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

Lecture – 46 Ternary Phase Diagrams and Tie Line Construction – II

So, we have discussed the two important rules for the tie line construction in the ternary phase diagrams. In this class, I am going to talk about the remaining rules. The third important rule is that, in an isothermal sections ternary tie lines will never intersect; correct. So, why it will never intersect? Let us see the problem.

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Before I talked about the problem, you know in a ternary system, the Gibbs phase rules says; so for a for a two phase zone like alpha plus liquid or liquid plus solid, a degrees of freedom is equal to two. There are two degrees of freedom; right? It is a bivariant system. That is very simple. If I know that if the degrees of freedom is given equal to c minus p plus 1 and there are three components of c is equal to 3. So, in a two phase region, there are two phases: solid plus liquid. So, there is phase number 2, so 3 minus 2 plus 1; that is equal to 2. This is a bivariant system; please remember that. Now, if suppose let me just - I will just go back to the board and explain it; that is very convenient.

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So, if I suppose draw; this is my liquid plus solid shown $1\ 1\ 1\ 2\ s\ 1\ s\ 2$. So, now, I draw one – one tie line $1\ 4\ s\ 4$. This is the s 4. Or, let me draw it properly. And, I draw another tie line, which is $1\ 5\ s\ 5$ these are the two tie lines which are drawn. Now, suppose I draw a tie line such way that it intersect $-1\ 6\ s\ 6$ in intersects. This is this construction is very clear to be understood. So, initially, I draw a tie line $1\ 4\ s\ 4$; another one $1\ 5\ s\ 5$, which are not intersecting. Now, I draw a tie line $1\ 6\ s\ 6$, which intersects $1\ 5\ s\ 5$ tie line in such way that these ends meet at s 4. Now, according to this tie line, $1\ 4$, $s\ 4$ and $1\ 6$, $s\ 6$; there are three phases, which are at equilibrium. $1\ 6$ composition liquid phase; solid phase $-\ s\ 4$ composition and $s\ 6$ composition. Three phases are in equilibrium. I am going to that construction. You might be wondering why. Very simple; tie line connects number of phases from one end to the other end; right? So, therefore, if this tie line $1\ 6\ s\ 6$, they are actually connecting the solid and liquid phases: one at $1\ 6$; other one is at $s\ 6$. Then, it is intersecting with $1\ 4\ s\ 4$; that means what? $1\ 6\ s\ 4\ s\ 6\ -$ three phases, two solid and one liquid phases at equilibrium.

And, as I told you just few minutes back, this is a two phase equilibrium zone, degree of freedom is 2. But, if three phases are in equilibrium, degrees of freedom will be 1. So, this will violate the Gibbs phase rule. So, in the sense, basically, I can tell that tie lines inside this isothermal section will never intersect with each other. If they intersect, this will violate the Gibbs phase rule. So, this is the rule number 3. The tie lines in isothermal sections will never intersect each other.

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Now, the fourth one, that is, the most important rule, which – for which I need to spend lot of time is known as Konovalov's rule – rule 4. Really very important rule – Konovalov's rule or rule 4. Why this is important? I have been telling you only qualitatively the tie line will rotate from one binary to the other binary. Tie line extended will never meet the corner. Tie line will not intersect. But, this we will tell you how it will rotate, how much it can rotate – all these stuff. Well, this rule says – let me just tell you exactly what is that. Tie lines rotate in a counter clockwise direction – counter clockwise direction as the temperature falls. Temperature will fall; right – from T 1 to T 2 to T 3, T 4. So, tie line has to rotate. So, tie lines will rotate counter clockwise direction as the temperature falls.

And, this rotation coincides; this rotation will coincide with the fall of temperature from C to B to A here. So, temperature is falling which ways? C has the as many temperature followed by B followed by A. So, temperature is falling like a counter clockwise direction. C to A to - C to B to A - this is a counter clockwise. If you look at the triangle, C to A to B is a counter clockwise direction. That is why it is to say tie lines will rotate in a counter clockwise direction as a temperature falls. And this rotation coincides with a direction from the highest point temperature to the lowest point, melting point component.

So, what is it? Let me just explain it. It is very simple. As you know, this is because solid is already seen in the (Refer Time: 06:42) melt in the primary component. Saying suppose solid C – solid is here; solid is rich in C than the liquid. It is very simple; liquid is more lean in C than the solid. So, if that is the case, I can write down; that means what? I can always. Well, let me just tell you this way. Solid is richer than the liquid, which is in equilibrium in that component. So, suppose solid is in equilibrium with component C. So, this will be richer in C than in liquid.

