Materials Science and Engineering
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Lecture – 12
Diffusion

Hello, friends. Today's lecture we will discuss the problem of diffusion. It is a very important topic for any engineering application, because lot of heat treatment which we do in a practice in industries diffusion is one of the most important process which takes place during the any heat treatment process ok.

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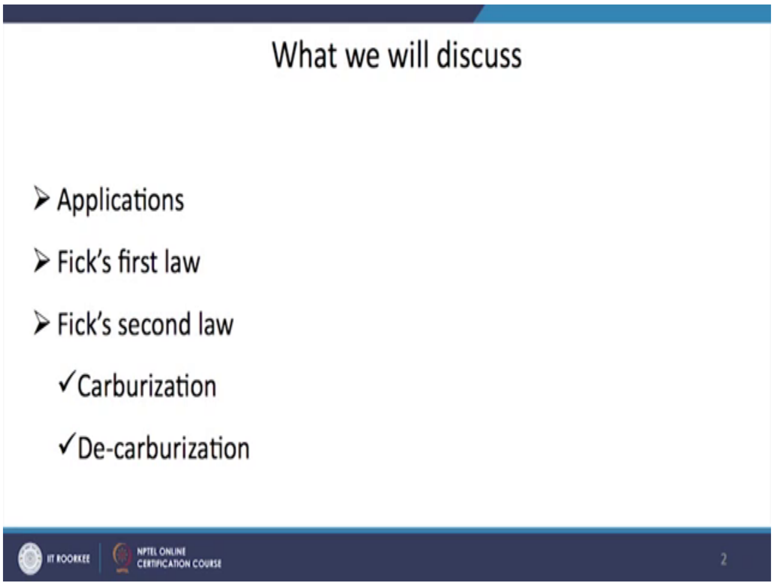

What we will discuss

- Applications
- Fick's first law
- Fick's second law
  - ✓Carburization
  - ✓De-carburization

So, we just want to understand this diffusion phenomena and we will like to see some of the applications of diffusion a process Fick's first law what do we mean by Fick's first law and Fick's second law and a couple of a application or where we use Fick's second law.

So, I will go through all this subtopic one by one. In terms of application as I told you that in lot of heat treatment processes diffusion is a very important process and a one of the process is what we have in industry is called carburization, ok. So, steel is a very well known material which is used in lot of applications a structural application spendy and to have higher strength on the surface and hardness on the surface, we do a process called carburization ok.

So, as the name suggests it involves the diffusion of carbon in steel ok. So, you may not be knowing this right now, but a steel is a alloy is an alloy and it is an alloy between iron and carbon. So, iron and carbon make an alloy which is called steel and a carburization means that we want to introduce or increase the a carbon percentage only on the surface of the any component to have more strength and more hardness on the surface ok, so, the process which we with which we do this is called carburization, ok.

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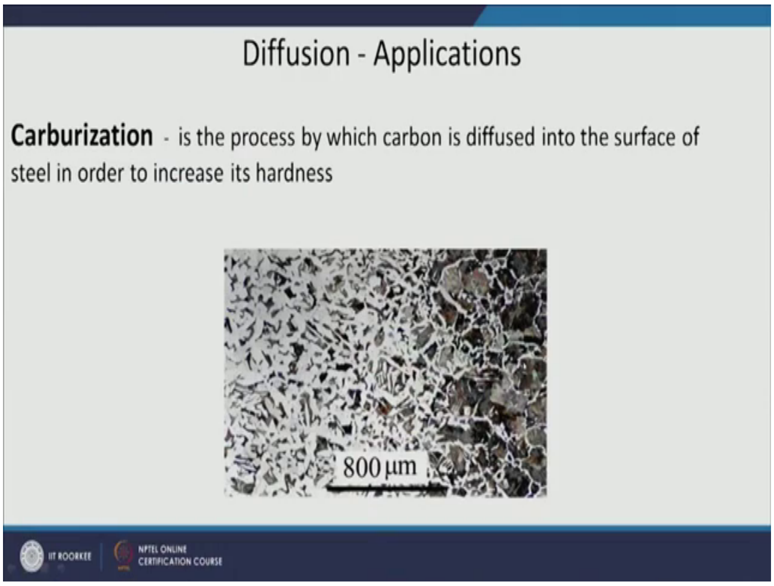

Diffusion - Applications

Carburization - is the process by which carbon is diffused into the surface of steel in order to increase its hardness

And, you can see the effect of this carburization in this particular microstructure you can see that there are more a white phases a proportion of white phase is more in this part in the interior of the material whereas, at the surface you see that there are more of dark phases ok, I am not right now telling you what is white or light phase or what is dark phase. But, at least we can see one thing here that the dark phase is more here and light phase is more here, that means, something has happened at this region which has increased the proportion of the dark phase and that is because of the carbon increase in carbon percentage and because of that actually the there is more paralytic type of microstructure here, ok.

These things we will see later on ok. So, at least we can see that one thing is that there is a change in the microstructure and that is because of the diffusion of carbon through the process called carburization.

