Heat Treatment and Surface Hardening (Part–1)

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Diffusion in Solids - 2

So, continuing our discussion and diffusion in the soiled state.

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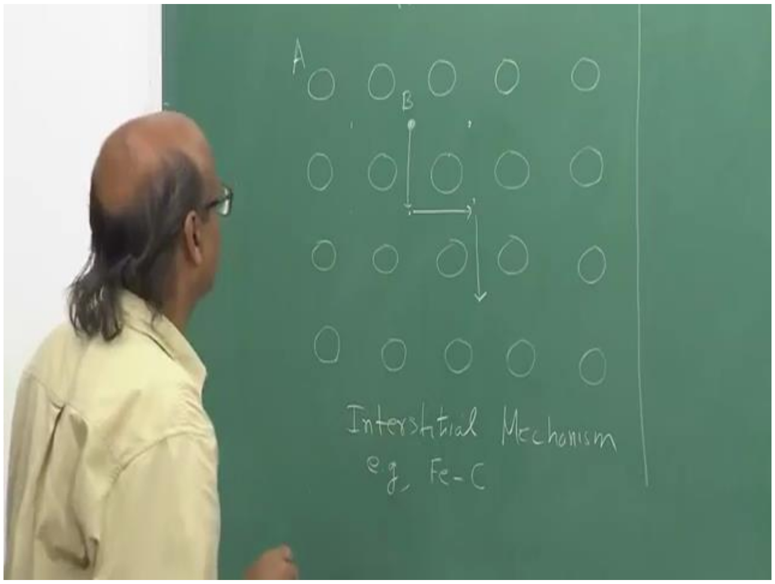

Let us first look at the mechanism of diffusion in the soiled state which had been a subject of controversy for several decades. So, here let us consider, let say a crystalline solids of let say A atoms which are arranged in a particular crystal structure. Here will just take a two dimensional view of this to understand diffusion. So, one possibility in the solid state is suppose along with this A atoms we also have B atoms in an interstitial solid solution. which means the B atoms are located at some interstitial side.

So, for example I have a B atom located here, now how can it move. So, it has to make a jump from one interstitial side to another interstitial side. So, these are all possible neighboring interstitial sides. So, it can make a jump to this side, it can make a jump to this interstitial side, but it cannot make a direct jump from this interstitial sides. So, for example it can jump to this interstitial side making use of the gap between the atoms of A.

Similarly the next jump could be in this direction, a third jump could be in this direction and eventually the B atom reaches here. So, this is the case where two dimensional random walk by the B atoms. Similarly one can imagine that in the three dimensional structure this B atom can move in the third direction as well. So, this is one possibility where the B atom is a lot smaller then the A atoms and this is what is called as the interstitial mechanism of diffusion.

Example of system where you would have an interstitial mechanism is one prominent example is the iron carbon system, where the carbon atoms or lots smaller than the iron atoms and hence the carbon atoms can diffuse or make jumps from one interstitial side to another interstitial side.

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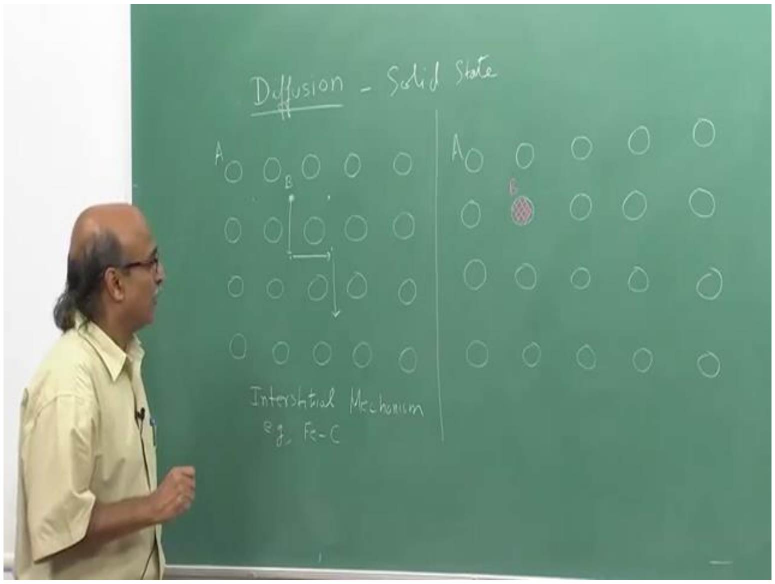

