Phase Transformation in Materials
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Lecture - 09
Heterogeneous Phase Equilibria

Students we have been discussing about these different free energy functions and models for calculating free energy of the solutions. Today we are going to extend that for the understanding of phase stability in heterogeneous systems.

I hope you have an some idea about heterogeneous systems; you know heterogeneous systems will always consisting of more than one phase. So, therefore, the stability of different phases will dictate the phase transformations. So, we are going to take examples of different systems and show you how we can find out the heterogeneous phase equilibria; and also find out the stability of different phases from the free energy composition diagrams and different temperatures. So, I am going to use you know board for little discussions. So, I request you to follow it very carefully. So, that you do not forget; because these free energy composition diagrams will be utilized in every chapter of phase transformations.

So, you must have an fair idea, about how to construct them and how to study these free energy composition diagrams. Let us suppose we have a system simple heterogeneous system consisting of two metals A and B. And for the sake of simplicity; let us assume a has A FCC crystal structure, B has a body centered cubic crystal structure. So, A has face center cubic crystal structure and B has a body centered cubic crystal structure. And because they have a similar crystal structure therefore, they will be miscible provided their atomic size differences are not very large.

And let us suppose that their atomic sizes differences are not very large electro negativities are similar because they are metals. So, therefore, miscible and solid solutions are possible. Now if I simply consider A and B mixed together and if I go to the board just for the sake of understanding.

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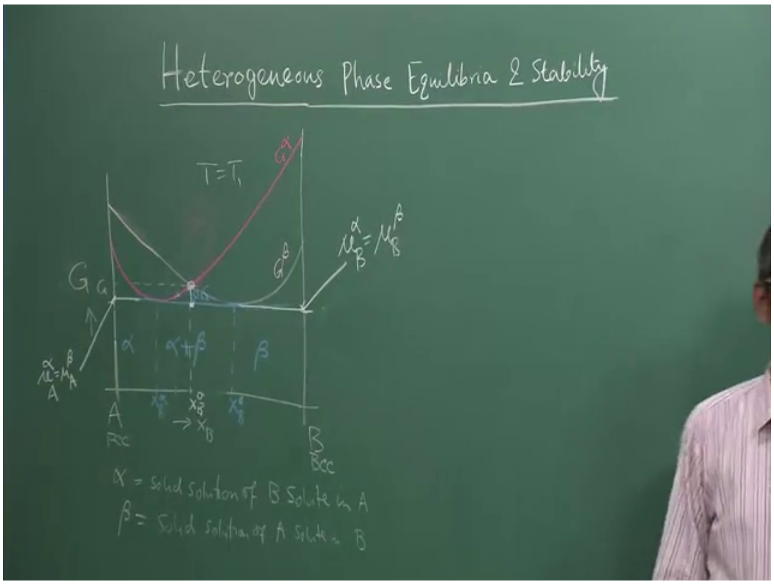

Suppose if I have A and B, and I am drawing this diagram which is which will be common for all your discussion. So, this is A end this is B end; and this is how B increases from 0 to 1 the fraction of B in to the alloy. Let us suppose that A is forming solid solutions with B alpha. So, alpha is a solid solution of on B solute in A correct; that means, alpha is nothing but A is solute solutions A is more B is less; that is why as B is less we call B as a solid, A as a solvent.

So, in books it will be written alpha the solid solution of B in A. The moment you see B in A; that means, B is a solid A is a solvent. Just like in a liquid solution suppose if I add take a water in a glass add sugar. The sugar is my solid, because I add very little amount of sugar in to water to get a solution. Similarly for metals it is the atom which is added a small quantity to a atom in the large quantity is called a solid; that is why B is called a solid, A is called a solvent. And let us also assume say A or; obviously, alpha solid solution and A as f center face centered cubic structure pure A.

So, therefore, alpha will also be face centered cubic structure that is how the solid solutions are defined. And let us suppose B sorry; beta it is a solid solution of A solid in B; that means, A beta is B reach solid solutions, A is added small quantity. So, we have form two solid solutions: one is alpha which is face centered cubic structure same as A and this is A reach, when we have a another solid solution beta which is B reach and it does a BCC crystal structure right, because it is B reach.

