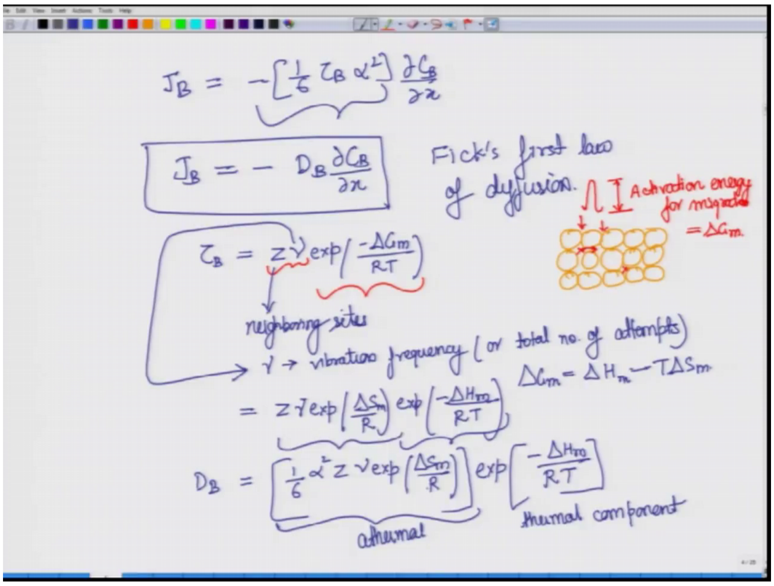
Defects in Crystalline Solids (Part-I)

Prof. Shashank Shekhar
Department of Materials Science and Engineering
Indian Institute of Technology, Kanpur

Lecture - 13
Non-Steady State Diffusion

So, let us get back to where we left last time.

(Refer Slide Time: 00:20)



$$J_B = -\underbrace{\left[\frac{1}{6}\tau_B\alpha^2\right]}\frac{\partial C_B}{\partial x}$$

$$\boxed{J_B = -D_B\frac{\partial C_B}{\partial x}}$$

Fick's first law of diffusion.

Activation energy for migration $= \Delta G_m$

$$\tau_B = \underbrace{z\nu}\,\exp\underbrace{\left(\frac{-\Delta G_m}{RT}\right)}$$

$z \rightarrow$ neighboring sites

$\nu \rightarrow$ vibration frequency (or total no. of attempts)

$\Delta G_m = \Delta H_m - T\Delta S_m$

$$= \underbrace{z\nu\exp\left(\frac{\Delta S_m}{R}\right)}\underbrace{\exp\left(\frac{-\Delta H_m}{RT}\right)}$$

$$D_B = \underbrace{\left[\frac{1}{6}\alpha^2 z\nu\exp\left(\frac{\Delta S_m}{R}\right)\right]}_{\text{athermal}}\exp\left[\frac{-\Delta H_m}{RT}\right]$$

thermal component

So, we derived this relation for flux, diffusion of flux and this has a form like this minus and this 1 by 6 tau B alpha square and then it is multiplied by concentration gradient and since the flux is going in the direction where the concentration is decreasing. So, there is a negative sign and together we have lumped it together to call it D B, the term is D B.

Now, there are a few more things that we need to learn at this stage, one is, what is this tau B? That we have already described as jump frequency. But this jump frequency can be further expanded to write like this; z into mu into exp minus delta G m by RT; where does this come from? So, let us say there are there is a site. So, let us draw. So, this is some material and over here. So, we were talking about interstitials. So, there are some interstitials and let me draw it with different colour. So, there is one interstitial over here let us say one interstitial over here.

So, now let us say this interstitial moves from here to over here. So, as you can see that this has lowest and this is a low energy position, this is a low energy position. Somewhere over here it will have to have higher energy and this will be your activation energy for migration. So, this is what I have tried to schematically draw here is the energy plot when it moves from this position to this position.

