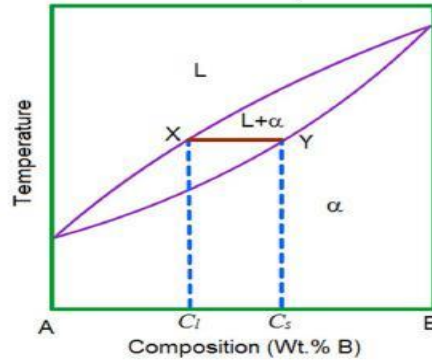


Module-2

SOLIDIFICATION



OBJECTIVES:

- To learn and understand the concepts of solidification
- Solid Solution and types
- Phase and phase equilibrium
- Nucleation and types of nucleation
- Crystal growth
- Phase diagrams

OUT COMES

The student should be able to understand the mechanism of solidification

Introduction

The solidification of metals and alloys is an important industrial process since most metals are melted and then cast in to a semi finished or finished shape. When molten metals are cast, solidification starts at the walls of the mould as it is being cooled. The solidification of alloy takes place not at a specific temperature but over a range of temperatures. While the alloy is in this range, it has a pasty form that consists of solid, tree like structures called dendrites and liquid metals. The size and shape of the dendrites depends on the cooling rate. The study of dendrites is important because they influence compositional variations, porosity and segregation and therefore properties.

Component – is either pure metal and/or compounds of which an alloy is composed. The components of a system may be elements, ions or compounds. They refer to the independent chemical species that comprise the system.

System – it can either refer to a specific body of material under consideration or it may relate to the series of possible alloys consisting of the same components but without regard to alloy composition.

Solid solution – it consists of atoms of at least two different types where solute atoms occupy either substitutional or interstitial positions in the solvent lattice and the crystal structure of the solvent is maintained.

Solubility limit – for almost all alloy systems, at a specific temperature, a maximum of solute atoms can dissolve in solvent phase to form a solid solution. The limit is known as solubility limit. In general, solubility limit changes with temperature. If solute available is more than the solubility limit that may lead to formation of different phase, either a solid solution or compound.

Phase equilibrium – it refers to the set of conditions where more than one phase may exist. It can be reflected by constancy with time in the phase characteristics of a system. In most metallurgical and materials systems, phase equilibrium involves just solid phases. However the state of equilibrium is never completely achieved because of very slow rate of approach of equilibrium in solid systems. This leads to non-equilibrium or meta-stable state, which may persist indefinitely and of course, has more practical significance than equilibrium phases. An equilibrium state of solid system can be reflected in terms of characteristics of the microstructure, phases present and their compositions, relative phase amounts and their spatial arrangement or distribution.

Kinetics of nucleation and growth

Structural changes in metallic systems usually take place by nucleation and growth whether it is just a phase change within one of the three states, or a simple structural rearrangement within a single phase, or a phase transformation. An equilibrium phase diagram presents the phases and phase changes expected under equilibrium conditions, but it provides no information about the rates of transformation. Although changes in pressure, composition, or temperature can cause phase transformations, it is temperature changes that are more important. From a micro structural standpoint, the first process to accompany a phase transformation is nucleation (i.e. the formation of very small particles or nuclei of the product phase from the parent phase) of the new phase particles which are capable of growing. The second stage is growth, in which the nucleated particles increase their size. The transformation reaches completion if growth of these new phase particles is allowed to proceed until the equilibrium fraction is attained.

Both nucleation and growth require that the accompanying free energy change be negative. Consequently, the super-heating or super-cooling that is necessary for a phase change is to be expected. That is a transformation cannot take place precisely at the equilibrium transformation

temperature because at that temperature free energies of phases are equal. In addition to temperature, two other factors that affect transformation rate – first, diffusion controlled rearrangement of atoms because of compositional and/or crystal structural differences; second, difficulty encountered in nucleating small particles via change in surface energy associated with the interface. Diffusion limits both the nucleation and growth rates in many cases.

