Heat Treatment and Surface Hardening (Part-II)

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Lecture - 15
Determining nucleation of phases using G-X plot

Let us start our lecture number 15.

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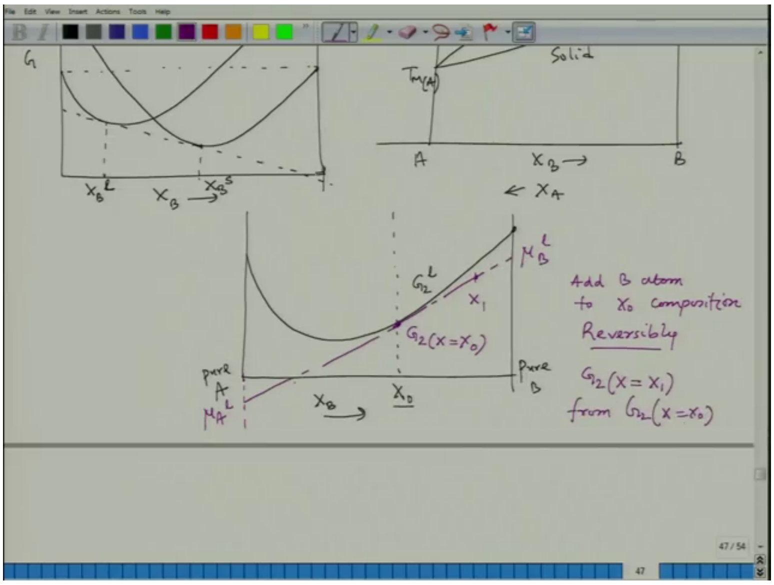

In till lecture 14 we have seen that how to get to phase diagram from free energy composition diagram and that to getting to the equilibrium concept; that means, where the chemical potential of a particular component is same, in both the phases at a particular temperature and pressure. Now we would look into free energy composition more bit more.

And we have to look into this free energy composition in depth and understand that, if we have some particular composition if we start with some particular composition of an alloy from liquid state, let us say in the beginning, let us consider the liquid state and then at, if I consider a particular composition whether that composition would yield solid phase; that means, the nucleation of solid alloy would be possible in that particular liquid at a particular temperature between the melting point of 2 pure components.

now we have seen the phase diagram that isomorphs phase diagram, this was the isomorphs phase diagram what we have drawn this is TM A this is TM B, and this is temperature this is XB this way XA, this way. This is pure A, but B this is liquid, liquid plus solid this is solid.

Now, let us consider at a particular temperature; what is the free energy composition plot. See if I see the free energy composition plot. So, let us say this is G 2 liquid this is G 2 solid this is G versus XB and if temperature is less than TM B and greater than TM A we would get this particular energy composition plots.

Now, from our earlier discussion we can see that if we have a common tangent, these 2 compositions are in equilibrium at that particular temperature. So, this is XB of liquid. So, this is XB of solid these 2 compositions are in equilibrium. At the same time in our previous discussion, we can also see let us say if we have one particular this is some G 2 line of some particular one particular phase. For example, let us say I consider a liquid phase let us say that is a liquid solution.

So, this is pure a side this is pure B side, I just put a line here just to refer this particular free energy composition diagram with reference to this straight line. Now any composition, if I start with let us say I start with some composition this X 0 with reference to B so; that means, this is composition in terms of XB. Now at this point if I draw a tangent, if I draw a tangent draw a tangent. This is this tangent is passing through this point this is nothing, but G 2 of liquid at composition X equal to X 0. And this is mu B of liquid, this is mu a of liquid. This is very clear.

Now, we have also seen that if I would like to go from these compositions to any other composition on this particular line, then I have to follow a reversible transformation. Let us say I would like to reach to a composition X 1. So, then I have to add B, I have to add B atom to this particular composition add B atom to X 0 composition reversibly. That way we can follow this particular line, and we can see that these particular point; that means, if I reach to X 1, then my composition trend would be nothing, but X equal to X 1 from G to X equal to x0.

But remember whenever I am doing this transformation. Actually, I am following equilibrium condition. And the system remains in liquid only thing is the composition is changing. Why?

