Diffusion in Multicomponent Solids
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Lecture 51
Interdiffusion Analysis of Multiphase Diffusion Couples

Welcome to 51st lecture of this Open Course on Diffusion in Multicomponent Solids. In the last class we have seen how the diffusion structures develop in a multiphase diffusion couple and how we can use them to get some information about phase diagrams. Now, in this class I would like to explain how we can analyze the diffusion profiles developed in a multiphase diffusion couple.

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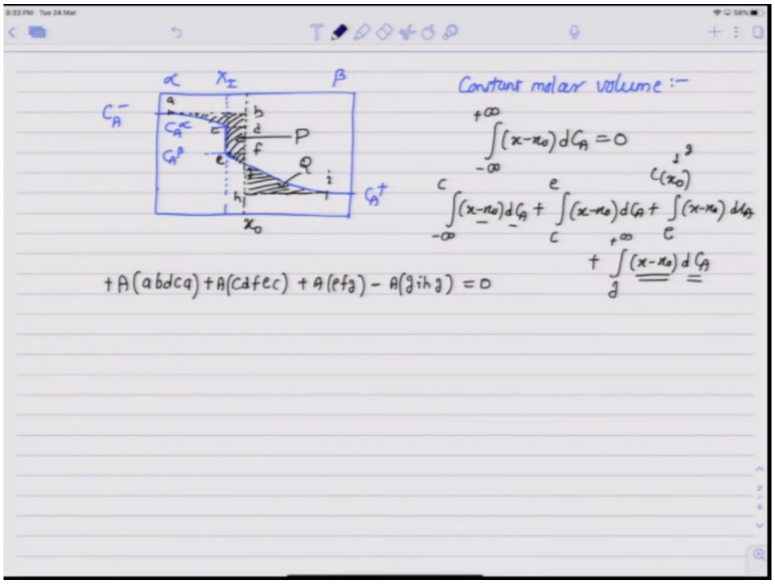

Constant molar volume :-

$$\int_{-\infty}^{+\infty}(x-x_0)\,dC_A = 0$$

$$\int_{-\infty}^{c}(x-x_0)\,dC_A + \int_{c}^{e}(x-x_0)\,dC_A + \int_{e}^{\overset{g}{C(x_0)}}(x-x_0)\,dC_A + \int_{g}^{+\infty}(x-x_0)\,dC_A$$

$$+A(abdca)+A(cdfec)+A(efg)-A(gihg)=0$$

So, let us consider one concentration profile in a multiphase diffusion couple, say this is $C_A^{-¿¿}$, this is $C_A^{+¿¿}$ and this side is α, this side is $\beta$and there is an interface at x_I which is let us assume a planar interface. So, there will be discontinuity in the profile at x_I so the profile would look something like this. So, this is C_A^α, this is C_A^β.

Now, we can use the same principles to analyze this as we used for the single-phase diffusion couples as long as we assume molar volume to be constant. So, for constant molar volume we know for finding the matano plane, which is the first task in the analysis of diffusion profiles, we can use the formula:

$$\int_{-\infty}^{+\infty} (x-x_o)\, dC_A = 0$$

Now, to understand this let us split this integral at different places. So, let us label these points, let us say this is the position of matano plane, x_o this is a, b, let us call this c, d, e, f, g, h, and i. So, let us split the integral at two positions: at the discontinuity in the concentration profiles and at the minterface.

So, we can write this to be:

$$\int_{C_A^{-\text{¿}}\text{¿}} c(x-x_o)dC_A + \int_c^e (x-x_o)dC_A + \int_e^g (x-x_o)dC_A + \int_g^{C_A^{+\text{¿}}(x-x_o)dC_A=0\text{¿}} \text{¿}$$

So, if you look at the first integral, this is area abdca and the sign would be $(x-x_o)$ is negative and dC_A is negative because C_A is decreasing, so there would be a positive sign. The integral from c to e would be again be positive as it is this area cdfec, and integral e to g at x_o is this small area efg with a positive sign, then the integral g to plus infinity would be this area gihg and there will be a negative sign because now $(x-x_o)$ is positive but dC_A is still negative. All of the area summed should be equal to 0:

$$A(abdca)+A(cdfec)+A(efg)-A(gihg)=0$$

So, this basically tells me that this total area, let us call this P should be equal to this area Q on the other side of the matano plane.

