Diffusion in Multicomponent Solids
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Lecture 42

Welcome back. So, far we have gone through the theory of diffusion. First we looked into the phenomenological aspect of diffusion. Then we went into details of the atomistics of diffusion. We looked at the atomic mechanisms of diffusion and also, we analyzed the diffusion process in terms of the atomic jump frequencies, which helped us to establish a correlation between the phenomenological coefficients and the fundamental atomic jump frequencies.

Next few classes I would like to take you over the experimental techniques that are used for determination of different types of diffusion coefficients. Now when you look into the literature on diffusion, you will come across various kinds of diffusivity terms and at times it is confusing. Most of these diffusivity terms we have already covered at different points in the class. But to summarize, I will briefly explain the different types of diffusivities which are used.

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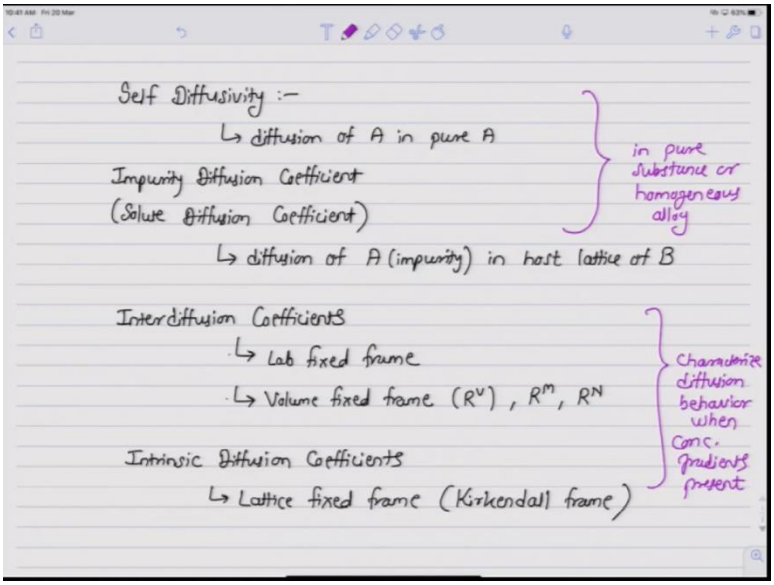

The most fundamental is the self diffusivity, or the self diffusion coefficient. It essentially refers to the diffusion of an atom in its own pure lattice. For example: diffusion of A in pure A. Second type of diffusivity is called the Impurity diffusion coefficient. This is also referred to as solute diffusion coefficient. And as the name suggest impurity diffusion coefficient is the diffusion

coefficient that characterizes the diffusion of an impurity atom in homogenous host lattice. We can define this as diffusion of A impurity in host lattice of B. Now the self-diffusion and impurity diffusion are essentially the diffusion phenomena that occur when there is negligible concentration gradient. In other words, these terms characterize the diffusion in a homogenous alloy. When there is concentration gradient present, then we also need to take into account the cross effects of different concentration gradients, which we have gone over. And then we have to define different diffusivity terms. So, when the concentration gradients are present we would like to define interdiffusion coefficients.

Now whenever there are concentration gradients presents, in presence or absence of external driving forces there will also be some drift associated with it. For example, we have seen even in the absence of any external driving force if the molar volume varies with composition, more precisely if partial molar volume of components varies with composition then there will be a drift because of the net volume flow. And hence in such cases we need to first fix the frame of reference. I have explained various frames of reference at the beginning of this class. When we talk about lab fixed frame of reference, the flux is measured with respect to a frame which is stationary. We had already talked about different frames of reference. Most widely used of it is the lab-fixed frame.

Now if we fix the frame of reference at the local center of volume such that the net volume flow is 0 at any plane, it is referred to as volume fixed frame of reference. This is also referred to as R^v. So, we can also measure the flux with respect to volume fixed frame and the diffusivity measured with respect to that would be the diffusivities with respect to volume fixed frame of reference. Typically for the assumption of constant partial molar volume, the volume fix frame coincides with the lab fix frame.