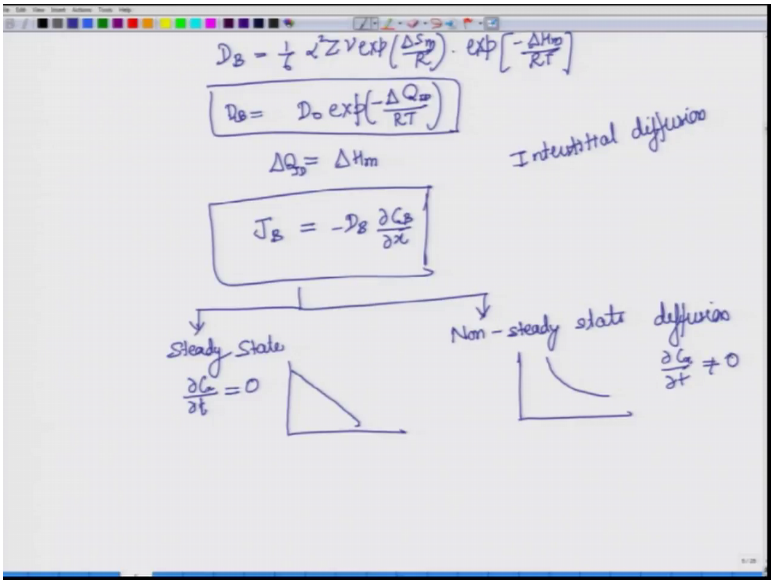
So, this is a one minima this is another minima and it has to go through energy activation energy, meaning it must be provided this much energy, before it can migrate and this is the term delta G m. And we can therefore, write it as pre x some pre exponential factor times exp this delta G m. Now what this term will denote is the number of the fraction of jumps that will actually take place; meaning, if delta G m is if the energy for migration is delta G m, then the total number of vibrations that will actually result in migration is this fraction.

Now, fraction of what? So, this is where this first term comes into picture this is z, this is the coordination number or site, neighbouring sites where this atom can move. So, this is telling you the number of look sites where it can move. What is nu? Nu is the in effect vibration frequency or that is total number of attempts you can say. So, nu is in any particular direction. So, in for one particular site it is nu. So, it is for z neighbouring sites it is z nu.

So, this is the z nu is the total number of attempts out of this fraction is that results in successful jump. So, that is where we get this relation tau B and now if we expand delta G m equal to delta G delta H m minus T delta S m we get, we can actually differ parts basically we can put together the thermal component and a thermal component separately and therefore, we will have something like this and this is z. So, this is the thermal component, this hole is the eternal meaning it does not get influenced by temperature.

And now when we put this back over here, what we get is that D B is equal to 1 by 6 alpha square z nu exp delta S m by R. So, this is like I said a thermal component and to it you multiply the thermal component, winning the one which will get affected or which denotes how this value will change with temperature. So, this is your. So, no matter what is the temperature, this value is supposed to stay like this.

(Refer Slide Time: 05:57)



So, let me rewrite this over here in a new page. So, this comes out 1 by 6 alpha square z nu exp delta S m by R, exp minus delta Hm by Rt, which can now be written like something like this D naught exp minus delta Q 1 d by R T where delta Q is equal to delta H m. So, in this particular case which is the interstitial diffusion, which is written as id. So, delta Q I d is equal to delta Hm meaning the activation enthalpy for migration this is equal to delta Hm and you would see why we are writing it like this because in the next part it will get changed.

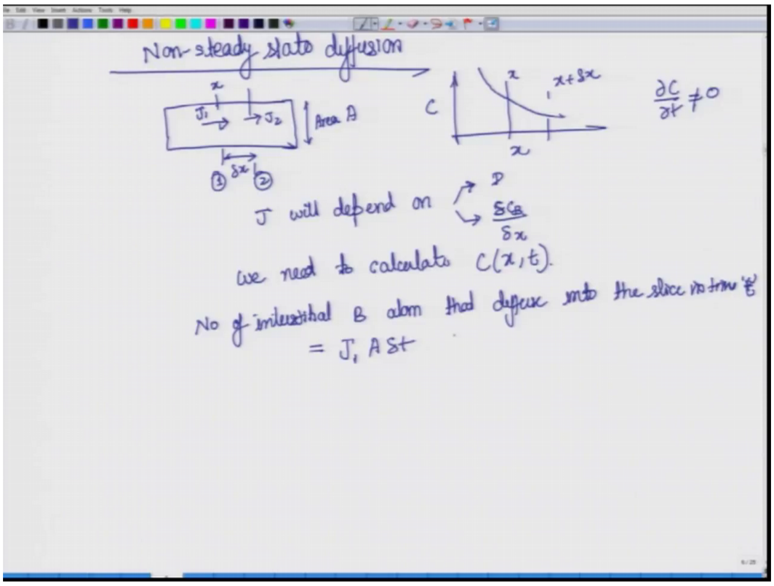
So, this is your form of the relation D B D B which is used to define the flux you remember. So, now, these are some 2 important relations with respect to interstitial diffusion. So, these are our relations which define interstitial diffusion.

