Phase Diagrams in Material Science Engineering Prof. Krishnanu Biswas Department of Materials Science and Engineering Indian Institute of Technology, Kanpur

Lecture – 48 Ternary Isomorphous Phase Diagram

Students today we are going to discuss about the solidification of these Isomorphous 2 phase alloy system, and we are also going to discuss about the some derivation of these Isomorphous ternary phase diagram. So, before that let me just take you some recap of this ternary phase diagrams.

The only important thing about ternary phase diagram is basically isothermal sections of the three dimensional space models. three dimensional phase model is; obviously, the best thing to use with, and the space model consisting of a equilateral triangle, you are on the horizontal plane, and the particle plane it has temperature axis, and the I have discussed with you regarding how to measure compositions, and how to draw this you know the space model. So, for the simple system like a ternary Isomorhous in which all the three components are forming Isomorphous system with each other, is shown here. This you see a b c as a ternary Isomorphous system.

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You can see clearly on this picture. Now as I told you one of the important aspects of these phase diagram is to take the two dimensional positions, and best way of doing is to

use the isothermal sections, at the section under a particular temperature. So, here suppose if I draw a section at t 1, and the way I draw is that I take a triangle, same to as a b c d and cut these ternary with space model with it is triangular at particular temperature equal to t 1. So, what I get is basically this kind of sections, you can clearly see, this is the one, that is another one that is what shown.

And then these two dimensional position will divide the triangle into three regions liquid solid and liquid plus solid in between. And the surface bounding as bounding curves between the liquid and liquid plus solid zone is known as liquidus position, and this 1 is known as solidus and therefore, I can draw tie lines between them; that is what is I discussed with you. Then I can actually take the section at different temperature you see it is done at t 2, I get complete different section then that and again section is similar like consisting of three zones liquid solid alpha and liquid plus alpha 3 zones demarcated. And if I take a sectional t 3 which is much slower than these liquid solidus temperature solidus curve then I get completely only alpha. There is no two phase liquid phase region; that is something I discussed with you in the last lecture nicely.

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Now, I can also I have also discussed with the vertical sections. Vertical sections are the sections which have taken at different ways. I can draw this triangle and. So, you what are the different ways we can take of vertical section; this is a b c. So, another way of taking bilateral section is drawing line, like e f draw a line parallel to a b and take a

section this will look like, this is I think this is what we are using y z let us do that y z here, or you can actually take one of that lines as like this a to c or b other which is small b. So, in these sections they will look like again similar to like a binary isomorphous phase diagrams. The whole diagram is section is divided into three zones liquid liquid plus alpha and alpha, but they are not, because we cannot draw tie lines here very simple. We can also have a section like this, this is suppose m n the same line, but like y z, but at an angle not parallel to a b, and I have shown you what are the thing ways it to look like.

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Another important aspect which I did not discussed with you is that, the free energy surface for the ternary Isomorphous system will look like this you know binary it is looking like this. For any for the Isomorphous system it will look like this right, this is your delta g this is a this is b x b and this is what is delta g l. Let see s is will also be looking like exactly similar, there will not much difference. So, therefore, whatever you see as curve, use if it curve invited parabola is x, is a surface parabolic surface that is what is we called Gibbs free energy surface.

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Now, let me just get into the basic theme of this lecture. We are going to discuss about the solidification view about ternary Isomorphous system, with both equilibrium and non equilibrium conditions. Well this is what is a ternary Isomorphous system; a b c phase diagram space model, three d space model. Now, I am going to discuss the solidification of the alloy composition x.

So, in a binary as I told you, if I wanted to discuss solidification of alloy binary between a b, what I do. I draw the vertical line x, composition x, then I start from the liquid, I discuss solidification of the alloy as I move inside the liquid plus solid and finally, into liquid; how I do I draw tie lines right; that is how I do not want to get back into again to it because I have done it discussed several times. Now, in a ternary what happens as you cool down the liquid from the high temperature, first thing it will do it will touch just like this point is touch on the liquidus surface, this will also touch here on the liquidus surface.