We can also define flux with respect to local center of mass or with respect to local center of number of moles of the components and those are called mass fixed frame or number fixed frame and on. Those are denoted as R^M and R^N. We can also determine the flux with respect to a frame of reference which is fixed to a particular lattice plane. It is then referred to as intrinsic diffusion. And the diffusion coefficients evaluated with respect to lattice fix frame are called intrinsic diffusion coefficients. And this is with respect to the lattice fixed frame. This is also known as Kirkendall frame of reference. These are various types of diffusion coefficients that we typically

encounter. Again the self and impurity coefficients basically characterize the diffusion in a pure substance or in a homogenous alloy. And the interdiffusion and intrinsic diffusion coefficients characterize the diffusion behavior of different components when there are concentration gradients present.

Note here, although the interdiffusion coefficients and intrinsic diffusion coefficients characterize the diffusion behavior in presence of concentration gradients, these coefficients are not functions of concentration gradients, but they are functions of composition only. In order for them to be material properties, they have to be functions of composition. If they depend upon concentration gradients, then they will not be material properties. And as we have seen through the theoretical relations as well as experimentally in several systems, these are the functions of composition. Whenever there is a concentration gradient present at each x coordinate, since the composition is different, the set of diffusion coefficients that we need is different. But still this set of diffusion coefficient depends upon composition and not the concentration gradient. That means if we are dealing with the same composition, no matter what is the concentration gradient at that composition plane, the set of diffusion coefficient should be same.

Look into some of the experimental techniques that are used for characterizing these various diffusion coefficients. Let us start with self and impurity diffusion coefficient in today's class.

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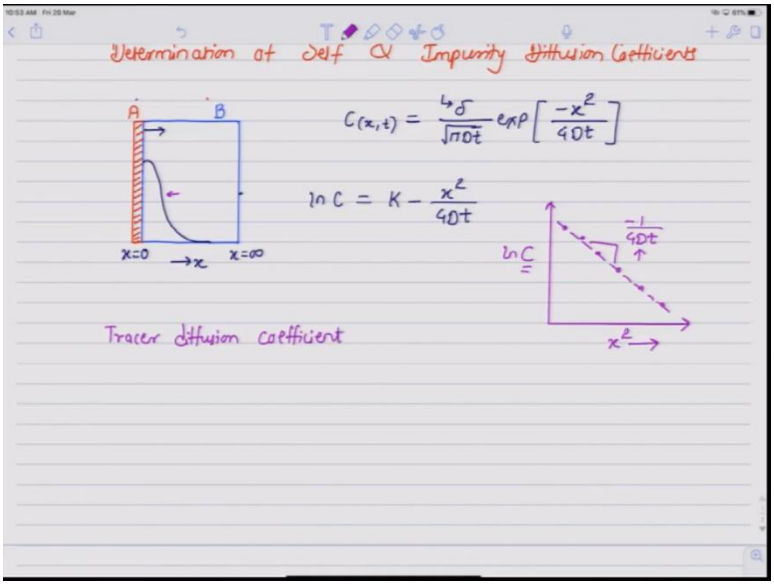

For determination of self or impurity diffusion coefficient, we can make use of solution to the diffusion equation that we derived in lecture 20 of this class. If you remember, we dealt with the boundary conditions of instantaneous planar source which is presented here in this diagram. We have in this case, a thin layer of A deposited on to a surface of pure B. Now this thin layer is really thin, so that its thickness can be assumed to be 0. If this assembly is annealed at a certain fixed temperature for certain time, A will diffuse into B and then it will develop some kind of profile like this, and we have derived the solution for this.