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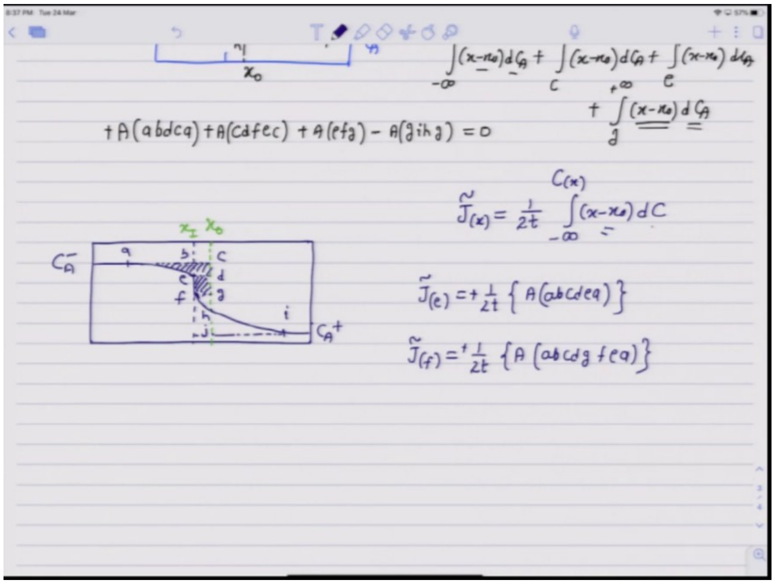

$$\int_{-\infty}(x-x_o)dC_A + \int_{c}^{+\infty}(x-x_o)dC_A + \int_{e}(x-x_o)dC_A + \int_{g}(x-x_o)dC_A$$

$$+A(abdca)+A(cdfec)+A(efg)-A(gihg)=0$$

$$\tilde{J}(x)=\frac{1}{2t}\int_{-\infty}^{C(x)}(x-x_o)dC$$

$$\tilde{J}(e)=+\frac{1}{2t}\{A(abcdea)\}$$

$$\tilde{J}(f)=+\frac{1}{2t}\{A(abcdgfea)\}$$

A similar procedure can be applied for finding the matano plane, the same equations can be used for finding fluxes as we used for single-phase diffusion couples, that is:

$$\tilde{J}(x)=\frac{1}{2t}\int_{-\infty}^{C(x)}\left(x-x_o\right)dC$$

So, if we consider again the concentration profile in a multi-phase couple, let us say this is $C_A^{-¿¿}$ and let us say this is the matano plane position here, let us say this is the interface position x_I where there is a discontinuity here. Let us label these points abcdefghij.

So, if you want to find out the interdiffusion flux at point e that is on the α side of the interface, we know it will be basically:

$$\tilde{J}(e)=\frac{1}{2t}\left\{A(abcdea)\right\}$$

and component is moving from left to right here so the diffusion flux will be positive which is also clear from the signs here $\left(x-x_o\right)$ is negative and dC is negative, so the flux would be positive.

After the discontinuity, that is on the β side of the interface what would be the interdiffusion flux? Now, $\tilde{J}(f)$ would be:

$$\tilde{J}(f)=\frac{1}{2t}\{A(abcdgfea)\}$$

as it will add another area here edgf and again it will be a positive value. The diffusion flux will keep increasing until the matano plane position similar to in the single-phase couple, after the matano position the sign of $(x-x_o)$changes and so the contribution of the further areas will be negative and hence the flux will start decreasing and there will be a maximum at the matano plane.

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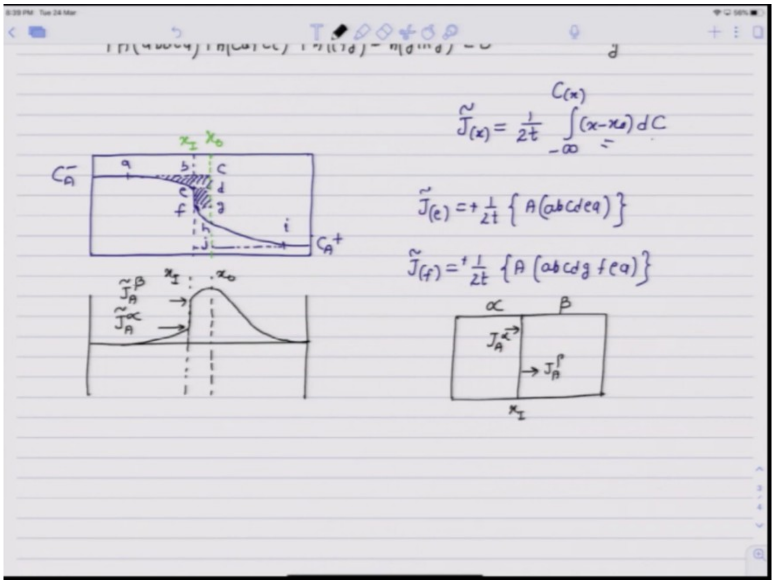

