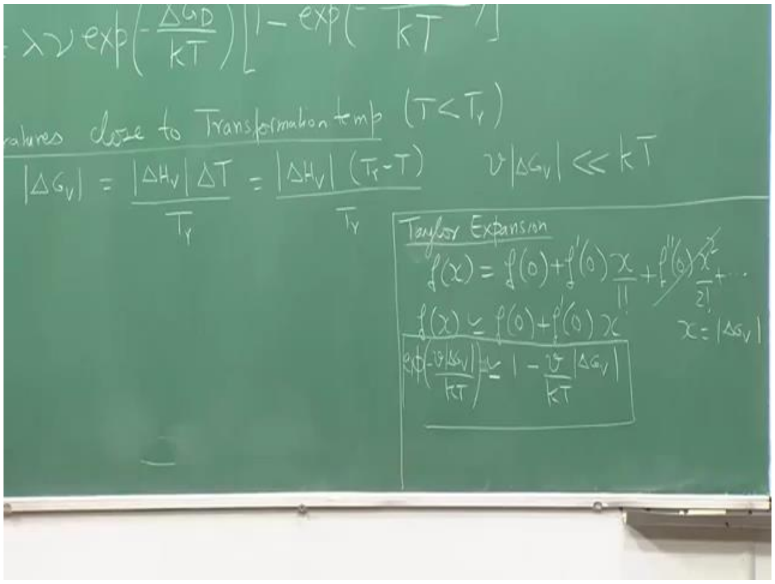

If I have a function f(x), for a function f(x) which I expand around x is equal to 0. The Taylor Expansion can be written as in in the form of an infinite series as f(0)+f prime (0)x upon 1 factorial + f double prime (0)x square upon 2 factorial and so on. Now for small undercooling means for small values of x here, I could neglect higher order terms and keep only the first 2 terms. So here x actually is nothing but delta GV. So using only the first 2 terms the approximation is f(0) + f prime (0) times x. Now what is f(0) well the function is exponential –v delta GV upon KT.

So x is putting this is 0, this is essentially 1, so this is equal to 1. Differentiate this find the derivative at 0 and the derivative is going to be –v upon KT multiplied by x and that is delta GV. So what this is telling us is that for v delta GV much smaller than KT, the function which is exponential –v delta GV upon KT can simply be approximated by this.

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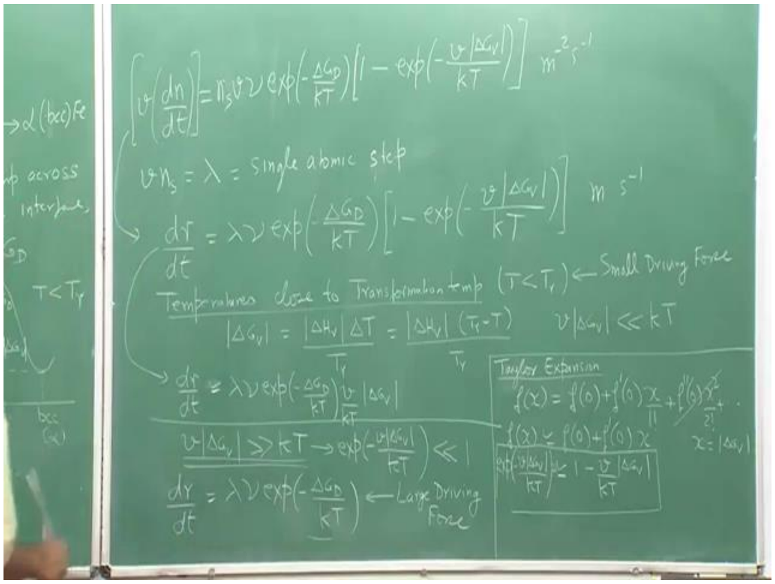

$$\left[v\left(\frac{dn}{dt}\right)\right] = n_s v \nu \exp\left(-\frac{\Delta G_D}{kT}\right)\left[1 - \exp\left(-\frac{v|\Delta G_v|}{kT}\right)\right] \; m^{-2} s^{-1}$$

$v n_s = \lambda$ = single atomic step

$$\frac{dr}{dt} = \lambda \nu \exp\left(-\frac{\Delta G_D}{kT}\right)\left[1 - \exp\left(-\frac{v|\Delta G_v|}{kT}\right)\right] \; m \, s^{-1}$$

Temperatures close to Transformation temp $(T < T_\gamma)$ ← Small Driving Force

$$|\Delta G_v| = \frac{|\Delta H_v| \Delta T}{T_\gamma} = \frac{|\Delta H_v| (T_\gamma - T)}{T_\gamma} \qquad v|\Delta G_v| \ll kT$$

$$\frac{dr}{dt} \simeq \lambda \nu \exp\left(-\frac{\Delta G_D}{kT}\right)\frac{v}{kT}|\Delta G_v|$$

$$v|\Delta G_v| \gg kT \rightarrow \exp\left(-\frac{v|\Delta G_v|}{kT}\right) \ll 1$$

$$\frac{dr}{dt} = \lambda \nu \exp\left(-\frac{\Delta G_D}{kT}\right) \leftarrow \text{Large Driving Force}$$

Taylor Expansion

$$f(x) = f(0) + f'(0)\frac{x}{1!} + \cancel{f''(0)\frac{x^2}{2!}} + \ldots$$

$$f(x) \simeq f(0) + f'(0)\, x \qquad x = |\Delta G_v|$$

$$\boxed{\exp\left(-\frac{v|\Delta G_v|}{kT}\right) \simeq 1 - \frac{v}{kT}|\Delta G_v|}$$

If I substitute this now this approximation into this my rate of growth dr by dt then can be approximated as lambda mu exponential – delta GD upon KT.