This is touching here on the liquidus curve, this is liquidus, and this is solidus. So, it touches on the liquidus curve here, on the ternary it will touch liquidus surface here, and what does it is what does it touch at temperature t 1 temperature t 1 here you see t 1, corresponding to point l 1 on the liquidus surface. Now, as it solidifies, here or I thing let me draw it here (Refer Time: 07:29) because you need to follow it up, and correlation between binary and the ternary is very important. So, x it should not be, it should be

parallel. So, let me draw it properly otherwise you will also make mistakes this is. So, I draw a line x, as it touches here I draw a tie line right.

So, therefore, solid which will form as composition s liquid as a composition l, or whether I like again same way alpha 1 l 1, that is what is shown here, this is the point on the liquidus surface l 1, it is a point on the l solidus surface alpha 1, because this is like a cone cell like this.

So, therefore, inside the diagram draw tie lines. So, therefore, the first solid which will form as composition given by alpha, as I cool it down the liquid, what will happen, the next temperature suppose t 2 this is t 1 then t 2, the solid will have composition given by alpha 2 a liquid will have composition l 2. Similarly I can draw at t 3 alpha 3 l 3 and finished done at t 4 alpha four l four. So, this is how the whole thing will be (Refer Time: 09:05). Now, as you know the solidification is over at l four severely solidification will go to get over at l four, because at l four solid will have a composition same as the overall alloy compositions. Now this is easier to follow, because this is the space model in three dimensional is very easy things to follow, but in real life everything will not be easy to follow. Thus the space model may be very complicated, and if this is the case how you are going to follow it up.

So, best way of following it up is to is to basically drop these positions on to these Gibbs angle, and this is what is done here and shown as zoomed view you see here. So, as you see the liquid composition is following on the liquidus surface, given by l 1 l 2 l 3 l four along these. Let me just draw it like a red curve. On the other is solid composition is following, followed by the point on the solidus surface and there giving by l 1 to l four, and sorry alpha 1 to alpha four, and alpha four and l 1 falls on each other that is obvious, because l 1 is the first solid liquid composition to start with before you start a solidifying, and alpha four is a solid composition which is finally, solidified. So, they will have same compositions. So, now, I can actually join this (Refer Time: 10:33) lines to draw the tie lines. The point is the way that is not we draw it here is that we can actually then calculate.

Suppose if I want to know the volume pressure of alpha, and at a temperature l 1 at temperature t 1, basically is minus cool minus cool means, why it is minus cool, because x is sitting exactly on l 1 only at l 2 sorry, only at l 2 temperature t 2, x lies on this point.

So, therefore, volume pressure of the alpha 2, will be l 2 volume pressure of alpha 2 l 2 l 2 x divide by l 2 x divide by alpha 2 alright, l 2 x divide by l 2 alpha 2 into 100; that is the volume pressure of alpha 2 sorry solid, solid alpha at temperature t 2. This is the length of these (Refer Time: 11:32) other one. Similarly, you can do the same thing. So, same thing can done here also, exactly same thing can be done here also; that is the reason actually we show it on to the ternary plot. So, now, let me go about the pore and explain you how the tie lines actually rotate. So, that is very important. So, let me just go to that pore. So, see I have drawn these things.

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So, let me just tell you this is alpha 1 l 1 l 2 alpha 2 l 3 alpha 3 l four alpha four. So, now, let me just see, see this is what is at this at temperature t 1, this is temperature t 2, t 3, and t 4. just to show you that that if I take the positions on at the Isomorphous sections at t 1 t 2 t 3 t 4 that is how it will look like. So, at t 1 you have this is the liquidus position, this is the solidus position and therefore, there are three zones l l plus alpha and alpha. I am not written l plus alpha let me write it. So, the tie line is falling like this l 1 to alpha, just now whatever picture I have shown you three dimensional model if I project it that this will look like this, and x is sitting exactly on 1 1 why, because this is starting alloy compositions.