$$\tilde{J}_{(x)}=\frac{1}{2t}\int_{-\infty}^{C(x)}(x-x_o)\,dC$$

$$\tilde{J}_{(e)}=+\frac{1}{2t}\{A(abcdea)\}$$

$$\tilde{J}_{(f)}=+\frac{1}{2t}\{A(abcdgfea)\}$$

So, if you draw the diffusion flux profiles, this is $x_I \wedge$¿this is x_o, you know the diffusion flux is positive, it increases and suddenly there is a jump at the discontinuity that is at the interface and then it increases again until the matano plane. At the matano plane it reaches maximum and then start decreasing. So, similar to the concentration profile there is also a discontinuity in the flux profile, so at the discontinuity we can say this is the flux of component A on the α side of the interface and this is the flux of component A on the β side of the interface.

If we look into the diffusion structure there will be a planar interface between α and β and A is moving from left to right, there will be some flux coming into the interface which is $\tilde{J}_A^\alpha$ exactly at the interface position, there will also be some flux leaving the interface into β, this we call as $\tilde{J}_A^\beta$. So, this is how the flux profile would look like in a multiphase diffusion couple.

We can similarly draw various types of flux profiles which I will give you in the exercises. Now, the question is how do we use this data. Once we evaluate the diffusion flux profile, how we can make use of it? Obviously with the multiphase diffusion couple using the same approach as for single-phase couples we can also determine the interdiffusion coefficients, so for binary single phase couple, it would be okay for determining interdiffusion coefficients at different compositions, for ternary we will need two couples with intersecting diffusion paths and so on.

However, the error would be more because we are assuming constant molar volume but in multi-phase couple by its nature there are at least two different phases present and the two phases would tend to have different molar volumes, and hence the error involved because of assumption of constant molar volume would be more. However, by knowing the fluxes and compositions at the interfaces, we can get a quantitative estimate of the velocity of the interface which is important for getting the idea about the growth rate of a phase. Let us see how we can go about it.

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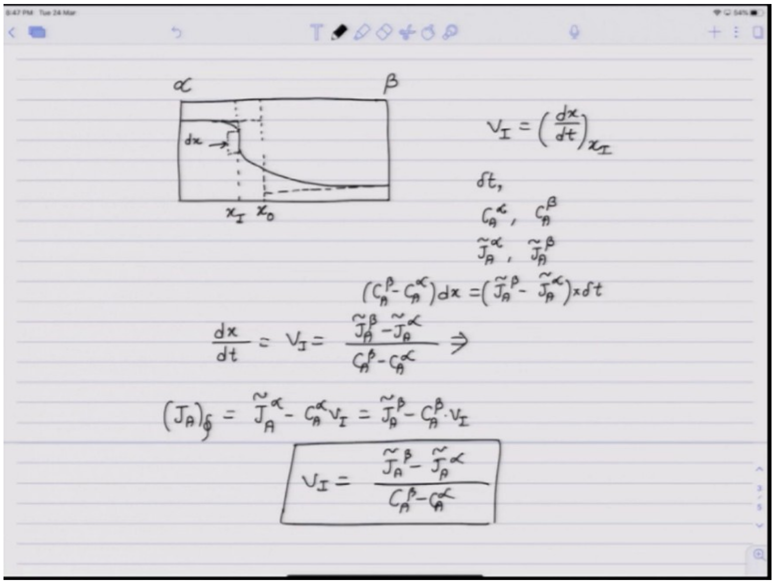

$$V_I = \left(\frac{dx}{dt}\right)_{x_I}$$

$\delta t,$

$C_A^{\alpha}, \; C_A^{\beta}$

$\tilde{J}_A^{\alpha}, \; \tilde{J}_A^{\beta}$

$$(C_A^{\beta} - C_A^{\alpha})dx = (\tilde{J}_A^{\beta} - \tilde{J}_A^{\alpha}) \times \delta t$$

$$\frac{dx}{dt} = V_I = \frac{\tilde{J}_A^{\beta} - \tilde{J}_A^{\alpha}}{C_A^{\beta} - C_A^{\alpha}} \Rightarrow$$

$$(J_A)_{\phi} = \tilde{J}_A^{\alpha} - C_A^{\alpha} V_I = \tilde{J}_A^{\beta} - C_A^{\beta} \cdot V_I$$

$$\boxed{V_I = \frac{\tilde{J}_A^{\beta} - \tilde{J}_A^{\alpha}}{C_A^{\beta} - C_A^{\alpha}}}$$

