Diffusion in Multicomponent Solids
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Lecture 46

Now that we have gone through various techniques for experimental determination of interdiffusion coefficients in binary, ternary as well as higher order systems. Today I would like to show you some examples from the literature in which they have actually determined the interdiffusion coefficients. We will start with binary. I will also give one example each from ternary, quaternary and quinary.

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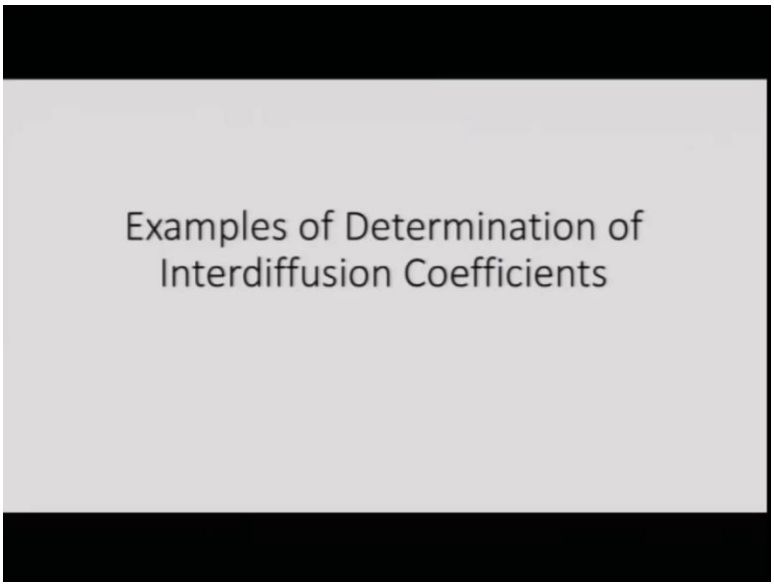

So, the following are examples of determination of interdiffusion coefficients from the literature.

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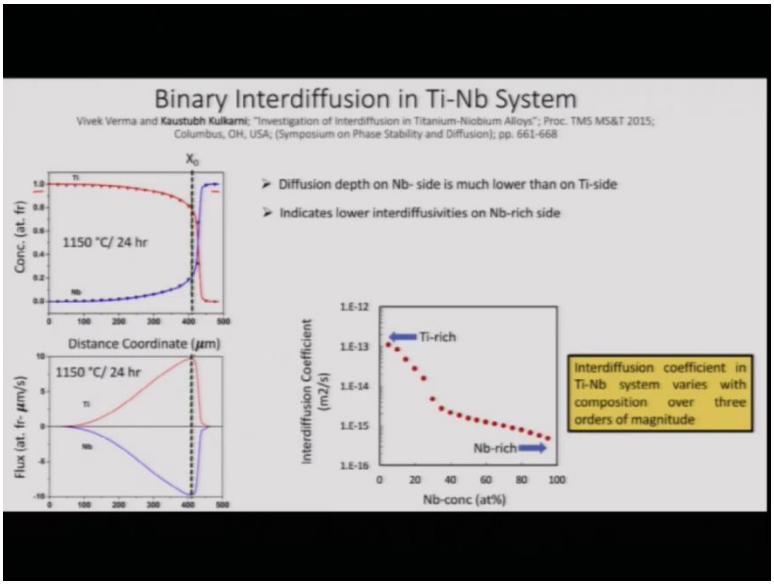

First, we look at a binary Titanium Niobium system. This we worked for determining interdiffusion coefficients as function of compositions at different temperatures. I have shown here one binary diffusion couple between pure Titanium pure Niobium. On the left side we have pure Titanium, right side we have pure Niobium.

The first figure here on top is the concentration profile. This diffusion couple was annealed at 1150 ℃ for 24 hours. As we can see, the diffusion depth on the Niobium side is much lower as compared to that on the Titanium side. This indicates that the interdiffusivities in the Niobium rich side are much lower compared to the interdiffusivities on the Titanium rich side.

We can see on the left side of the Matano plane x_o, the diffusion depth is about 400 microns. Whereas on the right side, that is, on the Niobium rich side, the diffusion depth is less than 100 micron. On the bottom figure here, we have shown the interdiffusion flux profiles. The red one is for Titanium. The blue one is for Niobium. These interdiffusion flux profiles were estimated based on the Dayananda's analysis that I discussed a couple of classes back. We can see as expected there is a minimum in the Niobium flux profile and maximum in the Titanium flux profile at the Matano plane. Again, as apparent even from the diffusion flux profiles, the diffusion depths are much smaller on the Niobium rich side.

