Phase Diagrams in Material Science Engineering

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Lecture – 11

Phase Diagram of Binary Eutectic Systems

Hello everyone. Today, we are going to start a new topic, that is, eutectic phase diagram. I think I have discussed about the binary isomorphous diagrams in detail and you have got a fair idea about the different facts of this phase diagram. You know, the binary isomorphous phase diagram, it looks somewhat like this.

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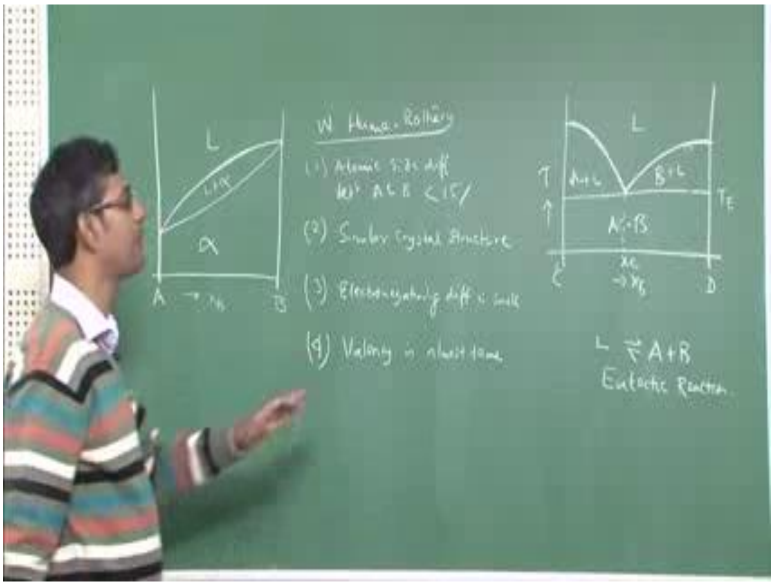

If I take a binary system A and B and plot (Refer Time: 00:46) composition and I get the phase diagram which looks like a lens. And this phase diagram has three zones - liquid and solid phase, and these two zones are surrounded by liquid plus solid or liquid plus alpha. Now, such a kind of phase diagram is possible only under certain conditions. And these conditions are very strict. So, first condition to be satisfied by the two components A and B is that the size difference or rather the atomic size differences between A and B should be less than 15 percentage. So, that means, the atomic size differences between A and B should be less than 15 percent. This is the first condition to be satisfied by the two components A and B for such a kind of phase diagram.

Second condition to be satisfied is that they must have similar crystal structures. Like A and B, so their cubic crystal structures with themselves or external crystal structures, similar means A can be f c c, B can be b c c or A and B both can be f c c or A and B both can be b c c or A and B both can be hexagonal, any other crystal structures by the way; like germanium and silicon both have diamond cubic structure. Then this (Refer Time: 02:19) both are (Refer Time: 02:21) other one is hexagonal crystal structures. So, they all form binary isomorphous phase diagram. So, similar crystal structure is the second condition to be satisfied; similar crystal structure.

Third thing to be satisfied is that the electro negativity difference between A and B should be very small. Why? Because if the electro negativity difference between these two components are very high, then there will be compound formation. Let us suppose sodium and chloride if you consider; sodium one component and then chloride in another component, then what will happen? They have huge difference in electro negativity. So, it will form sodium chloride structure. So, that means, electro negativity difference between two components must be very small - as small as possible to form isomporphous system. This is the third condition to be satisfied - electro negativity difference is very, very small.

The fourth condition to be satisfied is that the valiancy of these two elements or these two components should not be widely different. Like, suppose, consider element between, I will tell copper and nickel; the valiancy difference between these two elements are very small. So, therefore, valiancy should be similar or almost same. So that, you know, these are the conditions to be satisfied to form a binary isomorphous system. It is true for ternary system also, but for the sake of simplicity we have considered binary.

So, now, you know these conditions are developed by scientist known as William Hume Rothery, from Oxford University, long back. So, these are called Hume Rothary rules for formation of isomorphous phase diagrams or continuous solid solutions, but it is not possible always to satisfy all the conditions.

