Heat Treatment and Surface Hardening (Part–1)

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Lecture Number 21

Phase Diagram from G vs X plots

Hello everyone, today we will start our twenty-first lecture. And in the twenty-first lecture we will try to constitute phase diagram of course a simple one from free energy composition diagram in case of binary system. Now in the last two lectures we have talked about phase diagrams and we have also seen different kinds of phase diagrams in case of solid to liquid transformation, in case of solid-solid transformation, in case of solid to liquid we have taken example of isomorphous system where both the components are completely mixable in liquid as well as in solid over the entire composition range from 0 to 100 percent of the 100, 0 to 100 percent.

In the second one we have talked about eutectic system which one is also talking about liquid to solid transformation. And there we talked about transformation of one liquid to two different solids and then we also talked about peritectic transformation where liquid plus another solid they react together and forms another solid of different structures and then finally we talked about eutectoid transformation which talks about a solid transforming to two different solids and these transformation points as we have seen that the degree of freedom is zero which talks, which means that these points are invariant points.

And then we drew a phase diagram for iron carbon system and in that iron carbon system we saw three different reactions, one is eutectic another one is peritectic and there is another one which is eutectoid and we also saw that there is a steel part when the carbon content is up to two weight percent then it is called a steel part of the diagram and then from 2 to 6.67 percent carbon we call it a cast iron range. And in that particular phase diagram if you notice if you go back to lecture number 20, you will see that there are different phase zones and out of those phase zones you will see that we will be looking at the eutectoid part and the eutectoid part would be useful during the heat treatment of steels.

And that particular different heat treatments are there, for example annealing, normalizing, hardening then there could be speroidizing, there could be heat treatment like austempering, martempering there are different types of heat treatments, those will be only concentrating on the steel part of the phase diagram and that too the eutectoid section and it would also try to consider all most of the cases, it tries to consider this heat treatments would try to consider the eutectoid reaction. So that means one solid converts into two new solids and in case of steel part, we have austenite going into cementite and ferrite.

And these transformation would actually gives rise to a huge number of microstructural variations, and that actually affects the materials properties. And another part it is important that we have (dra) we have drawn that particular diagram on the basis of Fe3C presence. Now this Fe3C is a meta-stable phase, either stable phase in case of iron carbon system is iron and the another one is graphite, okay. But Fe3C is forming and Fe3C actually if you (pu) give sufficient time and also in the temperature range required for breaking of Fe3C, then Fe3C can break into two parts, one is iron another one is a carbon and that carbon is nothing but the graphite .

And in case of cast iron actually we try to break this Fe3C into iron and graphite and that is why you get different types of cast iron, for example one is grey cast iron, then another one is spheroidal cast iron or we call it sg iron and there could be another variety which is called malleable cast iron. And in case of the cast iron where we have Fe3C present, that means the meta-stable phase which is present in cast iron and the carbon content is more than 2 percent, that time that particular cast iron we call it white iron.

So but we are not looking at that part, but we just would like to mention that the iron carbon phase diagram in case if it has Fe3C presence, than it is called meta-stable phase diagram. So now we have just describe those things, now today our intention would be to find out phase diagram from free energy and composition part. So free energy and composition plot can be derived from the consideration of a ideal solution or you can also extend it to a real solution, but that part we are not going to discuss in greater detail, rather we will straight way come to see k how this G versus X plot look like in case a situation where it is a ideal solution, okay.