Now, next thing that we so, we have seen how this interstitial defect has led to diffusion, and we have derived a relation for this and this is how it comes down to. So, this is the flux the flux is proportional to the negative of of concentration gradient, and there is a proportionality constant this proportionality constant has a thermal component and thermal component. So, this is how it looks like. And the activation energy or that enthalpy is. So, activation energy is related to this D B and when we when we separate, the entropy term and the enthalpy term this is how this relation would look like.

Now, let us look at 2 different conditions for this one is steady state, and one is non steady state diffusion. So, when we say steady state, what does it mean it means that del

C by at any particular x by del t is equal to 0. Meaning the concentration at that particular x is not changing with time. And you will see that this will only be possible when you have a concentration gradient like this it has to be a straight line like this. However, if you have a concentration gradient something like this, will show that this is a del C by del t here is not equal to 0 which is what is called as non steady state.

(Refer Slide Time: 09:24)



Non-steady state diffusion

$$\frac{\partial C}{\partial t} \neq 0$$

J will depend on → D, → $\frac{\delta C_B}{\delta x}$

we need to calculate C(x, t).

No of interstitial B atom that diffuse into the slice in time 'δt'

$= J_1 A \delta t$

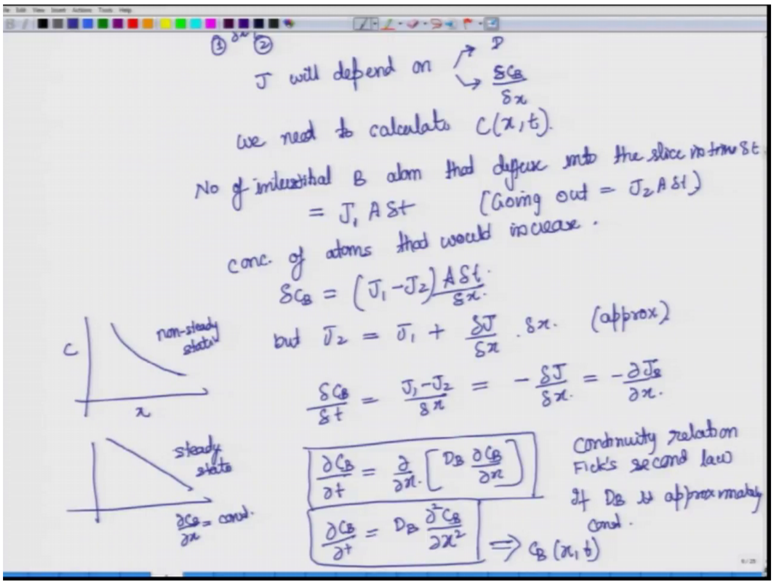
So, now let us move ahead to describe this non steady state diffusion. So, let us say this is a bar and for this the concentration gradient is given like this, cx, concentration is moving like this is we are talking about x, this is at some distance x plus delta x similarly we will draw here this is some distance x and this width is delta x. So, we will call this plane 1 we will call this plane 2.

So, let us say the flux of atoms across plane 1 is given as this J 1. So, the flux of atom across plane 2 and we can call it something as J 2 and let us say the area because we will need this which will get cancelled out eventually, but let us say that for now this area is a. So, now, this j we know will depend on 2 things, one is D, and the other is right now I am not writing in differential form because let us say we are talking about a little longer width. So, we are putting it like this delta cb by delta x.

Now, what we need to calculate we have already said that this is a condition where del C by del t is not equal to 0 therefore, we need to find or calculate C as a function of x and t. Now let us say that number of interstitial b atom that diffuses into the slice in this small slice is jJ 1 a delta t. So, J 1 is per unit area per unit time, and if we are giving it time t and we are talking about this area a then therefore, the number of interstitial atom that gets into this is that diffuse into the slice in time t. So, we have already described some time ok.

So, flux is number of atoms per unit area per unit time. So, we are talking about not number of atoms. So, we have to find what is the area and we have to find what is the time. So, we have both of the quantities here. So, this is J 1 A delta T ok.

(Refer Slide Time: 12:29)



① ②

J will depend on $\nearrow D$, $\searrow \frac{\delta C_B}{\delta x}$

we need to calculate $C(x,t)$.

