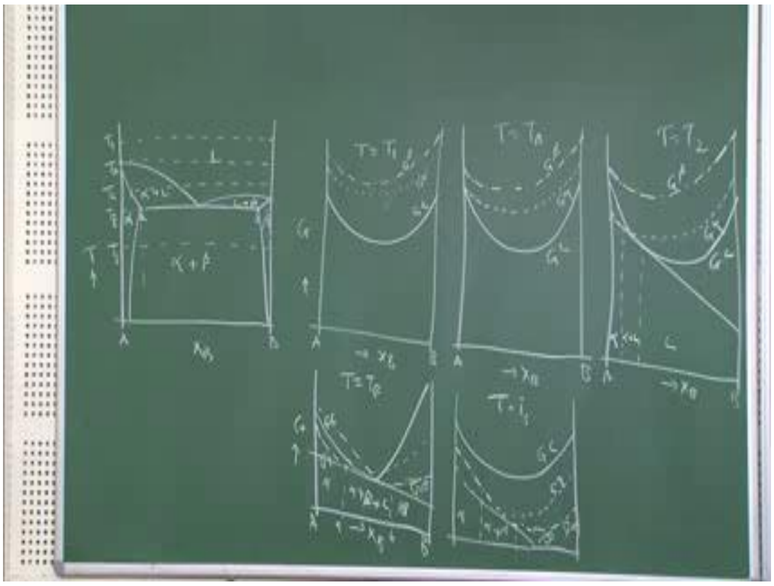
Phase Diagrams in Material Science Engineering
Prof. Krishanu Biswas
Department of Materials Science and Engineering
Indian Institute of Technology, Kanpur

Lecture – 14
Phase Diagrams of Binary Eutectic Two Terminal Solid Solution

Well, today is the last lecture on eutectic and I am going to talk abouT 2 important things here. First, I will talk about the free energy composition diagram for a typical eutectic phase diagram. Secondly, I will talk about the modification of a eutectic and the special emphasis will be on aluminum silicon eutectic.

So, you know that I have discussed three different types of eutectic phase diagrams, and I am going to take the most general one to give you how a free energy composition diagram looks like. And this is not the first time I am doing it here; I have done it for the isomorphous system in which I have shown you that the different free energy diagrams or free energies diagrams of different phases are plotted on a same curve as a function of temperature. So, at different temperatures we will draw it and show you. So, let me just to go to the board and show you how things will happen.

(Refer Slide Time: 01:29)



So, first I will draw a typical eutectic phase diagram with two terminal solid solutions. This is temperature axis; this is a composition axis; p o b and p o a and typical diagram will look like this. And for your information, this is the liquid, and this is the solid alpha, solid beta, these two are the two terminal solid solutions at A end and B end respectively, and this alpha plus beta, and this is alpha plus liquid, this is liquid plus beta. So, there are three two phase fields and three single phase fields.

So, we are going to draw the free energy composition diagram for these generalized eutectic phase diagram. You can draw it also very easily and as I show you the free energy composition diagram will be like this. It is G versus x b curve of all the phases present here at different temperatures. So, temperatures which we will select like this. We will select temperature like T 1, and this is T a, and then we will select a temperature here T 2. This is T - the eutectic temperature, and we will select the temperature at T three. These are all generalized temperatures, and basically, the way I have selected temperature is that, this will provide you different kinds of possibilities exist when you draw the free energy composition diagram.

So, what I mean to say is that at these temperatures, I am going to draw a free energy composition diagram, and show you that. So, what are these free energy composition diagrams? Let us restate again. These are actually free energy means free versus composition diagram at different temperatures, to show the relative dispositions of different free energy curves. What is with that? Suppose, at temperature T 1, I know that the phase stable is a liquid; all the composition from starting from p o a to p o b; now, to show that we need to draw the free energy composition diagram about liquid phase, solid alpha phase, and solid beta phase, and it is very clear. You have probably understood that because liquid is stable, all liquid is stable at T 1 temperature. So, the free energy of the liquid will be the minimum; the free energy of other two solid alpha and beta will be above that.

