Diffusion in Multicomponent Solids
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Lecture 26
Homogenization of Multicomponent alloys

Welcome back to this next lecture in the course on Diffusion in Multicomponent Solids. Last few classes, we have been solving diffusion equation for various boundary conditions including those related to infinite solid-solid diffusion couples, carburizing and also the instantaneous planar source. Now, we will look into boundary value problems which include finite boundary conditions or periodic boundary conditions.

And in today's class, we will consider another industry important process called homogenization. Most of the alloys when they are cast, exhibit some kind of segregation. There are 2 types of segregations, macro segregation, which is on a macro level, on a bigger scale, on the component level and micro segregation which is at the micro level or at the microstructure level. The macro segregation is something which we cannot get rid of, but the micro segregation which invariably occurs in most of the alloys after solidification has to be gotten rid of and homogenization is often used in order to get rid of the micro segregation.

Now, this homogenization treatment is governed by the process of diffusion and it is important to understand the various parameters which are basically driven by the diffusion. How the segregation takes place?

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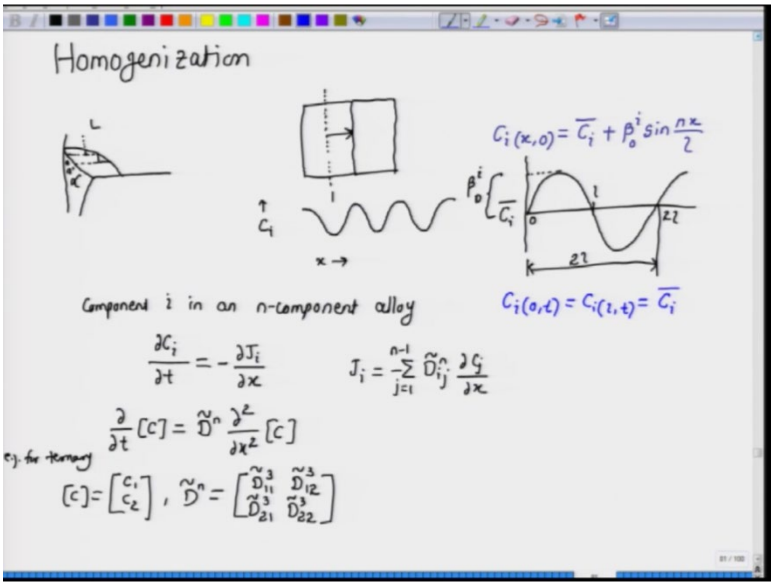


Homogenization

$C_i(x,0)=\bar{C}_i+\beta_0^i\sin\frac{\pi x}{l}$

$C_i(0,t)=C_i(l,t)=\bar{C}_i$

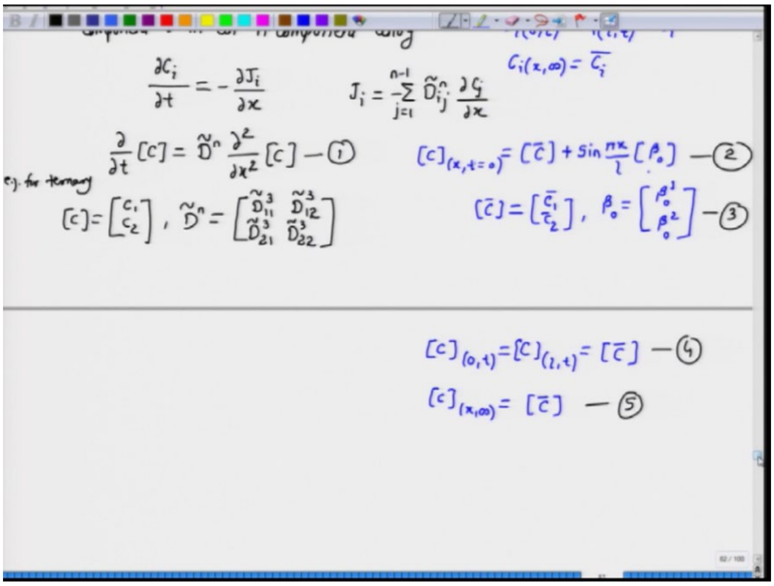
Component i in an n-component alloy

$\frac{\partial C_i}{\partial t}=-\frac{\partial J_i}{\partial x}$ $J_i=-\sum_{j=1}^{n-1}\tilde{D}_{ij}^{n}\frac{\partial C_j}{\partial x}$

$\frac{\partial}{\partial t}[C]=\tilde{D}^{n}\frac{\partial^2}{\partial x^2}[C]$

e.g. for ternary

$[C]=\begin{bmatrix}C_1\\C_2\end{bmatrix}$, $\tilde{D}^{n}=\begin{bmatrix}\tilde{D}_{11}^{3} & \tilde{D}_{12}^{3}\\ \tilde{D}_{21}^{3} & \tilde{D}_{22}^{3}\end{bmatrix}$



$C_i(x,\infty)=\bar{C}_i$

$\frac{\partial C_i}{\partial t}=-\frac{\partial J_i}{\partial x}$ $J_i=-\sum_{j=1}^{n-1}\tilde{D}_{ij}^{n}\frac{\partial C_j}{\partial x}$

$\frac{\partial}{\partial t}[C]=\tilde{D}^{n}\frac{\partial^2}{\partial x^2}[C]$ — ①

$[C]_{(x,t=0)}=[\bar{C}]+\sin\frac{\pi x}{l}[\beta_0]$ — ②

e.g. for ternary

$[C]=\begin{bmatrix}C_1\\C_2\end{bmatrix}$, $\tilde{D}^{n}=\begin{bmatrix}\tilde{D}_{11}^{3} & \tilde{D}_{12}^{3}\\ \tilde{D}_{21}^{3} & \tilde{D}_{22}^{3}\end{bmatrix}$

$[\bar{C}]=\begin{bmatrix}\bar{C}_1\\ \bar{C}_2\end{bmatrix}$, $\beta_0=\begin{bmatrix}\beta_0^1\\ \beta_0^2\end{bmatrix}$ — ③

$[C]_{(0,t)}=[C]_{(l,t)}=[\bar{C}]$ — ④

$[C]_{(x,\infty)}=[\bar{C}]$ — ⑤

For example, in casting there is something called as coring effect due to which the solute content in an alloy varies from center of the grain towards the exterior. Going over very quickly, this is the part of the phase diagram and this is the liquid region, alpha solid phase, this is the liquidus and this is the solidus.

When any alloy solidifies starts solidifying, the first solid that solidifies, has a lesser solute content which is given by this lets point a. As it solidifies further, the next solid that forms is little richer in the solute and on. If you look into the grain, the solute content varies from the center of the grain towards the exterior. Since the center is depleted in solid, if you draw the concentration versus x coordinate here, you will get a plot something like this. And when there is a grain nucleated next to the first grain, this pattern will be repeated. And you will see there is a kind of a sinusoidal distribution of the solute throughout the microstructure, considering that we are dealing with a single phase alpha. Ofcourse, if there is a second phase then there will be an interface, the concentration profiles will be different, but right now, we are considering only single phase. Now, to start with or immediately after the solidification, the concentration profile may not be exactly sinusoidal like this, but there will be some kind of repeating variations and as the homogenization start quickly, most of the time it will take the shape of a sinusoidal form.

