Phase Equilibria in Materials (Nature and Properties of Materials - II)

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Lecture - 32
Method of measuring phase diagram (cont…)

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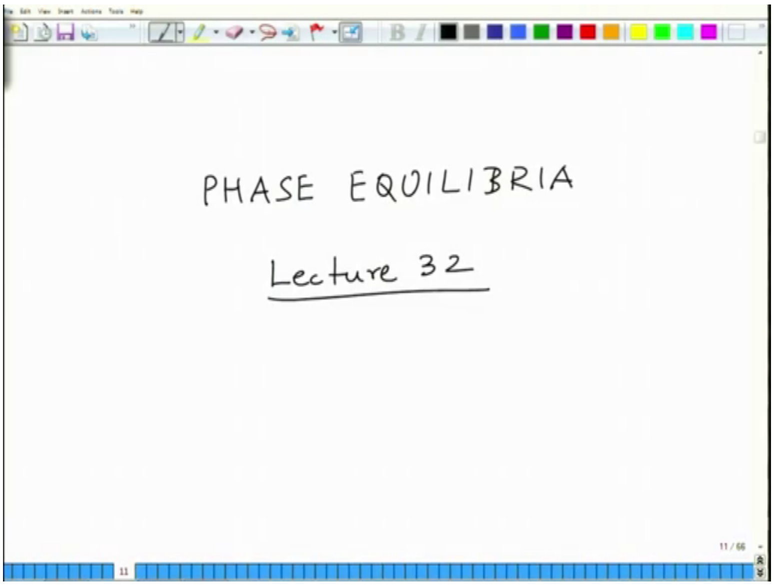

PHASE EQUILIBRIA

Lecture 32

So, now we will begin with the new lecture again this is lecture number 32 of Phase Equilibria course.

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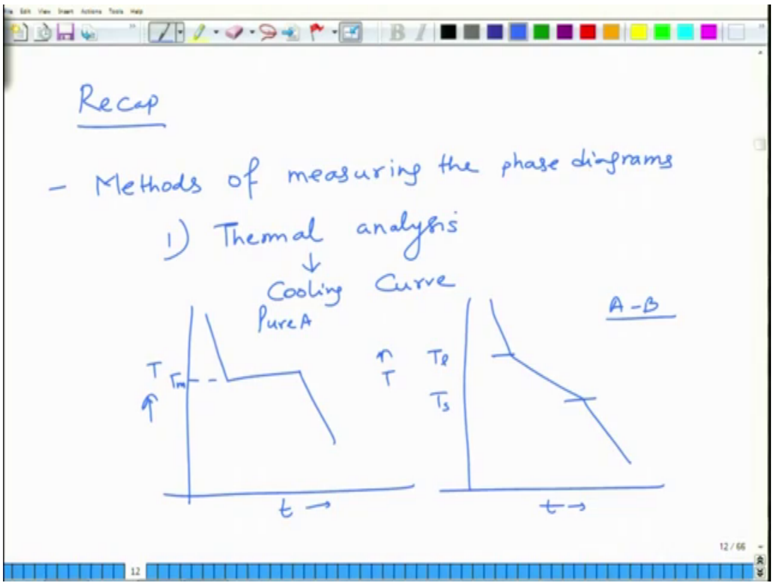

Recap

- Methods of measuring the phase diagrams
  1) Thermal analysis
  ↓
  Cooling Curve

So, what we did in the last lecture was to we looked at the methods of we introduced the methods of measuring the phase diagrams. So, what we basically introduced the first method as thermal analysis by measuring the cooling curves. And these are essentially you know, you can have a diagram like you can have a plot like this, time versus temperature for a pure metal or you can have put a two phase region, you can have something like this.

So, this is onset of solidification, this is the end of solidification, so, T liquidus, T solidus. And that is how you measure the and this is melting point, so that is how you measure the phase diagrams by stitched them, so this is for the fixed composition. So, this is for example pure A, this is for some A-B alloy. So, these curves are taken for different compositions and then they are stitched together to so you note down the liquidus and solidus temperatures. And then you stitch them a phase diagram.