So, let us draw that. So, I will draw free energy of the liquid first, which is by a solid line. This is free energy of the liquid. And, I will draw the free energy of the two solid phases alpha and beta; let me draw it like this. So, I will draw by alpha one by a dotted line and I will draw beta one also will be by a different dotted line. So, this is G, this is G alpha, and this is G beta, right. So, you can clearly see the if here the liquid phase is minimum at all composition from prior A to prior B. Shape of the p energy it remains same; that is, inverse parabolic; it does not change, and I told you why it should not change, because this is a depends on the entropy and enthalpy, and both of them are functions of the x b square. So, that is why they look like a parabola. So, that is very clear.

So, but the message is that whenever you are drawing free energy composition diagram in a particular phase diagram, you need to draw the free energy diagrams for all the phase, whether at a temperature T 1 only liquid (Refer Time: 5:45) stable or not, that does not matter. What is important is to show you the relative positions on this free energy curve; that is very important.

So, let us now do with at T a. So, at T a, as you can see, I have already done it for you. Isomorphous system at T a what is that going to happen? At T a you can see here only at temperature A, temperature at A end - that is compositions x b equal to zero at the pure A end, the liquidus alpha and liquidus solidus of alpha meets. So, that means what? The free energy curve of liquid and alpha will meet only at pure A end; others it will remain same. So, again, I draw liquid. So, as I told you only at A end liquidus of alpha and liquid will so, AG or free energy alpha liquid will touch; that is what you see here; it will touch; and beta will remain higher. That is how it will look like; very simple. And, these diagrams actually as shown are obtained from this, by looking at the phase diagram that is why it is very easy to understand.

Now, I will do it at temperature T 2 which is also very easy. temperature equal to T 2; this is A, this is B, x b. So, at T 2 you can see this is the most complex situations. At T 2 there is a composition range in which pure alpha is stable; there is a composition in which alpha and liquid is stable; and there is a composition range in which liquid is stable. So, there are three - one, two, and three domains. So, one is pure alpha, alpha plus liquid, and liquid. So, how to do that? Whenever you have a two phased field, I told you that both free energy curves will cross over each other.

So, that means, free energy curve alpha and liquid will cross over each other. So, how they do it? First, let me draw energy curve of the liquid; and alpha, obviously, because alpha is stable at the pure A end. So, alpha will be coming down. Sorry, this has to be drawn dotted line; otherwise, you will be getting confused; let us draw it. So, this is G alpha and beta is not stable at all. So, beta will be coming much above, because beta is not present here. So, this is the beta. So, because these two free energy between alpha and liquid are crossing each other, the real stability will be obtained by drawing a common tangent between these two. So, let me just draw a common tangent like this. So, if I draw a common tangent, it will cross at the, it will cut the liquid curve here and the alpha curve there.

So, this clearly tells me, very simply, that this is the stability join of alpha; this is stability join of liquid; this is stability join of alpha plus liquid. That is what you see in the phase diagram - alpha is stable here for the small composition zone or from here to there or from here to there and then alpha plus liquid and then liquid. So, one thing you understood whenever you have a two phase field and tie line at temperature T 2 passing through two phase field, these two free energy curves will cross over each other. And this must be done, otherwise you cannot have the field the condition that chemical potential at both the pure A and pure B ends satisfy the things.

So, anyway, let us do at temperature equal to eutectic temperature. At eutectic temperature, T E this is the classic temperature at which things are different and distinct. What will happen? At eutectic temperature three phases liquid and two solid phases are at equilibrium. So, that only possible (Refer Time: 10:12) n, you have common tangent between all the three curves. Drawn at a temperature at a composition and equal to composition given by these phase diagrams, let us draw it.

So, I let me first, because at new temperature you can see here till this composition - this point, from this to this, the solid alpha is stable; from these to these, solid beta is stable; only in this part all three phases are at equilibrium. So, let me just draw solid alpha curve, and then I draw the liquid, cross over liquid will be like this, and then I draw the beta. Let me just put it; this is alpha; this is liquid; beta will be, this is beta.

