

INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
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NPTEL ONLINE CERTIFICATION COURSE
Structural Analysis of Nanomaterials
LECTURE – 04
Phase Diagram: Determination of Phases
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Structural Analysis of Nanomaterials

Lecture- 04 Phase Diagram: Determination of Phases

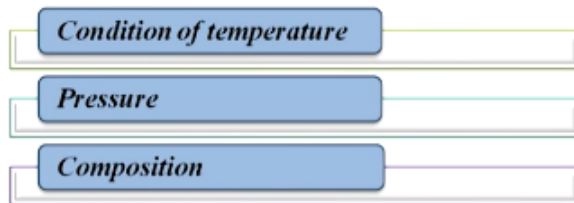


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Hello, in this particular lecture we are going to discuss about the phase diagram that means determination of the different phases from the phase diagram itself of various materials.

Why We Study Phase Diagram?

- ❖ Many material systems and alloy systems exist in more than one phases which depends on:



- ❖ Each phase will have different microstructure which is related to mechanical properties.
- ❖ Development of microstructure is related to the characteristics of phase diagram.
- ❖ Proper knowledge and understanding of phase diagrams will lead to:
 - ✓ Design and control of heating procedures for developing required microstructure and properties.

So first let us know that why we are going to study about the phase diagram? So generally in the many material systems and alloy systems exist in more than one phases which depends, I mean which depends upon so many parameters, what are those? First is called the conditions of the temperature, and then pressure, and the third one is the compositions, so first is that temperature, then pressure, and the compositions. So each phase will have different microstructure which is

related to the mechanical properties, yes, later we will see that one material can stay into different phases.

Development of microstructure is related to the characteristics of the phase diagram and the proper knowledge and understanding of phase diagram will lead to design and control of heating procedures for developing required microstructure and the properties, sometimes it may happen that we are heating that materials or maybe we are cooling down the materials so rapidly or maybe step by step so that we can get the different material characteristics at different temperature zone or maybe same material at different conditions will show us the different properties.

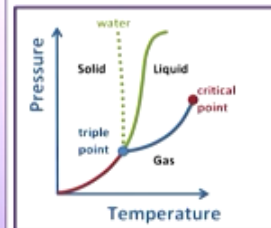
Phase Diagram:

Phase (solid, liquid, gas):

- Homogenous portion of system, physically distinct and mechanically separable.
- Phase have a definite boundary surface, so recognizable and separable.
- Different phases are given different names or symbols as:
 - ✓ α (Alpha), β (Beta), γ (Gamma) etc.

Phase Diagram:

- Graphical representation of various phase present in material system at various temperature and composition point.
- It is also called as **equilibrium diagram**.
- It has pressure on y-axis and temperature on x-axis.
- Crossing the lines or curves on phase diagram, a phase change occurs.



So what is phase diagram? So generally phase as we know it may be solid, it may be liquid or may be it maybe the gas, so it's a homogeneous portion of system physically distinct and mechanically separable, phase have a definitive or maybe definite boundary surface so recognizable and separable, different phases are given different names or symbols like alpha, beta, gamma, etcetera. So what is phase diagram? Graphical representations of the various phase present in the material systems at various temperature and composition point, it is also called as equilibrium diagram, it has pressure on the Y axis, so you can see from this and the temperature into the x-axis, crossing the lines or curves on phase diagram a phase change occur, so in this side you can see this is solid zone, then if you cross this line the liquid zone is coming and then again if you cross this boundary the gas zone is coming, so this is the generally the triple point where the three different phases of that particular materials is exist, and if you want to get the conditions of this point so simple we can get the temperature, and we can get the pressure, so at what pressure and what temperature the water or maybe that H₂O will exist into three different phases together.

Significance of Phase Diagram:

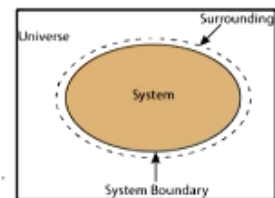
- To show the various phase present at different composition and temperature.
- To indicate equilibrium solid solubility of one element in other.
- To indicate temperature range over which solidification or liquidification of material system occurs.
- To indicate the temperature at which different phase start to melt.
- Amount of each phase in two phase mixture can be obtained.
- Useful in understanding the properties of materials in a heterogeneous systems.
- Provides valuable information about melting, casting and crystallization.

So what is the significance of the phase diagram? So first is that to show the various phase present at different compositions and temperature. Second to indicate the equilibrium solid solubility of one element in other. Third to indicate temperature range over which solidification or liquidification of material systems occur. Fourth to indicate the temperature at which different phase start to melt. Fifth amount of each phase in two phase mixture can be obtained. Sixth useful in understanding the properties of materials in a heterogeneous systems. And the seventh provides the valuable informations about melting, casting and the crystallization.

Basic Terminology Used in Phase Diagram:

1) System:

- Substances that are isolated and unaffected by their surrounding.
- It may contain solids, liquids, gases or their combination.
- It may have metals, non-metals separately or in combined form.
- It is capable of changing its composition, temperature, pressure, density etc.



2) Component:

- Pure metals or compounds of which an alloy is composed.
- Example: In **copper-zinc brass**, the components are **Cu** and **Zn**.
- Independent chemical species and components of a system may be elements, ions or compounds.
- It can exist in many phases:
 - ✓ *Water exists as ice, liquid water, and water vapor.*
 - ✓ *Carbon exists as graphite and diamond.*

3) System Variables:

- Parameters like composition (in terms of components), temperature 'T' and pressure 'P'.

So before going to start deeply into this particular lecture, just let us know some basic terminology which generally we are using for phase diagram, so first one is called the systems, so systems means substances that are isolated and unaffected by their surroundings, so here and this is the systems. It may contain solids, liquids, or maybe the gases or maybe their combinations, it may have metals non-metals separately or in combined form, it is capable of changing its compositions, temperature, pressure, density and so on.

What is component? Pure metals or compounds of which an alloy is composed, example in copper, zinc, brass, the components are copper and zinc, independent chemical species and components of a system may be elements, ions or compounds, it can exist in many phases like water exists as ice, liquid water, and the water vapor we know all, carbon exists as graphite and the diamond. Then system variables, parameters like compositions in terms of components, temperature T and the pressure P.

4) Equilibrium:

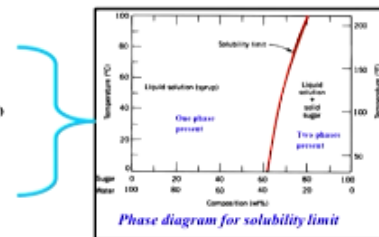
- State of minimum free energy under any specified combination of overall composition, temperature, pressure and overall volume.
- Once equilibrium is achieved, minor change in composition, temperature, pressure, volume within the system means an increase in free energy.

5) Degrees of Freedom:

- Also known as variance of system.
- It is the number of external or internal factors of system (temperature, pressure and concentration) that can be independently changed without altering equilibrium.

6) Solubility limit:

- Maximum concentration of solute atoms that may dissolve in solvent to for a solid solution.
- Example of solubility limit: **Sugar in Water**



7) Microstructure:

- Characterized by number of phases, proportions and manner of distribution of phases.
- Depends on: **Alloying elements, concentrations, heat treatment** (temp., heating/cooling rate).

Next equilibrium, state of minimum free energy under any specified combinations of overall compositions, temperature, pressure, and overall volume. Once equilibrium is achieved, minor change in composition, temperature, pressure, volume within the system means an increase in the free energy.

What is degree of freedom? It is also known as variance of system, it is the number of external or internal factors of system like temperature, pressure, and concentration that can be independently changed without altering the equilibrium.