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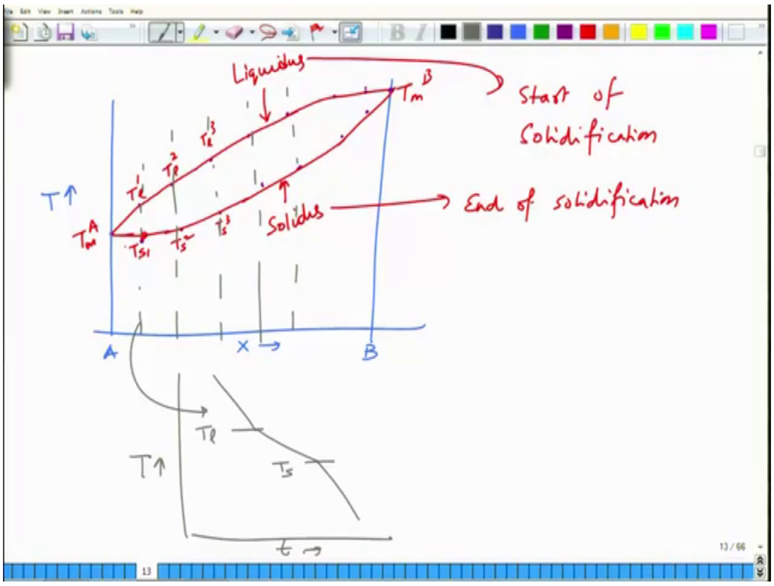

So, what you do is that using these curves. So, let us say for the pure metal, this is the melting point for the pure B, it is the melting point. Then in between you estimate points as this, this, this, this. So, these are the points that you obtain so, this is you can say T liquidus T solidus, T liquidus T solidus. So, this is 1, this is 2, this is T s 3, T l 3 and so on and so forth and this is T m A, this is T m B.

And if you stitch them together, you can construct a liquidus and solidus. So, it is not going very nicely, but something like that so, this point may be here. So, this is basically the liquidus and this is the solidus. So, this marks start of solidification and this marks the end of solidification. And these curves are obtained, so for each composition you are going to obtain a curve like this. This will be T l, this will be T s and this is what you have a stitched together.

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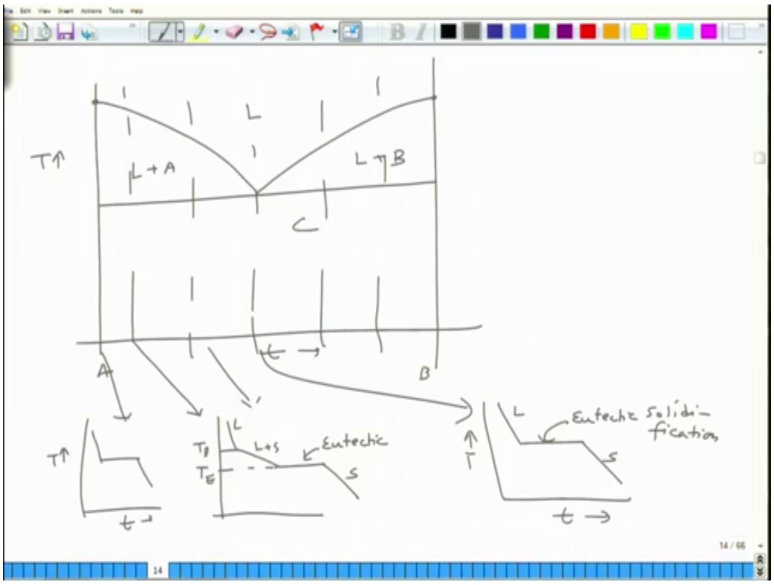

Similarly, if you want to obtain the similar curve for a eutectic phase diagram you will have, so this is temperature time. So, for a eutectic phase diagram with no solid solubility, you will have this kind of phase diagram let us say. This is liquid, liquid plus A, liquid plus B, and C, so for you have let us say these compositions. So, this is where we will have so we will have to begin with pure A, the pure A will have temperature like this.

