

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

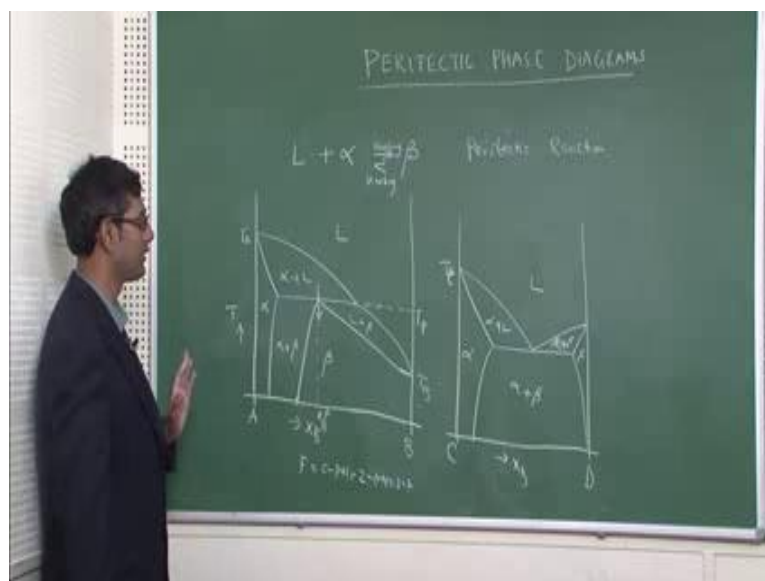
Lecture – 15
Phase diagrams of binary peritectic System – I

Well, today we are going to start on a new topic, that is, on the peritectic phase diagrams. And, as you know peritectic alloys are equally important like eutectic alloys. And, let me give you few examples. The copper and zinc, the classical brass is a peritectic alloy systems. There are about more than five peritectic reactions present in the (Refer Time: 00:40) copper and zinc system. Similarly, bronze, copper and tin in an alloy of, has peritectic reactions. Similarly, many industrially important are alloy.

Let us think of iron and carbon, classical steel has a peritectic reaction. And, peritectic reactions for the steel is, lies very low carbon concentrations as about point one three percentage of carbon; so that means that peritectic reaction is very general in the phase diagrams. And, many ceramic systems also have peritectic reaction. Like all the super conducting material, many of these have a peritectic reaction present. That is why it is very important, so that we understand the peritectic phase diagram and the solidification.

In the first lecture, I will just try to explain the phase diagram. And, show you how the things happen.

(Refer Slide Time: 01:40)



So, a classical peritectic reaction is given by liquid reacting with solid phase, giving rise to another solid phase. This is a peritectic reaction. This is very important reaction because most of the things (Refer Time: 01:57) depends on this reaction. So, please try to understand that here one liquid phase reacts with another solid phase; one solid phase leads to formation of another solid phase. Sometimes, it is written like this. There in cooling, it will form beta; there in heating, beta will disassociate into solid and liquid.

So, this kind of reaction can be represented in a phase diagram, in this way. Again, I draw the composition (Refer Time: 02:35) pure A, pure B and temperature. Ok. So, this diagram is completely different from eutectic. In eutectic phase diagram, you have seen there is a dip at the center. Here, it is not present. So, this is pure liquid; this is the melting temperature pure A, melting temperature pure B, alpha. This is alpha plus liquid; this is beta, alpha plus beta and liquid plus beta.

So, you can clearly see again there are three two phased field; liquid plus alpha, liquid plus beta, alpha plus beta, and three solid phase; liquid, alpha, beta. Same like eutectic systems. But, the diagram is completely different. In fact, this is not easy to draw. Sometimes, students face difficult in drawing the phase diagram. So, I, for generalization I am just drawing the phase diagram or eutectic here, so that you can keep it in. You can keep it here. This part you can send. This part varies, and there is a dip in the center. This is between C and D. So, you can clearly see the difference. It is not at all looking very similar. Rather, it is (Refer Time: 04:25) defined.

So, these kind of phase diagrams actually (Refer Time: 04:32) for systems, when you have a large difference in melting temperature between A and B. As you can see here T A is here, T B is there. Melting temperatures of A and B are large differences. So, whenever you have such a kind of large difference of melting temperatures, and interaction between A and B, which will come, which we will discuss later, is strongly negative. Then, you have this kind of phase diagram formations.