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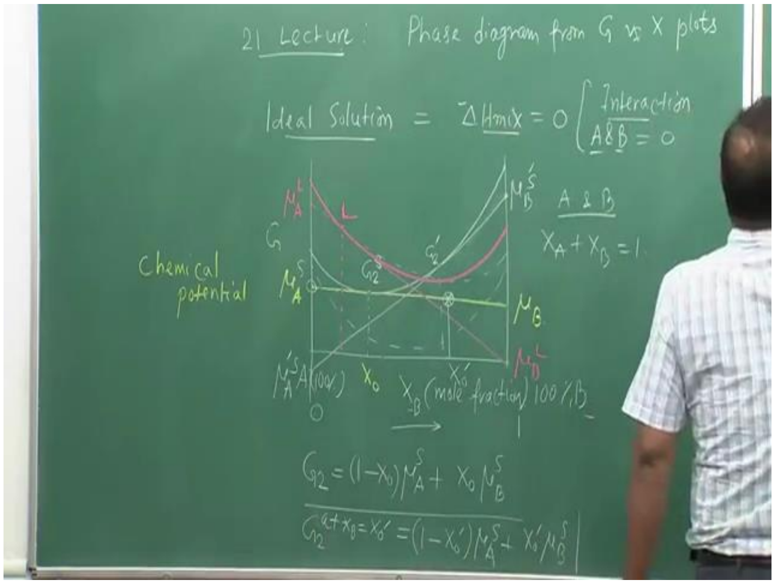

So in case of ideal solution, whenever we are talking about ideal solution, we mean and that del Hmix that means enthalpy of mixing is 0. So that means whenever two elements are mixed together, when they form a solution it can form either liquid solution or solid solution, that time this particular term would be zero, it means the interaction between the components, interaction between the components is zero.

So A and B, so if A metal and B metal are joined together or mixed together if they form solid solution, let us say this they form isomorphous system. So that means in the liquid as well as in solid in both the cases they have complete solubility. So that time the interaction between A atom and B atom is 0, and that particular condition we will consider, and that case the diagram for G versus X, X is basically mole fraction it has a nature like this, okay.

So it could have a different nature, it could have this, it could have this so but you will see that it is bending towards it is a curve nature, okay and this says that if this is 100 percent A and this is 100 percent B and if they form a solid solution or liquid solution, means we are considering isomorphous system that time this is the percentage of Xb or the mole fraction of B is gradually increasing. So this is Xb would be 0 here and Xb would be one here because finally both the things when they are mixed then Xa Xb equal to 1 since it is a fraction and it is a binary system A and B binary system.

Now if this is that graph, this graph tells that at any point on this graph indicate some free energy value and that free energy value can be found out from the tangent on that particular point over this graph, okay. So if I try to find out free energy at this point, so this point for example this is 2 G2 and the free energy would be if I draw a tangent, see if I draw a tangent and this tangent value would intersect 100 percent A and 100 percent B at two points and this particular point we call it as MuA and this particular point we call it as MuB. And this Mu is nothing but chemical potential**.**

And if this composition corresponds to X0, means the composition of Xb equal to X0, then we can take an equation for this straight line and that equation becomes this is that equation of this particular line, this is straight line because there is a tangent over this graph. Now if I try to find out what is the value of G2 prime that means the free energy at this composition again I have to draw a common tangent sorry not common tangent a tangent on this line on this point and it will cut here.

So this is a new MuB prime and this is MuA prime. And whenever we have this graph since we are considering complete solid solution, it is a graph for a particular phase, and let us say we considered that it is a graph for solid, okay. Now that means at any point if we try to draw a tangent over this graph, then this intersection points will be the Mu values the chemical potential of that particular component at this composition, okay for example if I try to find out what is the Mu of B, that is the chemical potential of B, the chemical potential of B would be at this composition would be this one and this chemical potential would be for that particular phase which is S solid.

And similarly this is also for S, similarly in this case, if I try to find out what is the chemical potential of solid, chemical potential of A in that solid, then this would be my value and that corresponds to this composition. Now, if I try to just for and that means here also we can make a change this would be for solid, this is (())(13:47) solid. Now similarly I can have plot for liquid free energy over this entire composition range because we are assuming a isomorphous system and where liquid solid solubility would be there from 0 percent B to 100 percent B.

And here also, I can have a graph like this so this is liquid. And similarly if I try to find what would be my chemical potential of A at this composition in liquid, so then I have to just draw a tangent again on this point over this liquid graph, this is the liquid phase this particular red graph which is G versus X plot for liquid phase. So this would be MuA and this is the liquid and similarly this one would be MuB liquid.

So like that way we can find out what is my equation for the free energy at any point over this graph for a particular phase if we know these two values, okay because this composition we know, these two values we know and we just put it here and find out what is equation for this straight line. Now just for sake of understanding this (eq) information would be useful later on when we try to find out the free energy difference for the transformation when we talk about a transformation from solid to solid, okay.