Then next one is called the solubility limit, maximum concentration of solute atoms that may dissolve in solvent to for a solute solution, so supposing in water I am adding the sugar, so here the sugar is the solute and the rest of the water is known as the solutions, so here if I am adding the sugar and sugar and sugar into the water, after certain time the sugar will not dissolve in to the water itself, so that is known as the solubility limit, so generally the solubility limit is sugar in water. And what is microstructure? Characterized by number of phases, proportions and manner of distribution of the phases itself, depends on alloying elements, concentrations, heat treatment maybe temperature or maybe the heating cooling rate, so in this case we are making the syrup which is liquid, as I was giving the examples of the sugar in water, so liquid solutions

syrup so this is the solubility limit or maybe the solubility line, so after that again if we add the sugar, so what will happen? Liquid solutions and solid sugar precipitations will be taking place inside the system.

Gibb's Phase Rule:

- Given by *Josiah Willard Gibbs* in 1870.
- Predicts the number of phases that will coexist within a system at equilibrium.
- It's a relationship between number of variable (F), number of element (C), and number of phases (P) as:
- Number of phases (P) can be determined as: $P + F = C + N$
 - ❖ Gas or gaseous mixture is single phase
 - ❖ Liquid is one, two and three phases
 - ✓ Two totally miscible liquids – single phase
 - ✓ A slurry of ice and water – two phases
 - ❖ Solid: A crystal is a single phase, an alloy of two metals is two phases (immiscible) and one phase (miscible).
- One use of Gibb's phase rule is in analyzing non-equilibrium conditions.
 - ❖ **Example:** a microstructure for a binary alloy is developed over a range of temperatures consists of three phases is a non-equilibrium. Under these circumstances, three phases will exist only at single temperature.

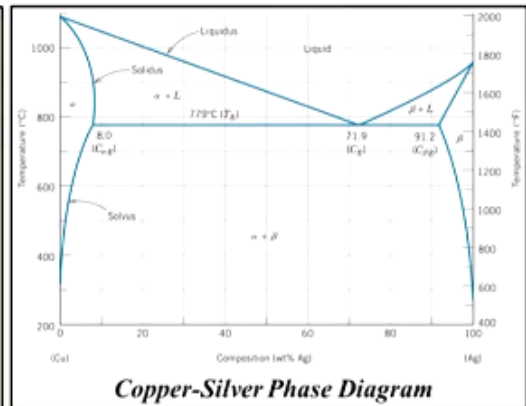
N = represents any two variable like temperature, pressure.

Now from where this phase actually has come, who is the inventor of that? So that's why it is called the Gibb's phase rule, because it is given by Josiah Willard Gibbs in 1870, predicts the number of phases that will coexist within a systems at equilibrium, it is a relationship between the number of variables F, number of elements C, the number of phases P, as number of phases can be determined as $P + F = C + N$, generally gas or gaseous mixture is single phase, liquid is one, two or maybe the three phases possible, two totally miscible liquids it is single phase, a slurry of ice and water is two phases, what is solid? A crystal in a single phase, an alloy of two metals in two phases, if it is immiscible and one phase if it is properly miscible.

One use of the Gibb's phase rule is in analyzing non-equilibrium conditions, what is the example? The example is a microstructure for a binary alloy is developed over a range of temperatures consists of three phases in a non-equilibrium, under these circumstances these three phases will exist only at single temperature.

Gibb's Phase Rule Example: **Copper-Silver System**

- The number of phase:
 - a) Consider case of single phase fields as (α , β and liquid region), only one phase is present, $P = 1$.
 - b) When two phases exist ($\alpha + L$, $\beta + L$ and $\alpha + \beta$ phase regions), $P = 2$.
 - c) For binary systems, when three phases are present, $P = 3$.
- The number of components is 2, Cu and Ag.
- Since pressure is constant (1 atm), parameter N is 1, where temperature is only non-compositional parameter.



a) $P + F = C + N$
 $1 + F = 2 + 1$
 $F = 2$

b) $P + F = C + N$
 $2 + F = 2 + 1$
 $F = 1$

c) $P + F = C + N$
 $3 + F = 2 + 1$
 $F = 0$

So now we are trying to give the Gibb's phase rule example for copper-silver systems, so in this particular case you can see that the compositions or the weight percent of silver it is increasing into this directions, here the silver percentage is 0, then 20, 40, 60, 80 and the 100, and the opposite is for the copper, in this particular case the copper is 100, then 80, then 60, then 40, then 20 and then 0, so copper is increasing into this directions, so in this particular case what is the number of phases? Considered the case of single phase fields as alpha, beta and the liquid region only one phase is present that's why $P = 1$, so in this case alpha it is only a single phase, liquid is one single phase and the beta is only single phase, but in this particular case you can see that alpha + L or maybe the beta + L or maybe the alpha + beta, so there are two phases exist, so that's why it is $P = 2$.

For binary systems when three phases are present that time $P = 3$, so the number of components is 2 that is copper and silver, since pressure is constant over here that is one atmospheric parameter n is 1, when temperature is only non-compositional parameter, so from the Gibb's rule first case if we consider the A, so for A $P + F = C + N$ in this case $P = 1$, $C = 2$ and $N = 1$, so here the $F = 2$, so in this particular case the F value is 2, in this particular case F value is 1, and in this particular case the $F = 0$, and what is F? The F is the number of variables.

Advantages:

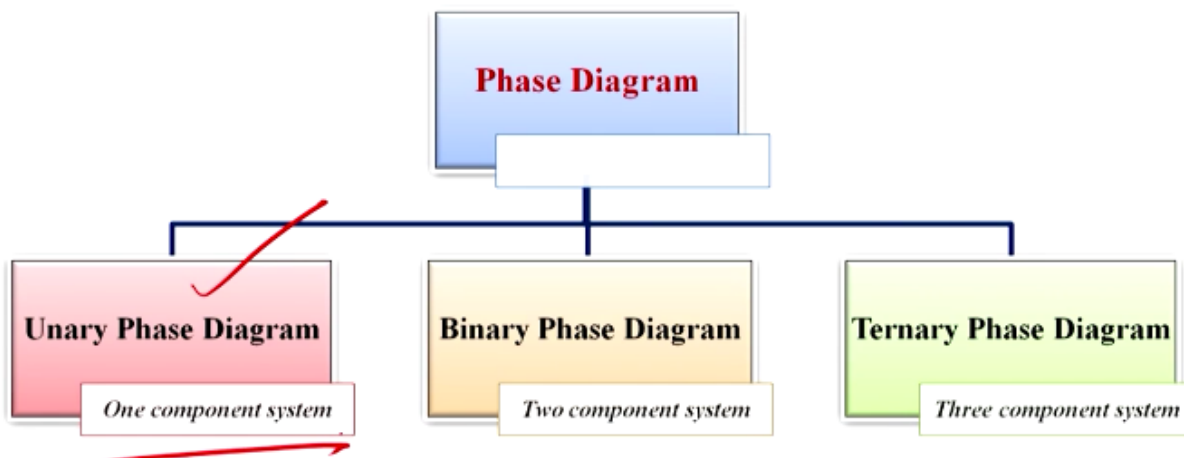
- ❖ Applicable to macroscopic system.
- ❖ Predicts the behavior of system with changes in intensive variables.
- ❖ Applicable to both chemical & physical equilibria.
- ❖ Simple method of classifying equilibrium states of matter.

Limitations:

- ❖ Applicable only for systems which are in equilibrium.
- ❖ Considers only number of phases rather than amounts.
- ❖ Under same condition of temperature & pressure, all phases of system must be present.

