Structure of Materials
Prof. Anandh Subramaniam
Department of Materials Science and Engineering
Indian Institute of Technology, Kanpur
Lecture - 32
Chapter - 07
Phase Diagrams

Today, we start the next chapter which is on Phase Diagrams, first let us start by playing a video.

(Refer Slide Time: 00:33)

In this video, we will see that a dendritic solidification of an under cooled melt of stearic acid, so in this we see that, there is a molten pool of stearic acid, which is a low melting material. And then, let the video replay then, I will show you some features of this, you see that there is a liquid melt in which there is a solid forming, this solid grows in the form of a dendrite, there is even a nucleation of a new crystal.

We will learn more about nucleation in the next chapter and then, there is this inter dendritic liquid. And finally, when the dendrites spreads over, all the liquid turns into a solid, there might be a little pool of liquid, let between the dendrites which also solidifies in the end. Therefore suppose, I freeze or pause my video at any point of time, you see that, there is a mixture of solid and liquid that means, the whole pool is neither fully homogeneously liquid nor fully solid, but there is solid in some regions like shown here.

In this region, there is solid and regions between the solid, so many such kind of solidification microstructures we will be considering in this chapter. But, suppose the final product I get, this I can call a microstructure, because there is certain future, there is certain morphology to the whole process which has taken place. So, we are in a good position after seeing this video of dendritic solidification of stearic acid from a under cooled melt.

We will technically define what is meant by an under cooled melt when we talk about phase transformations, but for now we will consider that, we are below the melting point of stearic acid. And this whole solidification is taking place at a temperature, which is kept constant below the melting point of this stearic acid. So, we start with the molten pool and this molten pool slowly solidifies, so we are in a position to take up the chapter on phase diagrams.

(Refer Slide Time: 02:33)

PHASE DIAGRAMS

EQUILIBRIUM PHASE DIAGRAMS

☐ Phase Rule
☐ Types of Phase diagrams
☐ Lever Rule

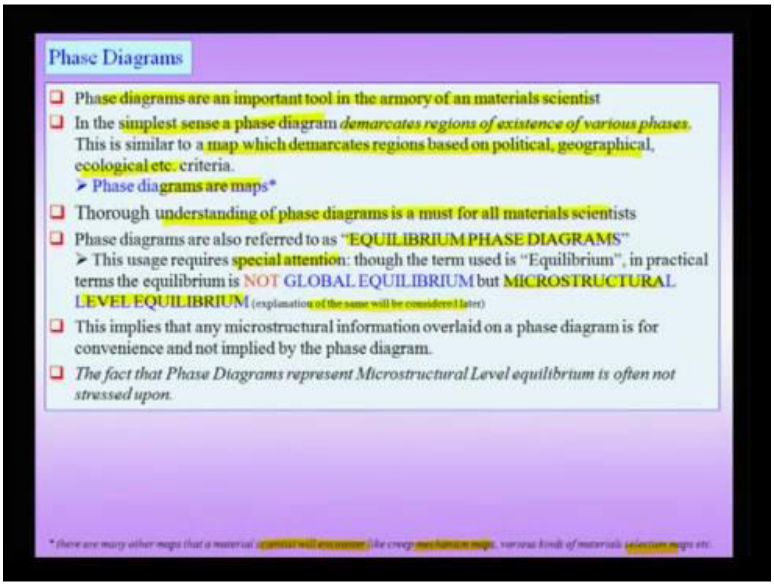
Advanced Reading

Alloy Phase Equilibria
A. Prince
Elsevier Publishing Company, Amsterdam (1966)

Phase diagrams are also called sometimes equilibrium phase diagrams, we will discuss this word equilibrium in the context of phase diagrams a little more in the coming slides. But, when whenever you use the word phase diagrams, typically we need equilibrium phase diagrams. In the context of this, we will learn about something known as the phase rule, we will take up some typical phase diagrams and we will understand, how to find out the fraction of the phase response using the lever rule.

There are many good text books in this area, there is even an ASM hand book or an ASM book published by ASM in this area, but the book by prince on alloy phase equilibrium is a good classic text in this area. But, most material science books or physical metallurgy books will definitely have a long chapter debuted to phase diagrams.

(Refer Slide Time: 03:17)



Phase Diagrams

- ☐ Phase diagrams are an important tool in the armory of an materials scientist
- ☐ In the simplest sense a phase diagram *demarcates regions of existence of various phases*. This is similar to a map which demarcates regions based on political, geographical, ecological etc. criteria.
  - ➤ Phase diagrams are maps*
- ☐ Thorough understanding of phase diagrams is a must for all materials scientists
- ☐ Phase diagrams are also referred to as "EQUILIBRIUM PHASE DIAGRAMS"
  - ➤ This usage requires special attention: though the term used is "Equilibrium", in practical terms the equilibrium is NOT GLOBAL EQUILIBRIUM but MICROSTRUCTURAL LEVEL EQUILIBRIUM (explanation of the same will be considered later)
- ☐ This implies that any microstructural information overlaid on a phase diagram is for convenience and not implied by the phase diagram.
- ☐ *The fact that Phase Diagrams represent Microstructural Level equilibrium is often not stressed upon.*

**there are many other maps that a material scientist will encounter like creep mechanism maps, various kinds of materials selection maps etc.*

First and for most we should note, that phase diagrams are an important tool in the armory of a material scientist. So, suppose there is a material scientist and he is wants to understand phase evolution behavior or and wants to understand, how what phases exist for a given composition at a given temperature and pressure then, he would rely on phase diagrams. There are extensive collection of binary and ternary phase diagrams in literature, there are dedicated hand books, which deal with phase diagrams.

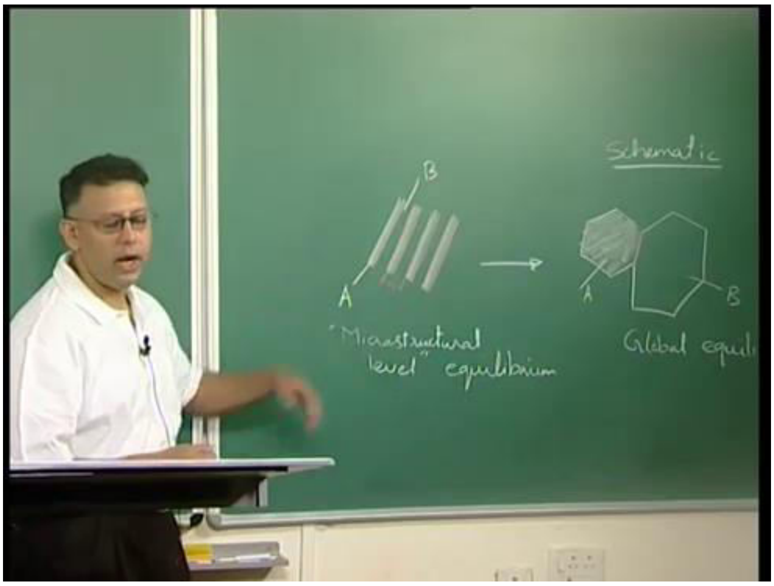
The other important tool, which will be the topic of the next chapter is something known as the T T T diagrams or the Time Temperature Transmission diagrams. If you want to understand a phase diagram in the simpler sense, we can think of it as a diagram, which demarcates various regions of existence of various phases that means, it is something like a map, which demarcates regions based on political, geographical or other criteria.

For instance, When you look at a map you know that, there is grass lands in some place, mountains in some place or you can say one country is in one place, another country is in a different place. Here, it is the map which demarcates different phase which exist, so in some sense the broader sense phase diagrams are maps. And we should note that, material scientists will encounter many more maps like creek mechanism maps, material selection maps etcetera, which form an important tool in the armory of a material scientist.

And therefore, a thorough understanding of phase diagrams is a must for all material scientists. As I pointed out, phase diagrams should also be called equilibrium phase diagrams and this usage requires a special attention. This is because, though we mean equilibrium, in practical terms the equilibrium we are considering, is not global equilibrium, but what we call as the micro structural level equilibrium.

So, we have defined a very functional definition of microstructure before, as a combination of phases defects, residual stress and their distributions. And equilibrium we typically talk about, which is described in phase diagrams, is not the global equilibrium. But, what we call micro structural level equilibrium, we will consider some more aspects of this in the coming slides.

(Refer Slide Time: 05:42)



But, 1 point I would like to mention for now that, suppose I have a combination of two phases say phase A which I am marking in a whitish color and a phase B which is the intermediate phase, so this is phase A and this is phase B. Now, obviously if you have a such a distribution of phases, which constitutes my microstructure then, there are lot of internal inter phases. So, there are these red lines are inter phases between phase A and phase B, these inter phases obviously cost energy to the system.

And if you allow the system, you expect that system to coarsen, in another words you expect, this wave length, say for instance this wave length A to increase. And in the ultimate limit, I would not like to have so many inter phases in the system and the global minimum, if you obtain it, you expect that the entire phase A could be present and I am drawing a schematic here, so this is the schematic.