And every time in order to find the nucleation rate, we need to find what is the free energy volumetric free energy change which is actually giving the driving force. So that will be required and for that we need to find out if this line, this line is given by this particular equation, I can also find out if I try to find out what would be my G2 at composition let us say X0 prime, so this composition is also line on the same line same tangent, so I just would shift this equation because these two term will not change because it is on the same line and these two are the two fulcrums, okay.

So now if we try to plot at Xb equal to X0 prime we have to just simply 1 – X0 prime MuA S+X0 prime MuB S. So what I am doing? I am just shifting my point from this place to this place equation does not change, only thing is my composition is changing, my equation remains the straight line equation, these two variables remain same this two points, only thing is I am changing the composition if I do this, I am actually indicating the same free energy line, okay and what does it mean? It means that on this line, on this line I can find what would be my G2 at any composition over this line, okay.

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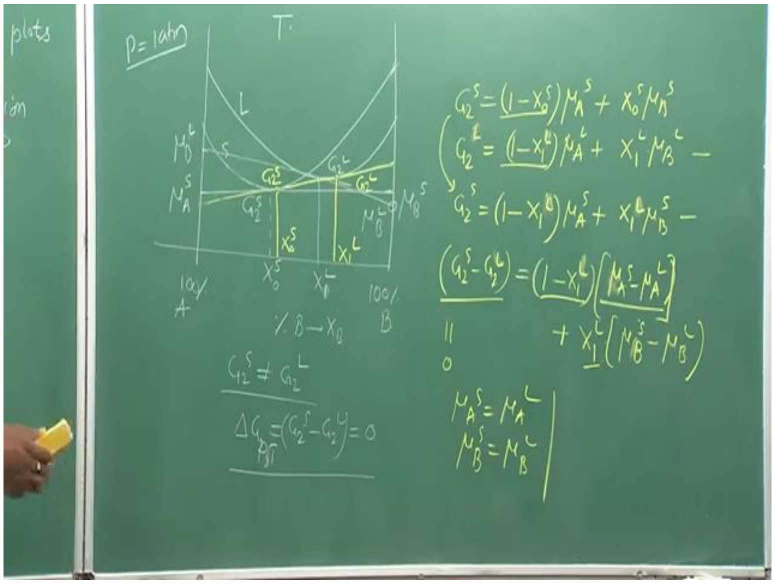

Now if I have this information, if I have the liquid and solid, then let us see an interesting situation, this is my liquid, let us say this is my solid and let say this is my liquid, now this is 100 percent A this is 100 percent B. Now if I draw a tangent at this point, so that means this is MuA S this is MuB S at composition X0 S and this is percentage of B which is in the form of Xb it is the mole fraction. Now if I try to draw another free energy, another tangent over this point, this is X0 liquid let us say X1 liquid. So now this value would be MuB liquid and this is MuB solid sorry it is a liquid phase because this line indicates the liquid.

Now when would you think that the alloy or the solution of this composition would you think that solution of this composition and solution of this composition would be in equilibrium, can they be in equilibrium? They cannot be in equilibrium, because here it is G2 S and here it is G2 liquid and G2 S not equal to G2 liquid, so this is not the condition for equilibrium and equilibrium means del G which is G2 S – G2 L should be zero. And we know that these are all drawn at pressure constant at let us say 1 atmosphere and this is drawn at a particular temperature T and we can change the T and accordingly this graph would vary, either it can shift downward or upward those things can happen.

So when would you think this thing can go to 0? This is only possible if we have a common tangent. So that means if we draw a tangent over this particular graph and that tangent cuts the other graph at some point, so then you can see so the it has cut the solid line here and the liquid line here. So these two points, these two points that means here we can find out G2 S and here also we can find out G2 liquid and interestingly the equation for the line, so if I consider this is so equation for this line if it is solid I can draw I can make this equation which is G2 solid, let me do it in yellow because I am giving a yellow line for a common tangent, G2 solid would be this is the composition let us say this is X0 S and this is X1 L.