So, they are many elements which will not satisfy. So for those elements, there will be deviation from these phase diagrams and one such deviation is eutectic. What is that? If I consider a eutectic phase diagram, simplest one, between suppose a component C and D, it will look like this. This is again liquid, solid, alpha plus beta, they are two solids, and I am just marking I will explain everything to you. So, what is C here? C here is that obviously is liquidus air, the liquidus air is this line, this curve; here the liquidus is this one. And you can clearly see that liquidus has a dip at the certain composition which is given by this, at a certain temperature which is given by this.

This is, as basically this kind of dip if it is present in the phase diagram, we call it as eutectic phase diagram. Why we call it eutectic phase diagram? Because if you have this kind of dip as a temperature equal to T e composition X e, so that means, at the temperature liquid undergoes a reaction during cooling leading to combination of two solid phases. Here it will be A and B. This will be A and B. Let me write down, otherwise you will be getting confused, because these are two pair components, therefore A and B. Please make this correction, liquid into A and B.

As this kind of reaction will happen, it will cool down from high temperature to low temperature through this composition. So, liquid will separate into solid phases A and B and this is known as eutectic reaction. This is known as eutectic reaction. And eutectic means easily meltable; in the Greek literature eutectic means easily meltable; that means, anything which melts very easily is known as eutectic. Why? Because if you look at this diagram this composition at X e melts at temperature T e but any other alloy composition will melt at high temperature. If I consider this alloy, the melting temperature of this alloy is this, and this alloy melting temperature is this which is higher than T e. So, that is why it is called easily meltable. It melts very easily at low temperature. So, it is called eutectic.

So, you understood that from this diagram, which is our isomorphous phase diagram, if these conditions are not satisfied, then we do not take this type of phase diagrams, whether we get deviations from these phase diagrams, and one such deviation is this which is given here; this deviation is the eutectic one in which there is a dip in the liquidus temperature, and the dip corresponds to eutectic reaction which is given by liquid into A plus B. So, I hope this is clear and this is type of phase diagrams are known as eutectic diagrams in the literature, because eutectic means easily meltable. That is why it is known as eutectic phase diagram.

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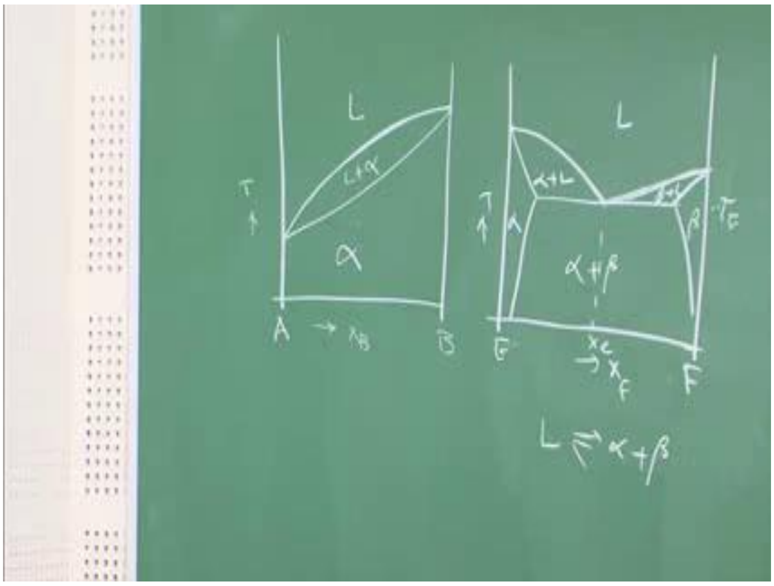

So, now, the most general eutectic phase diagram will be like this. We will discuss each of this separately; do not need to worry about it. The most (Refer Time: 08:26) one will be like this and it will have again a dip in the liquidus temperature. This is the liquidus; this is the dip. The difference between this and this is that there are two phased field. So, these are not A, B; these are like E and F. x f. The difference between these and these are; there are two phased fields at the ends - end corner - at the e reach and f reach part given by alpha and beta. This is obviously liquid. So, therefore, this will be given by liquid plus alpha and this will be given by beta plus liquid, and then, we have a phase field between beta and alpha, alpha plus beta. So, here again the eutectic reaction is given by, this is T e, here this is X e; eutectic reaction is given by liquid into alpha plus beta. While cooling, while heating this will melt like this, but we are not interested while heating, we are only interested while cooling.

So, this diagram will descend into this and from there you can get into this. That is what actually the most common - phase diagram in binary phase eutectic phase diagram in the literature you will find.