So, therefore, volume pressure of alpha is very small is zero actually almost. now if I go to temperature t 2 somehow into alpha as solidified, and the composition alpha 2 is given alpha is by alpha 2 and liquid is given by l 2, l 2, this is l 2 again three zones liquid, liquid plus alpha and alpha x is sitting there.

So, now, if I want to measure the measure the volume fraction of alpha this is nothing, but l 2 x divide by l 2 alpha 2 volume fraction of alpha is l 2 x divide by l 2 alpha 2 into hundred; that is what it is and x Is sitting inside these liquid plus solid zone, not only point l 2 a new one. Then if I come to temperature t 3 x is well inside this this position and if you see the position carefully it is starting from a reach end, because a here is b here is the highest melting temperature c has the lowest melting temperature, and a is the intermediate melting temperature. So, this is the highest melting temperature element next to these, next to these, and next to these things. So, what actually happens. You see here again x is inside this alpha plus liquid quite inside, and there are three zones liquid alpha plus liquid and alpha. So, again I can calculate volume fraction of alpha; that is why actually I wanted to draw it.

So, is basically l 3 x divided by l 3 alpha 3 into hundred, and if you look at this ratio this length is all little bit changing I know, but not much, but l 2 x is very small. on the other hand 1.3 x is large. So, therefore, volume fraction of alpha has increased. Now, if I go to the t 4 where the solidification has ended, alpha four and x is sitting on each other, and l four is here. So, volume fraction of alpha is volume percentage of alpha is l four l for x divided by l four alpha four that is nothing, but same as l four alpha four divided by l four alpha four into hundred that is nothing, but hundred percent alpha. So, that is why actually one can calculate the volume percentage of alpha as it solidification gets over. It is exactly same as the binary. Binary also you can do the same thing, exactly same thing. So, very easy to follow that is why I want lets wanted to draw this picture binary Isomorphous phase diagram liquid alpha, alpha plus liquid. So, if I follow it up I can draw this, this is my alpha composition of this is alpha 2 l 2.

So, I can calculate the same way here also I can do the same thing. Only thing I have to do is that to do the composition I need to draw parallel lines that I discussed with you when I showed you how to calculate volume fraction of phase, is in a two phase system. So, another important thing is that if you look at the tie lines what tie lines is shifting towards from b to a, is it they are going from here to there they are rotated this way from here to there rotated further this way. They have rotated further this way. So, they are rotating anti clock wise why they rotating anti clock wise very simple the melting temperature is changing b to a to c that is also anti clock wise. So, therefore, rotation of tie line is will exactly the same as will be following that melting temperature rotation of the elements that I discussed with you in the last 2 last class.

So, this is you must be able to I know clearly in vision that the tie lines rotates in a same way. So, whenever you draw this pictures on your note book or on the board, you must know how to follow it up which way the tie lines are rotate, and this is this is the major difference from the binary to the ternary. In the binaries your tie lines actually very simple very simple, they are always parallel to the horizontal axis, there is no rotation of tie lines. So, that is the major important thing you must, you know you must be able to follow very, in a very carefully duration of tie lines.

Although I said told you the tie line positions exactly depend on how would you measure experimentally, this has to be done experimentally, but theoretically as if for understanding the subject you will be able to follow it up if you know the melting temperature variations. here abc is b to a to c is what is the rotation of the melting temperature, and that is anti clock wise that is why the tie lines are getting anti clock wise rotating. this is what is shown in the next curve; exactly you see here tie lines are rotating at anti clock wise.

In this picture, and again to show you that this is the first tie line.

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The second line third one fourth one and the fourth case they sits on the alpha four.

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So, and this is all together I want to show you, this is the ternary space model, and these are the four Isomorphous sections where the solidification is shown. So, now, we can follow up this 1 very easily. So, let me just go back to my earlier picture I will keep it here and let me open that 1, and to show you my nicely art.

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So, this is what is the picture available in the book of align spins, and this is nicely done. Here actually two sections are cut off liquidus and solidus surfaces are cut off to show

you the inside ones. In fact, in from the book it is connected you can see here it is connected. So, here you can see if I follow this x l or s l 1 s 1 l 2 s 2 l 3 s 3 all are shown, and exactly same thing is shown on the Gibbs triangle.

