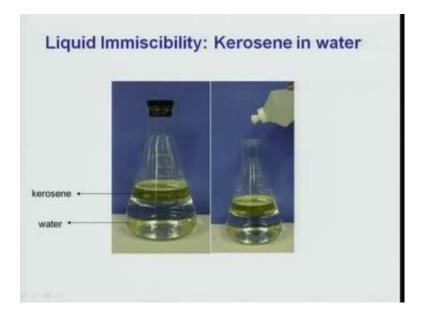
## Phase Diagrams in Material Science Engineering Prof. Krishanu Biswas Department of Materials Science and Engineering Indian Institute of Technology, Kanpur

## Lecture – 20 Microstructural Evolution of Monotectic Phase Diagram

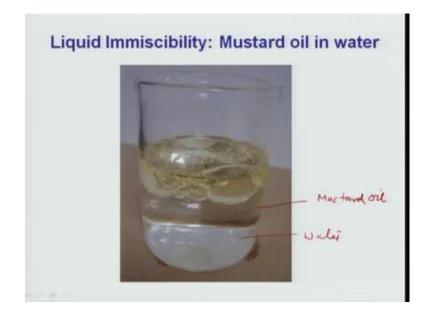
Hello everyone. So, we have been talking about or discussing about Monotectic phase diagrams and in the last class, I showed you the difference between the other phase diagrams and Monotectic diagrams lies in the fact that there is a concept called liquid phase invisibility and the liquid phase invisibility is what dictates the microstructure formation in Monotectic phase diagrams. So, before I really talk about the phase diagram, I would like to show the slides I showed you in the last class on liquid immiscibility.

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You know in our childhood would we have done experiments like putting kerosene in water in a beaker that is what is shown here. You see that if I put kerosene in water, kerosene is lighter than water and therefore, kerosene will float on water, but the fact is that kerosene and water does not mix with each other. That is the most important aspect

of the discussion today that these two liquids are immiscibility to each other. That means, they do not like each other at all and that is why they remain separate.



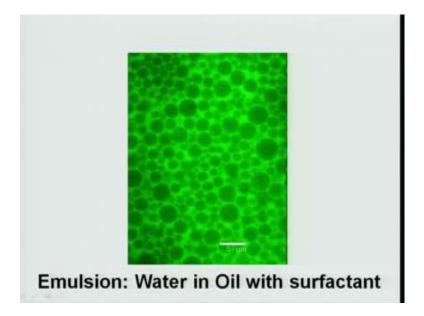
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Similarly, this is if we just take a mustard oil in your kitchen and put it into water and they will see that mustard oil will float in the water. That is because mustard oil is also lighter than water. So, the fact that these two liquids they remain separate, this is water and there is a boundary between mustard oil and water clearly tells us that at room temperature, these two liquids are immiscible. They do not like each other. So, they want to remain separate layers. Now, one can also do an experiment which I discussed in last class. I can take syrup like any cough syrup and put in a glass and then, water and oil together.



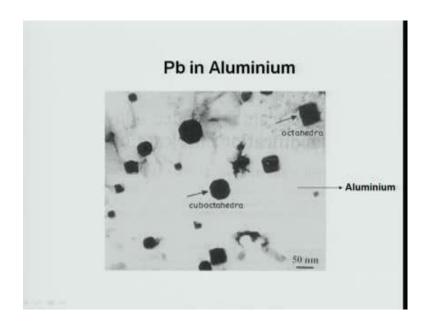
Then the all these three liquids will remain separate. They will not mix each other like you see this is syrup, this is water and this is the oil because syrup is heavier than water. So, it will settle at the bottom. So, now question is this. This is what dictates all the microstructural information and also the phase diagram in moderate system. So, you have to keep in mind these aspects. Please do not forget.

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So, then also have a situation in which if you add water and oil and stir nicely, then you will with a surfactant or without surfactant, it will happen surfactant is nothing, but which forms allowed to form bubbles like. So, it will form bubble or water droplets. Other oil droplets in water, these are oil droplets in water and will nicely mix in the way that they remain separate. They are each droplets of oil in water and that is known as emulsion. Emulsion is very common thing in Monotectic phase diagrams which we will discuss today itself and this is also very common in Monotectic phase diagrams.

