Phase Equilibria in Materials (Nature and Properties of Materials - II)
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Lecture – 31
Methods of measuring Phase diagram

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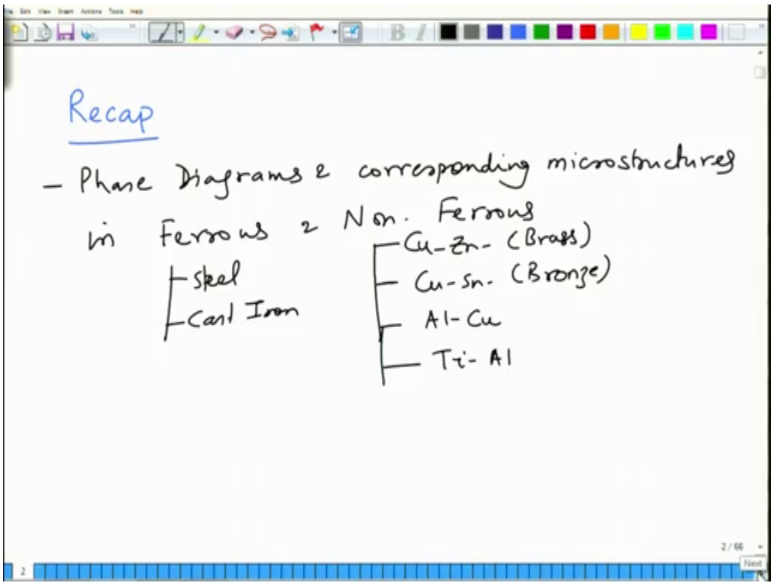

Recap

- Phase Diagrams & corresponding microstructures in Ferrous & Non. Ferrous
  - Steel
  - Cast Iron
  - Cu-Zn- (Brass)
  - Cu-Sn- (Bronze)
  - Al-Cu
  - Ti- Al

So good morning, again so we have this lecture number 31, today of Phase Equilibria, we will just first recap the last lecture and then. So, what we have done is we looked at the phase diagrams of phase diagrams and corresponding micro structures, microstructures in ferrous and non ferrous alloys.

So, we looked at in ferrous alloys, we looked at mainly steel and cast iron, these are 2 alloys from the perspective of engineering applications very important and then we non ferrous alloys category, we looked at aluminium zinc, which is brass. So, alpha and alpha beta brass, brass as we saw that it has lot of many peritectic reactions, because of huge differences between the melting points of 2, sorry copper zinc not aluminium zinc my apologies.

This is copper zinc and then we looked at copper tin, which was bronze. So, both of these systems show plenty of quite a few peritectic reactions, because of multi point differences and typically we operate for example, brass at compositions for relevant to alpha brass or alpha plus beta brass at knowledge of phase diagram is necessary to choose the appropriate composition for achieving desired microstructure. Similarly, in tin based materials copper tin based materials, we have phosphor bronze or we have a barium bronzes, which we have not discussed, but there are a lot of bronzes beryllium bronzes contained beryllium, tin bronzes contained tin, a phosphor bronzes contained tin and phosphorus and so on, and so forth.

So, these are again useful materials, they have again microstructure, which can be useful for example, delta phase intent based bronzes provides strength. So, if you are around the delta phase composition, then you have this 2 phase mixture, which provides you high strength to bronze and then we discussed we also looked at aluminium copper alloys and we looked at titanium aluminum. So, these are non ferrous alloys, which show by and large most of many of these systems, show peritectic and also at places eutectic reactions and knowledge of these phase diagrams is necessary to basically, correlate to the micro structural development, that you will obtain for a given alloy and then you can tune it by further carrying out phase transformations by changing the kinetics, which is not part of this course to (Refer Time: 03:01) them. So, this phase, so basically, the knowledge of phase diagrams tells you what are the equilibrium phases that you obtain? What is the equilibrium microstructure likely to be? But the morphology of microstructure will be changed by kinetics.

So kinetics is something, which will again play an important role in determining the microstructure, but the phase diagram will tell you, what are the equilibrium phases present, what are the temperatures, what are the compositions? They will help you in designing appropriate compositions. So now, we discuss in this lecture.