The second mechanism that operates in the solid states again, let us consider A atom with the certain structure. And in this case we have A atoms and along with a B atoms which have similar size to A atom and hence the B atoms are not going to be located in the interstitial side but they will form a substitutional solid solution.

So, some of the A atoms would get replaced by the B atom. Now this B atom has to move it cannot obviously move to a interstitial location that would be a that would take up the that would require a large amount of energy to get itself accommodated into a small interstitial side. However what can happen is the following.

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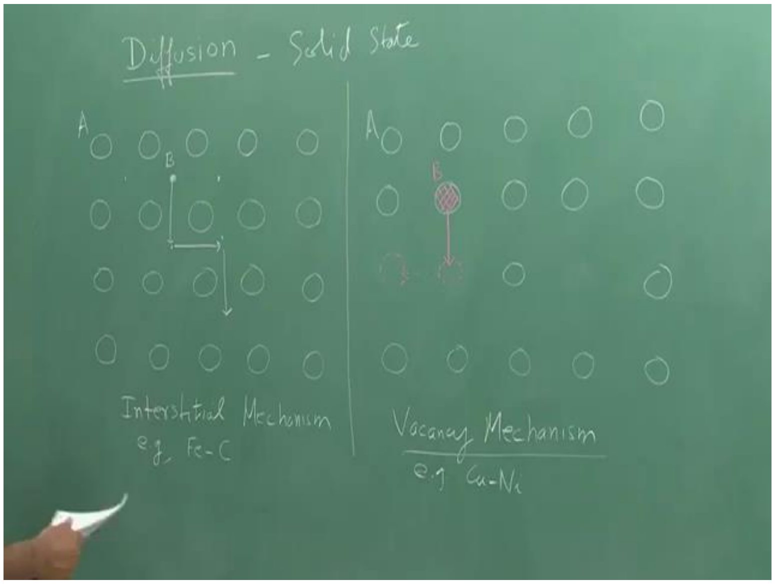

We all know that in the solid state all structures for temperature for finite temperatures would have some atoms missing. So they will have some vacant positions of water called as vacancies.

So, for example there can be an atom missing here, they are could an atom let us say missing here. It cannot jump from here to this vacant side but this B atom could make a jump to this vacant side and come to this position. Similarly if there was no atom here there are it can make a subsequent jump to this position and that is why how it is able to move from here to here in two successful jumps very clearly this would require a vacant side to be nearby.

So, in this particular two dimensional structure around this B atom where, where all it can make it can make jump to its 4 nearest neighbors if here here here or here provided at least one of them is the vacant side or at least one of them is a vacancy. So, this kind of diffusion which is extremely common is called vacancy mechanism and example of this could be, for example copper nickel. Copper and nickel form substitutional diffusion or substitutional solid solution at here if the copper atoms have to move through a nickel crystal or a nickel atom is to move through a copper crystal, it will have to find a vacancy in one of it is nearest neighbor positions.

Now in both cases, so these are the two cases by which diffusion in the solid state can be adequately described, at then eventually mathematically modeled to be able to determine the kinetics of diffusion how fast the atoms would move.

