Diffusion in Multicomponent Solids
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Lecture No 50
Multiphase Diffusion

Welcome to the 50th lecture of this open course on Diffusion in Multicomponent Solids. Now that I have introduced you to ternary isotherms in the last class, I would now like to start with studying multiphase diffusion. In single-phase diffusion we had diffusion couples with terminal alloys having the same phases to start with and even during the course of diffusion, there was no second phase developed within the diffusion zone.

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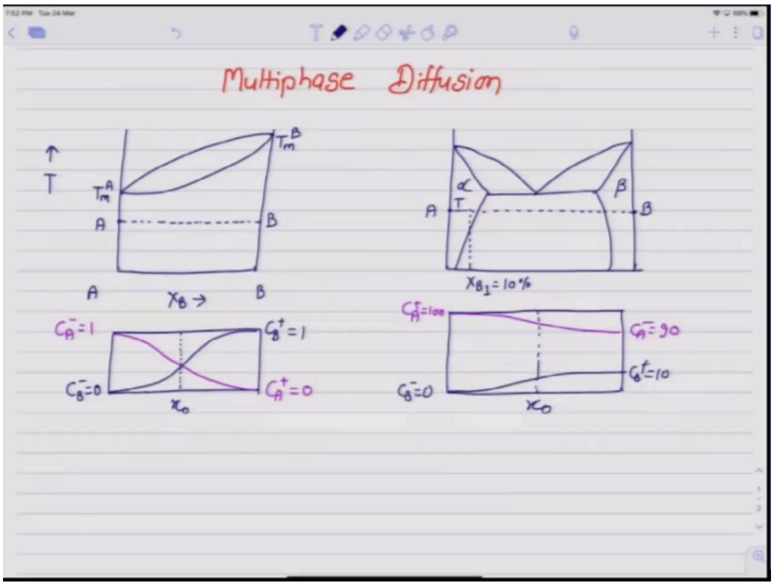

So, the simplest system for the case of single-phase diffusion is when there is a complete miscibility. So, if we consider an isomorphous type of phase diagram and if we assemble a diffusion couple between pure A and pure B at a constant temperature which is below the melting points of both A and B, we know that this would be a single-phase diffusion couple. So, this is the initial contact plane x_o. To start with, on the left terminal alloy B concentration was 0, on the right terminal alloy B concentration is 1 or 100 percent.

Similarly, on the left terminal alloy, the concentration of A is 1 and on the right terminal alloy concentration of A is 0. After the diffusion annealing at a constant temperature we know there will be a continuous concentration profile developed like this. This will be an error function type of profile for both the components. What happens if there are more phases existing in the composition range of pure A and pure B.

So, the simplest of it is eutectic system, so let us draw a eutectic system with some solubility on both A rich side and B rich side. So, if I consider a diffusion couple between pure A and some alloy with composition X_{B_1} at a temperature at which X_{B_1} exist as single-phase α. This is still a single-phase diffusion couple. Because as the diffusion starts there will be again continuous profiles developed and there is no formation of new phase at the diffusion annealing temperature being considered here.

So again, if you draw, to start with $C_B^{-¿=0¿}$, $C_B^{+¿¿}$is let us say $X_{B_1}=¿$ 10 mole percent of B. So this will be 10, the concentration profile would be something like this after diffusion annealing. This is x_o plane. For A we had $C_A^{-¿=100¿}$ and $C_A^{+¿=90¿}$ and again the error function type of profiles will be developed for both A and B. But what if at the same temperature, I assemble the diffusion couple between pure A and pure B here? Now, how would the diffusion structure look like? What is a diffusion structure? It is nothing but the microstructure that is developed within diffusion zone.

For a single-phase diffusion couple, diffusion structure is simple, there are not many features because it is all single-phase. So, at the most you can see some green boundaries if they exist but no precipitate or second phase. In multiphase diffusion couple, the diffusion structure is interesting and it does give lot of information about phase equilibrium. There may be multiple single-phase layers, there may be a 2 phase region or a 3 phase or multiple phase region depending upon how many components we are considering and so on. So, in this particular couple A-B how would diffusion structure look like?

