

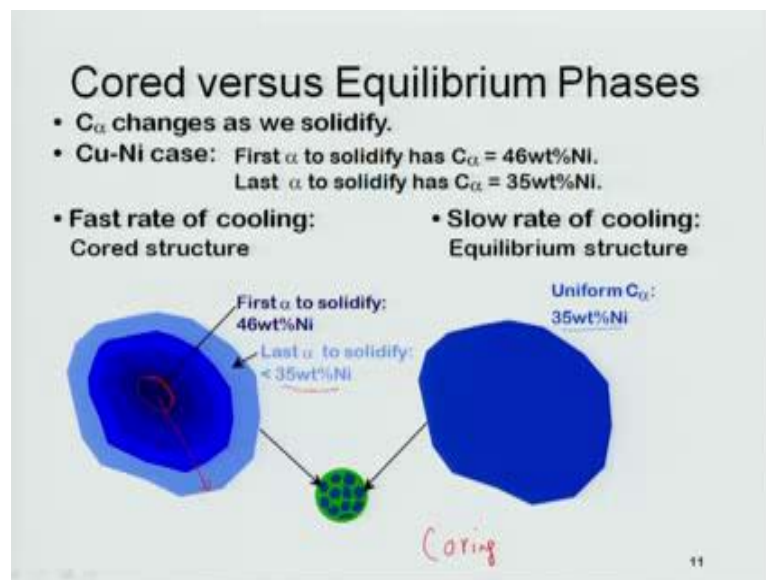
Phase Diagrams in Material Science Engineering
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Lecture - 10
Free Energy of Binary Isomorphous Phase Diagrams

In the last lecture on binary phase diagrams of isomorphous systems, we are going to discuss about how I have modified the phase diagram in the last class, and second thing I will discuss about the free energy versus composition diagrams of different types of binary isomorphous phase diagram.

Let us first discuss where we are finished in the last class. And I told you that if you take an alloy in a isomorphous system - binary isomorphous system - and start solidifying it, then depending on the type of solidification whether it is equilibrium or non-equilibrium, the microstructure evolution will be different. By equilibrium I mean slow cooling and by non-equilibrium I mean fast cooling. So, let us now do it again.

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In case of slow cooling, let us suppose we take copper-nickel system, and solidify the alloy of concentration 35 weight percent nickel using very slow rate of cooling. This is equivalent to equilibrium cooling. In that situation, we will get uniform solid of same composition as we started with and there will be no non-uniformity as far as composition is concerned. This is mainly because we cool slowly and by doing so we keep the sample

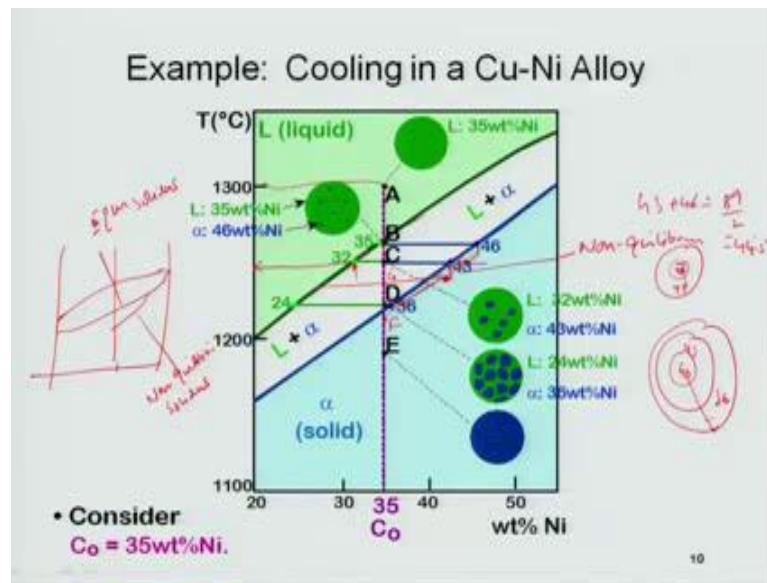
- solid plus liquid mixture, rather - at a particular temperature for a sufficiently long time. So that diffusing can happen and diffusion will out all the composition (Refer Time: 02:04) during slow cooling, but you know this kind of slow cooling process is never adopted in the industrial scale. So, therefore, we have to look into the microstructure evolution when you cool it sufficiently fast.