If you want to find the concentration of A at any position x at any time t, we can use the solution:

$$C_{(x,t)} = \frac{\delta}{\sqrt{\pi D t}} \exp\left[-\frac{x^2}{4Dt}\right]$$

where x represents the distance coordinate, that is the distance from the surface on which A was initially deposited. We have to remember, $x = 0$ is taken on the surface where A was initially deposited. Now this solution was valid for infinite boundary condition, which means it is assumed that the diffusivity and the diffusion time are such that this diffusant A does not penetrate all the way to the other end of B. And for all the practical purposes the other end can be assumed to be at $x = \infty$.

Then this parameter δ is nothing but the amount of A deposited per unit area initially. And if we consider unit cross section, it is assumed that throughout the thickness of B that amount δ remains the same. So, this solution can be used for getting the value of D for A in B. To simplify this if we take the logarithm on both side we get:

$$\ln C = K - \frac{x^2}{4Dt}$$

As δ is constant and we assume D is constant, only for that assumption we can derive this solution. this is constant. So, this is an equation of a line and if we plot $\ln C$ verses x^2, we will get a straight line with the slope of $\frac{-1}{4Dt}$. t is the diffusion time here. We know the diffusion time t and by determining slope we can get the value of D and this refers to the value of diffusivity of A in B. Here we assumed that D is constant but we know D is a function of composition. So, for this assumption to be true, one condition may be that the concentration of A throughout this diffusion profile has to be very very small. And since the concentration throughout is very small, the variation in D with x is not significant. Then we can apply this solution. This is true if the initial thickness of A deposited is very small close to 0. Now when this is true, we are dealing with diffusion of A in a very dilute solution of A in B. That means we are dealing with impurity diffusion of A in B. So, with this geometry, what we are going to get is the impurity diffusion coefficient of A in B.

Now second practical aspect, since the concentration at every plane is very small how do we determine these concentrations. Because we need to determine concentrations at many sections at many values of x. Typically, the tools that we use for measurement of concentrations are for example EPMA. They do not have resolution required for determining these concentrations at each plane as the concentration is going to be less then ppm.

So, how do we accurately measure these concentrations? Normal tools will not be able to that. And hence for these experiments, radiotracers of A are used. Why radiotracers are used? Because they emit gamma or beta rays and the count rate of the emission can be very accurately and precisely be measured. Since we use the radiotracers, the diffusion coefficient determined is commonly referred to as Tracer diffusion coefficient.

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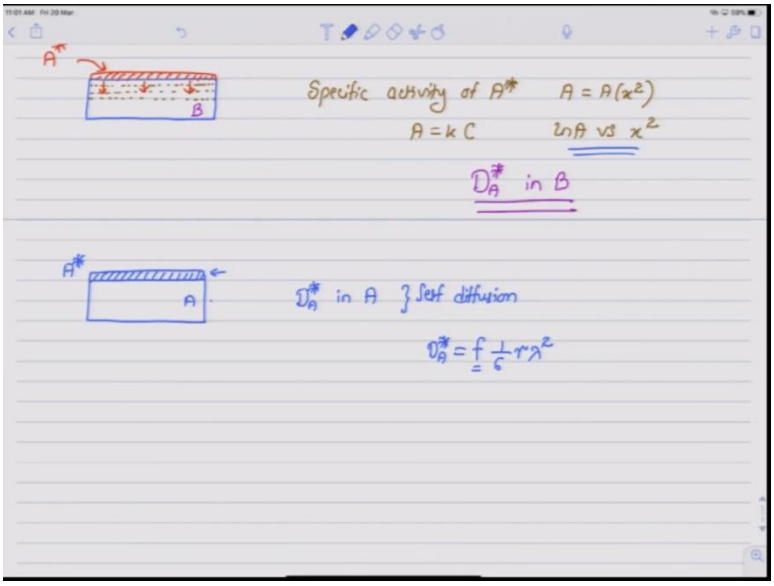

One can determine the impurity diffusion of A in pure B or in a homogenous alloy, in which A is an impurity. Right?It can be for example, diffusion of copper in pure nickel, or it can be diffusion of copper in a nickel zinc alloy. Of course the impurity diffusivity will be different in both the cases. But both are characterized as impurity diffusion coefficient of copper in that particular lattice or in that particular alloy.

