Diffusion in Multicomponent Solids
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Lecture 24
Nature of Concentration Profiles in Binary and Multicomponent Diffusion Couples

Keywords: Uphill diffusion, Constant diffusion coefficient, varying diffusion coefficient, binary system, ternary system, effect of relative magnitude and sign of cross and main interdiffusion coefficient, quinary high entropy alloy, varying partial molar volume

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Nature of Concentration
Profiles

Welcome to another interesting class of Diffusion in Multi-component Solids. In today's class we will see some of the features of concentration profiles that develop in a diffusion couple. We will look into both binary and multi-component diffusion couples.

Diffusion couple is a very important concept for this class. Throughout this class, we will use diffusion couples for various purposes, particularly for determination of interdiffusion coefficients and to see how the concentration profiles evolve in different types of infinite boundary conditions. So, it is important to go over some of the features of concentration profiles which are developed in infinite solid-solid diffusion couples.

We have already derived the solutions to diffusion equation with the boundary conditions as applicable for infinite diffusion couples. Today, we will see how the concentration profiles evolve and what are the different features.

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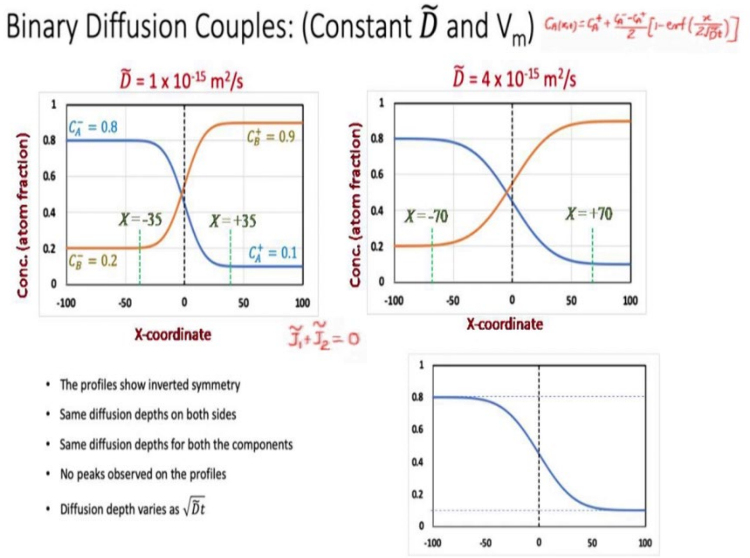

Binary Diffusion Couples: (Constant $\tilde{D}$ and V_m) $C_{A(x,t)} = C_A^+ + \frac{C_A^- - C_A^+}{2}\left[1 - erf\left(\frac{x}{2\sqrt{Dt}}\right)\right]$

$\tilde{J}_1 + \tilde{J}_2 = 0$

- The profiles show inverted symmetry
- Same diffusion depths on both sides
- Same diffusion depths for both the components
- No peaks observed on the profiles
- Diffusion depth varies as $\sqrt{\tilde{D}t}$

First we will look into diffusion profiles in a binary diffusion couple. Let us call the concentration at any position x as $C_{A\,(x,t)}$, concentration of component A at x and t is It is given by:

$$C_{A\,(x,t)} = C_A^+ + \frac{C_A^- - C_A^+}{2}\left[1 - erf\left(\frac{x}{2\sqrt{Dt}}\right)\right]$$

where C_A^+ is the concentration of the right side terminal alloy and C_A^- is the concentration of the left side terminal alloy. So, we are considering interdiffusion here and the interdiffusion coefficient is usually denoted by this symbol ~ on top of D. $\tilde{D}$ is the binary interdiffusion coefficient of the system that we are considering here. Above equation represent an error function type of solution. And this is the kind of profiles that develop in diffusion couple.

We have shown in the above figure, concentration profile of component A and concentration profile of component B. This hypothetical diffusion couple was formed by placing an alloy with 80 percent of A and 20 percent of B in atom percent on left side and 90 percent of B and 10 percent of A on the right side.

As you can see, the first obvious feature of this concentration profiles are: each concentration profile shows an inverted symmetry. To explain this further, if I consider the particular profile of component A here and this is the initial contact plane at x=0. If, I flip the concentration profile on the left side of this plane and repeat it on the other side, I get the entire concentration profile. That is the inverted symmetry. Of course, we have to rescale our concentration axis. In this case to get this inverted symmetry, I have to make $C_A^+ = 0$. Between C_A^- and C_A^+, this symmetry can be seen. It is also obvious from the kind of solution that we get for constant interdiffusion coefficients. Remember, first we are considering the case of constant interdiffusion coefficient. And throughout class today for all different concentration profiles, we will also assume that the molar volume V_m is constant. Towards the end of the class, we will see what happens if V_m varies with composition.

