Basics of Materials Engineering
Prof. Ratna Kumar Annabattula
Department of Mechanical Engineering
Indian Institute of Technology, Madras

Lecture – 33
Part 1 - Phase Diagrams (Allotropy, Eutectoid, and Peritectoid Reactions)

(Refer Slide Time: 00:13)

Welcome back. In the last class, we have completed the discussion on type 4, 5, 6 and 7 alloys. We have to looked at various reactions in the system when there is a liquid phase present - important reactions such as eutectic reaction, peritectic reaction, monotectic reaction - these are the kind of reactions that we have looked at.

Let us now look at the transformations that would happen in the solid state alone; that means, once the material is solidified, there may be further transformations for the solid within the solid state. We are going to look at four important solid-state transformations.

The four transformations are - allotropy, order-disorder transformation, and two special reactions - eutectoid reaction and peritectoid reactions, which give rise to new microstructure to the system.

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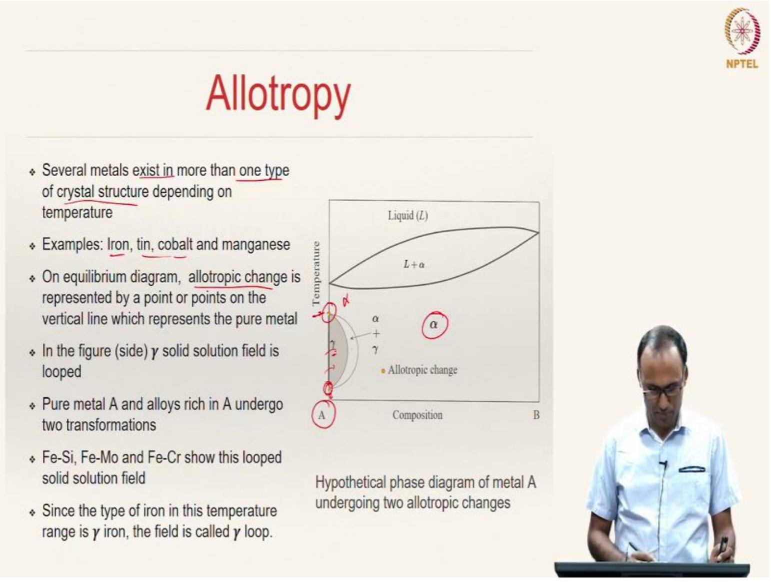

Several metals that we know of exist in more than one type of crystal structure depending on the temperature; at a lower temperature they exist in one kind of a crystal structure and if we increase the temperature, their crustal structure changes. Examples for such materials are iron, tin, cobalt and manganese.

Iron is known to have BCC at low temperatures; if we increase the temperature, the crystal structure of iron changes from BCC to FCC. On phase diagram, the allotropic change is represented by a point or a group of points on the vertical line. A point represents an allotropic change on the vertical line.

For instance, if you take pure metal A, here you see that this orange point represents the allotropic change; below this orange point this has an α-phase - that is one particular crystal structure, and above that it will change to γ-phase. So, between this orange point and this orange point, the material is in γ-phase; above that phase, the solid is in the α-phase.

Here you can see that γ-phase is looped in the phase diagram. Pure metal A or the alloys rich in A undergo two transformations; one at lower allotropic change and another one here. So, here is one allotropic change, here is another allotropic change.

The systems which show such a looped behavior - so, for instance, if you see here, you have an alpha phase changing to gamma and as a result, you will have a two-phase region. i.e., $\alpha +$

γ. Since in this region, the type of iron is called γ-iron and hence this is also called γ-loop, in the iron system.