With the nucleation of new particle, new interface is created between the particle and liquid. This interface will have positive energy that must be supplied during the transformation process. A tiny particle has a large surface area to volume ratio and therefore be unstable. Thus energy of the surface can effectively prevent the initial formation of a tiny particle. A particle said to have nucleated when it becomes stable and will not disappear due to thermal fluctuations. After a particle attained a critical size, it can grow further with a continuous decrease in energy. The surface energy is no longer a dominant factor in the growth process.

Nucleation

Homogeneous nucleation, the probability of nucleation occurring at any given site is identical to that at any other site within the volume of the parent phase. When a pure liquid metal is cooled below its equilibrium freezing temperature to a sufficient degree, numerous homogeneous nuclei are created by slow-moving atoms bonding together. Homogeneous nucleation usually requires a considerable amount of *under cooling* (cooling a material below the equilibrium temperature for a given transformation without the transformation occurring). Under cooling enhances the formation of nuclei that eventually grow. If f is the free energy change accompanying the formation of a spherical new phase particle,

$$\Delta f = \frac{4}{3} \pi r^3 \Delta g + 4 \pi r^2 \gamma$$

where r is the radius of the particle, g is the Gibbs free energy change per unit volume and γ is the surface energy of the interface.

Heterogeneous nucleation, the probability of nucleation occurring at certain preferred sites is much greater than that at other sites. During solidification, inclusions of foreign particles (*inoculants*), walls of container holding the liquid provide preferred sites. Irregularities in crystal structure such as point defects and dislocations possess strain energy. In solid-solid transformation, foreign inclusions, grain boundaries, interfaces, stacking faults and dislocations can act as preferred sites for nucleation as the strain energy associated with them will be reduced. The released strain energy can reduce the energy requirements for free energy change, f . Therefore, nucleation proceeds with a smaller critical radius. A majority of reactions are initiated by some type of heterogeneous nucleation which is common among the two types.

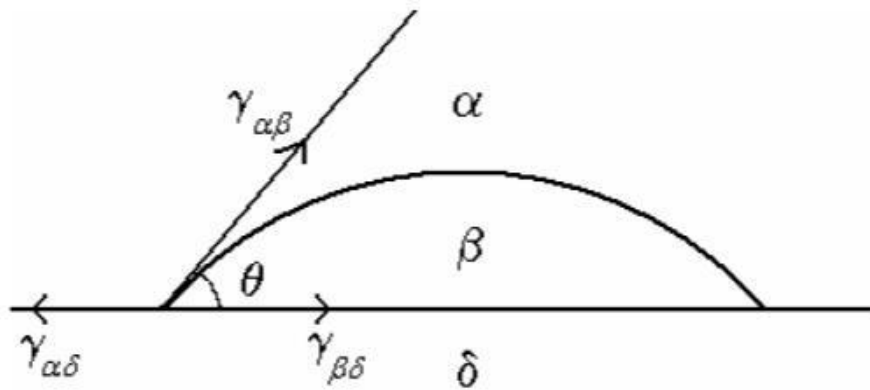


Figure-: Schematic of heterogeneous nucleation.

Crystal Growth

Many transformations occur as a result of continuous formation of critical nuclei in the parent phase and the subsequent growth of the particles. Growth is the increase in size of the particle after it has nucleated i.e. growth kinetics become important once an embryo has exceeded the critical size and become a stable nucleus. Growth may proceed in two

radically different manners. In one type of growth, individual atoms move independently from the parent to the product phase, thus it is diffusion controlled and is thermally activated. In the other type of growth that occurs in solid-solid transformations many atoms move cooperatively without thermal assistance. Growth that is diffusion controlled is more common the other. Growth usually occurs by the thermally activated jump of atoms from the parent phase to the product phase. The unit step in the growth process thus consists of an atom leaving the parent phase and jumping across the interface to join the product phase. At the equilibrium temperature, both phases have the same free energy, hence the frequency of jumps from parent phase to product phase will be equal to that from product phase to parent phase i.e. the net growth rate is zero. At lower temperatures, product phase is expected to have lower free energy, and thus a net flow of atoms from parent phase to product phase. This net flux of atoms results in interface motion i.e. growth rate is taken as the rate of increase of a linear dimension of a growing particle. As a function of temperature, the growth rate first increases with increasing degree of super cooling, but eventually slows-down as thermal energy decreases. This is same as for nucleation; however the maximum in the growth rate usually occurs at a higher temperature than the maximum in the nucleation rate.