So, the first feature is that each individual profile shows inverted symmetry when interdiffusion coefficient is constant. The second feature you can see, we get the same diffusion depths on both sides for any particular component. For example if we see component B on the left side it has penetrated about 35 μm. On the right side also it has penetrated about 35 μm. Moreover, the diffusion depths of both the components are same in a binary diffusion couple on both the sides. The reason for this is: we know that we have $n-1$ independent fluxes in an n component system. If we consider the volume fixed frame of reference, this interdiffusion coefficient $\widetilde{D}$ is in the volume fix frame of reference. And, we have only one independent flux in a binary system which means for constant molar volume:

$$\tilde{J}_1 + \tilde{J}_2 = 0$$

From this equation it should be clear that if the flux of a particular component goes to zero in a particular terminal alloy, the flux of other component should also go to zero. And both the components should show the same diffusion depths. So for binary diffusion, there is only one interdiffusion coefficient which characterizes the diffusion behavior of both the components. And, this binary interdiffusion coefficient should have a positive value, which means we will not expect any maxima or minima on any of the concentration profiles. So, there would be no uphill diffusion observed in a binary diffusion couple.

Now, what happens if I change the interdiffusion coefficients? On the right side here I have shown the binary diffusion profile. I have taken the value of $\widetilde{D}$ to be 4 times the one I used for previous profiles. For the first profile, we used:

$$\widetilde{D} = 1 \times 10^{-15}\ \frac{m^2}{s}$$

And, this hypothetical diffusion couple was annealed for 48 hours. For the second hypothetical diffusion couple, I am now using interdiffusion coefficient as:

$$\widetilde{D} = 4 \times 10^{-15}\ \frac{m^2}{s}$$

It is annealed for the same time that is 48 hours. Immediately, you can see the diffusion depths have increased. Obviously, from this equation one can recognize that the diffusion depth varies as $\sqrt{\widetilde{D}t}$. What it means is if I increase the interdiffusion coefficient by 4 times, the diffusion depth should be doubled, which can be seen if we compare the two profiles here. In the first profile, the total diffusion depth was about 35+ 35 on both sides, will be about 70 μm. In the second case, the total diffusion depth is 70+70 which is about 140 μm. If, I increase the diffusion coefficient to 4 times, the diffusion depths would be doubled assuming that the binary diffusion profiles were for constant interdiffusion coefficient.

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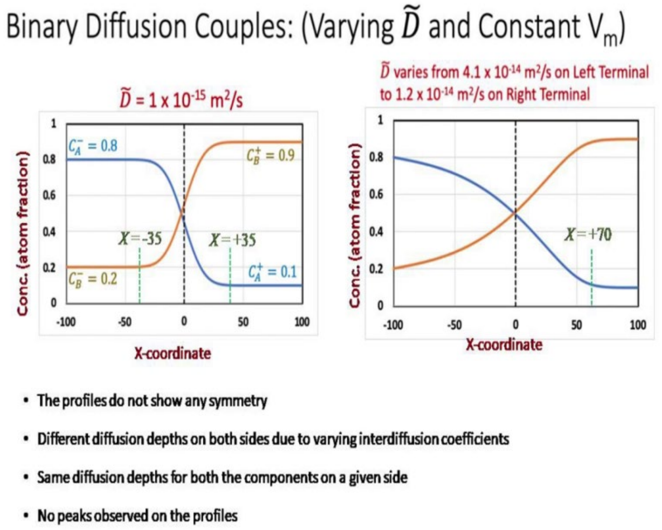

Binary Diffusion Couples: (Varying $\widetilde{D}$ and Constant V_m)

- The profiles do not show any symmetry
- Different diffusion depths on both sides due to varying interdiffusion coefficients
- Same diffusion depths for both the components on a given side
- No peaks observed on the profiles