To start with the distribution of concentration is given by this sinusoidal pattern. We will solve the diffusion equation. If I consider component i in an n component alloy, I have to solve the continuity equation:

$$\frac{\partial C_i}{\partial t} = -\frac{\partial J_i}{\partial x} \quad (1)$$

And we know J_i in an n component system is expressed in terms of n-1 interdiffusion coefficient:

$$J_i = -\sum_{j=1}^{n-1} \tilde{D}_{ij}^{n} \frac{\partial C_j}{\partial x}$$

If we substitute for J_i in continuity equation, we will get a coupled diffusion equation. And as we have seen before if we use the matrix approach, it simplifies the problem. If we write this equation in the form of matrix,, we can write:

$$\frac{\partial}{\partial t}[C] = -\tilde{D}^{n} \frac{\partial^2}{\partial x^2}[C]$$

after substituting for J_i. And we know this matrix C is a column matrix. For example, if we expand this for a ternary, we have 2 independent concentrations and four interdiffusion coefficients. So:

$$[C] = \begin{bmatrix} C_1 \\ C_2 \end{bmatrix}, \quad \tilde{D}^{n} = \begin{bmatrix} \tilde{D}_{11}^{3} & \tilde{D}_{12}^{3} \\ \tilde{D}_{21}^{3} & \tilde{D}_{22}^{3} \end{bmatrix}$$

This is the diffusion equation that we need to solve:

$$[C]_{(x,t=\,0)} = [\bar{C}] + sin\frac{\pi x}{l}[\beta_o]$$

and what are the boundary conditions. The initial condition is initially we have a sinusoidal pattern. We can represent for a component i at any x and $t = 0$ the sinusoidal pattern as:

$$C_{i(x,0)} = \bar{C_i} + \beta_o^i sin\frac{\pi x}{l}$$

where $\bar{C_i}$ is the average concentration about which the oscillations of concentrations occur, β_o^i is basically the amplitude of the pattern for component i and $2l$ is the period of the pattern. l is half the period. So the coordinate extend as: this is $x = 0$, $x = l$, $x = 2l$ and this repeats so that we have a periodic boundary condition. And what is the boundary condition? Since this is periodic boundary condition we know at $x = 0$, $x = l$, $x = 2l$ and on the concentration will not change. It will be same as the average concentration $\bar{C_i}$ at any time t:

$$C_{i(0,t)} = C_{i(l,t)} = C_{i(2l,t)} = \bar{C_i}$$

And there is one more condition, we know as the homogenization proceeds, the variation in concentration should slowly die down and so that ultimately we should get a uniform composition throughout the alloy. That uniform composition will be the average composition $\bar{C_i}$. We can write:

$$C_{i(x,t=\infty)} = \bar{C_i}$$

Now these conditions also we can write in the form of matrices:

$$[C]_{(x,t=\,0)} = [\bar{C}] + sin\frac{\pi x}{l}[\beta_o]$$

Where for a ternary system:

$$[\bar{C}] = \begin{bmatrix}\bar{C}_1\\ \bar{C}_2\end{bmatrix}, \quad [\beta_o] = \begin{bmatrix}\beta_o^1\\ \beta_o^2\end{bmatrix}$$

β_o is the column matrix of amplitudes of component 1 and 2. Similarly, we can express the boundary conditions in the matrix form as:

$$[C]_{(0,t)} = [C]_{(l,t)} = [\bar{C}]$$

And we have one more condition which also can be written as:

$$[C]_{(x,\infty)} = [\bar{C}]$$

So, we got the diffusion continuity equation in the form of matrix and which we have to solve with respect to this initial condition and these boundary conditions. We first need to decouple the equation for which we use the similar approach that we used previously for solving the multicomponent diffusion equation and we need a similarity transformation matrix which we call P for the interdiffusivity matrix.

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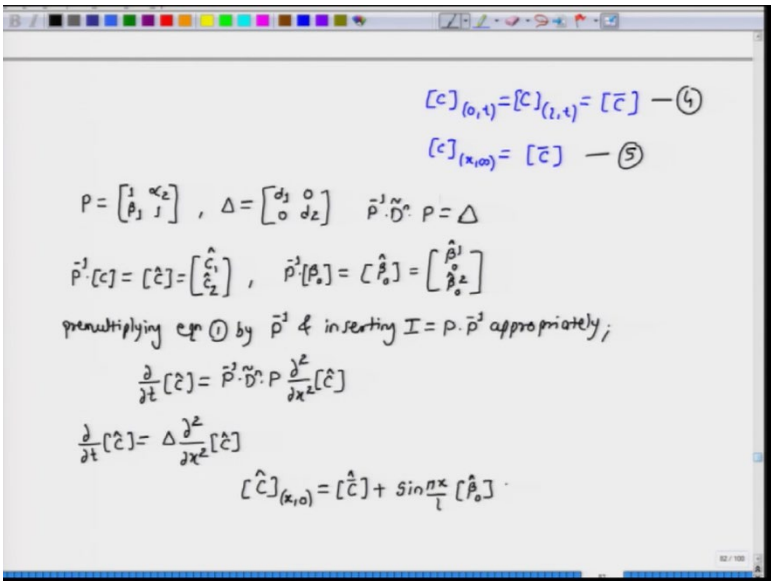


$$[c]_{(0,t)} = [c]_{(l,t)} = [\bar{c}] \quad — ④$$

$$[c]_{(x,\infty)} = [\bar{c}] \quad — ⑤$$

$$P = \begin{bmatrix} 1 & \alpha_2 \\ \beta_1 & 1 \end{bmatrix}, \quad \Delta = \begin{bmatrix} d_1 & 0 \\ 0 & d_2 \end{bmatrix} \quad P^{-1} \cdot \tilde{D}^n \cdot P = \Delta$$

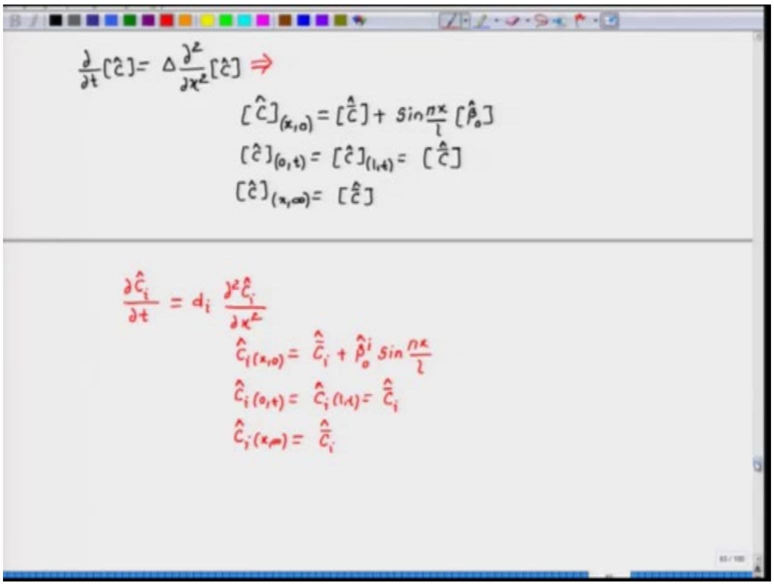
$$P^{-1} \cdot [c] = [\hat{c}] = \begin{bmatrix} \hat{c}_1 \\ \hat{c}_2 \end{bmatrix}, \quad P^{-1} \cdot [\beta_0] = [\hat{\beta}_0] = \begin{bmatrix} \hat{\beta}_0^1 \\ \hat{\beta}_0^2 \end{bmatrix}$$

premultiplying eqn ① by P^{-1} & inserting $I = P \cdot P^{-1}$ appropriately;