Let me just discuss about this phase diagrams in a little detailed manner. Here, the peritectic reaction happens at a temperature known as T P. This temperature and reaction is taking place here, in which alpha plus liquid reacting with each other and forming beta. This is where. So if you cool down this one, the way I have drawn the arrow, alpha plus liquid or liquid plus alpha, whichever way you say, reacts with each other and forms

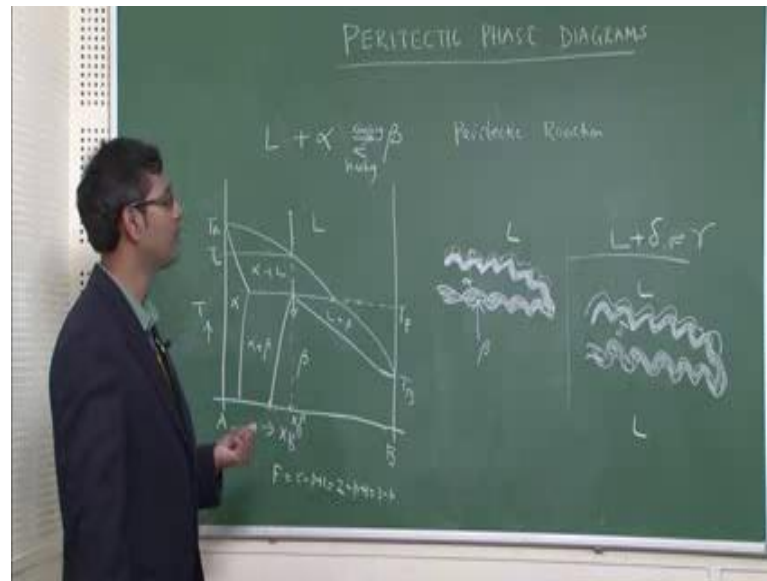
beta. This is where the reaction takes place. So, this is a horizontal line.

So, I told you; as I taught that any horizontal line in the phase diagram will give you the idea of phase of the reaction or some kind of reaction, at this temperature T_P or the composition given by test, which I can draw. This is X_B ; $X_B P$ is reaction happens. So that means, at this temperature T_P and composition X_P , an alpha liquid and beta, three phases are equilibrium. So, therefore degree of freedom here is 0. Why does a freedom has zero? Because we know degrees of freedom is given by $C - P + 1$. And, here there are two components. So two, C is two, $P + 1$, so three minus P . So, if there are three phases present here, so three minus three, P is three, so it becomes zero. So, degree of freedom is 0, at this point.

Now, similarly in the two phased (Refer Time: 06:37) where you have two phases alpha plus beta, alpha plus liquid beta plus liquid, degrees of freedom is equal to one. And, in the single phased field like beta liquid alpha, degrees of freedom is equal to two. You remember; you should remember that; same thing here also. The use of freedom at this point is zero. And here, they are, their degrees of freedom is equal to one. Other hand, in the alpha and beta and liquid regions, degrees of freedom is equal to two. So, there is some similarity between these and these, but the inside diagram is completely different from the eutectic one.

So now, upon knowing this, peritectic reaction is distinctly different from the eutectic. In eutectic reaction, two solid phases come out from the liquid. Here, one solid reaction in the liquid forms another solid. So, therefore this reaction is completely different. Now, I will tell you why it is this reaction is completely different. So, let me just rewrite it again. You have a peritectic reaction isotherm at temperature T_P , composition $X_P B$, in which liquid react with alpha giving twice the beta. Now, how does the reaction happens? Suppose, I have alloy which is solidifying this composition $X_P B$ public (Refer Time: 07:56).

(Refer Slide Time: 07:57)



So, I am drawing this vertical line and I am following it up. So, yes, if I am cooling it down from liquid, this is my liquidous L , T_L . Above liquidous, everything will be liquid. Only below the liquidous, alpha will start forming. And, alpha will start forming and alpha will grow like a dendrite in the liquid. This is alpha in contact to the liquid. In this temperature between T_L and T_P , alpha will go in the liquid like a dendrite. That is because this is the most easily formable shape possible in the liquid state.

Now, when a alpha, when the temperature of this system will go down below the T_P , alpha and liquid will react. And, if they react they will form beta. How the beta will form? Beta will form on the, at the interface between alpha and liquid like a layer. So, this is the beta layer, which will form in between alpha and liquid.

You can clearly see I am marking like a white chalk, using white chalk. This white layer is beta; which has formed because of reaction between alpha and the liquid. So, this is beta. So, this beta which is formed on the alpha will immediately stop the reaction. Why because as soon as the thin layer of beta forms on the alpha, the contact between alpha and liquid is gone. There is no contact, direct contact between alpha and liquid. So, any further increase of thickness of beta is not because of the peritectic reaction, but by peritectic transformation. What is that? Well, let us little bit do well on this matter.