Now, for constant $\widetilde{D}$ value, we can directly use the expression for concentration profiles which was error function type of expression, which we derived for the infinite boundary conditions. But, when $\widetilde{D}$ varies with composition, we cannot solve the diffusion equation straightaway or analytically. But we can solve the diffusion equation numerically with varying $\widetilde{D}$. In this slide I am comparing two couples. On the left side, I have the same hypothetical diffusion couple with constant value of $\widetilde{D}$ equal to:

$$\widetilde{D} = 1 \times 10^{-15}\ \frac{m^2}{s}$$

And the second on the right side are the diffusion profiles developed in a binary diffusion couple in which the interdiffusion coefficient varies with composition. How much it is varying? In the left terminal alloy, the diffusion coefficient is:

$$\widetilde{D} = 4.1 \times 10^{-14}\ \frac{m^2}{s}$$

It varies with composition. And, in the right terminal alloy, it has the value of:

$$\widetilde{D} = 1.2 \times 10^{-14}\ \frac{m^2}{s}$$

Now, the difference between the two type of profiles, when $\widetilde{D}$ is constant as against when $\widetilde{D}$ is varying is obvious. First is if we see the individual profiles, they do not show any kind of symmetry which is obvious because $\widetilde{D}$ is varying with composition. Also the diffusion depths are not same on both sides. In the left terminal alloy, the interdiffusivity values are higher than the right terminal alloy. And, we will see the diffusion depth is more in the left terminal alloy than in the right terminal alloy, which is also evident from the slopes of the concentration profiles. We can see the gradient in the concentration is shallower in the left terminal alloy and it is much steeper on the right terminal alloy.

Then, again since we only have one independent interdiffusion flux in volume fixed frame and assuming V_m is constant, we have:

$$\tilde{J}_1 + \tilde{J}_2 = 0$$

And on any side, both the diffusing species should show the same penetration depth or same diffusion depth. These diffusion depths are different on either side but at any given side the two components should show the same diffusion depth.

Again, no peaks are observed because we have a single diffusivity characterizing the diffusion behavior of both the components. And, we have only one independent component and one independent interdiffusion flux. Now, this was about the binary diffusion profiles. Let us see the nature of ternary diffusion profiles.

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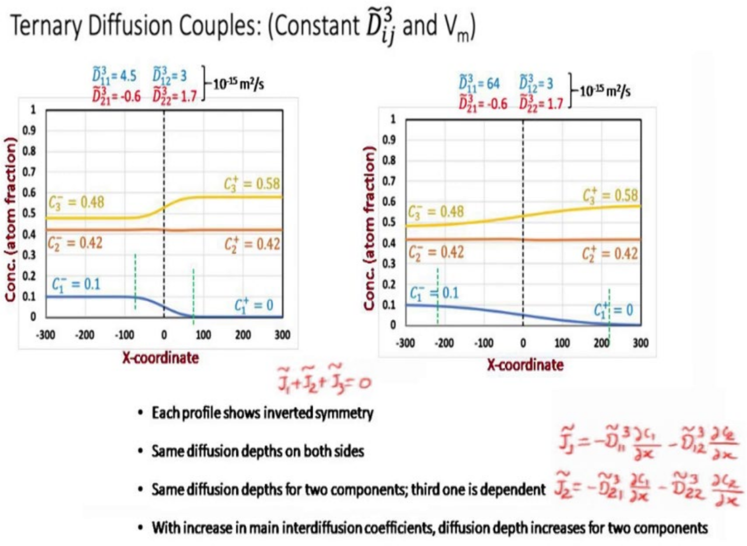

Ternary Diffusion Couples: (Constant $\tilde{D}_{ij}^3$ and V_m)

$$\tilde{J}_1 + \tilde{J}_2 + \tilde{J}_3 = 0$$

- Each profile shows inverted symmetry
- Same diffusion depths on both sides
- Same diffusion depths for two components; third one is dependent
- With increase in main interdiffusion coefficients, diffusion depth increases for two components

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

$$\tilde{J}_2 = -\tilde{D}_{21}^3 \frac{\partial C_1}{\partial x} - \tilde{D}_{22}^3 \frac{\partial C_2}{\partial x}$$

When I say ternary or a three component system, I have two independent interdiffusion fluxes. Based on Onsager's formalism of Fick's law I can write:

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

$$\tilde{J}_2 = -\tilde{D}_{21}^3 \frac{\partial C_1}{\partial x} - \tilde{D}_{22}^3 \frac{\partial C_2}{\partial x}$$