So, in a nutshell, I can write down this way -X A S – suppose it will be also a always X A L; right? And, I know that X A L, X A S plus X B S is equal to X A L plus X B L equal to 1; correct. So, therefore, X A S divided by X A S plus X B S is greater than equal to X A L divided by X A L plus X B L. That is nothing but dividing these two – these two things by 1; right. So, I can we write X A S divided by X A S plus X B S minus X A S greater than equal to X A L X A L plus X B L minus X A L. You must be wondering what is this. Well, very simple. If I reduce the denominator, the fraction value will increase; right. So, and here I am reducing the denominator in such way that X A S is greater than X A L, correct? So, therefore, this is will remain valid. So, I can write down X A S is equal to X divided by X B S greater than equal to X A L is of the plus X B S greater than equal to X divided by X B S greater than equal to X A L, this is what is your Konovalov's rule, so that because of this – the solid in which there is equilibrium will have higher concentration of A than B compared to the liquid.

And, if this is true, then the tie lines will rotate the way I said you. Tie lines in this case (Refer Time: 09:23) rotating counter clockwise direction as a temperature falls, because the solid, which is in equilibrium with the liquid is always richer in the component, which is higher melting temperature; correct. Solid which is a higher melting temperature – solid, which is in equilibrium liquid will be rich, which will be having more component, which has a higher melting temperature. In our case, solid will have more C than the liquid, because C is – has many temperatures. And, because of that, tie lines will rotate in a – rotation of tie lines will coincide as the melting temperature falls from highest to lowest. So, melting temperature is falling, how? Melting temperature is falling from C to A – B to A. So, because of this melting temperature fall, in this counter clockwise direction, tie lines also rotated in the counter clockwise direction. So, this is what exactly I just wanted to tell you.

Now, one can actually do these things in a much better way. What is that? Well, let me just do this construction. So, now, let me just draw an arbitrary tie line like this. This is s 1 1 1. And, the alloy composition is x - all other s 1 at (Refer Time: 11:19) Now, I join and extend this. So, this becomes s 1. I join these two points: C and X and extend this. This becomes x 1. I join these two points; extend this; this becomes 1 1. That is what I have done.

Very simple; I have this tie line -1 s; I am joining the point s with the corner c; joining the point x with the corner c; joining the point l with the corner c; and, extending, so that it meets on the AB things. So, now, this is the angle theta. It extend with the point – with the line connecting X and C in extended; correct. So, I need to see whether this angle or rotation is exactly proper or not in a real sense. How do I know that? That can be done using Konovalov's rule – the same concept. So, how it is done? Let me just take the book and read for you, because sometime also I forget. Or, rather I can do it with this. So, erase this part.

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Well, as you see here X A l divided by X C l here is equal to what? X A l is equal to what? $1 \ A - 1 \ A$ divided by A B; right? Because I have extended then and it is hitting here, 1 1 A is what is your A l 1 A l 1 C; yes, 1 - I made as mistake – better to keep this is the (Refer Time: 13:21) this is always happens. So, let us just change this corner A B C. So, X A l is l 1 C divided by A C. Similarly, X C l is what? $1 \ A - 1 \ I$ A divided by AC.

So, that is why I have written X A I; where, X C I is equal to 1 1 C divided by – opposite terms – 1 1 C divided by 1 1 A. Again X A s divided by X C s; s means solid; 1 means liquid, is equal to s 1 C divided by s 1 A; s 1 is here. s 1 C divided by s 1 A. So, as you know that, s 1 C here – s 1 C divided by s 1 A is greater than – s 1 C divided by s 1 A is greater than 1 1 C divided by 1 1 A. So, that means what? X A s divided by X C s is greater than equal to X A I greater than by X C I. So, I follow the Konovalov's rule. This is the Konovalov's rule; I follow the same rule.