If I suppose, supposing for cool; supposing fast enough, then what will happen is the cool kind of microstructure will develop; that means, layer microstructure will develop; each layer will have different composition. Like here, in this case, as we have drawn centre one has very high nuclear concentrations than the peripheral one. So, these each layer forms at each step of cooling. Suppose, if we cool at a rate of, suppose 100 Degree per minute, then at each 100 degree drop, one layer will form, and because of that, this kind of non-uniform compositional non-uniformity level is up in the microstructure, and this is known as coring in the literature. Coring means the center portion has higher content of nickel than the periphery. That is why it is called core or vice versa, the central portion has less copper than periphery.

And this kind of micro structural features are very bad as far as properties are concerned because this will lead to non-uniform property in the sample, and this non-uniform property is not expected, required, or not expected when you use in the real applications, thus to take care of these we need to do post processing of these alloys and that is nothing but an annealing treatment at a high temperature.

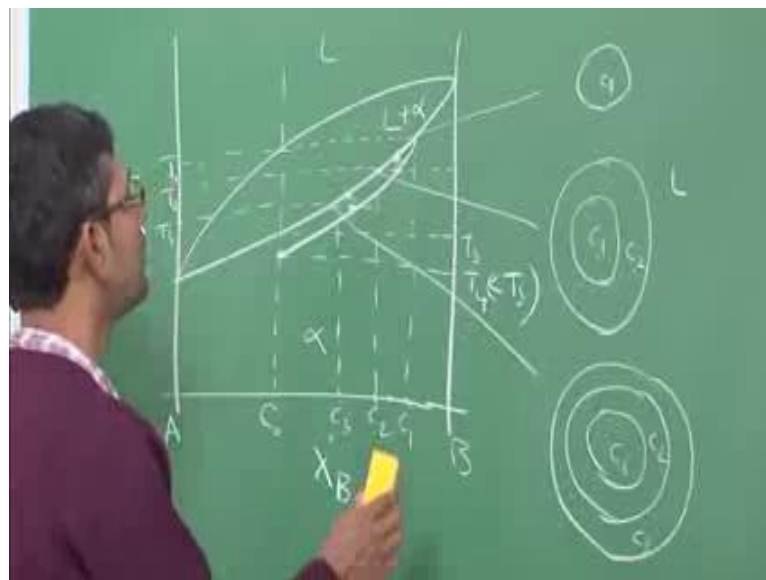
Temperature, obviously, should be better below the solidus temperature, so that it does not melt at all. And in that case, if you heat it for a long time, because of fast diffusion a composite will be annealed out. So, that means, we need to spend or we need to spend more money on such a kind of annealing of the samples and this will lead to extra cost. So, that this is a problem of fast cooling of isomorphous alloys, rather any alloys used as isomorphous type of phase diagrams which we will see in the integrated systems also.

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So, now, as I told you, you can use this concept and modify the phase diagram. So, I will do it nicely on the board; that is better for you.

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So, let us just take a simple binary phase diagram. And here, I draw this one in a big way. This temperature axis; this is the composition axis which is nothing, but XB or weight percent of the element B. So, if the phase diagram is like a lens, as I told you, lens, this is liquid, this is solid, this solid plus liquid or liquid plus alpha; alpha is a solid phase. So, as we see, if I take an alloy composition this one - C_0 - the first solid which will form

will have this composition, because the solid will form just below the liquidus. Now, as you go along, a dip in the temperature, different solid layers will form and this is the way it will happen.