$$\frac{\partial}{\partial t}[\hat{c}] = P^{-1} \cdot \tilde{D}^n \cdot P \frac{\partial^2}{\partial x^2}[\hat{c}]$$

$$\frac{\partial}{\partial t}[\hat{c}] = \Delta \frac{\partial^2}{\partial x^2}[\hat{c}]$$

$$[\hat{c}]_{(x,0)} = [\hat{\bar{c}}] + \sin\frac{nx}{l}[\hat{\beta}_0]$$



$$\frac{\partial}{\partial t}[\hat{c}] = \Delta \frac{\partial^2}{\partial x^2}[\hat{c}] \Rightarrow$$

$$[\hat{c}]_{(x,0)} = [\hat{\bar{c}}] + \sin\frac{nx}{l}[\hat{\beta}_0]$$

$$[\hat{c}]_{(0,t)} = [\hat{c}]_{(l,t)} = [\hat{\bar{c}}]$$

$$[\hat{c}]_{(x,\infty)} = [\hat{\bar{c}}]$$

$$\frac{\partial \hat{c}_i}{\partial t} = d_i \frac{\partial^2 \hat{c}_i}{\partial x^2}$$

$$\hat{c}_{i(x,0)} = \hat{\bar{c}}_i + \hat{\beta}_0^i \sin\frac{nx}{l}$$

$$\hat{c}_{i(0,t)} = \hat{c}_{i(l,t)} = \hat{\bar{c}}_i$$

$$\hat{c}_{i(x,\infty)} = \hat{\bar{c}}_i$$

We define the similarity transformation matrix P which is the matrix form by arranging the Eigen vectors of $\tilde{D}$ column by column. For simplicity, we write the Eigen vectors such that the diagonal elements are normalized to 1. delta is a diagonal matrix of Eigen values of $\tilde{D}$:

$$P = \begin{bmatrix} 1 & \alpha_2 \\ \beta_1 & 1 \end{bmatrix}, \quad \Delta = \begin{bmatrix} d_1 & 0 \\ 0 & d_2 \end{bmatrix}$$

And we know:

$$P^{-1}.\widetilde{D}^n.P = \Delta$$

Now, we convert the concentration from its original basis to cap basis. And we do that just like what we did for the diffusion couple problem. We pre-multiply the matrix C with P^{-1} which should give the matrix of concentration in new basis we call it a cap basis. P inverse times C gives:

$$P^{-1}.[C] = [\hat{C}] = \begin{bmatrix} \hat{C}_1 \\ \hat{C}_2 \end{bmatrix}$$

These are the concentrations in the new basis that is cap basis. Similarly:

$$P^{-1}.[\beta_o] = [\hat{\beta}_o] = \begin{bmatrix} \hat{\beta}_o^1 \\ \hat{\beta}_o^2 \end{bmatrix}$$

which is again a column matrix of amplitudes in the cap basis. Now with this, if we pre-multiply the diffusion equation (1) with P^{-1} and we know:

$$I = P.P^{-1}$$

We get:

$$\frac{\partial}{\partial t}[\hat{C}] = P^{-1}.\widetilde{D}^n \frac{\partial^2}{\partial x^2}[C]$$

Now, we smartly insert the identity matrix $I = P.P^{-1}$ in between. We have:

$$\frac{\partial}{\partial t}[\hat{C}] = P^{-1}.\widetilde{D}^n.P\frac{\partial^2}{\partial x^2}[\hat{C}]$$

Since, we are assuming constant interdiffusion coefficient, we can take the matrix P inside the derivative. What we get is:

$$\frac{\partial}{\partial t}[\hat{C}] = \Delta\frac{\partial^2}{\partial x^2}[\hat{C}]$$

We can do the similar operation for the initial and boundary conditions. For the initial condition which is written here, if we pre multiply by P inverse, we get:

$$[\hat{C}]_{(x,0)} = \left[\hat{\hat{C}}\right] + sin\frac{\pi x}{l}[\hat{\beta}_o]$$

And for the boundary condition again if we pre-multiply by P^{-1}, this will be:

$$[\hat{C}]_{(0,t)} = [\hat{C}]_{(l,t)} = \left[\hat{\hat{C}}\right]$$

And the last condition can be written as:

$$[\hat{C}]_{(x,\infty)} = \left[\hat{\hat{C}}\right]$$

If we expand the equation:

$$\frac{\partial}{\partial t}[\hat{C}] = \Delta\frac{\partial^2}{\partial x^2}[\hat{C}]$$

in terms of the individual components, we get an equation of the form:

$$\frac{\partial \hat{C}_i}{\partial t} = d_i\frac{\partial^2 \hat{C}_i}{\partial x^2}$$

Similarly, if we write the initial and boundary conditions in terms of the individual components, we will see that:

$$\hat{C}_{i(x,0)} = \hat{\hat{C}}_i + \hat{\beta}_o^i sin\frac{\pi x}{l}$$

$$\hat{C}_{i(0,t)} = \hat{C}_{i(l,t)} = \hat{\hat{C}}_i$$

$$\hat{C}_{i(x,\infty)} = \hat{\hat{C}}_i$$

What we are assuming here is that the period l is same for all the independent components which should be the case usually due to the way the microstructure evolves. Now, we need to solve this equation and we have periodic boundary conditions. So far, we used Laplace transforms, which was useful for solving the diffusion equation with infinite boundary conditions.

And now, we will use another approach which is useful in solving the diffusion equation with periodic boundary conditions and that is the principle of separation of variable.

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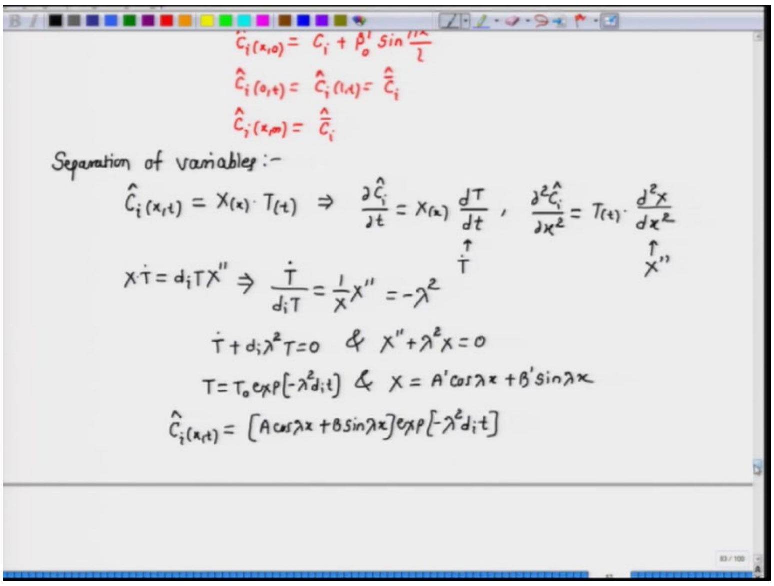