So, as you see here as, so I have formed a thin layer on the top of alpha thin layer, so between liquid and alpha. So, any kind of contact, direct contact between alpha and

liquid is not there. For a situation, for the reaction to proceed or reaction to go further, atoms in the alpha has to diffuse through this; has to diffuse through this layer of beta and come in contact with the liquid. The reaction is only possible, when there is a contact, otherwise reaction is not possible. And, here it is a liquid and solid. So, therefore direct contact is required. When there is there are no direct contact, all the way it is possible is that atoms in a solid alpha will diffuse through the layer of beta, come in contact with the liquid. And, when it comes in contact with the liquid, it forms another layer of beta, suppose this is the layer where a beta forms.

So, as it forms another layer of beta, the thickness of the beta will increase. So, if any, for any further reactions, atoms in the alpha again has to diffuse through this whole layer, come in contact with the liquid. And, the diffusion distance is time; is increasing. Why because thickness of the beta layer is increasing. As the diffusion distance in this increase, the time requires also increase; because diffusion, you know that distance is equal to \sqrt{Dt} , where x is the distance, t is the time and D is the diffusivity. So, as you increase x , these remaining constants same, time t increases.

Therefore as the time increases, you need more time for the atoms to diffuse from alpha to come in contact with the liquid. And after sometime, this time will be very large. So, therefore no further diffusion is possible. And under such situations, you will always have some leftover alpha in the microstructure, which you cannot help. There will be always some leftover alpha present in the microstructure because incomplete reaction, this is the problem with all peritectic reaction.

Peritectic reaction under normal cooling conditions will never get completed. They never get completed. And so, that is that creates problem in the industry, which we will discuss. One or two case studies we will discuss in the whole class in one of the classes. Where I will show you that returning this phase alpha, which is known as, which is this phase at a temperature lower than the (Refer Time: 12:26) temperature can create lot of problems in the properties of the material.

So, as you see here alpha is known as pro eutectic, pro peritectic phase that is like eutectic. I discuss pro peritectic phase; because it forms before the peritectic reaction, and beta is known as the peritectic phase, and because it forms after the peritectic reaction. So, you will have always eutectic, peritectic phase alpha retained in the

microstructure because of incomplete reactions of peritectic reactions of this kind. So because of this, it can create all kinds of problem as I told you.

Suppose, I generally just explain to you, the peritectic reaction, which is present in the iron-carbon phase diagram. Peritectic reaction based on iron-carbon can be written like this; liquid reacting with delta iron or delta rather, reacting with liquid and produce gamma. As you know that iron has three phases' alpha, beta and delta in the normal pressure, and, delta is BCC phased which is your iron and gamma is a FCC iron, alpha is also BCC phased.

Now in this reaction liquid plus delta going to gamma, same thing will happen. And, I will draw it again here. So, I have a delta dendrite coming in contact to the liquid. And as the reaction happens, this reaction happens at 1394 degree celcius temperature. As the reaction happens, you can see here that gamma will form like a layer around delta. This is gamma, so better to mark like a chalk, gamma. And as time goes, gamma layer will increase one by one. But, it cannot consume full delta. So, you cannot consume the full delta. Delta will retain. Delta will remain rather, in the microstructure. And so another; as you give more time, another layer of gamma will form. But, you know delta will retain because of entropic nature of the reaction.

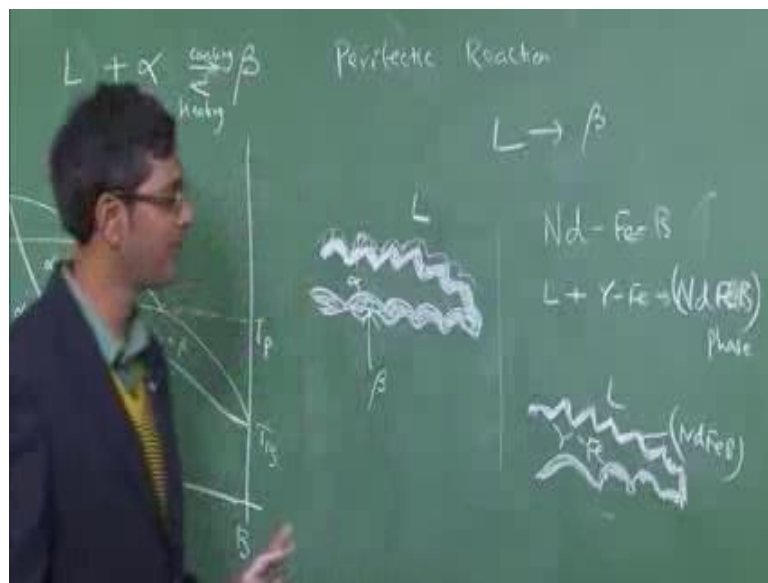
Now, suppose this whole microstructure is solidified and you are retaining it at your room temperature. At room temperature delta is not stable, but gamma is stable. Gamma will retain. They remain there. Delta or gamma is also not stable in here. But, gamma will undergo the other reaction to form paralite. Anyway, but delta is not stable at room temperature. Delta will form alpha iron at room temperature. Or, it may not form because of pressure effect. Whatever it is, this has, this will create a lot of problem in the final properties of the material because you ultimately, finally the steel what you want is alpha as a primary phase and paralite. You do not want anything else for the normal steels.