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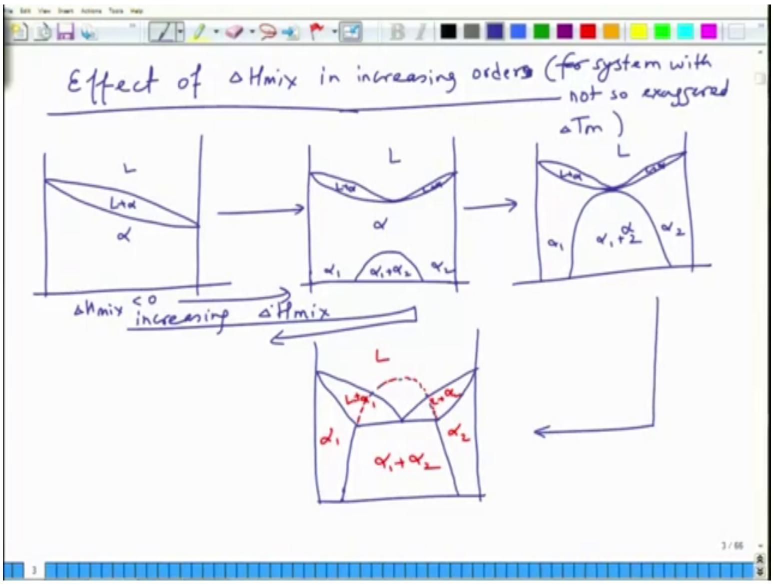

Effect of ΔH_{mix} in increasing orders (for system with not so exaggered ΔT_m)

So, before we move on to how to determine the phase diagram let me just briefly touch upon they; so, sort of a summary.

So, you can say effect of delta H mix. So, when you have. So for example, when you have 2 elements, which you have, complete solid solubility, but they do not have large difference in the melting points.

So, you start from this state, let us say liquid plus alpha and as you keep increasing to as you keep changing to higher enthalpy of mixing. So, as enthalpy of mixing keeps increasing order for systems, increasing order for systems with not so exaggerated, exaggerated delta T m, which means melting points are not vastly different. So, when you increase the free energy, enthalpy of mixing then the free in the phase diagram tends to split in such fashion, so that, you have this kind of behavior.

So this is liquid, this is liquid plus alpha again, liquid plus alpha, you have alpha and then you have alpha 1 alpha 2 and in between, you will have alpha 1 plus alpha 2, if you further increase the delta H mix, it changes to. So, this basically this region will keep growing. So, as it as it keep growing, it starts becoming bigger and bigger and this liquidus and solidus comes closer even further, this is liquid, liquid plus alpha liquid plus alpha again, you have alpha 1 alpha 2 alpha 1 plus alpha 2 and so as delta basically, what it means is that? As delta H mix is increasing, the solid solubility of 2 phases 2 elements within solid state, it is decreasing and as a result, they tend to phase separate and this phase separation increases as delta H mix increases and so, you can see that as delta H mix is increasing. This phase separated part is getting bigger and bigger in area and finally, when it becomes too high then, you have something like this. So, you have. So, this is just a schematic ok. So, you cannot take this as phase, it will have you know even certain variations.

So, it will have melting point something like that ok. So, the 2 phase region would have been like this, but it has merged with the liquidus and solidus as a result, you have liquid, liquid plus alpha 1 liquid plus alpha 2, this is alpha 1, this is alpha 2 and then you have alpha 1 plus. So, eventually this isomorphous phase diagram goes through this kind of solid state region at lower temperatures, phase separation at lower temperatures and then eventually, it converts it to a eutectic phase diagram.