I have to define 4 interdiffusion coefficients for a ternary system, $\tilde{D}_{11}^3$, $\tilde{D}_{12}^3$, $\tilde{D}_{21}^3$ and $\tilde{D}_{22}^3$. The superscript 3 here denotes that component 3 is being treated as the dependent component. Components 1 and 2 are the independent component. The flux of each component 1 and 2 is expressed in terms of the concentration gradients, $\frac{\partial C_1}{\partial x}$ and $\frac{\partial C_2}{\partial x}$. These are the concentration profiles of the 3 components developed in hypothetical ternary diffusion couple which was assembled between two terminal alloys. On the left side, the alloy had 10 % of component 1, 42 % of component 2, 48 % of component 3. On the right side, the alloy had 42 % of component 2 and 58 % of component 3. Components 1 and 2 are being treated as independent components here. And, component 3 is treated as the dependent component.

Again, this simulation was done for constant set of interdiffusion coefficient and assumption of constant molar volume. Because of the constancy of interdiffusion coefficient, we can see each individual profile shows inverted symmetry. Then, the diffusion depths should also be same on both the side for any individual component.

For a ternary case since there are two independent components and the third one is dependent, for constant value of V_m we have:

$$\tilde{J}_1 + \tilde{J}_2 + \tilde{J}_3 = 0$$

Even if one of the flux goes to 0 earlier than the others, then the other two should still satisfy this equation, which means at least two components should show the same diffusion depth. If not, all three. This is an important point because in ternary there are two independent components and the third one is dependent.

Now, in this particular couple you can see component 2 has the same concentration on both the side. If I want to write the flux of component 2, I can use above equation:

$$\tilde{J}_2 = -\tilde{D}_{21}^{3}\frac{\partial C_1}{\partial x} - \tilde{D}_{22}^{3}\frac{\partial C_2}{\partial x}$$

And, the set of ternary interdiffusion coefficient that was used to produce this profile is written here:

$$\{\tilde{D}_{11}^{3} = 4.5, \quad \tilde{D}_{12}^{3} = 3, \quad \tilde{D}_{21}^{3} = -0.6, \quad \tilde{D}_{22}^{3} = 1.7\ \} \times 10^{-15}\ \frac{m^2}{s}$$

The values are in $10^{-15}\ \frac{m^2}{s}$. Particularly for component 2, $\tilde{D}_{22}^{3}$ is the main coefficient which quantifies the contribution from gradient of 2 to its own flux. And $\tilde{D}_{21}^{3}$ is the cross coefficient that quantifies the effect of gradient of 1 on the diffusion of component 2. Both the independent gradients will contribute to the flux of 2. Even if there is no gradient of concentration for component 2 to start with, we can still expect some flux. But, in this case the profile is still almost flat. And, the reason being, the cross coefficient, $\tilde{D}_{21}^{3}$ is much smaller than the main coefficient, $\tilde{D}_{22}^{3}$ in its order of magnitude. Even though there is a gradient for 1, in first term, $\tilde{D}_{21}^{3}$ is very small. So, the cross effect is negligible here. The gradient of 2 is anyways 0 to start with and we get to see almost flat profile for component 2.

However, in a ternary couple we may expect maximum and minimum on one or more profiles which denotes the presence of uphill diffusion. We will see that in the later slide. But, now let us see what happens if I change the main interdiffusion coefficient. In this matrix now, if I increase the interdiffusion coefficient of 1, keeping the 3 components of the matrix same:

$$\left\{\widetilde{D}_{11}^{3} = 64, \quad \widetilde{D}_{12}^{3} = 3, \quad \widetilde{D}_{21}^{3} = -0.6, \quad \widetilde{D}_{22}^{3} = 1.7\right\} \times 10^{-15}\,\frac{m^2}{s}$$

We can see the diffusion depth of component 1 has increased. In the first couple, where the $\widetilde{D}_{11}^{3} = 4.5 \times 10^{-15}\,\frac{m^2}{s}$, the diffusion depth was about minus 70 + 70, about 140 μm. In the second couple, where $\widetilde{D}_{11}^{3} = 64 \times 10^{-15}\,\frac{m^2}{s}$, the diffusion depth is about -230 to +230 is about 460 μm. So, the diffusion depth of component 1 has increased.

But, you can see the diffusion depth of component 3 has also increased. The reason being, as I explained earlier, you have to satisfy this condition:

$$\tilde{J}_1 + \tilde{J}_2 + \tilde{J}_3 = 0$$

Since $\tilde{J}_2$ is almost zero throughout the diffusion profile, $\tilde{J}_1$ has to be equal to $-\tilde{J}_3$. Component 3 which is the dependent component here, responds to the changes in concentration of component 1. And, the diffusion depth of component 3 has also increased.

