# Heat Treatment and Surface Hardening (Part–1)

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**Lecture Number 32**

## Avrami Kinetics - 1

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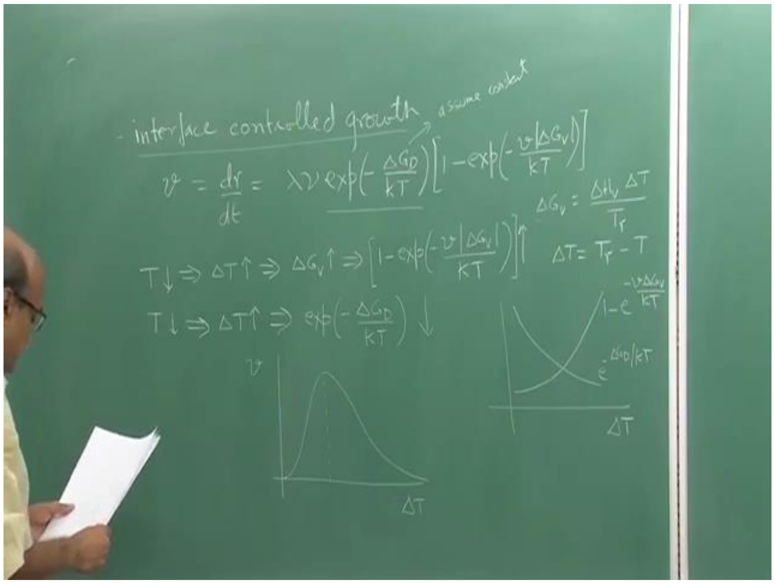

In this lecture I will make some concluding remarks regarding growth kinetics and let us consider interface control growth which the velocity of growth is dr by dt as we had seen in the last lecture is given by the following expression lambda mu exponential minus delta GD divided by KT times [1-exponential (-v delta GV divided by KT)] and all the terms in this expression you are already familiar with.

Now in this what I want to look at is that when the undercooling is changed as the temperature at which the transformation is taking place is lowered or the growth is taking place is lowered what happens to the growth rate. So let us see we have delta GD, we will assume is a constant or there is no significant change in delta GD with temperature of transformation. While delta GV as you know is given by the change in enthalpy per unit volume multiplied by the undercooling divided by the transformation temperature Tr.

So let us see what happens because delta T is the transformation temperature minus T and T is the temperature at which we are looking at the growth rate. So as the temperature at which we are looking at growth is reduced this implies the undercooling delta T increases. And very clearly from this expression delta GV would also increase. Now let us look at this term what happens to this term containing delta GV.

As delta GV increases implies that the exponential term reduces as delta GV in the exponent is uhh negative quantity here then I should make uhh I should wrote that I am taking the absolute value of delta GV here in the (expe) in the exponential. Hence if this term reduces the term 1-exponential –v delta GV divided by KT would also increase. Because exponential term reduces, so 1-exponential term will increase.

So as the temperature of growth is reduced temperature at which growth is taking place is reduced that means the undercooling is increased the term in the square bracket increases. Now let us look at the delta GD term what happens when the temperature is reduced or the undercooling is increased. Well that is straight forward that as the temperature T is reduced and delta GD being a constant the exponential term minus delta GD divided by KT has to reduce.

So we have here two terms one term with the increase in undercooling goes up the term in the square brackets while the second exponential term containing delta GD uhh reduces when the undercooling is increased. So if I plot this or I sketch it in a plot of these two terms uhh versus its delta T. So there is one term which is increasing which is 1-e to power –v delta GV divided by KT. The other term containing delta GD goes down with undercooling which is e to power –delta GD divided by KT.

Now this is to be expected because as the driving force delta GV goes up with undercooling the term in the square brackets goes up. While the delta GD term goes down very clearly is that (int) interface control growth the jump of atoms across the interface uhh become more difficult as at lower temperatures. So looking at these two opposing terms the overall growth velocity v versus the undercooling at initial stages at small undercoolings one term will dominate at higher undercooling another term will dominate at small undercooling.

