Heat Treatment and Surface Hardening - II

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Lecture – 29

Growth rate variation with undercooling and kinetics of overall phase transformation

In this lecture we will look at growth rate as a function of undercooling. Delta T which is the temperature at which the transformation is taking place minus the transformation temperature T r. So, suppose we will consider the 2 cases of interface controlled growth and diffusion controlled growths separately.

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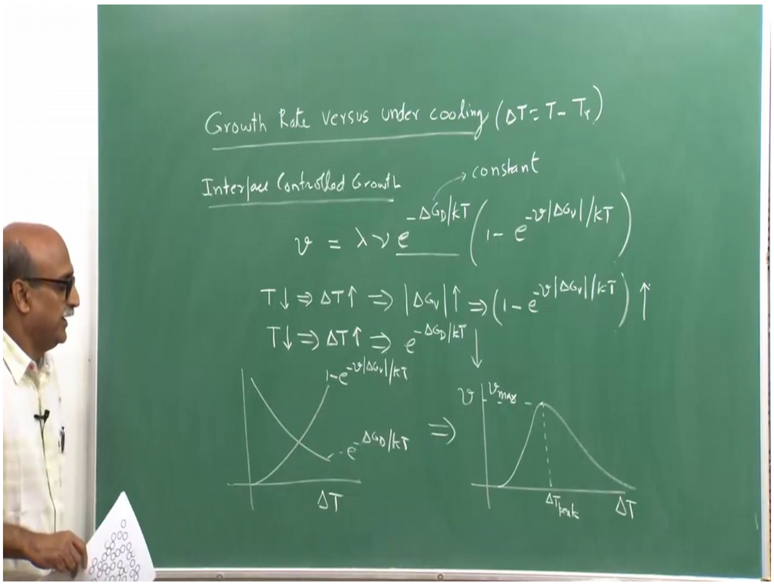

Growth Rate versus under cooling $(\Delta T = T - T_r)$

Interface Controlled Growth

$$\vartheta = \lambda \nu \underline{e^{-\Delta G_D/kT}} \left(1 - e^{-\vartheta|\Delta G_v|/kT}\right)$$

$\xrightarrow{}$ constant

$$T\downarrow \Rightarrow \Delta T\uparrow \Rightarrow |\Delta G_v|\uparrow \Rightarrow \left(1 - e^{-\vartheta|\Delta G_v|/kT}\right)\uparrow$$

$$T\downarrow \Rightarrow \Delta T\uparrow \Rightarrow e^{-\Delta G_D/kT}\downarrow$$

So, in the case of interface controlled growth as we had seen in the last lecture. The growth velocity v can be written as lambda nu e to power minus delta G D divided by kT multiplied by 1 minus e to power minus v delta G v divided by kT.

So, let us see what happens if I reduce the temperature at which growth is taking place. This results in a larger undercooling. And a larger undercooling would result as we had also seen in the previous lecture that the volume free energy change would increase. And if the volume free energy change increases then the term in the circular brackets 1 minus e to power minus v delta G v divided by k T would increase. So, this would have a contribution of increasing the growth velocity; however, we also have this term. If I look at reducing temperature increasing undercooling, and we can it is fear to assume that delta G D is fairly constant then increasing temperature in the denominator term here would result in this exponential term e to power minus delta G D by kT to go down.

So, here also as in the case of nucleation we have 2 terms with increasing undercooling one term increases the other term decreases. So, if I were to graphically illustrate this that as increasing undercooling. This is the term e to power minus delta G D divided by kT reduces while the second term 1 minus e to power minus v delta G v divided by kT this curve increases. And as a result combining both of these curves together.

We get the growth velocity or the growth rate as a function of undercooling to initially increase and then starts to reduce. With at some particular undercooling calling it as delta peak I get a maxima in the growth rate. So, just like nucleation in the case of interface controlled growth. We also have a peak in the growth rate like nucleation also we had a peak in the nucleation rate as we change the under cooling.