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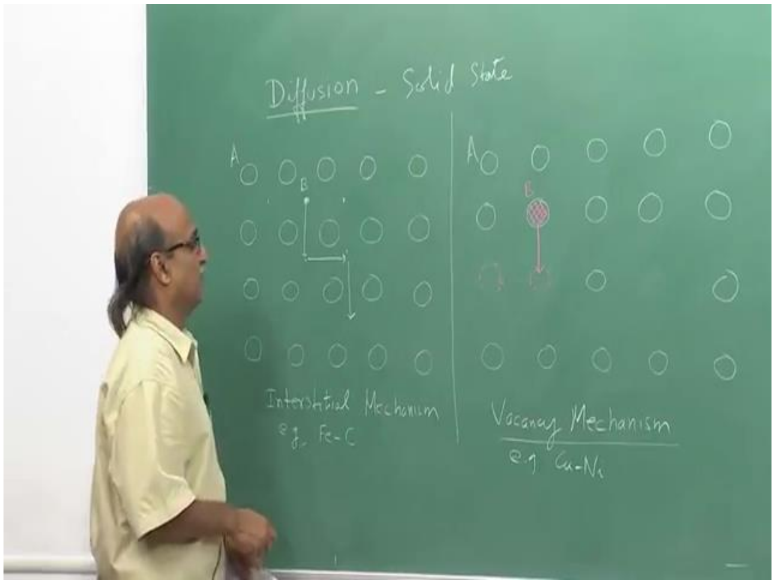

But it should be noted, that for an atom to jump from this location to a vacant side in the case of substitutional solid solution and in the case of interstitial solid solution for in B atom to jump from here to here, one should know.

Say example for example so one (intes) interstitial solid solution the gap between these two atoms is actually much smaller than the size of the B atom. In order for this atom to jump it has to squeeze through the two neighboring atoms in and therefore they would be a there would be an energy hill for this atom to migrate from this location to this location. So, it is still has to climb an energy hills.

Similarly here is well even though your vacant side all these atoms are quite closed, so they will have to be they will have to move away to give space for this B atom to jump and again it will have to go through a energy hill for making the jump. The difference in these situations would be that if B atoms are very few in number then it will always have a free interstitial side around it.

So, it does not have to look for a free interstitial side it will always have, so the only uhh only energy hill that it has to climb is, is squeezing these two at the neighboring atoms. On the other hand in the vacancy mechanism, first there is energy hill for the jump, second there is a chance whether the side is vacant or not.

So, there are two parameters that come in, there is a probability of a side being vacant that will have be to taken into account plus the energy required for the jump. So, looking at this way interstitial diffusion would typically be faster as compare to the diffusion by the vacancy mechanism and very quickly I can show you a simulation of the vacancy mechanism in this slide.

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Here what you see are the red atoms on the left and the black atoms on the right. They are all the sizes of the same order, hence the only way these atoms cam jump into the each, each other crystal structure is by a vacancy mechanism. And the white circles that you see are the vec vacant positions. Here I deliberately put a very high density or vacancy typically in the solid state the number of vacancies are much less in number and of course they increase as temperature has increased.

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So, if I look at this and I start the simulation these vacancies will start to migrate and will will start to jump around and you can see that the black atoms have started penetrating towards the left and the red atoms are have started penetrating towards the right.

So, this is a simulation of the vacancy mechanism and action, we will let it go on we will see towards the end how far things have changed in this, we have started with red atoms on the left and the black atoms on the right. Now let us, let us look at a quantitative picture of diffusion that how we can develop relationships for diffusion in orders to determine the kinetics of diffusion.

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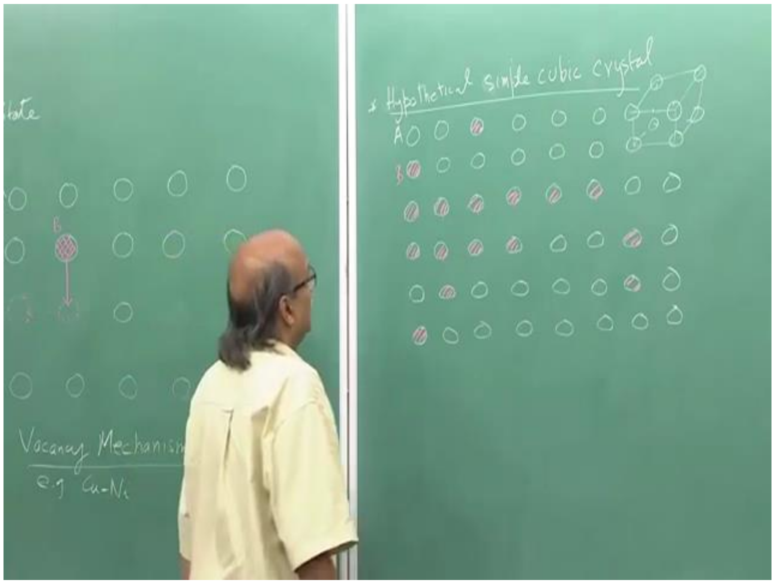

