Introduction to Materials Science and Engineering

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Lecture - 85
Atomic mechanisms of diffusion

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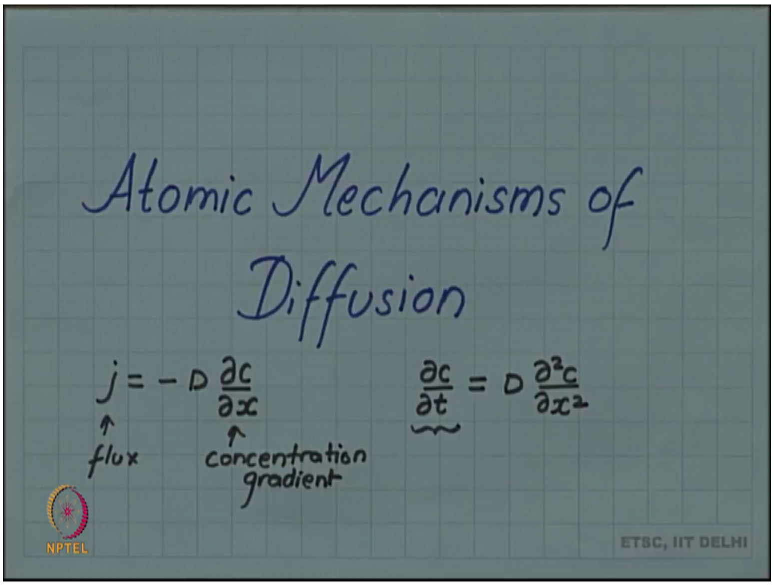

Atomic Mechanisms of Diffusion

$$\underset{\underset{\text{flux}}{\uparrow}}{j} = -D \underset{\underset{\text{concentration gradient}}{\uparrow}}{\frac{\partial c}{\partial x}} \qquad \underset{\sim}{\frac{\partial c}{\partial t}} = D\frac{\partial^2 c}{\partial x^2}$$

Let us now consider atomic mechanisms of diffusion. We have discussed two laws of diffusion, the two Fick's law. The first law which was j is equal to minus D del c by del x, and the second law, which was del c by del t is equal to D del 2 c by del x square. Both these laws are continuum laws, in the sense that these parameters the flux the concentration gradient for their definition, they do not require the existence of atoms; however, we know the existence of atoms now and we believe in them.

So, it is important to look at the diffusion process in terms of, what atoms are doing inside the crystal, how actually the atoms move to create this diffusion to create a change in concentration with time, which is in the part of second law and so, on. So, we will look at the atomic mechanisms two kinds of atomic mechanisms a distinguished.

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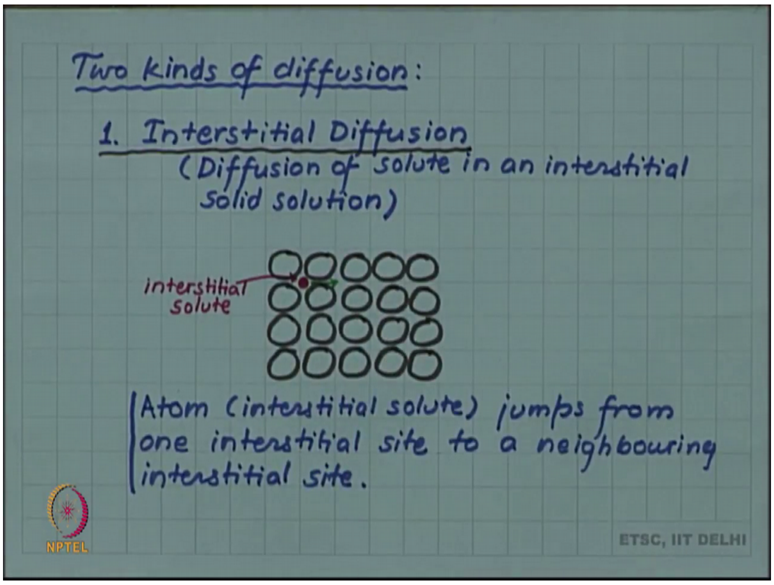

Two kinds of diffusion:

1. Interstitial Diffusion
(Diffusion of solute in an interstitial solid solution)

Atom (interstitial solute) jumps from one interstitial site to a neighbouring interstitial site.

So, let us call it two kinds of diffusion, which is based on the two kinds of solid solutions, which we have discussed. Recall, that we discussed interstitial solid solution and substitutional solid solution.