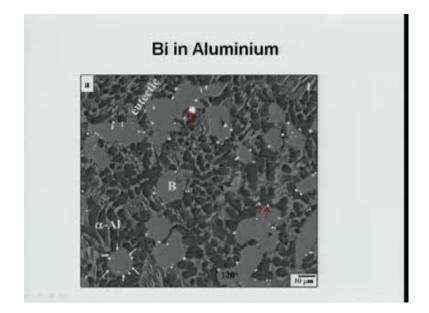
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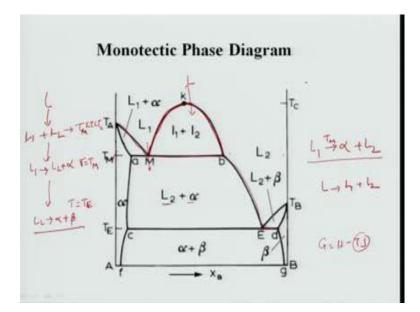
Now in metals or many of the phase diagrams which we discussed, we cannot see these things exactly in the liquid state because metals in the liquid state opaque to light and also very difficult to handle high temperature. So, what you see is in solidified state. Suppose lead and aluminium as I showed in the phase diagram in the last class, lead and aluminium they do not mix each other in solid state and liquid states either. So, because of this immiscibility, both in liquid and solid state what will happen is lead will come out as droplets.

As you see here these are the lead droplets in aluminium matrix. So, as you understand, lead is a very soft phase and has a very low temperature compared to aluminium. So, therefore, this kind of material is a good material for lubricating or fiction and applications because lead being a soft phase will act as a lubricating fling on the surface of the making in which the wire will happen which will impart the wire on this material. So, that is why is aluminium lead has a system become important. They are all Monotectic other from a system.

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Then, you can also tell, I can also show you another microstructure which is taken my own work. You can see here these are the bismuth droplets. The white color pictures, these are all bismuth. Each one is a bismuth droplet. These bismuth droplets actually form a moderate reaction, a complex aluminium silicon iron copper alike, but fact is that bismuth is miscible with aluminium, copper and iron and also probably silicon. So, bismuth comes out as a bismuth liquid and bismuth you know it melts at 2200 degree celcius temperature. Therefore, bismuth form remains a liquid and solidified at the end as the droplets and this also signature of liquid phase immiscibility.



So, let us now discuss the Monotectic phase diagram in detail giving knowing this background information. Let us now discuss that this is more general Monotectic phase diagram and I have drawn it in a board. We will discuss that. So, before that let me just discuss with you the monotectic phase diagram. The most important signature is the monotectic reaction and the reaction is like this liquid one going to solid phase alpha plus another liquid 2 and this happens at the temperature T m and T m is mentioned here. So, these is the monotectic point m on the phase diagram, but before that let me just explain you obviously the liquid surface is this one.

You can see here this is like isomorphous phase diagram. This parallel phase diagram from a m T a, this is like a isomorphs system and then what happen is this change you form a dome like structure m k b dome like structure and this is the immiscibility domain of the liquid. That means, if I take a liquid 1 which whose composition lies between m and b composition lies between a and b will undergo the miscibility on separations. That means the liquid 1 will separate into two liquids L 1 plus L 2 at any temperature below T c. T c is the critical temperature.

What is the meaning of that like suppose if I go back to mixture of kerosene and water at dome temperature that is immiscible? Now, if I heat it up, you know if I heat it up to 40

to 50 degree celsius temperature, it will be homogenously mixed liquid. That is because if heat it up an entropic of the system, the free energy increases. Why? It is because g is nothing, but h minus T s you know. So, T into s is the entropic condition to the free energy.

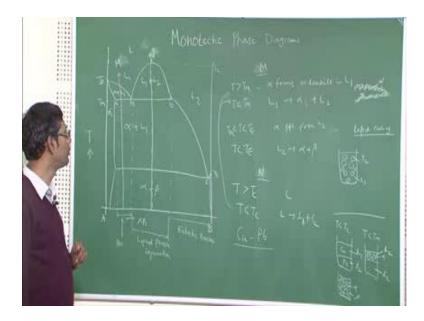
If these fellow increases, then g can be lower even though follow the value in the system, but g can be lower and by doing that you can actually harm homogenous solution liquid solutions at high temperature and that is what happens at temperature higher than T c temperature higher than T c. What will happen? These two liquids L 1 L 2 in a water mixture will mix nicely and form a homogenous liquid solution. If I think other way suppose if I take this homogenous liquid at higher temperature above T c and cool it down to this dome, it will separate into two liquids where composition given by m and b at the temperature T m.

So, these two liquids will be composition given by this part of the graph in k. Other one is given the composition in the form of graph k b at the temperature between T m and T c will form now this liquid L 1. Once if you cool it down further below the T m, this liquid L 1 undergo the monotectic reaction which I have written here L 1 going to 1 plus L 2 and that is what will happen. So, this at this temperature below this temperature L 1 will undergo this monotectic reaction formation of alpha and L 2.