$$C_i(x,0) = C_i + \beta_0' \sin\frac{\pi x}{l}$$

$$\hat{C}_i(0,t) = \hat{C}_i(l,t) = \hat{\hat{C}}_i$$

$$\hat{C}_i(x,\infty) = \hat{\hat{C}}_i$$

Separation of variables :-

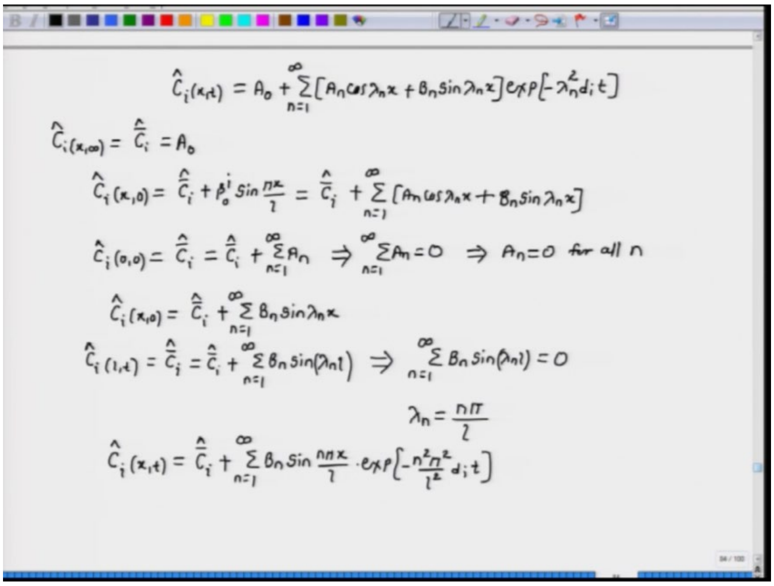
$$\hat{C}_i(x,t) = X(x) \cdot T(t) \Rightarrow \frac{\partial \hat{C}_i}{\partial t} = X(x) \underset{\overset{\uparrow}{\dot{T}}}{\frac{dT}{dt}} , \quad \frac{\partial^2 \hat{C}_i}{\partial x^2} = T(t) \cdot \underset{\overset{\uparrow}{X''}}{\frac{d^2X}{dx^2}}$$

$$X\dot{T} = d_i T X'' \Rightarrow \frac{\dot{T}}{d_i T} = \frac{1}{X} X'' = -\lambda^2$$

$$\dot{T} + d_i \lambda^2 T = 0 \quad \& \quad X'' + \lambda^2 X = 0$$

$$T = T_0 \exp[-\lambda^2 d_i t] \quad \& \quad X = A' \cos\lambda x + B' \sin\lambda x$$

$$\hat{C}_i(x,t) = [A\cos\lambda x + B\sin\lambda x]\exp[-\lambda^2 d_i t]$$



$$\hat{C}_i(x,t) = A_0 + \sum_{n=1}^{\infty}[A_n\cos\lambda_n x + B_n\sin\lambda_n x]\exp[-\lambda_n^2 d_i t]$$

$$\hat{C}_i(x,\infty) = \hat{\hat{C}}_i = A_0$$

$$\hat{C}_i(x,0) = \hat{\hat{C}}_i + \beta_0^i \sin\frac{\pi x}{l} = \hat{\hat{C}}_i + \sum_{n=1}^{\infty}[A_n\cos\lambda_n x + B_n\sin\lambda_n x]$$

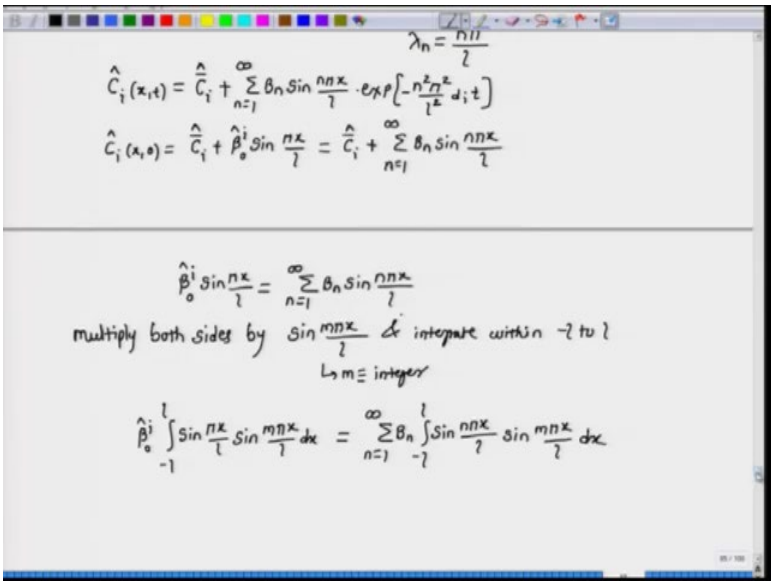
$$\hat{C}_i(0,0) = \hat{\hat{C}}_i = \hat{\hat{C}}_i + \sum_{n=1}^{\infty} A_n \Rightarrow \sum_{n=1}^{\infty} A_n = 0 \Rightarrow A_n = 0 \text{ for all } n$$

$$\hat{C}_i(x,0) = \hat{\hat{C}}_i + \sum_{n=1}^{\infty} B_n \sin\lambda_n x$$

$$\hat{C}_i(l,t) = \hat{\hat{C}}_i = \hat{\hat{C}}_i + \sum_{n=1}^{\infty} B_n \sin(\lambda_n l) \Rightarrow \sum_{n=1}^{\infty} B_n \sin(\lambda_n l) = 0$$

$$\lambda_n = \frac{n\pi}{l}$$

$$\hat{C}_i(x,t) = \hat{\hat{C}}_i + \sum_{n=1}^{\infty} B_n \sin\frac{n\pi x}{l} \cdot \exp\left[-\frac{n^2\pi^2}{l^2} d_i t\right]$$



$$\lambda_n = \frac{n\pi}{l}$$

$$\hat{C}_i(x,t) = \hat{\bar{C}}_i + \sum_{n=1}^{\infty} B_n \sin\frac{n\pi x}{l} \cdot \exp\left[-\frac{n^2\pi^2}{l^2} d_i t\right]$$

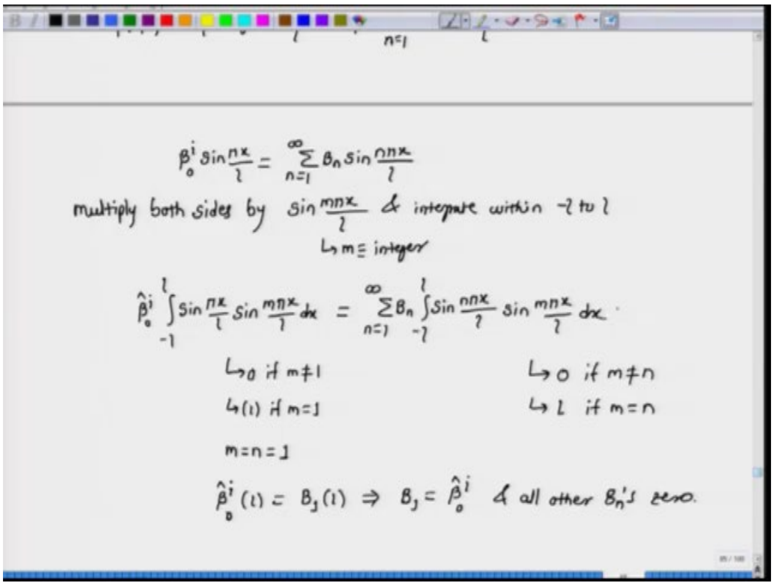
$$\hat{C}_i(x,0) = \hat{\bar{C}}_i + \hat{\beta}_0^i \sin\frac{\pi x}{l} = \hat{\bar{C}}_i + \sum_{n=1}^{\infty} B_n \sin\frac{n\pi x}{l}$$