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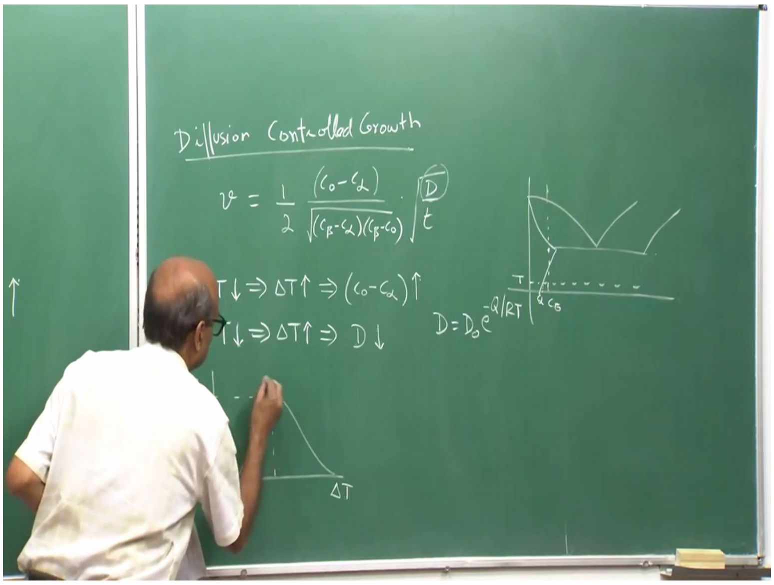

Let us also look at diffusion controlled growth, what happens in this case? In the case of diffusion controlled in the last lecture we had the growth rate written as v equals half c 0 minus c alpha the super saturation divided by square root of c beta minus c alpha times c beta minus c naught, multiplied by square root of D upon t. So, let us look at what happens here? As the temperature of transformation is reduced; that means, the undercooling is increased this result send, Let us say first let us look at super saturation.

If you look at the phase diagram it would be very clear to you that c naught minus c alpha would increase, let me quickly show this. This is c naught the chosen alloy and we are looking at growth rate at some particular temperature and this is c alpha we clearly as the temperature of transformation is reduced c naught minus c alpha would clearly increase. What other term is affected as the temperature is changed or the undercooling is changed? The coefficient of diffusion.

What is the coefficient of diffusion D? We all know that D equals D naught e to power minus Q divided by R T where Q is that active energy for diffusion T is a temperature R is the gas constant D naught is the frequency factor. And if temperature of transformation is reduced of the undercooling is increased, this would result in to the diffusion coefficient reducing. It would it fair to assume that Q and D naught are independent of temperature. And hence very clearly the exponential term e to power minus Q R upon R T s temperature is reduced would decrease because as the temperature is reduced the mobility of atoms also go down.

Here again we have 2 terms one term increasing the other term decreasing as the undercooling increases. And hence we get a very similar pattern of growth rate versus delta T that is it goes through a peak. So, what we have done? We have reviewed nucleation rate, we have reviewed growth and growth rate reviewed briefly the mechanism of both nucleation and growth and we have seen that in all cases whether it is homogeneous nucleation or heterogeneous nucleation the nucleation rate goes through a peak as undercooling increases.

In the case of a growth also whether it is interface control growth or diffusion controlled growth, the growth velocity also goes through a peak, yes the undercooling increases. So, at very small undercooling both nucleation and growth rates would be very low at very large undercoolings again both of them will be low and at intermediate undercoolings we will have a maximum in both nucleation and growth rate.

Now we would now combine these ideas of nucleation rate and growth rate to come up with the kinetics of the overall phase transformation.