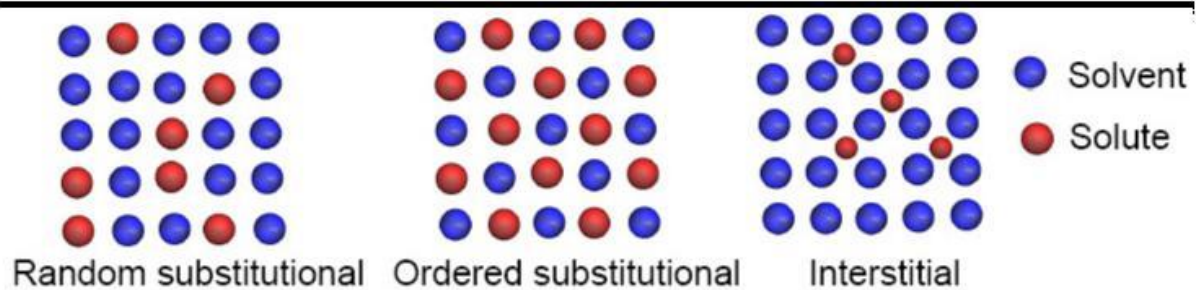
Solid Solution

When two metals are mixed together they form an alloy if one metal is soluble in the other one in solid state. Therefore, an alloy is a solid solution of two or more metals.

Primarily there are two types of solid solutions -

Substitutional – Solute atoms occupy the regular lattice sites of the parent metal (solvent). Substitutional solid solutions can be random (Cu-Ni) or ordered (Cu-Au).

Interstitial – Solute atoms occupy the interstitial positions (Steel – C solute atoms in Fe) .



Hume-Rothery Rules

Formation of substitutional solid solutions between two metals is governed by a set of rules known as **Hume-Rothery rules**

- Size difference between the atoms of solute and the parent metal should be less than 15%.
- The electronegativity difference between the metals should be small (minimum chemical affinity to each other).
- The solubility of a metal with higher valence in a solvent of lower valence is more compared to the reverse situation e.g. Zn is much more soluble in Cu than Cu in Zn.
- For complete solubility over the entire range of compositions the crystal structures of the solute and the solvent must be the same.

Phase

A phase can be defined as a physically distinct and chemically homogeneous portion of a system that has a particular chemical composition and structure.

Water in liquid or vapor state is single phase. Ice floating on water is an example two phase system.

Gibbs Phase rule

The number of degrees of freedom, F (no. of independently variable factors), number of components, C , and number of phases in equilibrium, P , are related by Gibbs phase rule as

$$F = C - P + 2$$

Number of external factors = 2 (pressure and temperature).

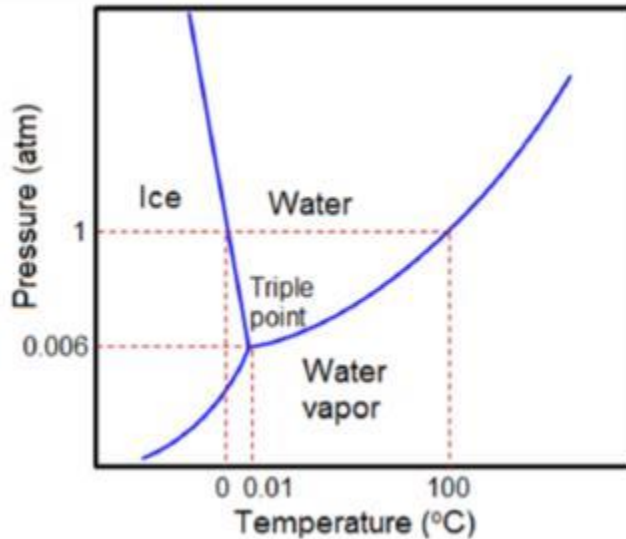
For metallurgical system pressure has no appreciable effect on phase equilibrium and hence, $F = C - P + 1$