So, if I draw the microstructure, suppose at this temperature T_1 , this is what I have shown you, it is T_2 , T_1 , T_2 , this is T_3 , and this is T_s , and T_1 is slightly below this a liquidus temperature. So, at T_1 you have a layer of composition given by suppose C_1 ; at T_2 this is given by C_2 ; at T_3 this is given by C_3 . So, at T_2 , here again I will have two layers - one is C_1 , other one is C_2 , and at T_3 if I draw it, this will have C_1 , C_2 , and C_3 . This kind of layers will form. As you see here, C_1 is reaching B, C_2 is little lower than C_1 , C_3 is much lower than C_1 , and all of these are lower than this C_0 origin alloy compositions.

Now, let us kind of investigate. At T_1 , we have two layers: one is the composition C_1 ; other one is composition C_2 . So, average composition of these two will depend upon the mass fraction of each one. So, for the sake of understanding or for the sake of simplicity let assume average composition of the, sorry, the mass fraction of these two - C_1 and C_2 - are 50-50 percent each. So, therefore, average composition of these two will lie in between these two points; obviously, in between these two points C_1 and C_2 . So, let us suppose it will lie on a center, here, correct.

So, this is what is my average composition of this solid which is in contact to the liquid. All these are in contact to the liquid except the one which is solidifying at solidus temperature T_s . So, because this is the average composition of these two, and now, this average composition point is lying above the temperature T_2 . You could remember that we have dropped the temperature from T_1 to T_2 to form this structure. So, therefore, only way I can adjust this is while dropping it vertical line here, if I draw a vertical line here which meets the tie line at T_2 . So, this will be my point. This will be the actual point of solidification will be lying at this point which is lying at the temperature T_2 , but composition is little higher than C_2 and lower than C_1 .

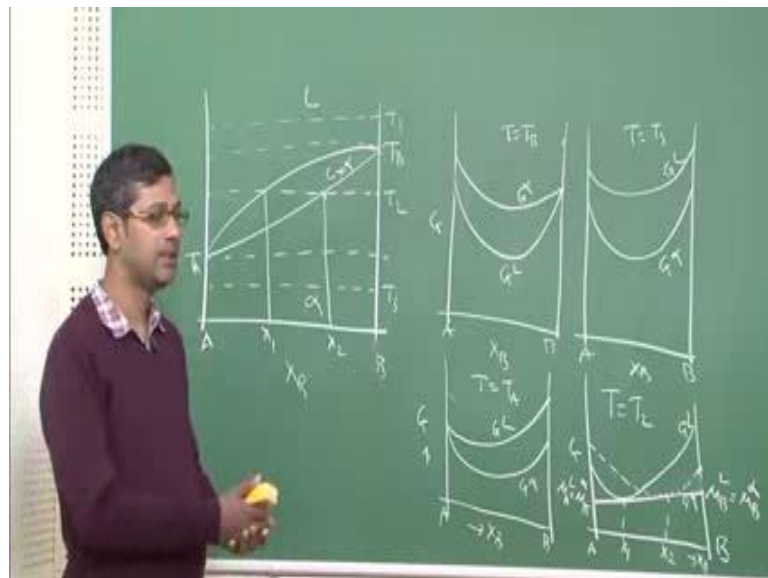
Similarly, same thing will happen a temperature T_3 ; we have three layers: C_1 , C_2 , C_3 , and if you assume each one is having same mass fraction, suppose 33 at mass fraction, 33 percent of mass. So, what will happen? Average composition will be one which will average of these three. So, it will be lying between C_3 and C_2 . So, somewhere there

supposes it lies. Now, because temperature is at T_3 , I only way I can do is I can drop a vertical line and get a point here. I can drop this one at C_3 and the wherever this T_3 line will connect, intersect with this point, I will get a new equilibrium point. Similarly, here also I will get somewhere there, somewhere there. So, if I join these three, I get a non-equilibrium phase diagram or non-equilibrium type of solidification behavior, indicated by this line, by this curve.