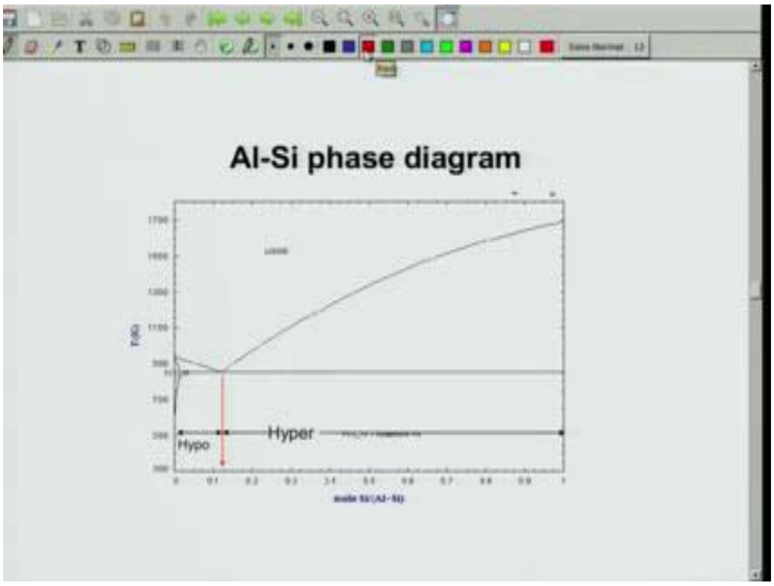
So, you can clearly see, although I have not been able to do properly, these three curves are common tangent to each other, and these two points which you see here - alpha plus liquid, beta - these two regions this is pure alpha; alpha is stable low as p energy; beta has a lowest free energy, in between three of them are that common tangent. So, therefore, this will be region of alpha plus beta plus liquid. That is what it is. Here alpha, beta, liquid - three figures are coexisting; that is why you can see there is a composition remain; this is stable; and these point - here - I can mark it a this is A, A; this is B. So, this is B on the phase diagram. O that is how it is done. So, therefore, add a temperature T all the three curves will be sitting in such a way that there you can draw a common tangent between them.

So, at T three, at T three it is not difficult, much easy. At T three liquid is not stable at all; at T three is at this temperature only alpha and beta are stable, but there is a two phased field alpha plus beta; therefore, alpha and beta, the free energy curves, will cross over. So, liquid will be above GL, and alpha, and then beta; beta is different. So, you can clearly see that alpha and beta are crossing about. So, there is a common tangent I can draw here between them. So, this is what is; this is alpha, this is alpha plus beta, and this is beta. Remember, this is G beta; this is G alpha (Refer Time: 13:29). So, you can always draw a common tangent between alpha and beta free energy curves, and then, you can show that the common tangent actually demarcates the regions the two phase region between the two single phase regions alpha and beta.

So, that is how actually the free energy composition diagrams for the eutectic systems are drawn. And I have shown you very clearly that this is important in the perspectives of understanding the phase diagrams and you can do it for other systems also.

So, let me just go back and start discussing about aluminum silicon alloy what will happen.

(Refer Slide Time: 14:15)



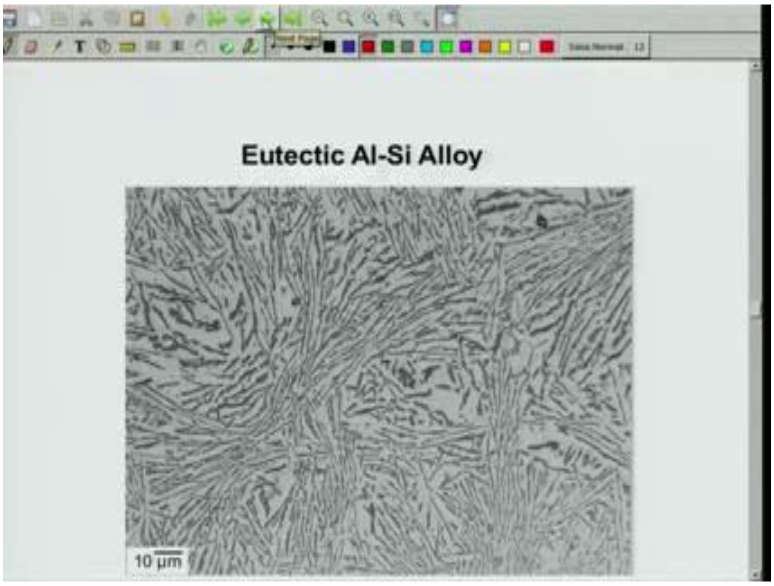
Al-Si phase diagram

And I told you that aluminum silicon is a very important alloy system, and this phase diagram is shown here, you can clearly see. It is classical phase diagram in a sense that there is a eutectic point here; there is a eutectic point at temperature; and composition is given by this; it is about 11.8 percent of silicon, and temperature is about 573 degree