So, if a solute atom diffuses in an interstitial solid solution, we will call it interstitial diffusion interstitial diffusion essentially diffusion in a diffusion of solute in interstitial solid solution. So recall let me create and interstitial solid solution. So, we have atoms of solute forming a crystal, so these black atoms my black atoms I am representing the host crystal, which is forming some crystal structure of course, I am making a two dimensional cartoon here in three dimensions they can form FCC or B c c crystal structures different kinds of crystal structures are possible as you know.

And then between the atoms there are the vacant sites, and in the vacant site a solute atom can sit. So, by red atom I am showing an interstitial solute. Now, this interstitial solute can jump from one interstitial site to another nearby vacant site. So, it can jump from this site to this site. So, that will create a movement of the atom and will of course, gradually will change the concentrations of atoms as the several of these atoms move.

So, diffusion happens by; so interstitial diffusion happens; so by atom jump jumping from; so atom interstitial atom interstitial solute atom jumps from one interstitial site to a neighbouring interstitial site.

So, this is the basic step, this will this jump this jump shown by the arrow here, is the basic unit of the diffusion and basic jump of the diffusion one single step and several of such steps of several atoms in the crystal will call the kind of diffusion which, then is governed by the Fick's laws.

So, this is our first kind of diffusion interstitial diffusion.

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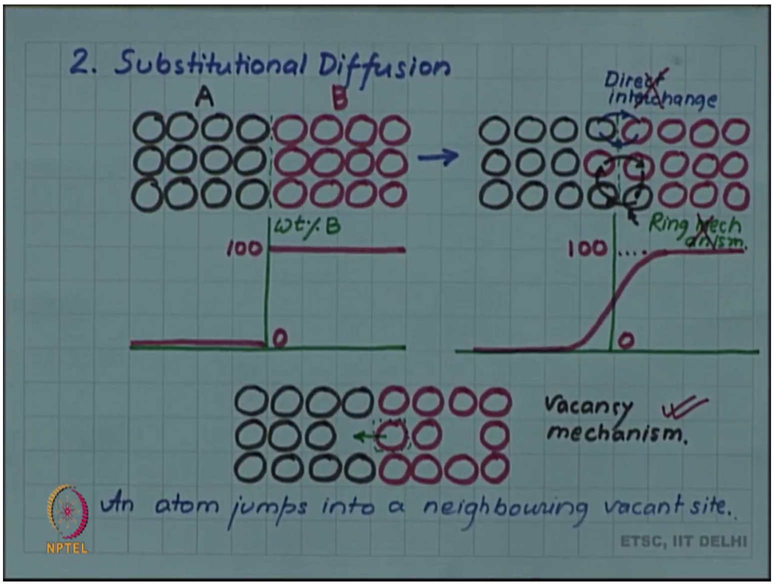

2. Substitutional Diffusion

An atom jumps into a neighbouring vacant site.

The next one the next type is substitutional diffusion, recall that the second type of solid solution, which we considered was substitutional solid solution. So, the corresponding diffusion will be called substitutional diffusion. Let me make a situation for substitutional diffusion, so I am creating what is known in diffusion literature as diffusion couple. So, I one side I have black atoms another side I have red atoms. So, two different elements they are representing two different elements.

So, for example, one can be copper, another can be nickel. So, we are keeping it general, let us called A atoms and let us call this B atoms, and they are meeting at an interface here in the middle there is the junction where they are meeting. So, if we represent the concentration profile in this system.

So, let us say that we are we are plotting weight percent B as our y axis and the x axis is the distance as seen in the diagram, then we find that on the A side there is no B, so you will have 0 B percent. So, it will coincide with the x axis whereas, on the B side you have pure B. So, you will have 100 percent B.

So, you have 100 percent B on the B side you have 0 percent B on the A side. So, this is the initial situation, but if you anneal this system, that is if you heat this system in a furnace for some time what you will find that diffusion has happened and the system will evolve to show you that sort of diffusion, we will then have some B atom migrating on to the A side, this kind of experiments have been done and one have observed this kind of situation. So, now, I am finding a B atom on what was initially the A side and correspondingly somewhere there will be an A atom on the B side.

So, across the interface you can now see that a migration of atoms have taken place or a diffusion has taken place. So, if one measures the concentration profile after some time, then one will find some B on the A side also. So, you will now have a concentration profile which will evolve something like this and it is governed by the solution of Fick's laws, which we have already discussed. So, we did not take this example, we took the example of carburization, but this example can also be solved using the error function solution which we have considered.