We can evaluate the binary interdiffusion coefficients as functions of composition over the range of compositions developed in the diffusion zone in this binary couple. At 1150 ℃, the

interdiffusion coefficients that we estimated can be plotted against the Niobium concentration as shown here. We can see there is a big difference in the interdiffusivities on the Titanium rich side compared to those on the Niobium rich side. As we go from Titanium rich side to Niobium rich side, there is about 3 orders of magnitude difference in the interdiffusivities. Close to Titanium rich side, the interdiffusivities are about $10^{-13}m^2/s$. Whereas, towards the Niobium rich side, they drop down to about $10^{-16}m^2/s$. There is a big variation of interdiffusivities with composition in this particular system, Titanium Niobium binary system.

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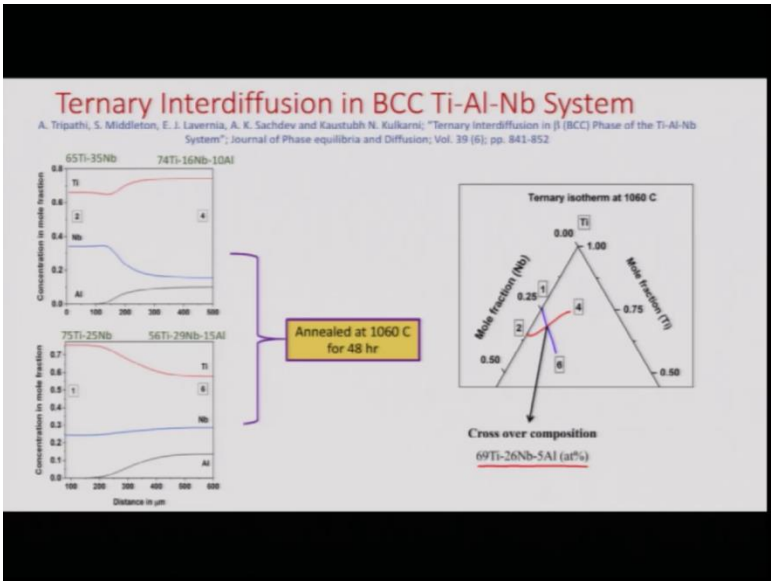

Next, we will consider a ternary example. This is again our group's work on Titanium Aluminum Niobium system. I have shown two ternary diffusion couples which were assembled at 1160 ℃ for 48 hours. The first couple on the left terminal alloy is 65 Titanium-35 Niobium, on the right side of the couple, the alloy, the terminal alloy is 74 Titanium-16 Niobium-10 Aluminum. These concentrations are in atom percent.

The second couple between alloy 1 and alloy 6 is shown at the bottom figure. On the left terminal alloy, we have alloy 1 with 75 Titanium-25 Niobium. On the right, we have alloy 6 with 56 Titanium-29 Niobium-15 Aluminum. In first couple, we can see the interesting features. There is a minimum on Titanium profile. There is a maximum on Niobium profile. Correspondingly there are also zero flux planes for Titanium Niobium. I have not shown the diffusion flux profiles here. Now, these two are the couples with intersecting diffusion paths.

If we plot the diffusion paths of these two ternary couples on the ternary isotherm, it will be like as shown above. The blue path is for couple 1-6. The red path is for couple 2-4. We can see they intersect at a composition. The composition corresponding to the crossover point is 69 Titanium-26 Niobium-5 Aluminum. Again, all the concentrations are in atom percent. We can determine the 4 ternary interdiffusion coefficients here by setting up 4 equations.