So, let us first try to see how we can get the velocity of interface. Again, I am showing a concentration profile in a multi-phase couple, x_I is the position of interface, x_o is the matano plane. On the left side I have α phase, right side I have β phase. So obviously as the diffusion progresses one phase has to grow at the expense of the other and hence the interface has to travel.

So, it is important to know at what rate this interface is traveling because that way we can estimate the growth rate of a particular phase. So, let us say this interface at x_I at time t is moving with a velocity V_I, so V_I is nothing but:

$$V_I = \left(\frac{dx}{dt}\right)_{x_I}$$

So, if I consider a very small element of width dx around the interface and since I am considering a unit cross sectional area, volume of this element is dx. Suppose, β is growing at the expense of α and in small interval of time δt, the small volume dx is converted from α into β. So, initially the small element had the concentration $C_A^\alpha$and it has changed in small interval of time δt to C_A^β.

And if $\tilde{J}_A^\alpha$is the interdiffusion flux of A at the interface on α side and $\tilde{J}_A^\beta$ is the interdiffusion flux of A at the interface on β side then we can write, since we are considering unit cross section, the mass balance as:

$$\left(C_A^\beta - C_A^\alpha\right) dx = \left(\tilde{J}_A^\beta - \tilde{J}_A^\alpha\right) \delta t$$

The final concentration C_A^β minus initial concentration C_A^α of the element times the volume of the element, which is dx, is equal to $\left(\tilde{J}_A^\beta - \tilde{J}_A^\alpha\right)$ times the unit cross section 1 times the time interval δt. Flux has a tilde sign because I am considering interdiffusion flux.

So, this tells me as δt tends to 0, $\frac{dx}{dt}$which is nothing but V_I should be equal to:

$$\frac{dx}{dt} = V_I = \frac{\left(\tilde{J}_A^\beta - \tilde{J}_A^\alpha\right)}{\left(C_A^\beta - C_A^\alpha\right)}$$

This equation can also be obtained by simply considering the frame of reference which is fixed to this interface. Since the frame of reference is fixed to this interface, the flux in that frame of reference let us call it $\left(J_A\right)_\varphi$ in the α phase should be equal to:

$$\left(J_A\right)_\varphi = \tilde{J}_A^\alpha - C_A^\alpha V_I$$

This we can also considered in the β phase and so we can also write:

$$\left(J_A\right)_\varphi = \tilde{J}_A^\alpha - C_A^\alpha V_I = \tilde{J}_A^\beta - C_A^\beta V_I$$

So the formula for V_I can be obtained as:

$$V_I = \frac{\left(\tilde{J}_A^\beta - \tilde{J}_A^\alpha\right)}{\left(C_A^\beta - C_A^\alpha\right)}$$

This is very important because this we can use this for analyzing the growth rates. So, for example consider the growth of a precipitate β in the matrix α.

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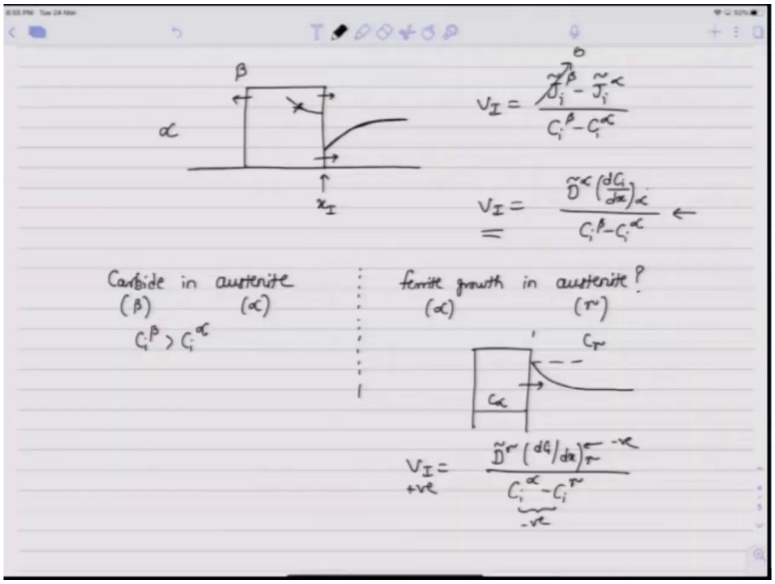

$$V_I = \frac{\overset{0}{\cancel{\tilde{J}_i^\beta}} - \tilde{J}_i^\alpha}{C_i^\beta - C_i^\alpha}$$

$$V_I = \frac{\tilde{D}^\alpha \left(\frac{dC_i}{dx}\right)_\alpha}{C_i^\beta - C_i^\alpha} \leftarrow$$