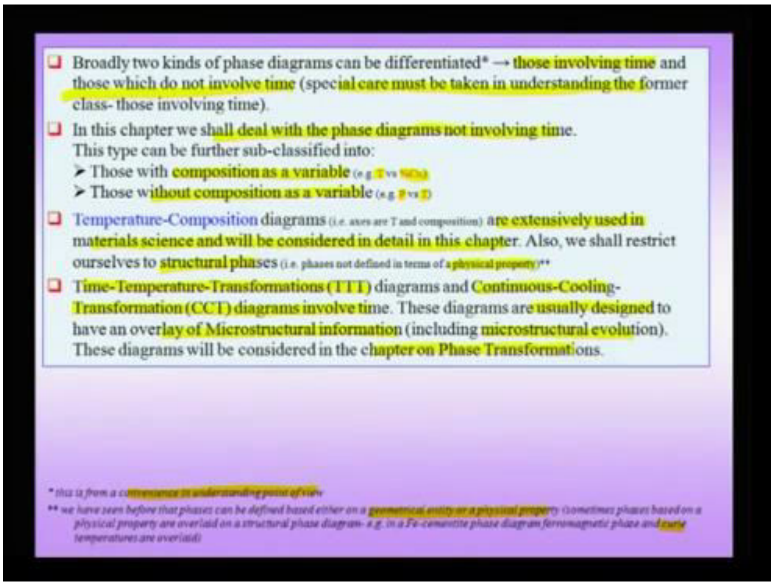
So, these are again a very crude schematic, what I would expect is that, the entire phase A will be one side, the entire phase B will be on the other side. The entire phase A will be what you call, bounded by a what we might call a wolf construction low energy surface so that, the entire surface energy of this becomes minimum. You would also expect that the surface energy of this phase B is also low and additionally, that the inter phase which is marked in the red color between A and B is also a low energy inter phase.

But, rarely we take a system from this configuration, which is a micro structural level equilibrium to a global equilibrium, so I can label this as the micro structural level equilibrium. So, rarely we allow the system to go from this to this, in other words whenever we are talking about phase diagrams, we do tolerate micro constituents and micro structures. And therefore, typically the phase diagrams, we consider are not global equilibrium phase diagrams, though we call them equilibrium phase diagrams, they are more at the micro structure level equilibrium phase diagrams.

And often you would note, that micro structural information is overlaid on phase diagrams and a important point to note is that, this is for convenience, this is for us to sort of extend utility of phase diagrams. And this micro structural information is not implied by the phase diagram and this aspect that phase diagrams represent micro structure level equilibrium is often not stressed up on.

So, this is very important thing to note, because often text books will start with the assumption that, you understand the fact that these are micro structural level equilibrium diagrams. And there will be no further mention of the fact that, these are not truly a global representation or the truly global equilibrium. And the additional fact, that truly speaking you there is no information in the phase diagram regarding the any micro structural information, this has been overlaid on the phase diagram, to make it more useful to get additional information out of the phase diagram.

(Refer Slide Time: 09:24)



- ❑ Broadly two kinds of phase diagrams can be differentiated* → those involving time and those which do not involve time (special care must be taken in understanding the former class- those involving time).
- ❑ In this chapter we shall deal with the phase diagrams not involving time.
  This type can be further sub-classified into:
  - ➢ Those with composition as a variable (e.g. T vs %Cu)
  - ➢ Those without composition as a variable (e.g. P vs T)
- ❑ Temperature-Composition diagrams (i.e. axes are T and composition) are extensively used in materials science and will be considered in detail in this chapter. Also, we shall restrict ourselves to structural phases (i.e. phases not defined in terms of a physical property)**
- ❑ Time-Temperature-Transformations (TTT) diagrams and Continuous-Cooling-Transformation (CCT) diagrams involve time. These diagrams are usually designed to have an overlay of Microstructural information (including microstructural evolution). These diagrams will be considered in the chapter on Phase Transformations.

** this is from a convenience in understanding point of view*

*** we have seen before that phases can be defined based either on a geometrical entity or a physical property (sometimes phases based on a physical property are overlaid on a structural phase diagram- e.g. in a Fe-cementite phase diagram ferromagnetic phase and curie temperatures are overlaid)*

Broadly two kinds of phase diagrams can be differentiated, those involving time and those which do not involve time, normally those involving time like the time temperature transformation diagrams are not typically called as phase diagrams. But, in the general sense from the point of view of convenience of understanding, they can also be classified as phase diagrams and special care must be made whenever you are talking about a phase diagram involving time.

Because, such a phase diagram has a directionality toward and therefore, whenever you are trying to understand information from diagram involving time, you should be more careful then that which is totally time independent. And in this chapter we shall deal with phase diagrams not involving time and this can further, be those which involve composition as a variable like you can talk about temperature, versus percentage of copper or percentage of an alumina or percentage, so it is a composition temperature phase diagram.

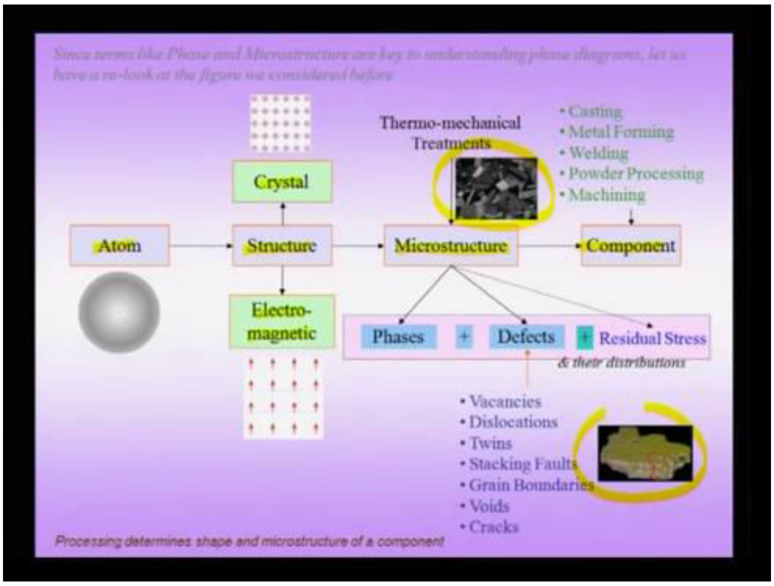
And those without composition as a variable that means, the variables are purely thermodynamic variables like pressure and temperature, the former one the one involving composition is what is called a typically a metallurgical or a materials phase diagram, which is you will encounter very frequently as a material scientist. And the later one is typically taken up more by the physicist, the temperature composition diagrams as I pointed are extensively use by in material science and we will consider this in a lot of detail in this chapter.

And we shall also restrict ourselves for now to structural phases like we will not consider phases based on physical property like, we had talked about before, that phases can be defined based on a geometrical entity or a physical property. And therefore, we suppose you talking about physical property, we may talking about for instance a ferromagnetic phase or anti ferromagnetic phase.

And if you are wanting to overlay additionally this physical information, then we will have to include, for instance curie temperatures need to be overlaid on a phase diagram. But, in this chapter we shall restrict ourselves to the definition of a phase, based only on structure and not on physical property and therefore, typically you will find, that I am not overlaying any curie temperature or Neil temperature on a phase diagram.

Time temperature transformation diagrams, which will be the basic focus of the next chapter and a close cousin of that, which is the continuous cooling transformation diagrams both of them involve time, these diagrams are usually designed to have an overlay of micro structural information. So, the very starting objective of these kind of diagrams is to have a micro structural information, overlaid and we also want to understand micro structural evolution and this, will be the topic of the next chapter on phase transformations.

(Refer Slide Time: 12:12)



Since terms like Phase and Microstructure are key to understanding phase diagrams, let us have a re-look at the figure we considered before

Processing determines shape and microstructure of a component

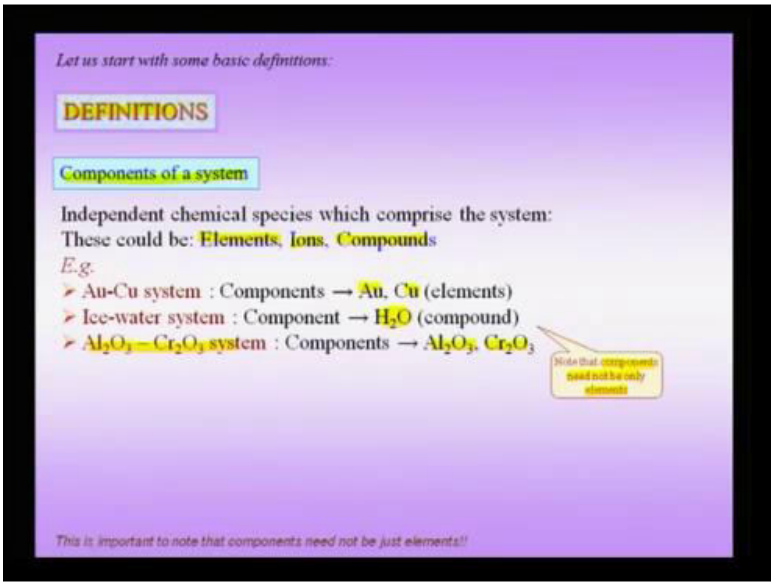
Now, we have defined the term microstructure before and its worthwhile to revisit some of the concept, the concept of a phase the concept of a micro structure and what you call revise the concepts. So, we have seen that we can start form an atom and we can go to the structure and the structure, can be based on crystal structure or as I pointed out on a physical property like an electromagnetic structure, then we go to the next scale, the scale of microstructure and finally, to the scale of the component.