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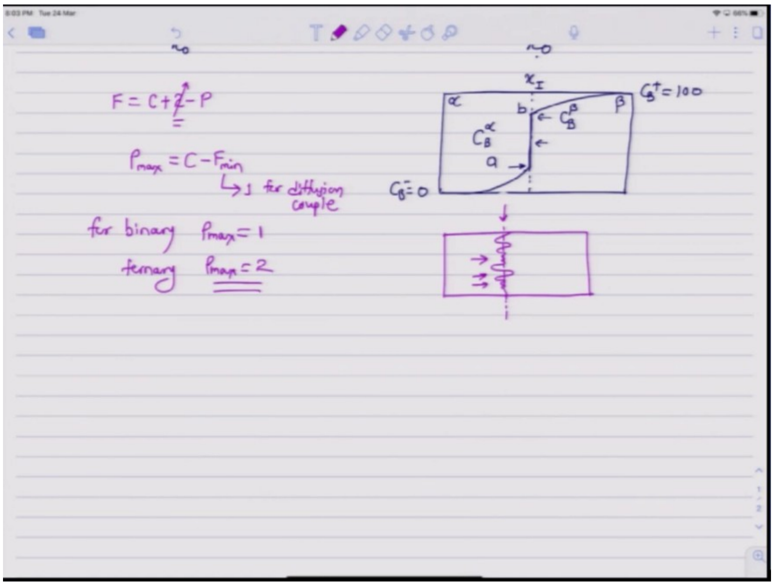


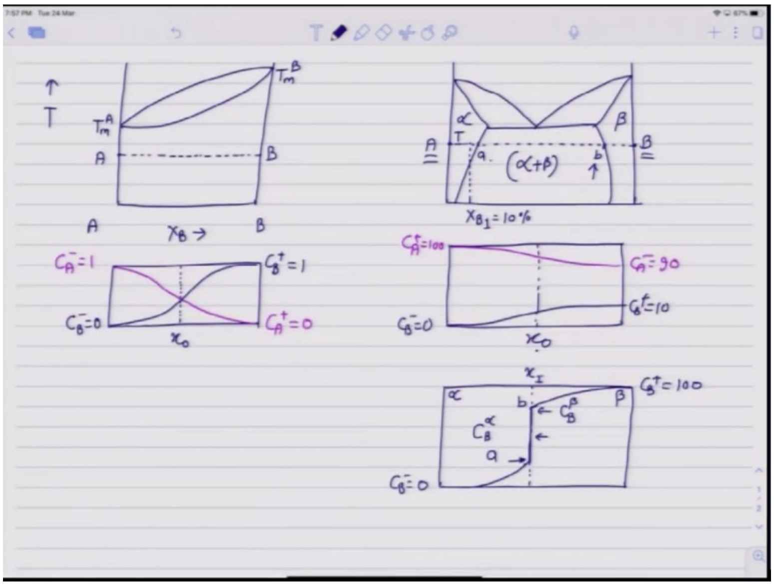
$F = C + \cancel{2} - P$

$P_{max} = C - F_{min}$

↳ 1 for diffusion couple

for binary $P_{max} = 1$

ternary $P_{max} = 2$



So, let us try to draw the concentration profile again here. So obviously, in this case A and B both have different phases to start with. So, on the left terminal alloy, I have phaseα, right terminal alloy I have phase β. So, there has to be an interface between α and β. So, let us denote this interface here as x_I. Now it has to be noted this x_I, the interface position is not necessarily same as the matano plane position x_o. We will talk about this in the next class how to determine x_o for this. But just remember now that x_I is not same as x_o. x_I is the interface position that is where the α transits to β within the diffusion zone. Now let us consider the concentration profile for B on the left terminal alloy, we have $C_B^{-¿=0¿}$, in right terminal alloy $C_B^{-¿=100¿}$. We know as we enter the diffusion zone from left side and in the terminal alloy $C_B^{-¿=0¿}$and then the C_B will start increasing and it will increase until the interface position is reached. What is the concentration of B at the interface?