Let us see the effect of cross terms or how diffusional interactions work in multi-component system or how diffusional interactions are important in a multi-component system.

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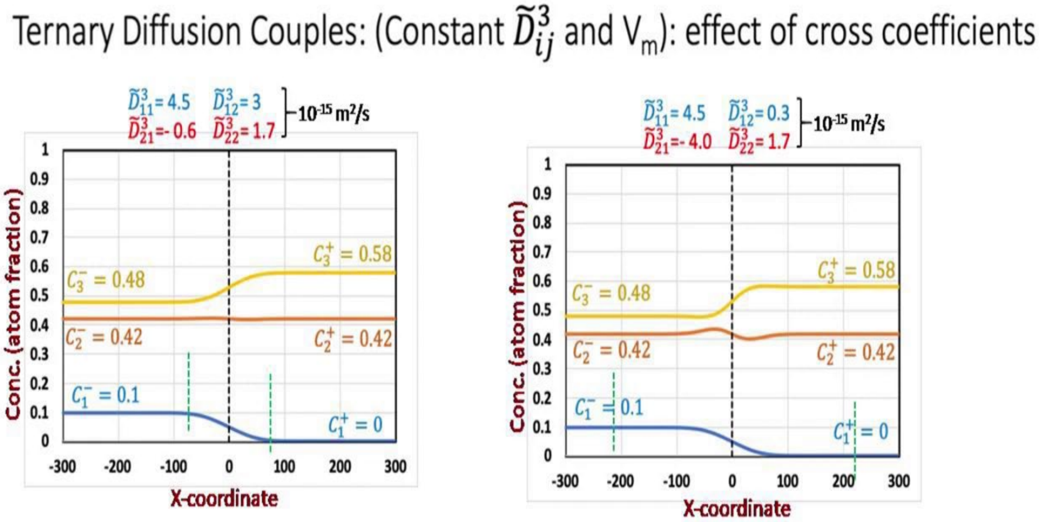

Ternary Diffusion Couples: (Constant $\tilde{D}_{ij}^{3}$ and V_m): effect of cross coefficients

On this slide, I am comparing two cases of the same diffusion couple or the diffusion couple formed with the same to two terminal alloys as described in the first previous slide. Now, here what I have done is, I have changed the cross coefficients. The first profile is same as I presented previously with :

$$\left\{\tilde{D}_{11}^{3} = 4.5, \quad \tilde{D}_{12}^{3} = 3, \quad \tilde{D}_{21}^{3} = -0.6, \quad \tilde{D}_{22}^{3} = 1.7\right\} \times 10^{-15}\ \frac{m^2}{s}$$

For the second case, I kept the main coefficient same but increased the cross coefficient b an order of magnitude:

$$\left\{\tilde{D}_{11}^{3} = 4.5, \quad \tilde{D}_{12}^{3} = 0.3, \quad \tilde{D}_{21}^{3} = -4.0, \quad \tilde{D}_{22}^{3} = 1.7\right\} \times 10^{-15}\ \frac{m^2}{s}$$

Now, in order to keep the matrix positive definite, I had to decrease the value of $\tilde{D}_{12}^{3}$. But, let us see the effect of this change in magnitude of cross coefficient of component 2. In the previous case, since the cross coefficient was very small and we started with the same concentration of 2 on both the terminal alloys, we saw that the concentration profile for component 2 was almost flat.

But, now since the cross coefficient has considerable magnitude, in fact the magnitude of cross coefficient here is higher than that for a main coefficient $\tilde{D}_{22}^{3}$. It gives rise to this kind of maximum and minimum in the concentration profile. In other words, component

2 is showing uphill diffusion because now the interactions are very strong which is reflected in the large magnitude of $\widetilde{D}_{21}^{3}$.

Now, the cross coefficient can be negative or positive. In this case, I considered negative cross coefficient. What if the coefficient was positive?