And if you look at a typical microstructure like the one shown in the diagram above, the term microstructure you see that there is a poly crystalline material that means, there are grain boundaries and in addition there are twin boundaries, which you would observe in this microstructure. Now, in a typical micro structure some of the features may be revealed at the level of the what, you may call the metallographic done or may not be reveal.

Suppose, you are looking at a typical scanning electron micrograph or an optical micrograph, then you would not observe dislocations on the other hand in a typical micrograph, you might observe grain boundaries like in if you look at the figure at the bottom, you would notice that this is sort of a three dimensional rendering done by taking progressive sections of a material and building up the images, you would notice that, there are these grain boundaries and these grain boundaries are going downward into the material which are seen in the section.

So, this concept of a micro structure will be the focus of these two chapter on phase diagrams and the chapter on phase transformations.

(Refer Slide Time: 13:44)



Let us start with some basic definitions:

DEFINITIONS

Components of a system

Independent chemical species which comprise the system:
These could be: Elements, Ions, Compounds
E.g.
- Au-Cu system : Components → Au, Cu (elements)
- Ice-water system : Component → H_2O (compound)
- $Al_2O_3 - Cr_2O_3$ system : Components → Al_2O_3, Cr_2O_3

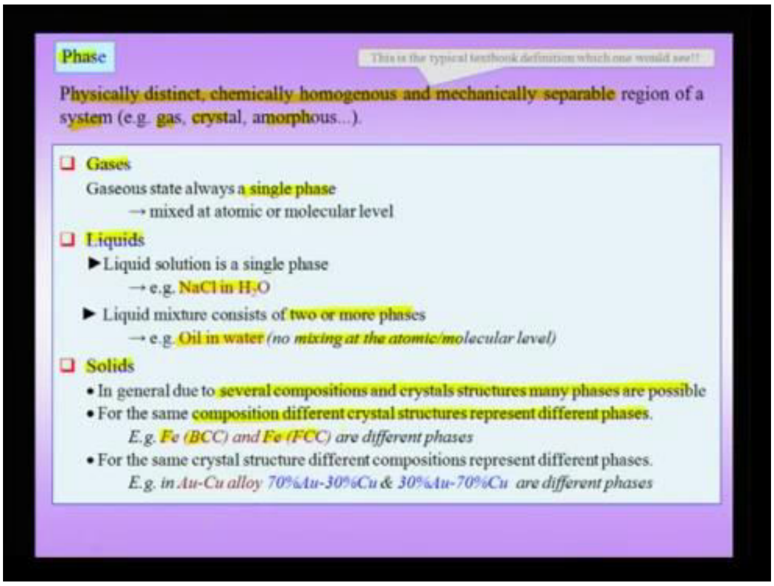
Note that components need not be only elements

This is important to note that components need not be just elements!!

Now, to start with lets have some definitions in place and the first one is what is a component of a system, the component could be and this is very important note elements And these elements for instance could be gold, copper could be sodium etcetera, they could be ions like for instance in a ionic system, you could be talking about ions components, they could even be compounds like for instance in the alumina chromia system, which we will take up some time the alumina and chromia both of which are compounds or components of the phase diagram.

So, it is important to note that components need not only be elements, this is some time not truly stressed up on, but it is important note and we will take up examples, that actually components can be elements ions or even compounds. And you could be drawing a phase diagram for instance a unary phase diagram for water, in this case the component is water which is a compound, so to emphasize it is important note that components need not be just elements.

(Refer Slide Time: 14:58)



Phase

This is the typical textbook definition which one would see!!

Physically distinct, chemically homogenous and mechanically separable region of a system (e.g. gas, crystal, amorphous…).

☐ **Gases**

Gaseous state always a single phase

→ mixed at atomic or molecular level

☐ **Liquids**

► Liquid solution is a single phase

→ e.g. NaCl in H_2O

► Liquid mixture consists of two or more phases

→ e.g. Oil in water *(no mixing at the atomic/molecular level)*

☐ **Solids**

- In general due to several compositions and crystals structures many phases are possible
- For the same composition different crystal structures represent different phases.

  E.g. Fe (BCC) and Fe (FCC) are different phases
- For the same crystal structure different compositions represent different phases.

  E.g. in Au-Cu alloy 70%Au-30%Cu & 30%Au-70%Cu are different phases

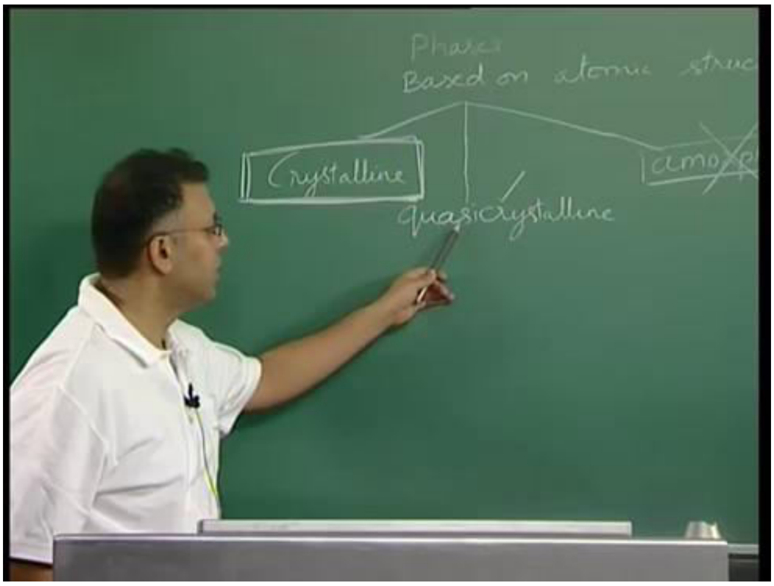
Typically you would encounter, the term phase in text books as defined to be something which is physically distinct chemically homogeneous and mechanically, separable region of a system like a gas phase, a crystalline phase, an amorphous phase and this is the typical text book definition. But, we will go ahead and use more definitions or more view points to understand this concept of a phase a little better in the coming slide.

Typically, if you look at gases then gases mix in all proportions, suppose I take nitrogen and organ I can take one percent of nitrogen with 99 percent of organ and mix it or I could take 99 percent of oxygen mix, it with 1 percent of hydrogen etcetera. And therefore, mixing at an atomic level at a intimate level is complete in the gaseous state therefore, the gaseous state always forms a single phase therefore, we should notice in liquids you could have for instance, sodium chloride in water which is basically taking salt and dissolving it in water, this solution is a single phase solution.

But additionally you could also have cases, where there are more than two phases for instance oil and water and there is no, mixing at the atomic level of oil and water and therefore, oil and water phases separate out and there is a distinct inter phase between the two phases. So, gases are always form a single phase liquids may mix like alcohol in water, liquids may dissolve solids and form a single phase or they could be separated out like in the case of oil and water.

Solids on the other hand are more interesting and rich, in general due to several compositions in crystal structures many phases are possible. And this is very important to note that is for the same composition, different crystal structures represent different phases. So, let me reiterate even though my composition, which could be pure ion for instance in the example below, if I change my crystal structure then they represent different phases like for instance iron BCC and iron FCC are different phases, silicon in the diamond cubic form, we saw we silicon in the amorphous form represent different phases.

(Refer Slide Time: 17:23)



Since, we are talking about the amorphous form a point may be noted here, that typically you would observe, that we had defined phases based on atomic structure to be crystalline, quasi crystalline and amorphous. Typically in phase diagrams, amorphous phases will not be formed and the reason is that, typically it is assumed that or its found that at least, there is one crystal structure for a given temperature and pressure, which will have a lower Gibbs free energy.