Now there are 2 sides for the interface. On one side there is phase α, on the other side there is phase β. If you want to determine the equilibrium compositions at temperature T in the two phase region, we draw this tie line which I have already drawn here and I mark where the tie line intersects the two phase boundaries. So, this tie line intersects at position a and $b$here and a represents the maximum solid solubility of B in α at temperature T.

And so, the concentration of B in α cannot exceed the concentration a and so at the interface on the α side, this concentration is a and we call this as C_B at the interface in the phase α. Similarly, if we come from the right side, in the right terminal alloy, the concentration of B is 100 percent and as we go towards the diffusion zone, B will decrease and we know the minimum amount of B that has to be there in β at temperature T is given by this point, b here. And so, where the concentration profile intersects this interface position, this concentration is corresponding to this point b here and we call this as concentration of B in β. So, as we can see there would be a discontinuity in the concentration profile at the interface. So, we have α on left side, β on right side and a planar interface between α and β. And on the concentration profile there will be a discontinuity.

The compositions on the two sides of the interface that is a and b here represent the equilibrium compositions of the two phases. We can assume local equilibrium at a planar interface and this is very important because it helps us in determining phase diagrams from the diffusion couple experiments. If we get planar interface, we get the two phases which are in equilibrium and we exactly get the tie lines between those two.

Now the question is we see a two-phase region on the phase diagram here but when I draw the concentration profile or the diffusion structure, I did not show two phase region. And the reason is because this is a binary system. Again, if we apply Gibbs phase rule:

$$F = C + 2 - P$$

Since I am considering constant pressure and the diffusion couples are isothermal couples that is at constant temperature so I can ignore this factor 2 which are basically for pressure and temperature. And I can write the maximum phases that can exist $P_{max}$is equal to:

$$P_{max} = C - F_{min}$$

F_{min} is the minimum degrees of freedom. Diffusion couples requires at least 1 degree of freedom that is, concentration gradient. Otherwise, there would be no diffusion and so F_{min} is 1 for diffusion couple and for a binary system we can see the maximum phases can be 1. So, in the diffusion zone of a binary diffusion couple only single-phase layers can form. There may be multiple single-phase layers within the diffusion zone but in a given layer there will exist only one phase. Two phase layers cannot form because of the constraint from the Gibbs phase rule. Also, the interface between the two different phases formed in a binary diffusion couple which is annealed at constant temperature has to be a planar interface. What happens if the interface is non-planar? A non-planar interface may look wavy like this.

Remember, when I say an interface, it is the cross section or it is the plane perpendicular to the diffusion direction which in this case is the plane going into the plane of paper. So, if you take a cross section along this non-planar interface and see its microstructure, we will see that there will be two phases existing in that plane and two phase layer is not possible in an isothermal binary diffusion couple. And hence, a non-planar interface cannot exist in a binary couple.

For ternary, it is possible because for ternary, P max is equal to 2. So, a two phase layer can form or there may be two single-phase layers having a non-planar interface between them. So, this is possible in ternary diffusion couple or even in quaternary or higher order systems but not in binary diffusion. So, this was about binary multiphase diffusion couples.