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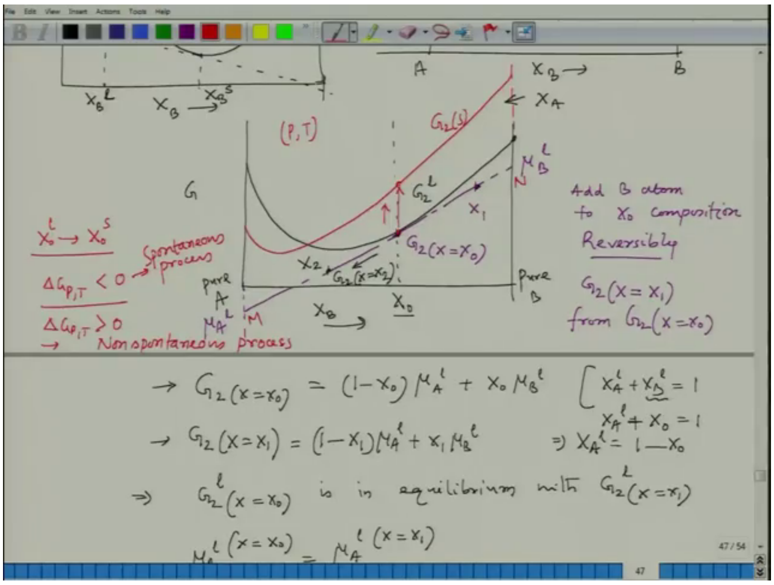

$X_0^l \rightarrow X_0^s$

$\Delta G_{P,T} < 0 \rightarrow$ Spontaneous process

$\Delta G_{P,T} > 0 \rightarrow$ Nonspontaneous process

Add B atom to X_0 composition Reversibly

$G_2(X = X_1)$ from $G_2(X = X_0)$

$\rightarrow G_2(x = x_0) = (1 - X_0)\mu_A^l + X_0 \mu_B^l \quad \left[X_A^l + X_B^l = 1 \right.$

$X_A^l + X_0 = 1$

$\rightarrow G_2(X = X_1) = (1 - X_1)\mu_A^l + x_1 \mu_B^l \quad \Rightarrow X_A^l = 1 - X_0$

$\Rightarrow G_2^l(x = x_0)$ is in equilibrium with $G_2^L(x = x_1)$

$\mu_A^l(x = x_0) = \mu_A^l(x = x_1)$

Because G 2 X equal to X 0 can be written as 1 minus X 0, mu a liquid plus X 0 mu B liquid. And we can write it XA plus X B. Since this is liquid. So, I can write it as 1 and here this is nothing, but nothing, but X 0 equal to 1. So, I can write X al equal to 1 minus X 0. And remember this is all are liquid compositions.

Now, if I try to move from here to this point, this point to this point. Then by G 2 X equal to X 1 would be 1 minus X 1 mu al plus X 1 mu bl. And then I can say that G 2 X equal to X 0 is in equilibrium with G 2 X equal to X 1. And remember both are liquid phase.

Why I can say this statement, I could see that from this 2 equation I could see that for both the free energy cases mu al when X equal to composition X 0 equal to mu al when this. Similarly, mu bl X equal to X 0 equal to mu bl X equal to X 1; so as per our equilibrium concept; that means, these 2 points are in equilibrium. These 2 points are in equilibrium. These 2 points means this one as well as composition X 1 and X 2 X 0 are equilibrium.

Similarly, if I try to go this way, and if I reach let us say X 2 composition, then what I have to do I have to take out B from X 0, because it is going towards a right side from X 0 reversibly to reach to this particular G 2 X equal to X 2 point. And there also this particular equilibrium constants are concepts are can be validated. So, we see that if we take any composition in this entire composition range, then that composition can go to any other composition keeping the liquid phase as a liquid phase, along the tangent line and those all composition will be in equilibrium.

now if I now combine this particular on this particular phase diagram this G versus G versus X diagram, if I introduce one more phase let us say I introduce solid phase on this particular diagram. Let us show if I put it with let us say different color let us say red color let us say I put a solid line, like this. Do you think that that solid would be able to nucleate from these liquid particular liquid compositions.

And in order to do that we have to see that whether these solid line this is G 2 of solid; that means, the solid solution that line whether that is below this particular tangent line this. Let us say I consider it is as M and N see this MN, line we have to see that whether that line is above this particular red solid solution line or some portion of this MN line is just reiterate, this we have to see whether this MN line is above this solid free energy line or MN line is below the solid free energy line.

Now if I have to form this particular, let us say these composition I need to form a solid and then I have to reach to this point in order to get solid. And if I would like to reach there to get a solid I could see that the free energy is actually increasing for any process; that means, here the solid X 0 composition liquid, if I try to follow X 0 of solid; that means, the X 0 composition is converting into solid X 0. Then I am saying there is a increment in free energy.

And as this particular process is done at particular composition pressure, until unless we see pt less than equal to less than 0 the process cannot be spontaneous. And if we see pt greater than 0 this is for spontaneous process. And this is for non spontaneous process. I see that if I have to go from solid liquid line to the solid line at the same composition I see there is a increase in free energy then that process cannot be spontaneous rather that kind of process cannot be possible thermodynamically.

similarly, if I try to see at any point at any point with reference to this MN line, everywhere if I have to get solid have to increase the free energy which is not thermodynamically feasible process; that means, if the condition of or the position of this solid solution line and liquid solution line are such as it is dictated in this particular picture solid phase will not fall. Because everywhere I am seeing that there is a increase in free energy which is not thermodynamically feasible process.

now situation could be different, if I change this particular point position that was initial alloy composition if I change from this side to this side; that means, initial composition let us see what happens there. Now I can draw the similar diagram.