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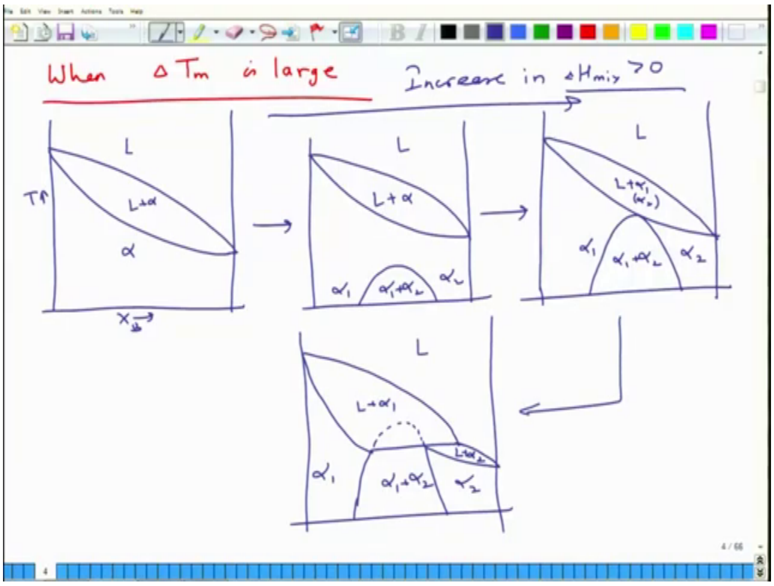

When the temperature difference is huge then this converts into you know the peritectic kind of system so, when delta Tm is large.

Then you know you start from this kind of system. So, you have substantial difference between the melting points, let us say ok. So, this is temperature this is x b, this is liquid plus alpha and as you increase delta H mix, this tends to again, show similar behavior. So, you have this kind of system L plus alpha 1 alpha 2 alpha 1 plus alpha 2 and axis is remain, axis remain the same. So I do not, I am not drawing labeling the axis and eventually it turns to something like this, as delta H mix further increases. So, it appears something like, this liquid plus alpha 1 and alpha 2 and then you have alpha 1 alpha 1 plus alpha 2 and then alpha 2.

And then finally, when it increases delta H mix increases even further. So, this is basically increase in delta H mix and which is greater than 0 ok. So essentially, what you have is you have this part, being as if you know. So, what you are going to have is something like this. So, this is liquid, this is liquid plus alpha 1 and then you have liquid plus alpha 2 here. So, this is alpha 1 plus alpha 2 alpha 1 alpha 2, this is liquid plus alpha 2. So, this is when you have large differences between the melting points of 2 elements and when delta H mix increases to greater than 0from being delta H mix lower than 0, when the vast effect, when the delta Tm is very large.

So, these are the 2 cases again, this is increasing delta H mix; so; obviously, for this case delta H mix is negative and then it increases further to becoming positive. So, this is the evolution of phase diagram that happens and so it is sort of it gives you better understanding of how do phase diagrams evolve or as to what is the effect of various parameters 1 phase diagrams, what is the expected when delta H mix is larger and delta Tm is large.

So, this is this completes basically the discussion of binary phase diagrams. So what kind of phase? So, what we had learnt is basically, thermodynamic basis of phase diagrams regular solutions, ideal solutions and you know real solutions and then we looked at the effect of delta H of delta and could change in the enthalpy of mixing and change in the entropy of mixing and then change in the mixing the sum of that the balance of these balance of delta H and delta S gives you, certain stable free energy like, free energy composition diagram and from those, you can determine the phase diagrams and we looked at variety of phase diagrams like eutectic, isomorphous, peritectic and so on and so forth and we also looked at various alloy systems.

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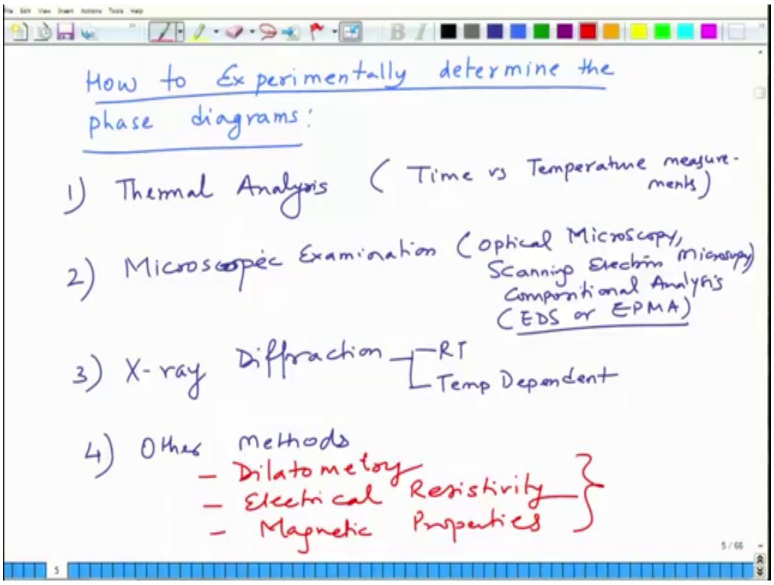

