# Non-Metallic Materials

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**Module - 02**
**Defects, and reaction kinetics of non - metallic materials**
**Lecture - 10**
**Phase diagram and microstructure evolution in Non – metallic materials**

Welcome to my course Non-Metallic Materials and this is part of the lecture of module-2 Defects and Reaction Kinetics of non-metallic materials, where I will be describing the phase diagram and associated microstructural evolution of non-metallic materials.

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To start with, the concept that I wish to cover is the phase rule particularly for the one component system that I will cover in the lecture. Binary system then I will take which is having two components system, and several types of binary system including complete range of solid solubility, eutectic diagram which is having partial range of solid solubility, but no intermediate compound in it. And also another category which is partial solid solubility is there, but intermediate compound forms there in.

So, these things will be illustrated, illustrated in this particular lecture. And additionally for particularly for the ceramic based system we will introduce the ternary phase diagram which is not very well defined in several textbooks which I have seen. And we will be introducing this details of the ternary phase diagram in this particular lecture.

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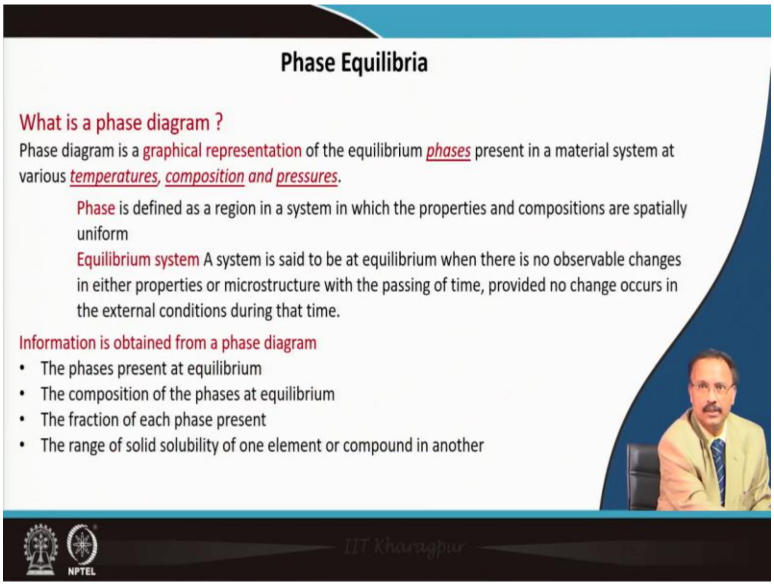


Now, the phase diagram is basically a graphical representation of the equilibrium phase that is there in a particular material system. This equilibrium phase present in the system at different temperature, composition of the material as well as in different ambient pressure. So, the phase that is defined as a region in the system in which the properties or the compositions are spatially uniform, so that is defined as a phase.

The equilibrium system is a system where there is no observable change either in the property or in the microstructure with time, so this remains constant. And this remains constant only to the extent when the external temperature and pressure they are remaining constant. So, either it should be isothermal or isobaric system when the equilibrium is talked about.

So, if you understand the phase diagram, you can understand that what are the phases that is present in the system at equilibrium, the composition of that particular phase. If multiple phases as present, for example, solid and liquid then what are the fraction of each of these phase, and the range of solid solubility to solid form a solid solution that also you can read from the phase diagram.

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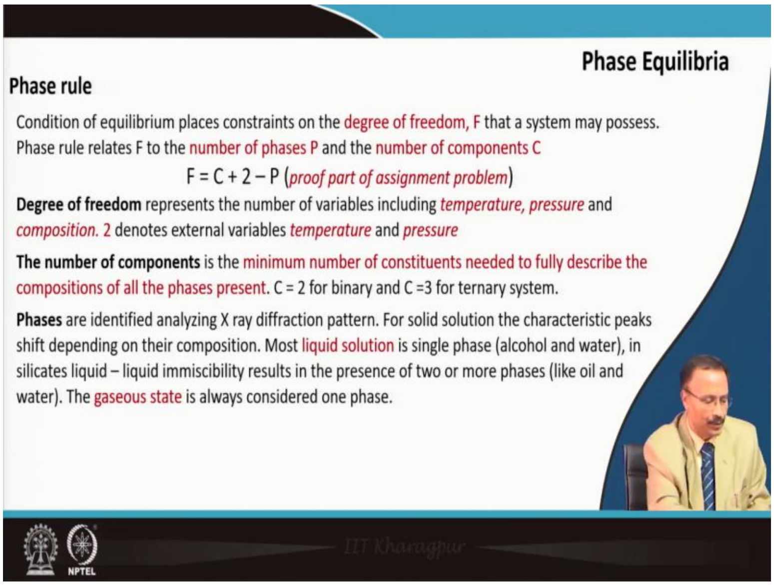


So, let us first introduce the phase rule and this phase rule as you can see in the relevant equation is related to the degree of freedom. Degree of freedom is denoted by F. Component of the system, if it is a single component system or multi component system three components system, so that is a part, and these 2 determines signifies the temperature and pressure, and P is the number of phase.

