Heat Treatment and Surface Hardening (Part–1)

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Lecture Number 31

Diffusion controlled growth

So in the last lecture we were discussing interface control growth of a stable nucleus and now we want to examine diffusion controlled growth. Where we had mentioned something about diffusion control growth where diffusion processes will be involved in controlling the growth rather than the interface processes.

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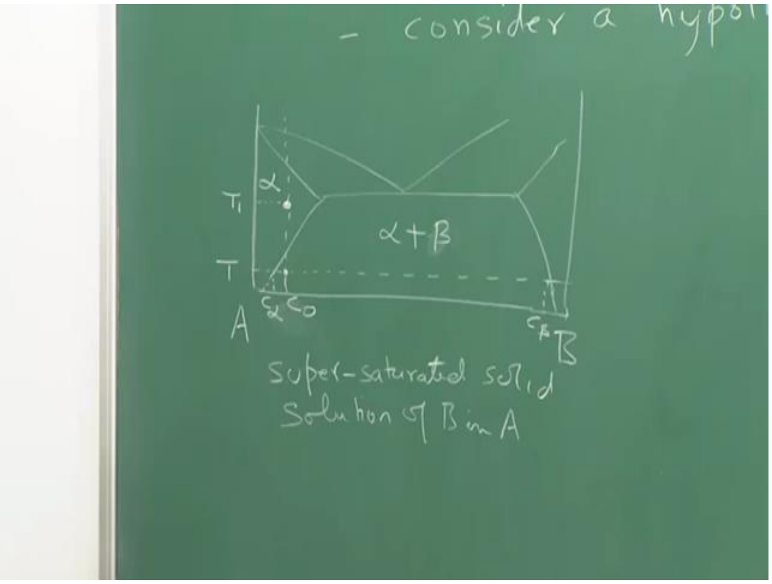

For this let us consider a hypothetical binary alloy. So the phase diagram for this alloy could be something like this. This is a alloy between two components A and B and let us say that we choose an alloy of composition C0 at a temperature let us say T1 we are in the single phase region is alloy and let the single phase region be alpha. Now imagine that we suddenly bring the temperature down to some temperature T. So we are at this point and we are now in the two phase alpha + beta region.

So what we have now is a super saturated solid solution of B in A. And hence this super saturated solid solution will tend to break and beta nuclei will form at this temperature T and once a stable nucleus form that phase will tend to grow then. So beta precipitates will grow and they should grow if you look at the equilibrium that is required, the alpha should have a composition of C alpha and the beta should have, beta precipitates that from should have a composition of C beta according to this phase diagram.

So this C alpha composition of alpha is in equilibrium with the beta of composition C beta. So we are talking about equilibrium kinetics here.

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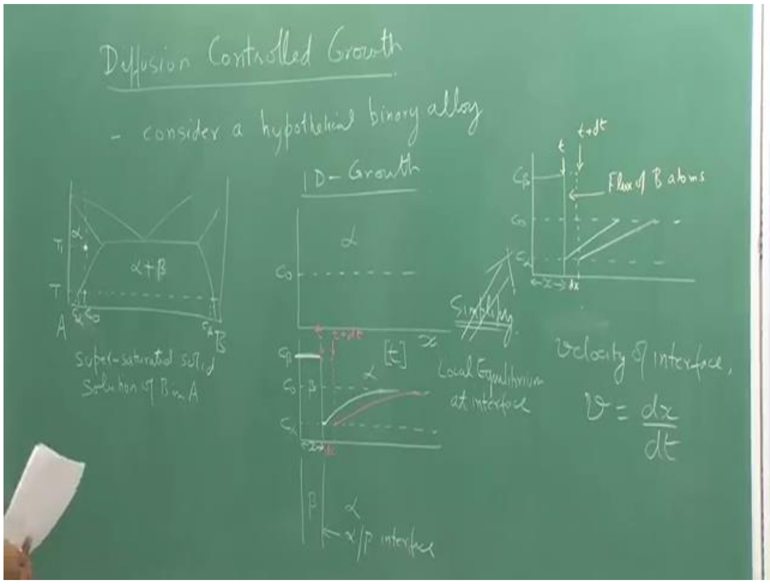

So let us try to model this as a one dimensional growth. So let us try to model this as one dimensional growth. So at time t is equal to 0 when we bring the alloy to temperature T, we (())(04:10) from T1 to T. So at time T is equal to 0 all one has is composition Cnot and we have only the alpha phase.

