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

Lecture – 19 Introduction to Monotectic Phase Diagram

So, today we are going to start on the new topic; that is monotectic phase diagrams, and we are going to discuss further the syntactic phase diagrams also, but before I do that I just like to take few minutes to discuss about the congruent melting and congruent transformations which are observed in a phase diagrams, just few minutes on that. I told you the congruent melting compounds are observe in the peritectic phase diagrams. I have given the example of aluminium nickel, aluminium magnesium phase diagrams where this kind of congruent melting system exist, but there are others where this kind of systems, this kind of phase diagrams exists. So, let us have a look of the phase diagrams.

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So, this slide, in this slide I am showing you four different cases; the first one is the case where, the phase diagram is isomorphous type, which you see here isomorphous type between a and b 2 components, but there is a composition x I have marked it by this way, in which alpha will melt congruently at this the melting temperature. So that means, for x

composition alpha will melt to liquid, without any change of composition. On the other hand on this side of this side if alpha wants to melt to liquid, within melting will happen of higher range of comp temperatures. So, therefore, a composition of alpha will directly not change to composition of liquid; that is the point I am trying to tell you.

So, this is frequently observed in some of these isomorphous systems. now question is this there are also phase diagrams in which such a kind of phases exist like this one c and d, c is source surface beta, or d also source surface beta in which, the with the congruently melting exists. You can see that beta melts with liquid at this composition, given by this point a arrow to liquid, without change of any composition. Similarly for this one also and this is like a g m g or l n I type of phase diagrams.

On the other hand there are peritectic points here peritectic point there on the both sides. Similarly here this eutectic there is a eutectic reaction. So, this is also widely observed in the peritectic phase diagrams, where a phase you will exist which a composition in the intermediate range here, like here and here, but it will melt congruently. The solid state also this kind of thing happens, like here alpha phase transform congruently to beta in solid state. Although I have I am not discuss anything about solid state so far, but this is also possible in solid state. And this kind of phase transformations are also seen in solid state phase diagrams, but if you do not understand like tried now this one. So, do not look into detail, later on will do that will, later on will discuss about this, but these two are important for you. These two phase diagram you should understand very clearly.

Now, solid state things it can be seen here that there is a congruent melting cong this is a phase to sigma for iron chromium system. iron chromium system has a you know important phase call sigma phase, which is a tetragonal structure, order or disorder depends on how we process, but the transformation form a liquid alpha iron to this is gamma iron, alpha iron means alpha solid solution of chromium and iron to sigma phase is, by congruent transformations this is solid state, just you show you. So, that is about the congruent transformations.

Now, I am going to start with this new topic and monotectic phase diagrams. monotectic phase diagrams are very different from what we have seen earlier; monotectic phase diagrams, and these phase diagrams are important for many applications that is why you we should discuss. Before that little is just take a few minutes to discuss suitable immiscibility in liquid. You know all of you, when your kid you have done this experiment a list, many of you have done that. suppose you this is a picture taken long back by myself and in which, you can see clearly see I have taken a you know basic kind of glass bottle, and we have poor liquids of different color yellow, blue, black, there is green and also, yellow again and red.

And these liquids are not immiscibility other, they are remaining stagnant, you can see here at each layer they are remaining stagnant. So, this is call immiscibility in liquid. You can take like, you can take you know sugar solution and syrup. Syrup means any medicine you can take; first you put sugar solution into this bigger, and then you put see here this medicine syrup, we will see they will not mix each other. Or you can take even you know this kind of things, I can draw it here, you can take initially water, and then you add kerosene here. So, what will happen, they will now be mixed each other, similar like petrol and water. So, why does these two liquids, or these different liquids do not mix, or not mix each other. Well the real reason is coming from the automatic mixing,

basically fact is like this. These two liquids like kerosene and water, the kerosene molecule does not like water molecule at all, there are (Refer Time: 06:58) each other; that is like you do not like some friend.

So, what will happen you will not mix to the (Refer Time: 07:03) or they will not even talk to him if you do not like you know you have. So, (Refer Time: 07:09) with him that have you not like to talk. So, in such a situation is call immiscibility. So, immiscibility means they do not mix each other at all, in liquid state it can happen in solid state also that will discuss later as part of the phase diagram, but initially, let us consider on liquid. So, if I put two liquids if did know mix each other, then we call immiscible liquid, mixing means there atomic limits about.