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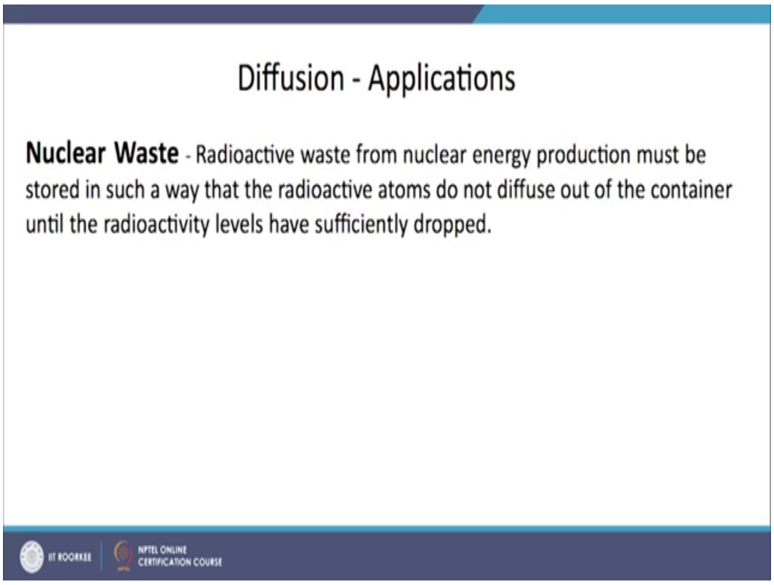

Diffusion - Applications

Nuclear Waste - Radioactive waste from nuclear energy production must be stored in such a way that the radioactive atoms do not diffuse out of the container until the radioactivity levels have sufficiently dropped.

Another very important area where diffusion is a very important process to understand is how you are going to dispose nuclear waste ok. So, after you take out the energy from these nuclear materials by the process of radioactivity they go into lower atomic number elements ok, but still after getting some energy out ok, whatever waste is there still it is a radioactive waste; that means, the radioactivity is still there. So, we have to contain this material in such containers that diffusion of this radioactive atom should not takes place from inside to the outside atmosphere, ok.

So, the thickness of the material or the properties of the material should be such that the diffusion of this particular radioactive element should not be very fast ok. It should take a sufficient amount of time ok. So, by that time the radioactivity of that particular element should come down and should be dropped to such a level that it is not a hazard to any human or any animal life ok. So, another very important area where we have to understand the diffusion process of this radioactive element through any material ok.

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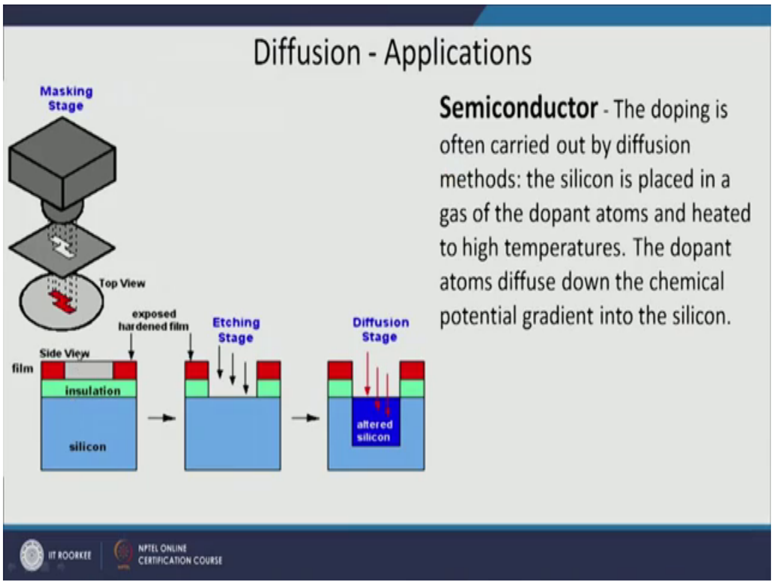

Diffusion - Applications

Semiconductor - The doping is often carried out by diffusion methods: the silicon is placed in a gas of the dopant atoms and heated to high temperatures. The dopant atoms diffuse down the chemical potential gradient into the silicon.

Third very important application is in preparation of semiconductors where through doping of a impurities the silicon is made either p or n junction and it is done through diffusion process ok. The process is shown here that wherever you want to have the doping that particular part of the silicon we remove this a one layer of insulating layer ok. So, that my material is exposed to any diffusing elements and that is how you alter the silicon as shown in this blue square here that the, because of doping the chemical composition of this particular square has changed ok. And, now it will behave either as a p type a semiconductor or n type semiconductor ok.

So, you can see that the wide variety of application from a very a material which is used in the structural application to a material which is used to contain this nuclear waste to a material which is used in a very sophisticated electronic application and everywhere you have this diffusion phenomena which is used to understand or used to which is used to bring about change in the material such that you can use it in a in an application ok, where these processes are very important ok. Now, we will like to understand the diffusion phenomena and to understand that we will right now take the example of a interstitial atoms ok.

