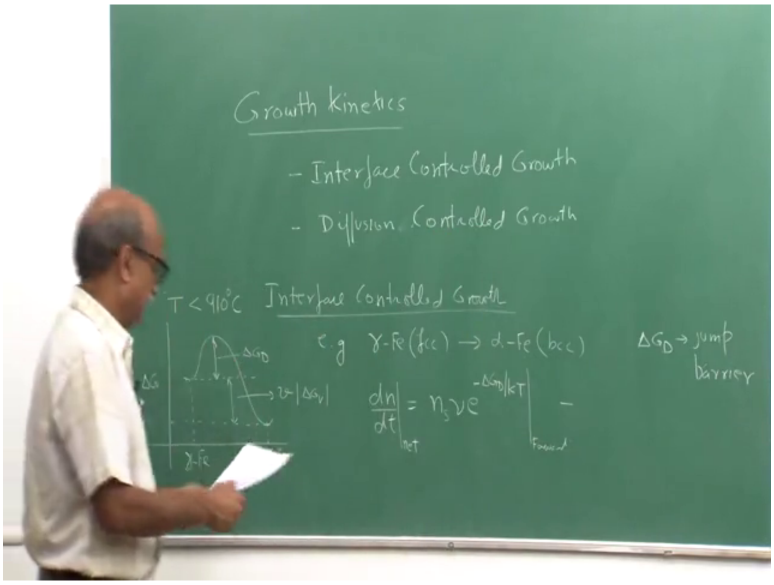
Heat Treatment and Surface Hardening - II
Prof. Kallol Mondal
Prof. Sandeep Sangal
Department of Material Science & Engineering
Indian Institute of Technology, Kanpur

Lecture – 28
Growth kinetics cont …

We, continuing with our discussion from the last lecture on growth kinetics.

(Refer Slide Time: 00:19)



We had divided growth kinetics into 2 processes depending on whether long range diffusion is a rate controlling process, or if the long range diffusion is not a rate controlling process then we get what is known as interface controlled growth and if the long range diffusion is the rate controlling process then what we call as the diffusion controlled growth.

So, today we will review what we are done in part one of this course the interface controlled growth first. So, in interface controlled growth for example, gamma iron which is a phase centered cubic structure on cooling below 910 degrees centigrade transformers to alpha iron which is a body centered cubic structure. So, this is a single component system in which a growth of a alpha nuclear that forms in gamma iron, then grows we are the mechanism of interface control growth that we had seen in the last lecture.

Now, in order to get to the growth kinetics under interface control we can look at the what is the barrier involved in jumping of an iron atom from the gamma side to the alpha nucleus, the alpha stable nucleus that is formed for it to grow. So, the barrier to jump is delta G D. So, this is the jump barrier from an for an iron atom to jump from the parent gamma phase to the product alpha phase. If I look at the overall changed free energy that is involved in the process of growth from gamma to alpha.

So, let us look at this diagram and understand this. This is gamma iron and this is alpha iron which is at a much lower energy state than gamma iron, and that is why the ferrite for other the body centered cubic iron should form from the gamma phase if the temperature is less than the transformation temperature that is 910 degrees centigrade. So, what is the barrier to jump for an atom from the parent gamma phase to the product alpha phase. This barrier is what we have called as delta G D.

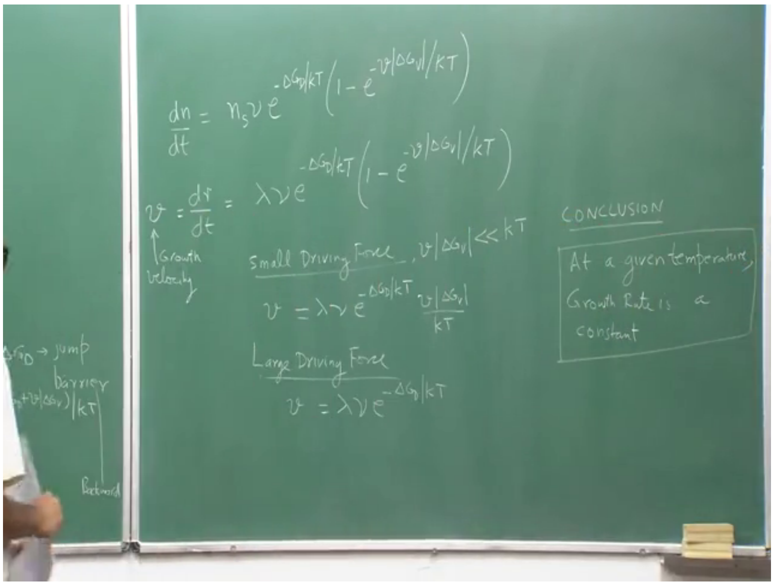
So, this is the energy hill that is involved for an iron atom to jump over this barrier and beyond this it will simply go down to a much lower energy level. And what is the difference between the energy level of gamma iron and alpha iron that is simply we already know is the volume of the product phase multiplied by the absolute value of the volume free energy change. So, hence clearly the thermodynamics favors the jumping of atoms from gamma to alpha. Now if you wish to now compute or other estimate or calculate what is the rate or what is the net jump rate of atoms from gamma to alpha.