So now what is the advantages? So generally applicable to the microscopic system predicts the behavior of system with changes in intensive variables, applicable to both the chemical and physical equilibria, simple method of classified equilibrium stages of matter, but of course there is certain limitations, what are those? Applicable only for systems which are in equilibrium, it's not possible for the non-equilibrium system, considers only number of phases rather than amounts, it will tell you the number of phases, but what amounts, it is difficult, under same conditions of temperature and pressure all phases of system must be present.

Classification of Phase Diagram:



Now if we see the classifications of the phase diagram so generally it is divided into three parts, one is called the unary phase diagram or maybe known as the one component systems, binary phase diagrams also known as the two components systems, ternary phase diagram which is known as the three component system.

1. Unary Phase Diagrams:

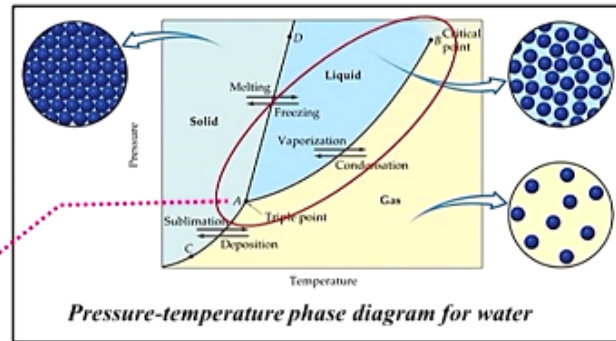
- Also known as pressure-temperature or P-T diagram.
- Simplest phase diagram, which is one component system.
- **Example:** water (H_2O), have regions for three different phases- *solid, liquid and vapor*.
- Two phases exist along each of the three phase boundaries.

Critical point:

- Point at which substance is indistinguishable between liquid and gaseous state.

Triple point:

- Point where all three phases coexist at low pressure and temperature.
- Also called as invariant point.



So what is unary phase diagrams, also known as pressure temperature or maybe the P-T diagram, simplest phase diagram which is one component system, example water H_2O have regions for 3 different phases, solid, liquid and vapor, two phases exist along each of the three phases boundaries, so I will give you the example. So in this particular case we are having that pressure into the Y axis and temperature into the X axis, so in this particular case this is the gas phase, this is the liquid phase, and this is the solid phase.

So now what is the critical point? So critical point at which substance is indistinguishable between liquid and the gaseous state, so in this particular point you cannot distinguish that the material is into the liquid phase or maybe the gas phase that is known as the critical point. And what is triple point? Point where all three phases, already I told in this particular point that solid, liquid, and gas three phases are present at that particular point, at low pressure and temperature also called as invariant point, also called as invariant point. So in this particular case if we move from solid to liquid that is known as the melting, if we move from liquid to solid that is known as the freezing, and then if we move from liquid to gas it is known as the vaporizations, and if we move from gas to liquid it is known as the condensations, and if we move from solid to gas that is known as the sublimations, and if we directly move from gas to solid that is known as the depositions.

Unary Phase Diagram for Metal: (Pure iron)

- Formation of different phases are function of temperature and pressure.
- At atmospheric pressure, three allotropic forms of iron exist:
- At very high pressure, a fourth form exists, called epsilon iron (ϵ) hexaferrum.

- ❖ α -Fe
- ❖ Gamma iron (γ) - austenite
- ❖ Delta iron (δ)

Delta iron (δ -Fe):

- ✓ As molten iron cools down, it solidifies at 1,539 °C into its δ allotrope, which has BCC crystal structure.
- ✓ δ -iron can dissolve as much as 0.09% of carbon by mass at 1,493 °C.

Gamma iron / Austenite (γ -Fe):

- ✓ As iron cools further to 1,394 °C its crystal structure changes to a FCC crystalline structure.
- ✓ In this form it is called gamma iron (γ -Fe) or Austenite.

Alpha iron (α -Fe):

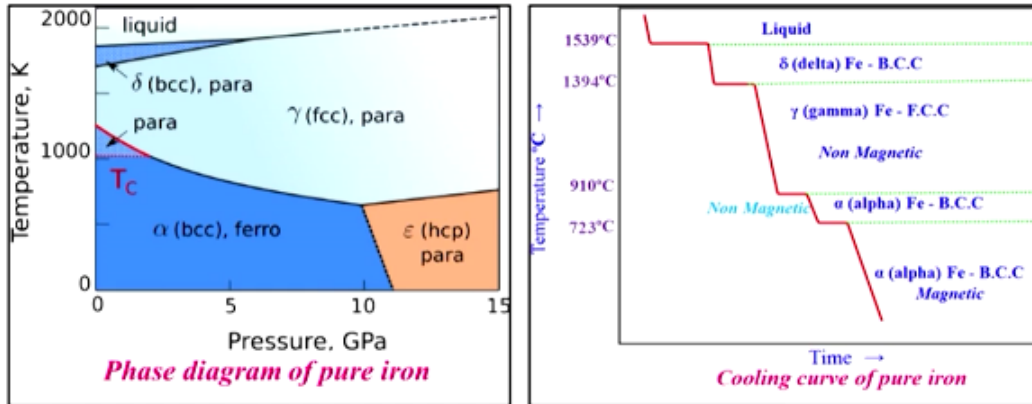
- ✓ Below 910 °C iron again adopts the BCC structure characteristic of α -iron, also called ferrite.
- ✓ The substance assumes a paramagnetic property.
- ✓ Carbon dissolves poorly in α -iron: no more than 0.021% by mass at 723 °C.

So now unary phase diagrams for metal, say suppose we are trying to give an example of pure iron, so formations of different phases are functions of temperature and pressure already I told, at atmospheric pressure three allotropic forms of iron exist that is known as the alpha iron, gamma iron, which is known as the austenite, and other one is called the delta iron. At very high pressure a fourth form exist called epsilon iron or maybe the hexaferrum.

What is delta iron? As molten iron cools down it solidifies at 1,539 degree centigrade into its delta allotrope which has BCC crystal structure, delta iron can dissolve as much as 0.09% of carbon by mass at 1,493 degree centigrade. What is gamma iron or maybe the austenite or maybe the austenite or maybe the gamma Fe, as iron cools further to 1,394 degree centigrade its crystal structure changes to a FCC crystalline structure, in this form it is called the gamma iron or maybe the austenite, and what is alpha iron or maybe alpha Fe? Below 910 degree centigrade iron again adopts the BCC structure characteristics of alpha iron also called the ferrite, the substance assumes a paramagnetic in property, carbon dissolves poorly in alpha iron, no more than 0.021% by mass at 723 degree centigrade, so you see one single material had different temperature just changing the temperature or maybe the pressure, it is behaving like different materials.

Epsilon iron / Hexaferrum (ϵ -Fe):

- ✓ At pressures above approximately 130 kbar and temperatures of a few hundred kelvin or less, α -iron changes into a hcp structure, which is known as ϵ -iron or hexaferrum.
- ✓ Higher-temperature γ -phase also changes into ϵ -iron, but does so at a higher pressure.