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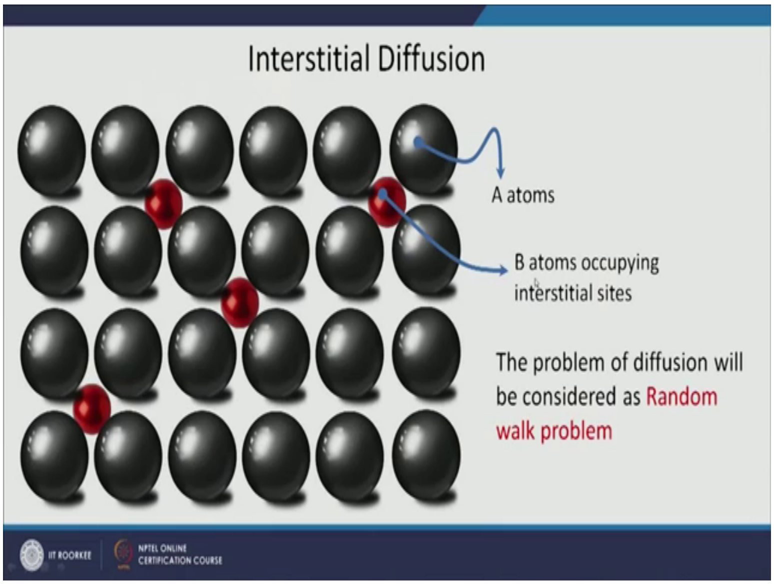

Interstitial Diffusion

The problem of diffusion will be considered as Random walk problem

So, basically one lattice is there where the host atoms are sitting and in the interstitial position your another type of a atom is sitting ok. So, we will call the host atoms as a atoms and the atom sitting in the interstitial position as b atoms ok. So, we will like to see that how this particular b atom will diffuse ok; diffuse means it has to jump from this site to the next site ok. And, the this problem of diffusion will be considered as a random walk problem ok. So, it is a random diffusion. So, there is no we are not kind of forcing the atom to go in particular direction ok, but this is a random walk problem ok.

So, but now in a some normal books generally available some misconception takes place that we assume that the atoms will be diffusing from an area where the concentration is more to an area where concentration is less so, that means, along the concentration gradient ok. The problem in this idea is that we do not know or how an atom will know that there is a concentration gradient ok.

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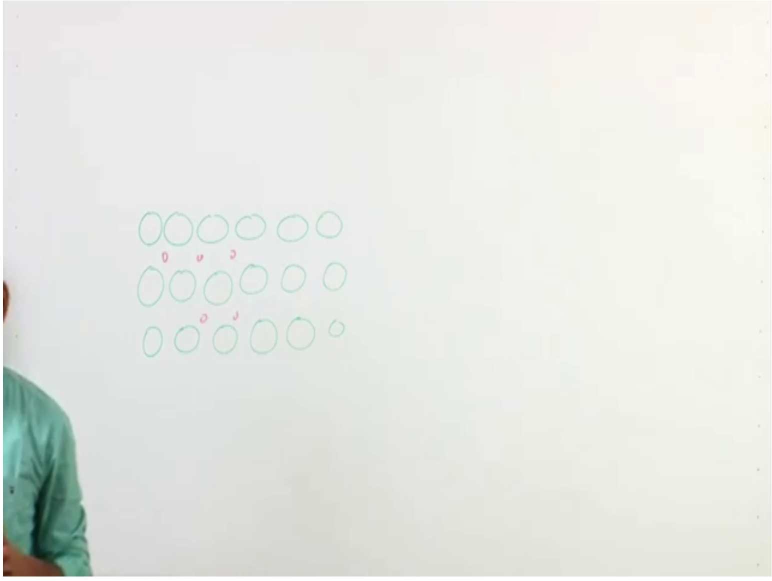

For example, suppose this is the lattice of atoms. I am just drawing a some a lattice and in this lattice in interstitial position suppose in this location, there are more interstitial atoms and later on the concentration of this interstitial atom is less ok.

Now, the question is that how these atoms know that there is a concentration gradient there or there is a less concentration they there ok; that means, how they are going to go and travel to that direction ok, how this atom will know that there is a less number of b atoms at this location ok. So, an atom cannot know it does not see what is going or what is beyond in beyond a immediate neighborhood ok. So, to tackle this problem is what we will call it as a random walk problem that I am saying that atom does not know anything only at what atom does is that atom jumps from one site to another site.

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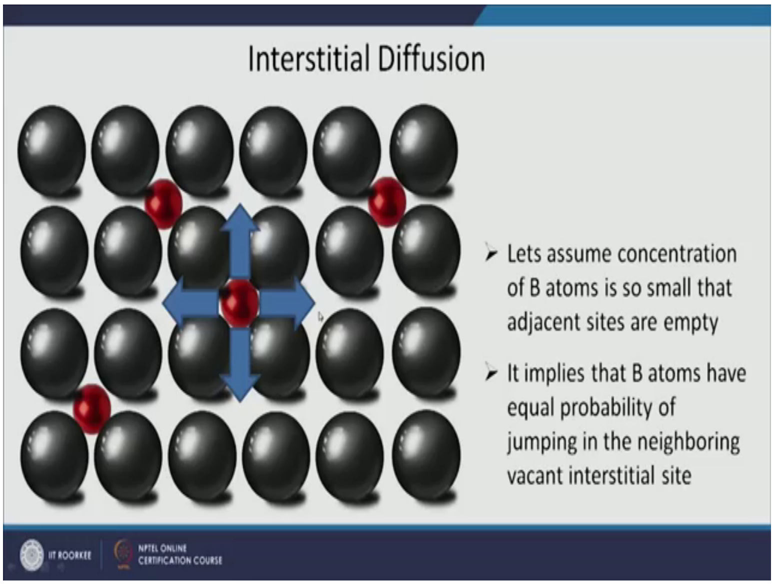

