Defects in Crystalline Solids (Part-I)

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Lecture – 15
Diffusion in Substitutional Alloys+Diffusion along Defects

So, J V plus J A plus J B is equal to 0 that is sum of all the fluxes must be equal to 0. What this is saying is that, vacancy can be treated as one of the constituent as far as flux is concerned.

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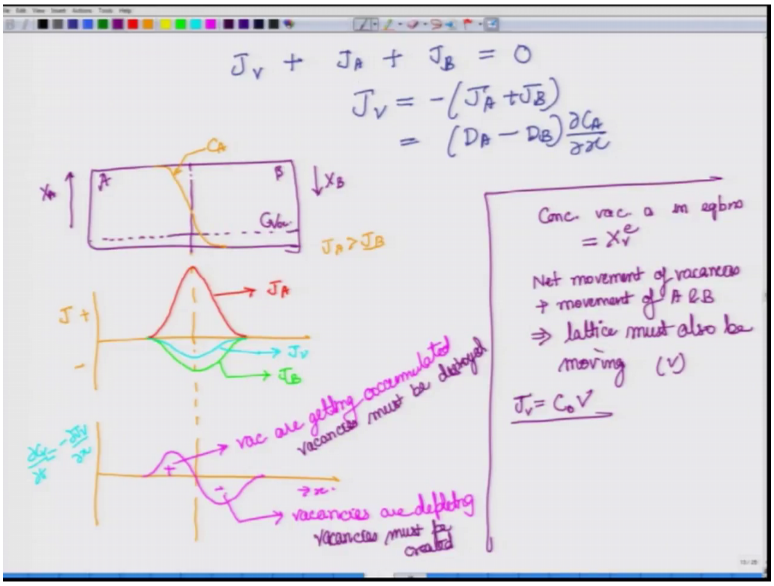

So, the sum of all the fluxes of all the constituents must be equal to 0. Otherwise, it would be like one side you are creating vacancies which is or not creating, but you are creating some gap vacancies will be created as we will see. So, there will in order to avoid that dilemma, this is you can say mass conservation relation that we will arrive at flux of all the 3 constituent should come to 0.

Therefore, J V is equal to minus of J A plus J B and which we derived last time in terms of del C A by del x. So, we can write it as. So, we have derived it in terms of del C A in the terms of constituent A.

Now, let us look schematically how this concentrations would vary, what is the meaning of thee fluxes, what is the meaning of the change in the gradient. So, we have a system let us say, where it was A to begin with this was B to begin with and this was the interface between these 2 and let us say that on the y axis the we will consider X A. So, obviously, on this side we have one X B and on in this side and this side we will count inverse of this. So, X B would be like this. So, X B is equal to 1 at this point X A is equal to 1 at this point.

But at the interface there will be diffusion taking place. And therefore, the final concentration would appear something like this. So, this is the concentration that we draw here for a atom. So, this is C A. Now, if we have concentration for C A or one of the concentrations, then we can also draw the flux how the flux would change. So, let us draw J.

So, this is positive flux meaning moving from left to right and negative flux meaning moving from right to left and this is where our assumption which does not change the generality of the equation which is J A is greater than J B. So, it will look like something like this. So, as you remember J A will be proportional to del C A by del x. Therefore, we have to take the concentration gradient. So, the co-gradient is highest at this point the flux will be highest at this point and it is lowest at these points. So, this is about A.

Now, the B component which is smaller would look something like this and remember B is moving in the opposite direction right to left. Therefore, we have shown it on the negative side. Now, if as you can see if J moving this side B is moving this side then there is a net imbalance and that net imbalance is balanced out by vacancies; so this is where vacancies come into picture. So, this is J V this is J B and this is J A. This is how flux changing which has directly related to the gradient of the concentration.

Now, so far everything is good. But now, let us how the cons how the vacancies would change with time. So, we know that del C V by del J V is equal to minus del J V by del x meaning if we take the another next gradient of this concentration. So, first gradient is J. If we take another gradient, then we will get how the concentration changing with time. So, this is what we will try to draw over here.