So, after some time; so we are now finding some B concentration also on the A side and there is some A concentration on the B side and that is, why the concentration of B has come down from 100 percent on this side, because some A atoms are now present there. So, the question is this diffusion has occurred, but what let to this diffusion, if you look at the diagram here there it is not obvious; how an A atom can get into the B side or how a B atom can get into A side, because everything a is well placed and interlocked into the crystal structure. Unlike, the interstitial diffusion which we talked about in the interstitial diffusion most interstitial sites are waiting.

So, I have an interstitial solute can jump into a neighbouring vacant interstitial site, but this is not a situation here, because all as I have shown here all positions are occupied by atoms, because they are sitting on their regular position, then how is this diffusion possible. This was an important question, which was discussed by early scientists working with the problem of diffusion and various kinds of mechanisms were proposed.

One such mechanism was the, so called ring mechanism or the direct exchange mechanism. So, in the direct exchange mechanism, they believed that something like this will happen that to a pair of atoms will exchange their position with each other of course, physically they will have to rotate around each other and we will have to distort the surrounding lattice.

So, that will require energy, but this kind of direct exchange. So, let us write this as a direct interchange mechanism. Another mechanism which was proposed was ring mechanism, in which a group of atoms this requires a group of atoms and then it was proposed that they interchange positions in a ring. So, one goes to the second position, second goes to the third, third one to the fourth and fourth one may come back to the first one and in this kind of ring if they move, then the positions will interchange and atoms will move to different locations.

So, this is this mechanism is the ring mechanism, but we will not go into the details actually experimental there are experimental observations, which negates both these and have been shown for example, it has been shown that they require much higher energy than is possible in diffusion processes. So, both these mechanisms finally, have been ruled out in the favor of a third mechanism, which is now the accepted mechanism for diffusion and that is the vacancy mechanism.

So, recall my diagram in fact, a drawing of diagram like this was incorrect, because I did not show the vacancies we have seen that vacancies are always in equilibrium. So, some sites have to be vacant sites. Now, I am showing a vacant site in the A lattice, they can be a vacant site in B lattice also.

So, there are some vacant sites in the crystal and then this is what aids diffusion, because an atom can jump into a nearby vacancy. So, if this red atom jumps into the neighbouring vacancy, you can see that it has entered into the B side and where it will where it has jumped from that original site will, then be left as a vacant site and some neighbouring atom can jump into that site and so on.

So, with this mechanism the diffusion is possible and it has been shown now. So, this is the vacancy mechanism, which means an atom jumps into a neighbouring vacant site. So, this is now the accepted mechanism. So, let us make a note on this. So, direct interchange and ring mechanism originally work were proposed and considered, but now have been ruled out in the favor of the vacancy mechanism, which gives have results which are closer to the experimental observations. Just let me; let me justify one statement which I made that for interstitial solute atom, there are lots of neighbouring interstitial sites which are already vacant.

So, here the vacancy problem was not there, because the vacant sites are naturally available. Let us justify this for the case of carbon.

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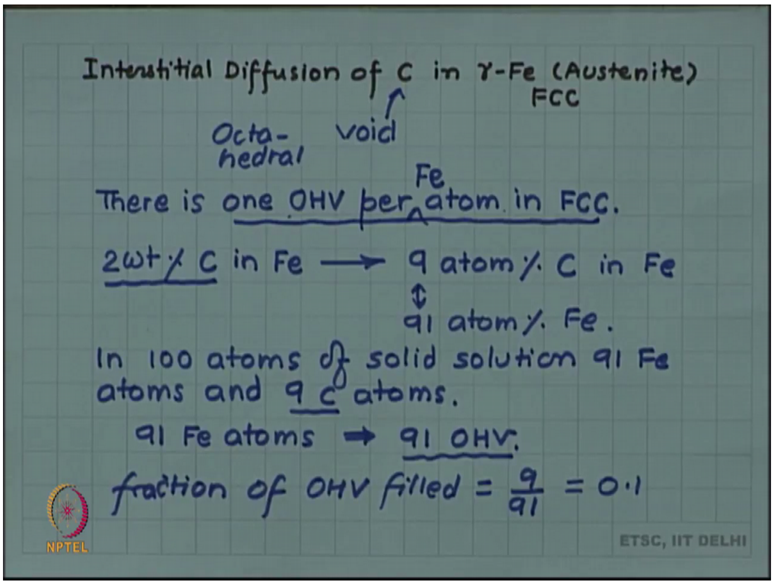

Interstitial Diffusion of C in γ-Fe (Austenite)
FCC
Octa-hedral void

There is one OHV per Fe atom in FCC.