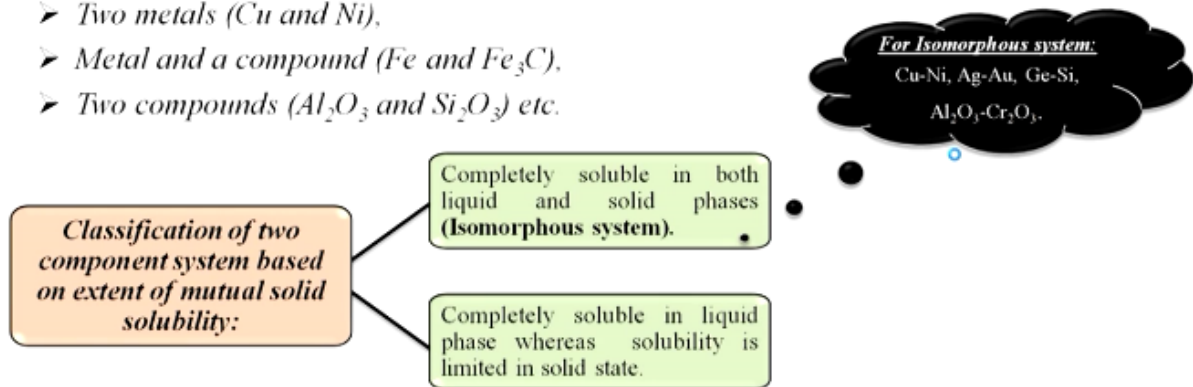


What is epsilon iron or maybe the hexaferrum? At pressure above approximately 130 kilo bar at high pressure, high pressure only it can exist, and temperatures of a few 100 kelvin or less, because temperature is also not too high. Alpha iron changes into a HCP structure which is known as epsilon iron or maybe the hexaferrum. High temperature, gamma phase also changes into epsilon iron but does so at a higher pressure, so this is the phase diagram of the pure iron and this is the cooling curve of the pure iron at 1539 degree centigrade it is liquid in stage, when we are coming it down the temperature around 1394 degree centigrade it is delta iron having the BCC structure, again when we are reducing the temperature it is forming the gamma iron FCC structure and it is non-magnetic in nature.

And then when we are reducing the temperature from 910 degree centigrade to 723 degree centigrade it is showing the alpha iron BCC structure, and then if it is below 723 degree centigrade it is alpha iron BCC but it is magnetic in nature, so you see only a single material at higher temperature it was non-magnetic when we are reducing the temperature it is became the magnetic one also the crystal structure from BCC to FCC then again BCC it is changing with time and temperature.

2. Binary Phase Diagram:

- Two component system, used in alloy designing.
- Pressure is constant, and independently variable parameters are temperature and composition.
- Two components can be:
 - Two metals (Cu and Ni),
 - Metal and a compound (Fe and Fe_3C),
 - Two compounds (Al_2O_3 and Si_2O_3) etc.



Then what is binary phase diagram? There are two component system used in alloy designing, pressure is constant and independently variable parameters are temperature and compositions, two components can be two metals either maybe copper and nickel it's just for an example, metal and a compound like iron and Fe_3C or maybe two compounds Al_2O_3 and Si_2O_3 , so these all are the examples, so classification of two component system based on extent of mutual solid solubility, one is completely soluble in both liquid and the solid phases that is known as the isomorphous systems, so for isomorphous systems example like copper nickel then silver and gold, then germanium silicon Al_2O_3 and the Cr_2O_3 , and another one is completely soluble in liquid phase whereas the solubility is limited in solid state.

- Extent of solid solubility in two element system can be predicted based on Hume-Ruthery conditions.
- If system obeys these conditions, then complete solid solubility can be expected.

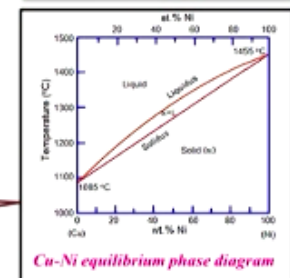
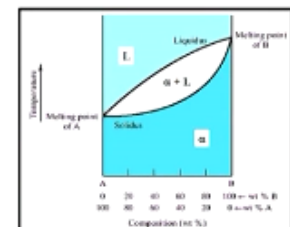
Hume-Ruthery conditions:

- ✓ Crystal structure of each element of solid solution must be the same.
- ✓ Size of atoms of each two elements must not differ by more than 15%.
- ✓ Elements should not form compounds with each other i.e. there should be no appreciable difference in the electro-negativities of the two elements.
- ✓ Elements should have the same valence.

So extent of solid solubility in two element system can be predicted based on Hume-Ruthery conditions, so that is one conditions it should satisfy that conditions if system obeys these conditions then complete solid solubility can be expected, what is Hume-Ruthery conditions? Generally the crystal structure of each element of solid solutions must be the same, size of atoms of each two elements must not differ by more than 15%, element should not form compounds with each other, there should be no appreciable difference in the electro-negativities of the two elements, and last element should have the same valence.

Binary Isomorphous System:

- **Isomorphous system** - complete solid solubility of the two components (both in liquid and solid phases).
- Three phase region can be identified on the phase diagram:
 - ✓ Liquid (L),
 - ✓ Solid + liquid ($\alpha + L$),
 - ✓ Solid (α).
- **Liquidus** line separates liquid from liquid + solid.
 - At temperature just below this line, crystals of (α) solid solution start forming.
- **Solidus** line separates solid from liquid + solid.
 - Only (α) solid solution exists at any temperature below the solidus line.



Example of binary system:

Cu-Ni, which exhibits complete solubility in liquid and solid state.

Now we are going to discuss about the binary isomorphous system, so isomorphous systems complete solid solubility of the two components both in liquid and the solid phases, three phases region can be identified on the phase diagram, it's called the liquid, solid + liquid that is alpha + L and the solid that is alpha, so in this particular case there are two materials like A and B, the melting temperature of A is here, and the melting temperature of B is here that is higher than the A, so in this particular case the weight percent of B is increasing, so in this case B point is 100% of B, and A point is 100% of A. So now after mixing if we heat the materials so that is known as the liquidus and this is known as the solidus, so at the time of heating this curve will generate and at the time of cooling this curve will generate, so this is the liquidus phase L, this is the solidus phase alpha and this is the combinations of the solid + liquid which is nothing but the alpha + L, liquidus line separates the liquid from liquid + solid at temperature just below this line crystals of alpha solid solutions start forming, and solidus line separates the solid from liquid + solid, only alpha solid solutions exists at any temperature below the solidus line.

Example of binary systems, like copper-nickel which exhibits the complete solubility in liquid and the solid state, say suppose copper the melting temperature is 1085 degree centigrade, for nickel it is 1455 degree centigrade, when we are heating the materials it is following this part and at the cooling it is following this part, and at the cooling it is following this part, so this is the liquid of this both the materials, this is the solid solutions of that particular materials and this is the zone where the solid + liquid phase are exists.

Interpretation of Phase Diagrams:

From binary phase diagrams we can determine:

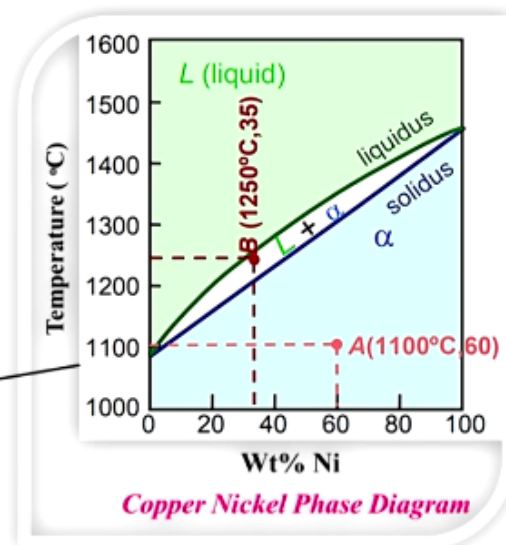
- (1) Phases that are present.
- (2) The composition of phases.
- (3) The percentage and fraction of the phases.

❖ If we know T and C_0 , then we can identify which phases are present.

