Heat Treatment and Surface Hardening - II

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Lecture - 21
Effect of ΔHmix on determination of phase diagrams (same crystal structure)

Let us start lecture 21.

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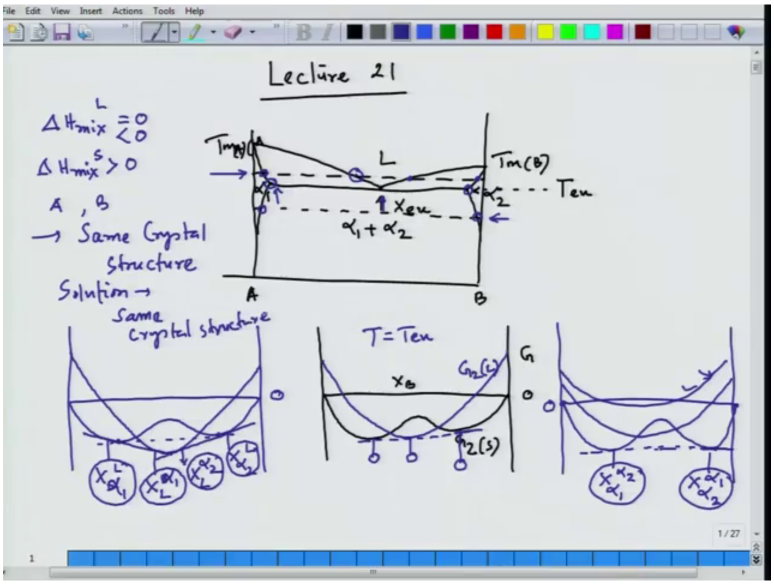

In our last lecture, we tried to draw and eutectic phase diagram. And that time our condition was that binary system E and B the constituents of that binary system have the same crystal structure. And in the solid state after forming the solution they have the same crystal structure in case of solution. And we tried to consider the situation when enthalpy of mixing for the liquid solution is negative or 0.

And, another case when enthalpy of mixing for solid solution is greater than 0, so because solid solution enthalpy of mixing is greater than 0; so we have experience of phase separation. So, we tried to see this is my eutectic phase diagram. This is my eutectic phase diagram. Where this is liquid this is alpha 1. This is alpha 2. And this is alpha 1 plus alpha 2 and this alpha 1 and alpha 2 both are the same crystal structure and this is my eutectic composition this is X 0 X eutectic. And this temperature is T eutectic; that means, eutectic temperature this side is A and this side is B pure side this is TMA.

This is TMA. Now we drew free energy composition diagrams at 3 different temperatures, one temperature was chosen this one another temperature was chosen this one. And the third temperature was the eutectic temperature. And we saw a situation that is the locally there equilibrium between different phases.

So, first thing if I try to see free energy composition diagram for a system where for the system is at temperature T eutectic. So, T eutectic both the pure states are in solid condition, but if those are of they are at solid condition then the solid line would be if I try to see this is a reference value which is 0, this is G access this is X B and there liquid would be because in the pure side the liquid would be higher free energy than compared to the solids free energy this is G 2 solid. If I try to draw free energy of liquid this is my free energy of liquid this is G 2 liquid. And now I have a common tangent at this at the compositions.

So, this composition this composition corresponds to this, this composition corresponds to eutectic composition. And this one indicates the composition on the B reach side. And this temperature is basically T eutectic. Now at higher than melting temperature we had a free energy composition diagram this is arbitrary 0 value here also if the temperature is higher than T eutectic; that means, the temperature why I am considering this. So, that case also on the pure site solid free energy should be lowered then the liquid free energy because pure side already it has from solid.

So, it will be again the similar pattern, liquid free energy line will be lower than the equilibrium free energy line; that means, the common tangent between this point and this point and the liquid free energy should be lower than that. So, that is what we have 2 phase common tangent this is X solid in equilibrium with liquid this is X liquid in equilibrium with solid. Now here I have considered I have considered alpha. So, let me put it at alpha 1, this is alpha 1 and this composition would be X liquid alpha 2 and this is X alpha 2 liquid. It means that this is the composition of alpha 2 of solid solution in equilibrium with liquid. So, if I see that those 4, 4 points. So, this the point which is nothing but X of alpha 1.