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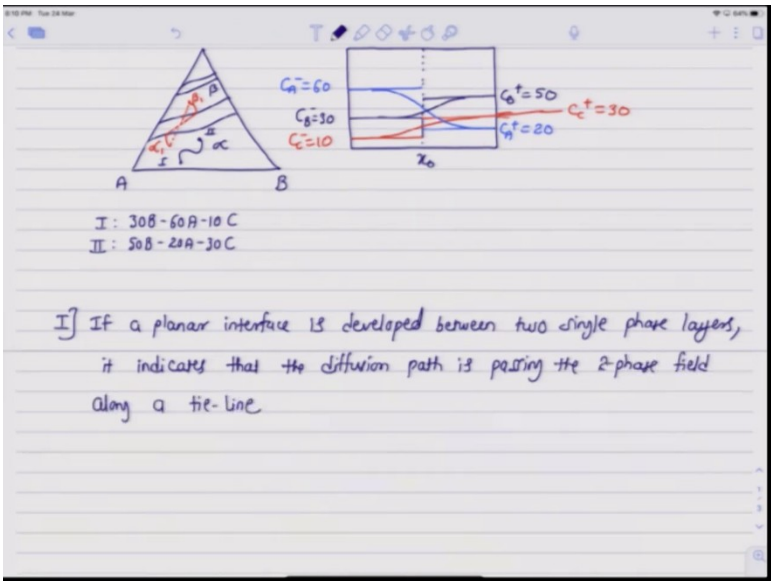

I : 30B - 60A - 10 C
II : 50B - 20A - 30C

I] If a planar interface is developed between two single phase layers, it indicates that the diffusion path is passing the 2-phase field along a tie-line

Now let us look into ternary multiphase diffusion couples. If I consider a ternary isotherm in which there is a big α solid solution region similar to what we have seen for copper, nickel, zinc system last class, there is also a β phase region here let us say. Now, if I assemble a diffusion couple between 2 alloys which lie completely inside the α phase region. Let us call this alloy 1, alloy 2. Suppose alloy 1 has composition 30B-60A-10C and alloy 2 had composition of 50B-20A-30C. We know this will be a single-phase diffusion couple with nice S shaped diffusion path and all the concentration profiles will be continuous. So, there will be no discontinuity in the concentration profiles. So, if I draw this concentration profiles here, this is the initial contact plane x_o. To start with B is 30 percent on left side so $C_B^{-¿=30¿}$, $C_B^{+¿=50¿}$, then $C_A^{-¿=60¿}$ and $C_A^{+¿=20¿}$ and $C_C^{-¿=10¿}$ whereas, $C_C^{+¿=30¿}$. So, after the diffusion annealing, there will be nice continuous profiles developed something like this.

However, if we form a diffusion couple between let us say alloy $\alpha_1$and β_1 here. So, to start with the two terminal alloys had different compositions, so they may develop two phase region in the diffusion zone or there may be a planar interface between α and β. So again, for mass balance the diffusion path has to cross the straight line joining the two alloys at least once, so this diffusion path may look something like this. The way the diffusion path passes through the two phase region, the diffusion structure may be different.

There are certain rules that help us to correlate the diffusion structure that is developed in the diffusion zone of an isothermal ternary diffusion couple with the features of the ternary isotherm. So, let us look at those. So, the first rule is that if there is a planar interface developed between two single-phase layers in a ternary diffusion couple, it indicates that the diffusion path is passing through the two phase region along a tie line.

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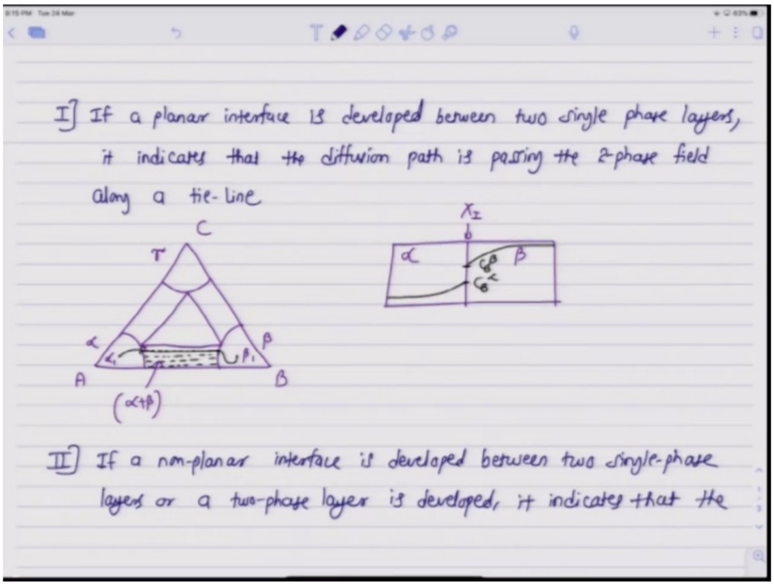