So, I just explain in detail binary. Here you have one, two, three, two phase fields - liquid plus alpha, beta plus liquid, alpha plus beta; and one, two, three single phase fields – liquid, alpha, and beta. Here we have one, two single phase fields; and one, two phase fields. So as compared to this we have three single phased fields here, and three, two phase fields here. On the other hand, here we have three two phase fields and only one single phase field, but anyway from there to here the most important increase is the number of two phase fields, alpha plus liquid plus liquid alpha plus beta it is three, here it is one. So that is the major difference from binary isomorphous to the binary eutectic systems.

Second important difference is that in this system we have a reaction, whereas there is no such reaction happening here. Here liquid slowly becomes solid alpha, but here, in this case, liquid undergoes a reaction and produces two alpha simultaneously; please remember these words – simultaneously. Liquid transforms to solid simultaneously and these two solids coming together leads to different kind of micro structures, different kind of micro structure features that we see, going to see, today itself. So, my basic point I want to stress upon is that, because of this reaction we have a large number of different kinds of micro structure development; whereas, here we do not that many. So that means, it gives you many opportunities to control the micro structure by this reaction, which we do not get in the isomorphous system. So, let me just get into the different kinds of phase diagrams and tell you how it is possible.

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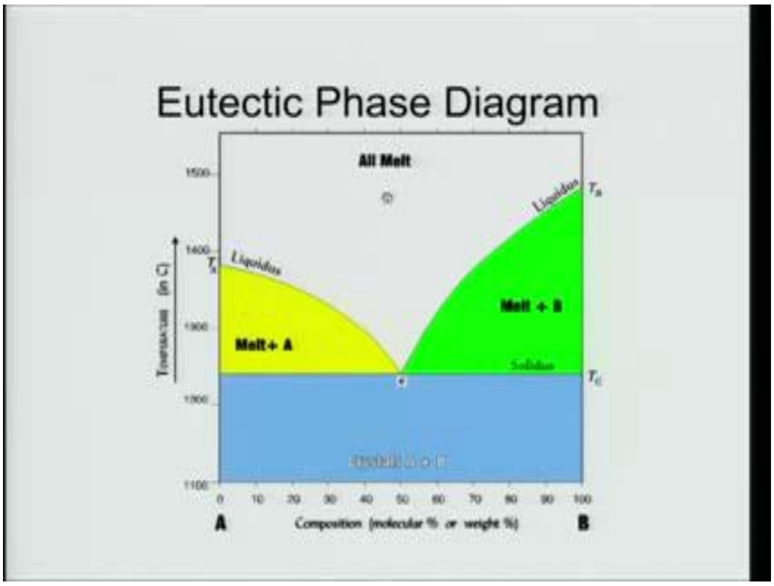

Eutectic Phase Diagram

So, this is the diagram I just discussed right now. This is the diagram I just discussed right now. You can see here this is the simplest possible diagram in which A and B are two components, it can be anything, and this y region is the fully liquid region, and then, you have liquidus - these two are the liquidus, one coming down to melt temperature p o a other one coming down from melt temperature p o b, and they meet at a temperature at a concentration e; they meet at concentration e and temperature T e; that is why we will take the temperature (Refer Time: 12:31) composition and same for these yellow color phase liquid plus A or melt plus A; on the right side, green color, it will be liquid plus B; and you have at the bottom, below the eutectic temperature, you have crystals of A and B or rather A plus B.

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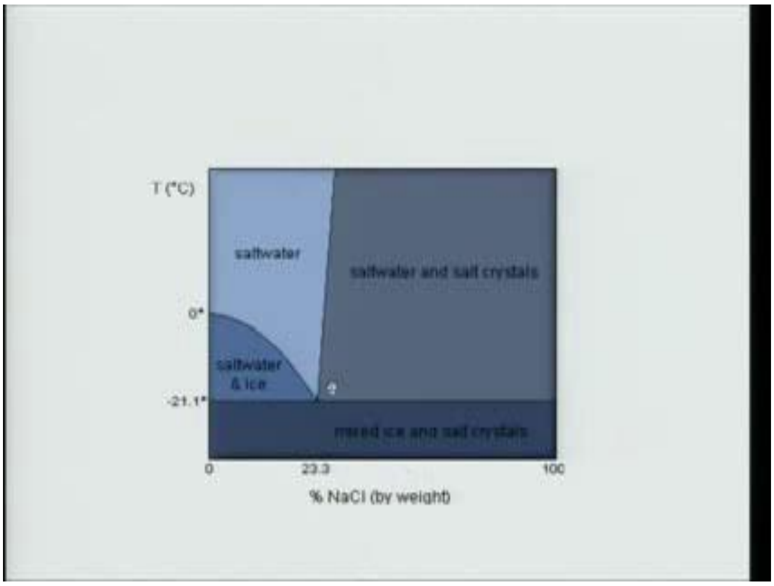