So, now let us now discuss further. So, as you see here we have got three important things happening here in this phase diagram which I list in the left side of this slide. First is that liquid which is at a high temperature is a single phase liquid undergoes the composition between two liquid L 1 plus L 2 here L 1 plus L 2 you can see here L 1 plus L 2 and this is what happens at monotectic in between T m and T c. What happen between T m and T c? Now, at T m this wall liquid L 1 will undergo to the monotectic reaction L 2 plus alpha. This will happen at T equal to T m correct and then from T m to T e, what will happen is this liquid L 2 will precipitate more alpha. Nothing will happen only precipitate more alpha. That is because the composition of the liquid is kept on increasing. So, that is why there will be more alpha phase formation. So, between this one L 2 to T e, more alpha phase precipitated.

Finally at T E what will happen is T E the L 2 will undergo the (Refer Time: 11:12) reaction forming alpha plus beta that is exactly going to happen if you follow the color composition between a and b. Obviously, any other composition beyond b that is beyond b means from this point to this point, what will happen? Only thing happen can happen is formation by (Refer Time: 11:30) reaction those will not undergo any kind of you know monotectic reactions or phase operations. So, now let me just go to the board and discuss with you the aspects I discussed. So, I have drawn the same phase diagram here on the board as you see here.

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Here this is the monotectic temperature, this is the mini temperature of a, this is the mini temperature of b and this is the monotectic temperature T m and this is the point m and this is the T c, the critical temperature. As you can see here, there are three sets of alloys we can see here. One I told you the alloy composition from these two; these alloys are not of any importance form monotectic systems because these alloys will not undergo the monotectic reaction or any kind of phase operation. These alloys will undergo monotectic reaction. So, therefore we will not discuss much on these alloys because they are not important to us.

On the other end, any alloy compositions between a and b will undergo monotectic reactions at T m, but there are distinct classes between this one is from this part to this part which have liquid phase operation. That means, one will add separate into two different phases, liquid phase separations and any alloy between a and m between a and m will not undergo liquid phase operations, but it will have monotectic reaction. Remember that this also, this set of alloys always undergo monotectic reaction, but liquid phase operation will not happen between a and m compositions. No liquid phase operation will happen, but both of them undergo monotectic reaction.

Now, let us take an alloy composition of these. Suppose I draw a vertical line and suppose this alloy composition I will discuss about as you see here if I take the alloy at this temperature, it is a fully 100 percent liquid L 1 not 1 l is above T c L 1. So, this liquid if you cool it below the liquidate temperature by this curve, this is more like a isomorphous phase diagram. This part of the phase diagram, these liquid will form alpha phase in the liquid L 1. So, this is a two phase tree alpha plus liquid.

So, these alpha phases will form like a density. This will go like dendrites like a tree like structure into the liquid and slowly the alpha phase composition will change by these by the solidities and liquid composition change. Now, at this temperature T m when the liquid temperature is point m, same way it will composition reach m this L 1 will undergo the monotectic reaction. So, at temperature T m above temperature T m, alpha forms as a dendrite in L 1.

Now, at temperature T equal to T m, there is a monotectic reaction or you can say at temperature little bit lower than T m because it will not happen at T m. It will happen at lower than T m liquid. It will undergo monotectic reaction leading to alpha plus 12. So, now we are going to form a new alpha, but this is not new alpha. It is same as this. Only difference is that this alpha is a little higher concentration of b than the alpha which is formed here.

So, what will happen actually you will have alpha as a dendrite at temperature above T m. Second way alpha which is formed here, this is primary alpha because it is formed earlier. So, second alpha which is formed here will be precipitating on this only. The

same way it will precipitate on little bit composition difference will be there, but this will be same as the earlier alpha. This is alpha. This alpha is formed by without any reaction by simply solidification from the L 1 and these alphas are formed by monotectic reaction.

So, between T m and T E in this temperature range, T less than T m, but greater than T E and between this temperature ranges, what will happen? Nothing will happen because the compositions at this point and at these points are different. More alpha will precipitate from L 2 alpha precipitates from L 2 the same. It will also form on the existing alpha. Nothing will happen. Only at temperature when the temperature reach below T e, what will happen is this liquid whatever given L 2 at T even small amount of liquid is left over because you can see here almost all liquid will be consumed by the monotectic reaction and the precipitation of alpha from the from the L 2, the liquid will undergo reaction leading to formation of alpha plus beta.

The point I am telling you this because we are going to see the microstructure. The point I am telling you this that because the effective point is sitting very close to b range or b end. What will happen because of this? The beta will be very large quantity. Alpha will be very small that you can see alpha is given by this arm and beta, sorry beta is given by this arm and alpha is given by this small arm. This only you can see here. So, alpha is very less. Because of that it will form daibos. Daibos means you will have alpha dendrites in which beta droplets will be present and nothing else in the microstructure. So, that is what will happen for any alloy composition sitting here.