This point is in equilibrium with alpha 1. And this composition is the liquid composition this is the liquid composition again in equilibrium with alpha 2. And this is the composition which is this one in equilibrium with liquid. And we had another consideration which is the temperature this one which is below T eutectic. So, that time again of solid would have a lower free energy, and if I take this is as a reference value now again this would be having a plot like this. So, this point and this point would go and meet 0 point, but the liquid line would be above this common tangent between 2 solid phases. So, this is X alpha 1 in equilibrium with alpha 2. This is X alpha 2 in equilibrium with alpha one, but the liquid line either it could be here or it could be here.

But it would be above that these 2 this common tangent line. So, we cannot have liquid phase as a stable phase. So, pa depending on the temperature, if that temperature is such that the liquid line goes up to a great extent and it can be temperature could be such that the liquid line could be little lower than that than this, but it should be above this common tangent line this common tangent line. So, that case we have to concentrations which are in equilibrium. This is nothing but this composition and this composition is nothing but these compositions. So, we had an eutectic phase diagram, where our conditions was condition were del h mix of liquid either it could be 0 considered as 0. Or it could be considered as less than 0 or del h mix solid another case is greater than0.

But, since we have a continuous solid solution line here crystal structure of A and B same crystal structures, same crystal structure. And the solution also has the same crystal structure solution. Or the alloy has got the same crystal structure. So, this is one situation, we have talked about.

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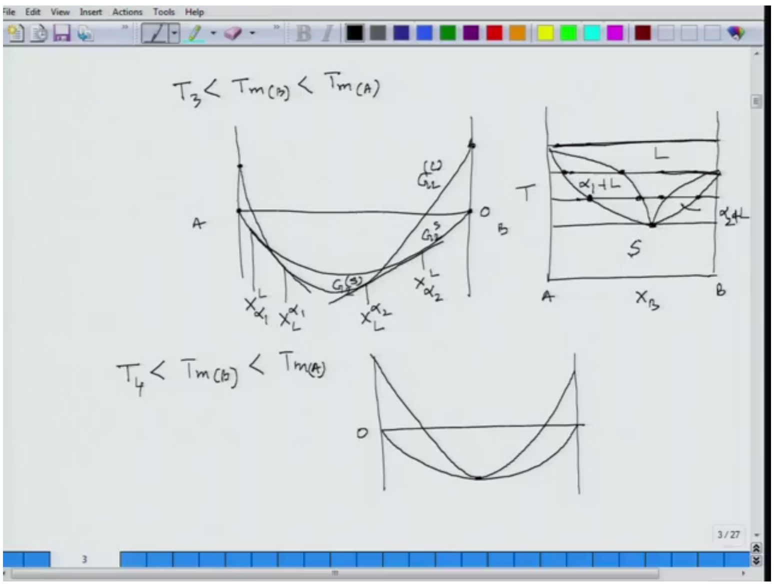

Now we have to get into another situation where my conditions are del h mix of liquid is very low and highly negative; that means, what does it mean if I try to see the construction of del G del h mix, this is my minus T del s mix. And since del h mix of liquid is very low; that means, very negative very much negative.

So, it might have very steep this is del h mix of liquid. So, now, del G mix would be just addition of these 2 and this would have a very deep del G mix. And accordingly if I try to see what happens to the del G 2; that means, this is G 1 I know this is pure AG a 0 G b0. So, if I try to see G 2 for that particular liquid phase then G 2 would be having very steep situation this is the G 2. Now if del h mix of liquid is negative, but not highly negative the only difference would be in the del h mix thing. So, if I try to plot del h mix of liquid lower negative. So, this would be this 1 minus T del s mix would change. So, del G mix would have a lesser dip and then G 2 also would have lesser dip.