No of interstitial B atom that diffuse into the slice in time δt

$= J_1 A \delta t$ [Going out $= J_2 A \delta t$]

conc. of atoms that would increase.

$$\delta C_B = (J_1 - J_2) \frac{A \delta t}{\delta x}.$$

but $J_2 = J_1 + \frac{\delta J}{\delta x} . \delta x.$ (approx)

$$\frac{\delta C_B}{\delta t} = \frac{J_1 - J_2}{\delta x} = -\frac{\delta J}{\delta x} = -\frac{\partial J_B}{\partial x}.$$

$$\boxed{\frac{\partial C_B}{\partial t} = \frac{\partial}{\partial x}\left[D_B \frac{\partial C_B}{\partial x}\right]}$$

Continuity relation
Fick's second law

If D_B is approximately const.

$$\boxed{\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2}} \Rightarrow C_B(x,t)$$

A So, nd similarly concentration of atoms that would increase is equal to; now if something is going in. So, similarly we can find what is going out and that will be equal to; so, going. So, I have missed this part this is going out will be equal to J 2 A delta t.

So, the concentration of atoms that would increase; so, the obviously, the number that is coming in is higher, because the consan there the concentration gradient is higher at x and lower at delta x x plus delta x. So, going in is equal to J 1 A delta t going out is equal to J 2 delta t where J 2 is smaller; so, now, J 1. So, the number of atoms that has increased over time is equal to J 1 minus J 2 a delta t.

But we know that J 2 is equal to and say sorry and we are talking about concentration. So, we have to divide by delta x. So, J 2 is equal to J 1 plus del j by del x into del x this is again approximate now putting this over there is del C B by del t putting the del t over here from this side to this side and J 1 minus J 2 this is to be divided by delta x.

So, we can get J 1 minus J 2 by delta x from here, which will be equal to minus del J by del x. Because we have divided by del x. So, this is over here which is now if we take it in the limiting case, then this will become minus del J B by del x or in other words del C B by del t is equal to del by del x we instead of J B we will put the what the relation we already know from first law which is equal to C B del C B by del x.

Now, this is what is called as continuity relation which is also commonly known as Ficks second law. Now here we can make an approximation that this quantity dV is, if dB is approximately constant through the range, then we can further simplify it to write it like this. So, both these relations would be called the continuity relation. Basically what it is saying is that the concentration overall concentration of the or the total number of atoms remain constant.

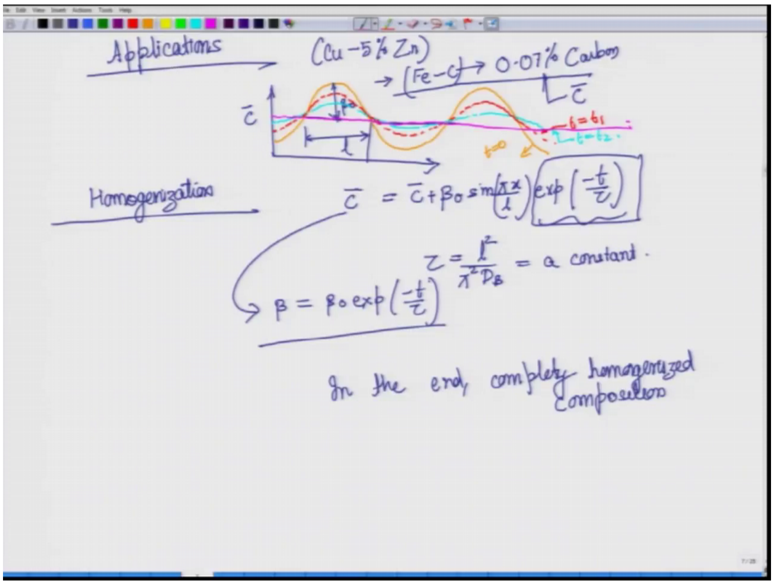
So, there is a particular flow of atom and we are just maintaining the continuity of this. So, you can see that where we started from we just started through that there is a concentration which is changing with x and therefore, there are 2 different fluxes at 2 different axes from there we get a relation like this, and what we are able to see is that therefore, del C B, but we can we are in a position to find a relation for concentration in terms of x and t.

So, this is in the differential form and when you solve it depending on the initial condition and the final conditions, then you will be able to get this will give you C B as a function of x and t. So, this will have to be solved depending on initial and final conditions.