So now, this is the concentration change in concentration vacancies with time and we are taking the gradient of this part and as you can see that gradient here would be. So, what does this mean? This means that, right now this is still x axis. So, this means that vacancies have been created or not created sorry vacancies are getting accumulated over here and over here vacancies are getting depleted. So, it is moving away the negative sign shows. So, this del C V by del t meaning it is negative which means that, it is decreasing with time and it is decreasing highest at this point lowest at this point and also at this point.

So, at these 2 this is a kind of a unique feature when you look in the diffusion in detail that there is the point where the concentration change is still 0 which is at this point, but anyways we will not discuss this is part of larger diffusion course. So, the vacancies are depleting over here and they are getting accumulated over here. But, remember what we what one of the major assumptions that we had was that the concentration of vacancy is in equilibrium concentration; which means that the concentration or vacancies must remain constant throughout. So, something like the vacancies must remain like this.

So, if we are taking about the concentration, the vacancy concentration must or C V must remain something like this and here we are showing that vacancies are getting accumulated here. We are showing vacancies are getting depleted. Therefore, over here, vacancies must be destroyed internally not externally, but the system must destroy the vacancies in some way or the other and here vacancies must be created.

So, those will happen by movement of dislocations and also of the latticides. So, there will be that movement of dislocations would lead to one side creation vacancies and on the other side destruction of vacancies. So, this is one thing. But, however, one what cannot be forgotten is that a net flux of vacancies is moving from right side to left side and this net movement of vacancies would imply at least in the local region plus the movement of vacancies plus the movement of A and B atoms implies that the lattice must also be moving.

So, this is a very important result which was also shown by Kerkendle. But, here because of the presence of these defects, vacancy defects you can re-understand now that the lattice the lattice must latticides must be moving which you would be able to see or observe in terms of the interface the interface between the A and B you would see that it has moved and that is how Kerkendle was able to show this.

Anyways, we will move on to. So that this is now, this is the lattice is moving. So, we can say that there is a velocity V and since it is the oral concentration. So, the total flux vacancies can like I said earlier, now can be related to this C naught V. So, this is the net movement of lattice velocity V which is related to the flux of vacancies. So, C naught V gets the vacancies. So, this is another very important result which now we will use to get to our inter diffusion coefficient. Now, this vacancy V J V also varies in some way as the sorry the flux of vacancies also varies in the same way as the flux of A and B.

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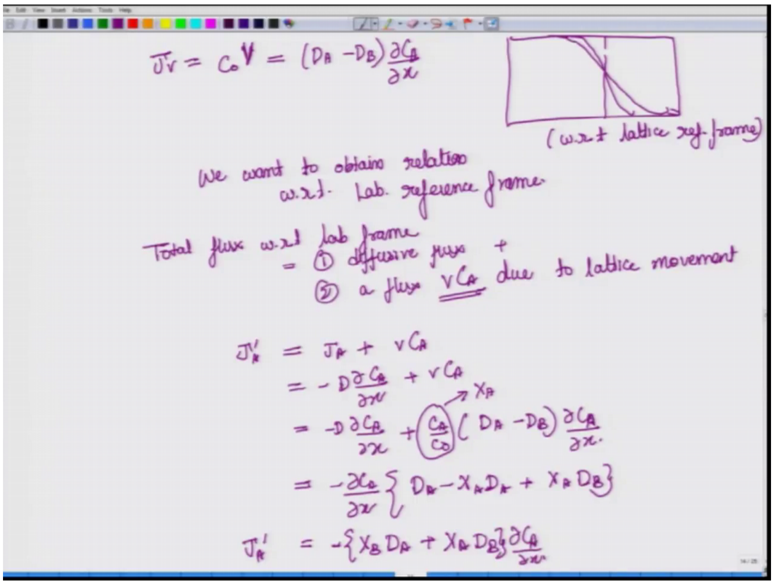

So now, let us see how we proceed to get the equation. So now, we have seen J V is equal to C naught V, but we had earlier said that this is equal to D A minus D B del C A by del x. So, here this part is saying that flux of vacancies is the same is treated similarly as flux of A and B. So, we had J V equal to minus J minus J B and here we saw that J V is equal to is what leads to the movement of lattice. So, we have a relation J V equal to C naught V and this will help us in getting the next stage of relation.