Now, if you take alloy composition here after this one, you will have that at temperature T c bill temperature T c for this alloy, I am talking about it. So, this is b and this is a. So, these things have happened for sorry this is 1. This is m 1 m or no composition m and n like one is transformed to liquid. So, this is for one. Now, m will have all these steps in addition to that before above T m or rather let us start above T c will have full liquid 1 and below T c l will call k.

You will undergo liquid free separation L 1 plus L 2. So, below T c the liquid l will then separate into two liquid phases, L 1 and L 2 just like kerosene plus water at high

temperature. They are homogenous liquid at low temperature. They would became two liquids and then, what will happen finally is this liquid L 1 will have composition given by this sum between a m and k and L 2 will composition given by b and k. That is all will happen, right nothing else. So, this will go back here. So, for the alloy we have added two more steps. So, 3 plus 2 is 5 different things will happen for the alloy n. This is for the alloy n. Sorry all mistakes will happen. This is for the alloy n. The alloy n is this one as you see here and addition to these three steps, there are two more steps taking place.

Now, question is this let us suppose take a system alloy system and I want to tell you because I am going to show you lot of microstructural copper and lead and if I take alloy composition for copper lead which lies like n, what will happen at below T c? These two copper region lead, this equation separate now as you know copper has a density of 8.9 gram per c c. Let density of about 11.8 gram per c c. Because of that in a container if you take these two this liquid, lead will be sitting at the bottom and copper will be sitting at the top because copper is lighter. Copper has density of 8.9 gram per cc and density of lead is 11.8 gram per c c. So, because of that there will be already separation of these. It will take place just like kerosene and water. Kerosene is lighter. So, it sits on top. Water is a heavier; it sits at the bottom.

So, this is suppose my L 1 and this is suppose my L 2 L 1 and L 2. So, as you see here L 1 because it is sitting at the top will undergo monotectic reaction at temperature T E T m. Sorry at temperature T m, this will undergo monotectic reaction. So, what will happen if I draw this picture correctly? So, this is T less than T c. So, it will form alpha. These are alpha and this is L 2 and this is L 2, correct. So, you got clear. So, this L 2 which is there will have almost same density as the bottom L 2 and this will just go down and because of that these dendrites which have form alpha. It is copper lead a v solid solutions alpha will float in the liquid.

Finally, these two will undergo monotectic reactions. So, finally, what will happen if I draw this picture? Finally, you have alpha dendrites and beta droplets into the microstructural form because reaction will lead to very small amount of beta, a very small amount of alpha and large amount of beta. So, therefore you will not see it and that

is what you are seeing in microstructure like aluminium lead. What you are seeing? You are seeing that these are the aluminium greens, large aluminium greens and within that you have beta or lead droplets present, correct. These are the lead droplets I have drawn here.

That is what exactly will happen in the real microstructural situations. This is what will happen and now question is this if you cool it slowly, this is going to happen, but if you cool it very fast, very fast means suppose if you use technique like rapid solidification then because of fastness of cooling, these two liquids will mix. That means they will form a mass. What will happen because of that? Suppose I can draw it here and show you by cooling rapidly, this is slow cooling. So, if rapid cooling happens, rapid cooling will lead to very interesting thing. It will lead to emulsion formation.

What is emulsion formation? You will have lead droplets or liquid lead droplets. This is one and this is one. This is known as emulsion. Instead for remaining two layers separate layers, they will form like droplets inside the liquid one and because of this droplet, because of these presence of droplets, they know the small droplets will do will remain there where one will again undergo monotectic reaction from further two droplets and finally, you will have very fine droplets of beta phase in the alpha. So, that is what happens in the solidification of this monotectic alloys and that is the reason I showed you one of the emulsions. So, it is very clear by looking at these phase diagram that we can understand the phase formations or solidification of this alloy m, also these alloy n. The distinct difference in between these two is that for this alloy, there is no liquid phase separation and for this alloy there is a liquid phase separation like one at the bottom I have drawn.

For this alloy, there is no liquid phase separation and only dendritic growth of alpha will happen and then, further reaction will take place, but on the other hand here you can form droplets and that is what I have shown you in the microstructures. I hope it is clear to you and you will be able to understand it by reading the books and by looking at the microstructure which I have shown in the last class. Now, only thing which I need to do is that to complete the monotectic things is only to show you the free energy composition diagrams which I will do in the next class and in that class also, I will talk about synthetic reactions because synthetic alloys are very less and therefore, will not discuss in details about the synthetic reactions. I will just show you how the reaction happens and what are ways it can develop in these alloys and subsequent to that we will go into the solid state reactions mostly steels and lead.