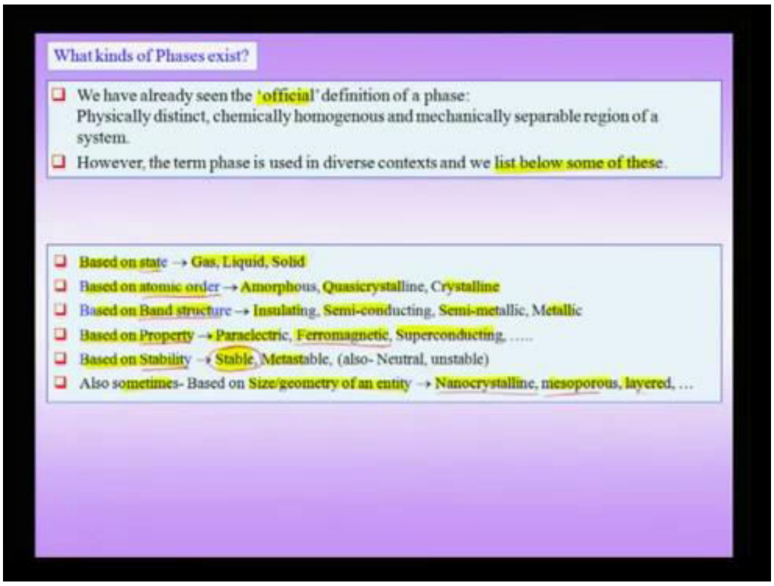
And in other words, its more stable than the amorphous phase and therefore, the amorphous phase, does not represent the equilibrium an equilibrium phase and therefore, they are typically not included in phase diagrams. Some quasi crystals are having postulated to be equilibrium phases and those, kind of quasi crystal may be included, but in typical phase diagrams, you would only find crystalline phases.

And therefore, in this chapter you will only focus, on crystalline phases in the phase diagrams therefore, as I was pointing out just to reiterate this slide once more, this drawing here that we shall consider only crystalline phase. As a part of the phase diagram though there is a possibility of even quasi crystalline phases, being stable or it was just being equilibrium phases, amorphous phases definitely do not find a place, in the phase diagram.

Now, I pointed out that if you have silicon, when you have silicon in two forms the amorphous form and the crystalline form, then these represent two different phases. In other words different polymorphs of the same element different represent different phases, also for the same crystal structure different compositions represent different phases that means, suppose I have an gold copper alloy and gold and copper dissolve in each other in all proportions that means, it forms an isomorphism system, as we shall see later 70 percent gold, 30 percent copper alloy.

Which is the say I call alloy 1 and say this is alloy 1, alloy 1 and alloy 2 represent different phases though both of them have the same components gold and copper, both of them have the same crystal structure, which is FCC. But, the proportion of gold and copper is different in these two alloys and therefore, these represent different phases, since now we have a different phases, either based on crystal structure or based on composition, therefore there is a rich variety of phases, which are possible in the solid state and these phases needs to be differentiated. As I pointed out we have a text book definition of a phase, which says that it is a physically distinct, chemically homogeneous and a mechanically separable region of a system like for instance a gas crystal or amorphous phases.

(Refer Slide Time: 20:39)



What kinds of Phases exist?

- ☐ We have already seen the 'official' definition of a phase:
  Physically distinct, chemically homogenous and mechanically separable region of a system.
- ☐ However, the term phase is used in diverse contexts and we list below some of these.

- ☐ Based on state → Gas, Liquid, Solid
- ☐ Based on atomic order → Amorphous, Quasicrystalline, Crystalline
- ☐ Based on Band structure → Insulating, Semi-conducting, Semi-metallic, Metallic
- ☐ Based on Property → Paraelectric, Ferromagnetic, Superconducting, ...
- ☐ Based on Stability → Stable, Metastable, (also- Neutral, unstable)
- ☐ Also sometimes- Based on Size/geometry of an entity → Nanocrystalline, mesoporous, layered, …

But, it is worthwhile to ask her, what kind of phases exist and in what could be the basis of definition of these, kind of different kind of phases. So, here we will list a few and its worthwhile to note these, because often when you read literature, when you read text book you might find usage of some of these terms, from school days we know that based on state, we can define a phase to be a gaseous liquid or a solid phase.

We already seen that based on atomic order you can have amorphous, quasi crystalline and crystalline phases, we also seen before that based on band structure, you could have insulating, semi conducting, semi metallic and metallic phases. For instance often you may lead literature, wherein they talk about phase transformation from a metallic phase or an metal insulated transformation.

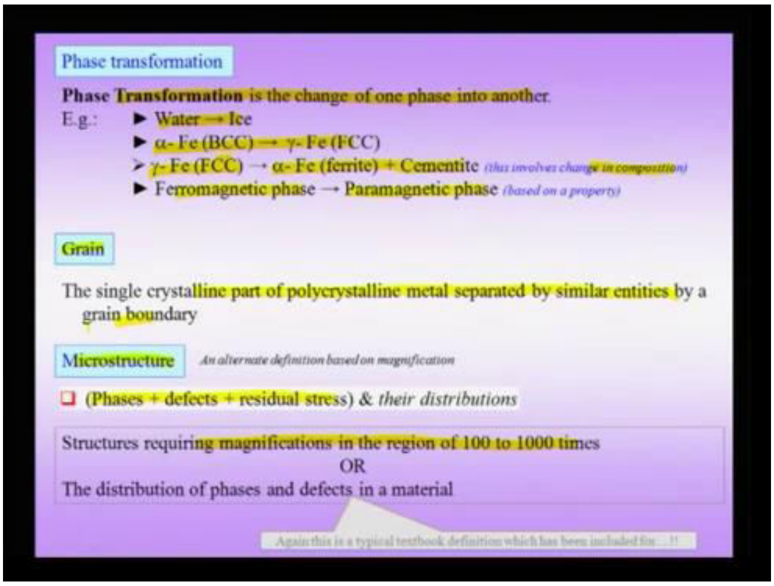
So, that means I talking about a metallic phase going to an insulator phase and this kind of a phase transformation, involves a change in the property and this property has been defined based on the band structure. Additionally you could have definitions of phase based on properties like people would, refer to ferromagnetic phases, super conducting phases, Para electric phases. And often you will note terms like, when you heat a ferromagnetic substance, it turns into a paramagnetic that means, a ferromagnetic to paramagnetic transformation can be considered as a phase transformation, which has been defined based on property.

Additionally, based on stability people also define phases like a stable phase, a meta stable phase and when we are talking about equilibrium phase diagram, our focus will be on the stable phases. But, sometimes the phase diagrams are extended to include meta stable phases, in the gamet of a phase diagram, but typically usually they are meant to include only stable phases.

Sometimes, you would also notice that people define phases based on size or geometry of the entity, like a nano crystalline phase, a mesoporous phase in which case the poor size is between, that in the nano crystalline and micro and nano regimes people even talk about layered phases etcetera. So, to summarize this slide typically, we have a sort you might call the official definition of a phase as seen here.

But, in diverse context, we may come across terminology which define phases based either on the state like a solid, liquid and a gas, there may be definitions based on atomic order like a quasi crystalline phase and within quasi crystals people, may talk about an icosahedral phase or a decagonal phase. And then there is definitions based on the band structure, like people may talk about metallic phase or an insulating phase, you could talked about a property based definition of a phase like a ferromagnetic phase or a Para magnetic phase. And you, could talk about a stable phase and a meta stable phase and I told you in this context, that the stable phase is what you typically mark in a equilibrium phase diagram. And additionally, you may talk based on size or some geometry of the entity as nano crystalline, mesoporous layered, etcetera.

(Refer Slide Time: 23:38)



Phase transformation

Phase Transformation is the change of one phase into another.

E.g.:
- Water → Ice
- α- Fe (BCC) → γ- Fe (FCC)
- γ- Fe (FCC) → α- Fe (ferrite) + Cementite *(this involves change in composition)*
- Ferromagnetic phase → Paramagnetic phase *(based on a property)*

Grain

The single crystalline part of polycrystalline metal separated by similar entities by a grain boundary

Microstructure *An alternate definition based on magnification*

❑ (Phases + defects + residual stress) & *their distributions*

Structures requiring magnifications in the region of 100 to 1000 times

OR

The distribution of phases and defects in a material

Again this is a typical textbook definition which has been included for ... !!

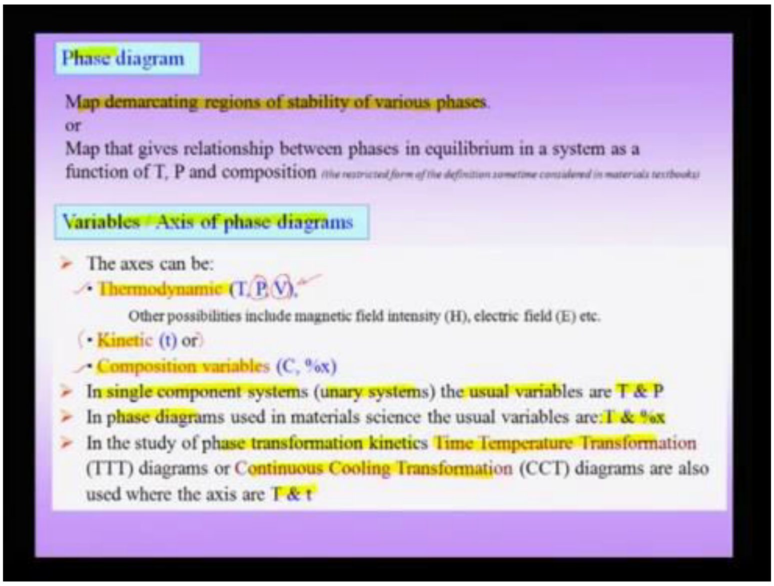
So, we have been using a term called phase transformation, so for and though it is obviously, we will consider few examples. Phase transformation implies a change of phase from one phase to the other for instance water to ice, which happens when you cool a system a water system, you can talk about alpha and BCC going to gamma ion when you heat, this alpha n. Additionally if you talking about gamma ion at high temperatures, which is cooled.