Interstitial Diffusion

- Lets assume concentration of B atoms is so small that adjacent sites are empty
- It implies that B atoms have equal probability of jumping in the neighboring vacant interstitial site

For example, in this slide you can see this atom is staying in this particular interstitial site ok. So, from this site it can jump to this next site or it can jump to this another interstitial site or maybe this site or this site and two sites which are in the this projection and outside this projection there will be six positions like this in which it can jump and we do not know where it is going to jump ok. So, taking from this idea we will try to derive the Fick's first law again in literature if you see in some books they will just say that the flux is proportional to concentration gradient and the proportionality constant is some diffusion coefficient which is wrong.

The equation is right ok, but this inference of this equation in this form is not right ok. So, the idea is that we have to understand this problem ok, saying that we do not know or the atom does not know there is a concentration gradient ok. Atom is only doing one thing it is jumping from one site to another site and it can jump to any site, there is no restriction for it to jump on on only in only one particular direction.

So, when I say that and there are some assumptions we are taking here that we are saying concentration is so small of B atoms in this particular alloy that for any atom there is always going to be an adjacent site which is vacant ok. So, concentration gradient is to a concentration has to be very small to take this assumption ok. So, we are dealing with very dilute alloys this and if we do that then we can say that b atom have equal probability of jumping in the neighboring vacant interstitial site ok. So, if for if all the neighboring sites are empty then my this atom can jump to any site and the probability is same ok. So, from there we will we will start the derivation for the Fick’s first law ok.

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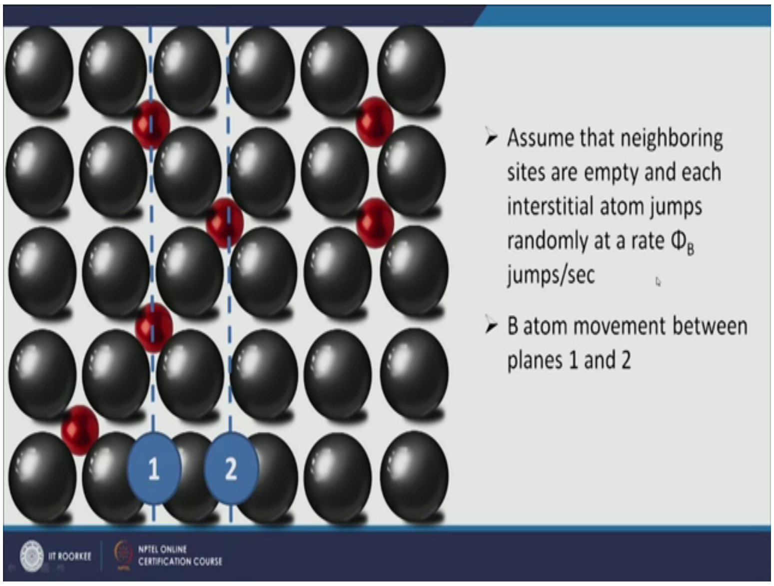

- Assume that neighboring sites are empty and each interstitial atom jumps randomly at a rate Φ_B jumps/sec
- B atom movement between planes 1 and 2

Let us start with this slide ok, I have drawn two planes here plane 1 and plane 2 and we are doing analysis only in these two planes ok. And, we are defining a jump frequency for this interstitial atom by phi B jumps per second ok. So, phi B jumps per second is the jump frequency. So, now, let us see what will be the b atom moment between this plane 1 and 2 ok.

So, as I told you that for each of this interstitial atom there will be six free sites in this particular lattice, if you change the lattice these numbers will change ok. Four you can see in this plane right now ok, one will be out of plane and one will be inside plane. So, there will be six sites where it can jump ok.

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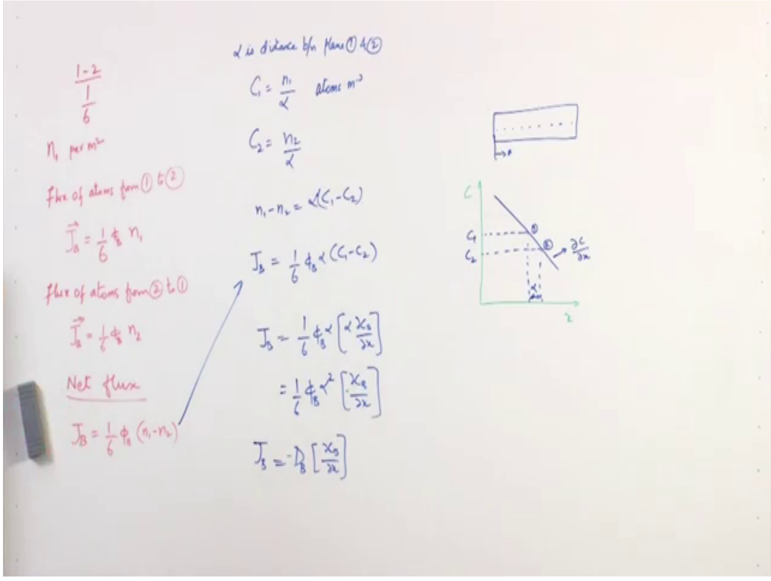