So, this is just a relation. So, degree of freedom usually is temperature pressure and composition. Number of components as I said that for single component system it is 1; for ternary system, it is 3.

And the phase usually for crystalline phase, you can identify by X-ray diffraction. If it is forming a solid solution, then the peak X-ray diffraction peak correspond to the pure material, this is slightly shifted either right hand side or left hand side depending on its lattice parameter change.

And for gaseous system, it is just mixture, so only one phase is present. And for liquid system, usually that is a one phase system, except in certain glassy liquid silicate base liquid you have the clear demarcation of the phase mixture. So, in that case probably two-phase you can consider.

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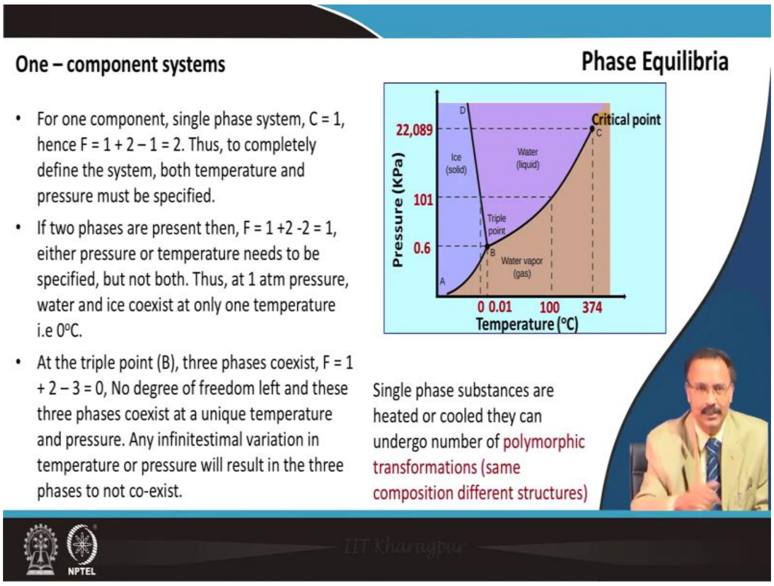


So, in single component system, component is 1, degree of freedom will be 1 plus 2 minus phase is 1. So, if the degree of freedom is 2, then the complete if you want to define a single phase system, then you will have to specify the temperature as well as pressure. When two phases are present, then your degree of freedom you put it in that equation degree of freedom is 1, so either temperature or pressure you will have to define.

For example, at 1 atmosphere, water and ice co-exists, all you, all of you know. So, at one temperature only one temperature – 0 degrees Celsius, you will have to mention that that, what is the temperature because pressure is 1 atmosphere. When it is a triple point, three phase coexist.

Again you go back to the phase rule which as a part of the assignment problem you need to prove the phase rule whatever I have described. So, at the triple point, you can see that F is equal to 0. So, you have no degree of freedom. So, you cannot change pressure, you cannot change temperature, you cannot change composition. So, it is a unique point.

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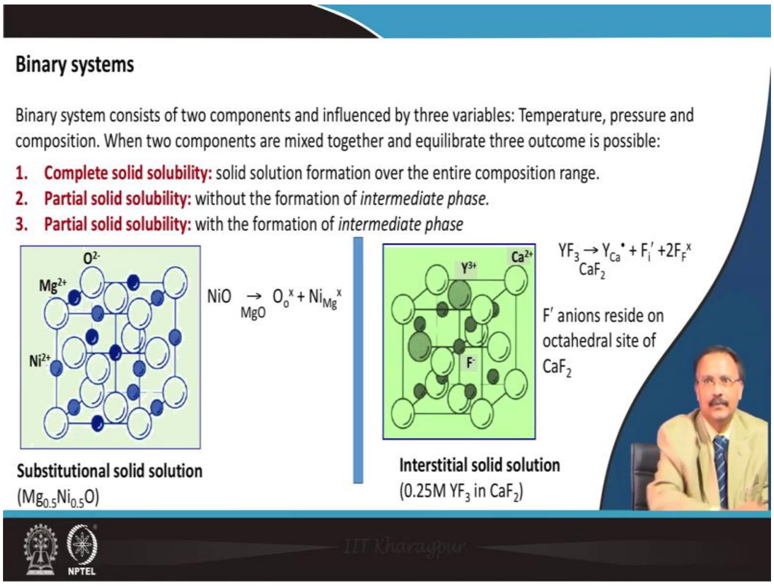


So, the polymorphic phase transformation, I will take part of the course for a single component system in the phase transformation lecture. So, single phase system in ceramic, it is important for barium-titanate, for silicon dioxide. So, we will be taking that details of the single component single phase diagram. So, for the binary system, you have three different possibility. One is a complete range of solid solubility. I talked about the defect.