Carbide in austenite
(β) (α)
$C_i^\beta > C_i^\alpha$

ferrite growth in austenite?
(α) (γ)

$$\underset{+ve}{V_I} = \frac{\tilde{D}^\gamma \left(dC_i/dx\right)_\gamma \leftarrow -ve}{\underbrace{C_i^\alpha - C_i^\gamma}_{-ve}}$$

So, this is β and the matrix is α, obviously the precipitation is occurring because the matrix is supersaturated with the solute, let us call the solute as i and hence the solute has to be transported from matrix to the interface, so there will be a concentration gradient with respect to this interface here and the concentration in the precipitate will be of course higher. So, let us say the concentration gradient here is something like this.

Now, as the β grows this interface is moving into the matrix. Similarly, the other interface is moving towards left and that is how the β precipitate would grow. So, to evaluate this growth rate it is important to understand the velocity of this interface and the velocity of this interface can be obtained by the formula that we derived:

$$V_I = \frac{\left(\tilde{J}_i^\beta - \tilde{J}_i^\alpha\right)}{\left(C_i^\beta - C_i^\alpha\right)}$$

Most of the time the precipitates are line compounds which means there is no concentration gradient within the precipitate and hence we can assume safely that $\tilde{J}_i^\beta = 0$ or rather close to 0. And so if we use Fick's law we can write:

$$V_I = \frac{\tilde{D}^\alpha}{\left(C_i^\beta - C_i^\alpha\right)} \left(\frac{dC_i}{dx}\right)_{\alpha I}$$

So, this would be $\tilde{D}^\alpha$ that is the interdiffusion coefficient in α times $\left(\frac{dC_i}{dx}\right)_{\alpha I}$ at the interface divided by $\left(C_i^\beta - C_i^\alpha\right)$. So, let us consider for example two different cases that will help us to understand how different concentration profiles are developed depending upon different transformations. So, if I consider precipitation of let us say carbide in austenite represented by β. It will be a similar case like this because carbide concentration is higher, so the precipitate concentration C_i^β would be greater than the matrix concentration C_i^α, considering matrix is austenite here represented by α:

$$C_i^\beta > C_i^\alpha$$

Since the carbide has to grow, this interface has to move from left to right that is from the precipitate side into the matrix which means V_I has to be positive. Since C_i^β that is carbide concentration is higher than the matrix concentration that means the gradient in α has to be positive also. And so this kind of gradient will be set up.

Physically also it can be understood because for the carbide precipitate to grow the carbon has to be transported from matrix towards the precipitate. And hence the carbon concentration gradient here with respect to this interface should be positive. What happens if ferrite is growing in austenite? Ferrite is α, austenite is considered as γ. So, in this case now ferrite has ofcourse lower concentration of carbon than γ or austenite. That means V_I the interface velocity here would be given by:

$$V_I = \frac{\tilde{D}^{\gamma}}{\left(C_i^{\alpha} - C_i^{\gamma}\right)} \left(\frac{dC_i}{dx}\right)_{\gamma}$$

Now, carbon concentration in ferrite is typically very, very small and so it can be taken as constant. So, still the same, similar formula can be applied. Now, in this case for the growth of ferrite again the interface velocity has to be from left to right that is positive but C_i^{α} here is less than C_i^{γ} and so that is why the gradient has to be negative. That means in γ the gradient will be developed something like this, a negative gradient, which is also understood again physically because ferrite has much lower carbon concentration than austenite and hence when the ferrite is growing in austenite, so the excess carbon has to be rejected into the matrix. And therefore, the negative gradient will be developed with respect to this interface here.

So, this is how we can use the multiphase diffusion analysis in actually determining the phase growth rates. Simple interdiffusion flux and concentration analysis help us to get to the interface velocity which in turn helps us to understand the growth rates. And that is why studying multiphase diffusion is important. We will stop here today, thank you.