For this composition you will have, so this is T l, this is T E ok. So, this is liquid, this is solid, this is liquid plus solid and this is eutectic transformation. And same will be obtained for this composition also and then for eutectic you will obtain this is liquid, this is solid, this is eutectic solidification. And same is going to be repeated on the other side. The trick the issues arise in phase diagrams, so you have a solvers region.

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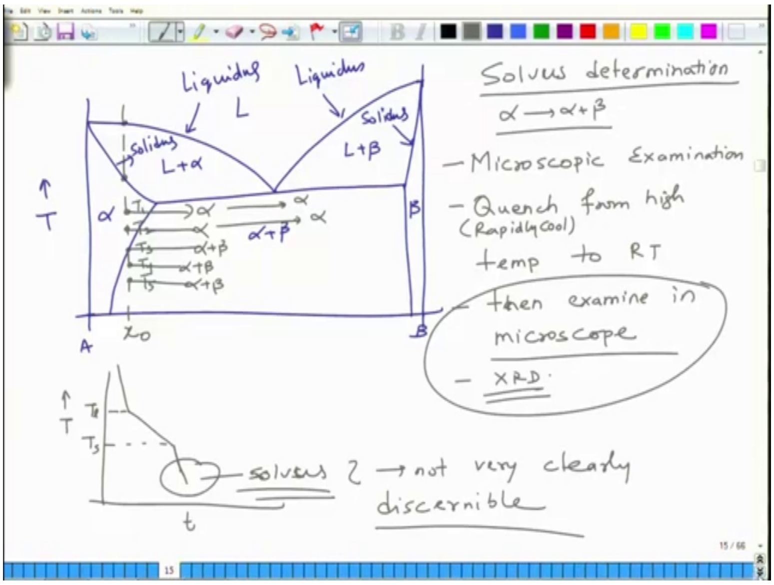

Solvus determination

α → α+β

- Microscopic Examination
- Quench from high (Rapidly cool) temp to RT
- then examine in microscope
- XRD

So, if you have a phase diagram like this, so you have a liquid, you have liquid plus alpha, liquid plus beta, alpha, beta and alpha plus beta so, this is liquidus you can measure it easily. This is liquidus, this is solidus and this is also solidus. These can be measured using the phase diagram, the cooling curves easily, point is when you come to this point, so let us say if I choose this composition, let me just remove this color.

If I choose this particular composition, then how do I so I can measure this, I can measure this. So, if I take this composition x naught let us say, so for this the cooling curve is going to be like this. So, you start from liquid phase, then you go into two phase region then you have eutectic, you have you do not have eutectic here. You get into a solid phase region ok, so you get into a solid phase region. But, then what happens here, here you start seeing some beta automatically. And this may not be very obvious in this cooling curve, because the chain temperature changes here or the slope changes here may be very insignificant.

So, this is fine T l, this is fine T s, but what will happen to solvers. So, solvers is not very clearly discernible, you cannot distinguish it very easily. So, solvers is generally so for solvers determination we generally use techniques, so this is since you are dealing in only solid state. So, you are going from alpha to alpha plus beta, so essentially it is alpha to alpha plus beta going through a solvers temperature you need to conduct microscopic examination.

So, what you need to do is that, you take your alloy at various temperatures. So, you heat your alloy to this point to this point to this point to this point to this point quench it. Quench means rapidly cool from let us say T 1, T 2, T 3, T 4, T 5 quench from quench means rapidly cool, which means like throwing in water ok. From high temperature to room temperature and then examine in microscope it works well with those systems, where this.

So, in this for example, here you will have alpha, here you will have alpha, here you will have alpha plus some amount of beta, this will be alpha plus beta and this will be alpha plus beta it is ok. So, as long as you are quenching, so if you quench from T 1, you should have alpha. If you quench from T 2, you should have alpha. So, it is as long as the high temperature phase is retained after quenching at lower temperature, so that you can see that it at this temperature, it was this phase.

However, if the system decomposes into the so if this alpha decomposes into alpha plus beta upon quenching, which means that it has very large driving force to form the beta phase, then you may not be able to obtain correct information. In such a case, so what you need to do is that when you do examine them in microscope and do XRD. So, X-ray will tell you about the structure of the phases, microscope will tell you about that difference in the morphology and their appearance, and compositions, and then you correlate this information together.