Here it is isotropic substitution. So, nickel oxide is replacing magnesium oxide, both are FCC structure. So, no additional defect point defect is being created. So, in this case, you can see a complete range of solid solubility will occur. For example, 50 atomic percent nickel is introduced in the magnesium oxide lattice.

In the second case, it is a fluoride base structure, calcium fluoride, and you are doping it with say yttrium. So, there is a charge imbalance. So, it will create yttrium when it goes to the calcium site, it is replacing the calcium as you can see here. So, to maintain the charge balance fluoride ion will come to the octahedral site. So, this is one example for interstitial solid solution. This is another example for the substitutional solid solution.

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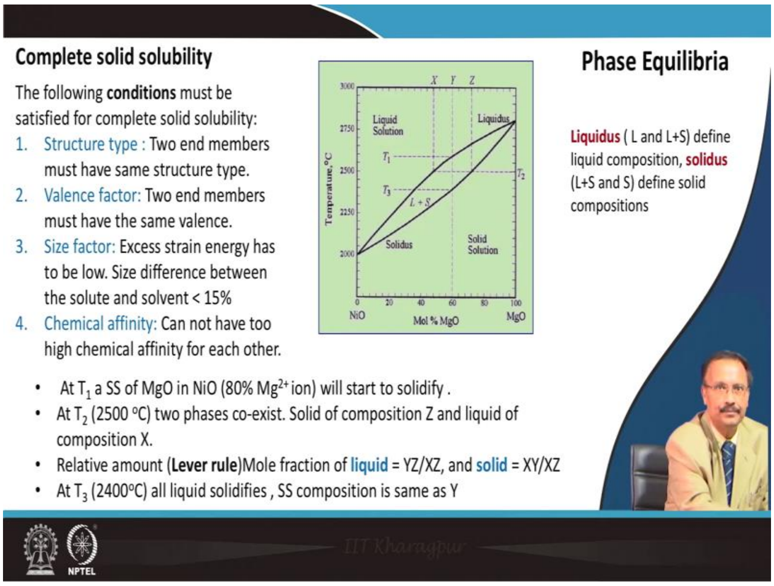


Now, in the complete range of solid solubility, there are certain rule it must be followed. If two component – two ceramic component forming a solid solution, then there should be structural compatibility. So, in this case nickel oxide and magnesium oxide both are FCC type. The constituent cation because anion is same.

So, constituent cation should have same valence. So, nickel and magnesium both are plus 2 valent. The size of this cation should be within 15 percent, so that there is no strain energy is involved, so that is another criteria. And they should not have a strong chemical affinity. If they have a very strong chemical affinity, then they will form a compound and not a solid solution. So, it will be a substitutional solid solution.

And let us see how you can read this particular diagram. So, if you take the point T 1 – this temperature, you see that when you cool a composition corresponds to this Y. So, once you cool, it will touch this line, this is called liquidus line, and the first phase of the solid will form. So, magnesium oxide in nickel oxide if the solid solution is made, so the first phase of solid will form at this point, and it will start to solidify.

And the composition you can directly get from this particular diagram. What is the composition? Then once you go to T 2 intermediate temperature which is about 2500 degree Celsius, the two phase will coexist one solid and another liquid. The solid will have a composition which is Z. So, you will have to cut this solidus line, and this will be the composition of the solid. And composition of the liquid will be read from the liquidus line.

And relative fraction of these two, you can identify from Lever rule. So, if you want to know the concentration fraction of the liquid, then you will have to take this length divided by the whole length. So, if you just want to know the liquid composition it will be YZ by XZ.

And if you want to know the solid which is formed, then it will be XY divided by XZ. Then at T 3 all liquid will solidify, and the composition will be same as the starting cooling composition. So, you can identify the composition of the solid, the liquid, as well as the fraction of solid and liquid.

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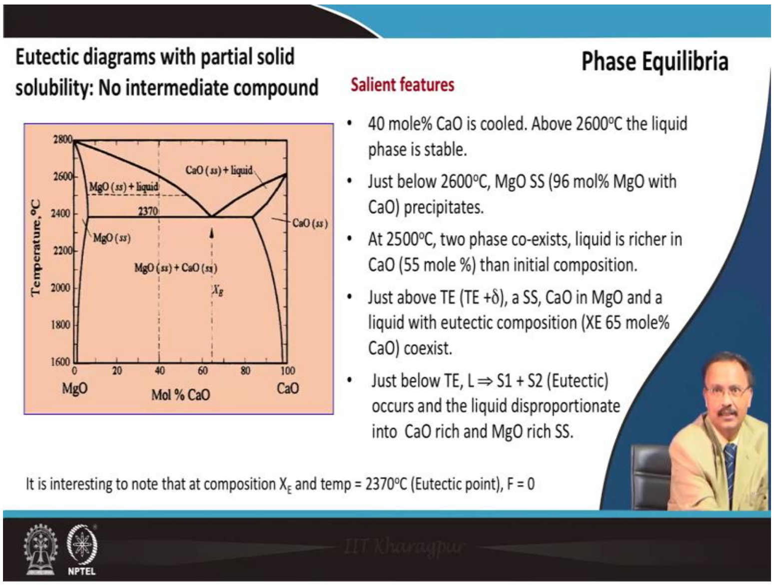