Celsius, and importantly you have a single phase zone here; alpha - which is solid solution of silicon and aluminum, but on the right side silicon inside there is no such thing; it is a pure silicon.

So, now, I know that the alloys which are important for industrial applications are the hyper eutectic alloys. Alloys which have compositions less than eutectic - hyper ones are not very interesting, because it contains hard silicon particles that make the alloy very brittle, not used.

(Refer Slide Time: 15:12)


Eutectic Al-Si Alloy

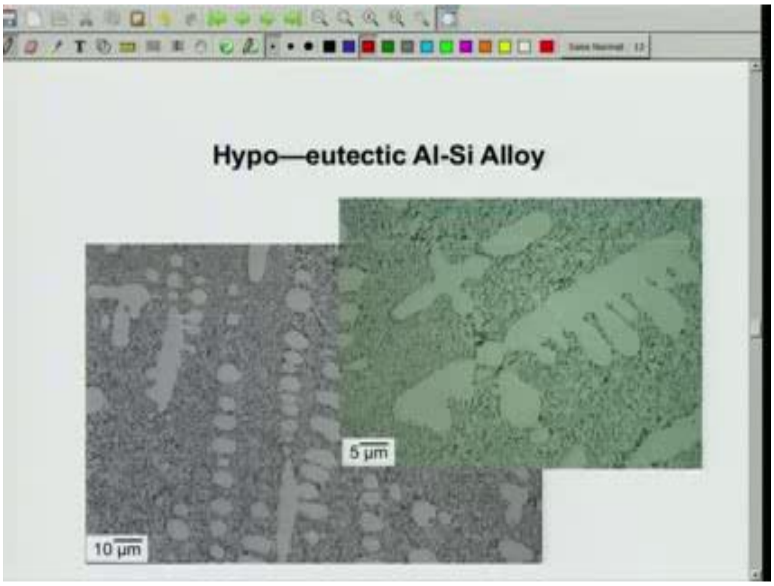
So, the next slide - this is the classical aluminum silicon alloy microstructure. I have shown you already. It contains continuous white aluminum matrix like thing, but it is not a matrix, it is specifically aluminum phase, and then you have a needle like silicon. Now, as I told you, silicon is very brittle. If I take a silicon piece, and just drop it on the floor, it will break shatter into pieces. And so, therefore, these needles are basically mixed alloy, brittle, not so good. So, we need to modify this microstructure.

And this is very important in a sense that you need a good machinability, good toughness, and ductility of the alloy when you are using it as an engine block for many of the car engines. So, then what is done, and this is suddenly pity in the metallurgy or metal (Refer Time: 15:58) that you had very small amount of sodium, strontium or (Refer Time: 16:04); and amount is very small; it is about point 1 percentage.

So, that means, that means if you use about 100 grams of the aluminum silicon alloy, you need about point 1 gram of sodium or strontium; sodium is Na; strontium is Sr or the (Refer Time: 16:23) metals or mixture of (Refer Time: 16:24) metals sometimes it is known as misch metal, m i s c h, misch metal. One, two, three; three different types of things are added or sometime together, sometime separately to modify the micro structure, to modify the silicon needles, and this has been discovered out of serendipity; nobody knew that it will happen; somebody probably had tried to add sodium into it, and then, found that microstructure do gets changed.

What is the change you see? Change you see is this. You can clearly see the alloy picture, this is 10 micrometer scale, and the needles are - silicon needles - are very big and quite thick also. On the other hand, if you had about point 1 percent silicon, the silicon needles become very fine, very very fine silicon needles become.