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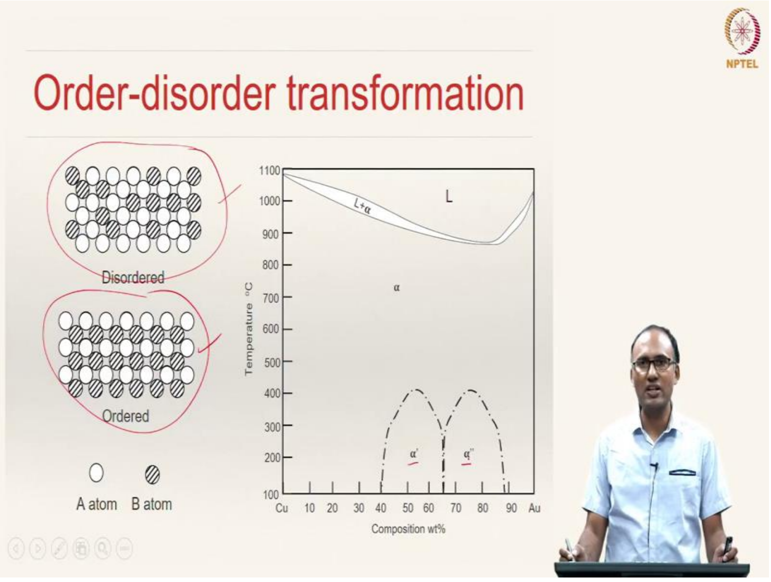

The next transformation is the order-disorder transformation. What do we mean by order-disorder transformation? If you look at the arrangement of atoms A and B, in the disordered system there is no specific order in which they are arranged. Whereas in an ordered system, they attain a specific ordering arrangement, as we can see in this figure.

If the solid solution has such an ordered structure, that is called an ordered solid solution; otherwise, it is a disorder solid solution. On phase diagrams, these solid solutions which are ordered are usually shown by dash-dot lines. Ordered solid solutions are usually designated using Greek letters, such as, α', α'', etc., or α', β', etc.

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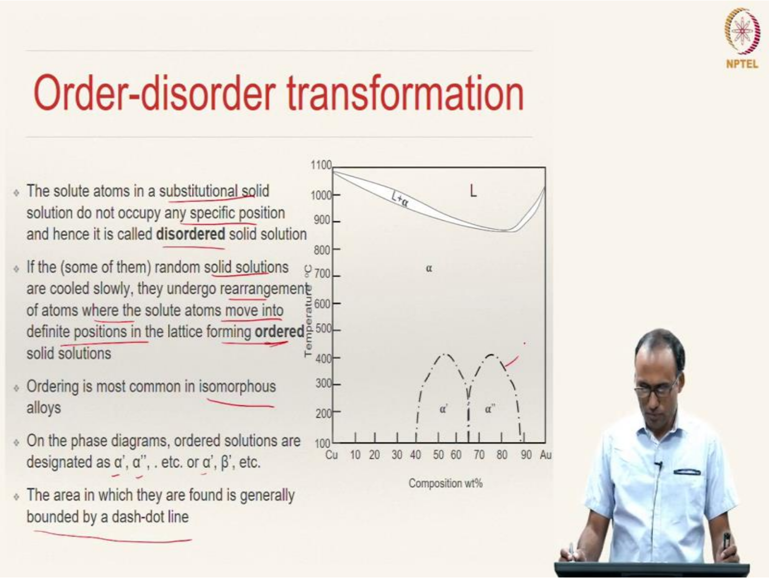

As we have already mentioned, solute atoms in a substitutional solid solution do not occupy any specific positions and hence that is called a disordered solid solution. If the random solid solutions are cooled slowly, then they undergo rearrangement of atoms, where the solute atoms move into definite positions in the lattice; that means, they are moving to a specific position, so as to give some order to the lattice structure. Such solutions are called ordered solid solutions.

Ordering is very common in isomorphous alloys. On the phase diagrams, ordered solution are designated as α', α'', etc., or α', β', etc. The area in which they are found is generally bounded by a dash dot line as we have shown here.

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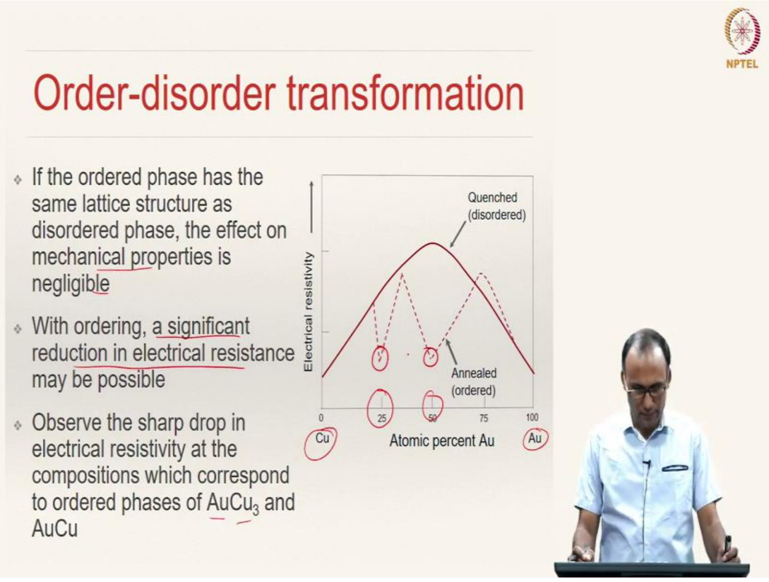