So, consider a hypothetical crystal, in fact hypothetical cubic crystal, in fact I will say simple cubic crystal to keep thing simple. So, these crystal may have A atoms and some B atoms uhh substituting the A atoms. So, let me first draw the picture of this, so I have atoms again put in a few simple cubic crystals and I am going to only going to draw a 2 D projection of the crystal.

So, let us say this is my 2D projection of lots of unit cells of the cubic crystal, see each one for example all I am seeing is 1 square here but this is you can imagine a unit cell here with atoms located at the corners and of course you can uhh you will have on each of these atom on the top as well and of course atoms at the bottom.

Let us consider and let us let me also put some B atoms in this. So, these whites once are A atoms and let us put some B atoms, something like this. And the way I have drawn it there is some kind of a concentration gradient. So, there are higher density of B atoms on the left and as you move towards the right the density of B atoms is reducing. If these B atoms are given a chance to jump then in the end this crystal should become homogenies where B atoms are uniformly substituting the A atoms all along the block crystal block.

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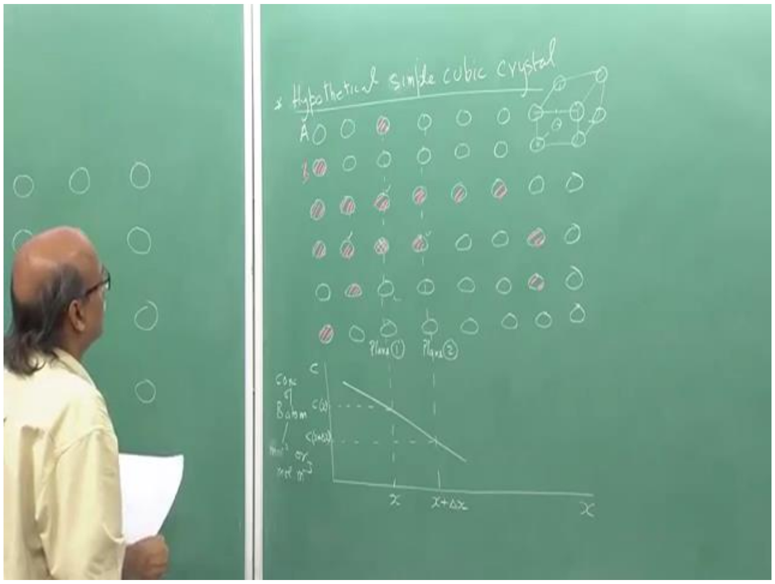

So, let us look at this concentration gradient, so this is the distance we move x, this is c the concentration of B atoms measured as number of B atoms per unit volume or it could be moles per meter cube and let us look at two atomic planes this is one atomic plane this is another atomic plane and let say this is how the concentration varies with distance of straight line. So, I have here let us say the location x, this is location x plus delta x concentration, let us say this is called this is plane one, this is atomic plane 1 this is the atomic plane two.

So, the concentration at x is cx concentration of delta x is c x plus delta x. Now consider any atom on plane 1, for example suppose I consider this atom, in which directions it can jump, how many direction are possible for it to jump. So, 1 has to look at what are the nearest neighbors of this atoms this being a simple cubic crystal it is nearest neighbor on this plan is is this one, this atom this at this position and so on. There are 4 positions here there will be fifth position on top, there is another atom at the top and there is another atom at the back side of it.