Then let us come to the next case which we call a eutectic diagram. And again I will try to explain the salient feature of this eutectic phase diagram. You start with a liquid which is having 40 percent of calcium oxide and start to cool it. So, as I said above 2600 degree Celsius, it is all liquid; liquid phase is stable. Just below 2600, magnesium oxide solid solution will form, and the composition will be about 96 percent of magnesium oxide. In calcium, little bit calcium will also be there.

Then at 2500 degree Celsius, this two phase will coexist. And liquid is richer in calcium oxide as you can see from this liquidus diagram. Just above this eutectic temperature point, there will be a solid solution, calcium oxide and magnesium oxide and a liquid with eutectic composition. So, this is the liquid eutectic composition it will form. So, the typical composition for the eutectic is 65 percent.

And once you cross the tie line, then two solid solution, one magnesium oxide solid solution. So, primary (Refer Time: 12:25) will be magnesium oxide little bit calcium oxide will be there, or calcium oxide solid solution these two will coexist. So, this phase throughout the region, there will be a coexist of these two phases. And why it is partial solid solubility, because up to this extent only MgO solid solution will be stable; and up to this composition only calcium oxide solid solution will be stable.

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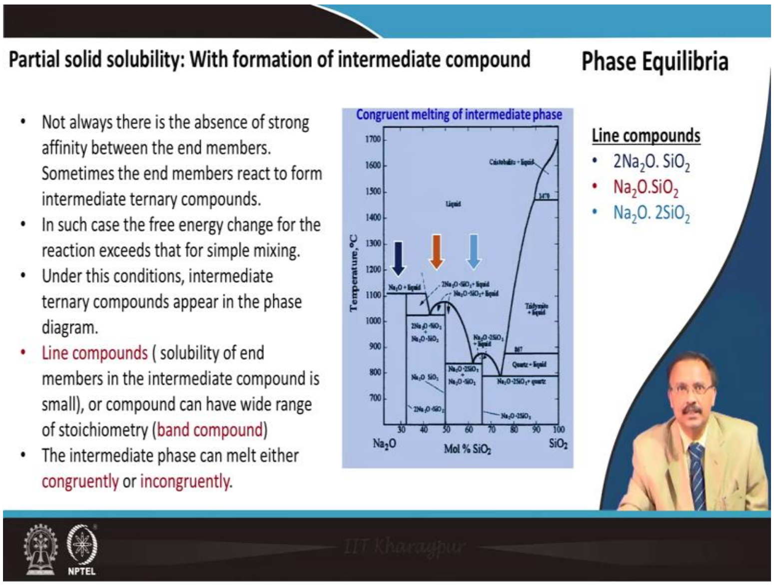


Now, let me describe a case where partial solid solubility with the formation of an intermediate compound takes place. So, now, it is not a perfect solid solubility some kind of intermediate compound is also forming. So, this is a typical diagram of sodium oxide and silicon dioxide. When I will take the glass part I will explain it in details. So, this is a typical phase diagram. And there is a little bit affinity between these two, so the phase will form.

So, here you can see we have considered three different phases of sodium oxide and silicon dioxide Stoichiometry, one is Na 2 O Si O 2 of different concentration. And in this case, we call it is a line compound. So, line compound means that if you change the temperature here, the composition is not changing and it is forming a liquid. For all these cases, this is valid. So, formation of the intermediate compound is there, but it is we call it is a congruent melting. So, when it melts, then the composition does not change as long as it is not melting the composition is not changing.

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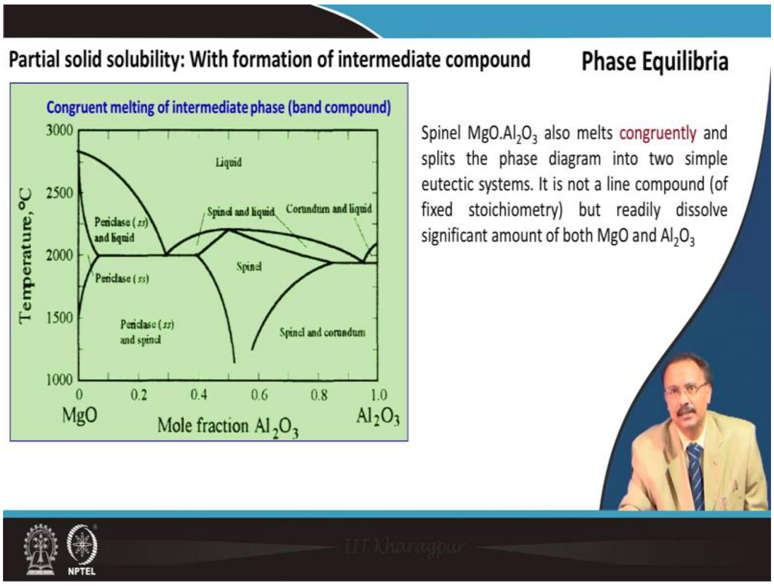