So, we take the substrate of B and its surface is metallographically polished very well. Then a thin layer of radiotracer A is deposited on to the polished surface. The radiotracer is usually denoted by the symbol star. And then the diffusion is allowed to progress by heating the assembly at the desired temperature for desired time. A diffuses inside, after the desired annealing time the sections are cut perpendicular to the diffusion direction and thin slices are removed. Specific activity of A^* is measured in each slice and the specific activity which is written as A is plotted as a function of x^2. That is a square of the distance from the surface.

The specific activity is directly proportional to the concentration of A^*. We can write:

$$A = kC$$

Since there is a direct proportion, we can very well $\ln A \ vs\ x^2$ instead of $\ln C \ vs\ x^2$. Because in both cases the slope should be same. By plotting $\ln A \ vs\ x^2$ and by determining the slope of the plot, we can get to the tracer diffusivity of A in B. It is usually denoted as D_A^* in B. It is the impurity diffusion coefficient of A in B. This tracer diffusivity refers to the impurity diffusion of

A in B. Now there are various ways in which the deposition can be done. The deposition of radiotracer can be done by either physical vapor deposition, that is by evaporation, by electro deposition, or it can be done by applying a solution of A^*on to the surface and drying. Similarly, there are various ways in which sectioning can be done after the diffusion experiment. If the diffusivity is larger, a large enough diffusion zone is created and we can go for mechanical sectioning. If the diffusivity is very small such that a very small diffusion zone is created then, one has to take the help of iron beam sputtering.

Now coming back to this geometry, here we are we talked about determination of diffusivity of A^* in B, what about self-diffusion? Self-diffusion is basically the diffusion of A in pure A. Now how do we identify, or how do we trace a particular atoms of A in pure A? Because all the atoms of A are indistinguishable. Here again the radiotracers or radioisotopes come to our help.

So for determining self diffusivity, we start with substrate of pure A and deposit a radioisotope of A on top. Now the radioisotope is almost similar to the normal isotope of A, except that it has a different mass. So, it is going to exhibit almost the same diffusion behavior as that of the regular isotope of A. And hence, A^* in A will characterize the tracer diffusion which can be taken as self-diffusion coefficient of A. For self-diffusion measurement we have this type of geometry, deposit a thin layer of A^* on A, rest everything is same. Determination of the specific activity of A by sectioning and plot $\ln A \ vs\ x^2$ to give the self-diffusivity of A, that is D_A^* in A. And this is the self-diffusion.

Now this D_A^* is not exactly the diffusivity determined by Einstein, which is given as:

$$D = \frac{1}{6}\gamma\lambda^2$$

in any cubic lattice. But we can relate it to the experimentally determined D_A^* by applying the correlation factor f. We have talked about this correlation factor f and we have even derived correlation factor in some of the cubic lattices, and this is a geometric factor. So:

$$D_A^* = f\frac{1}{6}\gamma\lambda^2$$

Now, I would like to show some of the reports from the literature which have determined the tracer diffusion coefficients of A in B. Some examples will be given from the literature on experimental determination of tracer diffusivities.