And you would observe a phase transformation in which, you will obtain an alpha ion and a cementite, we will take up these some of these things in detail later. But, it is important note, this gamma n splitting into alpha ion and cementite on cooling, involves a change in composition apart from a change in the phase. Because, the starting phase is gamma ion as FCC and the phases you obtain cementite is orthorhombic and ferrite is b c, you could heat a substance a ferromagnetic phase and produce the paramagnetic phase, which is a phase transformation based on property.

Another definition you need to consider, now which we have talked about before and therefore, we just briefly considered here that a grain is a single crystalline part of a polycrystalline material, separated by a grain boundary. Additionally we also we will be talking about two important terms, one is known as micro structure and other is the term called micro constituents, though in text books microstructure is typically defined as entities seen at a high magnification of about 100 to 1000 times.

But, here we have already made a functional definition, based on distribution of phases defects and residual stress. So, this is expected to be a functional definition, because this directly gives a handle on the properties.

(Refer Slide Time: 25:33)



Phase diagram

Map demarcating regions of stability of various phases
or
Map that gives relationship between phases in equilibrium in a system as a function of T, P and composition *(the restricted form of the definition sometime considered in materials textbooks)*

Variables / Axis of phase diagrams

- The axes can be:
  - Thermodynamic (T, P, V),
    Other possibilities include magnetic field intensity (H), electric field (E) etc.
  - Kinetic (t) or
  - Composition variables (C, %x)
- In single component systems (unary systems) the usual variables are T & P
- In phase diagrams used in materials science the usual variables are: T & %x
- In the study of phase transformation kinetics Time Temperature Transformation (TTT) diagrams or Continuous Cooling Transformation (CCT) diagrams are also used where the axis are T & t

So, we also defined a phase diagram to be a map demarcating regions of stability of various phases and typical variables, which you encounter or we may call the axis of a phase diagrams, can be thermo dynamic, kinetic or composition variables. And as I had pointed out typically, that the metallurgist deal with those phase diagrams, which involve thermodynamic and composition variables.

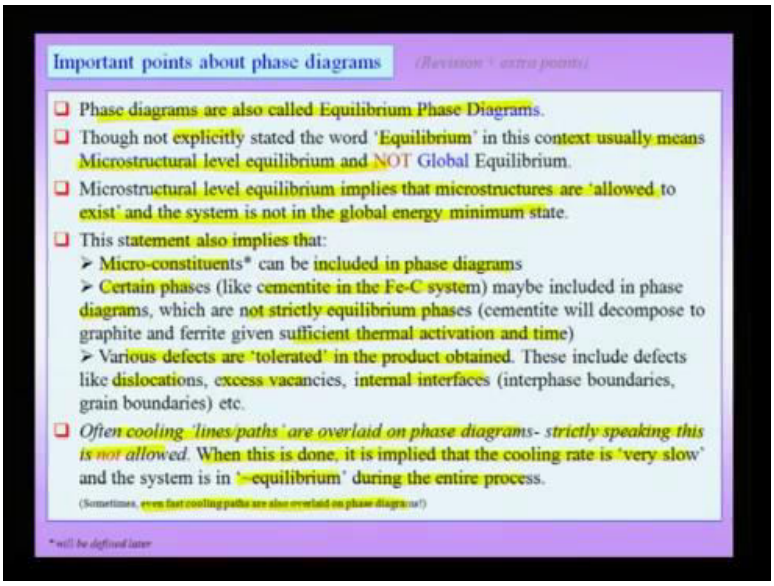
And typically metallurgists operate or material scientist, would drop his diagrams at one atmosphere pressure, but it is and typically do not draw diagrams which involve volume. But, it is possible to draw those diagrams and physicists tend to draw diagrams, which involve purely thermodynamic variables, involving a typically a single component, kinetic variables are typically not included in normal phase diagrams. As I pointed out they should be considered part of something known as time temperature transformation diagrams, which are also maps and which can also be considered as phase diagrams.

But, typically not included in normal chapters on phase diagrams, so to summarize access can be thermodynamic like temperature, pressure volume, they can be kinetic like time, they can involve composition variables like percentage of an component or this percentage could be in mole fraction could be weight percent. In single component systems which are also called unary systems, the usual variables are temperature and pressure.

So, you could also draw temperature volume diagrams, but the typical variables shows into plot, such unary diagrams are temperature pressure and we will see an example when on the coming slides. And as I pointed out the diagrams phase diagrams, drawn in material science temperature and percentage of one of the components, which could be in usually in weight percent or atomic percent forms the other axis.

So, whenever you interested in kinetics, only then we consider phase diagrams with time like the continuous cooling transformation or the t t diagram, wherein temperature and time are the variables. So, it is important to understand the variables, which are used in a phase diagram and these variables as, we have classified here turnout to be thermodynamic, kinetic or composition variables.

(Refer Slide Time: 27:35)



Important points about phase diagrams *(Revision + extra points)*

- Phase diagrams are also called Equilibrium Phase Diagrams.
- Though not explicitly stated the word 'Equilibrium' in this context usually means Microstructural level equilibrium and NOT Global Equilibrium.
- Microstructural level equilibrium implies that microstructures are 'allowed to exist' and the system is not in the global energy minimum state.
- This statement also implies that:
  - ➢ Micro-constituents* can be included in phase diagrams
  - ➢ Certain phases (like cementite in the Fe-C system) maybe included in phase diagrams, which are not strictly equilibrium phases (cementite will decompose to graphite and ferrite given sufficient thermal activation and time)
  - ➢ Various defects are 'tolerated' in the product obtained. These include defects like dislocations, excess vacancies, internal interfaces (interphase boundaries, grain boundaries) etc.
- *Often cooling 'lines/paths' are overlaid on phase diagrams- strictly speaking this is not allowed*. When this is done, it is implied that the cooling rate is 'very slow' and the system is in '~equilibrium' during the entire process.

(Sometimes, even fast cooling paths are also overlaid on phase diagrams!)

*will be defined later

So, let us revise some of the points regarding, the important points regarding phase diagrams and in addition, we will add a few more points which will strengthen our understanding of these. So, it will set the base ready for the slides, which are going to come next phase diagrams are also called equilibrium phase diagrams, though the word equilibrium is not explicitly stated, in this context it usually means micro structural level equilibrium and not global equilibrium.

Micro structural level equilibrium imply microstructures are allowed to exist and system is not, in a state of global energy minimum that means, suppose I take a micro structure I allow inter phases like in this diagram, multiple inter phases I may allow dislocations, I may allow residual stress to exist etcetera. And this implies, that I am not truly considering a global energy minima or global energy minimum, this statement also implies that micro constituents can be included in phase diagrams.

And we will see what, some examples of micro constituents in the coming slides, additionally certain phases. And one good example of this is the cementie phase in the ion carbon diagram are also included in phase diagrams, if you want to be very strict you will note that cementite is not strictly an equilibrium phase. In other words cementite will decompose to graphite and ferrite given sufficient thermal activation and time, that means, that cementite in the truer sense should not be include in a phase diagram.

But, you will notice that whenever, we draw an ion carbon phase diagram cementite is included, because it is a reasonably meta stable phase and continue to exist as cementite for long periods of time. And but truly if you allow it to transform into graphite and ferrite and as I pointed out various defects are tolerate, in the product obtained these defects are like dislocations, excess vacancies, internal interfaces, which include interface boundaries and grain boundaries.

Another important point, which will we have to note here and I will emphasize, it again when we actually do this operation is often cooling lines paths, are overlaid on phase diagrams. Now, whenever I am talking about an equilibrium phase diagram, I automatically imply the time is not a variable, given a certain composition, a certain temperature, a certain pressure, I would expect that a certain combination of phases in a very prescribed fraction should form.