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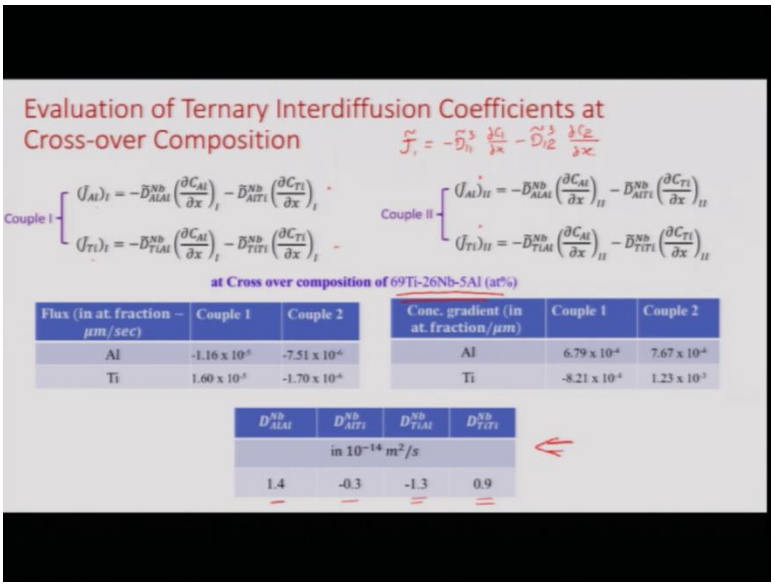

At the crossover composition in the first couple, we can write the equation for interdiffusion flux of Aluminum and interdiffusion flux of Titanium in terms of the 4 interdiffusion coefficients and the 2 concentration gradients. This is in 1 couple. We can write similar two equations in couple 2. So we get 4 independent equations which we can solve for the 4 coefficients. Here those coefficients will correspond to again this crossover composition.

In order to get an idea about what orders of magnitude the flux is, the gradients are, I have actually listed numerical values of interdiffusion fluxes in the left side table, of concentration gradients in the right-side table here. The fluxes for Aluminum and Titanium in couple 1 are about 10^{-5}. The units of flux noted here is atom fraction micron per second.

Remember when we write Fick's Law equation:

$$\tilde{J}_1 = -\tilde{D}_{11}^3 \frac{\partial C_1}{\partial x} - \tilde{D}_{12}^3 \frac{\partial C_2}{\partial x} \qquad (1)$$

We assume the molar volume to be constant. Now, in this equation, C_1 and C_2 are the concentrations which are in $\frac{moles}{cm^3}$, the flux unit is $\frac{moles}{cm^2 s}$. We can also express the concentrations in terms of atom fractions. If we express concentrations in terms of atom fractions, we can write:

$$C_1 V_m = X_1$$

X_1 is the atom fraction or mole fraction. If we divide both sides of Eq. (1) by V_m, we can express this equation in terms of gradient of mole fractions of the components. The unit of flux will change to atom fraction micron per second. But for this we have to assume that the molar volume is constant. We do this because it is easier to work with the atom fractions. Assuming molar volume constant, the volume fixed frame coincides with the laboratory fixed frame.

If we substitute these values of fluxes and concentration gradients in the 4 equations here, we can solve to get the 4 interdiffusion coefficients, the values of which are listed here. We can see the main coefficient of Aluminum is 1 order of magnitude larger than the cross-coefficient $\widetilde{D}_{AlTi}^{Nb}$. We have treated Niobium as dependent component here. For Titanium, the cross coefficient of $\widetilde{D}_{TiAl}^{Nb}$ is higher than the main coefficient of Ti, $\widetilde{D}_{TiTi}^{Nb}$. $\widetilde{D}_{TiAl}^{Nb}$ has a negative value. This means the interaction of Aluminum on the flux of Titanium is significant it is negative. It means the interdiffusion flux of Titanium is enhanced up the gradient of Aluminum and is reduced down the gradient of Aluminum. Aluminum has significant interaction on the flux of Titanium. This is what this indicates.

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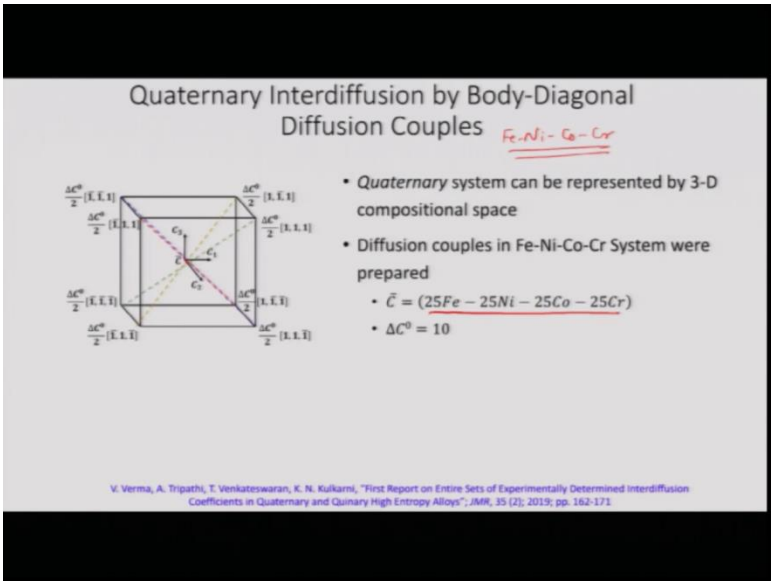