So, you can see here. This steel, this happens only with very low carbon concentration in the steel. And because of very low carbon concentration steel, these categories of steels are basically stainless steel. And therefore, this is very critical problem in a stainless steel. In all stainless steel, you can have this problem. And, infact there are other stainless steel containing the iron, chromium and nickel, then carbon. So, therefore there actually chromium can segregate and reacts with carbides and form chromium carbides. There is

another additional problem, which we will discuss later.

But from the perspective to peritectic reaction, you understand that this can create problem. Another example, I will give it to you which are very interesting. All the headphones, nowadays used for IPod, iPad or mobile phones have this very small magnet into the headphone. And, these magnets are actually very strong. And, most of these magnets come from China. And, China has the largest source of that material. And, that is why they have the monopoly. Almost, 96 percent market share is by China.

(Refer Slide Time: 16:39)



These magnets actually are this type; it contains neodymium, iron and boron. And iron, boron, most of the countries has. What you do not have is a neodymium. Neodymium is a rare earth metal. So, these alloys actually, these alloys actually undergo eutectic, peritectic reaction; liquid with gamma iron reacts and form a Nd Fe B phase. This alloy forms. Remember, this is the magnetic phase. All the speakers actually had magnets, which we used to listen music or listen and all kinds of other things. So, like we can use for other purpose also. There, this is the magnetic phase; this is the hard magnetic phase.

If you want to use, increase this strength of that you want to have more of this phase. But, as you here because of this peritectic reaction, you will have form gamma phase present; gamma iron, liquid. And then, this phase will form on the layer between gamma and liquid like this. But, as an engineer what do you want? You want this because the hard property, hard magnetic property is provided by this. This is what is this; Nd Fe B

phase. OK, Nd 12 Fe B actually.

So, because of that you want to have maximization of this particular phase in the microstructure. So, this will give you more energy product or stronger magnets, hard magnets. But, it will never happen because by peritectic reaction, there will be some gamma leftover. And, this gamma will create problem; because if this gamma actually (Refer Time: 18:30) room temperature will transform to alpha iron. And, alpha iron is a soft magnet. So, if you have a, you know, soft magnet inside this center of the hard magnet, this will reduce the strength of the hard magnet.

So, therefore there must be some solution to that. So, what I am telling you is that peritectic reaction creates problem in the industry actually. All this peritectic reaction like a stainless steel, I told you or in magnets, it creates problem. And, the main problem (Refer Time: 19:01) form is nature of the reaction. The reaction is such that it can create problem, which you have to deal with it. And that is why it is important to understand the peritectic phase diagrams very nicely. If you do not know the peritectic phase diagrams very nicely, you cannot control.

To give you a hint; because those of you who are intelligent enough or able to understand my lectures nicely, you can actually bypass this peritectic reaction. What is the minimum bypass? Which I will discuss detail in my next class. But, I am just giving you a hint. You can actually directly form beta from liquid, instead of alpha; that means, you can actually, you do not need alpha to form beta.

In normal classical peritectic reactions, you need alpha to form beta. Liquid is anyway present in the microstructure in alloys. So, you do not need alpha to form beta. So, you can actually directly go from liquid to beta. If this is possible, if this I can do it by under cooling the alloy, what will happen? Because there is no gamma iron present, liquid (Refer time: 20:06) Nd Fe B phase form on the liquid. There is no soft phase at the center of the obvious magnet, of the hard magnet. And, we can produce harder magnet.

This is the technology which is been mastered or which is been rather developed and mastered by the people in the world, especially in China. And, that is why they could make very strong magnets. And, those magnets actually are very useful and can be utilized for many applications. That is what is done normally in all the things. If you under cool the liquid strongly, you can get into this beta region. You can suppose under

cool the liquid, this much amount from liquid to beta, this much amount, I am talking about it. Then, you can have a, nucleation of beta is possible. And then, beta can easily go into the liquid and directly form it. You do not need alpha at all. That is exactly I am talking about to you, so that we can actually use this technique to control all the microstructures of peritectic reaction.

In the next class; I have introduced to you in this class the peritectic phase diagram, peritectic reaction, I have told you the problems of peritectic reaction, what are the issues can we normally see.

In next class, I am going to talk about the different varieties of peritectic phase diagrams followed by eutectic reaction, also I will talk about it and I will show you some microstructures, by the way. I will start with microstructure in the next class. And then, finally I will draw the free energy composition diagram for the peritectic reactions.