So, we the only thing that we have talked about here is the change in concentration. Now if you put this as a straight line what will happen? Del 2 C B by del x what will this become this quantity will become 0 del C by del x will become constant and del 2 C B by del x square will become 0 and therefore, you will see that del cv by del t is comes out to be 0. So, as I said that the steady state will only be possible when you have a straight line like behaviour for concentration. So, this is the steady state when del C B by del x is equal to constant, and whenever there is a curvature then you would know that it is non steady state.

Now, let us talk about some applications. So, now, we have seen the relation for Fick's first law and Fick's second law, which were derived assuming interstitial diffusion we will also talk about the other kind of diffusion, which is when you have substitutional atoms, but before that let us look at some applications.

(Refer Slide Time: 18:23)



Applications → (Cu-5% Zn)

→ (Fe-C) → 0.07% Carbon

$\bar{c}$

Homogenization

$$\bar{c} = \bar{c} + \beta_0 \sin\left(\frac{\pi x}{l}\right) \boxed{\exp\left(\frac{-t}{\tau}\right)}$$

$$\tau = \frac{l^2}{\pi^2 D_B} = \text{a constant}.$$

$$\beta = \beta_0 \exp\left(\frac{-t}{\tau}\right)$$

In the end, complety homogenized composition

Now, let us say you have cost an alloy, let us talk about a simple alloy like a copper zinc, which is supposed to be and we are talking about 5 percent zinc. Up to 30 percent zinc you are supposed to get single phase, but let us say that because of the casting condition or because of difference in the weight atomic weight of the 2, there is certain compositional difference from point to point and just as a matter of understanding or to understand this concept in a better way, we will assume that this concentration, let us say we are talking about zinc concentration then the zinc concentration should have been 5 percent which is given by c bar, but because of different conditions different solidification condition or like I said because of the mask conditions there may be some segregation and therefore, you end up with a constitution a compositional variation like this.

So, this is not desirable, we would have want that when you say copper 5 percent zinc, it is uniformly homogeneously distributed and therefore, comes the concept of homogenization, how does this homogenization takes place? It takes place by diffusion. So, right now copper and zinc they are not actually interstitial diffusion. So, what I will do is I will replace this example with let us say iron carbon where let us say we were we wanted only we are talking about as small as 0.07 percent carbon ok.

So, as you would see later that the equations are similar in form, only that the delta g value would change, but since we have only talked about interstitial diffusion. So, I will give I will just stay with this particular example which is where carbon stays as an interstitial.

And let us say with this is the 0.07 percent. So, this should have been your car this is carbon and this should be this will become your c bar and this is the maximum and minimum that is varying and this is a completely theoretical framework you are assuming a very you know you can say systematic fluctuation in the concentration, but this will let you understand what a homogenization means.

So, let us say this is the concentration C is equal to C bar plus beta naught where beta naught will become beta naught is nothing, but the amplitude. So, this is the wave 2, l will be the wavelength. So, l is the half wavelength. So, this is given here over here you could have as well write written is that written it as 2 pi by lambda where lambda would be the wavelengths times x, but since we have taken wavelength as 2 l. So, 2 cancels out and you are left with pi by l times x.

Now, here since it is also varying with time, you would be able to see that the solution for this once you put in that relation it will come out like this. So, now, what it is saying is that if we were looking at this, this is just telling you the concentration variation with x when you look into this is also telling you how the concentration, this part as if you ignore this part then it is only telling the concentration with x, and when you include this it is also telling concentration variation with time.

So, there you have t which is varying which is starts from 0 and changes, but tau is a constant. What is tau it is given by l square by pi square D B and it is equal to a constant. So, you can see all the quantities here is a constant. So, it is in this respect that you are calculating time.