❖ Examples:

$A(1100\text{ }^\circ\text{C}, 60\text{ wt\% Ni})$: 1 phase: α

$B(1250\text{ }^\circ\text{C}, 35\text{ wt\% Ni})$: 2 phases: $L + \alpha$

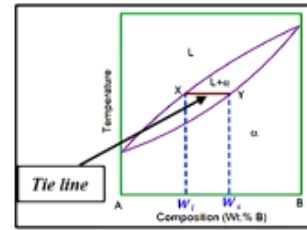


Now what are the interpretations we can do from the phase diagram itself, from binary phase diagrams we can determine phases that are present, the composition of phases and the percentage and fraction of the phases, how? If we know the temperature and C_0 then we can identify which phases are present over there, so here we are giving the examples, say suppose from the copper-nickel phase diagram if we remember the part last one, so suppose we are going to calculate this point or maybe the this points, so this point means it is around 1100 degree centigrade, and what is the percentage of the nickel? That is 60% of the nickel, so one phase that is alpha, and B this point, so what is that? This is the 1250 degree centigrade over here, and then it is 35 weight

percent of the nickel itself, so here two phases are present, because it is coming into the L + alpha region, so two phases are present that is L + alpha.

Tie line: (For determination of phase composition)

- Composition of individual phases in two phase region, can be found using a horizontal line (XY), called tie line.
- It is drawn and its intercepts on liquidus and solidus lines, W_l and W_s , are taken as composition of liquid and solid.



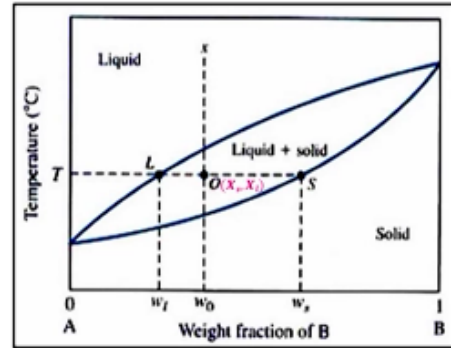
Lever Rule: (For determination of phase amounts)

- Gives the weight percent of phase in any two phase regions.

$$\text{wt. fraction of solid phase} = X_s = \frac{W_o - W_l}{W_s - W_l}$$

$$\text{wt. fraction of liquid phase} = X_l = \frac{W_s - W_o}{W_s - W_l}$$

where: W_o is weight percentage of alloy.
 W_s is weight percentage within the solid phase.
 W_l is weight percentage in the liquid phase.



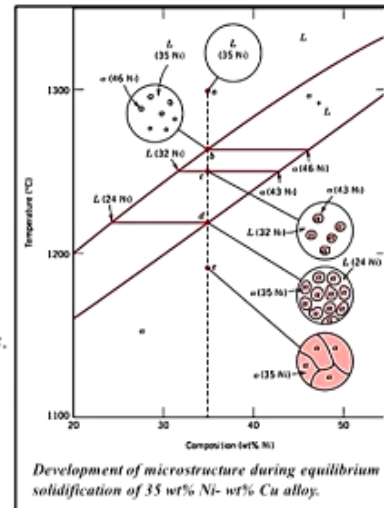
Now what is tie line? Say for determinations of phase compositions, so now compositions of the individual phases in two phase region can be found using a horizontal line called a tie line, so suppose I am making a tie line in between the solidus line and the liquidus line, so it is drawn and it intercepts on liquidus and solidus lines like W_l and W_s are taken as compositions of the liquid and solid, so through this simple we can get the compositions of W_l and we can get the compositions of the W_s itself, and this XY line is known as the tie line.

Now come to the lever rule, for determinations of the phase amounts, how we can calculate that, how much percentage of the phases are present inside the systems, gives the weight percent of phases in any two phase regions, weight fraction of solid phase that is X_s is equal to, because say suppose I made the tie line in between the L and S, so this point and this point and I am putting the tie line over here, now I want to know the compositions of point O, so L is known as the W_l it is coming from here, and it is W_s it is also coming from here, now I want to know the point O suppose it is X_s and X_l , so what is the weight fraction of solid phase, $X_s = W_o - W_l / W_s - W_l$, and what is the X_l ? That is $X_l = W_s - W_o / W_s - W_l$, so where W_o is the weight percentage of alloy, W_s is weight percentage within the solid phase, W_l is the weight percentage into the liquid phase itself, so by this way we can easily calculate the weight fraction of solid phase or maybe the liquid phase.

Development of Microstructure in Isomorphous Alloys: Cu-Ni alloy

Equilibrium cooling:

- ❖ Very slow cooling to allow phase equilibrium to be maintained during the cooling process.
- ❖ Very slow cooling give rise to cored structure as composition of melt continuously changes.
 - ❑ ($T > 1260\text{ }^{\circ}\text{C}$): start as homogeneous liquid solution.
 - ❑ ($T \sim 1260\text{ }^{\circ}\text{C}$): liquidus line reached, α phase begins to nucleate, $C_{\alpha} = 46\text{ wt\% Ni}$; $C_l = 35\text{ wt\% Ni}$.
 - ❑ ($T = 1250\text{ }^{\circ}\text{C}$): calculate composition and mass fraction of each phase.
 - ❑ ($T \sim 1220\text{ }^{\circ}\text{C}$): solidus line reached, nearly complete solidification. $C_{\alpha} = 23\text{ wt\% Ni}$; $C_l = 24\text{ wt\% Ni}$.
 - ❑ ($T < 1220\text{ }^{\circ}\text{C}$): homogeneous solid solution with 35 wt% Ni.



Now development of microstructure in isomorphous alloys, say suppose I am giving the example of copper-nickel alloy, once again so in the equilibrium cooling very slow cooling two alloy phase equilibrium to be maintained during the cooling process, very slow cooling give rise to cored structure as compositions of the melt continuously change, so in this particular case so this is the compositions, weight percent of the nickel and this is the temperature so in this particular case now we are going to know the characteristics of this line at different point, say suppose when we are talking about the 1260 degree, more than 1260 centigrade that means point A, so it starts as homogeneous liquid solutions over there, so it has been mention that L liquid with 35% of nickel.

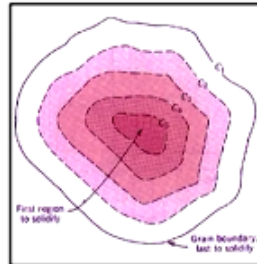
Now when T is more or less 1260 degree centigrade, so in this particular case liquidus line reached alpha phase begins to nucleate, so C alpha 46 weight percent of nickel and Cl 35 weight percent of the nickel itself, so this is the point, so it is talking about the B point, so this is A point, this is B point, and then T = 1250 degree centigrade so that is the point C, so calculate compositions and mass fractions of each phases, when we are talking about the D point, so D means T more or less 1220 degree centigrade, solidus line reached nearly complete solidifications, so C alpha = 23 weight percent of the nickel, and Cl = 24 weight percent of the nickel itself, and T that means the point E, so E is equal to, less than = 1220 degree centigrade, homogeneous solid solution with 35 weight percent of nickel it is taking place.

Non equilibrium cooling:

❖ Rapid cooling delays solidification but also leads to cored structures.

❖ Cored “Microstructures”:

- ✓ Interior is rich in high melting component.
- ✓ Exterior is rich in low melting component.