This is the common phase diagram between sodium chloride and water, where it has very interesting implication. If you look at this diagram, eutectic temperature for sodium chloride and water, this is pure water; this is pure sodium chloride; right side is pure sodium chloride; and you can see as you keep on adding sodium chloride at about 23.3 percentage of sodium chloride concentration, you have a dip in the liquidus, and this dip corresponds to eutectic temperature which is given by minus 21.1 degree Celsius. This is the reason in the northern hemisphere, when there is a snowfall, in order to melt the snow, people add sodium chloride. Why? Because snow normally melts or ice normally melts at 0 degree Celsius or above, but if you add sodium chloride into it, the melting temperature goes down to minus 21 degree Celsius temperature.

So, that means, you can easily melt down the ice or snow by adding sodium chloride and you can understand these things by using eutectic phase diagram. This is the beauty of eutectic phase diagram at a concentration of sodium chloride 23.3 weight percentage, at about minus 21 degree Celsius temperature; it forms a eutectic reaction in which salt water while cooling transform into mix of ice and salt crystals. So, that means, if I heat it up beyond 21 degree temperature, mixed ice and salt crystals, they will become water. So, that is what you want. You normally want to melt the ice in the northern hemisphere when there is huge snowfall. So, you sprinkle sodium chloride or common salt into the water.

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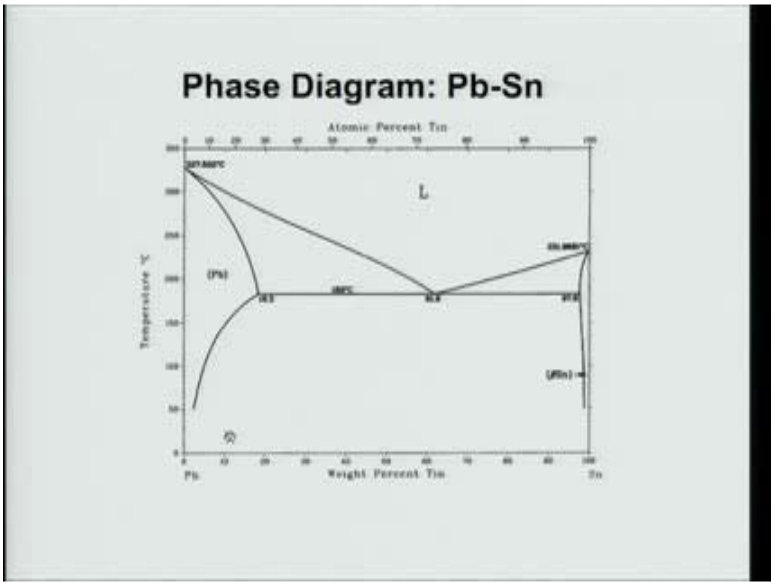

Phase Diagram: Pb-Sn

Now, the most common phase diagrams or the second one which I discussed in the board, in which there are two end phase fields: one is alpha, one is beta is the lead-tin solder. Lead-tin is a very classic example of eutectic system. Why? Because lead-tin alloys are used to make solders in any kinds of device you want to make, whether it is a computer, it is a mobile phone or anything; the soldering element is lead-tin alloy. And if you look at this phase diagram, lead-tin alloy at about continuous 61.98 percent of tin, it melts at 183 degree Celsius temperature, this is the melting temperature. So, that means, it melts at a much lower temperature, we can easily join or solder two pieces of coil or cable in electronic device. That is why it is widely used as a solder material in the electronic device and it is very important.