So 1 – X0 S MuA solid + X0 S MuB is solid and this is G2 S G2 L equal to 1 – X1 liquid MuA liquid + X1 liquid MuB liquid. So that means these two equations are indicating same line and then if it is same line and you see that these two terms are, so I can if I take this one, I can as per this particular shifting of points I can also shift there and that time I can write G2 S equal to 1 – X1 S if I take this composition to this composition in case of solid, so I can write this as per that conversion. So from this, now you see if I try to see G2 S – G2 L would be equal to 1 – X1 S Xa S – MuA S – MuA liquid + X1, sorry this composition is liquid so solid initially solid but I can also take it as liquid.

Because this is telling the same composition, so I can covert to liquid, similarly I can convert this one to be liquid MuB S – MuB liquid. So these two terms are same values and this are giving the same line, so this value becomes zero, okay and then when it can be zero? Because these two terms are not changing, only thing is if separately MuA S equal to MuA liquid as well as MuB S equal to MuB liquid that is the condition for equilibrium. So that is why people say, that is why it is said that common tangent gives the equilibrium.

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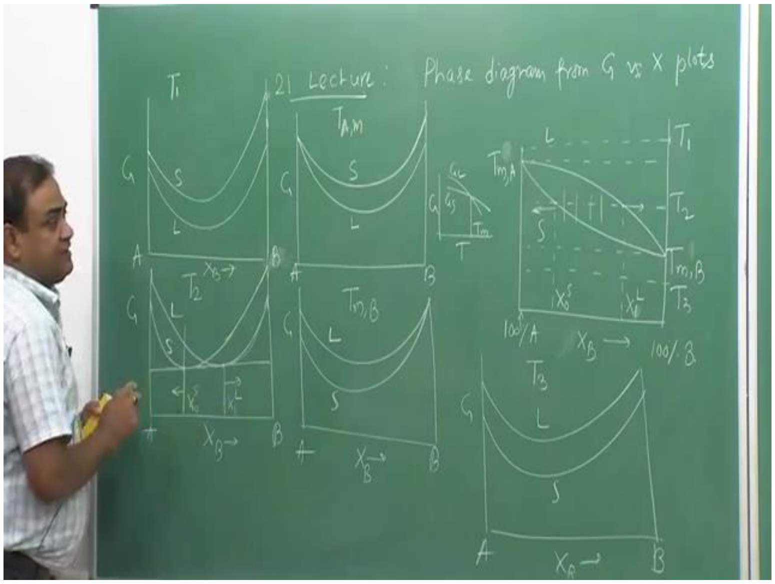

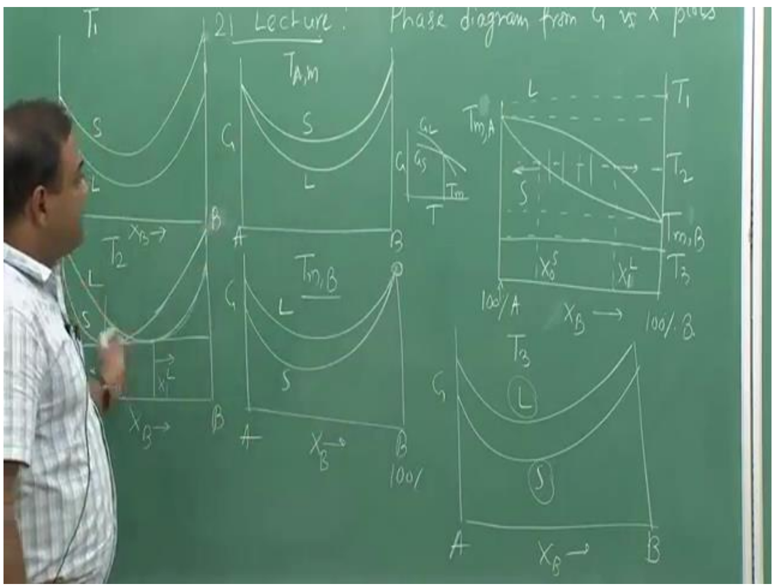

Now if I draw the equilibrium, if I try to draw equilibrium at different temperatures I could get the phase diagram for isomorphous, let me draw that, so let us draw of an isomorphous phase diagram where it is liquid solubility and solid solubility is there from 100 percent A to 100 percent B. Now if I try to draw this free energy composition diagram for (loc) liquid and solid phase, at this temperature T1 since at this temperature T1 liquid is stable, so the free energy of liquid graph will be below solid free energy graph these are all free energy composition graph this is the composition, this is free energy.