We can figure that out and let us call that as d n pi d t the net jump rate the net jump rate would be the difference between the forward jump rate of atoms from gamma to alpha minus the backward jump from alpha to gamma. So, for atoms to jump from gamma to alpha the energy barrier is only delta G D while for the atoms to jump from alpha to gamma the energy barrier is some total of delta G D plus v times the absolute value of delta G V.

So, writing this down n s which is the number of atoms that is surrounding the alpha phase, as we had seen in the formation of the stable nuclear also. N s is the number of atoms that is surrounding in the gamma iron surrounding the alpha iron. These are the atoms that can jump from gamma to alpha multiplied by the by frequency multiplied by e to power minus delta G D by k T. We had already seen such kinetic expressions being written in the last lecture. So, this is the forward rate. There will be some number of atoms that can jump from alpha to gamma, but the energy hill is much bigger for them. And hence the backward rate would become n s nu e to power minus delta G D plus v times delta G V divided by k T, this constitutes the backward rate.

So, the difference would give you the net jump rate in the forward direction from gamma to alpha. So, just simplifying this a little bit.

(Refer Slide Time: 07:32)



D n by d t now can be written as n s nu e to power minus delta G D divided by k T multiplied by I taken this term common, I can write this as 1 minus e to power minus v delta G V divided by k T. Now instead of writing this rate in terms of number of atoms jumping from gamma to alpha we would write to convert this into a growth rate in terms of a measure of distance, and hence if I consider a spherical nuclei which is growing. Then it is radius of change which is d r by d t which you can we can also call it as the velocity of transformation in terms of meters per second. So, d r by d t can be written as in a very similar way lambda nu e to power minus delta G D divided by k T and the same bracket term, 1 minus v to power minus v delta G V divided by k T. Here lambda is essentially atom to atom distance.

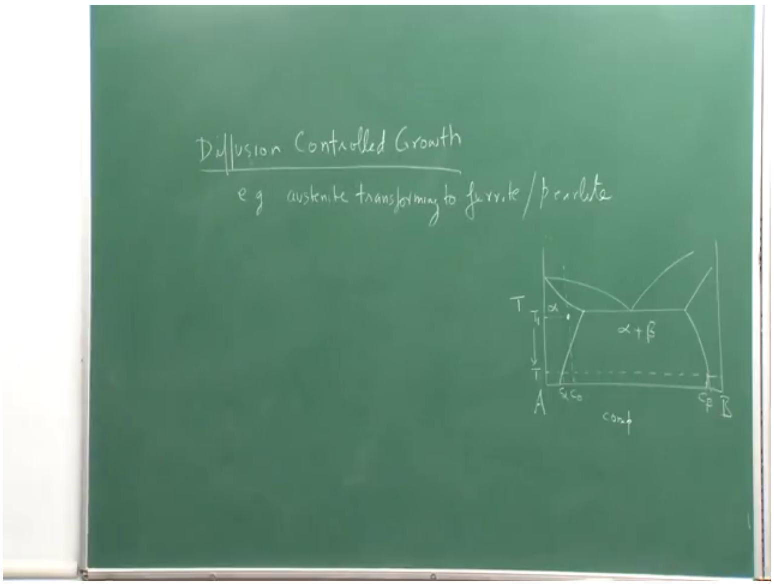
And hence we are able to now right growth in terms of a growth velocity. So, this could be considered as growth velocity. If I look at this expression we can try to see, what happens for small driving force? Small driving force means that the term v delta, G V is much, much smaller than k T. Now this if you are had a very small driving force then I can simplify this write the velocity or the growth velocity. S simply lambda nu e to power minus delta G D divided by k T times velocity multiplied by delta G V upon k T. That is the term in the brackets can be approximated by v delta G V upon k T.