Now, I will draw I will basically know the different parameters of alpha and beta. So, I can calculate the free energy functions of both. And let me just draw it using different colored chalks that is will help you I will take all the colored chalks from here. So, that I know it is easy for me to show you different aspects of that. So, first thing I will draw is the alpha solid solutions free energy curves. And we know the free energy curves. So, free energy is plotted on the X axis that is G here. So, this is free energy versus composition diagram. And this diagram is at temperature let us say T 1.

This diagram is a say taken as a temperature T 1. Now for the alpha; let us suppose free energy curves looks like this; obviously, free energy curve for both alpha and beta will looks like inverted parabola. And this I have shown in the books I am showing you for detail analysis, because it will make you clear so; that means, the alpha of free energy curve will start from A end and go and reached here; let us extend it further, because that is otherwise it will create misconceptions correct; is always because alpha solid solutions. Now so, this is G alpha. Now for beta again similar thing will happen. So, once I have measured and got this free energy functional and plotted at temperature T 1 from A reach to B reach in and I get 2 separate curves.

Now it is very clear because free energy tells you relative stability; that A reach solid solution alpha is stable till this point, this cross over point you can clearly see this is a cross over point here in which A any solid solution is stable. And beyond this crossover point b reach solid solution beta is stable; am I clear? Very clearly seen that the relative positions of the free energy curves if you compare alpha has other (Refer Time: 07:06) lower free energy compared to beta phase from a reach in to this cross over.

Similarly, from this cross over to the B reach in beta has a lower free energy, because of these alpha is stable from this to these, beta is stable from this to this, but you know if you clearly look at it at the cross over; actually this looks like that, but this is not a correct picture; the correct picture is little different, but if I look like that will carefully there is a cross over. Cross over means free energies are equal at this point so; that means, both the free energies would be stable. When the free energies are equal at this point; that means, both the phases will be stable, correct; let us suppose for your understanding; if you do not know thermodynamics only at this point both the phases are stable, because free energies are equal correct, but you can clearly see that even if that is the case. So, this is my value of free energy.

Suppose G or both; both will be same. So, I write G the free energy of the system consisting of certain amount of alpha, certain amount of beta, because both are stable correct, but if you clearly see that it can still lower if free energy further; very clearly, why? Because, it can decompose into two phases of composition alpha this composition and beta of this composition and then I can draw a line.

So, average free energy will be given by this point now so; that means, even though the cross over point tells you that free energy of both the solid solutions are equal and; that means, the solid solutions of alpha and beta alpha of this curve having this much of say let us suppose this much of B and beta of this much of A will be stable; from this diagram, but that is not the case, because system can always decompose more alpha and more beta. And then reduce is free energy; it can further do that you can further go and reduce it to this point. That is what you can do? Because there were free energy of that system will be by given that this point. So, initially it was this point, then it reduces to this point, and then it reduce to this point. So, further it can lower down the free energy in the system.

Am I clear this is very important concept? So, now, question is that how far we can go down. Thus will be clear to you; once I little bit erase that part and explain to you. It is very clear that if; I erase these things and draw a nice plot then it will be clear that if I draw a common tangent between these two, then I will be touching the lowest portions of these free energy curves.

And therefore, it cannot reduce any further below, because I cannot draw a straight line like this and it is not fair; it is not going to be mathematically correct; so it can reduce free energy by this much delta G by actually forming a solid solutions of alpha having this much compositions X B alpha and this much composition of beta, correct; it can do that. So, very clear whenever we have a cross over between two free energy curve this is a very golden rule; that means, that there is a range of composition in which alpha and beta together stable.

So, that is why it is here both alpha and beta stable, but in this range alpha is stable in this range beta is stable why; because beyond this point it is this free energy curve which is lower than this alpha. So, below this point below X B alpha it is the alpha free energy curve which is lower positions then the beta. So, therefore, alpha is stable from any reach end or pure A end to X B alpha compositions, beta is stable from X B beta to B end. In between both alpha and beta are stable.