But as a nucleus forms and then it starts to grow we have a picture like this. So I have Cnot here. I have let us say slab of beta that is formed, so I have a slab imagine situation like this, this is my beta, this is my alpha, this is my alpha beta interface. And this is of thickness x and this is at some time t. This composition of the beta that forms, so this is beta out here is alpha this composition is C beta.

The equilibrium composition from the phase diagram. And let me mark the equilibrium composition from alpha here, so let us assume local equilibrium at the interface. If we assume local interface at the interface what does this mean that in this region the beta would have the (co) equilibrium composition of C beta. And out here alpha at the interface would have a composition equilibrium composition of C alpha.

And far away from this bets precipitate the composition will in inside alpha would be Cnot. So hence the composition or the concentration profile within the alpha would be something like this. So it will as one moves into the alpha away from the beta precipitate the concentration inside the alpha would increase and reach the starting alloy composition of Cnot. This is at some time [t].

Now after an elapse of time dt, so this is at time t. At time dt this beta precipitate will grow by a by an amount dx and the composition profile in the alpha would also change like this. So this so the interface at time t was here, interface at time t+dt has moved by a distance dx. So this is the situation that we have. Now in order to solve this in a kind of a simplistic manner just to show (how) what is the growth kinetics in this we make a (simp) we make a small simplification.

And the simplification is that instead of assuming a curve profile like this which actually is given by a complex function called the error function. We assume this profile to be a straight line. So let me redraw this picture, so simplify, so in this simplified picture the situation can be represented like this. This is Cnot, this is C alpha and within the alpha phase I have a linear concentration profile.

And when the after time dt the interface moves by a distance dx. So from a time t the interface is here, at time t+dt the interface is moved by a distance dx. The profile becomes something like this. And that way the interface will keep moving now what is our objective here. Our objective here is to find out the velocity with which this interface will move and how the distance or or the distance of the interface changes as a function of time.

So the velocity of the interface v is simply dx by dt. So our objective here is to find this and that would give us the growth kinetics. So we will look at this simplified picture and attempt to solve this problem. Now what are the processes that are happening remember this is diffusion controlled process that we are looking at so not interface controlled so the jumping of the atoms across the interface is a very fast process and therefore we can neglect it and the rate is essentially controlled by the rate of diffusion of atoms.

In this case one would need B atoms to diffuse, so there will have to be a flux of B atoms diffusing across the interface in order for this interface to grow or what this interface to move or for the precipitate to grow. So let us look at it what is the flux of B atoms, at what rate can B atoms move towards the interface that flux.

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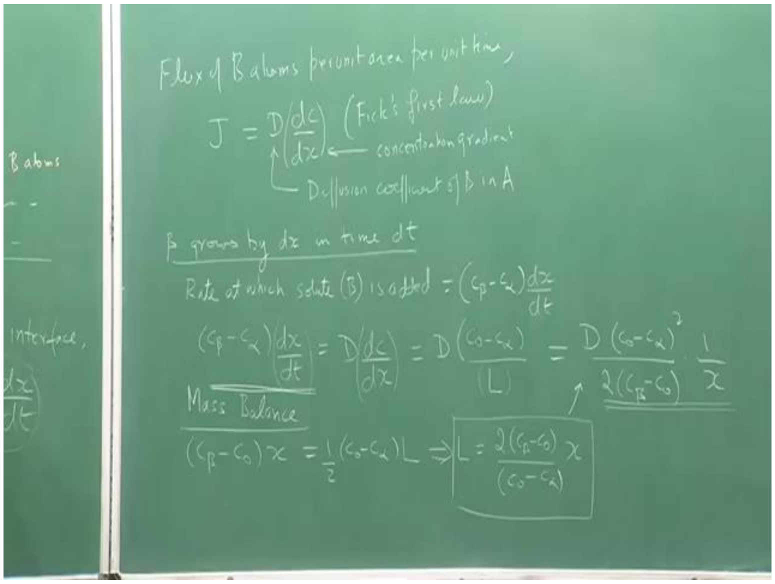