We have a small driving force the growth velocity will be small. At large undercoolings the jump of atoms across the interface become difficult hence again we will have a smaller growth rate.

And infact if we compute this putting in (so) some appropriate values for a given system we would get a curve for growth velocity something like this which will have a peak at a certain undercooling.

So this is very similar to what we observed in the rate of nucleation as well that for a specific undercooling the nucleation rate went through a peak. Now this was for interface controlled growth a similar kind of situation would exist for diffusion controlled growth as well. In the case of diffusion controlled growth that we have seen in the last lecture.

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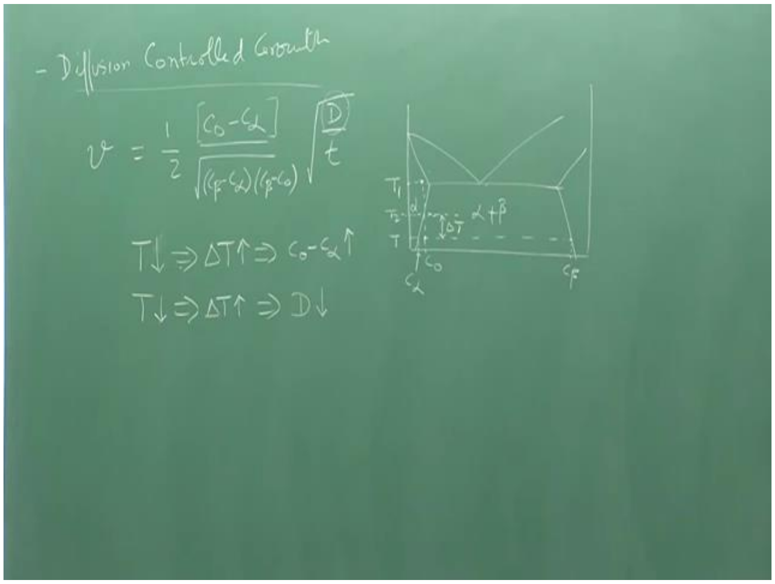

- Diffusion Controlled Growth

$$v = \frac{1}{2}\frac{[C_0 - C_\alpha]}{\sqrt{(C_\beta - C_\alpha)(C_\beta - C_0)}}\sqrt{\frac{\boxed{D}}{t}}$$

$$T\downarrow \Rightarrow \Delta T\uparrow \Rightarrow C_0 - C_\alpha\uparrow$$

$$T\downarrow \Rightarrow \Delta T\uparrow \Rightarrow D\downarrow$$

The growth velocity v was written as half C0-C alpha divided by square root of (C beta – C alpha) times (C beta - Cnot) times the square root of D by t, where D was a diffusion coefficient, t is a time and in this case we had seen that this growth what we had called was a parabolic growth.

And the term C0, C alpha, C beta came from the phase diagram and if you look at it we have chosen a composition Cnot and taken some temperature T1 and then we suddenly cool down to some temperature T. Obviously at this point we had if this is the alpha phase this is alpha plus beta that at this point at this temperature we had (hun) hundred percent alpha by ess quenching it time T equal to 0.

And it obviously was super saturated alpha because the alpha composition as per the phase diagram should be C alpha and similarly the beta that would precipitate out would have the composition C beta. Now the amount of super saturation as you can clearly see will depend on the amount of undercooling delta T in uhh in this case. Very clearly if this let us say if this temperature was T2 then at temperature T2 the undercooling is 0, delta T0 and the C alpha composition will correspond to Cnot composition and the supper saturation term in the numerator here would be 0. And hence the growth velocity will be 0.

As the temperature is lower you will have a certain finite super saturation which will increase so this super saturation will tend to increase the growth velocity. However as we increase the undercooling that means we reduced the temperature. So if temperature is reduced this leads to as I said just now delta T going up. This leads to C0 minus C alpha the super saturation going up.