So, this is also known as tangent to curve rule, why; because I am drawing a tangent to I am drawing a tangent to the two curves this is known as tangent to curve rule; that is why we always draw this tangent to the curves common tangent to the curves. And this also allow us to explain that in heterogeneous system; if I extend these lines which I have been discussing with you for long time, that this will heat B reach end here A reach end here these are the two points.

And, I know that if I had draw a tangent to the curve that you should do yourself as a part of homework; if I draw a tangent to the free energy curve this if this hits the A reach end means this point tells me that this is a chemical potentials of A, because it is tangent to both the curves. So, therefore, A in alpha must be equal to A in beta, right; similarly this is also hitting here. So, therefore, I can write chemical potential of B in alpha must be equal to chemical potential B in beta so; that means, if I draw a common tangent, I can clearly explain a satisfy all the thermodynamics conditions to these phase equilibria.

So, it is very clear if I have a phase mixture whose free energies are equal at this composition at this point let us suppose this composition is X B at this point X B zero let us suppose it will decompose in to two solid solutions still the compositions of the solid solution will reach these two points. And these two points therefore, can be obtained simply by drawing a common tangent to these curves.

This is very important concepts, because in the next this lecture also next lecture I am going to use this concept extensively to arrive at stability stable composition range for the different phase mixtures, and I would like you to be having a very very clear idea, how I am drawing it? And how I am explaining it? So, it is very clear if I drop draw the common tangent I reduce the free energy further from this point to this point this is my free energy of this mixture now. So, free energy mixture is at least lower for the free energy of given by this cross over point by delta G and this is possible only by decompositions of and of forming these two solid solutions. So, that is let us keep this diagram that tells you the basic concepts and I told you how the free energy the chemical potential can also been equated in this way.

Now, I go one by one at least few phase diagrams. And explain you how things will happen? You know phase diagrams as I told you the very basic important all things in the phase transformations because phase diagram. So, tells you how the different phases will evolve and how they are going to transform. So, we will take some of the phase diagrams and show you how we can use this free energy composition diagrams to explain or in a different phases and the tough (Refer Time: 14:23) First. phase diagram which I will take I will draw here.

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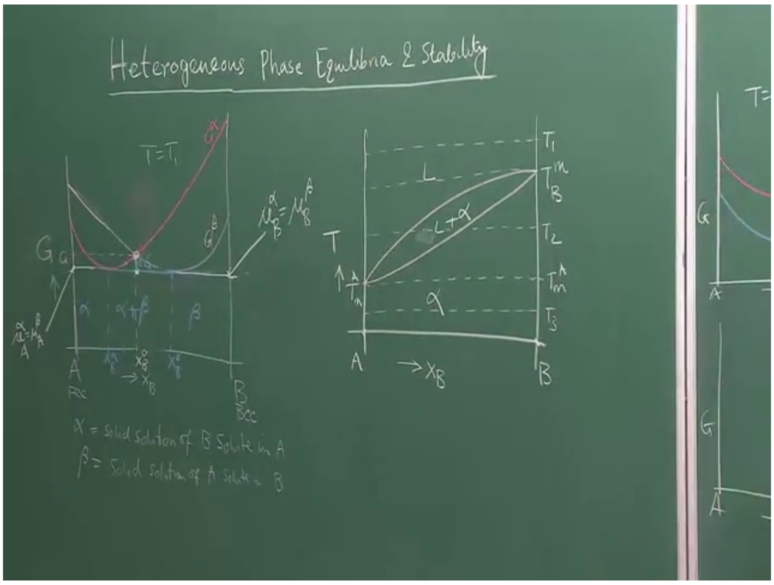

So, that you can understand; is the simplest possible phase diagram metallurgy or material science. Suppose I have two components A and B this is A reach; that means, this is of the A pure this point is A is 100 percent pure this point B is 100 percent. And B is increasing from this end to this end. So, therefore if I write in faction B is here 0, B is 1 here, A is here 1, B is 0, A is 0 there.