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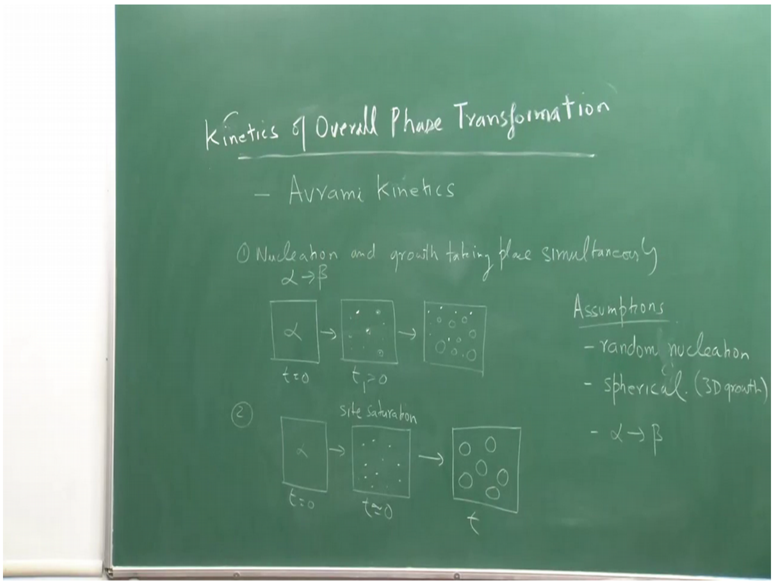

Kinetics of Overall Phase Transformation

- Avrami Kinetics

① Nucleation and growth taking place simultaneously
$\alpha \rightarrow \beta$

Assumptions
- random nucleation
- spherical. (3D growth)
- $\alpha \rightarrow \beta$

So, coming to the kinetics of overall phase transformation, we come to the well known kinetic theory called the avrami kinetics, this also have been dealt in great detail in part one of the course. So, avrami kinetics take both the growth rate and the nucleation rate combine them together to come up with a very neat relationship between the fraction transformed as a function of time.

Now one can imagine several scenarios. For example, one can consider nucleation and growth taking place simultaneously. So, there for a situation like where alpha phase is transforming to the beta phase at t is equal to 0, we only have alpha at some time t 1 greater than 0, I have some nuclei form and some of the older nuclei also have undergone growth. And as time progresses further I will have different nuclei which have nucleated at different times, grown to different sizes and fresh nucleation also take place.

So, this is one kind of scenario one can imagine. And in this we may have a constant growth rate or we may have a parabolic growth rate. We may have a constant nucleation rate or we could also have varying nucleation rate as well. A second scenario one can consider is at t equal to 0 we are the alpha phase, and within a very small fraction of time nucleation is complete. So, essentially at t equal to 0 itself more or less a nucleation is complete. Now this is a possibility in a situation where heterogeneous nucleation is taking place and there are limited nucleation sites for heterogeneous nucleation. So, those sites quickly get saturated.

So, there is site saturation taking place, and then after that these nuclei all the nuclei simultaneously grow. And this is a this is a picture at some time t. This way one can build many different scenarios, and they can be combined together into what is known as the avrami relationship. There are some assumptions involved in this avrami analysis. The key assumption as nucleation takes place randomly.

So, random nucleation. The nuclei that are formed are spherical. So, we are saying that is 3 D growth, but there are 2 D growth possible one D growth also possible. And alpha is transforming to beta in the form of precipitates.