I] If a planar interface is developed between two single phase layers, it indicates that the diffusion path is passing the 2-phase field along a tie-line

II] If a non-planar interface is developed between two single-phase layers or a two-phase layer is developed, it indicates that the

So, let me draw another type of isotherm here to understand this, so let us say there are 3 single-phase zones here and on the A rich side we have α, B rich side we have β and C rich side let say we have gamma. There will be a 3-phase region or tie triangle, say if I assemble a diffusion couple between $\alpha_1$and β_1 and if I see a planar interface after diffusion annealing between α and β, this is the interface position x_I, that means the diffusion path is crossing the $\alpha + \beta$ phase field which is this phase field along a tie line.

So, the tie line in $\alpha + \beta$ region would look something like this and if I draw the diffusion path it may look something like this. First it passes through α phase field, then it passes along the tie line then it enters the β region S. So, the diffusion path may look like this with its segment within the 2-phase region being parallel to a tie line or along a tie line. This is important because a tie line represents equilibrium compositions of the 2 phases in equilibrium.

And hence, we can determine the equilibrium compositions of the 2 phases at this temperature or essentially by determining the composition profiles we can determine the tie line of the $\alpha+\beta$ 2-phase field. So, if I draw the concentration profile here, let us say for B it may look something like this and these two compositions C_B^{α} and C_B^{β} are basically the equilibrium compositions given by this tie line.

So, this helps us in determining the phase diagrams. Second rule, if a non-planer interface forms between 2 single-phase regions or if there exist a 2-phase region in the diffusion zone it indicates that the diffusion path is passing through the 2 phase region across the tie lines.

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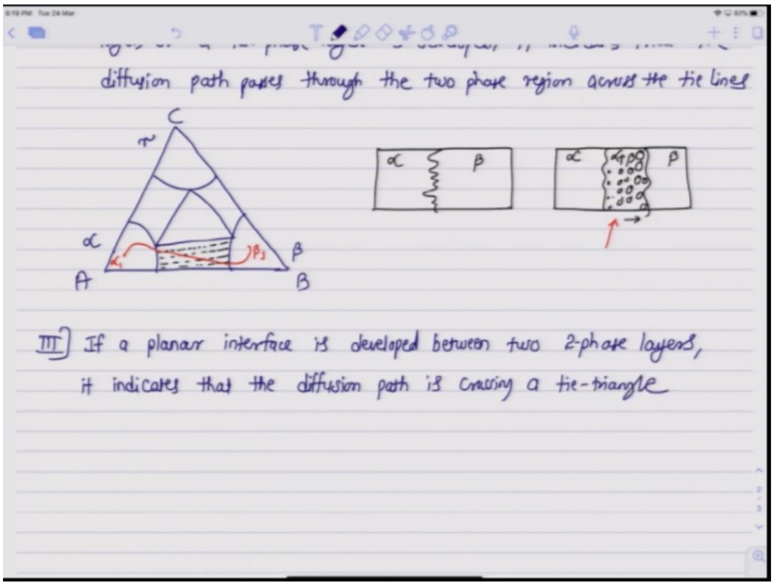

diffusion path passes through the two phase region across the tie lines

III] If a planar interface is developed between two 2-phase layers, it indicates that the diffusion path is crossing a tie-triangle

So, if I assemble couple between $\alpha_1$and β_1, the tie lines in this would look something like this and if the diffusion structure shows a non-planer interface between α and β or a 2-phase region, basically 2 phase region is a mixture of α and β phases. Obviously, as we go towards β rich side, the density of β precipitates will keep increasing. So, the matrix here in this 2-phase region is α, precipitate is β. So, in any of these cases we accept that the diffusion path will cross $\alpha+\beta$ region across the tie line. So if we draw the diffusion path it may look something like this. So, basically the segment of diffusion path within the 2-phase region is across the tie lines.