How to Experimentally determine the phase diagrams:

1) Thermal Analysis (Time vs Temperature measurements)

2) Microscopic Examination (Optical Microscopy, Scanning Electron Microscopy) Compositional Analysis (EDS or EPMA)

3) X-ray Diffraction — RT
— Temp Dependent

4) Other methods
- Dilatometry
- Electrical Resistivity
- Magnetic Properties

Now, what we going to determine is so the first thing is how to determine these phase diagrams? So, what we are going to see here is how to experimentally determine the phase diagrams? All right, so we have various methods. So, the first method very commonly used this thermal analysis. So, basically this means doing time versus temperature measurements and experiments. Second technique, which is commonly used is microscopic examination and microscope examination of microstructure is basically, microscopic examination means examination of the microstructure using appropriate techniques such as optical microscopy, scanning electron microscopy and this is also associated with the compositional analysis of course, using techniques such as energy dispersive spectroscopy or energy electron probe microanalysis.

So, these 2 techniques can give you 2 very fairly good picture of composition local compositions and then we have third technique, which is related to structure of the phases is X ray diffraction while SEM and optical and scanning electron microscope can tell you call it qualitatively about the differences in the phases, the exact difference is between the structure of the phases can be found using X ray diffraction. So, X ray diffraction can be carried out both at room temperature as well as temperature dependent to understand phase evolution and then correlate it to the time temperature measurements and microscopic examination.

And then finally, there are some other measurements, other methods, which are also useful especially in solid state. So, these are for example, Dilatometery, which basically utilize and change in the volume and dimensions and then change in electrical resistivity and then change in magnetic properties. So, these are 3 methods, which we generally use to analyze the phase generally, use these are a few method that we use to analyze the evolution of phase diagrams, how the phase diagram can be determined?.

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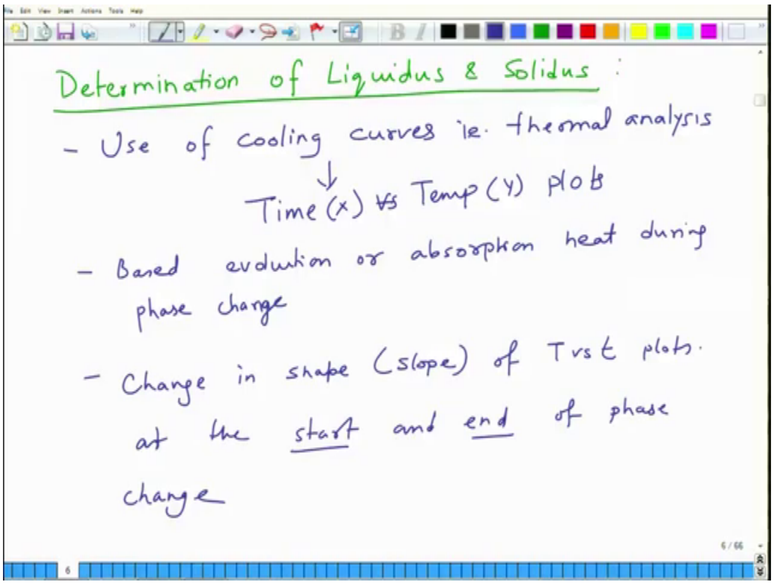

Determination of Liquidus & Solidus :

- Use of cooling curves ie. thermal analysis
  ↓
  Time (x) vs Temp (y) plots
- Based evolution or absorption heat during phase change
- Change in shape (slope) of T vs t plots. at the start and end of phase change

So, let us first look at, how we determine? determination of liquidus and solidus ok. So basically, we are looking at a phase diagram like a isomorphous phase diagram. So basically, what it uses is something called as use of cooling curves, that is you thermally analyze a material and cooling curves are nothing but, time versus time on x axis versus temperature, y axis plots. So, when you cool a solid or when you heat a saw, when you cool a liquid or solid and when you heat a solid to liquidus temperatures, you money to the time temperature as a function of time and these curves are called as cooling curves and these are essentially based on the principle is based on evolution the change in the shape, change in the profile of these curves is based on evolution or absorption of heat.