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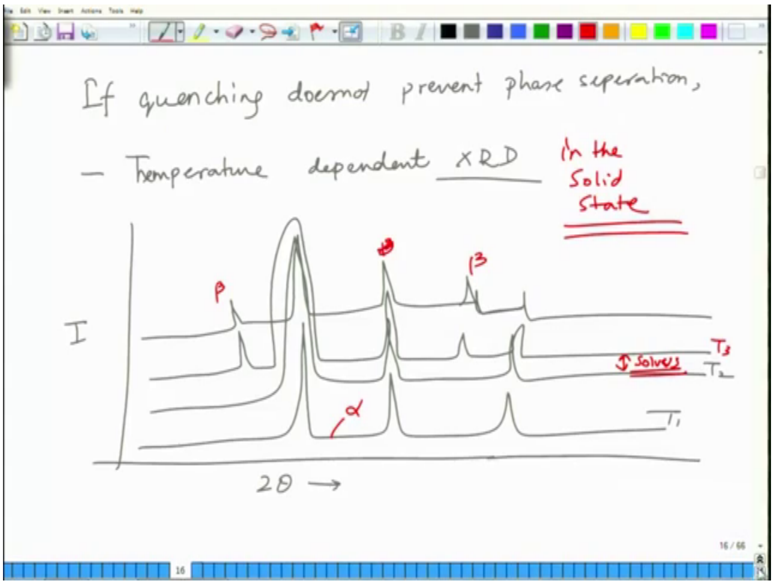

If quenching doesnot prevent phase seperation,

- Temperature dependent XRD in the Solid State

However, if quenching does not prevent phase separation, which is the stable at low temperature, then you need to do temperature dependent XRD. So, basically you take X-ray diffraction pattern. So, X-ray diffraction pattern is 2 theta versus in density so, let us say you have a pattern like this ok. And so this is at T 1, then at T 2 also it shows similar sort of pattern, but at so this is T 2 then at T 3, it starts showing some other peaks, and then at T 4 again you will have.

So, basically this phase let us say is alpha phase and then you start seeing the peaks of beta phase sorry beta phase. So, this is how you, so that the appearance of new peaks in the X-ray diffraction pattern as the phase transformation happens. So, this is where somewhere between T 2 and T 3, you will have solvers and this is in solid state. So, temperature dependent XRD in the solid state to determine the solvers line so, this is how you determine the phase diagrams using thermal analysis.

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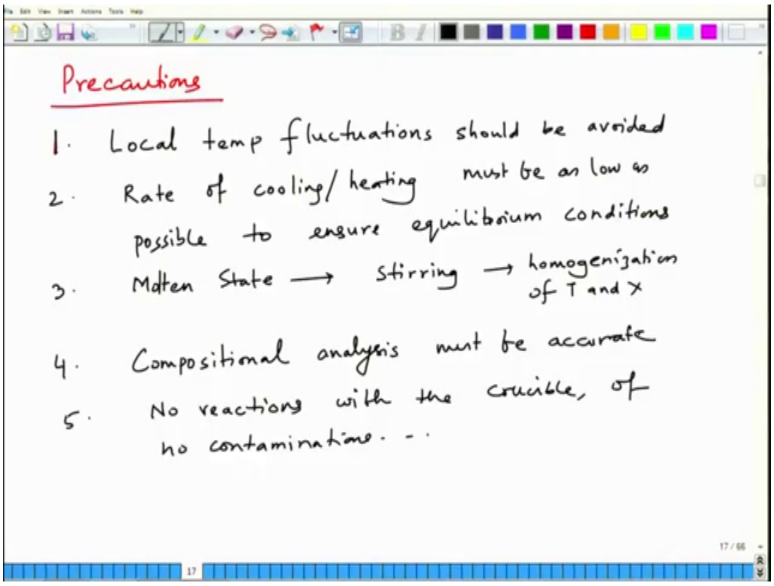

Precautions

1. Local temp fluctuations should be avoided
2. Rate of cooling/heating must be as low as possible to ensure equilibrium conditions
3. Molten State → Stirring → homogenization of T and X
4. Compositional analysis must be accurate
5. No reactions with the crucible, of no contaminations . . .