Like miscible liquid using for isomorphous system like, if I take sugar solution and coffee. if I add sugar into coffee sugar solution into coffee, what will happen? Both of them will mix together nicely. So, this is call miscibility, but on the other hand if you add kerosene into water, they then never go into mix each other and that is why it is known as immiscibility. It is opposite to miscibility. And monotectic phase diagram (Refer Time: 08:04) phase diagram actually lies on this concept of immiscibility in the phase, in the system.

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So, this experiment was done again. You can see here this is emulsion; emulsion of oil with in water, what is that? Very simple suppose if I take with you kerosene put in a oil, and then I am take a stare air an (Refer Time: 08:31) mix what will happen. Kerosene both will become droplets and they will get inside the water. But if you take a good picture of that you might thing that if I stare nicely it will liquid will react, a liquid will mix together. No they never mix, but what will happen is that if the process you are going create small droplets of kerosene and discuss in small droplets will get inside the water, but remain as a kerosene; that is what is known as emulsion, you can see here these are kerosene, kerosene droplets in water, all of them, but they are not mix with water, water is remaining as water. This also happens if you make is you know add soap into water and stare will from soap bubbles.

In soap bubbles also air and the liquid they did not mix each other. So, this is also emulsion. so; that means, what if any if I take two liquids and try to mix them by application of force or whatever, I never will be able to mix him at room temperature. Thus understandable, because they do not like each other at room temperature, they would never try to bound each other, to mix it they have to form bound automatically. If they do not from bound they will not mix each other, and this is the basis of the phase diagram. Now question is that you may ask why well (Refer Time: 09:51) they do not like each other thermodynamically what will happen. Thermodynamically what actually happen is that (Refer Time: 09:56) energy has two components g equal to h minus t s where h is the enthalpy, and s is the entropy and t is the temperature

Now, I told you that entropy will always you know allow two things to mix, because if I mix two things together entropy of the system will be higher, or other system will try reduce energy by increasing their predominates, or increasing by entropy, but enthalpy depends on bone energy. So, if two molecules do not like each other they are not forming bond each other, enthalpy will be positive and high. if there is the case when g of a system will be very high, because h is positive and high and it can actually (Refer Time: 10:47) if this is positive and high it can (Refer Time: 10:49) the negative contusion of entropy, and g will be positive; that is why g is positive then you cannot make the system thermodynamically stable, and then you cannot actually mix them together; that is the idea.

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So, now how do we represent such a kind of phase diagrams? Well this is what is shown here, for real phase diagram between lead and aluminium, this is represented by dome. You can see here this is a dome. Liquid positive immiscibility is represents by a dome. You know is just like a temple, or just like a you know in European cities you have cathedrals, and in those cathedrals whether is like call a dome, and because cathedrals has like a dome like structure, this like structure. So, this is like that. So, whenever you thing about it a phase diagram.

You also remember you want to think about the dome. So, what is the meaning of this dome? Meaning of this dome is this; you know this is the function of temperature verses composition. As I told you g is equal to h minus g s. So, as low temperature, because of the immiscibility of two liquids; h will be very higher and positive and. So, high that it can overtake the negative effect of entropy, but you know entropy has a temperature term t. So, as you increase the temperature more and more, this temperature will increase the entropy contribution. In a high temperature what will happen, because of this very high contribution, it can take over the entropy contribution enthalpy contribution. So, at a low temperature entropy is very higher than t s. So, g is positive, but at a low temp this is at low temperature, low means relatively low temperatures.

I write lower temperatures, higher temperature, and higher temperature h sorry. The higher temperature enthalpy entropy t into s will be higher than h, because of the t if a t there t into s and in that case g can we may taken negative. So, that is what higher temperatures, they can mix that if you take kerosene and water mixture keep on hitting after sometime it will mix whatever 40 degree Celsius it starts mixing, but do not take beyond 65 degree Celsius kerosene will burnt, so it can create accident or create an accident. So, that is the thing will happen. So, if you keep on hitting the systems, after sometime the entropy effect, because of t t is there here as a multiplication factor will be keep these stronger than the enthalpy which is positive because of disliking of the atoms and it will be mix. So, that is why see there is a critical temperature this is call critical temperature t c r (Refer Time: 13:47) which is a simple miscible liquid.