So, there are thus with this I think you have got a fair amount of, I will say not fair I will say good idea about how to follow solidification path of this alloys. Now question is this. This is what will happen when you solidify under equilibrium conditions, but suppose if you solidify under non equilibrium conditions how are the things will valid. Well non equilibrium condition means diffusion in the solid is low, liquid it is possible to not have a good diffusion and mixing because of convection, but solid it will not be.

So, therefore, it has a binary, as you know in a binary we call it a coring effecting, because solid is in diffusion in solid is low; therefore, the every temperature if you from a solid it will remain at the composition. it will it will not basically get (Refer Time: 20:00) with the next solid, or let me just explain you taking this picture very nice, this is very nice picture here.

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So, what I mean to say is that this is suppose at t 1 this is t 2 this is t 3. So, whatever solid I form at t 1, will have compositions given by this point. So, I write down alpha 1. So, as I cool it down from t 1 to t 2 I form another solid layer with a composition alpha 2. So, the problem in the non equilibrium cases that you do not provide enough time for these two solid to homogenize, you write, because these two solid has different composition right. Can you see alpha 1 is (Refer Time: 20:44) b than alpha 2. So, therefore, in order to homogenize them the b has to diffuse from alpha 1 to alpha 2, and these diffusion is solid is not allowed, because of the non equilibrium nature of the possessing. So, it is; obviously, the last solid which will form will have a composition given by alpha 3 will be forming another layer alpha 3.

So, that that is way you are developing a composition get into the center to the periphery; and that is why it is call coring same thing will happen here also, it may more complex here only we have only one element is getting you know compositional variation from the center to the periphery, but there in the ternary we have two elements can be also. So, this is basically done this way. So, at the t 1 there will be no much thing happening, because you have only going to form the solid at t 2, let me just draw it. So, the effect of non equilibrium things it will be.

So, on little bit ahead this is. So, this is I call alpha 2 this is I call alpha 2 prime, can you see that this is alpha 2 prime. So, same thing will be happening here also. Let me draw it carefully. So, and this is alpha 3 prime, this is alpha 3 alpha 3 is sitting on this solidus curve alpha 3 prime is little bit I have the solidus curve, and here again; obviously, this is alpha four, and this is alpha four prime this is alpha. So, as you clearly see the solidification will not over get over at alpha four or t t 4. It will go down actually temperature turn the t 4, and probably actually it will be, I have to draw another section, and this will be little bit down, sorry is a little bit angular.

So, this will be some l 5 alpha five. So, that is what it is happens here also. The way we represent the solidification sequence is prime dotted line like this, and the end of solidification temperature will be t 4. Similarly, here in solidification temperature will be t five, because we are showing already t 4 temperatures above. So, final 1 will be there. So, that is how actually things will happen. So, one of the way of showing this solidification non equilibrium manner is, just extend this tie line, little bit ahead; obviously, why because it will be more reaching the component which is the highest melting temperature, as you see is b is highest melting temperature compound sorry (Refer Time: 23:49) component.

So, it will be reaching that slowly it is shifting; obviously initially it was reaching that then it is shifted to in between a and b, finally, it is shifted to a b c also, and finally, it will solidify at compositions which is different from the original, which will be same as the original like compositions, but (Refer Time: 24:13) at low temperature like this. So, that is how actually we show the variation of the, you know solidification sequence in the non equilibrium manner. So, and this is very important, because this is of this is the easiest phase diagram I am discussing with you. I would like you to understand and try to you know think about it these diagrams, can be used to understand the ternary solidification of different solidification of different ternary alloys.

Well in the next lecture, although I thought of discussing about ternary or the three phase equilibrium, because I am already discussing in this diagrams of two phase equilibrium. Two phase means, liquid to alpha a liquid plus alpha there is 3 phases, third phase is existing here. So, I am going to discus about that, but before doing in the like next class I will also show you some variation of these Isomorphous diagrams, perceivably for 5 minutes. So, the next 20 minutes I will discuss about these three phase three phase equilibrium