$$\hat{\beta}_0^i \sin\frac{\pi x}{l} = \sum_{n=1}^{\infty} B_n \sin\frac{n\pi x}{l}$$

multiply both sides by $\sin\frac{m\pi x}{l}$ & integrate within $-l$ to l

$\hookrightarrow m \equiv$ integer

$$\hat{\beta}_0^i \int_{-l}^{l} \sin\frac{\pi x}{l} \sin\frac{m\pi x}{l}\, dx = \sum_{n=1}^{\infty} B_n \int_{-l}^{l} \sin\frac{n\pi x}{l} \sin\frac{m\pi x}{l}\, dx$$



$$\beta_0^i \sin\frac{\pi x}{l} = \sum_{n=1}^{\infty} B_n \sin\frac{n\pi x}{l}$$

multiply both sides by $\sin\frac{m\pi x}{l}$ & integrate within $-l$ to l

$\hookrightarrow m \equiv$ integer

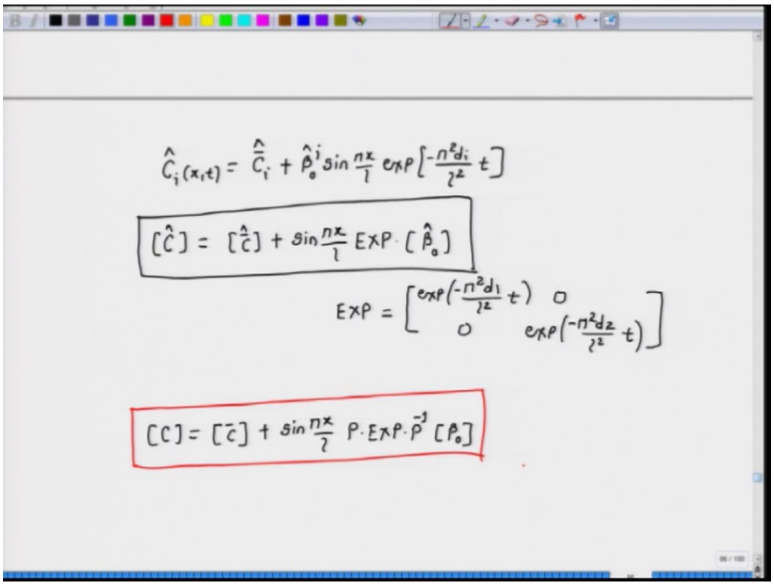
$$\hat{\beta}_0^i \int_{-l}^{l} \sin\frac{\pi x}{l} \sin\frac{m\pi x}{l}\, dx = \sum_{n=1}^{\infty} B_n \int_{-l}^{l} \sin\frac{n\pi x}{l} \sin\frac{m\pi x}{l}\, dx$$

$\hookrightarrow 0$ if $m \neq 1$ $\qquad\qquad$ $\hookrightarrow 0$ if $m \neq n$

$\hookrightarrow (l)$ if $m = 1$ $\qquad\qquad$ $\hookrightarrow l$ if $m = n$

$m = n = 1$

$\hat{\beta}_0^i (l) = B_1 (l) \Rightarrow B_1 = \hat{\beta}_0^i$ & all other B_n's zero.



$$\hat{C}_{i(x,t)} = \hat{\bar{C}}_i + \hat{\beta}_0^i \sin\frac{nx}{l} \exp\left[-\frac{n^2 d_i}{l^2} t\right]$$

$$\boxed{[\hat{C}] = [\hat{\bar{C}}] + \sin\frac{nx}{l} EXP \cdot [\hat{\beta}_0]}$$

$$EXP = \begin{bmatrix} \exp\left(-\frac{n^2 d_1}{l^2} t\right) & 0 \\ 0 & \exp\left(-\frac{n^2 d_2}{l^2} t\right) \end{bmatrix}$$

$$\boxed{[C] = [\bar{C}] + \sin\frac{nx}{l} P \cdot EXP \cdot P^{-1} [\beta_0]}$$

What we assume is that $\hat{C}_i$ at any x and t can be expressed as a product of two functions: one which is the function of only x and the second which is the function of only t. Let us call it $X(x)$ and $T(t)$. $\hat{C}_i$ at any x and t can be given as:

$$\hat{C}_{i(x,t)} = X(x).T(t)$$

This means I can write:

$$\frac{\partial \hat{C}_i}{\partial t} = X(x)\frac{dT}{dt} \quad , \quad \frac{\partial^2 \hat{C}_i}{\partial x^2} = T(t).\frac{d^2X}{dx^2}$$

And since T is function only of t, I can replace $\frac{\partial T}{\partial t}$ as the ordinary derivative $\frac{dT}{dt}$. Similarly, I can replace the partial derivative with again ordinary derivative because X is only function of x. This derivative with respect to t, we usually denote with dot on top of the function T and first derivative with respect to x we denote by prime, double prime for second derivative. If we substitute this in the diffusion equation, what we see is:

$$X.\dot{T} = d_i T X'' \quad , \quad \frac{\dot{T}}{d_i T} = \frac{1}{X} X''$$

Now this is interesting, because what you see in this equation, the left hand side of this equation is function only of t and the right side is function only of x. So, left hand side and right hand side are basically independent of each other. This equality, therefore, will be valid only when both the sides are equal to a constant.

Let us call that constant as $-\lambda^2$:

$$\frac{\dot{T}}{d_i T} = \frac{1}{X}X'' = -\lambda^2$$

We basically get 2 ordinary differential equation, one only in T, the other only in x and those I can write as:

$$\dot{T} + d_i\lambda^2 T = 0 \qquad and \quad X'' + \lambda^2 X = 0$$

The solution for the first one can be expressed as:

$$T = T_o \exp(-d_i\lambda^2 t)$$

And solution for x can be expressed as:

$$X = A'cos\lambda x + B'sin\lambda x$$

If we substitute these solutions in the respective equations for T and X, the function $\hat{C}_{i_{(x,t)}}$ can be written as:

$$\hat{C}_{i_{(x,t)}} = (Acos\lambda x + Bsin\lambda x)exp(-\lambda^2 d_i t)$$

Here, I have combined the constants T_o and A' to get A and T_o and B' to get B. Now, we know the linear combination of solutions is also a solution. If there are infinite number of values of λ_n for which the solution is satisfied, then their summation should also be a solution. I can write:

$$\hat{C}_{i_{(x,t)}} = A_o + \sum_{n=1}^{\infty}(A_n cos\lambda_n x + B_n sin\lambda_n x)exp(-\lambda_n^2 d_i t)$$

This A_o is basically the value of A_n when $\lambda_n = 0$. So, this is the general solution that we have obtained for $\hat{C}_i$. Now, we need to find these constants. If we use this condition:

$$\hat{C}_{i_{(x,\infty)}} = \hat{\hat{C}}_i$$

If we substitute $t = \infty$ in this equation, I get:

$$\hat{C}_{i_{(x,\infty)}} = \hat{\hat{C}}_i = A_o$$

If we use the initial condition now:

$$\hat{C}_{i(x,0)} = \hat{\hat{C}}_i + \hat{\beta}_o^i sin\frac{\pi x}{l}$$

On substituting $t = 0$ general solution for $\hat{C}_i$ should be equal to:

$$\hat{C}_{i(x,0)} = \hat{\hat{C}}_i + \hat{\beta}_o^i sin\frac{\pi x}{l} = \hat{\hat{C}}_i + \sum_{n=1}^{\infty}(A_n cos\lambda_n x + B_n sin\lambda_n x)exp(-\lambda_n^2 d_i t)$$