For large driving force the growth velocity becomes for large driving force this term becomes very small much smaller than 1, and hence that this term can be neglected and hence the growth velocity simply becomes lambda nu e to power minus delta G D divided by k T. Now looking at any of these expression whether this expression or this expression or this expression.

There is one conclusion that we can draw directly from here and that is that a growth velocity is not a function of time. So, for a given temperature growth rate is a constant. So, one major conclusion regarding interface controlled growth is that at a given temperature, growth rate is a constant. Now let us examine we have seen we have briefly reviewed.

How interface controlled growth works. Now let us examine and compare this with diffusion controlled growth, which is a little bit more involved as you shall see.

(Refer Slide Time: 12:56)

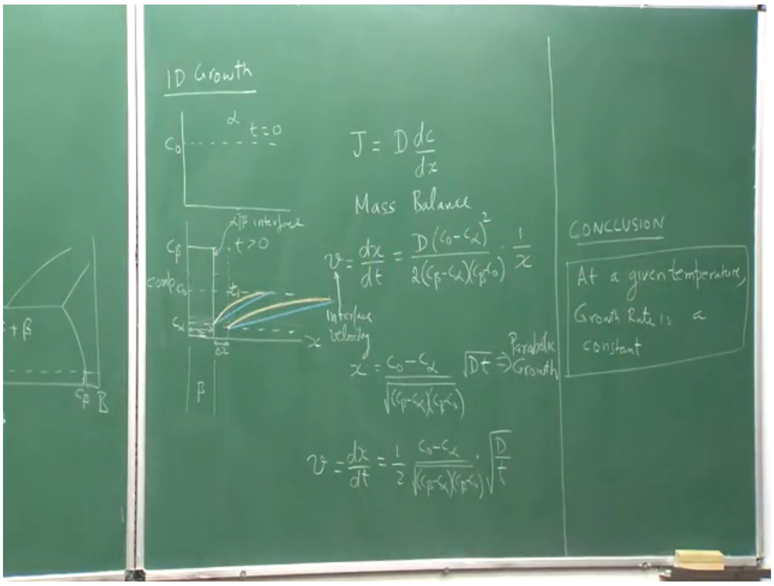


So, looking at Diffusion controlled growth. So, examples of this one important example of this is austenite transforming to ferrite or pearlite. So, for that matter diffusion controlled growth will be present in may los systems, where long range diffusion in the parent matrix would become important. So, consider a hypothetical binary system A B. Let us say that we have alloy A B of composition c naught on this phase diagram. And we start we hit this alloy at to a temperature of T 1.

So, that the entire sample is a single phase sample of let us say alpha phase. We suddenly quench the sample or we rapidly lower the temperature of this sample to some temperature T. So, we go from T 1 to t very rapidly effectively in no time. As a result we reach this point; however, no transformation is taking place and we get a supersaturated solid solution of B in A, and let me mark out the equilibrium composition that are expected at T we expect to get an alpha phase of compositions c alpha and beta precipitation of composition c beta. So, this is the 2 phase alpha plus beta phase field.

Now looking at this system. We have at time T is equal to 0 let me draw this diagram separately that if I look and I am going to look at one dimensional growth of beta in alpha.

(Refer Slide Time: 16:25)



So, at time T equal to 0 when I rapidly change the temperature from T 1 to t I have alpha everywhere of composition c 0. After sometime T, I will get a following situation, I will get some beta that is formed of composition c beta. So, I have a linear growth of the beta phase, and beyond this is the distance x. And it has grown by a distance x for some time T greater than 0. Let me also mark out if this is the composition c naught, let me also mark out the composition on this diagram of c alpha.