So, I change the orientation of this tie – tie line and I check by using Konovalov's rule. You might be thinking how exactly measures this angle theta. Well, that cannot be measured by – that cannot be measured using Konovalov's rule directly. That has to be done using experiments. So, one has to do experiments with liquid of composition, this solid of composition – this and find out these two composition points. But, at least it says which way it is going to be rotated. As you see, this is anti clockwise – clockwise rotation from B to A to C. Here actually B has a higher melting temperature than A and C. So, that is what is actually the Konovalov's rule's concept. So, Konovalov's rule actually is very very important in the sense that, it tells you the orientation of this tie lines; also it tells you even the directions of the rotation of the tie lines that temperature drops from liquid from highest to lowest melting temperature; solve the components.

So, as the temperature drops, it sells you to do the things. So, these are the two important rules I told you. So, these four important rules I will tell you. There is a fifth rule, but this is not so severe, not so serious. All these rules are nicely written in this book. And, I do not need to do that again further. If you have any questions, you can buy the – follow this book or the other book, which I have given; otherwise, one can actually look into that. So, now, I am going to talk about – because we have discussed only the bio – the isothermal sections; we need to discuss also the projections of this solidus and liquidus and the vertical section and polythermal sections. So, as you know, we can actually also projects these solidus and liquidus surfaces at different temperatures on to the Gibbs triangle. This is exactly shown here.

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So, this is what is your solidus-liquidus surfaces. And now, if I take sections at different temperatures -T 1, T 2, T 3, T 4, T 5, T 6, T 7, T 8 and I can plot them; let me just tell you – where is that? It is not there. If you have a second, draw it and show you.

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So, they are very simple. Let me just draw it. This probably I could not add into the slides.

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So, I have only discussed you the isothermal sections and then the tie line concept came. And, that is what we discussed in detail. There are several more projections possible. One is another one is the second position is the liquidus and solidus surfaces can be projected on that angle. So, suppose I have three dimensional model and I want to project solidus and liquidus surfaces – so, at different temperatures. So, I am projecting this is liquidus – solid line and this is solidus. Please remember these are done at different temperatures. This is at T 1, so 1 1 s 1; 1 1 2 and s 1 s 2. Let me just jot. So, then this is s 1 s 2; this is 1 1 1 - 1 1 - 1 1 are better; s 1 s prime. This is 1 2; 1 2; s 2 s 2 prime; 1 3 1 3prime; s 3 s 3 prime; 1 4 1 4 prime; like that. So, basically, these are what? These are at different sections.

In one section, I am drawing like this. So, these same things are projected on the Gibbs triangle at different temperature. This is supposing at temperature T 1; and then, I draw another one. So, I am drawing these different sections -1, 2, 3. This is at temperature T 1; this is at temperature T 2; I am drawing these sections at different temperatures. And then, all the sections are projected on to the Gibbs triangle – all of them. That is what is the liquidus solidus surface position – its means. So, what it means? It means that I take this – I draw these triangles at different temperatures at T 1, T 2, T 3, T 4, T 5, T 6, T 7 or T 8 – whatever different temperatures. And then, I can give these sections at different isothermal sections. And then, all these isothermal sections are projected on to the Gibbs triangle. That is what I am doing.

So, as you understand step-by-step way, first thing I did – I took one section – isothermal section. How I have done that? I have taken a triangle at the temperature T equal to T 1 parallel to the Gibbs triangle and just pass it through the phase diagrams – three dimensional models. And, because I passes through three dimensional model, it cuts the liquidus surface at two points -1111 dot; and, solidus surface at two points -s1s1 dot -s1 prime; right. Now, this becomes my projection of the solidus and the liquidus surface at temperature T 1. I can do the same thing at temperature T 2 and subsequently lower temperatures. Once I get all of them, I can put all these sections. This is nothing but liquidus and solidus surface projections; understand? So, at different temperatures, whatever section I get I have plotted to the projections.

This is very important, why? Because this tells you how the liquidus-solidus surfaces are changing as a function of temperature. Here actually they are not changing at all, because it is a isomorphous system. Therefore, there is no change. But it might be possible in some – some diagrams; this will change. And, there is this one will allow us to know how this orientation is changing. That is what is I wanted to convey. So, in this class, in a nutshell, what have I told you? I talked about you all the rules and regulations of the tie lines for the isothermal sections. And, as the position formalism, I tell you how to project liquidus-solidus surfaces on to the Gibbs triangle.

In the next class, I am going to talk about two important positions: one is of article section; other one is a poly thermal section. And subsequently, we will go forward looking into the how the solidification of the ternary alloy will take place. We will discuss about that. Then finally, we will move into eutectic systems. Let us stop it here.