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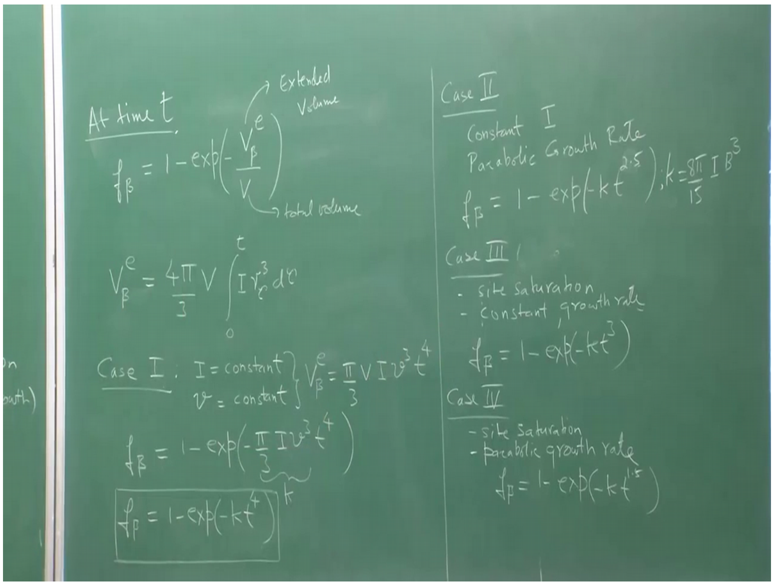

At time t

$$f_\beta = 1 - \exp\left(-\frac{V_\beta^e}{V}\right)$$

$$V_\beta^e = \frac{4\pi}{3} V \int_0^t I r_\tau^3 \, d\tau$$

Case I : I = constant, v = constant

$$V_\beta^e = \frac{\pi}{3} V I v^3 t^4$$

$$f_\beta = 1 - \exp\left(-\underbrace{\frac{\pi}{3} I v^3}_{k} t^4\right)$$

$$\boxed{f_\beta = 1 - \exp(-kt^4)}$$

Case II

Constant I

Parabolic Growth Rate

$$f_\beta = 1 - \exp(-kt^{2.5}); \quad k = \frac{8\pi}{15} I B^3$$

Case III

- site saturation
- constant growth rate

$$f_\beta = 1 - \exp(-kt^3)$$

Case IV

- site saturation
- parabolic growth rate

$$f_\beta = 1 - \exp(-kt^{1.5})$$

So, avrami relationship the avrami analysis shows that at time t, at time t the fraction of beta transformed is given by 1 minus exponential minus v beta e divided by v. Where v beta e is termed as the extended only. For a review of this you can go back to the to my lectures in the part one of this course, in which each of these terms and the extended term in particular is dealt in detail. And v is the total volume. Then it was also shown that the extended volume v beta superscript e can be written as 4 pi by 3 times the total volume times integral 0 to t.

So, v beta e is extended volume at time t the extended volume of beta. So, which is equal to 4 pi by 3 times the total volume into an integral term which integrates from 0 to t the nucleation rate I multiplied by the size of the size of the beta precipitate that is formed R tau which means the size of the beta precipitated formed at time t is equal to tau. So, R T

Q that is coming from the volume with the particle time d tau. So, you are integrating all the nuclear that are formed throughout continuously as the transformation is progressing. So, tau is wearing from 0 to the instead of time t.

Now, with just these 2 expressions we are dealt several situations. Instance case one of the avrami analysis which is the simplest case where we consider that I is a constant the nucleation rate is a constant throughout the transformation, and the growth rate or the growth velocity v is also a constant throughout the transformation. In this particular case, v beta extended the extended volume becomes pi by 3 times v times the nucleation rate times cube of the growth velocity small v multiplied by t to power 4. If we take this plug this into the into this expression f beta at and compute what would be f beta then f beta simply turn out to be 1 minus exponential of minus pi by 3 I times v cube times t to power 4. Where pi by 3 I and v cube as you can see these are constants, and they can be locked in one single constant k and hence f beta the fraction of beta transformed at time t is given by 1 minus exponential minus k T to power 4. This is a case where nucleation and growth are a constant. A second case, case 2.

Suppose we have constant nucleation rate, while the growth rate is parabolic. So, we have parabolic growth rate. In this case fraction of beta transformed is a function of time is given by 1 minus exponential minus k T to power fi by 2, or simply I can write this is t 2 power 2.5 where k is equal to 8 pi by 15 times a constant nucleation rate times a constant growth constant B and this growth constant B is coming from diffusion controlled growth, which includes terms like super saturation diffusion coefficient etcetera. A third case is a situation which we have which we discussed here, that site saturation has taken place and essentially at time t is equal to 0 all nucleation is complete.