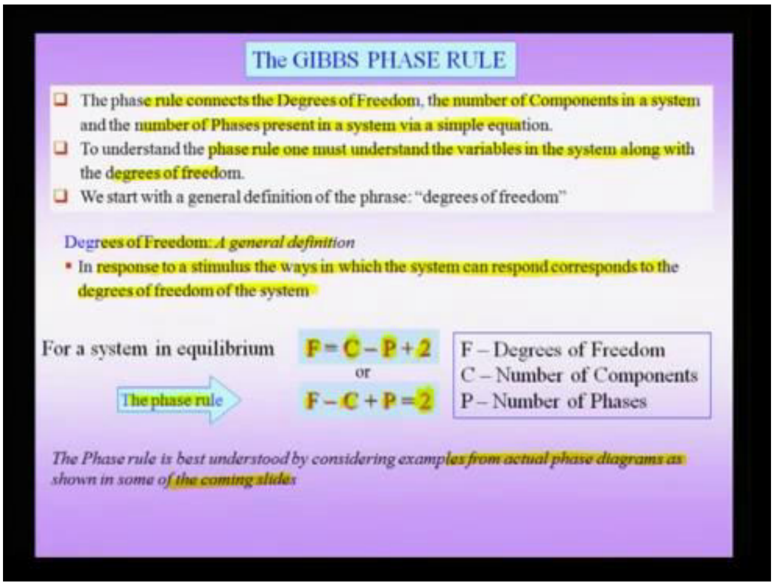
And however, long I wait these fraction should remain unaltered that means, I know what are the phases, which are going to coexist at a given temperature, pressure and composition. And that combination is not going to be altered, even if I wait for a long period of time and therefore, in a typical phase diagram, which does not involve time there is no scope of introducing cooling curves. As I pointed out though we have these phase diagrams involve in time, which are called the T T T diagrams or the C C diagrams, they will not form a part of this chapter.

And therefore, safely for now we will talk about those diagrams, which do not involve time and overlaying any cooling curves on these diagrams is technically not a correct thing to do, strictly speaking this should not be done. But, this is done to actually improve the utility of the phase diagram and when, this is done it is implied that the cooling rate is very slow. So, therefore, whenever we overlay cooling, lines on a phase diagram and this is an additional dimension to the phase diagram, of time this adds an additional dimension to the phase diagram.

And the interpretation has to be very carefully done, that this cooling rate is assumed to be very slow and at least the system is in some kind of a equilibrium. During the entire process, sometimes very rarely even fast cooling paths are overlaid on phase diagrams and caution should be exercised when you are doing this, because then the interpretations or the original phase diagram are known no longer any no longer valid, where time plays no role.

So, to emphasize this last point again, whenever you are overlaying cooling lines or cooling paths on phase diagrams, it is expected to or it is understood that the cooling rate is very slow, it is understood that you are actually extending the utility of the phase diagram, beyond its very strict usage sense. And the system is assumed to be in equilibrium during this entire cooling process, next we come to an important point which is known as the Gibbs phase rule in the context of phase diagrams.

(Refer Slide Time: 32:38)



The GIBBS PHASE RULE

- ☐ The phase rule connects the Degrees of Freedom, the number of Components in a system and the number of Phases present in a system via a simple equation.
- ☐ To understand the phase rule one must understand the variables in the system along with the degrees of freedom.
- ☐ We start with a general definition of the phrase: "degrees of freedom"

Degrees of Freedom: *A general definition*

- In response to a stimulus the ways in which the system can respond corresponds to the degrees of freedom of the system

For a system in equilibrium

The phase rule

$F = C - P + 2$

or

$F - C + P = 2$

F – Degrees of Freedom
C – Number of Components
P – Number of Phases

The Phase rule is best understood by considering examples from actual phase diagrams as shown in some of the coming slides

The phase rule which is also called a Gibbs phase rule, connects degrees of freedom the number of components, in a system and the number of phases, present in a system via a simple equation to understand the phase rule, one must understand the variables in the system, along with the degrees of freedom. So, in this context the degrees of freedom is a technical term and we will try to understand, what does this imply in the context of a phase diagram.

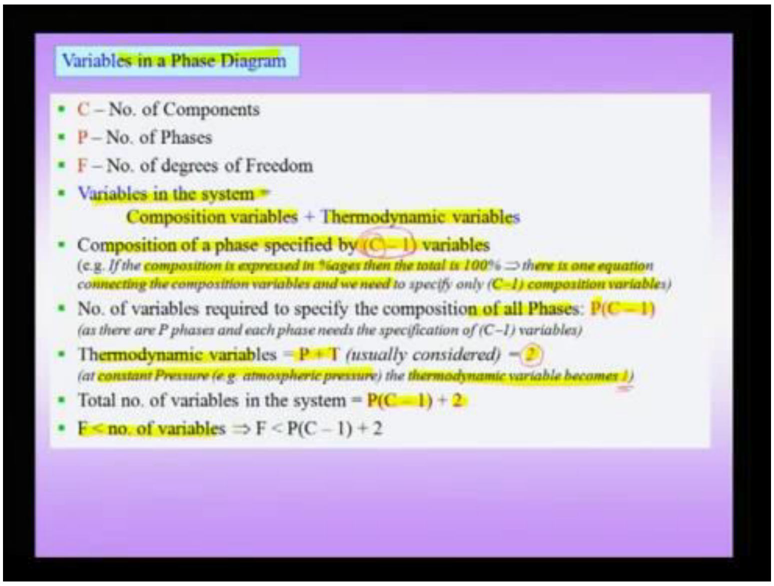
In general suppose, we are not particularly talking about phase diagrams, the general definition of degrees of freedom is that in response to a stimulus, the number of ways in which a system can respond, corresponds to the degrees of freedom of a system. In other words suppose, I have an object like this and I have a stimulus, which is the force which is pushing then obviously, this object as a whole cannot move along the x direction.

But, it can rotate along this, so this is one degree of freedom, this rotation and maybe there is a little tolerance in this direction a rotation in the other direction. But, because of the constraint this cannot move totally, as a whole rigid body along towards the direction of the camera therefore, you can think of degrees of freedom, that it is the ways in which a system can respond in response to a stimulus.

But, in the context of a phase diagram as we shall see, that the degrees of freedom has a very specific meaning. And we shall try to understand, the phase rule by considering examples from actual phase diagrams, in which we will see in the coming slides the Gibbs phase rule states that the degrees of freedom, f is number of components in the system minus the number of phases in equilibrium plus 2.

Now, in other words I can write that f minus c plus p is equal to 2 and this 2, as we shall see comes from the two thermodynamic variables temperature and pressure. So, the Gibbs phase rule is a simple equation, which connects the number of degrees of freedom with the number of components, the number of phases, which are in equilibrium and the thermodynamic variables which are 2 in number.

(Refer Slide Time: 34:54)



Variables in a Phase Diagram

- C – No. of Components
- P – No. of Phases
- F – No. of degrees of Freedom
- Variables in the system =
  Composition variables + Thermodynamic variables
- Composition of a phase specified by (C – 1) variables
  (e.g. *If the composition is expressed in %ages then the total is 100% ⇒ there is one equation connecting the composition variables and we need to specify only (C–1) composition variables)*
- No. of variables required to specify the composition of all Phases: P(C – 1)
  (as there are P phases and each phase needs the specification of (C–1) variables)
- Thermodynamic variables = P + T *(usually considered)* = 2
  (at constant Pressure (e.g. atmospheric pressure) the thermodynamic variable becomes 1)
- Total no. of variables in the system = $P(C - 1) + 2$
- F < no. of variables ⇒ $F < P(C - 1) + 2$

What are the variables in a phase diagram, we need to understand before we understand the degrees of freedom, the variables in a system are composition variables plus thermodynamic variables. Suppose I want to specify their composition of phase I need c minus 1 variables to describe, the composition of a phase why, because suppose I have an a a b c phase diagrams, then the total of all the percentages of a plus b plus c is 100 therefore, there is one equation connecting the various phases the composition of various phases.

And that is why, I do not need c composition variables, I need c minus 1 composition variables to describe, the composition of a phase to reiterate, the composition of a phase is prescribed by c minus one variables. Because, if the composition is expressed in percentages, the total percentage is 100 percent or if expressed in fractions the total fraction will add up to 1, that is there is one equation connecting the composition variables.

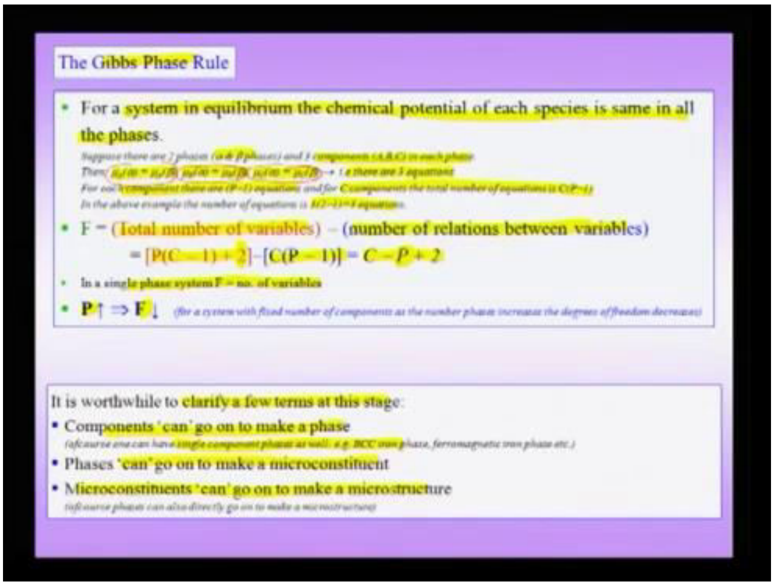
And therefore, we need to only specify C minus 1 variables to specify the composition of any given phase and therefore, suppose I have P phases in a in equilibrium like for instance, I drawn a diagram on the board. Some time, back in which there were 2 phases in equilibrium say it is phase A and phase B, it could be phase alpha and phase beta. In that case, if there are P phases then, I need the total number of variables, I need to specify the composition of all the phases is P times, C minus 1 for each phase.