And the other effect of temperature being reduced as the undercooling is increased would lead to the diffusion coefficient D also reducing. We will see in subsequent lectures how D varies with temperature but this point or time I will simply leave it that as the temperature goes down the undercooling goes up, the diffusion coefficient D goes down. So again we have two opposing terms here one increasing with increase in undercooling the other decreasing with uhh increasing undercooling.

And hence in this case as well we will get a nucleation rate which would be something similar to what we had shown for the interface controlled growth. Now with these few words I will stop the discussion on growth kinetics and now the next thing I want to take up in this lecture is the rate at which the phase transformation will take place. The overall kinetics of phase transformation.

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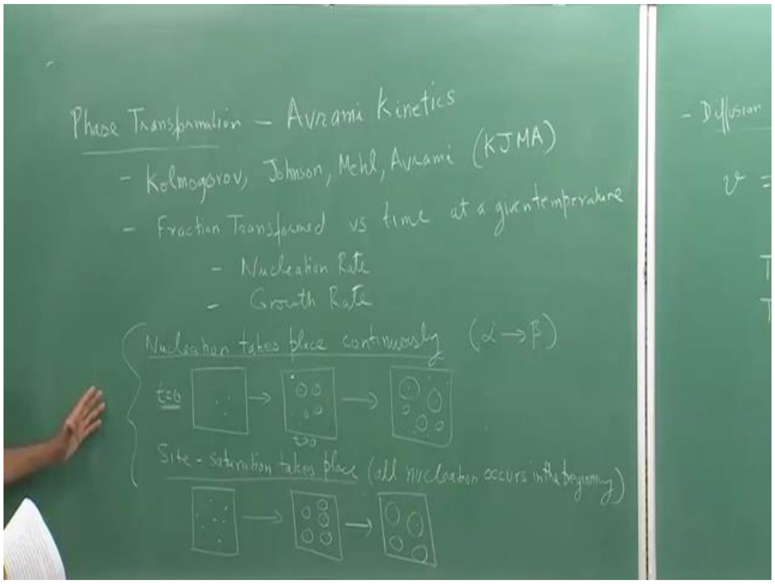

Phase Transformation – Avrami Kinetics

- Kolmogorov, Johnson, Mehl, Avrami (KJMA)
- Fraction Transformed vs time at a given temperature
  - Nucleation Rate
  - Growth Rate

Nucleation takes place continuously ($\alpha \to \beta$)

Site - saturation takes place (all nucleation occurs in the beginning)

So let us look at how we approach this problem. So we are going to look at overall phase transformation in terms of what is also known as simply Avrami Kinetics. In short it is called Avrami Kinetics but there are several researches which have worked on this and it is also known as Kolmogorov, Johnson, Mehl, Avrami Kinetics or in short (KJMA) kinetics. And what we are deduce from here is simply Fraction Transformed versus time at a given temperature.

Now what should this fraction transformed as a function of time depend on clearly the rate of nucleation and the growth rate. It will of course depend on many other parameters such as if there is a temperature gradient uhh uhh in the material that will uhh play a role but, we are assuming that we are going to do this and look at it uhh at a given constant temperature.

We already know now that the phase transformation first involves nucleation and then wants a stable nucleus forms then growth of that nucleus. So we can have several scenarios in the way uhh phase transformation would take place. For instance we can have a scenario where nucleation takes place continuously. That is nucleation take uhh is taking place continuously and at the same time the nuclei which are formed are growing continuously.

And let us say that there is a phase alpha which is transforming to beta. So this can be pictured that we have some nuclei formed at time t is equal to 0. Many of these nuclei would grow and at the same time new nuclei are forming. So this is t equal to 0, this is at some time t greater than 0 and this will just continue. And there are fresh nuclei which are always available.

So nucleation is taking place continuously and at the same time the nuclei are growing. Another situation can be that there are only limited sites for nucleation and as a result site saturation takes place. And the extreme case of this site saturation could be that all nucleation occurs in the beginning. So we have a situation where we have nuclei forming right in the beginning and after that no more no further nucleation takes place.

And we have only nuclei which are growing. As time increases the size of these nuclei are increased. So these are two kind of scenarios we would look at and see how they affect the overall kinetics of phase transformation. So now let us look at how we can derive the transformation kinetics in a quantitative manner with whatever we have learned so far.