So, this is G 2 when this condition is del h mix of liquid is less than 0. And in this case in this case it is del h mix of liquid less than less than 0. So, now, these situation when it arises then we have a much deeper G 2. And another situation could be del h mix of solid is equal to 0. So, automatically according to this explanation G 2 of solid solution would have less steeper G 2. Now, let us say I consider a situation T which is greater than T m of a greater than T m of b; that means, the melting point of a is higher than melting point of B, means when a cool down from a temperature which is beyond the melting point of A, and has we cool down the first solid phase that would appear is basically the pure A.

Now, if the temperature is greater than TMA and greater than TMB. So, everything would be liquid for the entire composition range. So, our composition free energy composition plot, if I try to plot this is my arbitrary 0 value this is the reference value and then solid liquid. I can say that this is pure liquid pure liquid A and pure liquid B. So, this is my liquid line G 2 which is G 2 liquid which is very steep and solid line should have appeared higher than this because at that temperature, I cannot have any solid. So, solid line would be like this this is G 2 of solid. Now this is G this is X B. So, now, second situation T is TMA, TMB then the temperature is such that the pure A side I would always get a phase pure A solid and on the B side I must get pure B in the form of liquid.

So, if I try to draw this free energy composition diagram this is arbitrary 0 reference on the a reach side or a side pure A pure A should be solid if I considered to be 0. Then the liquid should be above that because the temperature is such that, this is lower than the temperature melting point of a. So, the a should appear in the pure condition and where as on the B reach side since the temperature is beyond the melting point is greater than the melting point of B. So, there the liquid would be the several stable conditions. So, the liquid line, I can draw it like this whereas, the solid line on the right side this is pure B side B reach side solid must have higher free energy because then only B can appear as a liquid.

So, this is G 2 liquid this is my situation, this is G 2 solid. So, now, I have a common tangent here. So, this is composition X alpha with liquid in equilibrium with liquid and this is X liquid in equilibrium with alpha. Now third condition I can have which is T less than TMB less than TMA so; that means, on both pure A and pure B side I must get solid pure solid of both the components both the elements. So, that time if I arbitrarily draw that particular situation this is 0 it is a reference point. Now this is let us say I start with pure solid because I must get pure solid when T is less than TMA this is a reach and this is B reach. So, the solid will start here and similar on the right side also I must get solid B because the temperature is less than TMB. So, the B also would solidify in the pure condition.

So, now solid line is like this. So, on the pure side liquid lines are like this. So, G 2 this this is G 2 solid since the liquid has got a very steave G 2 line. So, so this G 2 liquid and this is G 2 solid. So, if I see the equilibrium condition, I have this equilibrium at the same time I can have one more equilibrium like this. Now this composition is X alpha in equilibrium with liquid this is X if I considered to be alpha 1 because on the both the sides I am I am getting alpha phase because the free energy line is continuous and they have the same crystal structure. So, this is, but in order to distinguish between to those 2 solids because these 2 solids have different a content and different B content one is a reach another one is B reach. So, that time I can put it as X alpha 2 in equilibrium with liquid and this is X liquid in equilibrium with alpha 2, and this is X liquid in equilibrium with alpha 1.

And now if we go down further the temperature is such which is still TMB is less than TMA I can have a situation the free energy situation free energy line, this is my solid line this is 0 arbitrary reference whether liquid line can just touch at this point. So, now, if I put all these compositions whatever we have drawn. Till now 4 temperatures this is let us let us go back to this this is temperature, one this is temperature 2. This is temperature 3 and this is temperature 4, if I try to draw there this is X B. This is A this is B pure side. Now I would get a if I try to plot all those temperatures with this temperatures, I just draw 4 temperatures. And here I get this 2 points and then I get these 2 points.

First one is I do not get any points. There actually I do not get any points there because every time it is a liquid stable. So, here I get 2 and I do not get anything, but here I get this this and this 4 points. And finally, I get this. So, if I try to do it complete we would get a plot like this. So, this is liquid this is temperature this is alpha 1 plus liquid this region is alpha 2 plus liquid. And this is solved which is alpha. So, I am getting a situation when I am having you see, because the liquid free energy line is G 2 line is very steep that is what I could get the liquid stability at a very low temperature. Now this situation becomes opposite if I consider.