So, now this is a classic eutectic phase diagram, the second type I showed you, where we have a two ends; one is a lead region, other is the tin region; you have a lead, solid solution known as alpha of p v within first bracket, and on the right side you have beta team solid solution within bracket first bracket beta team or beta whatever will be fine. Anyway, by the way, tin exists in two forms alpha and beta, and this transformation happened at 281 degree Kelvin, and this is a very important phase transformation for many of this historical perspective, which I will discuss maybe later.

So, these are the two ends, which are solid solutions just like either we have isomorphous systems, and between that we have a binary, we do have a binary eutectic phase diagram existing. So, therefore, these phase field, which I am showing here, is basically liquid plus alpha; this one is liquid plus beta; and this one is alpha plus beta; alpha is lead solution, beta is steel solid solution.

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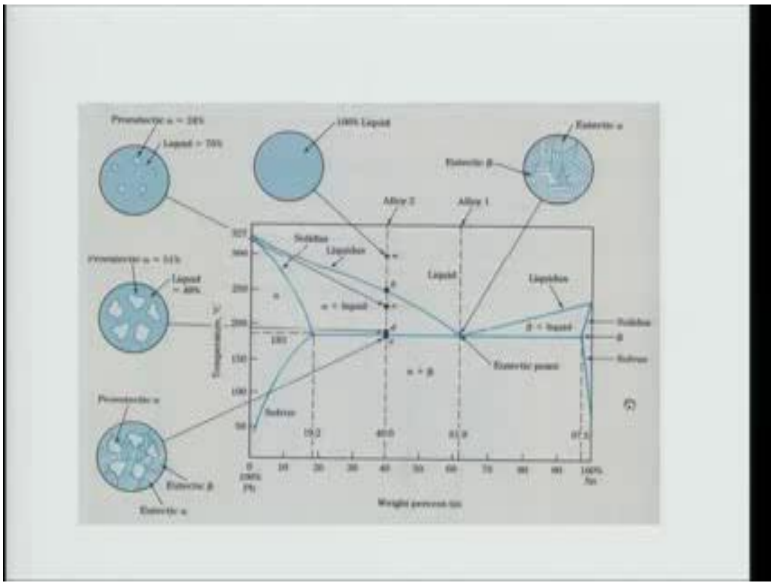

So, now after knowing this, let us now discuss little bit more, and because this is a very important and I must go back to board, and explain you from the start. So, as you see here, I put the phase diagrams, nicely. So, now, let us consider and apply phase rule - Gibbs phase rule here.

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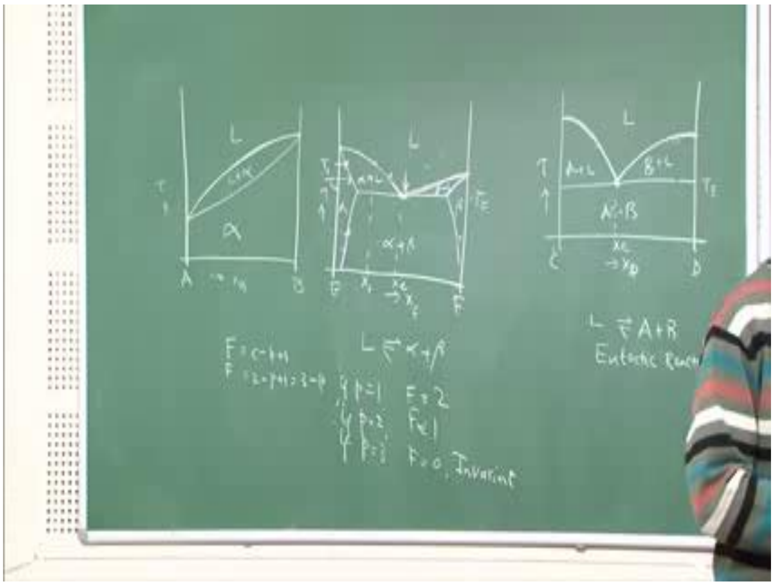

I know that Gibbs phase rule is given by f is equal to c minus p plus 1, when pressure is kept constant and that is why one comes. Remember, when the pressure and temperature, both are varying it will be two. So, c is, small c, is the number of components, this is the number of phases and F is the (Refer Time: 07:20). So, here c is equal to two because it is a binary system. A, B or E, F or C, D - there are two components. So, there are two components say two plus minus p plus one is basically three minus p; that is the value of f. I hope it is clear. c is the number of component – two; p is the number of phases.