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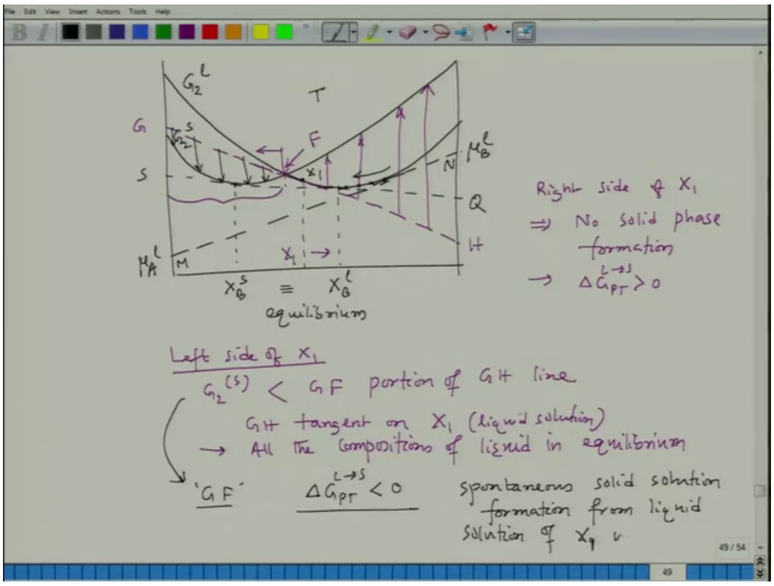

Right side of X_1

$\Rightarrow$ No solid phase formation

$\rightarrow \Delta G_{PT}^{L\rightarrow S} > 0$

Left side of X_1

$G_2^{(S)} <$ GF portion of GH line

GH tangent on X_1 (liquid solution)

$\rightarrow$ All the compositions of liquid in equilibrium

'GF' $\Delta G_{PT}^{L\rightarrow S} < 0$ spontaneous solid solution formation from liquid solution of X_1 ✓

This is G 2 of liquid; this is G 2 of solid. Now last time we consider the composition here. So, that is what this is mu bl, this is mu al. And every time we see that any composition starting from M and N would not lead to solid phase formation. Because every time I say that in order to form solid have to increase the free energy.

But now if I start changing the initial composition when the temperature let us say I take a particular alloy I take it beyond the melting point of B that is everything would be liquid and it will be miserable all the time and that composition if I drop gradually. I can also change those compositions as per my wish and if I sip this particular composition on this particular G 2 line. And everywhere if I keep drawing a tangent, there will be a point when the tangent on the composition of the liquid solution would cut the solid solution free energy line at a particular point.

so; that means, it becomes these tangent which is let us say st sq composition sq, sq, sq tangent line these tangent line is a common tangent between solid solution as well as liquid solution free energy composition line, or the curve graph I would say. And I could see that this composition and this composition they are at equilibrium. So, this is XB solid this is XB liquid. These 2 compositions are equilibrium.

So, if I have to and that moment this is at a particular temperature t which where this sq common tangent can be drawn on 2 points of solid and liquid lines liquid free energy composition curve. And that time these 2 compositions will coexist this is the equilibrium concept. Now as I am going from this composition and going along this particular G 2 free energy curve, once I let us say I reach to this particular composition.

So, this is let us say composition X 1. I can also draw a draw a tangent at that point over this G 2 line. So, if I draw that, this is that line. I could see the right side of this particular composition X 1 every time the solid G 2 line is above this tangent line on this X 1 composition. I can term it as gh.

So, if I try to go on the right side every time I see that I had increased the composition to reach to the increase the free energy to reach to the free energy line for solid. So; that means, right side of X 1, no solid phase. Since there delta gpt greater than 0, for liquid to solid formation, but on the left side of it left side, X 1 situation would be different between this point to the left of this point.

So, now left side of it I could see between this to this point G to s is less than and if I give a notation to this point as f G F portion of G H line. And G H line is what? G H line is tangent on X 1 liquid solution is indicating all the compositions of liquid in equilibrium.

hence between G and f line between, this I could see that there is a situation where this condition is met. So, spontaneous solid solution formation from liquid solution of X 1 is possible.