So, simple possible phase diagram will be will be like isomorphous system and this axis y axis all this temperature you should know that; temperature I then centigrade on Kelvin. So, let us now write it. So, let me just you know draw the phase diagram. So, phase diagram will be like a lengths. Here A has a lower melting temperature than the B, this are the melting temperatures A and B T m A, T m B and this is a lengths stable phase diagram, surprisingly liquid either solid solution alpha. And within the lengths we know both liquid plus alpha are stable. I am not going to spend any time on that, because this I discussed in my earlier course; as there in the books. Now, how do I explain thermodynamically, that there will be alpha sorry; alpha phase here liquid phase here alpha plus beta alpha plus liquid here.

so let us take free energy composition diagrams like this are different temperature. Let us suppose I take at this temperature T 1, I take at this temperature T m B, I take at this temperature T 2, I will take at this temperature T m A and I take at this temperature T 3. These are the horizontal lines just like a tie line of a phase diagram. So, I have taken 1 temperature above the milli temperature both that is T m B, and T m A that is a T 1, I have taken at temperature which is exactly T m B, I have taken a temperature in between the liquid plus alpha, that is T 2 take a temperature thermal temperature T m A and a temperature T 3 which is very low temperatures where only the alpha phase is stable at (Refer Time: 17:10) phase diagram.

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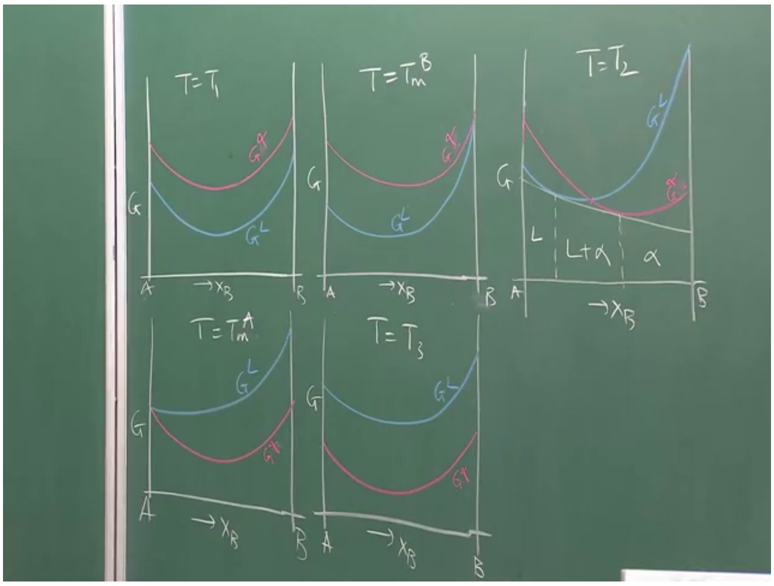

So, let me just draw this free energy composition diagrams; here on this board. So, how many diagrams will be there? 5 because 5 temperatures 1, 2, 3, 4, 5 this is also T m A. So, I will draw 5 diagrams, 3 at the top and 2 at the bottom. So, for each case this is free energy. So, G, G, G and this is A, this is B; well you draw any diagram you must be first leveling your axis; this is otherwise there is no point in showing the diagram. Though I am drawing at temperature T will be one first.

So, I have obviously, first thing I have to look at is that in this phase diagram there are only two phases possible. One is a liquid solution other one is a solid solution alpha. And we always put solid solutions as a Greek alphabet as to the phase diagram, why? Because these Greek alphabets are easy to use and also this be convention say starts with alpha go beta or gamma delta slowly one by one form in the Greek alphabets series. So obviously, at temperature T 1 its tells you that a liquid is the stable phase you can see here alpha is not stable at all.

So; that means, at all compositions from A reach to B reach alpha free energy curve will be sorry; liquid phase data will be lower. So, liquid I am drawing using a blue color liquid, and because liquid is the only stable alpha is not stable. So, alpha will free energy curves will be the higher position relatively; stability tells you whichever is the lower position that phase is most stable that is very easy very easy to understand there is no cross over; there will be no cross over because it is only the alpha phase is stable.