1-2

$\frac{1}{6}$

n_1 per m^2

Flux of atoms from ① to ②

$\vec{J}_B = \frac{1}{6}\phi_B n_1$

Flux of atoms from ② to ①

$\vec{J}_B = \frac{1}{6}\phi_B n_2$

Net flux

$J_B = \frac{1}{6}\phi_B (n_1 - n_2)$

α is distance b/n Plane ① & ②

$C_1 = \frac{n_1}{\alpha}$ atoms m^{-3}

$C_2 = \frac{n_2}{\alpha}$

$n_1 - n_2 = \alpha(C_1 - C_2)$

$J_B = \frac{1}{6}\phi_B \alpha (C_1 - C_2)$

$J_B = -\frac{1}{6}\phi_B \alpha \left[\alpha \frac{X_B}{\partial x}\right]$

$= \frac{1}{6}\phi_B \alpha^2 \left[\frac{X_B}{\partial x}\right]$

$J_B = -D_B \left[\frac{X_B}{\partial x}\right]$

So, in terms of probability I can say that it has one sixth probability of jumping from plane 1 to plane 2 in one particular direction it has only probability of by which is one sixth ok. So, there is one sixth probability of an atom jumping from plane 1 to 2 ok. So, from 1 to 2, if I want to say that what is the probability that is one sixth ok. Now, suppose if there are n n 1 atoms of B per meter square of plane 1, if I assume that there are n 1 number of atoms per meter square so, I will write per meter square in plane 1 ok. Then, flux of atom in 1 second from 1 to 2, what will be the flux of atom from flux of atoms from 1 to 2? Ok, that will be given by J B that is the flux we are defining here J B equal to 1 by 6 ok, in the direction of that it the probability is 1 by 6, phi B is the number of jumps per second an atom does ok.

So, in plane 1 to 2 it will be 1 by sixth of phi B ok, it if it if it does phi B number of zones per second. So, in a particular direction it will be 1 by 6 into 5 B and if there are what is the number of atoms we have in plane 1. So, that many atoms will jump from plane 1 to plane 2 ok. This will be the flux ok. Now, I can do the same analysis from plane 2 to 1 ok. So, flux of atom atoms from 2 to 1 I will again write J B equal to 1 by 6, same probability will be there again jump frequency is same for these atoms also, only thing which will change is the how many number of atoms are sitting in plane 2 ok. So, only those atoms can jump; obviously, in plane 1 ok.

So, now, we have flux from 1 to 2 and we have flux from 2 to 1. So, I can now have that what will be the net flux ok. Net flux will be the difference between the 2. So, now, I will write J B is equal to these things are common so, 1 by 6 phi B and n 1 minus n 2 ok. So, it depends on what is the number of atoms in plane 1 and what is the number of planes in n 2. So, now, you can start seeing that maybe we are started talking about concentration gradient ok, because there will be different number of atoms in plane 1 and plane 2 depending upon their concentration ok.

So, now I will like to define the concentration at different planes ok. So, I will define a concentration C 1 is equal to n 1 by alpha ok; I think I have not defined the alpha here. The alpha is distance between plane 1 and 2 that is the distance between plane 1 and 2. And, suppose we if we are talking about a unit area ok, then I can say that the concentration will be given by in plane 1 will be given by n 1 by alpha atom atoms per meter cube ok per unit volume.

Similarly, I can define the concentration in plane 2 as n 2 by alpha. Now, why we are interested in concentration is, because in when we talk about materials or when we do any calculation we talk about concentration ok, we do not talk about number of atoms ok, that we do not know ok. How many number of atoms are there when we make an alloy when we try to have a measurement of concentration ok. We get concentration in terms of how many atoms per unit volume are there it can be atomic percentage maybe sometime you express the concentration in terms of weight percentage.

So, right now it is the atomic percentage a in at number of atoms in a given volume and C 2 will be concentration in and number of atoms in a given volume again atoms per meter cube ok. So, now, I have defined C 1 and C 2 here ok. So, I will use that to define or to change the this particular equation here ok. So, now, equation-3 becomes n 1 minus n 2 will be written as alpha C 1 minus C 2 ok. So, I can replace it here ok. So, this equation will become now, this particular equation will become now J B 1 by 6, phi b alpha C 1 minus C 2 ok.

Now, we will like to bring the concentration gradient as I told you ok. So, C 1 minus C 2, I want to express in terms of concentration gradient ok. So, if you want to see concerned or I if I want to plot the concentration. So, I will plot it like this. This is concentration on y axis, this is x distance ok. So, suppose if I take a bar here a bar here; basically, I am finding out the concentration at different points as a function of x what is the concentration and that I have plotted ok. So, suppose that plot is coming like this ok, that is a concentration gradient then and this will be this concentration gradient can be given by this the slope of this will be del C by del x ok.