(Refer Slide Time: 17:16)


Hypo—eutectic Al-Si Alloy

Not only that, you also find some amount of aluminum which is alpha aluminum which is present in the microstructure. It is shown in the high resolution view here; you can see the micron values five microns now. So, you can modify the silicon needles or eutectic rather, very fine scale, and as you know it will make something very finer scale ductility and stability both improves. So, by making this is fine now we improve the ductility, we improve the toughness, at the same time we do not change the strength much. So, this is what you want, this is what the industry people what, they want a wonderful material which will be used for many applications, and that is what you see here, but you know that the important part is this - in all these microstructures you see presence of alpha aluminum dendrites; so, that means what? That means, this alloy is not behaving like a eutectic alloy; it has become a hyper eutectic alloy.

So, this particular phenomenon of modifying this eutectic microstructure, modification of the eutectic microstructure, from a course - this microstructure like this - to a fine one like this is known as modification in the literature, and this is routinely done in the industry nowadays. And this can be explained using free energy composition diagram, again, but I will not go into that details, but let me tell you what actually happens.

If you add sodium or if you add some amount of strontium or whatever it is – sodium, strontium or any misch metal or metals like that, they actually hinder the growth of silicon metals. Remember, silicon is a metalloid; it has its own growth problems; unlike other metals like aluminum, copper it cannot grow very nicely. It cannot grow nicely in the sense that when atoms actually jump and sit on the surfaces of silicon they cannot get attached along any plane; they need to be attached along certain twin boundaries, and I am not going to give details into those, because those will lead to, you know, different discussions deviating from the actual syllabus of the course, but you can read, these are very interesting.

So, sodium actually poisonous to the growth of silicon needles, sodium sits on the silicon needle and it has been observed that it poisons. Basically, it does not poison that, it removes the phosphorous; sodium, strontium, whatever is the elements they scavenge out the phosphorous in a melt, and if they scavenge on the phosphorous in the melt, the silicon cannot nucleate very easily. So, what is the scavenging out? What actually happens is that if I add sodium, strontium, or some misch metal into the melt, it reacts with phosphorous in the liquid which is present, and you may be thinking - where from the phosphorous come? That is a very good question. Phosphorous actually comes from a liquid itself; from the ore.

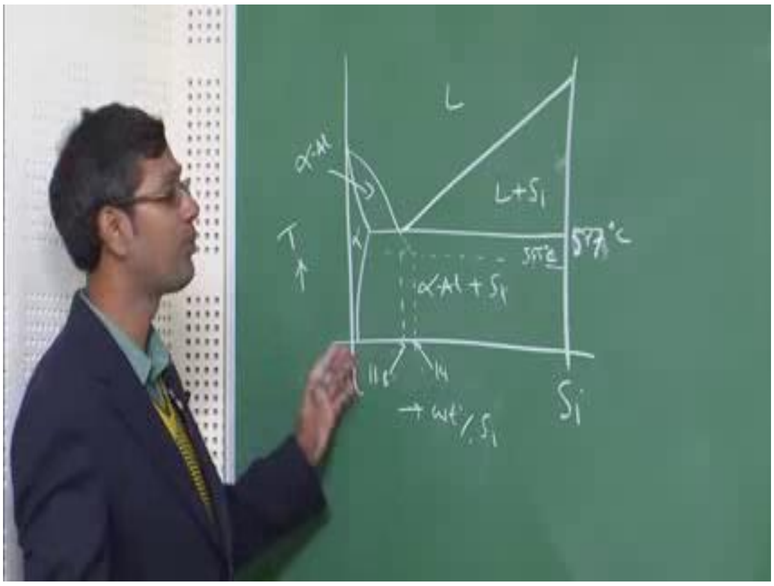
Aluminum silicon alloys whenever prepared we had the (Refer Time: 20:11) aluminum and (Refer Time: 20:14) aluminum will have lot of phosphorous into it, and this phosphorous actually for react with the aluminum from aluminum phosphate, and on the aluminum phosphate, silicon needles nucleate and grow and become very long. So, therefore, if I had sodium or if I had strontium, and this sodium is (Refer Time: 20:34) react to this phosphorous and remove the phosphorous from the liquid. So, that aluminum phosphate cannot form. If the aluminum phosphate cannot form, the silicon cannot nucleate on aluminum phosphate. So, therefore, the (Refer Time: 20:48) silicon is prolongated and this lead to very finer silicon needles in the microstructure. That is what you see here, very fine silicon needles are there; very (Refer Time: 20:59) structure. So, that is how things happen.