In this way, I could clearly see although I start solidifying at T_1 , it will never finish at T_s or the solidification temperature; it will be a little lower and temperature lower than the T_s , which is T_4 . T_4 is lower than T_s . I hope this is clear. These are actually in the books they draw this line, but never indicate, never tell how this line actually appears. This line appears a non-equilibrium processing of this alloys because of the things I told you right now, because of this average composition issues at temperature T_3 ; T_2 , T_3 are much lower; that is why it happens. So, now, it is very clear to you.

The next thing what I will do is that can I actually explain this kind of phase diagram using; I remove everything and redraw using three of the composition diagrams.

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So let me just draw it again and explain you. Suppose I draw this phase diagram again T verses composition, A and B ends, and this was my diagram. Remember this is the (Refer Time: 10:17) temperature of A, this is the (Refer Time: 10:19) temperature B, many times you write T_a , T_b (Refer Time: 10:22) temperature; liquid, solid alpha, liquid plus

solid. Now, I am asking myself the questions, that can I explain this phase diagram using free energy composition diagrams.

Suppose I draw different temperature tie lines, this is at T_b , this is at T_1 , this is at T_2 , and this is at T_a . T_a is here, and this is at T_3 . And suppose, I have been asked to draw the compositional, pre-composition diagrams at each of this temperature. What are these diagrams? Let me just write down G versus X_B at temperature T_1 . And I told you, that the composition that if you have here G , where is the function of compositions in a parabolic pair? The curves will be like here a inverted parabola, like this.

So, now the question is this - when you want to draw free energy composition diagram of any system, this is the binary isomorphous system, first thing you have to realize how many phases are present. You can clearly see there are two phases present - alpha and liquid. See, in all these diagrams there must be two curves - one for the alpha, other one for the liquid; there must be, otherwise this will not be complete. And, in all these diagrams, you do not care about what are the values of G . we only care about the related this position of these curves; related position of these curves are only required; that is what is expected from the point of view of you, that you understand that the positions of this free energy composition diagrams curves will be depending on what kind of phase are present.

So, let me just give an example. Suppose at the temperature T_1 , I can clearly see liquid is stable, solid is not stable. So, solid is not stable because there is only complete liquid (Refer Time: 12:18) single phase liquid phase field. So, therefore, this will have lower efficiency than the alpha. So, suppose this is my G_L , L stands for liquid, G_L , L stands for liquid. So, obviously, solid one will be above G_{α} , why? Because alpha phase has higher efficiency than the solid liquid, you can clearly see liquid is more stable. So, therefore, liquid have lower efficiency.

So, phase which has lower efficiency that is more stable one; I have already explained to you in the different classes. So, similarly, at T_3 , T_3 is very easy, again similar type, but only thing it will happen is that, it will get reversed. So, how it will get reverse? Because at T_3 alpha is stable, liquid is not stable. So, therefore, alpha will be lying at lower, alpha liquid will be sitting above, alpha is stable at all compositions at T_3 . So, therefore,

alpha curve will be lower than GL a liquid curve. This is very easy. Anywhere you can understand.

Now, let me first explain what will happen at T_b . I will just remove these plots and do it again. I will keep this one because these two are similar at T_b . At T_b you can clearly see that 2 curves - liquid and solidus - are meeting at point T_b . That means, at this position, at this position means at pivot B end and temperature T_b , both liquid and alpha are stable, both are coexisting, that is why these two curves are meeting together. So, how we can do that? So, you can first, but other compositions, all the other compositions except at pivot B all the other composition liquid is stable, liquid is more stable, you can see a liquid is there. So, I can draw liquid curve first because liquid is stable more. Solid one I will draw in such way that it meets at point pure B. These two curves are meeting at a point pure B, we know that if these two curves meet at point pivot B, at B which is corresponding to pure B; that means, (Refer Time: 14:37) of alpha and liquid are the same; that is what is the case.