What is the implication of this ordered solid solutions to the properties of the alloys? If the ordered phase has the same lattice structure as the disordered phase, then the effect on mechanical properties is negligible. However, with ordering, a significant reduction in electrical resistance may be possible.

For instance, if you see here, you are having copper-gold system. In the copper-gold system, the solid line represents the electrical resistivity as a function of alloy composition and you see the solid line represents for the disordered solid solution.

For an ordered solid solution, you can see that at the compositions $AuCu_3$ corresponding to this data point and AuCu corresponding to this data point, you have a sharp drop in electrical resistivity. We see that conductivity has increased significantly for the ordered solid solution.

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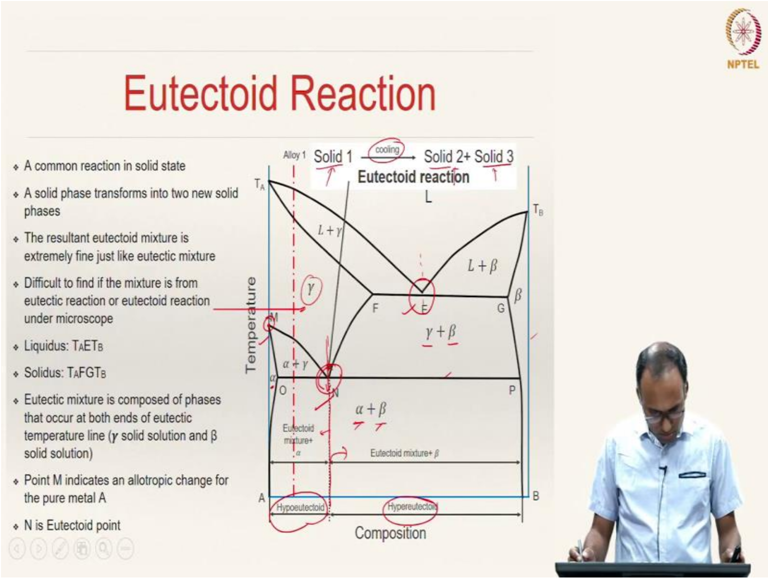

The next reaction that we are going to discuss about is the eutectoid reaction. What is eutectoid reaction? The name of eutectoid reaction is very close to another reaction that we have studied previously, that is eutectic reaction.

There is a difference between eutectic and eutectoid reactions. The reaction formula looks exactly the same except that a wherever there is a liquid in the eutectic reaction you replace that with a solid, then that becomes eutectoid reaction - because it is a solid-state reaction.

Eutectic reaction is the one in which a liquid upon cooling gives two solids. Now, you represent liquid with a solid. If a solid 1 upon cooling gives solid 2 and solid 3 - two different solids, such a reaction is called eutectoid reaction. It is a common reaction in solid state. Here, a single-phase is transforming to two new solid phases - that is important.

The microstructure of the eutectoid mixture under a microscope looks very similar to eutectic mixture - as alternate layers of A and B or α and β. And hence, it is difficult to find if the mixture is from eutectic reaction or eutectoid reaction, because their microstructures look very similar.

In this particular phase diagram, the liquidus line is $T_A ET_B$, and solidus line is $T_A FGT_B$. This is the eutectic reaction, wherein the liquid transforms to two solids γ and β. However, point N represents the eutectoid point where γ transforms to two solids.

As we have discussed, the point N represents the eutectoid reaction wherein a single solid phase γ when upon cooling gives two solid solutions α and β. So, this line OP represents eutectoid temperature or eutectoid reaction line; N is eutectoid point.

Again, in this diagram, here you have α-phase and at point M, it is changing to γ-phase. So, M is your allotropic point as we have discussed previously for allotropic reaction.