Flux of B atoms per unit area per unit time,

$$J = D\left(\frac{dc}{dx}\right) \quad \text{(Fick's first law)}$$

$\left(\frac{dc}{dx}\right) \leftarrow$ concentration gradient

D ← Diffusion coefficient of B in A

β grows by dx in time dt

Rate at which solute (B) is added $= (C_\beta - C_\alpha)\frac{dx}{dt}$

$$(C_\beta - C_\alpha)\left(\frac{dx}{dt}\right) = D\left(\frac{dc}{dx}\right) = D\frac{(C_0 - C_\alpha)}{(L)} = \frac{D\,(C_0 - C_\alpha)^2}{2(C_\beta - C_0)}\cdot\frac{1}{x}$$

Mass Balance

$$(C_\beta - C_0)x = \frac{1}{2}(C_0 - C_\alpha)L \Rightarrow \boxed{L = \frac{2(C_\beta - C_0)}{(C_0 - C_\alpha)}x}$$

So that I am talking about so flux of B atoms per unit area per unit time. If I call that as J, then this is given by D dc by dx. Now what is this relation, this infact is called the Ficks First Law which we will be discussing in subsequent lectures. For now let us take this relationship as it is D is called in this case the diffusion coefficient of B in A, dc by dx is the concentration gradient which is our simplified approach. If you look at this diagram the concentration gradient is a constant because we have assumed a linear profile of concentration.

So this is the rate at which B atoms are going to move per unit area per unit time. The velocity of the interface is dx by dt. So at what at what rate the essentially solute is getting added B atoms are getting added to beta. So we say that beta grows by dx in time dt. So then rate at which solute that is B atoms is added is equal to well look at the amount of B atoms that are added which is nothing but C beta minus C alpha.

But here the concentration was C alpha this is this concentration you can think in terms of moles per unit volume. So C beta minus C alpha multiplied by dx by dt, so the concentration let us say is in moles per unit volume multiplied by the velocity of the interface dx by dt and units for this would simply be we would become in terms of flux of B atoms in moles per unit area per unit time.

So this is the rate at which B atoms are getting added, this is the rate at which B atoms are arriving at the interface. And obviously for this rate and for this velocity the two have to match, have to balance. And therefore I can simply write C beta minus C alpha dx by dt to be equal to D dc by dx. Now let us look at it what is dc by dx go to my simplified representation here dc by dx is the slope of this line and that is nothing but Cnot minus C alpha divided by some length L, ok. So I write this as D times divided by L.

Now what do we do with this relationship we have we wanted to find this so this is a unknown quantity for us. C beta, C alpha we know from the phase diagram, I know D the diffusion coefficient of B in A. I can get from there is a huge database of values of this diffusion coefficient D or it can be obtained from experiment. So the other unknown quantity that is left is L.

I do not know what is this distance L. How do I find this distance L, well that is actually quite easy in this system there are no atoms going out of the system, no atoms coming into the system there has to be a mass balance atoms are conserved. So if the concentration have increasing here it is decreasing elsewhere. And hence if I look at this simple diagram, this area should be equal to this area for mass balance.