So, there will be total of 6 positions, it can jump to any of these 6 positions provided there is a vacant side available. Now, I want to find out overall what is the flux of B atoms jumping from plane 1 to plane 2.

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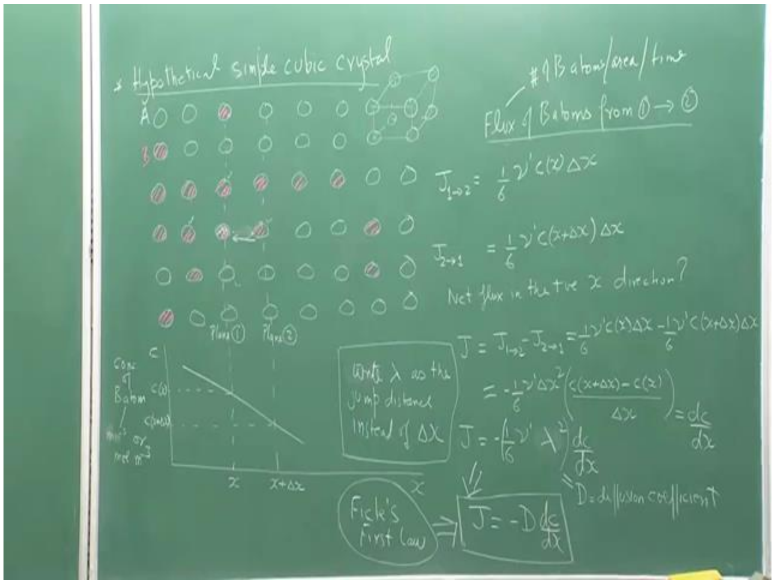

So, flux of B atoms from plane 1 to plane 2, the flux of B atoms from plane 1 to plane 2 could be written like this, first let see the units incidentally for flux would be number of B atoms per unit area per unit time. Let us say we are looking at a unit cross section of a unit area, then the volume that is in between plane 1 and plane 2 is simply delta x.

The area of cross section being unity, multiplying with c x the concentration which is number of atoms, B atoms per unit volume are the total number of atoms B atoms on plane 1 per unit area of the plane. So, so many atoms can jump from 1 to 2 but of course not all of them are going to jump, so there is a certain jump frequency that this is the rate at which B atoms are jumping. So, let me call that frequency as new prime, this is exactly the same jump frequency that I used in the random walk problem of the last lecture.

So, this is the total number of jumps per unit time, per unit area of B atoms in plane 1. However not all jumps will take a B atom for plane 1 to plane 2. Some of the jumps, for example if this is the atom that considering it can jump here it can jump here at the top atom or at the bottom total of 6 possibilities out of which there is a only 1 possibility which will take this B atom from plane 1 to plane 2.

So, out of total of 6 possibilities only 1 possibility will uhh move this atom from 1 to 2, hence the probability of an atom jumping from 1 to 2 is 1upon 6 and of course this jump frequency which would take into account the position being vacant etc uhh would also be there. We are going to talk about more in detail regarding the jump frequency later.

So, this gives me the flux from 1 to 2 of B atoms per unit area per unit time. Now similarly B atoms can jump from plane 2 to plane 1 in a similar situation. In that case the total number of atoms available per unit area is c x plus delta x, concentration in plane two multiplied by the volume would give me number of B atoms in the plane 2 per unit area multiplied again by the jump frequency and multiplied by 1 upon 6 because again there is only one jump which would take an atom from plane 2 to plane out of the 6 possible jumps.

Hence this is the flux of B atoms per unit area per unit time from 2 to 1. So, I have now flux od at B atoms going from plane 1 to plane 2, I have flux of B atom going from plane 2 to plane 1 out of these. So, what is the net flux, so net flux in the positive x direction. So, the net flux in the positive x direction let me call that as J and clearly this is J 1 to 2 minus J 2 to 1. If I write this so this is simply 1 by 6 new prime c x delta x minus 1 by 6 new prime cx plus delta x time delta x. This is equal to and let me write it and rearrange it a little bit and let me write it like this minus 1 upon 6 new prime delta x times c x plus delta x minus cx.