The precautions that you need to take during thermal analysis is 1, we need to have local temperature fluctuation should be avoided. So, basically we need to maintain the as uniform temperature as possible, which means that rate of cooling or heating depending upon whether you take in heating or cooling cycle must be as low as possible to ensure equilibrium to ensure equilibrium cooling or heating conditions equilibrium conditions.

Then 3rd is if you are in molten state, then you need so molten state may often require stirring. And this is stirring tends to uniform homogeneous the melt and equilibria the temperature as well as composition. So, for homogenization of temperature and composition and then the compositional analysis must be very accurate, so must be accurate. And then number 5, you should not have any no reactions with the crucible in which you are holding the material or no contamination, because any fluctuations in composition or changes in composition will alter the cooling curves and phase diagram etcetera.

So, these are the precautions that you must take to obtain these cooling curves for given compositions. And then you stitch the cooling curves and then you extract the values of solidus and liquidus temperatures from the cooling curves. And then put them on the temperature composition diagram for each of the composition and then a stitch them together to obtain phase diagram. So, this is how you determine simple phase diagram, at least if not the complex ones.

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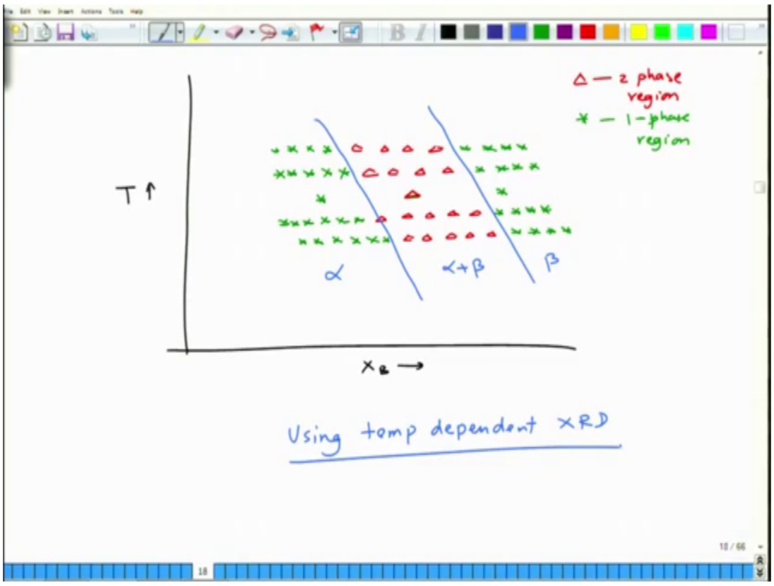

There are some other methods which one can use to determine the phase diagram. So, for example, I was telling you about the X-ray diffraction use. So, for the X-ray diffraction of solvers line for instance, so, let us say this is X B versus temperature. So, let us say we have this triangle as a 2-phase region and this star as single-phase region. And I have some initial data point that you know for this composition, I have single-phase region for this composition, I have 2-phase region.

So, let us say I put here and then for this composition I have a single-phase region. Now, what I do is that I do this analysis at various temperatures. So, I do this, so I can take data points at various points and I find that you know my two phase region, my phase existence is something like this. So, I do at a few temperatures below and above and we obtain so, similarly you do for a temperature above also.

And then you see that you know the phase boundary is something like this. So, you have this as a phase boundary between the two phase region so, this is alpha let us say, this is alpha plus beta, and this is beta. So, this is how you determine the phase boundaries between two phase boundaries between solid in the solid state between single-phase and 2-phase regions. So, this is using temperature dependent XRD ok.