Same thing will happen at T_a . T_a , the free energy curves of alpha and liquid will be opposed reverse because liquidus solidus alpha is stable in all compositions except at point A, appear A where liquid and alpha both are coexisting. So, therefore, I can draw this here at the bottom, at T equal to T_a , this is the alpha curve - G alpha, and liquid will like this. At pure A, we can scale is C, pure A both the curves are meeting. So, that means, I have cover almost all; at T_1 , at T_3 , at T_a , and T_b . Only thing I did not cover, the most interesting thing, is at temperature T_2 . Temperature T_2 you can see till T_2 tie line passes through from liquid, liquid plus solid to solid. That means it crosses the two-phase region, form one side phase, one is pure.

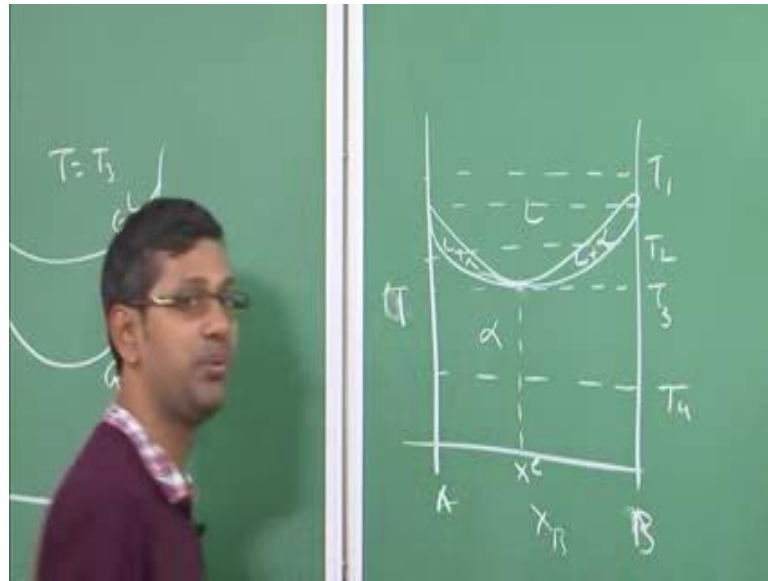
So, one single phase region to other single phase region, in between it passes through a two-phase region. So, that means, this is only possible when these two curves will cross each other. This kind of situation only possible having these two curves are cross each other; otherwise, this is not possible. How? Let me just draw it and just show it to you. This is what it is. So, I can clearly see liquid is stable, you seen. So, liquid curve will going like this, and solid curve will be going like this; this is what I am saying. So, this one is liquid, this is solid, and so that means, or rather let me just write different, rather it will be confusing to you. Dotted one is solid and solid one is liquid. We can clearly see the have crossed over each other.

So, whenever you have such a kind of change, whereas this tie line passes from single phase into another single phase into a two phase, then it will, this indicate they will cross, and equivalent composition of the solid liquid which are the cross sections of the tie line with this liquidus and the solidus. So, this is suppose, x_1 , this is x_2 , can only be known if I draw a common tangent between these two. So, this is x_1 , this is x_2 . Am I clear? This is what it is. Why you have common tangent? That is because common tangent will allow me to set the equilibrium condition is equal to this equilibrium. What is that? At this point, both the chemical potential at A, in both the phases solid and liquid are equal; that means, μ_A in liquid is equal to μ_A in alpha, here. Similarly, here μ_B in liquid is equal to μ_B in alpha. So, we satisfy these conditions of heterogeneous equilibrium that I have derived, before I derive the Gibbs phase rule by drawing a common tangent, by drawing a common tangent.

So, this is very important, this particular curve at temperature T_2 is very, very important as far as this kind of phase diagram is concerned. So, therefore, I will like to tell you that this is a very, very important exercise. Normally, this exercise is done in reverse way. That is first we get this diagrams, then from there you draw the phase diagram. In actually all the software, they will allow you to draw this phase average composition diagrams at different temperatures.