Phase Diagrams

One component system

The simplest phase diagram is the water which is a one component system. It is also known as pressure-temperature or P-T diagram. Two phases exist along each of the three phase boundaries.

At low pressure (0.006 atm) and temperature (0.01⁰C) all the three phases coexist at a point called triple point.

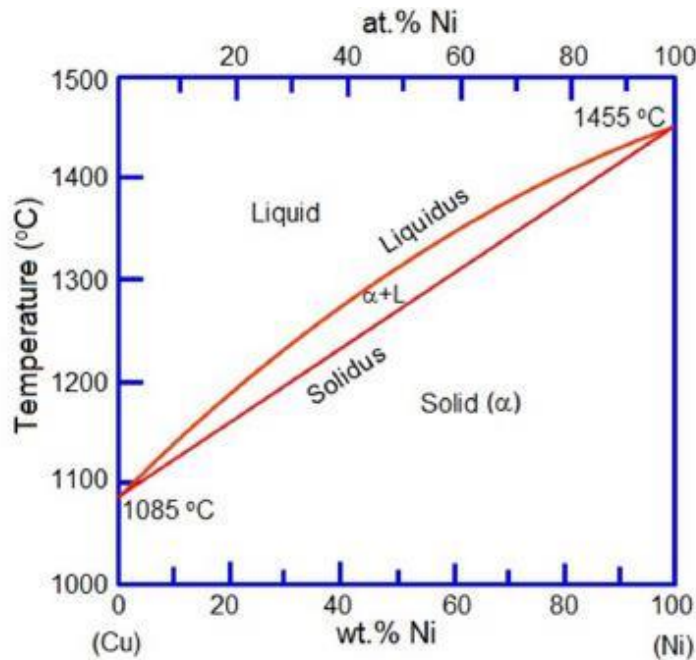


Water phase diagram

Binary Phase diagrams

A binary phase is a two component system. Binary phase diagrams are most commonly used in alloy designing.

The simplest binary system is the Cu-Ni which exhibits complete solubility in liquid and solid state.



Cu-Ni equilibrium phase diagram

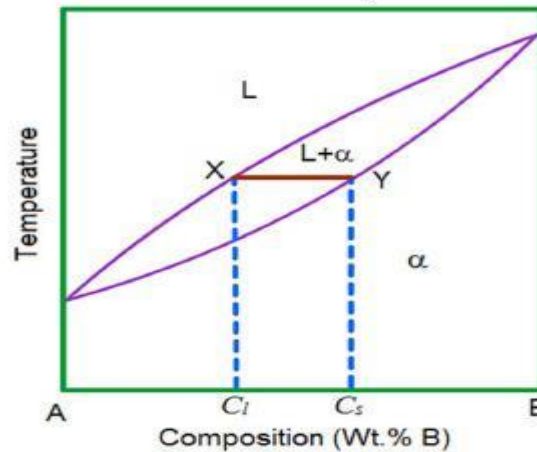
- The line above which the alloy is liquid is called the liquidus line. At temperature just below this line crystals of α solid solution start forming.
- The line below which solidification completes is called solidus line. Hence, only α solid solution exists at any temperature below the solidus line.
- The intermediate region between liquidus and solidus lines is the two-phase region where liquid and solid coexists.

- It can be noted that the two metals are soluble in each other in the entire range of compositions in both liquid and solid state. This kind of system is known as 'Isomorphous' system.

The Tie line

The composition of phases in the two-phase region is not same.