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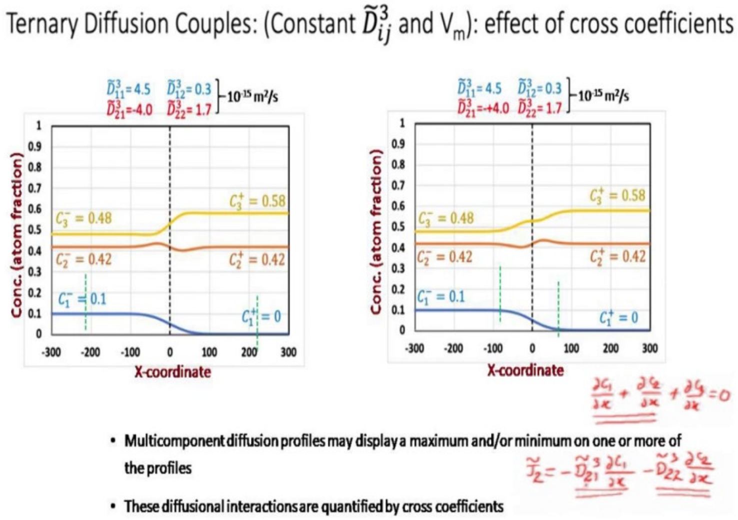

Ternary Diffusion Couples: (Constant $\widetilde{D}_{ij}^{3}$ and V_m): effect of cross coefficients

$$\frac{\partial C_1}{\partial x} + \frac{\partial C_2}{\partial x} + \frac{\partial C_3}{\partial x} = 0$$

- Multicomponent diffusion profiles may display a maximum and/or minimum on one or more of the profiles
- These diffusional interactions are quantified by cross coefficients

$$\tilde{J}_2 = -\widetilde{D}_{21}^{3}\frac{\partial C_1}{\partial x} - \widetilde{D}_{22}^{3}\frac{\partial C_2}{\partial x}$$

In this slide, I am comparing two cases. Again, in the first case, coefficient of $\widetilde{D}_{21}^{3}$ is negative whereas in the second case, it is positive:

$$\left\{\widetilde{D}_{11}^{3} = 4.5, \quad \widetilde{D}_{12}^{3} = 0.3, \quad \widetilde{D}_{21}^{3} = -4.0, \quad \widetilde{D}_{22}^{3} = 1.7\right\} \times 10^{-15}\ \frac{m^2}{s}$$

$$\left\{\widetilde{D}_{11}^{3} = 4.5, \quad \widetilde{D}_{12}^{3} = 0.3, \quad \widetilde{D}_{21}^{3} = 4.0, \quad \widetilde{D}_{22}^{3} = 1.7\right\} \times 10^{-15}\ \frac{m^2}{s}$$

And, if you compare the two concentration profiles, we can see the positions of maximum and minimum on concentration profiles of 2 are flipped as I changed the sign of its cross coefficient.

In the first case, the maximum was on the left side whereas minimum on the right side. In the second case, minimum is on the left side and maximum is on the right side. Now, it has also affected the concentration profile of component 3 right, because not all concentration gradients are independent. We can write for constant molar volume:

$$\frac{\partial C_1}{\partial x}+\frac{\partial C_2}{\partial x}+\frac{\partial C_3}{\partial x}=0$$

If I am treating 1 and 2 as independent component, 3 is the dependent component. If the gradient of 2 changes and you can see there is not much change in the concentration profile of component 1, the concentration profile of dependent component 3 also has to change in order to satisfy this equation. This is how the diffusion interactions can give very interesting concentration profiles and these diffusional interactions are quantified in terms of the cross coefficients.

Now, let us see what this negative and positive signs means. For example if I write the equation for interdiffusion flux of component 2, we can see the contributions is from both, the main term, which is this $\tilde{D}_{22}^{3}\frac{\partial C_2}{\partial x}$ and the cross term $\tilde{D}_{21}^{3}\frac{\partial C_1}{\partial x}$.

Now, let us suppose $\tilde{D}_{22}^{3}$ is positive and the concentration gradient to start with is negative. The second term in effect is positive. Now, if $\tilde{D}_{21}^{3}$ is negative and the gradient term of 1 is also negative, which is the case here, then the first term becomes negative. So, it is decreasing the flux of component 2 or it has a reducing effect because the second term is positive, the first term is negative, which means, the interdiffusion flux of component 2 is reduced down the gradient of 1. And, it is enhanced up the gradient of 1.

How is it enhanced up the gradient? Up the gradient means, if by any chance in a couple, if the gradient of 1 was positive, then this total first term will be positive and it will add to the second term. And, it has an additive effect. That means the negative value of cross coefficient $\tilde{D}_{21}^{3}$ enhances the interdiffusion flux of 2 up the gradient of 1 and reduces down the gradient of 1.