Now, in this case, you see that here also two eutectic phase diagram with partial solid solubility is there. The system is magnesium oxide and aluminium oxide, so that is there. So, intermediate, there is a phase which is formed. And we call it is a bent phase formation, it is not a line composition. So, you have a composition spread here in between. So, basically magnesium aluminate spinel is forming. And once the magnesium aluminate spinel forms, it also melts congruently.

So, if you take this composition, for example, it will melt here and you will get the composition of the melt from this place. So, it this spinel composition will not change right. The spinel composition will remain same. So, it will be a fixed stoichiometry. So, significant amount of magnesium oxide and aluminium oxide they form this kind of spinel reaction takes place, but they melt congruently, the composition does not change upon melting.

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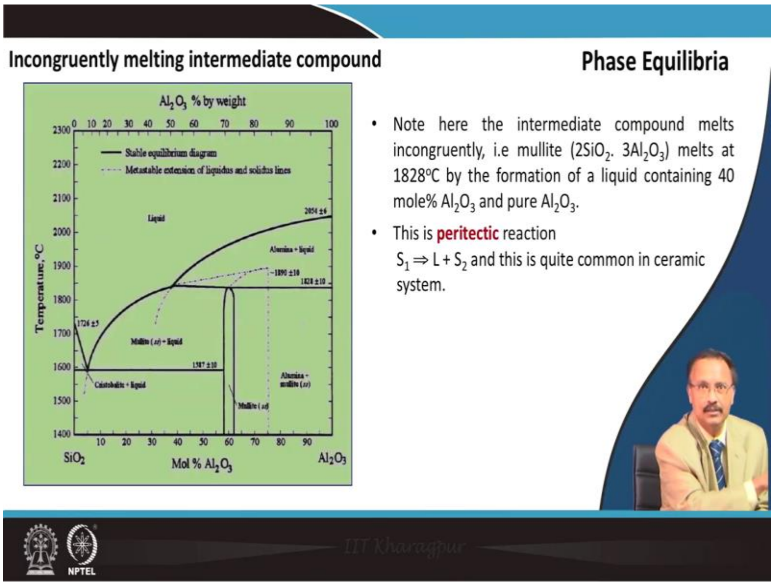


But here it is also a bent diagram as you can see. But when it melts then the composition is no longer similar, so for example, this mullite, I am talking about when it melts then the composition is somewhere here, somewhere here, this composition you can see which is very different. So, this reaction, this temperature, whatever reaction is taking place this is known as peritectic reaction.

When a solid of say mullite, it is converting to another solid of different composition and a liquid, so this mixture is there. So, for ceramic system, this is very common. So, peritectic reaction which is incongruent melting of a bend phase that is quite common in ceramic system, and alumina silica system this is a prominent example.

You can identify the eutectic point also otherwise the silica you see the silica when it is alumina is mix to it, then its melting point reduces. So, this part is a lower melting point of the eutectic system, and also peritectic reaction corresponding to this peritectic temperature is also there in this particular system.

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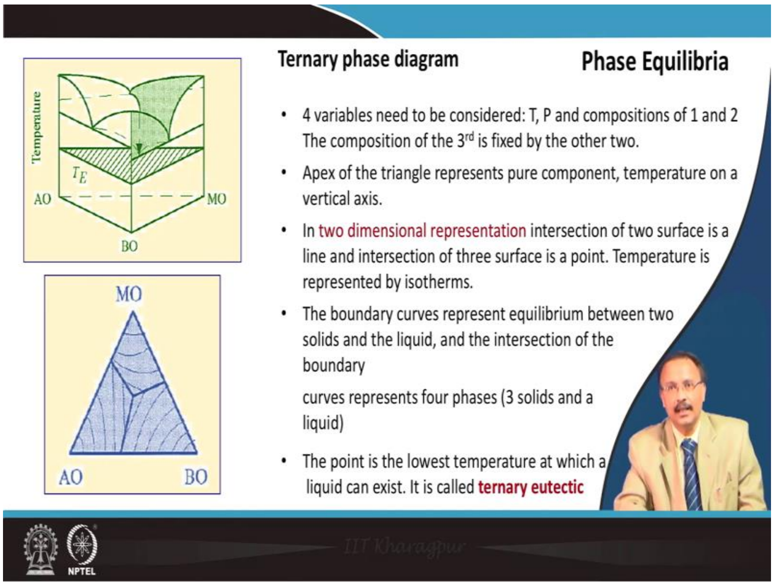


Now, we will talk about the ternary phase diagram, where there are three component which is present. So, you have three component present, and temperature, and pressure. So, totally there are five variables. If you consider the pressure remain constant, then there are four variable system.