This phase diagram shows the allotropy and it also shows eutectoid reaction - the solid-state reaction, but it also has eutectic reaction in the liquid phase. This is what you call eutectoid alloy, and left to that are called hypoeutectoid alloys, right to that are called hypereutectoid alloys.

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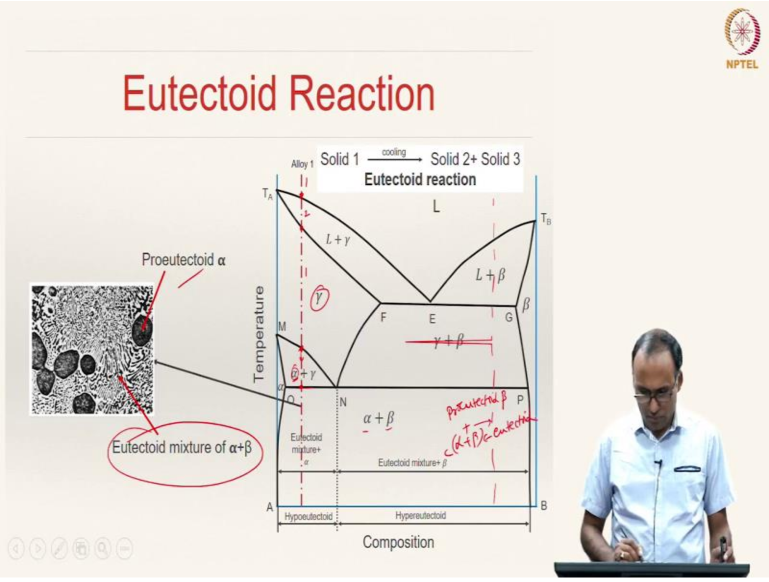

Alloy 1 which is in the liquid state to begin with, starts solidifying at this point, and then continuous to solidify. The solidification finishes here, and then the liquid would have transformed to γ - it is a single-phase region. So, here it is single-phase region, this is two-phase region, again this is single-phase region. It actually cools down in the single-phase region and again hits this line MN.

Here, the γ again starts entering two-phase region - $\alpha + \gamma$; but this is not a eutectoid reaction because it is not happening at constant temperature. Instead, what is happening is the γ is going to precipitate out α, and the α composition gradually increases.

Until this point is reached, that is eutectoid point, you have proeutectoid α, and at this point, the whatever γ that is remaining, will undergo the eutectoid reaction giving rise to eutectoid mixture of α and β.

The final microstructure will have proeutectoid α and eutectoid mixture of α and β. Similarly, if you have another alloy that is solidified here, it will have proeutectoid β + eutectoid mixture of α and β -- $\alpha + \beta$ - that is eutectoid mixture.

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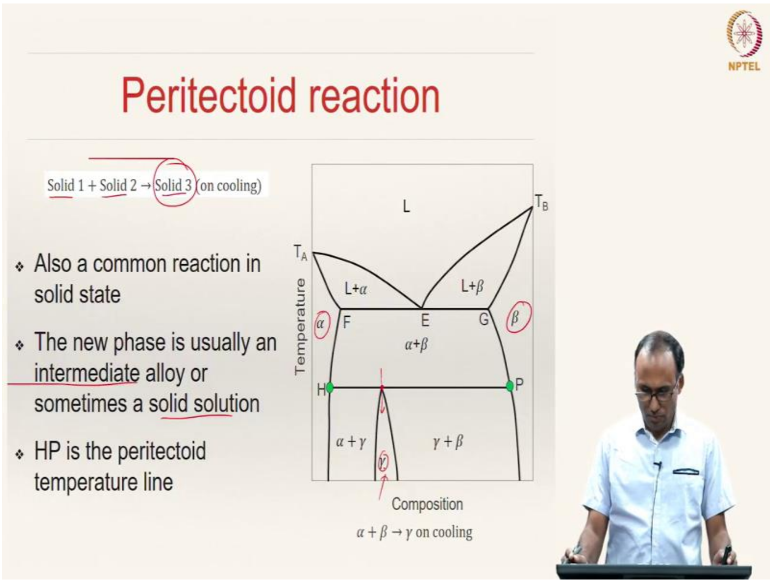

In this diagram, we will try to demonstrate the peritectoid reaction. So, peritectoid reaction is the one in which two solids, solid 1 and solid 2 upon cooling gives you solid 3.