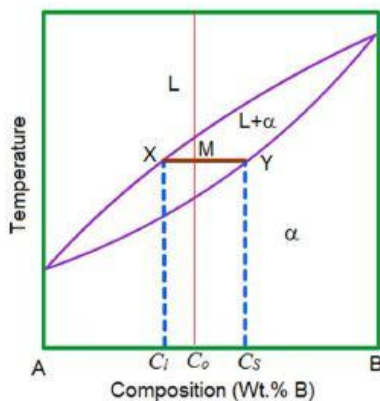
To find the composition of the individual phases in the two phase region, a horizontal line (XY), called tie line, is drawn and its intercepts on the liquidus and solidus lines, C_l and C_s , are taken as the composition of the liquid and solid respectively.



Lever rule

The relative fractions of the phases at a given temperature for an alloy composition C_o is obtained by the lever rule. This rule gives the fraction of a phase by the ratio of the lengths of the tie line between C_o and composition of the other phase to the total length of the tie line. For example, fraction solid, f_s is given by

$$f_s = \frac{MX}{XY} = \frac{C_o - C_l}{C_s - C_l}$$



Similarly fraction liquid, f_l

$$f_l = \frac{MY}{XY} = \frac{C_s - C_o}{C_s - C_l}$$

Phase diagrams- Limited solubility

Not all metals are completely soluble in each other. Distinctions can be made between two types of solid solutions with limited solubility – (i) **Eutectic** and (ii) **Peritectic**.

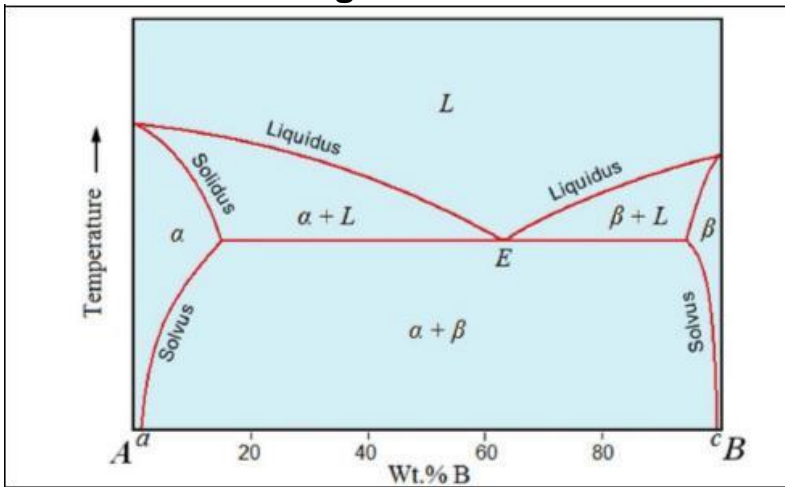
When the melting points of two metals are comparable, a eutectic system forms while a peritectic results when melting points are significantly different.

A eutectic reaction is defined as the one which generates two solids from the liquid at a given temperature and composition, $L \rightarrow \alpha + \beta$

Peritectic is Liquid + Solid 1 \rightarrow Solid 2 ($L + \alpha \rightarrow \beta$)

In both the cases three phases (two solids and a liquid) coexist and the degrees of freedom $F = 2 - 3 + 1 = 0$. This is known as invariant ($F = 0$) reaction or transformation.

Eutectic Phase diagram



Three phases ($L + \alpha + \beta$) coexist at point E . This point is called eutectic point or composition. Left of E is called hypoeutectic whereas right of E is called hypereutectic.

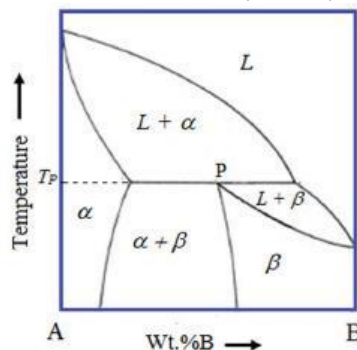
A eutectic composition solidifies as a eutectic mixture of α and β phases. The microstructure at room temperature (RT) may consist of alternate layers or lamellae of α and β .