With a similar logic, if $\tilde{D}_{21}^{3}$ was positive, it would have reverse effect. The positive value of cross coefficient, $\tilde{D}_{21}^{3}$ means the interdiffusion flux of 2 is enhanced down the gradient of 1 and reduced up the gradient of 1. This is how the diffusional interaction can affect the concentration profiles in a multi-component system.

Now, let us look into some of the real multi-component concentration profiles. I will give you couple of examples.

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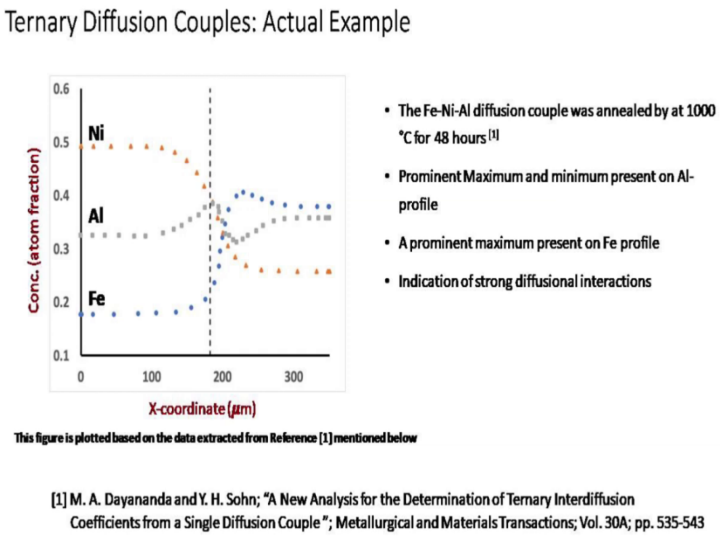

Ternary Diffusion Couples: Actual Example

- The Fe-Ni-Al diffusion couple was annealed by at 1000 °C for 48 hours [1]
- Prominent Maximum and minimum present on Al-profile
- A prominent maximum present on Fe profile
- Indication of strong diffusional interactions

This figure is plotted based on the data extracted from Reference [1] mentioned below

[1] M. A. Dayananda and Y. H. Sohn; "A New Analysis for the Determination of Ternary Interdiffusion Coefficients from a Single Diffusion Couple"; Metallurgical and Materials Transactions; Vol. 30A; pp. 535-543

The first one is an iron-nickel-aluminum ternary diffusion couple taken from this reference here by Dayananda and Sohn. Profiles are plotted by extracting the data from this reference. You can see in this particular couple between two iron-nickel-aluminum alloys, the aluminum profile is characterized by very prominent maximum and minimum. Also the iron profile is characterized by a very prominent maximum here on the right side of the initial contact plane which is also referred to as Matano plane. It means strong diffusional interactions exist in this iron-nickel-aluminum system.

This particular couple was diffusion annealed at 1000 °C for 48 hours. As we see the prominent maximum and minimum on aluminum and prominent maximum on the iron profile, this indicates strong diffusional interactions in this system. And, this was actually evidenced in terms of large values of a cross interdiffusion coefficient in the system, as reported in this reference. Particularly, $\widetilde{D}_{NiAl}^{Fe}$ and $\widetilde{D}_{AlNi}^{Fe}$ here are very highly negative and have large magnitudes.

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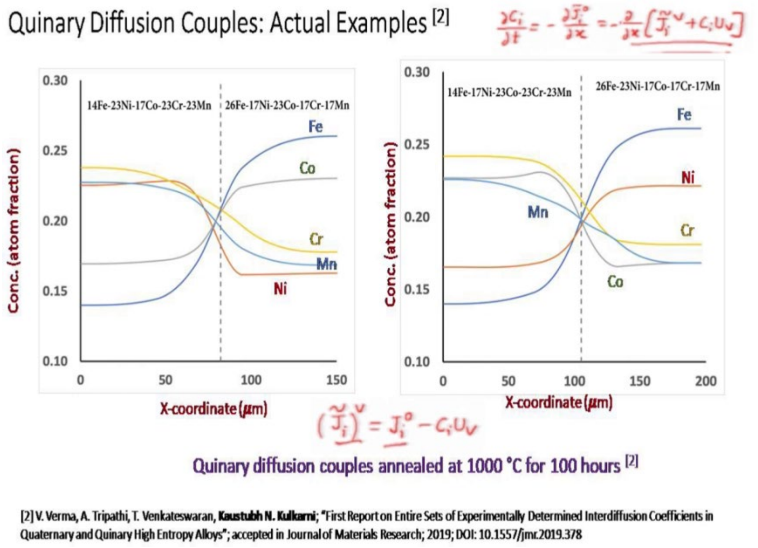