So, actually you need a three dimension, three-dimensional figure to identify a eutectic diagram. So, if these three component you consider AO, BO and MO, then it is a eutectic reaction that is taking place here as you can see. So, you have three eutectic reaction that is going on, and this vertical axis corresponding to this temperature.

So, if you take one particular temperature, then you have a denotation of this ternary phase diagram as this equilateral triangle. Where the first phase boundaries are determined by the solid lines, this is a two-dimensional representation. So, intersection of two surface is a line and intersection of three surface is a point here. And the temperature is represented by this isotherm.

So, as you can see in this diagram, the lowest point here – the lowest eutectic point is known actually is the ternary eutectic.

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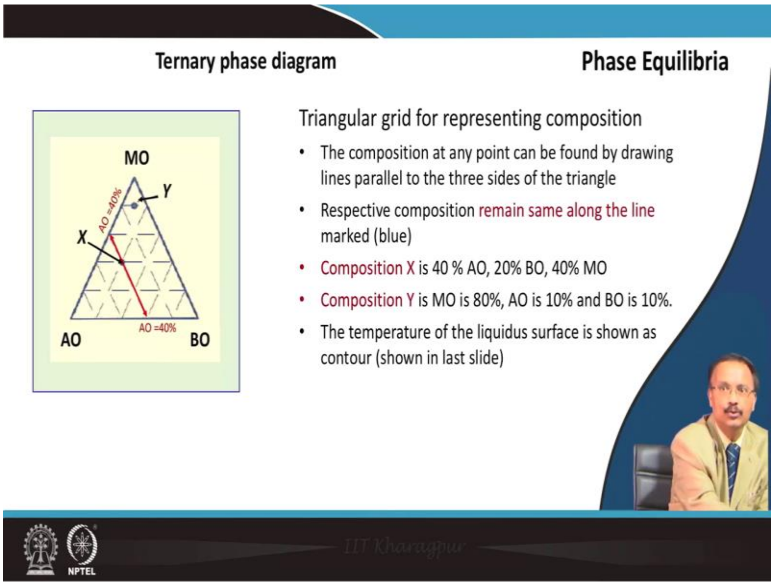


Now, we will learn how to read this ternary phase diagram. So, in order to read the composition of a system in ternary phase diagram, you will have to draw this equilateral triangle. And at any point say X, this composition if you are interested to know, so you will have to draw parallel lines here. So, one parallel line correspond to this particular line.

And if you draw this, you can draw another parallel line – this one, and another parallel line – this one. So, you draw this, and particularly I would like to draw your attention about this point. Here in this point, it is the locus of composition AO where the composition remain fixed here right.

So, always it is 40 percent. Here it is 40 percent; here also it is 40 percent. So, this composition x here it is 40 percent of AO, and similarly you can identify through the other two locus point that the composition of BO is 20 percent and concentration composition of MO is 40 percent.

Similarly, you try to work out what happens for this y. Again you draw three parallel lines and read this composition, where MO you will find 80 percent, AO is 10 percent, and BO is also 10 percent. So, the temperature it is correspond to one temperature; and in different temperatures, you have the contour which I showed in the last slide.

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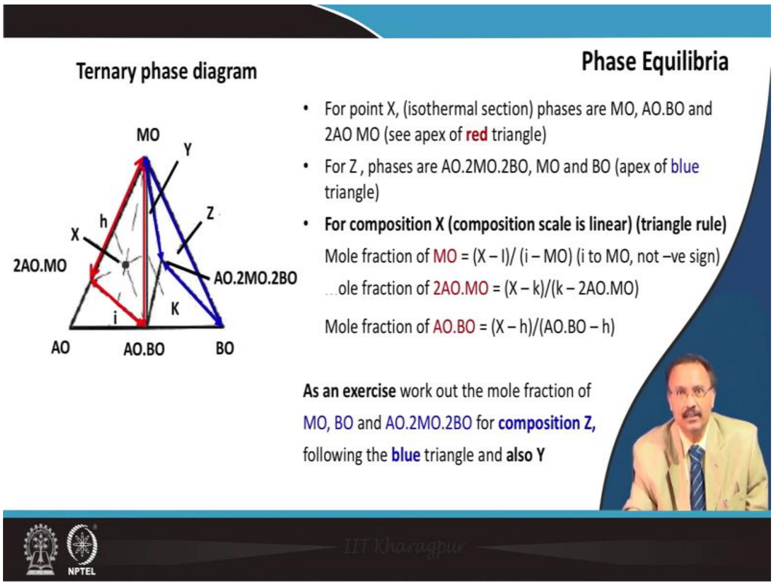


Now, in ternary phase diagram, again for a eutectic reaction, you can identify the mole fraction of this constituent phase. So, in that case, you will have to draw a triangle. For example, if you want to know the composition of X, then this X is basically within this particular triangle which I have marked rate. So, this is also an isothermal section and it constitute phase which is MO, then AO, BO, and 2 AO and MO. So, it is lying in between this.