So, now you have a concentration at two points C 1 and C 2 at plane one and two for example, this is C 1, this is C 2, this is C 1, this is C 2, this is at plane 1 this is at plane 2 and the distance between these two planes this is equal to alpha as we said alpha is distance between plane 1 and 2 ok. So, now, if I want to define what is C 1 minus C 2. So, basically what I will ta[ke]- two I will take the slope multiplied by alpha that will give me the difference between the two concentration.

So, the delta y will be equal to delta x into the slope, our standard definition ok so, that I will replace here now. So, now, J B is equal to it will be 1 by 6 phi b alpha and now it will be C 1 minus C 2 will be alpha n 2 del C B by del x and if I take alpha out it will become 1 by 6 phi B alpha square del C B del x and now, I will say that this is my diffusion coefficient. So, J B will become the diffusion coefficient of B and ok. So, that is what you usually get that the flux is proportional to the concentration gradient and it is multiplied by the diffusion coefficient of atom b and this is for interstitial diffusion ok.

So, as you can see, that I have taken the slope as a constant slope here ok.

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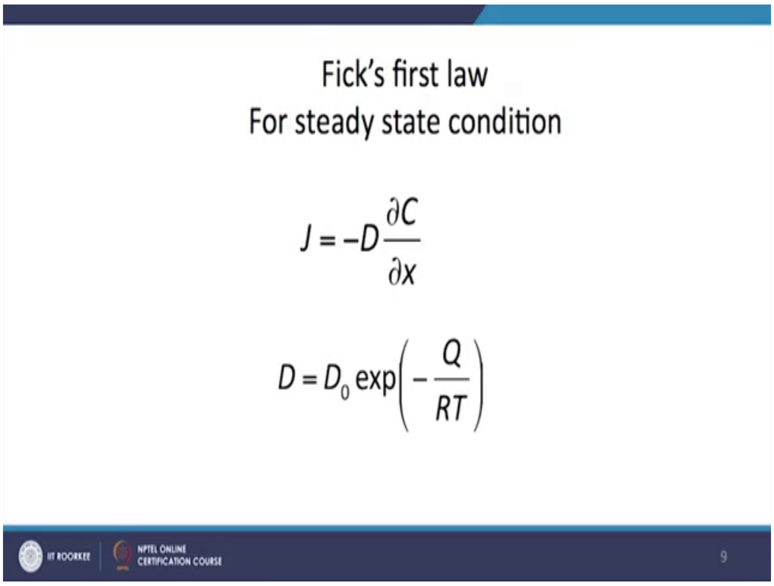

Fick's first law

For steady state condition

$$J = -D\frac{\partial C}{\partial x}$$

$$D = D_0 \exp\left(-\frac{Q}{RT}\right)$$

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So, the Fick’s first law which is which you are getting here this is for steady state condition ok. What do we mean by steady state condition is, that as a function of time my concentration of at any point will remain same and it is not going to change ok. So, that is my steady state condition, that there is no buildup of concentration as a function of time and this is what we say is Fick’s first law.

So, for steady state condition there is a Fick’s first law which is given as we are just derived. I am sorry we I did not put the sign here actually because it is a negative slope you will have a minus sign here and you will get a minus sign here and D is given by as you can see on the slide basically D, D is D naught exponential minus Q by RT ok.

So, this is my Fick’s first law. I am not doing the derivation for the Fick’s second law because I just wanted to bring the flavor of this random walk problem and how we can use that to derive Fick’s first law and there are some misconceptions sometime you find in book that they do not clearly specify that ok. The Fick’s second law deals with the non steady state condition and in that what do we mean by non steady state condition is that the flux will chan[ge]- sorry the concentration at any point will change as a function of time. So, there is a accumulation of atoms or depletion of atoms as the or change in the concentration at a particular point as a function of time ok.

When you see this particular curve, it is not going to give you change in the concentration at a particular point with the time ok. Then, you will get the non steady state condition if in terms of this particular graph I want to see that I will show you.

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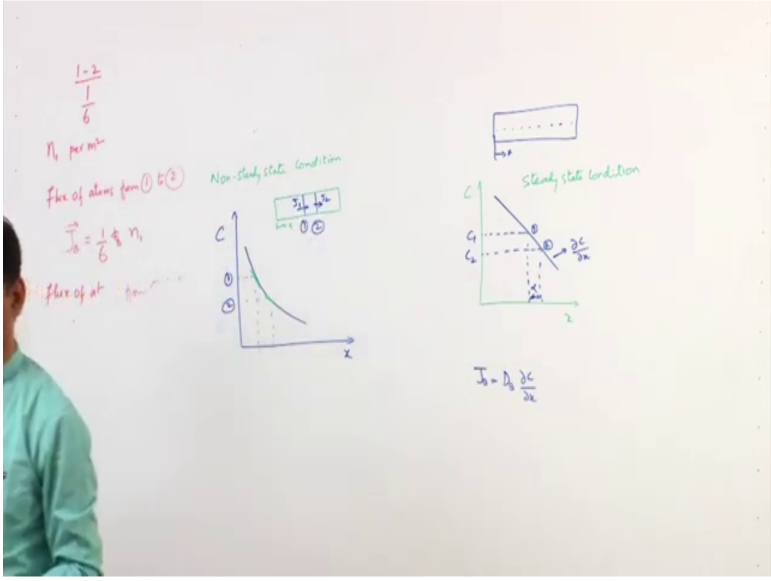

So, this is for steady state condition. For non steady state condition, the graph will be like this. This is my concentration this is the distance x ok, let me plot the block here this distance x and the graph will be like this ok.