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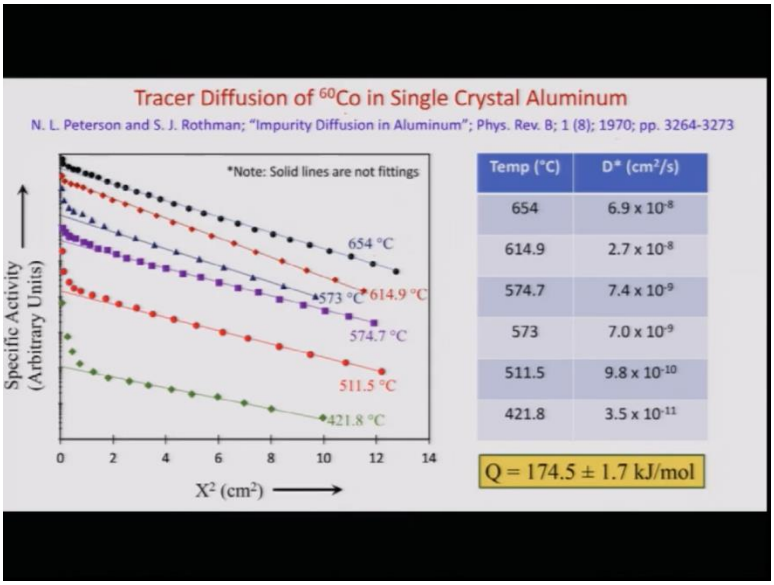

The first example is from the work reported by Peterson and Rothman back in 1970, on impurity diffusion in aluminum. They have reported various tracer diffusivities in aluminum. I would like to take the example of Impurity diffusion of cobalt that they have reported. They used cobalt 60 isotope for this. They deposited this cobalt isotope by evaporation on the single crystal aluminum substrate. Using single crystal aluminum gives precisely the bulk impurity diffusion coefficient, because there is no interference from grain boundary diffusion.

These are the profiles of specific activity versus distance square, as they have reported. Now these data points may be a little bit inaccurate because I have extracted the data from this paper and re-plotted here. Also, note that the straight lines that I have shown are only indicative, they are not the actual fittings. So, we can see they have done the experiments at various temperatures including 650 ℃, 614.9 ℃, 573 ℃ down to 421.8 ℃.

Most part of each dataset can be fitted by a straight line as expected. However, near to the surface that is close to $x = 0$, we can see each of the plot deviates from the straight line, and it shows some upward curvature. And the reason for this as they have mentioned is because of the oxide layer that quickly tends to form on aluminum surface. The tracer which is deposited on this oxide layer has to first diffuse through this oxide layer which is very slow. And hence, the initial part of each of the curve shows an upward curvature here.

However, they fitted the later part with a straight line which essentially gives the impurity diffusion of cobalt in aluminum. By determining the slope we can get to this D^*_{Co} in aluminum. With this the diffusivities determined at various temperatures as reported by them are presented here in this table.

We can see over the temperature range of about 421 ℃ to about 654 ℃ , the impurity diffusion of cobalt is varying over three orders of magnitude. With this they also evaluated the activation energy for impurity diffusion of cobalt in aluminum, which comes out to be about:

$$Q = 174.5 \pm 1.7\ kJ/mol$$

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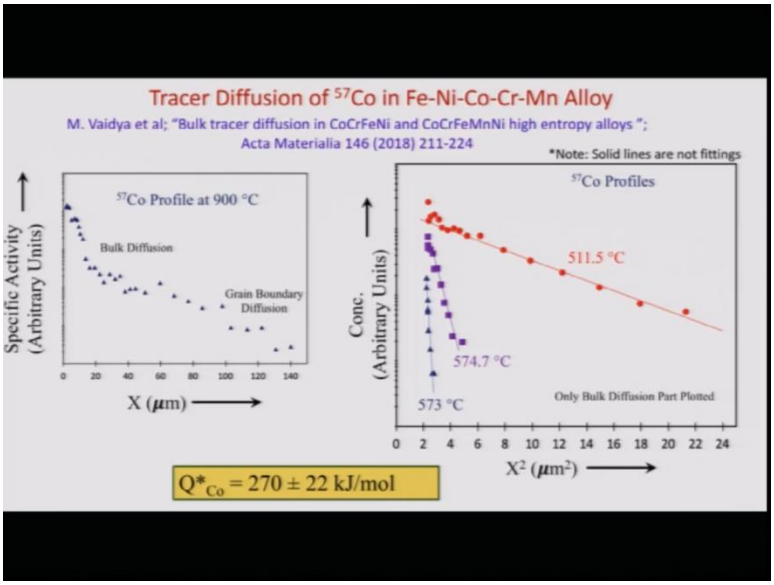