Now liquid free energy graph is below solid free energy graph at all the compositions and it means that the liquid would have lower free energy of solid all the time from 100 percent A to 100 percent B, it also means that the liquid would be stable as we have seen that the free energy the lower free energy substance would be stable compare to the higher free energy type. So now over this entire range we have liquid, so that is what we have seen from this composition to this composition everywhere it is a liquid phase, okay.

Now this is at temperature T1 as we have seen there are different temperature, we can draw the composition free energy graph from if we know the Mu which is the chemical potential. Now if I try to see what happens at this temperature which is the melting point of Tm, TmA that means the melting point of pure A. So whenever we reach that point, it suggest that if it is 100 percent A first solid would appear in the liquid and that would be 100 A if we take this composition, so we have to take this composition. So then the graph nature looks like this.

So at this point both the phases have the same free energy as we have seen before that if have G for a particular single component system, this is the graph we have seen, this is G liquid, this is G solid, so this is my Tm which is the melting point, similar thing happens here, so that means both the phases would have same free energy at this point, that means the free energy difference is 0. So here I would appear, I would get first A, okay the A pure A would start coming out in the form of solid.

So that means, here if try to see at this point I would get the first solid, but apart from this composition rest of the compositions liquid free energy is below solid free energy, so liquid would be stable. That is what we are saying, apart from this rest all compositions liquid is stable. Now come back to the composition situation where we are taking T2 for the entire composition range. And that T2 is see that once if we take any composition within this range any compositions, if we take any composition that composition would distribute into a liquid and solid phases.

And that particular liquid and the composition of solid would be this one, and the composition of liquid would be this one and these two phases are in equilibrium, why? Because the common tangent if we draw, if we draw this common tangent for liquid phase and the solid phase free energy I see that these two compositions are in equilibrium because they are falling on the same line and this condition is satisfied and then we say that this are in equilibrium.

Okay, similar situation we can also see here at T2, so that means the (ss) if we see this particular diagram nature along this common tangent, this composition and this composition both are at equilibrium because they are falling on the same common tangent. And then what does it mean? That below this you see all the solid free energy graph is below liquid, below this composition if we see and on the right side all the liquid composition because this is liquid graph is below free energy for liquid at different composition between this to this liquid is below the solid.

So (lept) left to this all will be solid, right to this line would be all liquid. So that is what we are seeing that left to this all are solid and right to this all are liquid. So and what happens in between? In between the liquid is distributed into solid and liquid of this composition X0 S and X1 S X1 L. So this X1 is the composition for liquid and X0 is the composition of solid. So that is what we are seeing this is X0 S and this is X1 L. Now once we come to TmB this particular temperature, we find the situation becomes like this where everywhere I see that the solid free energy (carv) curve is below the liquid free energy curve.

So that means the solid free energy would be lower than the liquid free energy and solid would be stable over the entire composition. But at this point, these two lines are cutting which is 100 percent B and 100 percent B case the same situation is taking place. So here the B would appear the B solid would appear at this composition and (ther) that means 100 percent B composition if we take, this would be mine situation where at this temperature B would start coming if we take 100 percent B. so here both the liquid and solid free energy lines are matching and rest of the places everywhere solid free energy is below liquid free energy and rest of the (se) cases everything would be solid.

So this is my melting point of B and rest all is solid. Now once we come to T3, you see the solid free energy at all the compositions is lower than liquid free energy and that is what we have all the solid, no liquid anywhere and we see it is all solid pictures. So that way we try to draw a composition free energy diagram and from that we can derive a phase diagram, okay. So now this particular thing you can also take it to draw eutectic phase diagram, you can also draw eutectoid phase diagram, you can also draw peritectic phase diagram, okay so you can see that how we can draw, phase diagram from G versus X plots, thank you.