If we evaluate this again at $x = 0$:

$$\hat{C}_{i(0,0)} = \hat{\hat{C}}_i = \hat{\hat{C}}_i + \sum_{n=1}^{\infty} A_n$$

So we get:

$$\sum_{n=1}^{\infty} A_n = 0$$

Now if this has to be true for all values of A_n, then all A_n should be equal to 0, only then this will be true. So:

$$A_n = 0 \quad for\ all\ n$$

We can write:

$$\hat{C}_{i(x,0)} = \hat{\hat{C}}_i + \sum_{n=1}^{\infty} B_n sin\lambda_n x$$

Now I use the second boundary condition that is at $x = l$:

$$\hat{C}_{i(l,t)} = \hat{\hat{C}}_i = \hat{\hat{C}}_i + \sum_{n=1}^{\infty} B_n sin\lambda_n$$

Again this means:

$$\sum_{n=1}^{\infty} B_n sin\lambda_n = 0$$

Either all B_n have to be 0 which will yield a trivial solution or the second sin term has to be 0. For the second case to be possible:

$$\lambda_n = \frac{n\pi}{l}$$

$\hat{C}_{i(x,t)}$ will be given by:

$$\hat{C}_{i(x,t)} = \hat{\hat{C}}_i + \sum_{n=1}^{\infty} B_n sin\frac{n\pi x}{l} exp\left(-\frac{n^2\pi^2}{l^2} d_i t\right)$$

Again, if I write at t =0 this should be equal to:

$$\hat{C}_{i(x,0)} = \hat{\hat{C}}_i + \hat{\beta}_o^i sin\frac{\pi x}{l} = \hat{\hat{C}}_i + \sum_{n=1}^{\infty} B_n sin\frac{n\pi x}{l}$$

which is from the initial condition and this should be:

$$\hat{\beta}_o^i sin\frac{\pi x}{l} = \sum_{n=1}^{\infty} B_n sin\frac{n\pi x}{l}$$

Now to obtain the values of B_n, what we do? We multiply both sides by $sin\frac{m\pi x}{l}$ and integrate within the interval $-l$ to l. Here m is an integer. We get:

$$\hat{\beta}_o^i \int_{-l}^{l} sin\frac{\pi x}{l} sin\frac{m\pi x}{l} = \sum_{n=1}^{\infty} B_n \int_{-l}^{l} sin\frac{n\pi x}{l} sin\frac{m\pi x}{l}$$

since B_n are constants. Now, it will be clear why we did this, because the integral on the right hand side, if we look at it, it has a value:

$$0 \;\; if \; m \neq n \;\;\; , \;\;\; l \;\;\; if \; m = n$$

Similarly, on the left hand side, it is a similar integral with $n = 1$ here. So, this has a value:

$$0 \;\; if \; m \neq 1 \;\;\; , \;\;\; l \;\;\; if \; m = 1$$

In effect if both sides are 0 then it would not help. So we should have:

$$m = n = 1$$

and in which case the value of the integrals will be l. I can write this equation as:

$$\hat{\beta}_o^i(l) = B_1(l)$$

$$\hat{\beta}_o^i = B_1$$

and all other $B_n = 0$. We got the solution for $\hat{C}_i$ which takes the form:

$$\hat{C}_{i(x,t)} = \hat{\bar{C}}_i + \hat{\beta}_o^i sin\frac{\pi x}{l} exp\left(-\frac{\pi^2 d_i}{l^2} t\right)$$

And we can see if we write for all independent components, this can be expressed in the matrix form as:

$$\hat{C} = \hat{\bar{C}} + sin\frac{\pi x}{l} EXP. [\hat{\beta}_o]$$

We will define soon what is the matrix E $EXP. [\hat{\beta}_o]$. And this EXP is a diagonal matrix with these exponential terms along its diagonal. For a ternary system this is:

$$EXP = \begin{bmatrix} exp\left(-\frac{\pi^2 d_1}{l^2} t\right) & 0 \\ 0 & exp\left(-\frac{\pi^2 d_2}{l^2} t\right) \end{bmatrix}$$

So, we got the solution for the concentrations in the cap basis. Now, we want to convert back to the original basis, we do a reverse operation. If we pre-multiply both sides by the matrix P, we get:

$$[C] = [\bar{C}] + sin\frac{\pi x}{l} P. EXP[\hat{\beta}_o]$$

But if we insert $P^{-1}.P$ in between, we get:

$$[C] = [\bar{C}] + sin\frac{\pi x}{l} P. EXP. P^{-1}[\beta_o]$$

So, this is the solution that we have got for homogenization in an n component alloy for which the initial concentration profile was represented by the sinusoidal form:

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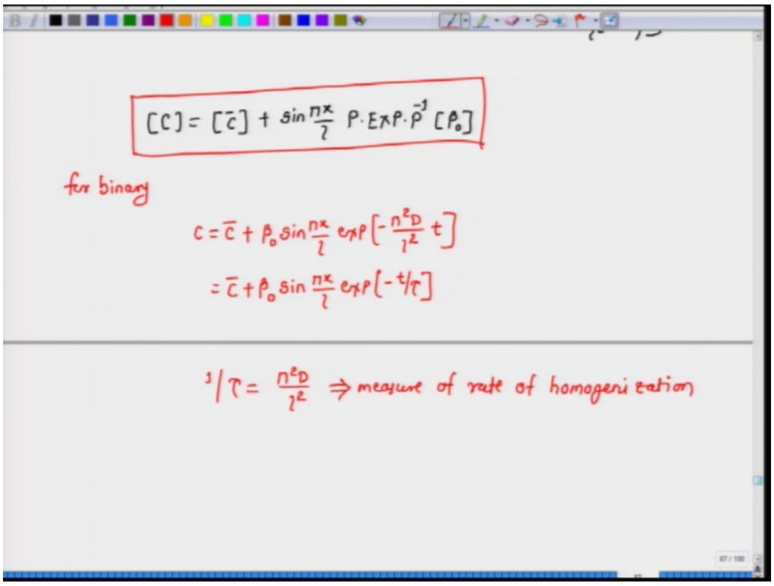

$$\boxed{[C] = [\bar{C}] + \sin\frac{\pi x}{l}\, P \cdot ExP \cdot P^{-1}\, [\beta_0]}$$

for binary

$$c = \bar{c} + \beta_0 \sin\frac{\pi x}{l} \exp\left[-\frac{\pi^2 D}{l^2} t\right]$$

$$= \bar{c} + \beta_0 \sin\frac{\pi x}{l} \exp\left[-t/\tau\right]$$

$1/\tau = \frac{\pi^2 D}{l^2} \Rightarrow$ measure of rate of homogeni zation

For binary this will reduce to, as we need just one concentration variable:

$$C = \bar{C} + \beta_o sin\frac{\pi x}{l} exp\left[-\frac{t}{\tau}\right]$$

Where:

$$\frac{1}{\tau} = \frac{\pi^2 D}{l^2}$$

and it has a unit of per second. D is $\frac{m^2}{s}$, l square is meter square. So τ is basically a measure of rate of homogenization. We can see the rate of homogenization depends on the diffusivity: higher the diffusivity, higher will be the rate of homogenization and it varies inversely with l^2. The rate of homogenization will be higher for smaller period. If we have 2 different segregation patterns with the same amplitude, but if they have different periods, the segregation pattern with lower period will homogenize faster.