We have also applied the Body-Diagonal diffusion couple technique to evaluate interdiffusion coefficients in quaternary and quinary system. Let us look at the quaternary system first. We wanted to evaluate the interdiffusion coefficients in the Fe-Ni-Co-Cr quaternary system at the equimolar composition that is at 25 atom % of each Iron, Nickel, Cobalt Chromium.

$\bar{C}$, which is the average composition, is equimolar composition which is shown here.$\Delta C_o = 10$. Based on this, we could prepare 4 independent diffusion couple across the 4 Body-Diagonals. As only 3 are needed for quaternary system, we prepared the 3 couples.

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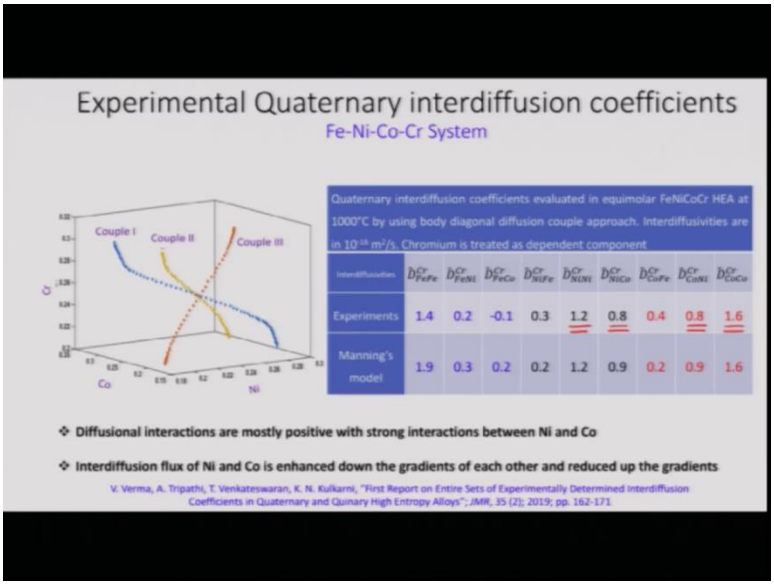

On the left side plot here are shown the diffusion paths of the 3 couples. Remember in quaternary system, we have a 3-dimensional composition space because there are 3 independent concentration variables. So quaternary isotherm is a 3-dimensional figure. You can see 3 diffusion paths of the three couples, Couple 1, Couple 2, Couple 3. They are intersecting at one common composition. The composition uncertainty of intersection was less than 0.1 atom % which is well within the experimental error.

We can set up the desired 9 independent equations and solve for 9 quaternary interdiffusion coefficients at the equimolar composition. We obtained the 9 coefficient to be as listed in this table here. We can see that significant interactions exist between Nickel and Cobalt. If we look at the cross-coefficient $\widetilde{D}^{Cr}_{CoNi}$, it is 50 percent of the value of $\widetilde{D}^{Cr}_{CoCo}$, which is the main coefficient.

If you look at $\widetilde{D}^{Cr}_{NiCo}$, it is positive and close to the value of main coefficient $\widetilde{D}^{Cr}_{NiNi}$. Which means Nickel Cobalt exhibit strong diffusional interactions in the quaternary Iron-Nickel-Cobalt-Chromium system. Their interdiffusion fluxes are enhanced down the gradients of each other and reduced up the gradients of each other.