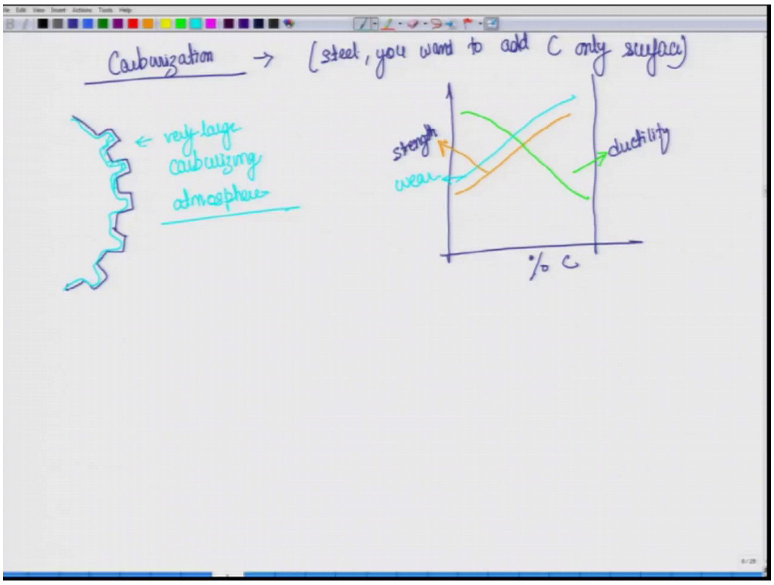
Now, what will happen when you increase time, what how should this plot change? This according to this solution that you have obtained if you solve using the relation we derived earlier you would get something like this. So, this is let us say this is t equal to 0 this is t equal to t 1, and you can you realize that here imagine that when you go to even higher time it will become something like this. So, what is changing here? It is the amplitude.

So, basically you can also write a relation for how the amplitude is changing and you can say beta is equal to beta naught, which is the amplitude at the very beginning exp minus t by tau and this is nothing, but concentration at x equal to l by 2. So, basically if you start from l equal to 0 here x sorry x equal to 0 here and then x equal to l by 2 is what you are getting from this relation. So, this is the same thing, but we are only putting x equal to l by 2 and you will get how the amplitude is changing with time.

So, in this particular problem, the way we have framed it what is changing is primarily you know not primarily only the amplitude, but that itself is now making the concentration homogeneous. So, here you can imagine the variation was from plus beta naught to minus beta naught, and that has changed from a much to a much smaller quantity let us say it is one-fourth of beta naught, so, one-fourth of beta naught to minus one-fourth of beta naught.

So, that is how this homogenization is taking place. So, in the end what you will get? Completely homogenized in terms of composition and if I want to plot it over here then let us this should be the ideal final solution. So, the concentration has bit reached the expected value across the volume. So, here we have looked at only 1 x or in only one direction one d. So, these are these problems are being solved in one d, but the same can be extended to three dimensions.

(Refer Slide Time: 25:59)



Carburization → (steel, you want to add C only surface)

Next example that we will look at is carburization. Why would you want to carburize something? Now again this is example related to steel. So, in steel you add you may want to add carbon, only on surface why because when you add carbon what happens this is. So, if we plot percentage carbon and if you plot strength, then you would see that strength actually increases up to certain value.

On the other hand if you look at ductility. So, at this point you would be imagining very good carbon percentage, we can keep the carbon percentage throughout the material very high and we will get very high strength, but then when you look at the ductility plot then you would realize that it is not always a good thing your ductility would drop sharply with increasing carbon percentage.

So, what is happening is that maybe the total toughness is same, but this material when you have very high percentage of carbon, if it develops cracks it will fail very easily and therefore, it will not be suitable for any component. And therefore, you do not want the material ductility to drop, but at the same time you have you are getting much higher strength and along with that you are also getting very good wear resistance. So, wear resistance also increases. So, this is ductility this is strength and the light blue one here is wear.

So, another important characteristics, when you increase carbon percentage, which is actually direct effect of increased strength is that wear resistance increases now let us say you are talking about gears on the surface the gears are in continuous contact with the other gears they mesh. So, they move and slide onto each other what does that do; that means, that it is slowly eroding each other. And therefore, you need high strength and high wear resistance on the surface.

And from this plot, you can see that if the carbon percentage was very high then wear resistance would be high strength would be high, but at the same time you do not want the gears to fail from interior. So, what you can do is that have carbon concentration high only at the surface and not in the interior and therefore, this process of carburization comes into picture.

So, now if you are talking about let us say. So, this is a gear, what you want is that carbon is high only up to certain region only near the edges why would you want to increase carbon concentration throughout the surface throughout the bulk that will make it brittle. So, you would increase carbon concentration only on the surface and this is done by exposing it to very large carburizing atmosphere. And hence you would be able to get very high concentration only on the surface.

So, we will look at how this particular carburization process not how, but the diffusion mechanics of this particular process carburization in the next lecture, and in the meantime it will be good if you can try to go through and the this process carburization and understand what is what does it actually do and what it and how is it useful. So, I will see you in the next class.