So, you basically latent heat of melting or you know heat change related to phase changes solid in the solid state. So, basically, absorption or evolution of heat during phase change; so, this change this heat could be evolved or absorbed depending upon liquid solid state transformation during heating or cooling or solid to solid transformation, if there is a large heat change involved and so on and so forth and what we basically analyzes? Analyze the change in shape of the curve shape means, slope of T versus t plot at the start and end of phase change.

So, when the phase change happens you notice the change in the shape, which is basically the slope of time versus temperature plot at the beginning or at the end. So, it depend if you if you cooling or heating you look at corresponding points of. So, if you are cooling for example, liquid solid you look at the start of solidification end of solidification and if you are heating it, then you are looking at start of like melting and end of melting as the phase change.

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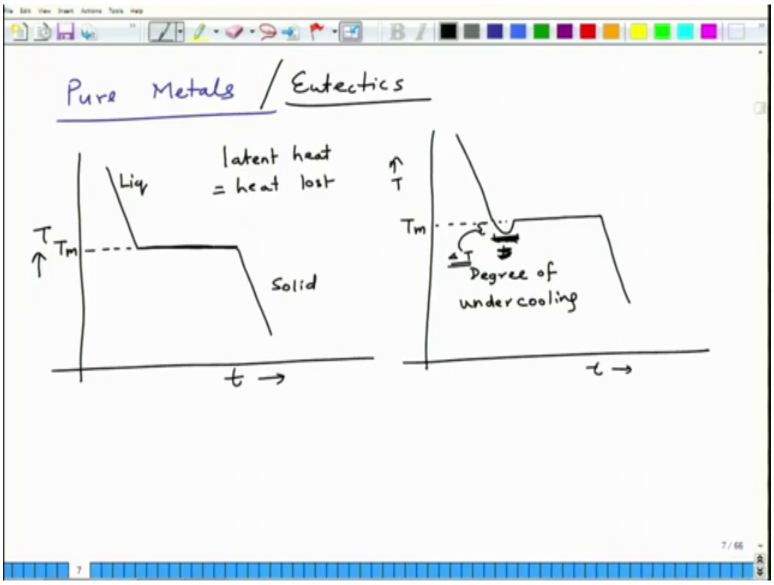

So, there are various curves that you may encounter during this plot. So, for example, for pure metals for pure metals, you might have a plot like this. So, this is time versus template. So, there is the time on x axis, temperature on y axis and for pure metals plot like this is obtained.

When you do not have any; so, this flat region basically, is the signature of solidification. So, in this state, so, at high temperature it is in liquid state, at low temperature it is in solid state and at the melting point, it is this temperature versus time plot is flat and what this means is that basically, whatever the latent heat that evolved was equal to heat, that was lost during cooling to the atmosphere to the ambient. So, this latent heat evolution is equal to heat of heat, that is lost and that is what maintains this temperature as constant. In some cases, in case of pure metals, you might observe that you have this plot with certain degree of under cooling before it shows.

So, this is what is you can say the melting point and this is what is degree of under cooling. So, under cooling is basically, this delta T . So, not this, this one. So, before it again becomes, flat again and this degree of under cooling is required, because as you will see in phase transformations, you need to form a stable nuclei and that formation of a stable nuclei requires, some energy and that energy comes through extra under cooling as a result, you require to cool the material a little bit lower than, it is melting point before you come back to it is melting point and solidification.

So again, these are the 2 kinds of plot that, you observe in case of pure metals similar plot is also observed in case of eutectics for example, because eutectics also have fixed, melting point as a result.