So from simple mass balance idea the two areas are equal so what is this area this is simply a rectangle and this area is C beta minus Cnot multiplied by x. And this is equal to the area of this triangle that is there which is half Cnot minus C alpha multiplied by L. So now I can write down an expression for L and that is simply rearranging the terms 2 C beta minus Cnot divided by Cnot minus C alpha multiplied by x. So this is the value of the unknown quantity L.

So if I substitute this in this I will get D times Cnot minus C alpha Cnot minus C alpha square upon 2C beta minus Cnot times 1 upon x. So this is the rate at which solute atoms are getting added and that is equal to this on the right hand side. Now this should be at this in fact is a fairly easily quantity to solve is a very simple differential equation.

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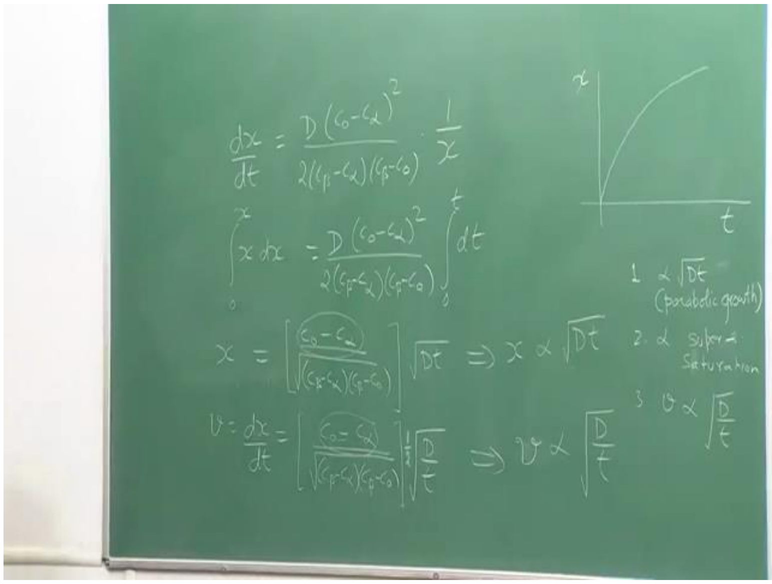

$$\frac{dx}{dt} = \frac{D(C_0-C_\alpha)^2}{2(C_\beta-C_\alpha)(C_\beta-C_0)} \cdot \frac{1}{x}$$

$$\int_0^x x\,dx = \frac{D(C_0-C_\alpha)^2}{2(C_\beta-C_\alpha)(C_\beta-C_0)} \int_0^t dt$$

$$x = \left[\frac{C_0-C_\alpha}{\sqrt{(C_\beta-C_\alpha)(C_\beta-C_0)}}\right]\sqrt{Dt} \Rightarrow x \propto \sqrt{Dt}$$

$$v = \frac{dx}{dt} = \left[\frac{C_0-C_\alpha}{\sqrt{(C_\beta-C_\alpha)(C_\beta-C_0)}}\right]\frac{1}{2}\sqrt{\frac{D}{t}} \Rightarrow v \propto \sqrt{\frac{D}{t}}$$

1. $\propto \sqrt{Dt}$ (parabolic growth)
2. $\propto$ super-saturation
3. $v \propto \sqrt{\frac{D}{t}}$

So let me rewrite this as dx by dt equals D times Cnot minus C alpha square upon 2 times C beta minus C alpha times C beta minus Cnot times 1 upon x.

Solving this integrating both sides xdx equals D times (Cnot minus C alpha) square upon 2 times (C beta minus C alpha) times (C beta minus Cnot) 0 to t dt. And this gives me x to be equal to Cnot minus C alpha upon square root of (C beta minus C alpha) times (C beta minus Cnot). Just simple rearrangement of terms and this gives me how x varies as a function of time.

So the interesting thing is this tells me that x is directly proportional to square root of Dt. Where D is a diffusion coefficient and t is the time. And now if I look at velocity which is dx by dt well that would be same constant term Cnot minus C alpha upon square root of (C beta minus C alpha) times (C beta minus Cnot) square root of D by t. And that is simply that x is directly proportional to not x but the velocity v is directly proportional to square root of D by t.