So, I call this as a case where site saturation has occurred, and let us say along with this the growth rate is parabolic. In this situation the avrami relation becomes f beta equals 1 minus exponential minus k T to power 3, where k would be different from the con the constitution of k would be different from what we saw in case one and case 2. Now I am sorry this expression is not for parabolic growth rate, but this is for constant growth rate. The last case, case 4 we have site saturation, and we have parabolic growth rate. Here the avrami relation becomes 1 minus exponential minus k T to power 1.5. So, in all the 4 cases case 1, case 2, case 3, case 4 as you can see the time exponent is different.

So, looking at this and that can be various other combinations and one can analyze. And hence we can write the general form of the avrami kinetics.

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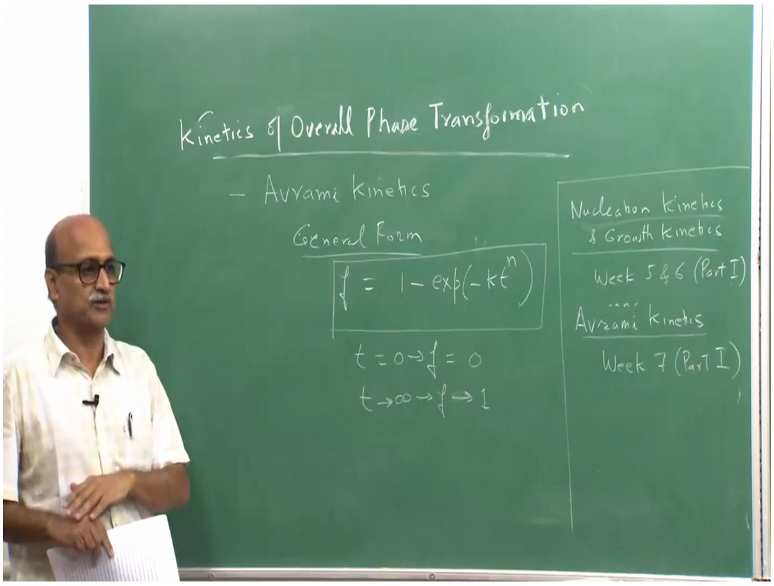

And the general form of the avrami kinetics is written very simply as f the fraction transformed from parent to the product phase, f is equal to 1 minus exponential minus k T to power n, where n and k are some constants which were governed by what kind of mechanisms are involved in nucleation and growth.

Now, all of this so far what we have done have been dealt in great detail this cases are also been done in great detail in part one of this course, and if you wish to review of all this material then you can go to the site which gives you the lectures for part one of the course. And for nucleation discussion on nucleation kinetics look at lectures. In fact, not just nucleation, but nucleation as well as growth kinetics. Look at lectures under week 5 and 6, part one of the course for a discussion on avrami kinetics look at lectures under week 7 of the part one of the heat treatment, and surface hardening of this course. Now what I intend to do and this would be the subject to the next lecture?

We will look at this avrami equation in some detail. First purely as a mathematical function, how this function varies how f varies as a function of time? What effect does the parameter n and k have on the function? And we will also look at the various we will also look at the overall what kind of a transformation characteristics we expect? Because as you know that both nucleation and growth vary may vary as a function of time. So, overall how this function varies with time? We will have a look at this very briefly. If you will notice when time t is equal to 0 the fraction transform as expected has to be 0, can when does 100 percent transformation take place? Well, that only takes place as time t tends to infinity then f tends to 1. For instance complete 100 percent transformation from alpha to the beta of x.

So, we will see how the fraction approaches one as time progresses. And then using the avrami kinetics we will come to the important topic of time temperature transformation diagram and then following that we will come to continuous cooling transformation right. We will stop here.