2wt% C in Fe $\longrightarrow$ 9 atom% C in Fe
$\updownarrow$
91 atom% Fe.

In 100 atoms of solid solution 91 Fe atoms and 9 C atoms.

91 Fe atoms $\rightarrow$ 91 OHV.

fraction of OHV filled $= \frac{9}{91} = 0{\cdot}1$

So let us say interstitial diffusion of carbon in gamma iron austenite. We have discussed these phases when we were discussing the iron carbon phase diagram, so and gamma iron if you recall is FCC face centered cubic. So, if we have carbon and the carbon, carbon goes into when we were discussing the voids, you probably discussed this also that this goes into the void and the void it chooses is the octahedral void. So, carbon goes into the octahedral void of FCC iron.

So, if you now recall, when we discussed void we said that there is there is one octahedral void; let me right OHV for octahedral void per atom in FCC. Now let us consider we also saw in the phase diagram that the maximum amount of solute which you can put in gamma iron is about 2 weight percent. So, let us consider that particular case. So, 2 weight percent carbon in iron, if you calculate this in terms of atom percent, you will get around 9 atom percent carbon in iron carbon is lighter.

So, a for a given weight there are more carbon atoms than iron atoms. So, 2 weight percent carbon, if you calculate the atom percent you will get 9 atom percent carbon, which means equivalently 91 atom percent iron. So, in 100 atom let us calculate for 100 atoms; in 100 atoms of solid solution, there will be 91 iron atoms and 9 carbon atoms, but we have one octahedral void per atom and what atom per iron atom, because that is the host atom. So, a for every iron atom there is an octahedral void. So, for 91 iron atoms I will have 91 octahedral voids atoms will imply 91 octahedral void.

So, you can now see you have 91 octahedral voids, but only 9 carbon atoms. So, even with the maximum concentration, only the fraction of octahedral voids filled is 9 by 91. So, that is about one-tenth you can see, it is about 0.1. So, only 10 percent of the sites are filled 90 percent of the sites are vacant.

So, when I saw when I show you a diffusion system like this 90 percent probability of a neighbouring site to be vacant is existing, if you have the maximum amount of carbon. In most have a practical steels the carbon concentration will be much less and in mild steel it can be 0.2 percent or 0.1 percent.

So, you can imagine that the probability of finding a vacant site will be very very high. So, interstitial diffusion this vacancy problem does not come and one does not consider it difficult for an interstitial salute to find a vacant sites whereas, in substitutional solution the presence of vacant site is important for diffusion and the vacancies are in very low concentration you should remember, that we have discussed that and we derive an expression for vacancy and we found that the vacancy concentration can be anywhere like 10 to the power minus 10.

So, only one site in 10 to the power 10 sites are vacant. So, since vacancy presence of vacancy is very rare, it will be very low probability for an atom to find a nearby vacant site.

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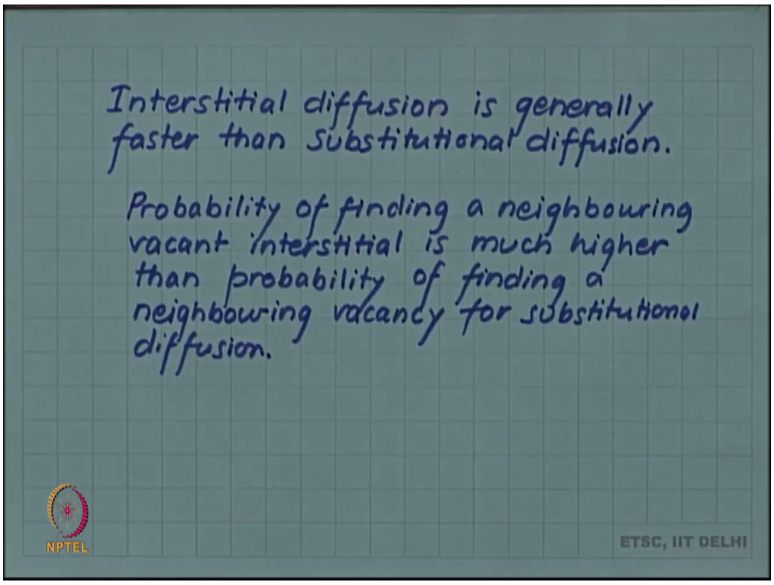

Interstitial diffusion is generally faster than substitutional diffusion.