Quinary Diffusion Couples: Actual Examples [2]

$$\frac{\partial C_i}{\partial t} = -\frac{\partial \tilde{J}_i^{o}}{\partial x} = -\frac{\partial}{\partial x}\underline{\left[\tilde{J}_i^{v} + C_i u_v\right]}$$

$$(\tilde{J}_i)^{v} = \underline{J_i^{o}} - C_i u_v$$

Quinary diffusion couples annealed at 1000 °C for 100 hours [2]

[2] V. Verma, A. Tripathi, T. Venkateswaran, **Kaustubh N. Kulkarni**; "First Report on Entire Sets of Experimentally Determined Interdiffusion Coefficients in Quaternary and Quinary High Entropy Alloys"; accepted in Journal of Materials Research; 2019; DOI: 10.1557/jmr.2019.378

This is another example. Two quinary diffusion couples I am showing here. It is taken from this reference recently published in JMR. The first couple was assembled between a quinary alloy. Quinary means 5 component system. On the left side, we have 40 iron, 23 nickel, 17 cobalt, 23 chrome, 23 manganese. The concentrations are in atom percent and the right side- 26 iron, 17 nickel, 23 cobalt, 17 chrome and 17 manganese. And, these are the concentration profiles developed in this quinary diffusion couple. And, important to note here is the nickel profile. We can see a nice maximum here on the left side and there is a minimum on the right side of the initial contact plane here. Similarly, in the second diffusion couple which was assembled between 14 iron, 17 nickel, 23 cobalt, 23 chromium, 23 manganese and, 26 iron, 23 nickel, 17 cobalt, 17 chromium and 17 manganese, the concentrations being in atom percent. On cobalt profile, we can see a maximum and minimum here. And, this indicates the presence of strong diffusional interactions in this system. This particular system, iron-nickel-cobalt-chrome-manganese is a very important system. It has recently gained a lot of importance, particularly in high entropy alloys in which diffusion is one of the most debated topics.

These couples actually show there exists strong diffusional interactions in high entropy alloy systems, particularly this one, iron-nickel-cobalt-chrome-manganese. If you want to know more, you can refer to this paper.

We have also characterized the interdiffusion coefficients. A quinary interdiffusion coefficient matrix has $(n-1)^2$ or 16 terms. A quinary composition is characterized by 16 interdiffusion coefficients in volume fixed frame of reference. These are some of the examples of multi-component diffusion couples and the concentration profiles developed in these couples.

Now, as I said, for all the discussion so far in this class we assumed molar volume is constant because we used for many of the profiles the analytical expressions derived by solving the diffusion equation which was:

$$\frac{\partial C_i}{\partial t} = -\frac{\partial \tilde{J}_i^o}{\partial x}$$

Now, if molar volume is not constant, then $\tilde{J}_i^v$ which is basically the flux in volume fixed frame of reference can be expressed in the terms of the flux in stationary frame of reference as:

$$\tilde{J}_i^v = \tilde{J}_i^o - C_i U_v$$

where U_v is the velocity of the volume fixed frame with respect to stationary frame. Now, whenever I write this continuity equation, you have to remember the flux here is in stationary frame of reference. The continuity equation applies for the stationary frame of reference. If I have to solve this equation, I have to substitute in terms of the volume fixed frame of reference as:

$$\tilde{J}_i^o = C_i U_v + \tilde{J}_i^v$$

If U_v is 0, which is the case when molar volume is constant, then you can see the volume fixed frame and the stationary frame would coincide. Or, the fluxes determined in any of the frames will be the same. And we can directly substitute here and solve this equation. But if U_v is not 0, which is the case when molar volumes vary with composition or more specifically when partial molar volumes vary with composition then, we have to account for this term U_v.Again, U_v is also function of x and, this becomes a complicated equation to solve. Then continuity equation cannot be solved straight away.

And, that is why we assumed the molar volume was constant so that we can simplistically show some features of the concentration profiles using the analytical expressions. Ofcourse, for varying case of binary interdiffusion coefficients we solved the diffusion equation numerically, again for constant molar volume case.

I think that should be all for now. I will explain in more detail what happens if or how we solve for U_v when the partial molar volumes are not constant. But, that will come later in the class.