And we substitute this expression to this. And one would get the term v upon KT times delta GV. So what this is telling us is that for small undercooling the growth rate is directly proportional to the driving force delta GV. Now what could happen when the driving force is very large. Here this was the situation where the driving force is small. What would be the situation when the driving force is large, what does that mean that means that v delta GV is much larger than KT.

If this happens then what about the term exponential –v delta GV upon KT, well exponential –v delta GV upon KT sets there is a negative exponent. This is going to be much much smaller than 1. And if this is much smaller than 1, this term for large driving force that this could be neglected and hence the rate of growth then becomes simply lambda mu exponential – delta GD upon KT.

This is the situation for large driving force and of course in between there will be whole range of growth rates in between which would simply be given by this expression.

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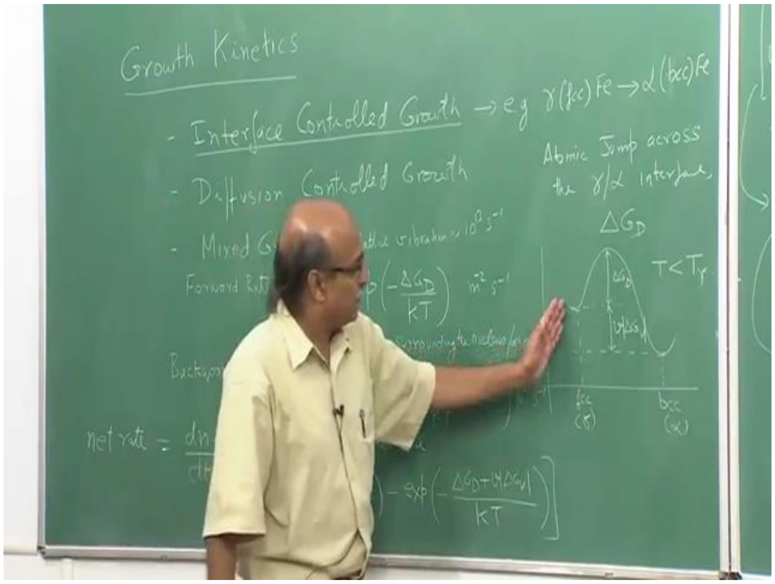

Now what can we conclude out of all this that we have done, that if we have interface controlled growth than one thing is clear that at a given temperature the growth rate will be a constant. We can assume the growth rate to be a constant.

But growth rate itself is going to change with temperature or change with undercooling. But if we were to model the rate of or the kinetics of the overall phase transformation. Then and if we knew that we had interface control growth then in that situation we can simply assume the growth rate to be a constant. So this is one kind of of a controlling mechanism for growth of a stable nucleus.

Now this is likely to happen in systems where single components system where there is no diffusion involved or in those systems where diffusion is very fast. But for some reason the atomic jump across the interface is difficult which means delta GD is very large. And it can happen, then in that case also one would get interface controlled growth. Even though there would be diffusion involved.

But the diffusion process is much faster or you can say the atomic jump across the interface is much smaller and hence in that situation we would have interface control growth and we can say that the growth rate would be a constant for given undercooling. Now this was all that I wanted to discuss regarding interface control growth and thh in the next lecture let us look at diffusion controlled growth.

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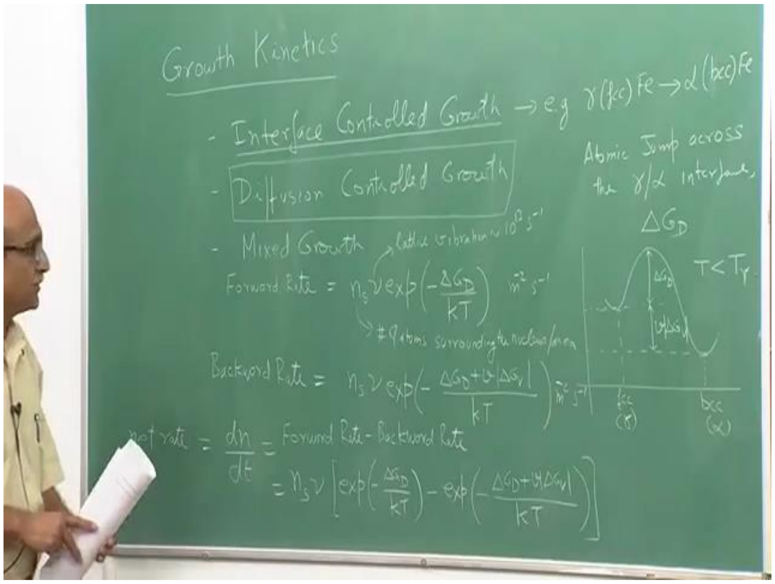

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And this is quite important and we would also find that the growth rate will no if we have diffusion control then growth rate will no longer be a constant. It itself is going to vary with time. So with this I will stop here and will continue in the next lecture.