And since, there are p phases in equilibrium, it is going to become p times c minus one the thermodynamic variables are pressure and temperature and therefore, the number is fixed at 2. And often, we will draw materials phase diagrams at constant pressure and this pressure is usually, the atmospheric pressure and therefore, at constant pressure, the atmospheric pressure, the thermo dynamic variable, reduces to just 1, therefore, even though in general I have two variables, which I need to take into account.

But, given the fact that most of the metallurgical phase diagrams are drawn at one atmosphere pressure I have just one thermodynamic variable, which I need to take into account. Therefore, the total number of variables in a system becomes P times C minus 1 plus 2 and as I pointed out these variable system are a sum of the composition variables and the thermodynamic variables.

And the degrees of freedom in a system have to be less than the number of variables, so because that is the maximum limit, set is the number of variables in the system and therefore, the degrees of freedom, always have to be less than the number of variables in the system.

(Refer Slide Time: 37:56)



The Gibbs Phase Rule

- For a system in equilibrium the chemical potential of each species is same in all the phases.
  Suppose there are 2 phases (α & β phases) and 3 components (A,B,C) in each phase
  Then: $\mu_A(\alpha) = \mu_A(\beta)$, $\mu_B(\alpha) = \mu_B(\beta)$, $\mu_C(\alpha) = \mu_C(\beta)$ → i.e. there are 3 equations
  For each component there are (P−1) equations and for C components the total number of equations is C(P−1)
  In the above example the number of equations is 3(2−1)=3 equations.
- F = (Total number of variables) − (number of relations between variables)
  $= [P(C-1)+2] - [C(P-1)] = C - P + 2$
- In a single phase system F = no. of variables
- $P\uparrow \Rightarrow F\downarrow$ (for a system with fixed number of components as the number phases increases the degrees of freedom decreases)

It is worthwhile to clarify a few terms at this stage:
- Components 'can' go on to make a phase
  (ofcourse one can have single component phases as well: e.g. BCC iron phase, ferromagnetic iron phase etc.)
- Phases 'can' go on to make a microconstituent
- Microconstituents 'can' go on to make a microstructure
  (ofcourse phases can also directly go on to make a microstructure)

So, the Gibbs according to the Gibbs phase rule for a system in equilibrium, the chemical potential of each species, is same in all the phases. Therefore, suppose I have two phases say for instance the alpha, and beta phases. And each one of these phases is a contains three components like for instance a b and c that means, I am talking about taking three components, which could for instance be three elements copper nickel and gold.

And I could form two phases out of these for instance, the alpha phase and the beta phase then if these phases are in equilibrium, the chemical potential of each species like for instance a in the alpha phase, has to be same as the in the beta phase. And we had noted, before if the chemical potential is not same, then this will lead to diffusion of say species a from the higher chemical potential say for instance. Suppose the chemical potential of a in alpha is higher and if it happens, to be lower in beta then a will flow from tend to flow from a to alpha to beta.

But, suppose they are in equilibrium, then the chemical potential of a in alpha has to be same as the chemical potential of a in beta. Similarly the chemical potential of b in alpha has to be same, as the chemical potential of b in beta and similarly the chemical potential of c in alpha has to be same, as the chemical potential of c in beta that means, there are three equations, three constraints based on the fact that the two phases alpha and beta are in equilibrium.

And the fact that, each one of them has three components a, b and c as a part of its alloy for each component, there are p minus 1 equations as we had noted before and for c components. The total number of equations, as we noted before are c into p minus one in the example above where in I considered alpha and beta phases. And a b c components the number of equations, I obtain is three equations which I have been listed here, so the three equations are equation number, one would be this equation number, two would be this equation and equation number three, would be this equation.

Therefore I have three equations, which plays constraint on the two phases alpha and beta in equilibrium therefore, the degrees of freedom can be or the total number of variables in the system minus, the number of relations between the variables. So, the total number of variables, we already derived is P into C minus 1 plus 2 assuming that I am for, now considering a system in which pressure and temperature, the two variables are both variable and the number of equations, as I have seen here is c into p minus 1.

So, simplifying this we can obtain C minus P plus 2, as the number of degrees of freedom of the system and in a single phase system, f is equal to number of variables. So, if I increase the number of phases, as seen from this equation if P increases, the number of degrees of freedom comes down therefore, at a given temperature. And pressure may be that there are two phases in equilibrium, suppose I am talking about a binary phase diagram.

But, at a certain different temperature and pressure, there may be three phases in equilibrium and if you are talking about, three phases in equilibrium the number of degrees of freedom will come down. We will actually perform some calculations to understand, this fact that how the degrees of freedom changes depending on the number of phases, which are in equilibrium.

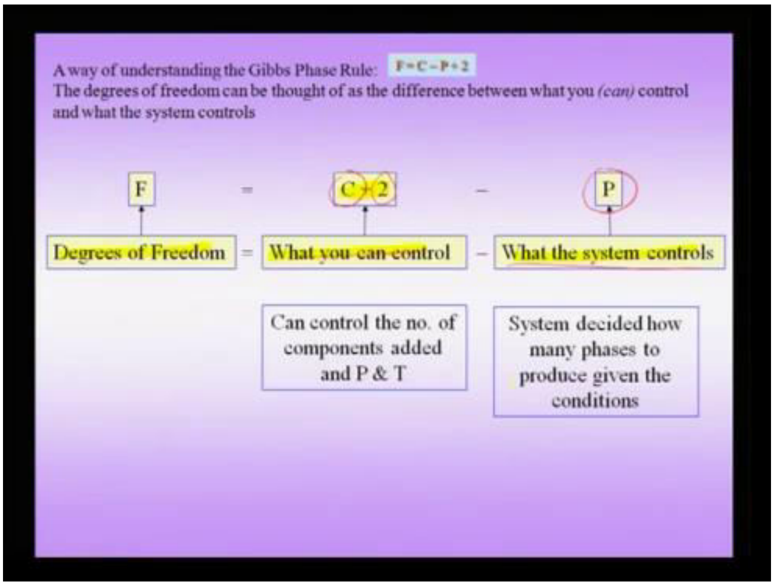
So, you have seen that degrees of freedom is c minus p plus 2 and this aspect can simply we derived from the fact that degrees of freedom is the difference between, the total number of variables. And the number of relation between variables, which are the constraints and these relations, can be obtained noting that the chemical potential of any given species or any given component, is same in all the phases in equilibrium.

So, to review and clarify a few terms at this stage components, can go on to make a phase of course, you have already noted there are single phase components as well like the BCC ion phase or the ferromagnetic ion phase, phases can go on to make a micro constituent. And we will take up a few examples of micro constituents in the coming slides and finally, micro constituents can go on to make a microstructure and this microstructure gives us a handle on the properties.

Therefore, so for we have introduced quite a few technical terms in our understanding of phase diagrams, we defined a component we have defined a phase, we have defined a phase based on multiple parameters, like based on state atomic order band structure etcetera. We have tried to understand the term microstructure, we have tried to understand the variables or axis of a phase diagram.

And we also using, that concept of a degrees of freedom and using the number of phases and components, we have also defined what is known as the Gibbs phase rule. And we have tried to understand the Gibbs phase rule, based on the fact that the chemical potential of various species, have to be same in the phases in equilibrium. Now in just to understand the Gibbs phase rules, a little more that, you can actually think of the Gibbs phase rule.

(Refer Slide Time: 43:38)



A way of understanding the Gibbs Phase Rule: $F=C-P+2$

The degrees of freedom can be thought of as the difference between what you *(can)* control and what the system controls

$F = C+2 - P$

Degrees of Freedom = What you can control − What the system controls

Can control the no. of components added and P & T

System decided how many phases to produce given the conditions

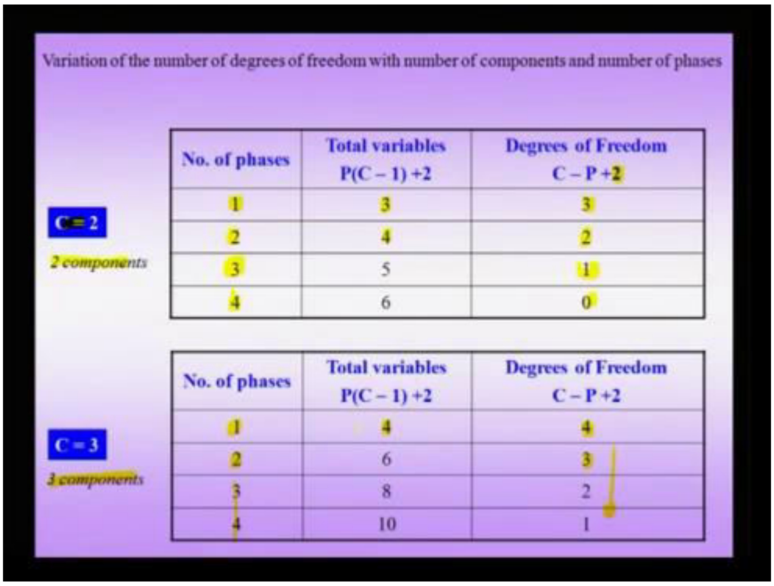
As the degrees of freedom being equal to the difference between, what you can control and what the system controls. For instance suppose I have put together say c components like for instance, I could be adding copper nickel and iron and forming or for, now let me simplify, this by taking just copper and nickel, I added then therefore, I have two components.