So one thing is clear that growth rate is not a constant at at a given temperature in fact it is going to be a function of time. And if I plot for example x versus t if I plot for example x versus t, I will get a curve like this. So as growth is taking place the rate at which growth is taking place is continuously reducing with time.

So in fact points to note here 1 that growth is proportional to root Dt and hence this is called parabolic (grow) growth. 2 if you look at this Cnot minus C alpha, this is super saturation when you suddenly quenched from T1 to T the alpha concentration was still Cnot. So growth is proportional to super saturation, so higher the super saturation higher is the rate of growth.

As you can see in the velocity also it is Cnot minus C alpha which is the super saturation. And third I have already mentioned velocity is proportional to square root of D by t which mean velocity reduces as time increases. Now why is velocity reducing or the growth rate is reducing with time.

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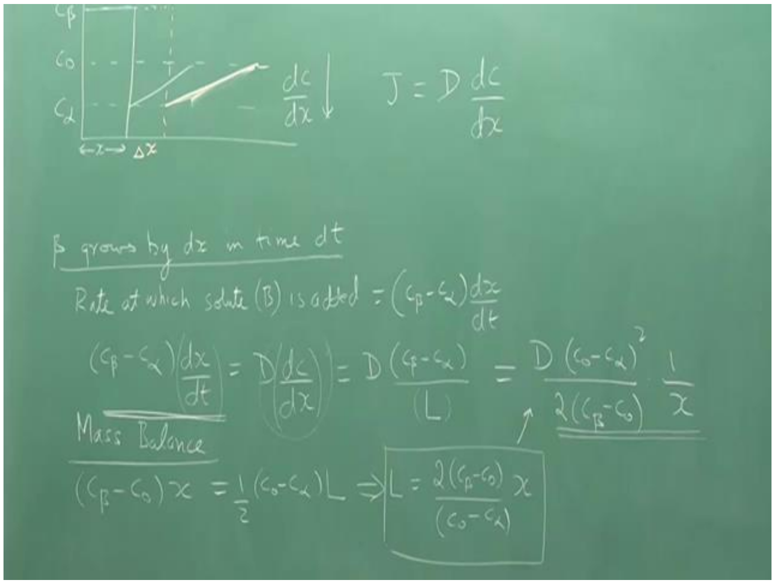

$$J = D\frac{dc}{dx}$$

β grows by dx in time dt

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Mass Balance

$$(C_\beta - C_0)x = \frac{1}{2}(C_0 - C_\alpha)L \Rightarrow \boxed{L = \frac{2(C_\beta - C_0)}{(C_0 - C_\alpha)}x}$$

This could be understood if I relook at this diagram that as the beta precipitate is growing so I have Cnot, I have C alpha, out here I have C beta this is my beta has grown by x and the concentration profile is this. Now as growth take place let us say it has grown by delta x the profile would become something like this. The slope this is a straight line that this slope will reduce, that is dc by dx reduces with time.

As dc by dx reduces with time, remember the flux which is given by diffusion coefficient time gradient of concentration. So if the gradient of concentration is reducing the flux of B atoms are reducing. So if I look at this, this is reducing and hence dx by dt has to reduce. So this is the reason why growth is reducing with time. So this is what in this lecture what we have discussed is diffusion controlled growth.

So in the last in this lecture in the previous lecture we have discussed 2 mechanisms of growth, the interface control growth and diffusion control growth. Interface control growth tells us that the growth rate will be constant for a given undercooling while in the diffusion control growth, growth rate is not a constant for a given undercooling infact it keeps reducing as a function of time.

With this we finish our discussion on kinetics of growth and what we have done in the last several lectures is we have understood nucleation rate and what factors control it. We have understood to some extent in the last two lectures, growth rate the two together will have to be considered to get overall transformation kinetics of phase transformation. So with this I stop here in this lecture, thank you.