Now, so, next part that we need to realise is that we are said that the lattice is whatever velocity or concentration we are talking about so far. What we are talking about is with respect to sample reference frame, not even sample reference frame actually with respect to lattice reference frame. So, these concentration change in the concentration.

So, for example, when we said that the concentration is varying like this and overtime, it should go like this. We are assuming the lattice is we are setting on the lattice and hence watching this displacement or watching this change in the concentration. But, now we want to shift or we want to obtain relation with respect to laboratory frame of reference.

Now, the with respect to laboratory frame of reference, what you need to realise is that total flux can now be con assumed to be contributing contributed by 2 parts total flux with respect to lab frame one is the usual that we know is the diffusive flux. That we have already accounted for plus the second one is a flux v C A due to when we are talking about the concentration change in A, there is also a change in concentration because of the movement of the lattice.

So, that will be the presented by v C A. So, this is a rational term when we move on to the lattice frame of reference. So, flux v C A due to lattice movement. So, we can denote this flux with respect to lab reference by this prime. This prime denotes lab reference frame flux this is equal to J A which is our diffusive flux plus this quantity v C A which is because of the movement of the lattice. And this can be written as minus D A del C A by del x plus v C A and we have seen the relation for V over here.

So, we can change it to minus D and when you put them together what you will get is D A minus X A D A plus X A. This is X A; this quantity is X A. So, this gets multiplied by X A D B and when you look at this 1 minus X A. So, this becomes X B times da. And therefore, our relation is like this X B D A plus X A D B into del C A by del x. So, let me rewrite it.

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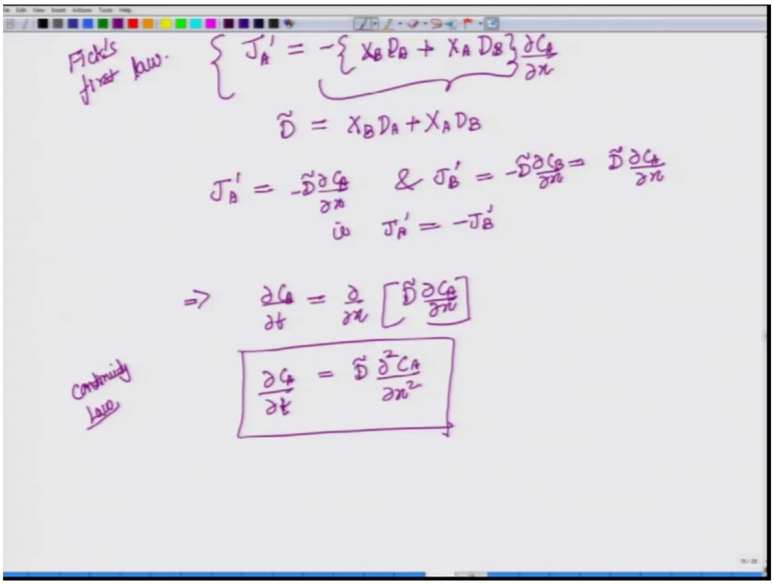

In the new page, now this quantity is something which is combination of 2 diffusivities and this is usually termed as inter diffusion coefficient. So, you can put something like this which is inter diffusion meaning something which is related to the presence of diffusivity of A in B. Now the diffusivity of A in A is different, diffusivity of A in B is different, diffusivity of A in C is different. So, they have to be careful.

So, this is a quantity which is being predicted only for diffusivity of A in B. And therefore, this is written like this of course, this it helps that you can expand it in this form. This way, once you know this you can also relate it with third component C and so on. So, this is and this becomes our Fick's first law.

Now, J prime we know can also be written as del C A by del x. So this, has come down to similar form of equation. So, you see that the overall formalism of the equation is still same only that what goes inside coefficient or the pre factor D. So, that is that has changed when we move from interstitial diffusion to self-diffusion to substitutional diffusion and J B prime is equal to minus D or you can still express it in terms of C A.

So, the negative sign goes away because C del C A by del x is inver minus of del C by del x; and this also means that in this reference frame J A prime is equal to minus J B prime. So, you can see that in the laboratory frame of reference this J prime is equal to J B prime and if you want to write the continuity law, it is similar just that instead of the D A or D B. Here, we will have inter diffusion coefficient and depending upon whether it is constant or not you can take it out.