Now as you cool it down, entropy if I it will not be strong and (Refer Time: 13:57) temperature as I told you, this two liquid this single liquid will separate in to two liquids; that is what if. So, if I take a, suppose kerosene and water mixer at lower temperature within below this temperature t c r; there will be separate kerosene and water, but at high temperature there will be single liquid. So, if I cool this one from lower to high, one liquid will separate into two liquids that is what is shown. So, this is the most important part of a monotectic phase diagram. Now, I prove these where things will happen later on, like if you cool it down further. If you cool it down below the melting temperature of the lead liquid solid lead will come out living behind liquid and finally, there is a eutectic reaction here which you cannot see, everything will become solid.

Now, in a classical phase diagram, which is more generalized one, is shown here. As you see here this is a t c I discussed with you, and k is the top most point of the dome. I told you dome, because this is like a dome in a temple or in some, this is like a dome. So, here this generalize, because you see here there is a solid solution call alpha, at the a (Refer Time: 15:11) there is solid solution call beta at b (Refer Time: 15:15), and then this is the point m at which the monotectic reaction happens. What is the monotectic reaction? Monotectic reaction is l going to L 1 going to L 2 plus alpha. Let me first explain little bit more. Well so; that means, if I take a single liquid here which is present, because (Refer Time: 15:35) within a single liquid because of strong entropy effect I told you. So, below that temperature it will separate into L 1 plus l two. Can you see here L 1 plus L 2 and within the dome; obviously, if this is two phase field the single phase field l, one single phase field L 2 will exist on both sides.

Now, this L_1 by a monotectic reaction this is a monotectic reaction will separate into L_2 plus liquid L 2 plus solid alpha; correct that is what you see here at m one if you cool it down it become L 2 plus alpha. So, this is known as monotectic reaction. This looks like eutectic reaction. What is eutectic reaction? Eutectic reaction is l going to alpha plus beta. Here what happen we have replaced beta by l 2 and l by l 1. So, they look like similar, but their formation everything is completely different; that is the beautiful part of the phase diagrams. So, this monotectic reactions is a very important, because l is the formation of alpha in the liquid of l 2, correct and then what will happen from these mode this is the monotectic temperature, t m is the monotectic temperature.

So, this is a critical temperature at which beyond which everything will become single phase liquid below which this l will separate into l plus l 2 l 1 plus l 2, and in the monotectic temperature L 1 separates into 12 plus alpha. And from t one to t e that is a eutectic reaction that is why t e shown, t one to t e nothing will happen except the more and more alpha will form, and composition of liquid will follow this line, because this is the liquidus, this is the whole thing so liquidus.

And at the temperature t l 2 will undergo at temperature t e l 2 under the eutectic reaction become alpha plus beta. So, I can write down from this is a t m and liquid at t c. So, t m the melting temperature (Refer Time: 17:37) monotectic reaction happens, and from t m to t e this is t e, alpha will be precipitated, one more alpha will precipitated that is what will happen, nothing else will happen no reaction. So, in the whole process you can see here you can track the solidification how are things will happen, and then we will discuss case by case in detail manner to give a perspectives of s u (Refer Time: 18:00) phase diagram, which is a classic and useful phase diagram.

Cu-Pb Phase Diagram

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Copper liquid copper liquid phase diagram has monotectic reaction at this temperature; that is 955 you can see here. So, here l 1 become alpha plus l 2, and this is the l 1 plus l 2 phase field, forget about this dot this lines, they have (Refer Time: 18:24) to composition thinks, and then there is a eutectic reaction present here. Not here, here, reaction present there in this point and 99.94 percent is of the lead, is very close to lead, pure lead composition that is why it cannot be seen, this is a classical. Now, look at let us look at some of these micro structures. So, I am going to show you several micro structures; one is thirty percentage, this is the one, this is thirty percentage lead, sorry thirty weight per atom percent. Lead is not this one I am wrong, atom percentage. So, 30 atom percentage lead these arrow.