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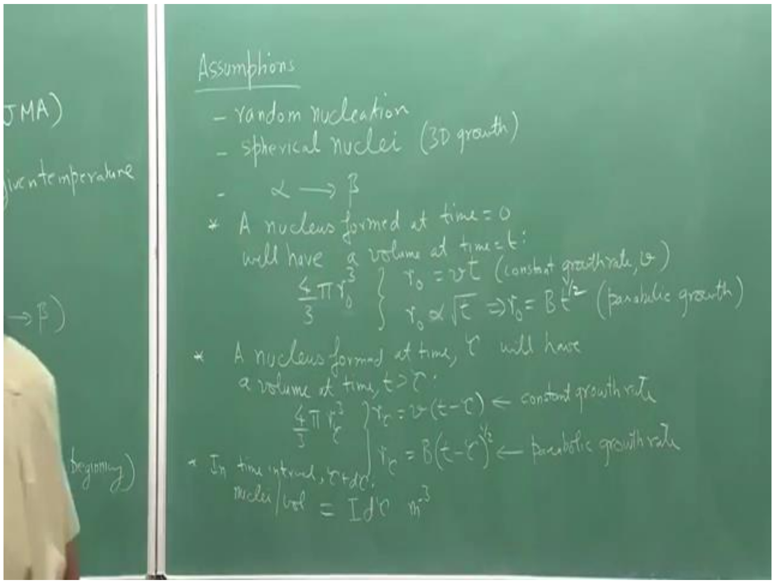

Assumptions

- random nucleation
- spherical nuclei (3D growth)
- $\alpha \longrightarrow \beta$

* A nucleus formed at time = 0 will have a volume at time = t:

$$\frac{4}{3}\pi r_0^3 \begin{cases} r_0 = vt \text{ (constant growth rate, } v) \\ r_0 \propto \sqrt{t} \Rightarrow r_0 = Bt^{1/2} \text{ (parabolic growth)} \end{cases}$$

* A nucleus formed at time, $\tau$ will have a volume at time, $t > \tau$:

$$\frac{4}{3}\pi r_\tau^3 \begin{cases} r_\tau = v(t-\tau) \leftarrow \text{constant growth rate} \\ r_\tau = B(t-\tau)^{1/2} \leftarrow \text{parabolic growth rate} \end{cases}$$

* In time interval, $\tau + d\tau$:

nuclei/vol $= I d\tau \quad m^{-3}$

So we will make some assumptions first and the following assumptions which are fairly reasonable is that nucleation takes place randomly. And uhh for the sake of simplicity let us assume spherical nuclei. And obviously for (())(18:57) to grow that means we are also saying that basically there is 3D growth not a 1 dimensional or 2 dimensional growth. And we have a phase alpha in which beta precipitates are forming. So let us see how we can work out quantitatively the phase transformation dynamics.

A nucleus formed at time 0 will have a volume at time equal to t. As since it is a spherical nucleus at time is equal to t, its radius becomes r0. So the volume would be 4 by 3 pi rnot cube. The subscript 0 here denotes there is nucleus formed at time 0. Now of course if we are saying that nucleation is taking place continuously then you will also have nuclei forming at other times.

Now what about r0, what would be at time equal to t. What would be the size r0, well that depends on what model of growth one would take suppose it was interface control growth then we had seen that in the case of interface control growth we could assume that the growth rate is constant. In that case r0 would simply be equal to the velocity times the time t. So this is constant growth rate v.

If it was parabolic growth rate then r0 would be proportional to t to power half or square root of t which implies that r0 can be written as some constant B times t to power half. Where B is a constant which would include terms like the diffusion coefficient and other terms that we had seen in the last lecture. So this is parabolic growth. Similarly a nucleus formed at time tau will have a volume at time t greater than tau as 4 by 3 pi r tau cube. Where the subscript tau in this case indicates that the nucleus formed at time tau.