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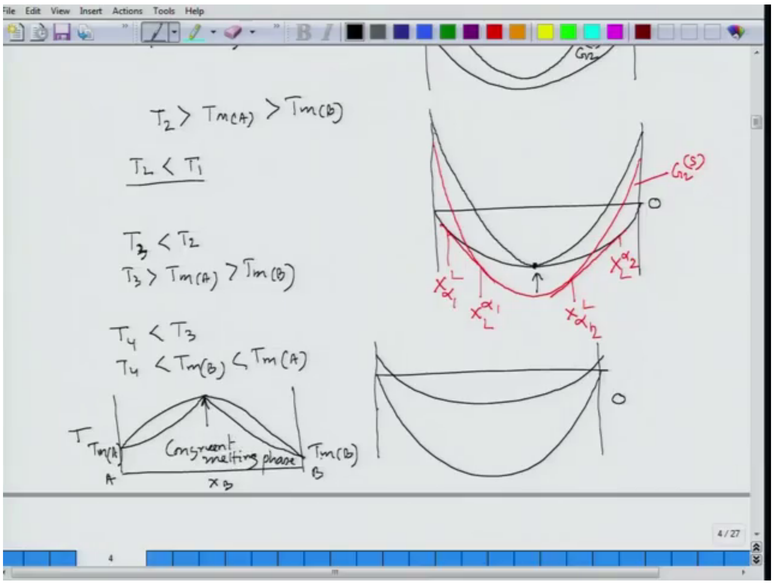

Del h mix of solid to be less than less than 0, and del h mix of liquid is either 0 or less than 0.

So, that situation, I would request you to just solve this you can get help from the thermodynamics book of cascle. So, there the phase diagram would look like. So, this will be my liquid this will be my solid this is alpha 1 plus liquid. This is alpha 2 plus liquid this is X B, this is temperature and that time I am getting point which has the maximum that solid has the maximum melting point. It is called congruent phase now in case of a system, where now the situation would be reverse if we consider this conditions. The solid del h mix is very negative highly negative, whereas, del h mix of liquid is either 0 or slightly negative that time I would have much steeper free energy line for solid solution, but less steeper free energy line for the liquid solution.

So, once a situation would be let us say the temperature is vary is basically higher than TMA and higher than TMB. That time, I would have a free energy plot if I consider this is might arbitrary 0 value, then for the entire composition range the solution would be liquid. This would be G 2 of liquid, but since del h mix of solid is highly negative. So, G 2 which is G 1 plus delta G mix for solid, which will be very steep. I can have G 2 of solid like this. Now if temperature is such that it is greater than TMA and greater than TMB, this is T 1. This is T 2 still, but T 2 is less than T 1 that time this liquid line would move off and the solid line would move down. So, then I can have a situation like this. This is arbitrary 0 because both the sides pure An pure B both are liquid because the temperature is such that pure metals such that should be should be in the liquid condition.

So, this is my liquid line, but the solid situation is such the solid is just touching the liquid line this point. So, at this point this composition of solid would appear in equilibrium with the liquid. Now if I decrease this temperature further T 3 is less than T 2, but T 3 is greater than TMA greater than TMB, that time I could have a situation like this on the same diagram situation could be like this. So, that time this is G 2 of solid. And then I would have 2 phase 2 equilibrium common tangent. So, this is be my X alpha 1 in equilibrium with liquid this is X liquid in equilibrium with let us say the on the other side B reach side I considered alpha 2. So, this is alpha 2 this should be my X liquid alpha 1 this composition would be X alpha 1 liquid.

And finally, I would get a situation I will get a situation T 4 less than T 3, but T 4 is less than TMA less than TM, TMB less than TMA. That case I would have a situation like this, this I can do it here. So, solid line would be steep and the liquid line would go like this. So, that case everything would be solid and my phase diagram would look like because T B side, this is a side this is TMA this is TMB. So, I would get a comp a phase diagram like this and this point is called congruent melting phase.

So, let us stop here. We will continue our discussion in our next lecture.

Thank you.