And additionally I can also control the temperature and pressure, at which I hold this components for instance, I could hold it at one atmosphere pressure at 500 degrees Celsius or I could change the temperature and make it, 700 degrees Celsius and increase the pressure to two atmospheres. Therefore, I control the two, the number 2 here, which is the pressure and temperature. And I can also control the number of components, I am adding into the system for instance, I could add one component, I could add two components, I could add four components.

But, after having done this and controlling the temperature and pressure, the system will decide that how many phases, does it throw out this is not under your control. Because that is decided by the system for instance, suppose I hold water at 50 degree Celsius then I know there is going to be a single phase water, at coexisting that, is the single phase the p is 1.

But, suppose I take water to 0 degrees, then I know that water and ice will coexist therefore, the number of phases the system throws out is 2 and therefore, the difference between, what you control and what the system controls can be thought, of as the degrees of freedom of the system. And so this is an alternate way of understanding, the Gibbs phase rule, that is the freedom or the degrees of freedom is what, you control minus what the system throws out or what the system controls.

(Refer Slide Time: 45:34)



Variation of the number of degrees of freedom with number of components and number of phases

C = 2

2 components

No. of phases	Total variables P(C – 1) +2	Degrees of Freedom C – P +2
1	3	3
2	4	2
3	5	1
4	6	0

C = 3

3 components

No. of phases	Total variables P(C – 1) +2	Degrees of Freedom C – P +2
1	4	4
2	6	3
3	8	2
4	10	1

So, let us take for instance two component system, in which case c equal to 2 and also compared with three component system and see what happens, when the number of phases increases. So, if you have a two component system and the number of phases, is one then the total number of variables is p into c minus 1 plus 2, which is 3 and the degrees of freedom is 3, which is nothing, but c minus p plus 2.

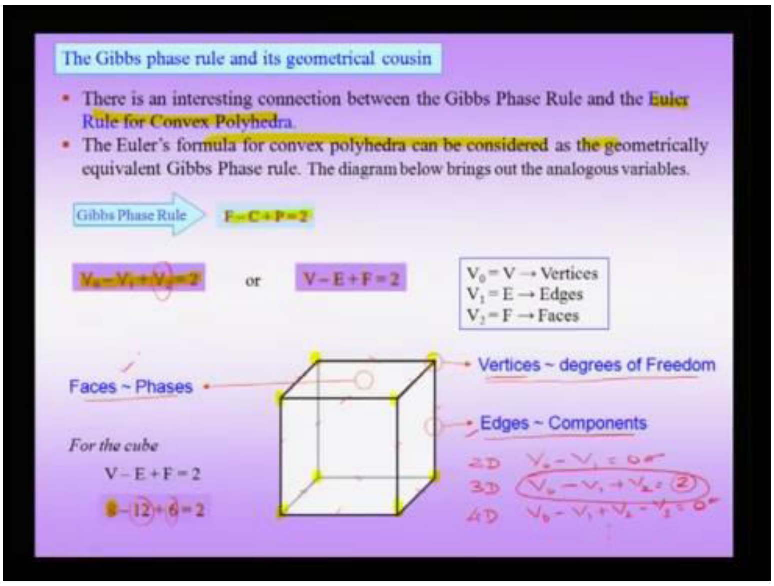
So, c is 2 here phases p is 1, so 2 minus 1 was 1 plus 2 is 3, but suppose the number of phases increases to 2, then the total number of variables, increases to 4 and correspondingly, the degrees of freedom reduces to 2. And in a two component system, suppose I have four phases in equilibrium, the degrees of freedom falls down to 0. Similarly, in a three components system I can evaluate that, suppose I have a 1 phase.

And the total number of variables, becomes p into c minus 1 plus 2, which is 4 and correspondingly, the degrees of freedom which is, now 3 minus 1 2 plus 2, which is 4. But, you would notice that, suppose I have a system in which, there are two phases in equilibrium in a three component system, the number of degrees of freedom comes down to 2 3 and then progressively, as the phases increase my degrees of freedom comes down.

Now, in a two component system, suppose I am using a reduced Gibbs phase rule, in which case the p minus e c minus p, plus 1 in this case you would notice that, if three phases are in equilibrium already the degrees of freedom, will become 0 therefore, most often than not we will be talking about two components system, which we will be taking many example like the iron cementite system or many more systems, you will notice that when there are three phases in equilibrium, the number of degrees of freedom, become 0, that is because I am not using, this temperature and pressure both as variables.

But, I am using a reduced Gibbs phase rule, wherein only one variable is there, which is temperature pressure is assumed to be constant at one atmosphere.

(Refer Slide Time: 47:50)



The Gibbs phase rule and its geometrical cousin

- There is an interesting connection between the Gibbs Phase Rule and the Euler Rule for Convex Polyhedra.
- The Euler's formula for convex polyhedra can be considered as the geometrically equivalent Gibbs Phase rule. The diagram below brings out the analogous variables.

Gibbs Phase Rule → $F - C + P = 2$

$V_0 - V_1 + V_2 = 2$ or $V - E + F = 2$

$V_0 = V \rightarrow$ Vertices
$V_1 = E \rightarrow$ Edges
$V_2 = F \rightarrow$ Faces

Faces ~ Phases

Vertices ~ degrees of Freedom

Edges ~ Components

For the cube

$V - E + F = 2$

$8 - ⑫ + 6 = 2$

2D $V_0 - V_1 = 0$

3D $V_0 - V_1 + V_2 = ②$

4D $V_0 - V_1 + V_2 - V_3 = 0$

Now, there is a curious resemblance between, what you might call the Gibbs phase rule and there is a geometrical cousin of it, which is known as the Euler rule for convex polyhedral, Though this is this particular slide is not very important from the point of view of phase diagrams. But, it is an interesting observation and this topological, analog of the Gibbs phase rule is interesting to note, the Gibbs phase rule says F minus C plus P is equal to 2.

And the Euler formula for convex polyhedral, can be written as V 0 minus V 1 plus V 2 is equal to 0. Now, V 0 for instance suppose I am talking about a cube, V 0 is the number of vertices and for a cube, there are 8 vertices. And suppose v 1 represents the number of one dimensional entities in this polyhedron, which happens to be line segments and there are for instance 12 line, 12 edges to this 1 2 3 4 5 6 7 8 9 10 11, there are 12 edges, which is shown here and V 2 represents 2 number of two dimensional entities in this polyhedron, which are number of phases.

And these phases, happen to be 6 in number and therefore, if I add number of vertices 8 subtract, the number of edges which is minus 12 and add the number of phases, which is F which is 6, then I get the number 2. So, I can have an analogy between, the Euler rule for convex polyhedral and the Gibbs phase rule, where in I can consider, the vertices as number of degrees of freedom, the edges as the components of the system and the phases, at the phases of which are in equilibrium in the case of the Gibbs phase rule.

Now of course, the Euler rule can also be written for various dimensions, for instance suppose I am talking about this is, now a three dimensional. But, you can also write down for two dimensional objects and in two dimension, it will become V 0 minus V 1 is equal to 0. So, suppose I talk about two dimensional polygons a triangle or a square or a pentagon, then the number of vertices minus number of edges is 0. Because for all polygons regular polygons for, now the vertices and edges are equal in number in this is in two dimensions in three dimensions.

I can write down V 0 minus, V 1 plus, V 2 is equal to 2 in 4 dimensions, you can write down as v 0 minus V 1 plus V 2 minus V 3 is equal to 0 and so forth. So, you note that in every odd dimension the right hand side, becomes 2 and in every even dimension the right hand side is 0. So, this is of course, the generalized Euler rule across various, dimensions and the one of immediate relevance is the 1, which we connect to the Gibbs phase rule, which is V 0 minus V 1 plus V 2 is equal to 2 and we do.

So, as I point out by taking equivalence between vertices and the degrees of freedom, the edges and the components and the phases and the phases in a system in equilibrium. So, there happens to be this interesting, correlation between the Gibbs phase rule and its geometrical cousin, which is the Euler rule for convex polyhedral.