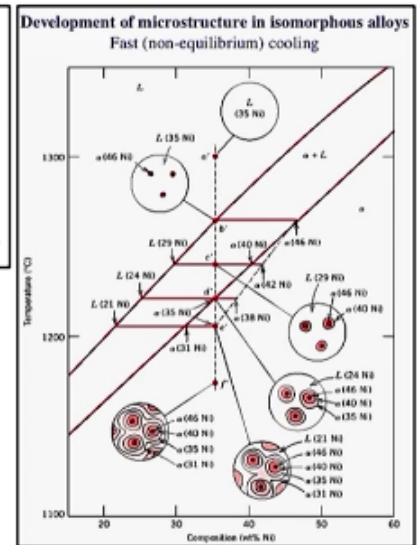


❖ Development of microstructure during the non-equilibrium solidification of a 35 wt% Ni-65 wt% Cu alloy outcome:

➤ Segregation:

- ✓ Non-uniform distribution of elements within grains.

➤ Weaker grain boundary if alloy is reheated.



Till now we are discussing about the equilibrium cooling, now we are going to discuss about the non-equilibrium cooling, so generally the rapid cooling delays solidification but also leads to cored structures, cored microstructures means interior is rich in high melting component here in this particular case, exterior is rich in low melting component, so that temperature is going from low to high.

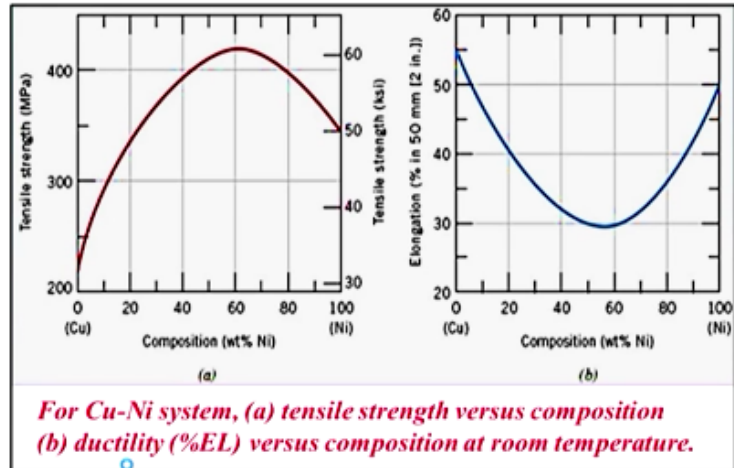
So development of microstructure during the non-equilibrium solidification of a 35 weight percent of nickel and 65 weight percent of copper alloy outcome, so in this particular case you can see that inside is alpha 46% nickel, then so initial 46% nickel then top of that 40% nickel, then top of that 35% nickel and the outside is 31% nickel, so this is for the non-equilibrium of cooling, so it's having different temperature zone, so we can see the segregations that means non-uniform distribution of elements within grains, and weaker grain boundary if alloy is reheated several times.

Mechanical Properties of Isomorphous Alloys:

- For copper nickel system, effect of solid solution strengthening on:

- Tensile strength
- Ductility (%EL).

- Increase in strength and hardness by addition of other component and curve passes maximum.
- Ductility decreases with addition of second component and curve exhibits a minimum.
- A solid solution exists over all composition for this system.



What are the mechanical properties of the isomorphous alloys? For copper-nickel system, the effect of solid solution strengthening on tensile strength and ductility, that means percentage elongations. Increase in strength and hardness by addition of other component and the curve passes the maximum, so in this particular case the tensile strength is increasing up to 60 weight percent of the nickel, and then after that it is decreasing for 100% nickel. Ductility decreases with addition of second component and the curve exhibits a minimum, a solid solution exists over all composition for this system, so in this case also the elongation had break at 0% nickel was the maximum then after that it is drastically reducing at 60% and then slowly slowly again it is increasing at 100% nickel.

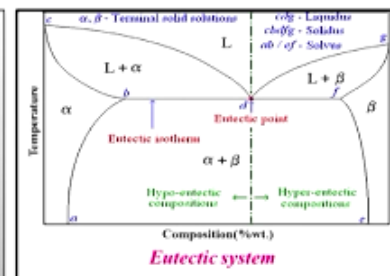
Binary Eutectic Systems:

Eutectic systems:

- Eutectic Reaction - Generate two solids from the liquid at a given temperature and composition.
$$L = \alpha + \beta$$
- Eutectic system always has a specific alloy, as **eutectic composition**.
- It freezes at lower temperature than other compositions.
- At '**eutectic temperature**', two solids form simultaneously from a single liquid phase.
- Eutectic temperature and composition determine a point on phase diagram as '**eutectic point**'.

General rules:

- The melting point of eutectic alloy is lower than that of components (eutectic = easy to melt in Greek).
- At most two phases can be in equilibrium within a phase field.
- Three phases (L, α , β) may be in equilibrium only at a few points along the eutectic isotherm.
- Single-phase regions are separated by 2-phase regions.



Now we are going to discuss about the binary eutectic systems, so for eutectic systems generally eutectic reactions generates 2 solids from the liquid at a given temperature and compositions, so from liquid generally 2 solid formation is taking place that is $L = \alpha + \beta$, eutectic system always has a specific alloy as eutectic compositions, it freezes at lower temperature than other compositions, at eutectic temperature 2 solid form simultaneously from a single liquid phase, eutectic temperature and composition determine a point on phase diagram as eutectic point, so this is known as the eutectic points, so in this particular case from liquid generally 2 solid formations $\alpha + \beta$ is taking place directly, and this is known as the eutectic isotherm so that is the constant temperature range over there.

Three Phase Reactions:

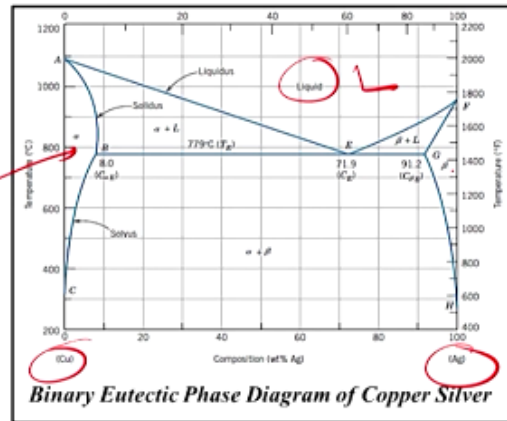
Reaction	Symbolic equation	Schematic Presentation
Eutectic	$L \rightarrow \alpha + \beta$	
Peritectic	$\alpha + L \rightarrow \beta$	
Monotectic	$L_1 \rightarrow L_2 + \alpha$	
Eutectoid	$\gamma \rightarrow \alpha + \beta$	
Peritectoid	$\alpha + \beta \rightarrow \gamma$	

So there are phases like alpha, then beta, the liquid phase, then alpha + beta and L + alpha and L + beta, so general rules the melting point of eutectic alloy is lower than that of the components that means eutectic = easy to melt in Greek, that is the meaning of the eutectic. At most two phases can be in equilibrium within a phase field, three phases like L, alpha, and beta maybe in equilibrium only at a few points along the eutectic isotherm. Single phase regions are separated by two phase regions, if it is 3 phase reactions, so in that case eutectic $L = \alpha + \beta$, so in the last slides if you remember $L = \alpha + \beta$, so that is the short formations, here is the alpha, here is the beta, and L it is changing into the alpha + beta. If it is peritectic then alpha + L it is coming to the beta, if it is monotectic then $L_1 = L_2 + \alpha$, for eutectoid that is gamma goes to alpha + beta, so gamma goes to alpha + beta, if it is peritectoid then alpha + beta goes to gamma, so alpha + beta it is going to gamma.