Now, what does it mean, if you see as we derived in the Fick's first law that J B is equal to D B del C by del x; that means, my flux of a atom is dependent on the concentration gradient the slope of the curve. Here, the slope is constant that is why it is a steady state condition; now, here my slope is changing. So, if you see at this point suppose I want to see at this point and I want to compare it with this point the slope is something like this, here the slope is like this ok. So, here the slope is more. So, the flux of atom will be coming more ok.

So, let us say if this is my plane 1, this is my plane 2 and suppose, I draw these two planes here plane 1, plane 2. So, J 1 let us let me call this as J 1, ok. The flux J 1 from going from plane 1 towards plane 2 and there is J 2 coming out of plane 2 ok. Now, the slope is more in case of 1 and slope is less in case of 2. So, there will be more flux of atom going from plane 1 and they volume in between and there is a less number of atoms coming out of this volume and going out ok. So, now, that means, if I have more flux coming in less flux going on between plane 1 and 2 what will happen there will be an accumulation of atoms and this accumulation will mean means that there will be change in the concentration of this particular element as a function of time.

So, after some constant interval if I want to measure what is the concentration here, the concentration will keep changing, whereas, in this first case the concentration will remains same it will not change as a function of time because the slope is constant ok. So, Fick's second law deals with the non steady state condition and which tells me that there will be change in the concentration as a function of time and which is the more practical up which has more practical application because in normal experiments or normal applications the it is always going to be a non steady state condition ok.

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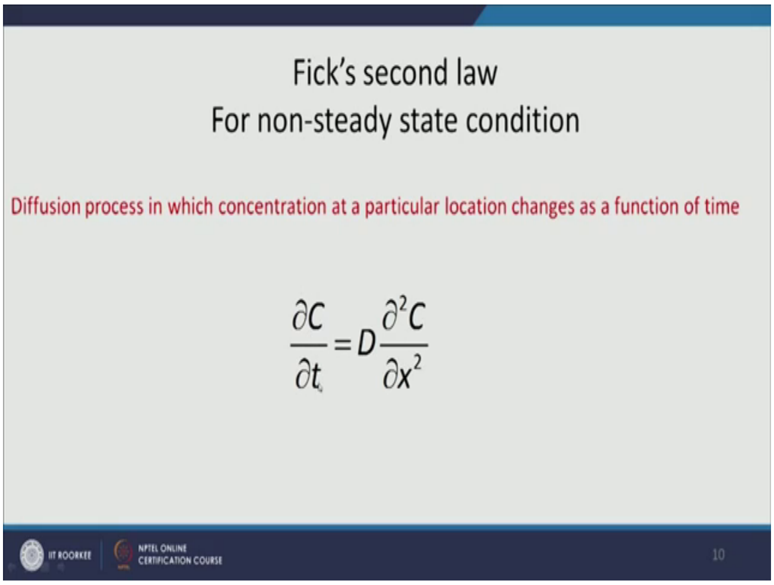

Fick's second law

For non-steady state condition

Diffusion process in which concentration at a particular location changes as a function of time

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

So, for a Fick's second law this is the equation as I told you the concentration will change as a function of time. So, del C by del t is equal to D and this is the curvature of the curve between the concentration in x del C del square by del square C by del x square will give you the curvature of the curve between C and x ok. So, it will depend on the curvature and of course, the diffusion coefficient and the concentration will change as a function of time.

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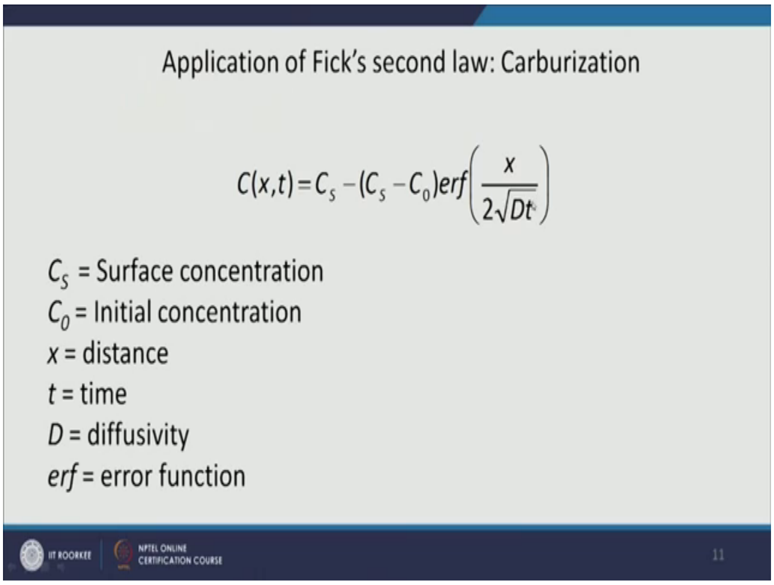