So, assuming that it is constant over the range of interest this becomes. So, this is the continuity law which is also known as Fick's second law. So now, we have looked at diffusion in all the 3 cases; one was the interstitial diffusion, then we looked at substitute self-diffusion and then we looked at in a substitutional law the diffusion. So, this has given us given us decent understanding of how the these defects have or display a important property which is mass flow. Now, let us look at another important aspect which is interaction of these phenomena with other defects.

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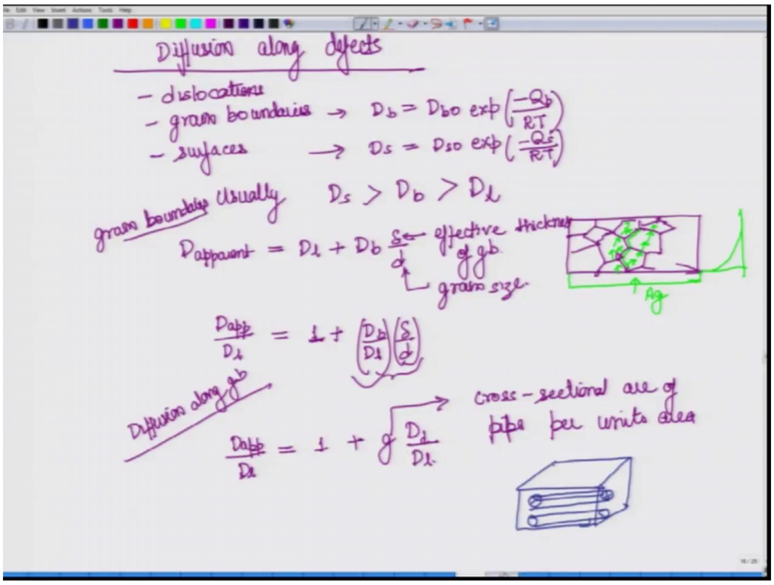

For example, we will quickly look at this part which is diffusion along defects. Now, we have seen that diffusion itself is a phenomena dependent or exhibited by defects which is like point defects vacancies or interstitial defects that may be there now this diffusion itself can also be affected by other defects. So, for example, your vacancy is jumping, but how will the vacancy. Now so far we have considered vacancy is jumping inside a lattice, but how will this vacancy jumping be effected if we are talking about dislocations a grain boundary.

So, what kind of defects? We are talking about something like dislocations grain boundaries even surfaces like I remember I told you in the beginning lecture that even surfaces are a defect because, there is no continuity. And if you look at the general form of the equation, you will not be able to differentiate you would see that this relation is still same.

And if you look at the surfaces and in matter of general comparison you would you should also know that usually D S surface defects or the diffusion through the surface will be greater than diffusion through grain boundaries which will be greater than diffusion through lattice boundaries. We will look at this location also separately not in much detail just to give you a brief understanding in these cases. For example, let us say we are talking about grain boundaries the in grain boundaries you can get a D apparent meaning let us say you have a polycrystal material. So, I will not draw any more, but you understand now that let us say we have a concentration of something or let us say we are putting in some component here may be silver. Now, you want to know how this concentration of the silver varies with the thickness.

So, there will be a very large concentration over here. So, we are drawing on the x over here this is the x axis, this is the distance and y axis is the concentration. So, it will vary something like this, but over here which is the diffusivity that we have to take is the question and what you will realise is that like we have said grain boundary diffusivity is greater than lattice. So, a lot of diffusion will take place like this and also some will take place like this, so because there is ba bulk. So, from bulk to the grain and again from the grain to grain boundary to the lattice again lattice to the boundary from here.

So, there are different paths for diffusion to take place which will be a mix of lattice diffusion and grain boundary diffusion and hence we need to define a term D apparent and this D apparent is given by this D lattice plus D B delta by D where what is delta delta is effective thickness of grain boundary. Let us say, we have a very large diffusivity of grain boundary, but we have a very large thickness of grain boundary. But, it is still if the thickness overall thickness of the grain boundary is very small, then it will not contribute to the total mass transfer and that is where this picture this type of relation comes into picture and this D would is grain size.