That means there is no equilibrium between α and β and with this we get an idea about the phase boundaries but we will not get an idea about the tie lines but still these structures would be helpful. Then the third rule says, if there exist a planer interface between two 2-phase layers in a ternary diffusion couple it indicates that the diffusion path is passing through a tie triangle. Obviously when there are two 2-phase layers, for example, here let me write it down first.

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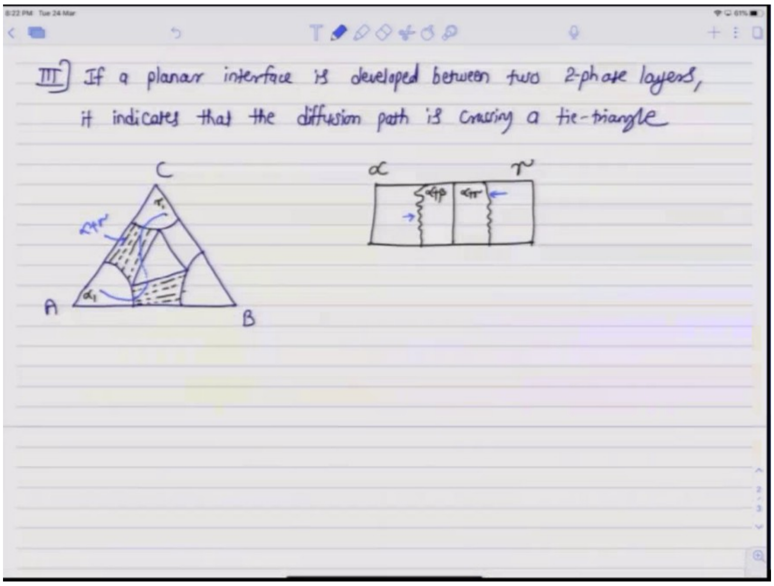

III] If a planar interface is developed between two 2-phase layers, it indicates that the diffusion path is crossing a tie-triangle

So, suppose if diffusion couple is assembled between let us say α_1 and γ_1. What this says is there exist two 2-phase regions and there is a planar interface between two 2-phase regions. So, there will be planar interface and on two sides there will be 2-phase region. So, obviously within the 2 phase regions there have to be 3 phases. There cannot be 4 phases because it is not possible based upon the Gibbs phase rule. A 4-phase equilibrium in an isothermal ternary diffusion couple is not possible.

So, this may be $\alpha+\beta$ in one side and $\alpha+\gamma$ on the other side. So, if this is the case we can see how the diffusion profile will look like. So, first the diffusion profile has to be in the α phase region and then it is entering $\alpha+\beta$ 2-phase field in which it will pass like this, and then it is going into $\alpha+\gamma$ region. So, it has to pass through this ternary triangle in between. Then it passes through $\alpha+\gamma$ region and finally enters the γ phase field. So, this is how the diffusion path may look like.

Obviously, since there is no direct interface between α and β here, so within the $\alpha+\beta$ region the diffusion path has to cross across the tie lines and hence this interface is non-planar. Similarly, as you can see as the diffusion path is entering from the tie triangle side and then entering into γ region, so the diffusion path again has to pass through the $\alpha+\gamma$ phase field here across the tie line and hence the interface between $\alpha+\gamma$ and γ should also be non-planar.

So, this is how we can get an idea about phase diagrams and their features based upon the diffusion structures developed in multiphase diffusion couples and this has been used by our group for developing phase diagrams for getting information about phase diagrams including aluminium-magnesium and even in the quaternary system of iron, nickel, cobalt, copper. Now, next question is how do we analyze the multiphase diffusion profiles for interdiffusion fluxes and inter diffusion coefficients. So, that we will cover in the next class. Thank you.