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So, if I do that what I will see. I see this is copper, and this is lead, these black things are lead, and you can see lead droplets are joining and form the continuous layer; that is what you see here. And if you process differently there are different to the processing that is what I am now discussing here. You have to understand the lead and copper there is a large density differences, density difference of the order of you know copper density of eight point nine and lead density of - 11.5, something around that. So, because of that lead will segregate at the bottom, you know when you solidify something.

So, that is why they will form such a kind of structure, which is not good pointer structure for applications, but if you process the (Refer Time: 19:46) lead solidify you can create list droplets of lead in uniform distributing the micro structure. You can do better here you can see this is done in space, space station that is why this is better. And if you if you do (Refer Time: 19:59) experiment you can see, even this droplets are actually this integrated like a (Refer Time: 20:04) in stability. So, you can create same alloy different micro structure by posting different.

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Now, if a take a 35 percent alloy, lets me this one sorry this one which is that 35 percent, which is at the center of this dome, this is the dome that is the center. So, what will happen? You can see here also you can create in space station nice distribution of micro structure; we will discuss later how it is done. Other case is you can create such a kind of (Refer Time: 20:32) decomposed micro structure you can see, (Refer Time: 20:35) decomposed means this like one like micro structure. These are the lead droplets and some of the case lead droplets have joined together and form, here also, this is the one, this is the one correct, and if you are not processing properly what will happen is that, these lead they will found long needle like things separate join together that is possible.

Now, there are some other examples let me show you; like this is again from betas beta this method is zinc, you can see here there is a dome here, and that dome indicates one liquid phase going to liquid two and liquid one and liquid two, and then there is a monotectic reaction here, sorry monotectic reaction there; that becomes liquid plus zinc s c p. So, let here look at micro structure you can use this kind of system to create nano structures.

You can see this is the nano structure lead this much lead this much zinc micro structure, where these are actually this much, and this is zinc, the matrix is zinc, and this particles are this much correct, and this actually nano size particles you can see here, there is a steps involved and. So, this is possible to create.

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And other is last example I show you aluminium thin, aluminium thin has a, you know classic phase diagrams. It does not show, these are liquid, it does not show miscibility gap. But I does not show, if you know difference miscibility gap means liquid one liquid (Refer Time: 21:59) two liquid it is not present, but you can see the shape of the liquidus is such that, it clearly suggest there is a miscibility gap present between this meta stables, if you cool it rapidly this liquid will separate into two liquids and then solidify into that.

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So, to a give examples, if I take aluminium 5 8 percent in the alloy, you can clear see these are the tin, and this is aluminium continuous matrix you can create this as a tin droplets again, and this is aluminium, this continues here. Actually some silicon is added to modify further, so that is this miscibility happens much easily. So, what I mean to say is that in this class, that I will not go to (Refer Time: 22:41) today. What I mean to say in this classes that (Refer Time: 22:44) miscibility allows us to generate different kinds of micro structures by using this phase diagrams.

I have shown you for copper lead, I have shown you for aluminium tin, I shown you for (Refer Time: 22:54) zinc, and you know these particular alloy systems are useful; like copper and lead alloy is use for a cell lubricating bearing, why because lead is a very soft and ducktail phase. So, this will act as a anti lube, anti friction or anti. This is like a

lubricant, when you have a where (Refer Time: 23:15) like in case of fan you have a cell lubricating bearing present fans rotating at of high speed you need a bearing, and the bearing will wear out for long time if you do not use this cell lubricating bearings.

So, most of the cell lubricating bears will have anti monia or lead present. This anti monia lead has are the low melting metal alloys or metals which are present like a droplets of particles, and they are act as a lubricant. (Refer Time: 23:39) is a 327 degree celsius. So, at high temperature it becomes soft, when you have wear and tear action patient and you can have a better for parties. So, but base for parties comes when the distribution is like this, very small particle distributed in the matrix for the copper.

So, with this next class I am going to discuss, I will take a ah monotectic phase diagram and discuss the each of the solidification phenomena for monotectic, hyper monotectic, hypo monotectic alloys and then go further in to this. But remember the important thing is to connect the micro structure with the phase diagram. If you are able to do that in the process of this course, then you will be a master; otherwise this is not going to help you much. You have to connect both of them phase diagram on the micro structure. Next class will discuss further.

Thank you.