So, the relative ratio between these 2 sizes is what tells you the importance of D B. If this is a very small quantity, then you can imagine this will not contribute. If this is sufficiently large, then this will start to contribute because anyways this is a very large quantity.

So, this can also be written as D app by D L meaning relative with respect to lattice diffusivity how different it is. Then, this will give you a much better idea what how these 2 are related. So, you can see that D apparent is 1 plus some quantity. So, obviously, what it is saying is that D apparent will be always greater than D lattice, but by how much will depend upon this quantity and in particular delta by D because D B is almost always orders of magnitude higher than D lattice.

Now, what is the coordinating ratio between delta by D will W A will decide with over all factor this particular factor. And therefore, you can decide what will be the; you can find out predict what will be this diffusion profile look like. And similarly, we can look for diffusion along on the very same line without going again into details. We can look at diffusion along grain boundaries and it will look something similar here instead of 2 factors. We have a g which I will show you what it means. So, this is D dislocation by D lattice and g is of pipe per unit area; what is this pipe we are talking about.

So, let us say we have again a crystal like this and inside these crystals you have defects dislocations like this. So, along this we will form a pipe along which the diffusion would be much faster. So, the diffusion will take place along these pipes and this g is talking about cross sectional area of pipe per unit area.

So, basically if this is the total area, what is the sum of all the areas of these cross sectional pipe is what this g factor denotes. So, as you can see if you have large dislocation density going from 1 g factor will again be much larger. And therefore, this relation would look like this and here this will be a very strong contribution.

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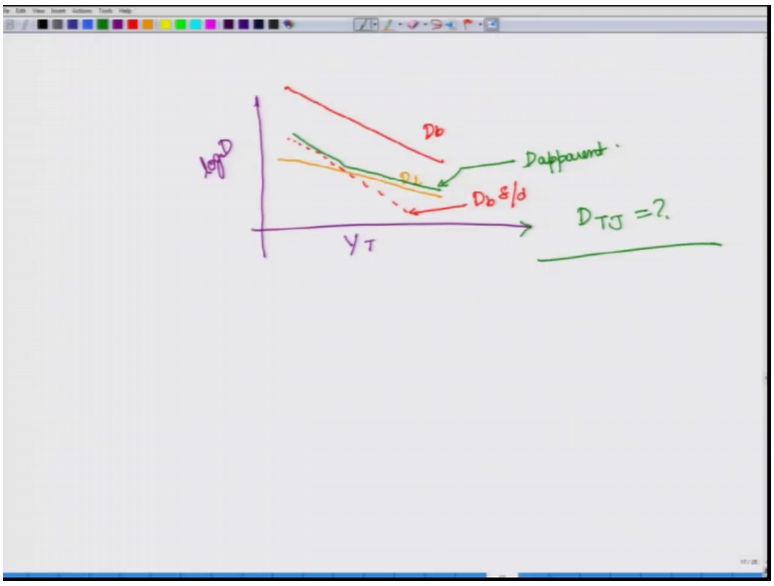

Now, we will summarize. Now, we will summarize this diffusion aspect with one last drawing which shows you how the diffusion actually varies with or when we said that diffusion through surface is larger than diffusion through boundary and it is much larger than diffusion through lattice. So, this is the diagram which will give you this understanding. So, here let us say this is temperature which is given by 1 by t and this is log of D.

So, the lattice diffusion would be somewhere like this grain boundary diffusion would be somewhere like this. Now, this into this grain boundary diffusion; so this is D B, this is D lattice. Now into this D B; we will multiply the factor delta by D. And therefore, this will become something like this. So now, this is D B into delta by D.

Now, you can see that there is a particular temperature at which beyond which this boundary is boundary diffusivity is higher the slopes are usually in this fashion that it becomes more important that at high temperature and lattice diffusion is important at lower temperature. And therefore, the effective diffusivity would be like this. So, this will be a D effective or D apparent and I will leave you with a thought how diffusivity through triple junction would come into this picture, where should it come to this is the end of week 3 and at the same time, this is also the end of point defect.

So, we have looked at quite many aspects of point defects and in particular, we went to one of the phenomena represented by this which is diffusion in a greater detail. So, we have looked at several of these aspects. And next, we will move on to another defect which is the dislocations. So, see you in the week 4.

Thank you.