If I multiply and divide by delta x then I have this, this term is nothing but the slope of this line and the slope of this line can be simply be written as dc by dx on the concentration gradient. Hence, the net flux becomes minus 1 upon 6 new prime delta x square times dc by dx. Let us look at this term and in fact before this let me also replace, let us instead of let us write the jump distance, write lambda is the jump distance instead of delta x.

So, replace this delta x by lambda square, lambda is this delta x or this is nothing but the distance between atoms and I in the last lecture also I had taken lambda is the distance between the atoms so I have just replace delta x with lambda. This term is circular brackets has a jump distance squared multiplied by the jump frequency and this we would call it as a some kind of a parameter D which is what is known as the diffusion coefficient. So, from here the net flux is minus D dc by dx and this is called as the Fick’s First of diffusion.

Note the negative sign here and note the slope of this line, the slope of the line is minus and this minus will become plus and the flux would be in the positive x direction from higher concentration of B atoms to lower concentration of B atoms. A little bit about units in this equation or Fick's first law.

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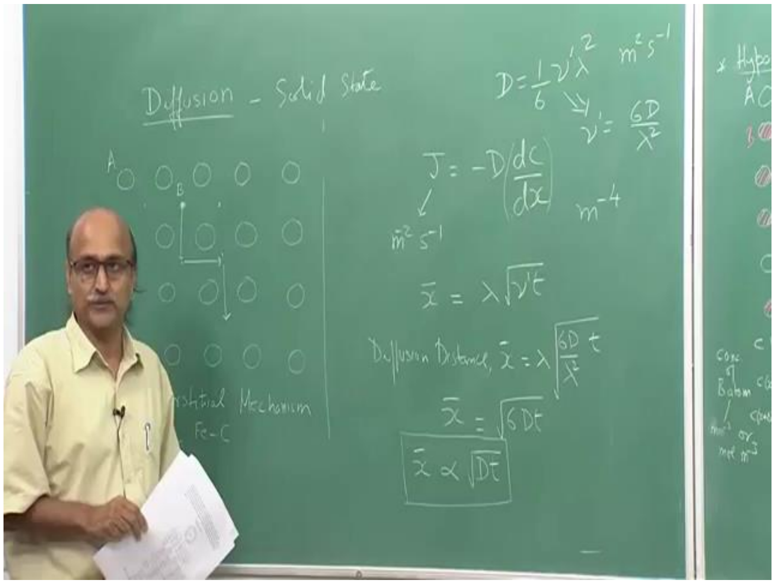

So, this is my Fick's first law, flux is equal to minus D dc by dx. if you look at it D itself, we have written as 1 upon 6 new lambda square. This has units of distance square per unit time. So, typical unit for D diffusion coefficient is meter square per second. If you look at units of this, this is number of atoms per unit volume, the number of atoms per meter cube and this itself is meter. So, the units of dc by dx is meter to power minus 4, and if you look at the units of this clearly we have the put the units for D, put the units of this the units of flux J is simply meter square per second. So, number of atoms moving in a certain direction through a plane of unit area in 1 second.

Finally, let me reconcile with what we are done in the last lecture. In the last lecture diffusion distance if you recall the relationship, we had written this relationship as x bar is equal to lambda square root of new prime t. And here the diffusion coefficient is 1 by 6 times new prime lambda square. So, from here I can write new prime as 6D upon lambda square, will substitute in this the diffusion distance, x bar becomes lambda square root 6 D upon lambda square time t or simply x bar is equal to square root of 6 D t.

Now this factor of 6 is coming simply because we have taking the simple cubic crystal, if we had taken some other crystal this factor would be different. So, in general the diffusion distance x bar is proportional to square root of D t. This is also an important proportionality that keeps cropping up whenever we have diffusion. So, in this lecture I have introduced the Fick’s First law will go ahead with this and continue our discussion in the next lecture and introduced what is called as the Fick’s second law. Thank you.