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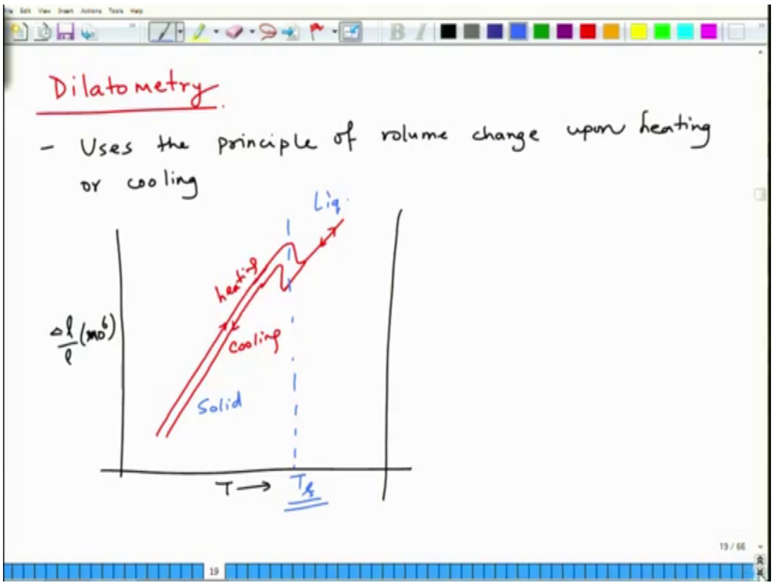

Dilatometry

- Uses the principle of volume change upon heating or cooling

Now, let us look at some of the auxiliary or other methods that are used for phase diagrams to assist with phase diagram identification. So, the first method that we use is called as dilatometry. This dilatometry is essentially based on uses the principle of volume change upon heating or cooling. So, what you have here is you make a plot of change in dimension versus temperature. So, this is delta l by l and this is typically in microns ok. So, let us say into 10 to power 6 ok and you measure these. So, you and this is let us say temperature what you do is that you first increase this you measure that so everything is going to increase longer as you increase.

So, volume will increase as a function of increase in temperature. And then at certain point, you will have change in volume in this fashion as it goes to liquid state and then we cool it, it undergoes this kind of behavior. So, something like that you will obtain, so this is heating, this is cooling.

So, you will have solid state in this region, you will have liquid state in this region, there is some hysteresis that you will observe during the phase changes that will occur. They are specially significant in the solid state, but this can tell you about changes in the transformation transition temperature. So, this is for example, a change in the transition temperature that you will obtain by dilatometry. So, this is let us say T c that the critical temperature of transformation, when this case T solidification or T melting.

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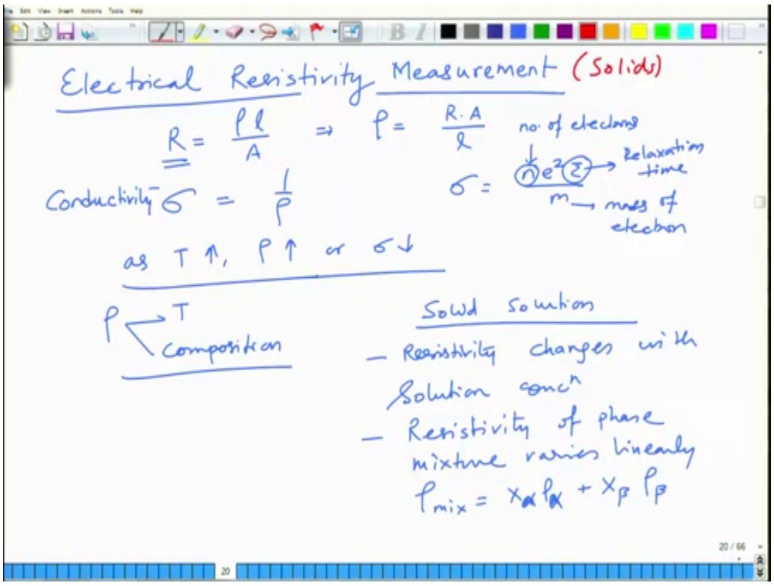

Electrical Resistivity Measurement (Solids)

$\underline{\underline{R}} = \frac{\rho l}{A} \Rightarrow \rho = \frac{R \cdot A}{l}$