There are other theories also. In fact, to be frank, this this not completely understood in materials and metallurgical engineering - how actually things happen. The other theory is that in (Refer Time: 21:14) aluminum, you can have iron as long as the impunity in aluminum alloys. And iron within the aluminum and silicon can form iron aluminates - a l f e s i type of phase, and these a l f i s e type of phase, then can prolongate or rather make the nuclei system silicon difficult and that is why a silicon becomes finite.

Anyhow, let us forget about iron, let us only think about that in aluminum silicon alloy you have phosphorous present, and this phosphorous it reacts with the aluminum and form aluminum phosphate. And this aluminum phosphate helps in nucleation of silicon. That is why you have easy nucleation of silicon, and it goes very fast. But, whenever, you add sodium or strontium or other metals, it reacts (Refer Time: 22:01) as phosphorous removes the phosphorous from the melt, so that aluminum phosphate cannot be formed, and because of the silicon nucleus is difficult, I mean silicon is very difficult to nucleate, then it will not grow large, it will remain finer scale, and that is how thing happens.

This can be explained very easily using the phase diagram data. Let me just go back. Let me see whether I have it here. I do not have. So, let me just back and explain it using a phase diagram. So, what does it mean is that, if I have a problem in nucleation of silicon in a liquid, so what it will do? It will basically lead to more under cooling.

(Refer Slide Time: 22:45)



So, that means, if I have an aluminum silicon phase diagram like this, this is aluminum, silicon, pure, correct? Sorry. This will be up, this is silicon has a (Refer Time: 22:58) detector. So, this is silicon; this is x s I or mole fraction of silicon; this is aluminum; this is temperature; this is liquid; this is alpha aluminum plus silicon; this is liquid plus silicon; this is alpha aluminum; and this will be alpha aluminum. This is what is a phase diagram looks like.

Now, the moment you add silicon and this composition actually sits at 11.8. Let me remove this lesser point of silicon. I do it 11.8 percent of silicon and this temperature is something like 573 degree Celsius, sorry 577 degree Celsius, not 73. I hope you can see it carefully Celsius. It is that you get a temperature; you get the composition.

Now, the whenever I add sodium, sodium or strontium or some other metals to modify it, now what does it mean is that it the eutectic temperature and composition shifts to higher, composition shifts to higher, it becomes actually 14 percent. So, this is 11 - original one, 11.8 and this one is 14 at temperature with percent, and this temperature is 555 degree Celsius. So, that means what? If you make this silicon nucleus difficult, it requires for that 22 degrees of (Refer Time: 24:28). Difference between 577 and 555 is 22 degrees. So, this is and leads to change the eutectic composition to 14 atom percent. So, therefore, the eutectic alloy which was originally eutectic alloy now has become a hyper eutectic alloy. Is it clear? This becomes a hyper eutectic alloy, and because of this hyper eutectic nature, it forms high as alpha aluminum dendrites in the liquid. That is the how you see alpha element dendrites in the microstructure which I have shown you.

So, basically what it boils down is that, in a short way, that if you add sodium, strontium or something it basically makes the growth or nucleation and growth of silicon difficult. Physically growth of silicon makes it difficult, and that is why you need more under cooling, because you need to provide more energy to the system, and then, it becomes a high pure higher the, you know, this same alloy which was (Refer Time: 25 :28) aluminum silicon, when you add sodium it will become hyper eutectic alloy. And you get to see some lot of aluminum dendrites, and as you know, aluminum is actually very soft metal. So, therefore, aluminum dendrites will make this alloy soft, ductile, and tough. At the same time, as the eutectic has become final, it will also lead to high strength, and high ductility, and toughness. That is how actually want to explain the modification of a eutectic alloys.

With this I will stop the discussion eutectic. In the next class, I am going to discuss about eutectic reactions, and move over.