Application of Fick's second law: Carburization

$$C(x,t)=C_s-(C_s-C_0)erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

C_S = Surface concentration
C_0 = Initial concentration
x = distance
t = time
D = diffusivity
erf = error function

Now, there are two applications of these as I told you carburization is one and application of Fick's second law in carburization the equation which we which we are going to use ok, right now I am not doing any problems ok, but we will take up that in an in our assignments ok. So, the change in the concentration as a function of distance and as a function of time will depend on, what is the concentration at the surface of the of your material, what is the initial concentration of your material and what is your diffusivity total time you are exposing your material to that particular element and what is the distance at which you are trying to find out the concentration ok. So, it will depend on all these parameters ok.

There is a another term here coming which is called error function ok. So, because these are these type of equations you do not get definite integration what we do is we use a statistical function which is called error function to find out the solution ok. So, that is why we are using and this error function here you will see this kind of error function in other applications also I think in heat conduction also you must be having this error function coming into equation ok. This is for decarburization, ok.

The earlier equation was for carburization. Same thing can happen if you heat treat a material in a atmosphere, where instead of carbon you have some other atmosphere. Let us say, oxygen ok; in normal atmosphere you are doing heat treatment then what will happen, carbon from inside the material will diffuse out and carbon will react with oxygen and for may form carbon monoxide or carbon dioxide and this carbon will keep on diffusing and you will have a layer on the surface which is having less number of carbon atoms ok. So, this we call as decarburization and this is the solution for that which you can use to find out how much will be the de carburized layer.

Then, one small comment on there is another type of diffusion ok. We are not doing it because these are the two most important one for a practicing engineer who has a mechanical background ok, that is why I am not going into some other aspects of diffusion here ok.

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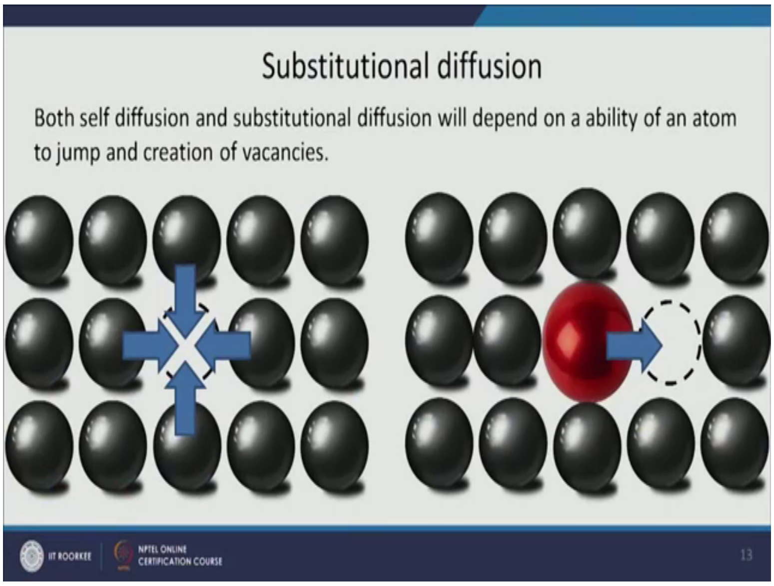

Substitutional diffusion

Both self diffusion and substitutional diffusion will depend on a ability of an atom to jump and creation of vacancies.

I am just giving one last comment on some other type of diffusion which also takes place which is not interstitial ok. So, it can be a substitutional diffusion and in this there are can be two cases one is where self diffusion of atoms takes place; so, you can see that there are there are at all the lattice points same type of atoms are there and there is a vacancy ok. So, now, these atoms they have a vacant site on which they can jump ok. So, now, they are defusing you can understand it as a diffusion process similarly again you have a vacancy here in the lattice and there is a substitutional atom is there which is occupying the regular position ok. So, they those atoms are called substitutional atoms and this atom can jump into this vacant site ok.

This is the two other type of diffusion in case of interstitial diffusion the interstitial sites are always present. In case of this diffusion which is dependent on vacancies you can understand that vacancy is a strong function of temperature it increases exponentially with temperature. So, where you need vacancies ok, so, it the diffusion process will depend on both the ability of an atom to jump from one site to another site and there should be a creation of vacancies to do that ok. So, this both will come together to have any diffusion.

So, we use the interstitial diffusion idea first to derive the Fick's first law and from there we said that you can also get Fick's second law and we saw that there can be two a very important applications of Fick's second law is in finding out what is the time and a distance for a for a carburization process or decarburization process and what will require if you have a substitutional diffusion? So, one can be self diffusion the same atoms can diffuse, if vacancy is there; another case, a substitutional atom can be there ok, where you have a vacant site and the diffusion is taking place in that vacant site ok. So, with that I will stop this lecture.

Thank you.