So, what happens then at temperature T equal to T m B, add the multi temperature of B you clearly see our liquid is stable all throughout except A tap at B and here there is a both the curves actually meeting liquidus and solidus so; that means, free energy curves will also meet at the temperature, because both must have it must be stable alpha liquid at the B end. So, that is only possible when; so I draw first the liquid. Now, I draw the alpha is stable all through except at the B reach end oops it is no something wrong this must be alpha.

So, I can clearly see at the B end only these two curves are meeting; that means, free energy of the solid alpha solid solution and the liquid l solid solutions are same value at this temperature, so because they are meeting only at the point. So, there is nothing there is no cross over only meeting point. So, there is no point in drawing common tangent. Now what happens when I draw a temperature T equal to T 2, that is the temperature between these two phase fields. So, what will happen let us see what happens? So, first; obviously, because both the phases are stable that must be a cross over as I told you from there. For the first diagram it is very clear that the cross over.

So, liquid and alpha so, liquid will be sorry this is alpha not liquid; and correct you have to raise (Refer Time: 21:54) otherwise it will not match. So, first let me draw with the liquid G L and I will draw now the alpha. This very clear the liquid stable at the beginning in the A reach end some part, then liquid plus alpha stable and then alpha is stable. So, that is why this cross over point here. So, now, once I have a cross over point I need to draw a common tangent, because I told you the reason for that just now. So, I draw a common tangent, and this common tangent will divide the whole region in to three parts

So obviously, this is liquid because you see the liquid free energy curve is a lower positions; this is again making mistakes this will be alpha again . So, therefore, this is add liquid and then again beyond these compositions alpha is stable. So, alpha and between this two the phase mixture of alpha and liquid stable; that is what you see in the phase diagram so; that means, it is very clearly sense you that in the temperature regime between T m beta and T m A, these two phase mixture will be stable. We will draw first the T m A then it will be much clear. So, at T equal to T m A, if I draw the free energy curves you can clearly see alpha is stable all throughout except that at the A end both liquid and the alpha phase the liquidus and solidus curves are meeting. So, let me just draw it.

Therefore, alpha is stable alpha will be always lower position and liquid will be always higher positions only at this point they will meeting, because at this point A point this two are this meeting so; that means, both solid and liquid is stable; that means, at the melting point of A both the solid and liquid will be stable; that is obvious and (Refer Time: 24:12) cells says it was ice and water are stable.

So that is means very clear from T m B to T m A only this cross over will take place that below T m A T m B and above T m A only this crossovers will take place and the reason, why? The because of that the alpha and liquid both will be stable. And this one last temperature which is T equal to T 3; obviously, all throughout alpha is stable. So, I draw it alpha and liquid this is opposite to this T 1 this positions of the curves so; that means, I by using with my free energy composition diagrams I can explain the phase stabilities in this phase diagrams.

So, few things you must remember one; that free energy curves are always inverted parabola that I explained you, why? Second, that relative position of the free energy curves will tell you the stability which very stables more; it will have free energy positions lower than the stable or not stable. Third whenever we have a cross over the free energy curves that indicate that there is a composition reaches range in which both the phases will be stable or all the phases will be stable rather it can be that 3 phase's curves will be crossing over.

So, then three phases will be stable also, but here because as very simple phase diagram easy to understand only two free energy curves of crossing over. So, crossing over means there is a composition range in which both alpha and liquid is stable. And four things will first remember; that these free energy curves must be done for one end to another end never ever leave in between.

Because, that is does not look good. Obviously, the free phase may not be stable from pure A end to pure B end, but free energy curves can be drawn, because we can relish obtained the free energy information's of free energy curves free energy functionals can be obtained and plot it. So, in a Nutshell, I just wanted to show you that how this free energy composition diagrams can be used for simple phase diagrams. Now in the next lecture, I am going to take you some more examples. So, that you feel more confident and you can yourself draw it.

So, that moment you draw yourself in a notebook; while reading listening to this lecture; you will have more confidence of doing that; because phase stability, phase diagram, phase stability and the transformation of the phases they all actually related to thermodynamics and kinetics. And thermodynamics is best explained in material science by drawing diagrams. And this is one such critical diagram, which you must learn very well.

Next we will do the eutectic phase diagrams that I will show you in the next class.