Conductivity $\sigma = \frac{1}{\rho}$

$\sigma = \frac{\overset{\text{no. of electrons}}{\downarrow} \; \boxed{n} e^2 \boxed{\tau} \rightarrow \text{Relaxation time}}{m \rightarrow \text{mass of electron}}$

as $T \uparrow$, $\rho \uparrow$ or $\sigma \downarrow$

$\rho \begin{cases} \rightarrow T \\ \text{Composition} \end{cases}$

Solid Solution

- Resistivity changes with Solution concn
- Resistivity of phase mixture varies linearly

$\rho_{mix} = X_\alpha \rho_\alpha + X_\beta \rho_\beta$

Now, other method that people generally uses the measurement of electrical resistivity. Now, electrical resistivity basically so we know that R is equal to rho l upon A, which is this is the resistance and this is the resistivity. The resistivity is a function of we can say R into A divided by l. So, as you as the composition changes and resistivity is related to and resistivity is equal to conductivity, which is inverse of conductivity. So, conductivity sigma is equal to 1 over rho and sigma is equal to n e square tau over m, where n is the number of electrons is the electronic charge tau is the relaxation time and m is mass of electron.

Now, electrical conductivity is because of motion of free electrons in the metals. And as you increase the temperature, the relaxation time in the materials in the metals typically goes down, because of higher scattering or thermal scattering of electrons. As a result electrons cannot conduct as easily as they would conduct at lower temperature. And hence, you have lower conductivity, which means resistivity as the temperature increases the resistivity also increases or you can say sigma decreases, because of higher thermal scattering.

Resistivity is also a function of composition as you change the composition, the composition leads to changes in relaxation time as well as changes in the number of electrons. And these two put together again change the conductivity so; resistivity is a function of temperature as well as composition. So, when you measure the resistivity of alloys, so change in so basically in solid solutions what happen is that solid solutions resistivity changes with solute concentration ok.

And generally is speaking resistivity of phase mixture varies linearly. So, basically row mixture is equal to X A rho A rho alpha plus X alpha rho alpha, which is the weight fraction of X alpha and resistivity of alpha phase and X beta and rho beta. So, this is this will follow generally rule of mixtures. And as you go from single phase to 2 phase region, there are abrupt changes in the resistivity.

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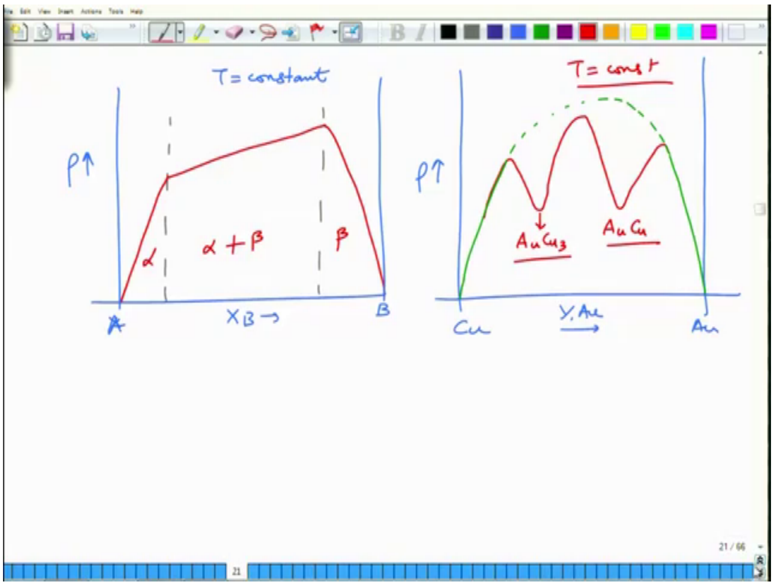

So, for example you might have a situation like this for a 2-phase region at a constant temperature so, this is temperature is constant. So, when you measure resistivity as a function of X B, let us say A B. So, we have we can have a situation like this resistivity may vary in this fashion this and then it can go like this and then it can again come down like this.