From there you can draw the phase diagram, but here you have seen another way, because you know the phase diagram so, therefore, there is no point. So, here we are showing you that from the phase diagram we can actually get an idea about the relative positions of the free energy composition diagram of different phases. If you think about a real phase diagram further many, many phases. So, in each of the diagram, so, if they draw the phase, the free energy curves for each of this phases, and it becomes really complex. So, that is what I would like to concentrate on this simple case and do it.

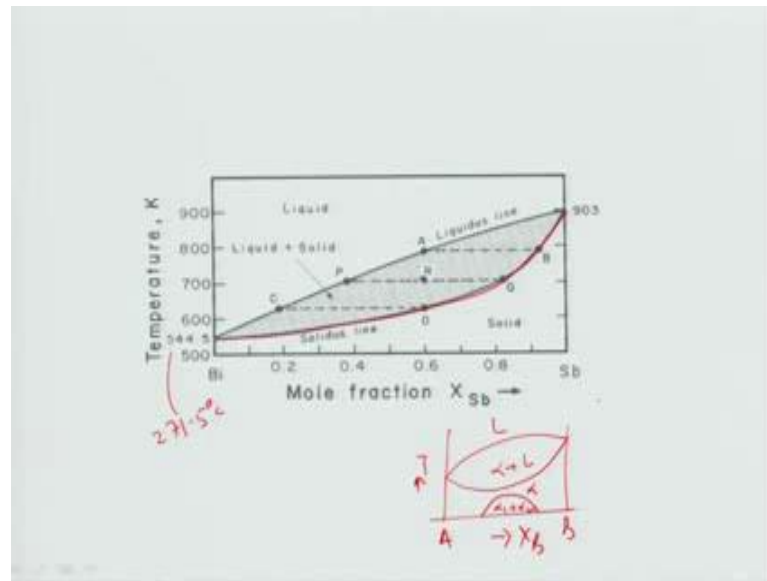
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In fact, this is a phase diagram where we are really interested you can try on this phase diagram, which will part of your assignment also, this phase diagram T versus X_B ; liquid, alpha, liquid plus alpha, liquid plus alpha. Here these two, these two curves liquids and solids, are meeting at this point; this is X_B that point they meet. So, try at different temperatures. This temperature, T_1 , T_b , also at this temperature T_3 , this is T_2 and obviously, T_4 . If you try, then you can draw these things very clearly, then we will be; I will be taking an impression that you can do it.

And now, in the next couple of minutes, whatever I have, what I am going to show you is the few.

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Let me see, I have phase diagrams is there. So, this is phase diagram of this mole fraction antimony. Here is very clearly written everything. Temperature is given in Kelvin. So, you can see here this (Refer Time: 20:25) about 544, that is equal to 271, 271.5 degree Celsius (Refer Time: 20:39) is. And an antimony mole is at 903 degree Celsius, that is about 623 Celsius. So, here you then see the solidus is this line, liquidus is this line written, and the points on solids are A, P, C is because A, P, C solids) are D, Q, B and you have liquid plus solid.

But peculiar nature of this phase diagram is that this liquidus looks very, very clear, and convincing; solidus is having in flexing point. So, whenever you see such a kind of miscibility gap point solidus, that indicates there is a (Refer Time: 21:25) gap, and that is why actually many of these binary phase diagrams; I will draw and show you. Many binary phase diagrams having such a kind of staff like this, liquid plus alpha, liquid will have a miscibility gap alpha one plus alpha two. This is very, very common in this kind of phase diagrams; please remember that.

So, that is what I am showing that this any phase diagram of this type has such a kind of liquidus like this, with inflection point, then that means there is a miscibility gap. In the copper-nickel also has the lower temperatures; similarly (Refer Time: 22:08) antimony has; many other also. And then germanium-silicon does not have; germanium-silicon phase diagram is very simple; there is no inflection point, both the curves are similar.

Therefore, I request you to explore the different isomorphous phase diagrams and try to solve different problems. Anyway, in the assignment also we will give lot of problems, so that you can solve it.

In next class, we will discuss start discussing about eutectic phase diagrams and let us see how we can move.