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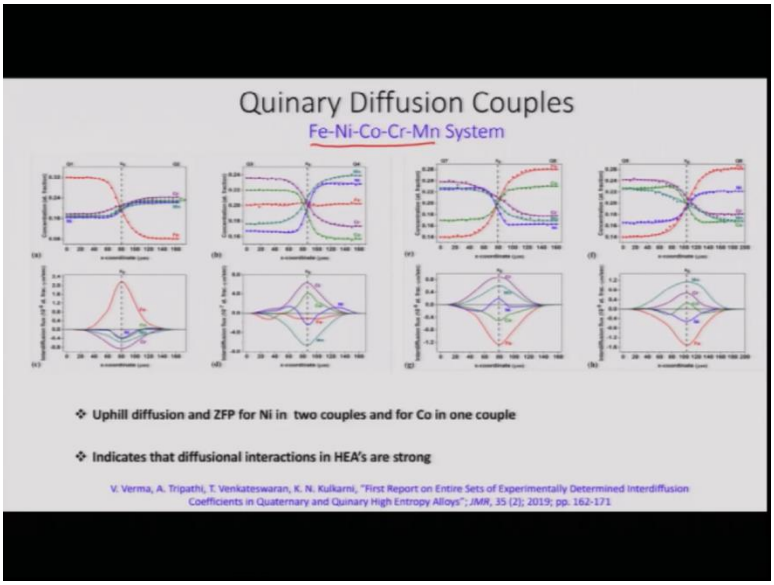

Then we can also extend the Body-Diagonal diffusion couple technique for a quinary system, that is, a 5-component system. We were interested again in the equimolar composition of Iron-Nickel-Cobalt-Chromium-Manganese system because this is the most studied high entropy alloy system. So, we prepared the 4 Body-Diagonal diffusion couples required for estimating 16 quinary interdiffusion coefficients. The concentration flux profiles of the 4 couples are shown here. At the bottom are the flux profiles, on the top are the concentration profiles. We can see interesting features in 3 of the couples.

In the second couple you can see there are two zero flux planes developed for Nickel. The third couple also has two zero flux planes developed for Nickel, the 4^{th} couple exhibits two zero flux planes for Cobalt. Correspondingly you can see there are maxima minima on the Nickel and Cobalt profiles in the respective couples. The strong diffusional interactions are again expected based on this maxima, minima and the zero flux plane features.

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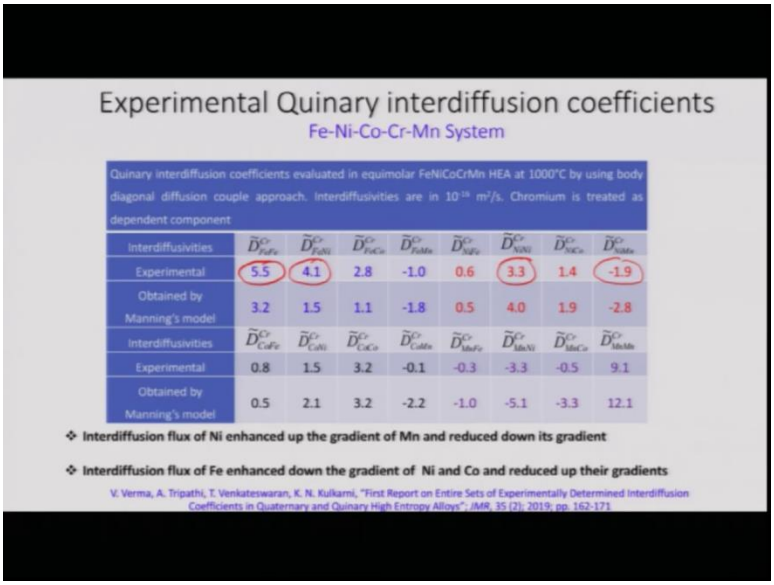

We evaluated the 16 interdiffusion coefficients and they are listed here. Very strong diffusional interactions are observed. If you look at specially $\widetilde{D}_{FeNi}^{Cr}$, it is almost same as $\widetilde{D}_{FeFe}^{Cr}$. $\widetilde{D}_{FeNi}^{Cr}$ is positive. It means in this quinary system, interdiffusion flux of Iron is enhanced down the gradient of Nickel and reduced up its gradient.

You can also look at $\widetilde{D}_{NiMn}^{Cr}$ which is negative and same order of magnitude as main coefficient $\widetilde{D}_{NiNi}^{Cr}$which means again, the interdiffusion flux of Nickel is enhanced up the gradient of Manganese and reduced down its gradient. This way, we can actually determine the entire sets of interdiffusion coefficients in various systems using the approaches that I explained in the last class. In this class, I showed you some of the actual applications from the literature. We will stop here for today. Thank you.