Similarly, for Z, if you take this particular composition, there also three phases are there; one is AO, then 2 MO, 2 BO, MO and BO, apex of the blue triangle. So, this one is another one. Similarly, for other composition also you can identify. So, if you take the composition X, then you will have to apply a triangle rule corresponding to this triangle.

So, mole fraction of MO, this is given by X and i, this line divided by the whole line which is MO and i. So, do not confuse this thing as a negative sign. So, this is just these two lines.

Similarly, mole fraction of 2 AO and MO, this also you can determine by X k line and k 2 AO MO line. Similarly, mole fraction of AO BO – the other component, also you can identify from this triangle rule. So, as an exercise I leave it to you to determine the composition of Z. So, Z is somewhere here and you will have to take the triangle corresponding to this composition which will constitute AO, BO, and 2 MO BO, and you can have the phase fraction of each constituent phase in this phase diagram.

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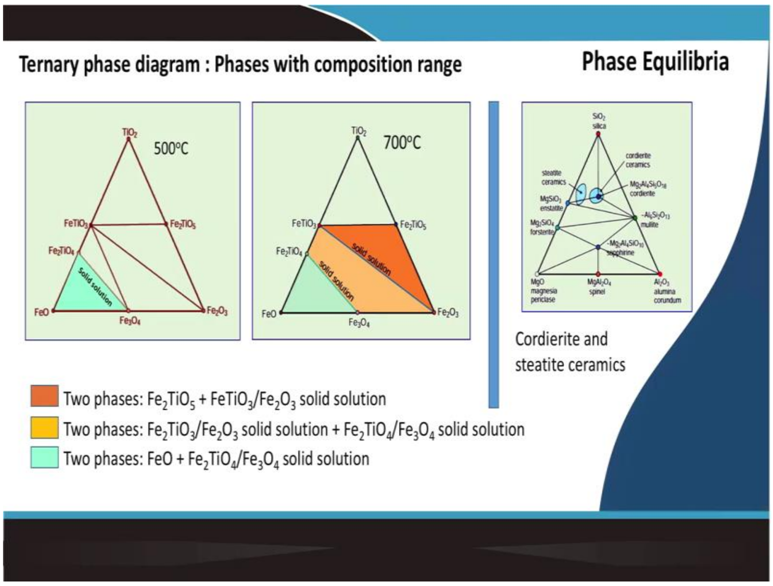


Sometimes, it also follows a solid solution not always it is a single compound. So, it also forms a solid solution. So, one example I have cited in this system titanium oxide, iron oxide and Fe 2 O 3. So, these three compositions if you take, the intermediate composition several phases forms – this Fe 2, Ti O 5, Fe Ti O 3.

So, these two phase, it forms a solid solution. So, they are not a separate phase like three component phase diagram. So, it forms a solid solution. So, basically in the shaded area there are only two phases present.

So, this is at a particular temperature as I told that if you increase the temperature, it is basically the section of the equilateral triangle. So, it is forming a solid solution at 500 degree Celsius. If you raise the temperature, then the other constituent phase they will also start to react, and they will also start to form the solid solution. So, there will be a bent in between if you change the temperature from low to high temperature.

So, in this case, if you go to 700 degree Celsius, then you have two phase corresponds to Fe Ti O 3, and Fe 2 O 3 that is one solid solution, and Fe 2 Ti O 4 and Fe 3 O 4 another solid solution. So, like this, you have the solid solution, so it is a complete range of solid solution. In many of the ceramic system, this complete range of solid solution does not form.

So, one important example is silicon dioxide, magnesium oxide and aluminium oxide phase diagram. It is a very complicated system it is not that easy to understand, but you can appreciate that so many phases it forms; I can and each are industrially important phase like steatite ceramics, good dielectric, enstatite, forsterite. So, there are several phases forms, intermediate phases forms.

And sometimes at a particular composition of this three component phase, we have the formation of a compound, we have a formation of a solid solution and it is marked by this region right. And the same triangle rule can be applied to know the fraction of each solid phase in this diagram. So, this is just an example that it forms different sets of composition in a as a part of this triangular phase diagram.

So, both for binary and triangular try ternary kind of phase diagram, the basic concept will remain same, because you will have to apply Lever rule to know the fraction of the liquid and fraction of the solid in the phase diagram.

And then from the phase diagram, you can read the respective composition of the liquid and solid phase above the tie line. And in the tie line, you cannot apply the Lever rule. But just above or just below the tie line, you can apply the Lever rule to know the corresponding phase fraction either liquid-solid or solid-solid phase fraction.

So, in order to clarify this idea, you will have to solve certain assignment problem because reading is one thing, understanding the concept, so that is one thing. And I think that if you try to read the phase diagram following my lecture, it will be clearer to you what exactly I meant, and how to apply the Lever rule; and also in the ternary system how to identify the phase fraction.