Okay, this is the solution that we have obtained. Now, let us study the features of the concentration profiles that develop during homogenization in order to understand how the homogenization proceeds based upon the solutions that we have derived. Let us first consider for binary and then also for a ternary system, so that we will understand how the cross diffusion term make important effects.

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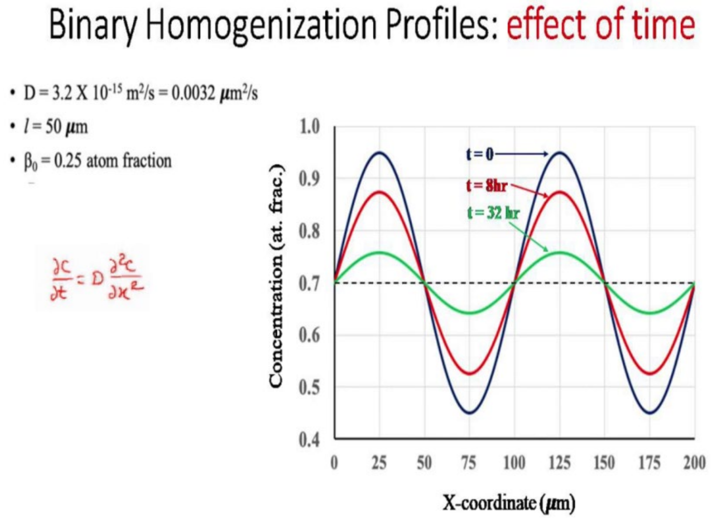

Binary Homogenization Profiles: effect of time

- $D = 3.2 \times 10^{-15}$ m²/s = 0.0032 μm²/s
- $l = 50$ μm
- $\beta_0 = 0.25$ atom fraction

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

Let us first consider the binary case. This figure shows the concentration profiles that are developed at different times of homogenization in a binary alloy and the parameters that we have taken for the simulation are:

$$D = 3.2 \times 10^{-15}\,\frac{m^2}{s} = 0.0032\,\frac{\mu m^2}{s}$$

The period is taken as 100 μm or:

$$l = 50\ \mu m \quad , \quad \beta_o = 0.25\ atom\ fraction$$

β_o is the amplitude and the average concentration is 0.7 atom fraction. This blue profile is the initial concentration profile. The profile is oscillating between the maximum value of 0.95 and the minimum value of 0.45. This is at t equal to 0, if we use the equation that we derived and simulate at different times, let us say at 8 hours the profile is represented by this red curve, at 32 hours the profile is represented by this green curve. We can see as the homogenization time proceeds, the amplitude keeps dropping. The fluctuations are getting lower and lower so that with time the profile is tending to flatten out. If we consider a particular period and let us look at the 2 sides of the half of the period. On the left side, you will see the curvature of the profile is negative. And for constant diffusion coefficient, we know:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

If the curvature is negative means, $\frac{\partial C}{\partial t}$ is negative, which means the concentration should drop. Whereas on the right side of this half interval, we see that the curvature is positive and the concentration should increase with time. At x equal to 0, l, $2l$ and on, the curvature is 0 and the concentration should be constant, which is the average concentration $\bar{C}$. This was the effect of time. Now, let us understand the effect of period and the diffusivity.

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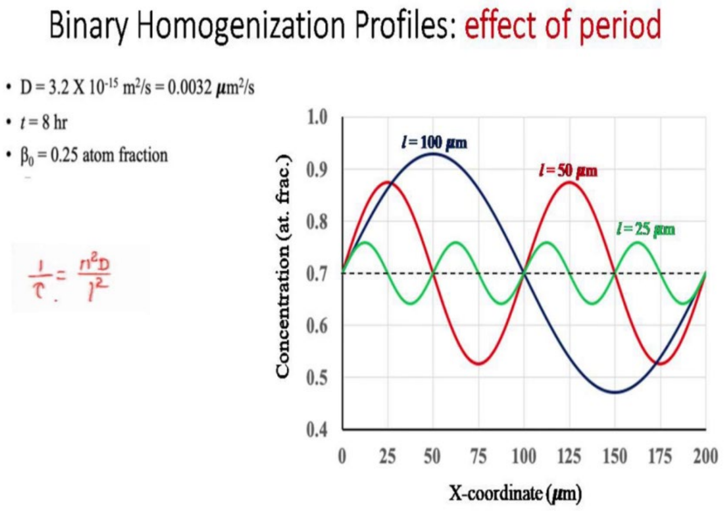

Binary Homogenization Profiles: effect of period

- $D = 3.2 \times 10^{-15}\ m^2/s = 0.0032\ \mu m^2/s$
- $t = 8$ hr
- $\beta_0 = 0.25$ atom fraction

$\frac{1}{\tau} = \frac{\pi^2 D}{l^2}$

We know the rate of homogenization was given by:

$$\frac{1}{\tau} = \frac{\pi^2 D}{l^2}$$

The rate is inversely proportional to l^2. Obviously as the period increases, the rate of homogenization should decrease. Again these are the concentration profiles with the similar parameters that we used for earlier profiles. The same value of diffusivity, β_o and $\bar{C}$ and at t equal to 8 hours, we have simulated for different periods. At $t = 8\ hr$ this is the profile for l equal to 100 micron, the red one is for l equal to 50 micron and the green one is for l equal to 25 micron. After the same time of homogenization, although we started with the same amplitude and the same average concentration, we see that the profile with the lower period homogenizes faster. Then, obviously as the rate of homogenization is $\frac{\pi^2 D}{l^2}$, as the diffusivity increases, the rate of homogenization should also increase.

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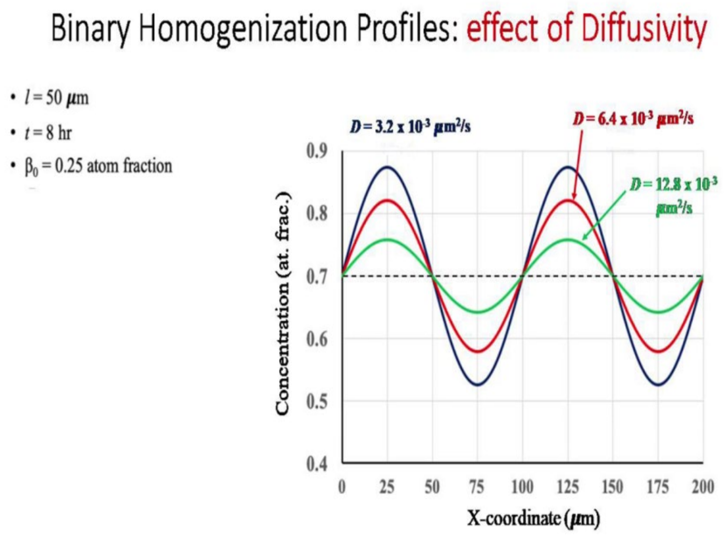

Binary Homogenization Profiles: effect of Diffusivity

- $l = 50\ \mu m$
- $t = 8$ hr
- $\beta_0 = 0.25$ atom fraction

With the same parameters at t equal to 8 hours and the half of the period-50 micron for different values of diffusivities, the profiles are shown here.

Blue one is for $D = 3.2 \times 10^{-3}\ \frac{\mu m^2}{s}$, red one is for the double the diffusivity and green one is for 4 times the original diffusivity. And we see as the diffusivity increases, the homogenization rate is increased. This was for binary. Now let us look into a ternary profile.