Binary Eutectic Phase Diagram:

- Comprises of three single phase regions:
 - ✓ α - solid solution of Ag in Cu matrix,
 - ✓ β - solid solution of Cu in Ag matrix,
 - ✓ L - liquid.
- Three two-phase regions as: ($\alpha + L$, $\beta + L$, $\alpha + \beta$).
- Eutectic reaction for Cu-Ag:** $L(C_E) \longrightarrow \alpha(C_{\alpha E}) + \beta(C_{\beta E})$
 $L(71.9 \text{ wt\% Ag}) \xrightleftharpoons[\text{heating}]{\text{cooling}} \alpha(8.0 \text{ wt\% Ag}) + \beta(91.2 \text{ wt\% Ag})$
- Solvus line** separates one solid solution from a mixture of solid solutions.
- Solvus line shows limit of solubility.
- Eutectic or invariant point** - Liquid and two solid phases coexist in equilibrium at eutectic composition C_E and the eutectic temperature T_E .
- Eutectic isotherm** - the horizontal solidus line at T_E .

Based on eutectic reactions, $L \rightarrow \alpha + \beta$ which occur at a temperature below melting temperature of either component.

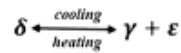


Now we are discussing about the binary eutectic phase diagram, so its comprised of three single phase regions, say alpha solid solutions of silver in copper matrix, now we are going to give the example of the copper and silver, so beta solid solution of copper in the Ag matrix and the L is the liquid, so this is the L, this is the alpha which is nothing but the solid solution of Ag in copper matrix, it is the solid solution of copper in the Ag matrix, so it is the composition weight percent of the Ag, so 3, 2 phase regions like alpha + L, beta + L and the alpha + beta are present over here, eutectic reaction for copper Ag like L to alpha + beta, so generally 71.9 weight percent of Ag, if we do the cooling or heating means both way that can be possible, so alpha = 8 weight percent of the Ag, so in this particular case, in this particular point and beta is 91.2 weight percent of the Ag are present, so solvus line separates one solid solutions from a mixture of solid solutions, so this is known as the solvus line, so solvus line shows the limit of solubility, eutectic or invariant point liquid and two solid phases coexist in equilibrium at eutectic compositions C_E and the eutectic temperature T_E , so this is the C_E is taking place in this particular point and this is the T_E that is 779 degree centigrade. Eutectic isotherm the horizontal solidus line at T_E , so that is known as the, this one, so this is known as the eutectic isotherm.

Eutectoid and Peritectic Reactions: (Copper-Zinc system)

Eutectoid reaction:

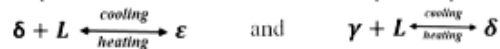
- One solid phase δ transforms into two other solid phases (γ and ϵ) upon cooling as:



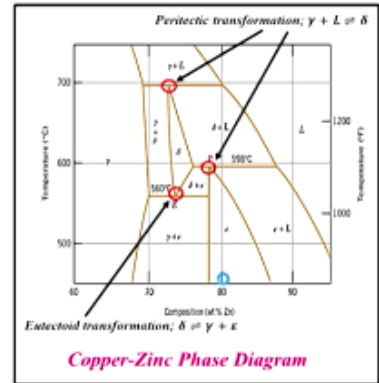
- Reverse reaction occurs upon heating
- It is called eutectoid reaction & invariant point E is eutectoid.
- Horizontal tie line at 560 °C is eutectoid isotherm.
- Eutectoid reaction is also found in Fe-C diagram.

Peritectic reaction:

- Liquid and one solid phase transform into second solid phase upon heating as:



- Peritectic exists the Cu-Zn system at point P (598 °C & 78.6% Zn-21.4 wt% Cu).
- One of the latter peritectics exists at about 97 wt% Zn at 435 °C where in η phase when heated transforms to ϵ and liquid phases.
- Three other peritectics found in Cu-Zn systems, reactions which involve β , δ , γ intermediate solid solutions at low temperature.



Eutectoid reaction:
(560 °C, 74 wt% Zn)
Peritectic reaction:
(598 °C, 78.6 wt% Zn) and
(698 °C, 74 wt% Zn)

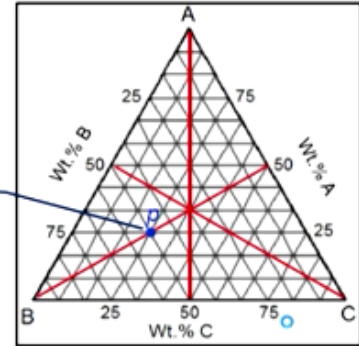
Now we are going to discuss about the eutectoid and peritectic reactions for the copper and zinc systems, so this is the copper and zinc, both are having different melting temperature, so in the eutectoid reactions one solid phase delta transform into two other solid phases that is gamma and epsilon upon cooling as, so delta cooling or maybe the heating it will form the gamma + epsilon, so reverse reactions occurs upon heating, it is called the eutectoid reactions and invariant point E is eutectoid, so in this particular case this is the eutectoid point, so in this case what happened? This delta is changing into the gamma + epsilon, horizontal tie line at 560 centigrade is the eutectoid isotherm so this is the eutectoid isotherm, eutectoid reactions is also found in iron, carbon diagrams, and when we are talking about the peritectic reactions liquid and one solid phase transforms into second solid phase upon heating as delta + L cooling or heating it is changing into the epsilon, so in this case what happened? So if you see this particular point so what is happened? Delta + L region is changing to the epsilon so this is the case, so from here to here or maybe gamma + L is changing into this delta.

Peritectic exist the copper-zinc system at point P that is 598 degree centigrade and 78.6% zinc, 21.4 weight % of the copper. One of the latter peritectics exists at about 97 weight percent zinc at 435 degree centigrade wherein eta phase when heated transforms to epsilon and liquid phases. Three other peritectic found in copper-zinc systems reactions which involves beta, delta, gamma intermediate solid solutions at low temperature, so in this case eutectoid reactions at 560 degree centigrade with 74 weight percent of zinc, peritectic reactions at around 598 degree centigrade with having 78.6 weight percent zinc and 698 degree centigrade, so this is the zone, it is 698 degree centigrade, so 74 weight percent of the zinc.

3. Ternary Phase Diagram:

- Three component system and constructed using a equilateral triangle as base.
- Ternary compositions are within the triangle.
- Composition lines on the triangle is constructed from projections of surfaces.
- Pure components at each end of triangle.
- Binary alloy composition represented on edges.

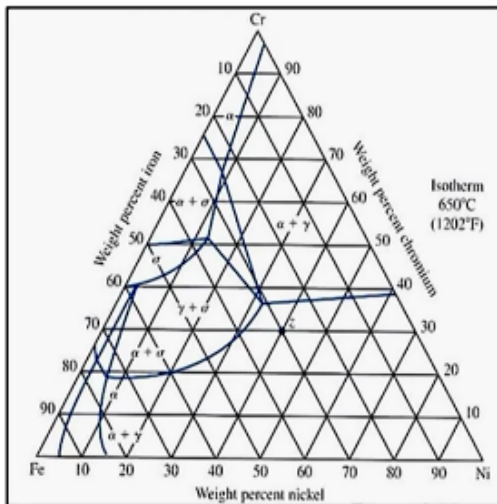
- Temperature varies along the height of prism and composition triangle is an isothermal section.
- Composition of any point in the triangle is determined by drawing perpendiculars from corners to opposite sides and measuring the distance of point along the perpendicular.
- **Example:**
 - ✓ Point *p*, lies on isocomposition line 25% A along the perpendicular A-50.
 - ✓ Percentage of A in alloy is 25%, B is 50% and C is 25%.