It is easy to remember peritectoid reaction, because the peritectic reaction is liquid + solid gives you another solid. So, you remove liquid with a new solid i.e., solid 1 + solid 2 gives another solid, upon cooling. This is also a common reaction in solid state, like eutectoid reaction.

The new phase that is formed from these two phases is usually an intermediate alloy or sometimes a solid solution. Here, you can see that the line HP is the peritectoid temperature line. So, here $\alpha + \beta$ would transform to γ on this line. If you take this particular alloy, $\alpha + \beta$ is transforming to another intermediate phase called γ.

If you see carefully here, now you can understand why we call α and β as terminal solid solutions - because you also have an intermediate solid solution called γ here.

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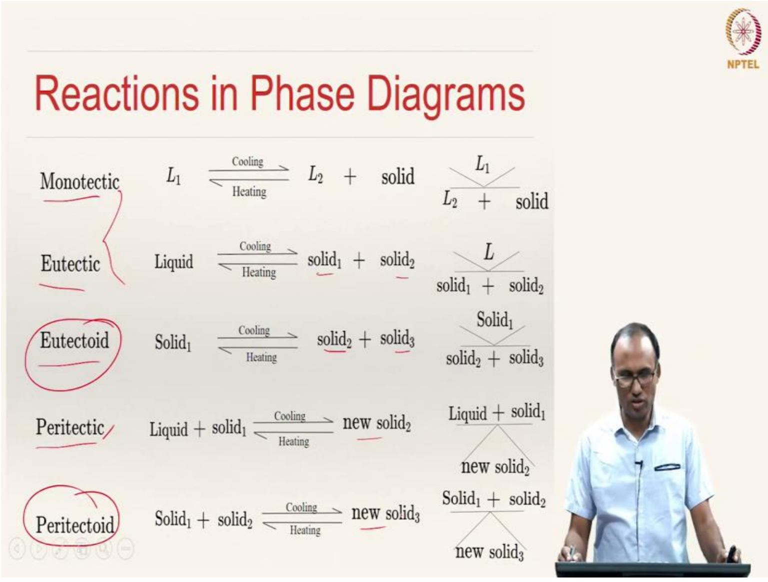

So far, in this course, we have discussed these five reactions - monotectic reaction, eutectic reaction, eutectoid reaction, peritectic reaction, and peritectoid reaction. Eutectoid and peritectoid are solid state reactions, and the other three also involve a liquid phase in their reactions.

The monotectic reaction is liquid when cooled gives a liquid and another solid. Eutectic reaction - a liquid when cooled, will give two solids; eutectoid reaction - a solid when cooled gives two solids; peritectic reaction - a liquid and a solid gives a new solid; peritectoid - two solids when cooled give a third solid.

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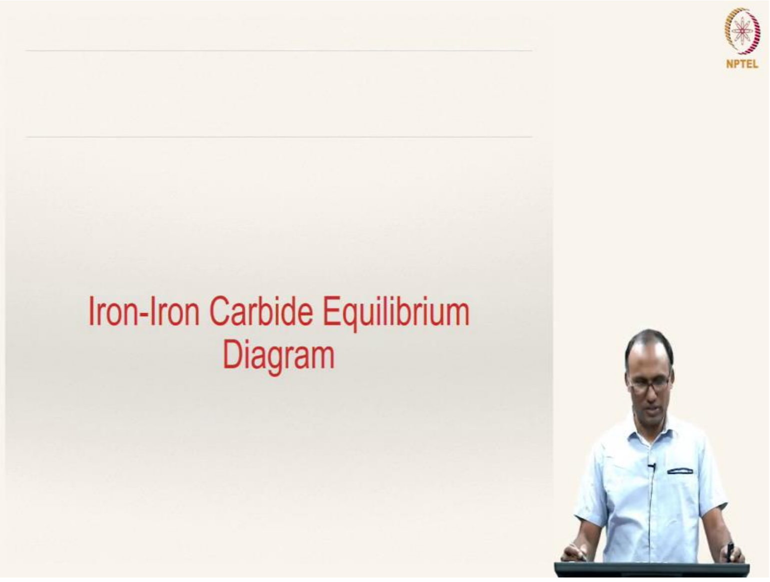

With that, we have also discussed different types of solid-state reactions that one would come across when we are dealing with phase diagrams. The next topic that we are going to discuss is a specific material system phase diagram, that is iron-iron carbide equilibrium diagram.