Now I would also like to present a very recent report on tracer diffusion experiments. This is from the work of Vaidya and group. They determined the tracer diffusion coefficients of all the constituent elements in the quaternary Co-Cr-Fe-Ni and quinary Co-Cr-Fe-Mn-Ni alloys, at the equimolar concentrations. These are very popular these days and are referred to as high entropy alloys. Diffusion is one of the most debated topic in these high entropy alloys.They determined the tracer diffusivities of each of the constituent elements in these two alloys. Here I am showing the plots of cobalt 57 isotope activity versus distance as presented by them. Again the data points may be not very accurate because I have extracted the data from the paper and re plotted here.

We can see on this plot of specific activity versus distance, there are two distinct slopes on this plot. The first part refers to the bulk diffusion which is characterized by a higher slope. Since the

slope is $\frac{-1}{4Dt}$, higher slope refers to the lower diffusivity. The later part corresponds to the grain boundary diffusion. Because they conducted the experiment in poly crystalline materials, it is also possible to determine the grain boundary diffusion. They have done it, I will not discuss it here, I will just focus on the bulk diffusion. They plotted the bulk diffusion portion.

Specifically for cobalt I have shown here at three different temperatures. Again the data are extracted and re plotted here, just like the last plot the solid lines here again are not the actual fittings, but they are just indicative. We can see this data can be fitted with a straight line and hence the impurity diffusion. And hence the tracer diffusion coefficient of cobalt can be determined in this alloy.

This I have shown in the Co-Cr-Fe-Mn-Ni alloy. Now since, cobalt is also a part of the host lattice, this will be referred to as self-tracer diffusion coefficient of cobalt in this particular high entropy alloy. And with this, they determined the activation energy of cobalt to be:

$$Q = 270 \pm 22\ kJ/mol$$

They have also done the experiments of tracer of each of the constituent element.

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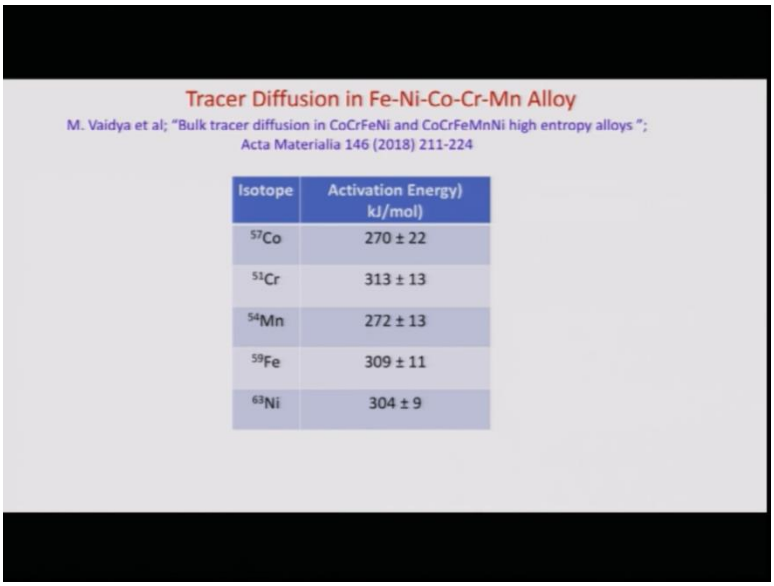

And in this particular quinary system the activation energies that have been reported by them are listed here. They used cobalt 57, chromium 51, manganese 54, iron 59 and nickel 63 isotopes. We can see the activation energy of cobalt is the lowest, whereas the activation energy for

diffusion of chromium is seen to be the highest. These are some of the examples that I have shown from the literature. And this was about the determination of self or impurity diffusion coefficients by tracer technique. In the next class, we will talk about interdiffusion.