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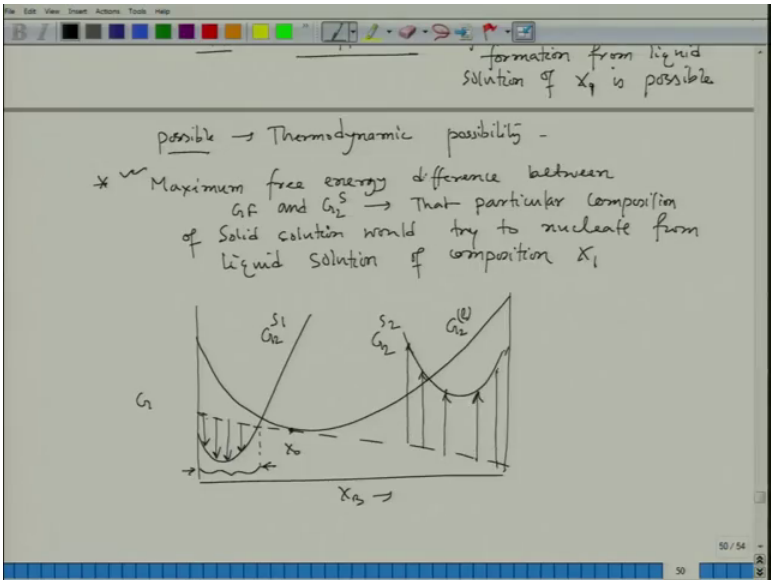

formation from liquid solution of X_1 is possible

possible → Thermodynamic possibility -

* Maximum free energy difference between G^f and G_2^S → That particular composition of Solid solution would try to nucleate from liquid solution of composition X_1

And this possibility is possible means thermodynamic possibility.

So, again if we go back, I could see that when the composition is taken composition of the initial alloy is taken at this point. At no point between P or A to p or B, I could get solute phase solid phase because every time I have increase the free energy which is indicating that the process of the transformation is non spontaneous. So, no solid phase formation thermodynamically.

But when I reach to this composition xbs and xbl, yes there is an equilibrium between solid and liquid and these 2 compositions of solid and liquid would be in equilibrium. We cannot definitely say that whether solid would form or not because that time the free energy difference is becoming 0, but once I take the composition between XB s and XB l, let us say X 1 here I could see that some portion of that tangent line on X 1 is above the solid solution line.

And that leads to the condition which is del gpt. Liquid to solid transformation is less than 0 so; that means, it indicates that thermodynamically this is a feasible process. And we could see solid phase formation from liquid. Now interestingly if we see that from this G 2 f point any compositions can be possible, but now we have to decide which phase as the highest probability to form. And that can be decided by the difference in free energy.

Now, if we see this difference in free energy, I will just find out why are the difference of free energy between this G F line and G 2 of solid line is maximum. That phase would like to nucleate first from the liquid composition of X 1. So, now, if I write it down, then the maximum free energy difference between G F and G 2 solid that particular composition of solid solution, would try to nucleate from liquid solution of composition X 1.

So, this is a very important aspect because finally, what why we are doing all this we have to calculate what is the free energy difference. When a particular alloy is taken and the second phase would appear. So, free energy difference for the second phase which is termed as delta gm how to find that particular value. And this gives that indication that what should be the value of that particular delta gn. Or free energy for nucleation.

Remember, free energy of nucleation and the free energy free energy difference for nucleation or free energy difference for overall transformation, these 2 are entirely different quantities. We will discuss those part little later, but first let us understand this particular issue that why we have to draw a tangent over that composition point on a liquid line in the case of liquid solid transformation for an alloy. And then we have to consider those compositions where the tangent over that composition line on G 2 of liquid is higher than the solid free energy line. And that is what we have considered here.

Now the same concept can be used to find out that if there are 2 solids which are possible in a system from a particular liquid composition, then which solid would appear that can also be found out by constructing free energy composition diagram for liquid as well as both the solids. Let us say I consider a situation like this, this is my liquid line G 2 liquid and they are all let us say 2 solids which could be possible from the liquid. One is let us say G 2 of solid one, the another one is let us say G 2 of solid 2.

If I start with the composition at this point, then again I have to draw a tangent on that particular point this is G versus XB. And here also I could see that from this below this particular portion of that tangent on this composition X 0, this is the initial composition of the liquid what we have considered is one free energy line is below that between this to this.

So, these particular solid one could be a possibility, but what happens to s 2, but if I try to see s 2 every time if I have to form s 2 from that particular liquid composition, I could see that there is increase in free energy. So, for s 2 delta gpt greater than 0; for S 1 if I give a notation as oq S 1 delta G pt between oq less than 0.

So, S 1 is possible s 2 not possible. So, the S 1 could form from the particular X 0 composition if the situation is this that is this is at some temperature t pressure equal to 1 atmosphere. So, that time S 1 is a possibility for the portion formation from liquid, but s 2 cannot form because for s 2 formation, I have to increase the free energy which is not possible. So, this also gives an indication that which phase would come out from a particular composition of liquid.

So, we will just take it up in our next lecture and discuss more on this. And finally, we will start counting what is the free energy for nucleation in case of (Refer Time: 31:35) systems.

Thank you.