Now what we expect is that in this region beta will have the equilibrium concentration dictated by the phase diagram of c beta. Very far away from this alpha beta interface my composition is going to be c 0, but locally we will have equilibrium; that means, we expect at the interface the alpha composition to be of c alpha. N s be go away from the interface into the alpha phase the composition will move towards c naught. And I can draw this concentration profile within the alpha phase something like this. So, this is at some time let us say T 1. Now after some more time has elapsed the beta will grow further, by let us say or distance delta x.

Hence now say composition at this this new interface of alpha beta. The local equilibrium will hold and the alpha composition at the new alpha beta interface would be c alpha. But as we move into the phase they would be a concentration will move towards, and well within into the alpha phase we will again reach c naught. So, that is how the beta phase will keep growing and the concentration profiles will also change. Now once we have this this picture this model of the growth of beta through a diffusion controlled process, which means that now B atoms have to diffuse over long range from within the alpha phase to the interface, and then those atoms have to jump across the interface to enable beta to grow into the alpha.

So, essentially the growth is going to be controlled by the time it takes for the solute atoms to move from large distances in the alpha phase right to the alpha beta interface. So, what is that how can I calculate at what rate they would be that atoms will be moving that to simpler given by the fixes first law that the flux of B atoms in the alpha phase would be given by the diffusion coefficient d times the concentration gradient in the alpha phase dc by dx. Now these profiles the concentration profiles that are shown here in this model, these are the actual concentration profiles that are expected. And their functional dependence can be obtained. In fact, the solution to this concentration profile is the error function.

Now, that makes the calculation derivation on this model to be quite complicated, hence we make a very simplifying assumption. And that simplifying assumption is as follows, that instead of taking these kind of concentration profiles we assume that the profiles are can be assure to be linear in the alpha region like this. There for the flux j then becomes a constant at all x, and that makes the subsequent derivation very, very simple at end. And that simple model also gives us very close to the actual picture that is showed in the model. So, using this the flux equation and also knowing that invoking mass balance that no mas is added or lost by the system, using these 2 we arrived at the following expression for velocity of the interface.

So, velocity of the interface v, v is equal to dx by dt is given by the diffusion coefficient d times c 0 minus c alpha square upon 2 times c beta minus c alpha times c beta minus c naught times 1 upon x. This equation was derived in detail in the lecture or the part one of this course. We integrate this we arrive at the following expression for x how x or the thickness of the beta phase changes as a function of time, and that is given by c naught minus c alpha divided by square root of c beta minus c alpha times c beta minus c naught times square root of d t.

This shows this being a constant at a given temperature the concentration she c naught c alpha c beta are already taken from the phase diagram and they are fixed. X is directly proportional to square root of dt. And hence this is also called as called as a parabolic growth. And then the interface velocity v dx by dt becomes if we simply differentiate this as half c naught minus c alpha divided by square root of c beta minus c alpha times c beta minus c naught times square root of d upon t; that means, now the velocity is proportional to square root of the diffusion coefficient divided by time. This equation very clearly shows in contrast to the interface controlled growth that at a given temperature growth rate was a constant.

If interface controlled growth mechanism is present; however, in the case of the diffusion controlled growth velocity clearly is the no longer constant, but it varies as a function of time. And In fact, it gradually reduces as the transformation or the as the growth progresses. So, this is a very important factor to realize that the 2 mechanism a interface controlled growth rate diffusion controlled growth gives us a growth which is dependent on time. What else what other conclusion can I draw from this expression that I have written. If I look at c naught minus c alpha this is at a temperature t c naught minus c alpha represent the super saturation at time T is equal to 0. That is the growth velocity is directly proportional to the super saturation, higher the super saturation we expect higher the growth velocity.

Now, the conclusion that the growth rate reduces as a function of time why should that happen of course, mathematically this comes out that it reduces as time progresses, but that can also be seen from this model of diffusion controlled growth, this is at sometime T 1 this profile this profile is at sometime T 2 which is greater than T 1. If I look at the 2 slopes as time progress the slope of the concentration profile or the concentration gradient slope is reducing if I look at the fixes equation which gives me the flux. So, flux is directly proportional to the concentration gradient. Hence as time progresses the concentration gradient dc by dx is reducing.

So, flux is reducing and therefore, the growth velocity is reducing. Now in the next lecture we will briefly look at how under cooling will affect the growth rate that as I change the temperature to different temperatures under cooling, how under cooling affects the growth rate that we will have a look and then we will look at the overall kinetics of phase transformation. We will stop here.