Probability of finding a neighbouring vacant interstitial is much higher than probability of finding a neighbouring vacancy for substitutional diffusion.

So, this leads to the general relationship let us write down that interstitial diffusion are faster than interrstitial diffusion is generally faster than substitutional diffusion substitutional diffusion. And this is related to the fact that probability of finding probability of finding neighbouring vacant interstitial is much higher, then probability of finding neighbouring vacancy for substitutional diffusion.

So, this is a general observation. Let me end this video with one more consideration of the movement of atom during diffusion the energy consideration.

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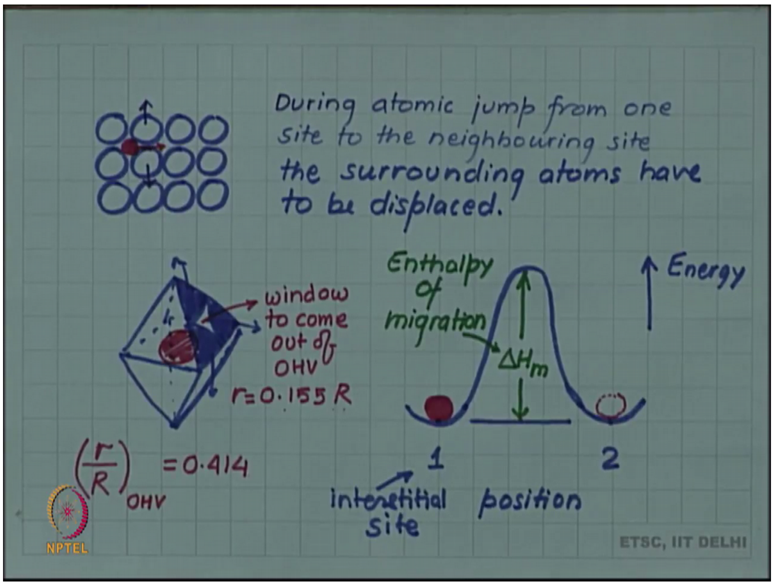

During atomic jump from one site to the neighbouring site the surrounding atoms have to be displaced.

So, let us look at it again from the interstitial diffusion point of view. When a solute atom wants to jump from one neighbouring site to the nearby neighbouring site the neighbouring site may be vacant and may be ready to accept, but the path requires distortion of the neighbouring atoms, because the path is narrow and unless and until these atoms move out to allow this atom this will not go through.

So, this distortion requires energy. So, during atomic jump from one site to the neighbouring site; during the atomic jump from one site to the neighbouring site the surrounding atoms have to be displaced I am showing it in this two dimensional cartoon, but in the 3D case also which we considered for example, octahedral void you can recall that; let me try to draw a schematic of an octahedral void. So, it is made up of 8 triangular faces like this and there are 6 atoms setting at the 6 corners.

Now, if you look at; so the void is in the center and there is an atom setting there and the void size, if you remember that the largest atom which can fit the void ratio for the octahedral void that is 0.414. So, about 40 percent size of the host atoms that interstitial atom of a 40 percent size can fit into this octahedral void, but then the host atoms are setting at the corner.

So, the host atom will be occupying the corner sites, if I fill this to represent the host atoms, so you can see that this may red interstitial atom have to jump out of this window. So, the window available to jump out to the neighbouring site is this one, but this window size you can show is only 0.155 R. So, this ratio is only 0.155. So, although a larger atom can fit inside, but when it is trying to come out of this octahedral void to some nearby site, then it has to displace these near neighbouring atoms, these neighbouring atoms have to be displaced out to increase the size of the window and come out.

So, this will create a distortion and in terms of energy you require energy of the system to increase. So, if we now let us call this to be an interstitial site one and this to be a neighbouring interstitial site, then on both these sites and let me try to and the y axis is energy and this is position. So, I am drawing now discuss is the location of interstitial site and we are saying that an atom from one interstitial site will jump to the neighbouring site. In terms of energy both these sites are local minimum for the interstitial atom.

So, the interstitial atom can set happily either on site 1 or on site 2, but to jump from site 1 to site 2 either in this two dimensional diagram or in this three dimensional picture you can see that it has to displace the neighbouring atoms and that will increase the energy of the system. So, that increase in the energy which, so by this energy hill.

So, an energy barrier exists in movement from site 1 to site 2. And in terms of enthalpy, this energy barrier is written as delta H m the enthalpy of migration. So, we will use this enthalpy of migration in the next video, where we will derive the Fick's first law by atomic mechanism.