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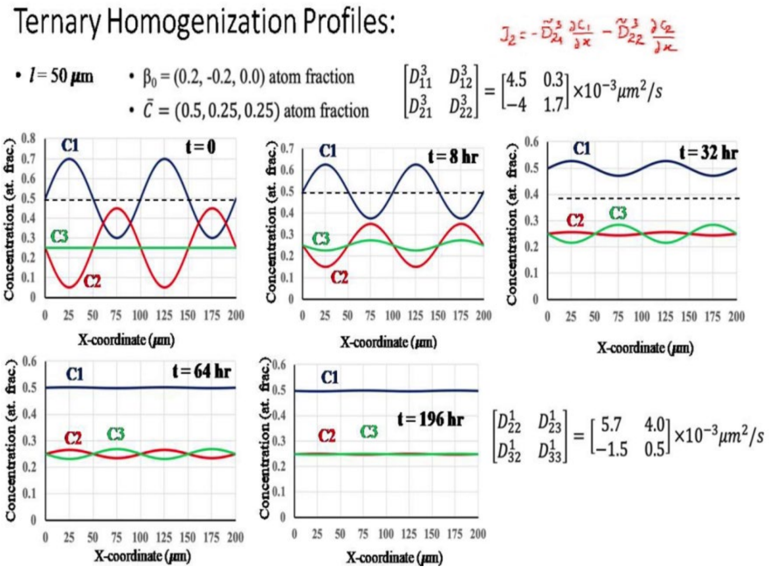

Ternary Homogenization Profiles:

$J_2 = -\tilde{D}_{21}^{3}\frac{\partial C_1}{\partial x} - \tilde{D}_{22}^{3}\frac{\partial C_2}{\partial x}$

- $l = 50\ \mu m$
- $\beta_0 = (0.2, -0.2, 0.0)$ atom fraction
- $\bar{C} = (0.5, 0.25, 0.25)$ atom fraction

$$\begin{bmatrix} D_{11}^{3} & D_{12}^{3} \\ D_{21}^{3} & D_{22}^{3} \end{bmatrix} = \begin{bmatrix} 4.5 & 0.3 \\ -4 & 1.7 \end{bmatrix} \times 10^{-3} \mu m^2/s$$

$$\begin{bmatrix} D_{22}^{1} & D_{23}^{1} \\ D_{32}^{1} & D_{33}^{1} \end{bmatrix} = \begin{bmatrix} 5.7 & 4.0 \\ -1.5 & 0.5 \end{bmatrix} \times 10^{-3} \mu m^2/s$$

Now, in ternary means we have 2 independent concentrations. So, the 2 concentrations can vary independently, third one will be just a dependent component or will just respond to the variations in the first two. The average concentration that we have taken for the ternary is:

$$\bar{C_1} = 0.5\, mole\ fraction$$

$$\bar{C_1} = 0.25\, mole\ fraction$$

$$\beta_o^1 = 0.2\, mole\ fraction$$

$$\beta_o^2 = -0.2\, mole\ fraction$$

which means C_1 and C_2 are varying in the opposite direction. This is the initial profile for C_1 and this one is for C_2. C_1 is varying from the maximum value of 0.7 to the minimum value of 0.3 periodically. And C_2 is varying in the same interval, the minimum value of 0.05 to the maximum value of 0.45. And you can see, C_3 is constant throughout. To start with, there was no variation in C_3. It was uniformly distributed. Now, one would tend to think, since C_3 is constant, it should remain constant throughout the homogenization treatment. But that is not true because of the cross effects. Although the gradient in C_3 is 0, but there exists gradients in 1 and 2. And the cross interdiffusivity term would come into effect. Here we need 4 inter diffusion coefficients for ternary. The values that we are used assuming of course, the constant values are given as:

$$\begin{bmatrix} \widetilde{D}_{11}^3 & \widetilde{D}_{12}^3 \\ \widetilde{D}_{21}^3 & \widetilde{D}_{22}^3 \end{bmatrix} = \begin{bmatrix} 4.5 & 0.3 \\ -4 & 1.7 \end{bmatrix} \times 10^{-3} \frac{\mu m^2}{s}$$

Now, we see we have simulated the concentration profiles at different times at t equal to 8 hours, 32 hours, 64 hours and 196 hours. As we go at 8 hours, we see the amplitudes of 1 and 2 have decreased and interestingly C_3 to start with was constant, but it has now developed the undulations. As I increase the time, the undulations of C_3 have increased, C_1 is homogenizing very fast. Of course, the main diffusivity of component 1 is much higher compared to the main diffusivity of 2. C_1 is homogenizing much faster.

And, as I go to 64 hour, what we can see? C_1 has completely flattened out, but C_2 which looked to be flattening out between 8 hours to 32 hours has now reversed its undulations and this is the interesting effect which has occurred because of the interactions. Now, we will try to understand how. To start with, if we look at the $\widetilde{D}_{21}^3$ and $\widetilde{D}_{22}^3$ value, $\widetilde{D}_{21}^3$ is very highly negative or its magnitude is higher than the main coefficient of 2. We expect that interaction of 1 on 2 will be great. But, we can see, because the flux of J 2 is given as:

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

the gradient of 2 is also high to start with, both the gradients are higher and C_1 is flattening out very fast. The interaction effect of 1 and 2 are not very obvious here. And by the time, C_1 has flattened out, the gradient in C_3 has picked up. And the interaction of 3 on 2 have come into effect. Now to understand those interaction I need to convert diffusivity matrix. This matrix is represented with component 3 as dependent, I can convert it to a matrix with component 1 as dependent because we want to analyze component 2, 3.

If I convert it to component 1 as dependent, this is the matrix that we have got:

$$\begin{bmatrix} \widetilde{D}_{22}^1 & \widetilde{D}_{23}^1 \\ \widetilde{D}_{32}^1 & \widetilde{D}_{33}^1 \end{bmatrix} = \begin{bmatrix} 5.7 & 4.0 \\ -1.5 & 0.5 \end{bmatrix} \times 10^{-3} \frac{\mu m^2}{s}$$

And what we see, $\widetilde{D}_{32}^1$ is much higher than $\widetilde{D}_{33}^1$, it is a negative and an order of magnitude higher. And the interaction of 2 and 3 becomes very important. At the same time, the gradient of 3 was very low to start with, and that is the reason, if you write the similar equation for $\tilde{J}_3$ in terms of $\widetilde{D}_{23}^1$ and $\widetilde{D}_{33}^1$ with component 1 as dependent. You will see, although C_3 was flat to start with, but there was a gradient in 2 and which caused the development of undulations in

C_3. By the time C_1 has flattened out, C_3 has developed a profile and now the effect of 3 on 2 would come into picture. And we can see $\widetilde{D}_{23}^{1}$is almost similar to $\widetilde{D}_{22}^{1}$. And that is why the undulations of C_2 have reversed in this case.

So, here the direction of undulations are reversed and slowly this will flatten out. And this is very important in ternary and higher order system. This cross terms plays important part. If we do not consider this cross terms, we would have missed this effect of the undulations that have been developed in C_3. Where would this be very important?

For example, if C_3 was constant initially and let us assume that it was below the solubility limit of 3 in the alloy. But since these undulations developed and if it happens that this concentration tries to exceed the solubility limit of component 3 in the alloy, then we expect the second phase to precipitate out. If we ignore these effects, we would completely miss the second phase precipitation and we will wrongly predict the microstructure.

This is just one example why the cross terms are important. Okay, we have developed the solution for homogenization for n component system. We applied it to binary and ternary and we also have seen the behavior of concentration profiles during homogenization treatment. Alright, we will stop here for today. Thank you.