So, this would be for example, transition between alpha to alpha plus beta to beta phase. So, this could be one sort of thing you can obtain, you may also have scenarios like this. Especially in a lawyers where inter metal x form such as copper gold alloys so, let us say you have copper gold system with gold percentage increasing. And the disordered solid solution will show a behavior like this. But, what happens is that when you mix gold and silver together, gold and copper together, some at few compositions they make ordered solid solutions.

And what happens is that in those cases, the conductivity varies resistivity changes like, so it shows a spikes. So, these spikes, so these are much sharper spikes exam so, this could be for example A u C u 3 or this could be because of A u C u. So, they are not exactly on the composition axis, but so this is how you may have the changes in the resistivity depicting the formation of various phases in the phase diagram. So, this is so you can you so again at a constant temperature.

So far at various temperatures as a function of compositions, you can vary the resistivity and may make a map or resistivity. And this may help you especially in the solid state map out the changes in the resistivity giving you temperature versus composition diagram.

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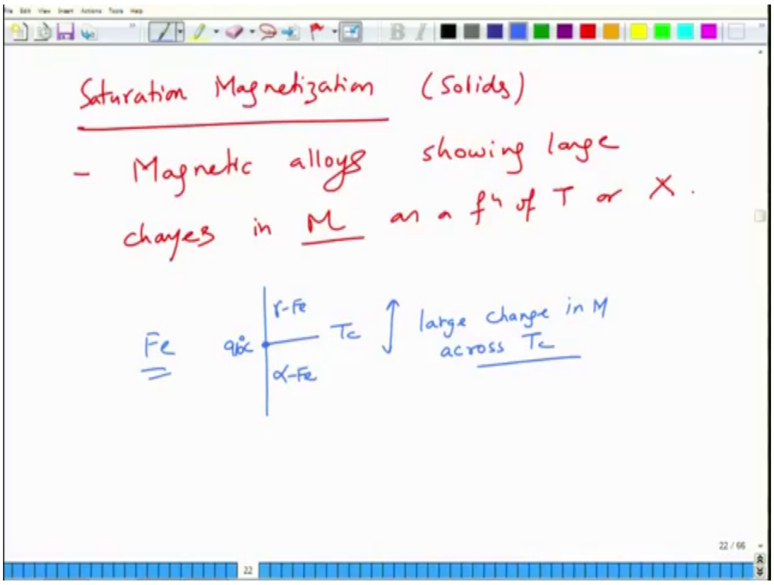

Saturation Magnetization (Solids)

- Magnetic alloys showing large changes in M as a f^n of T or X.

Third thing that one can do especially for magnetic systems is measurement of saturation magnetization. Essentially what we are saying is that we measure the functional properties of the materials. So, magnetic so this is again, you will do in solid state the previous ones was also in basically in the solid state. So, here it is mainly important for magnetic alloys showing large changes in magnetization M as a function of temperature or composition ok.

So, for example when you go from let us say for if you let us say look at iron ok, so iron shows a transition at so this is 900 and 10 degree centigrade. So, iron goes from alpha iron to gamma iron and this is a magnetic transition of iron. So, it goes from ferromagnetic to paramagnetic state as you heat it, so that there is a large change in so you can say there is a large change in M across T c. And this could also happen as a function of composition, so again you can map out the phase diagram by measuring these functional properties.

So, essentially what we have done in this lecture is we have looked at various methods of that are used to determine the phase diagrams of simple metals and alloys. And the techniques that we follow our thermal analysis, which means measuring the cooling curves as a time versus temperature plots for pure metals as well as for alloys.

And then mapping out liquidus and solidus temperatures to construct the phase diagram, and seem this can be done for both isomorphous, eutectic systems, measurement of solvers is a lot more difficult in the solid state. As a as a result you complement various techniques microscopic techniques, X-ray diffraction, temperature dependent X-ray diffraction as well as with drystivity and dilatometry or magnetization method techniques to complement the information make a make a phase diagram with the accurate data. And measurement of composition is very critical in these things, it should be accurate.

So, this is what we had done in past few lectures. Now, in the next lecture what we will do is that we will measure, we will present a case study, suppose you are given certain amount of data. And then based on that data how do you construct a phase diagram and determine various aspects. And so this we will do that in the next class.

Thank you very much.