And what would be r tau in a very similar manner are tau for a constant growth rate would be v times the elapse time since tau. And which would be v times t minus tau, this is constant growth rate. While if we are assuming parabolic growth rate then are tau can be written as the constant B times t minus tau to power half. So this is parabolic growth rate. Now we have nucleation taking place continuously so what would be the number of nuclei forming in the time interval tau to tau plus zeta.

So the in time interval tau + zeta, the number of nuclei per unit volume would be the nucleation rate at time tau times zeta. And its unit would be per meter cube, where I is a nucleation rate and number of nuclei per meter cube per second. Now we have to combine all of these results to obtain the Avrami kinetics in the following way. So let us consider a system with volume V.

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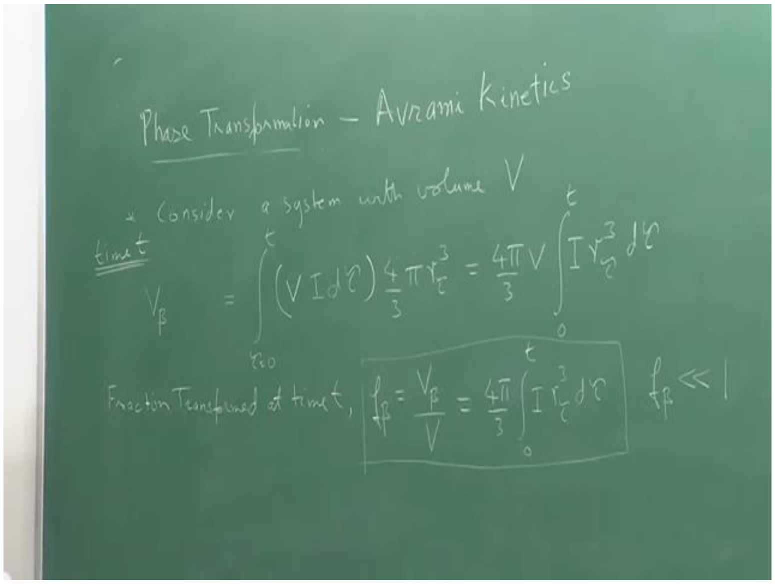

Phase Transformation – Avrami Kinetics

* Consider a system with volume V

time t

$$V_\beta = \int_{\tau=0}^{t} (V I d\tau) \frac{4}{3}\pi r_\tau^3 = \frac{4\pi V}{3}\int_0^t I r_\tau^3 d\tau$$

Fraction Transformed at time t, $\boxed{f_\beta = \frac{V_\beta}{V} = \frac{4\pi}{3}\int_0^t I r_\tau^3 d\tau}$ $f_\beta \ll 1$

So the total number of nuclei that will be formed in the time interval tau + d tau, would become V times I times zeta. And the nuclei that are formed at time tau they will have a volume 4 by each of those nucleus will have a volume 4 pi by 3 r tau cube. And we are looking at this situation at some time t greater that tau, in that case this would be the total volume of the nuclei at time t which was (form) all those nuclei which are formed at time tau this would be the total of all those nuclei.

Now as these nuclei are forming continuously from right from time t is equal to 0. We need to sum all of these contributions and summing all these contributions simply means we integrate this from tau is equal to 0 to sometime t and this would be the total volume of the beta phase that would form at time t, which I can take out the constant terms out which is 4pi by 3 V and leave everything inside the integral we would be left with I, the nucleation rate times r tau cube zeta.

This gives me that what is the fraction transformed at time t, so this is at time t. The situation fraction transformed at time t would be f beta. The fraction of beta that is formed which is V beta divided by the total volume of the system. So I divide the right hand side by V, I will be left with 4 pi by 3integral 0 to t I r tau cube zeta. So this is one expression we have got but there are some issues with this expression.

This works for fraction of the betas formed for very small fraction so very much less than 1. For larger fractions of beta this relationship will not be valid. Now why is that, I will give you some time to think about this. So at this point I will close this lecture and we will discuss it in the subsequent lecture as to why it works for small fractions and what do we have to do to make it work for large fractions, thank you.