Now we are going to discuss about the last one that is called the ternary phase diagram, so this is basically for the three component system, so and constructed using a equilateral triangle as a base, so ternary compositions are within the triangle, compositions lines on the triangle is constructed from projections of surfaces, pure components at each end of triangle, binary alloy compositions represented on edges, so in this particular case you can see that is pure A, that is pure B and the pure C, and this is the equilateral triangle.

Okay, temperature varies along with this A line, this line, temperature is varies, height of prism and composition triangle is an isothermal section, composition of any point in the triangle is determined by drawing the perpendiculars from corners to the opposite and measuring the distance of point along the perpendicular, so from each point we are drawing the perpendicular line from each corner and then we are calculating, say suppose we are going to calculate further this point, so at point P lies on isocomposition line of 25% of A, so in this particular case why it is 25% of A? Because this is the case, so here A is 25% perpendicular to A-50, percentage of A in alloy is 25%, now B come to this, so how we are going to calculate the percentage of B? So that is B, and what is C? C is also the 25%, so we are calculating getting A percentage is 25%, B

Iron-Chromium-Nickel Phase Diagram:



- Isothermal reaction takes place at 650 °C for this system.
- Composition of any metal at any point on phase diagram can be found by drawing perpendicular from pure metal corner to opposite side and calculating the %length of line at that point.

is 50% and C is the 25%, best example is that iron, chromium, nickel phase diagram, so in the isothermal reaction takes place at 650 degree centigrade for the systems, so here the three pure components iron, nickel, and the chromium then varying percentage here is the weight percent of the nickel is varying, inside is the chromium and this side is the iron, so from here easily we can calculate the different phases over there.

Compositions of any metal at any point on phase diagram can be found by drawing perpendicular from pure metal corner to opposite side and calculating the percentage length of line at that point, and the temperature is increasing into this directions.

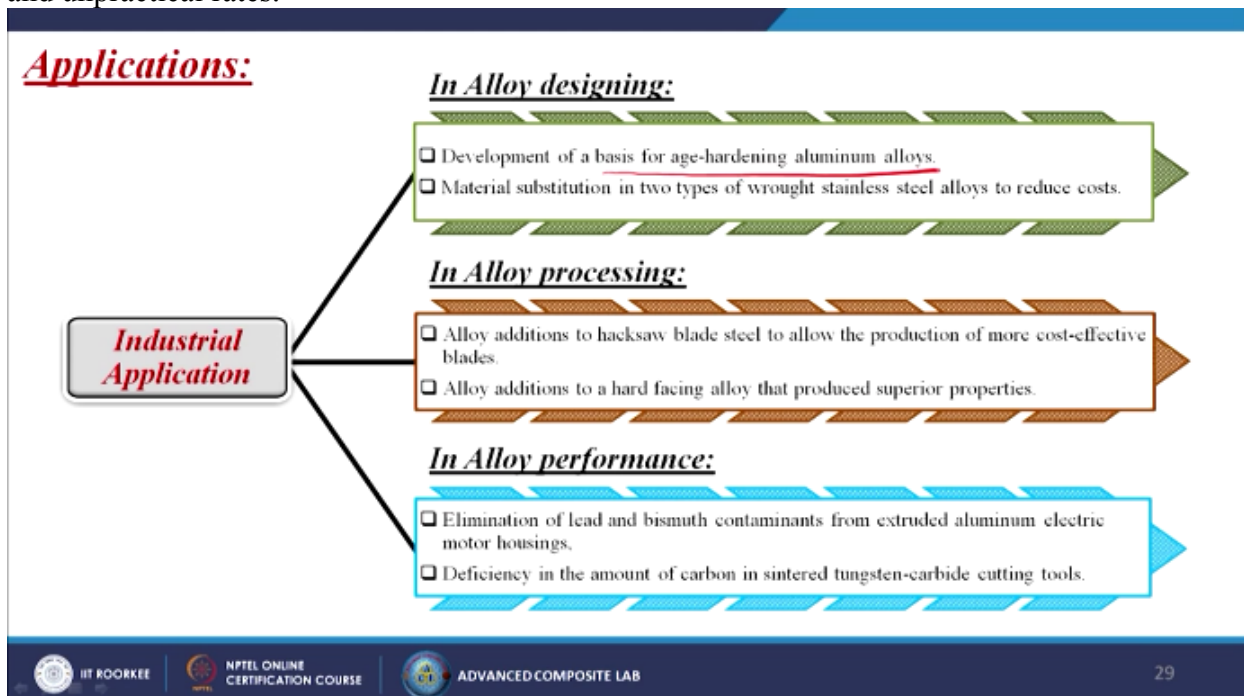
Uses of Phase Diagram:

- Used to predict temperature at which freezing or melting begins or ends for any specific alloy composition in an alloy system.
- To predict the safe temperature for hot working or heat treatments.
- To determine the number of phases, type of phases, and composition of phases present in any given alloy at a specific temperature.
- To calculate the relative amounts of the phases present in a two-phase alloy.
- To describe the freezing or melting of an alloy.
- To predict the microstructure of an alloy at a given temperature.
- To choose the alloy composition to develop the best properties.

Limitations:

- ❖ Unable to indicate the time period required for the attainment of equilibrium.
- ❖ Equilibrium conditions are maintained only if heating or cooling is carried out at extremely slow and unpractical rates.

Now we are going to discuss about the uses of a phase diagram, used to predict temperature at which freezing or melting begins or ends for any specific alloy compositions in an alloy system, to predict the safe temperature for hot working or maybe the heat treatments easily before going to start the experiment we can easily understand that what temperature we can achieve this kind of properties or maybe the material and so different properties or maybe thermal properties or maybe the electrical properties, to determine the number of phases, types of phases and composition of phases present in any given alloy at a specific temperature, to calculate the relative amount of phases present in two phase alloy, to describe the freezing or melting of an alloy, to predict the microstructure of an alloy at a given temperature, to choose the alloy compositions to develop the best properties, yes, but of course there is certain limitations, what are those? Unable to indicate the time period required for the attainment of equilibrium, and equilibrium conditions are maintained only if heating or cooling is carried out at extremely slow and unpractical rates.



Now what are the applications? Generally there are several types of industrial applications in alloy designing, development of a basis for age hardening aluminum alloys, material substitution in two types of wrought stainless steel alloys to reduce costs. In alloy processing, alloy additions of hacksaw blade steel to allow the production of more cost effective blades, alloy additions to a hard facing alloy that produced the superior properties.

In alloy performance, estimation of lead and bismuth contaminants from extruded aluminum electric motor housings, deficiency in the amount of carbon in sintered tungsten carbide cutting tools, so there are several types of applications.

Summary:

- Phase diagrams are useful tools to determine the number of types of phases present, composition, weight fraction of each phase at a given temperature and composition of system.
- Binary eutectics and binary eutectoids allow for a range of microstructures with different properties.
- The microstructure of an alloy depends upon:
 - ✓ Its composition
 - ✓ Whether or not cooling rate allows for maintenance of equilibrium.
- Important phase diagram, phase transformation include:
 - ✓ Eutectic, eutectoid and peritectic.



Now we have come to the last slide of this particular lecture, so we have to summarize the whole lecture, so in this particular lecture we have discussed about the phase diagram, which is a very useful tools to determine the number of types of the phases present, compositions with fraction of each phases at a given temperature and compositions of the system itself, binary eutectics and binary eutectoids allow for a range of microstructures with different properties, the microstructure of an alloy depends upon its compositions, whether or not cooling rate allows for maintenance of the equilibrium, important phase diagrams, phase transformations include eutectic, eutectoid and peritectic, we have discussed in this particular lecture. Thank you.

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