So, I have a very selective assignment problem I have selected. So, that in that assignment problem, if you solve it, these things will be much clarified along with if you read the chapter that I will suggest at the end of this lecture.

And particularly different types of phase reaction whatever is happening, whatever I told – complete range of solid solubility, eutectic reaction, peritectic reaction, forming an intermediate compound with congruent melting or forming an intermediate compound with incongruent melting. So, once you start solving those problems, this idea will get clarified.

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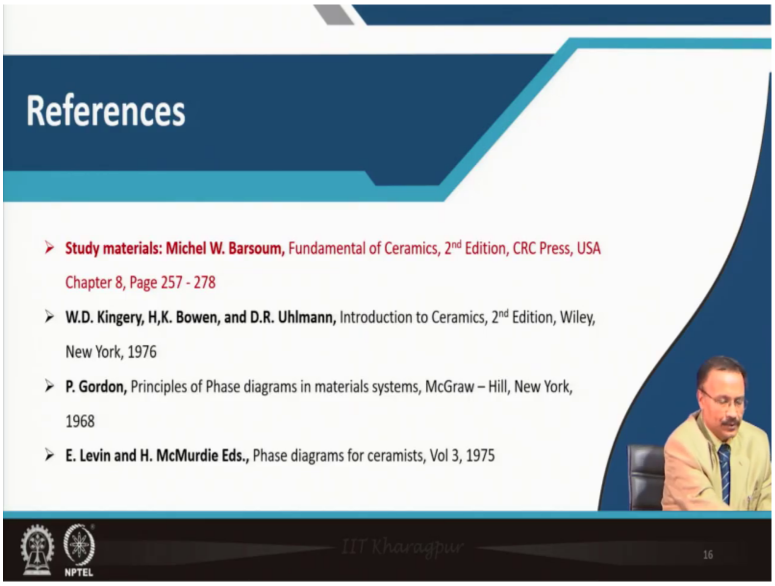


So, the reference for this particular phase diagram book is mostly from Barsoum book, we have taken the concepts and it is chapter 8 of the Barsoum book. And other than that there are several good text W. D. Kingery is one book which exclusively cover various types of phase diagram.

I would like you to go through those phase diagram, and try to understand that where the eutectic reaction is taking place, where the peritectic reaction is taking place. So, as I said earlier that in case of the eutectic reaction, you have a liquid and suddenly it forms a solid. So, solid to liquid transition is there; there is no in between liquid plus solid fraction.

In case of peritectic reaction, it starts from a solid and it ends up with a liquid, and another solid which is having a different composition as compared to the initial solid. So, all this reaction you will be able to understand if you go through several types of phase diagram.

And the book by Gordon that is also another good reference book, but I will suggest you to solve the assignment problems to better clarify your ideas.

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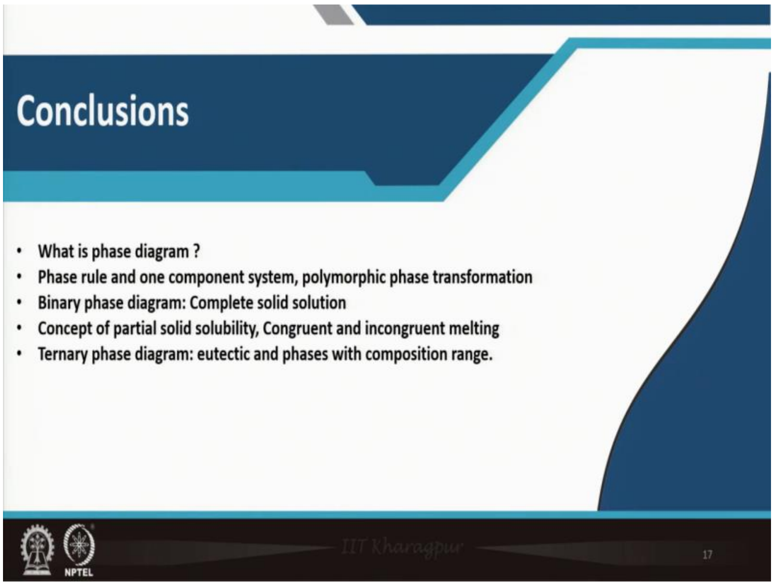


So, in this lecture, I covered what is the phase diagram, and then I covered what is the phase rule for one component system. And polymorphic phase transformation I just introduced, but when I will be talking about the phase transformation lecture when I will be talking about, then this will be clarified more different types of polymorphic phase transition.

Then I have introduced the binary phase diagram, and particularly the complete range of solid solution. Then the concept of partial solid solubility; and in congruent and congruent melting I tried to elucidate. And finally, ternary phase diagram with eutectic phase mainly I have covered; and to some extent, the solid solution also I have covered.

Thank you for your attention.