Now, let us apply this in single phase fields of these binary eutectic systems. There are three: alpha, beta, liquid. So, we have a single-phase field, that is when p is equal to one, if p is equal to one, then f becomes three minus one, two. So, what does it mean? I explain you in this case; that means, I have two degrees of freedom; that means, I can vary both temperature and composition, but I will not be; I will be in the same phase field. You can take any point here, you can buy the compositions or you can buy the temperatures like this, but still you are in the same phase field. So, that is what is the case for again alpha and beta. Same thing will happen between alpha and beta phase field.

Now, if p is equal to two, what will happen? F is equal to 1, c minus p; 3 minus 2 will be 1. If F is equal to 1, what does it mean? That means that there is phenomenal to one. So, if I go to the two phase fields, suppose alpha plus beta, let us do it for alpha plus liquid. Suppose, if I go here, now if you can see that if I choose a composition, supposed it is a composition x one. So, now, I can clearly see that at x 1, at any temperature t 1, my composition of solid and liquid are fixed. Similarly, at mean temperature t 2, my composition of solid and liquid are fixed. These two are; this is a third line connecting solidus and liquidus; solidus composition will be like this, liquidus composition will be like this. I have explained you already at the (Refer Time: 19:19) temperature which connects the two solidus and liquidus, the cross-section points will be the composition of solid for the solidus and liquid for the liquidus.

So, what I mean to say is that if I choose a composition, a composition I choose, I do not have any freedom of choosing the temperature, because composition of the solid or liquid are given. Or if I choose a temperature, suppose this one, t two, composition of solid and liquid are fixed. So, either way I have only one freedom. I can either choose a composition or a temperature, I cannot choose both of them together; if I choose, then I will be getting out of the two phase field. Now, the classic thing will come, and this is the same thing for alpha plus beta. I will choose a composition, this arises the temperature.

You can see here the compositions are given by these two lines, and if I choose the composition also, the temperatures are given, the temperature will be fixed. But classic thing will come if I consider pressure to be p to be three; if p to be three means f is equal to zero; p means number of phases, the number of phases of two; that means, you have basically three phases present, and degrees of freedom will be 0. What is that corresponding to? That corresponds to this point. At this point I am marking an arrow. At this point all the three phases – alpha, beta, and liquidus coexisting, and that is why p will be three. So, that means, at this point I have no degrees of freedom. If I simply change my temperature little above or below, I will be out of this point; and if I change the composition, it will be this way that way; I will be out of this point.

So, question is this - that this point is having degrees of freedom equal to zero and known as invariant point. I cannot vary anything here - invariant point. So, that is the definition of an invariant point; the invariant point here, no degrees of freedom. Here only zero degrees of freedom. Remember, in any reactions which involves three phases whether it is liquid going to alpha, beta, or any other phases, you have no degrees of freedom present; you have only zero degrees of freedom present. This is a very important concept as far as the (Refer Time: 21:39) phase is concerned.

So, you can actually apply phase rule here itself, here also at on this point if degrees freedom is equal to zero, and in these two phases field, degrees of freedom is equal to one, and single phase field, degrees of freedom is equal to two. So, therefore, as compared this, you have a one extra point, that is the eutectic point. At the eutectic point, you have degrees of freedom is equals zero. In this binary isomorphous diagram nowhere your degrees of freedom can be zero. So, we start seeing these isomorphous diagram to be zero only from eutectic phase diagram; that is what you should remember in your, all your lectures.

So, now, I think I will now discuss about the phase formations, and before I do that, because we will discuss in detail in the next class, before I do that, let me just tell you that this particular phase diagram which I discussed – lead-tin, there are three types of alloys to be present or discussed. The one which is made one, alloy one, is eutectic alloy. So, we will discuss the eutectic alloy first. And there are alloys whose composition is less than eutectic composition; that means, between these point - this is one point of the these horizontal lines - and the eutectic point, these are called hypo eutectic; hypo means less than eutectic. On the other right side ones, from 61.9 to this point to 97.5 this is called hyper eutectic alloys; hyper means more. So, that means, if I have to discuss the solidification or the (Refer Time: 23:17) of these alloys, I should consider one hypo, one eutectic alloy, another one hyper eutectic alloy.

So, this is the end of this lecture. In the next class we will discuss about the (Refer Time: 23:31) of these alloys, which are marked here in this diagram in detailed manner.