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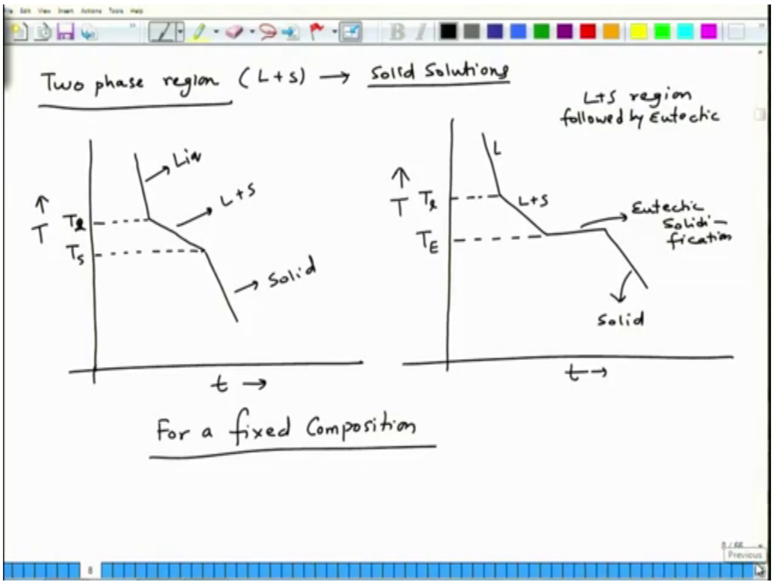
Two phase region (L+s) → Solid Solutions

For a fixed Composition

So, any reaction which undergoes a fixed at a constant temperature, you you are expected to obtain similar sort of curve and then for 2 phase regions. So, you can say 2 phase region, liquid plus solid region. So, if you have solid solution for instance ok. So, if you have in case of this is in case of solid solutions. So, again time versus temperature.

So what you obtain? Typically is you have this liquid, which cools and at the so, at the onset of solidification it changes shape, before it goes back to a sharper slope again. So, this change the point of the point, where the slope change begins, is the T s that is start of solidification or you can say like T l, we can say this is the basically start of solidification means liquidus and the point at which the solidification ends is basically, according to phase diagrams the solidus. So, this is the solidus point and this is for a fixed composition for a fixed composition. So, you take many you take a, you take many compositions of an alloy you take let us say, 0 to 10 percent, you take 20 compositions, every 5 percent interval.

You obtain such cooling curves starting from pure a to pure b at every 5 percent of b and then you stitch them together to obtain phase diagram. So, you will have to conduct many such experiments for various kinds of compositions and if you have alloy with liquid plus solid region with solidification culminating into eutectic followed by eutectic kind of behavior then, you will have a mixture of these 2. So in the beginning, you will have liquid cooling, then liquid plus solid and then again, you will have a eutectic reaction followed by. So, this would be your eutectic temperature T E this would be the start of solidification that is T l and so, this is liquid, this is liquid plus solid, this is the eutectic solidification and this is solid.

In this case, this would be liquid, this would be liquid plus solid and this would be solid. So, these are the these are the few different kinds of curves that, you are expected to obtain as you stitch them as you as you as you obtain various cooling curves.

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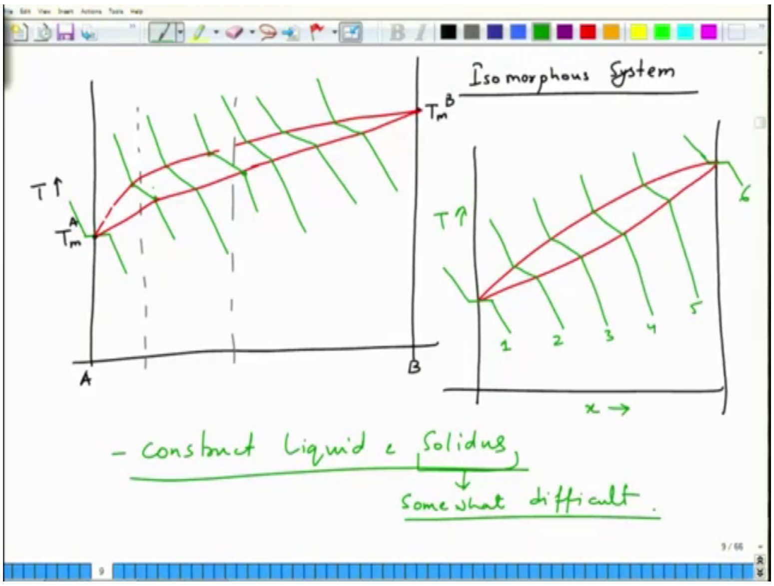

- Construct Liquid & Solidus → Somewhat difficult.

So now, let us say, you have a system for which you want to draw the cooling curves and so, what you do is that basically, you have let us say. So, this is A and B, let us say we have a isomorphous system and this is temperature. So, I obtained cooling curves for different compositions. So, let us say, we start from pure A, which has a melting point A and this has a melting point T m B.

So, for Tm A, when for the pure metal, the cooling curve is going to be something like this. So, this is going to be, the first point that I obtain in terms of where the solidification happens. So, this is the Tm, now as you go to as you go to another composition. Let us say, I go to this composition for this composition. Let us say, the curve is going to be you have curve like this and then this, you have one of this point, another of this point, then you have another one. Let us say for this composition, you start with. So, we have to be really careful so that, we do not end up going to down.

So, we have. So, if you just join them together. So, it is probably. So, it is gone little too up. So, if you join these points together, let me just use a different color, I think if you join these points together for example, this with this and if you keep doing it, you will obtain something like you know is it does not look very neat, but this is what you are going to obtain. So similarly, if you draw a cooling curve, it will look like, this for example, if you draw for this composition, it will look like this. So, draw for this composition it will look like this.

So, this is how you have cooling curves. So basically, if I redraw it, a little better, you have you have this phase diagram and cooling curves are going to look like, this is for pure metal on both sides and for these you are going to have something like. So, this is for composition, let us say, you are going to have different compositions. So, 1, 2, 3, 4, 5, 6 and when you stitch them together, you get a nice phase diagram ok. So, this is how you make a phase diagram by looking at the cooling curves of various systems and now what we are going to do is, that we are going to. So, this way, what you can do is that, if you if you do experiments in this way, you can construct liquidus and solidus ok. Construction of solidus is a little tricky because, what happens is that when you reach the solid often because of so this is somewhat difficult, because of compositional variances that occur as a result of non equilibrium cooling.

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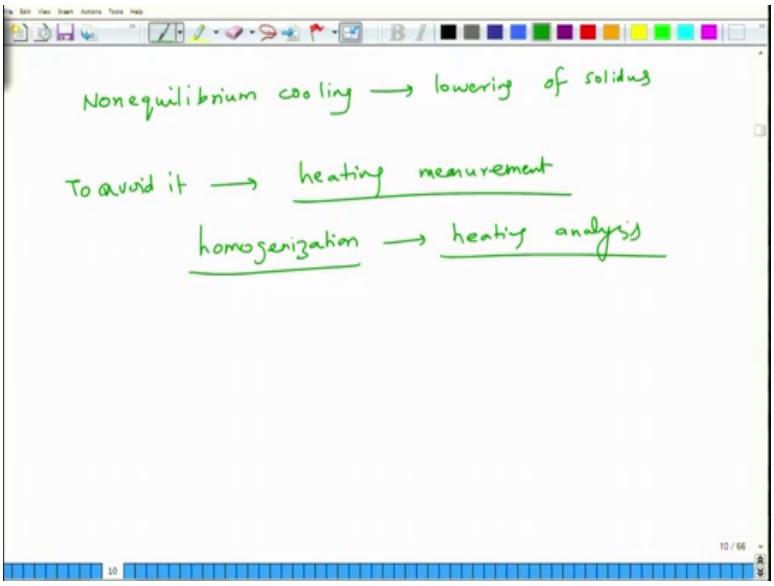

Nonequilibrium cooling → lowering of solidus

To avoid it → heating measurement

homogenization → heating analysis

So, non equilibrium cooling, which I explained that it creates con composition differences, this live gives right lowering of solidus. So as a result, measurement of solidus is somewhat tricky. So, what you what you do is that basically, to avoid it or to get better results, you do during heating. So heating measurements, because what you do is that, when you do heating. So, before you before you do heating, you homogenized alloy. So, homogenization follows by. So, you have homogenization, homogenization will remove the coring effects and then you do the heating treatment.

So, heating analysis and that will give you the better estimation of the solidus, it will be slightly higher than, what you observe during the cooling cycle. So, what we have done in this lecture is we have looked at how the phase diagram is measured, analyzed using thermal analysis by measuring cooling curves of alloys for both pure metals. So, you have different type of poly curves of pure metals and eutectics and different curves for liquid and solid regions, what we will do is that we will now, look at some more aspects of this measurement of phase diagrams, before we move on to the next topic of ternary system.

Thank you very much.