In **hypoeutectic** alloys the α phase solidifies first and the microstructure at RT consists of this α phase (called proeutectic α) and the eutectic ($\alpha + \beta$) mixture. Similarly hypereutectic alloys consist of proeutectic and the eutectic mixture. The melting point at the eutectic point is minimum. That's why Pb-Sn eutectic alloys are used as solders. Other eutectic systems are Ag-Cu, Al-Si, Al-Cu.

Peritectic Phase diagram

$L + \alpha \rightarrow \beta$. An alloy cooling slowly through the peritectic point, P , the α phase will crystallize first just below the liquidus line. At the peritectic temperature, T_P all of the liquid and α will convert to β . Any composition left of P will generate excess α and similarly compositions right of P will give rise to an excess of liquid.

Peritectic systems – Pt - Ag, Ni - Re, Fe - Ge, Sn-Sb (babbitt).

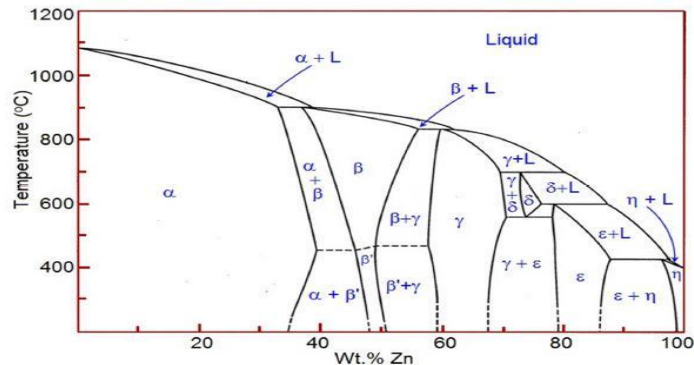


Phase diagrams with intermediate phases

Binary system can have two types of solid solutions/phases – *terminal phases* and *intermediate phases*. Terminal phases occur near the pure metal ends, e.g. α and β phases in the eutectic system. Intermediate phases occur inside the phase diagram and are separated by two-phase regions. The Cu-Zn system contains both types of phases. α and η are terminal phases and β , γ ,

δ and ϵ are intermediate phases. Intermediate phases form in ceramic phase diagrams also. For example, in the $\text{Al}_2\text{O}_3 - \text{SiO}_2$ system an intermediate phase called mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) is formed.

Intermediate phases - Cu-Zn Phase diagram



Cu-Zn phase diagram. α and η are terminal phases and β , γ , δ and ϵ are intermediate phases.

Summary

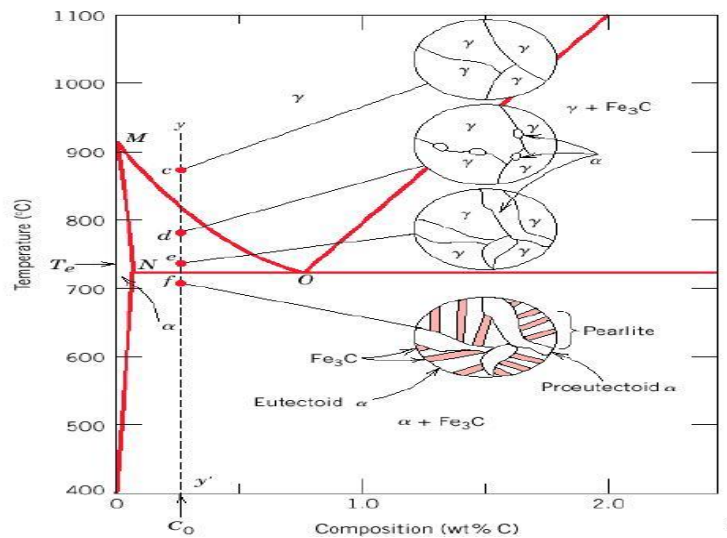
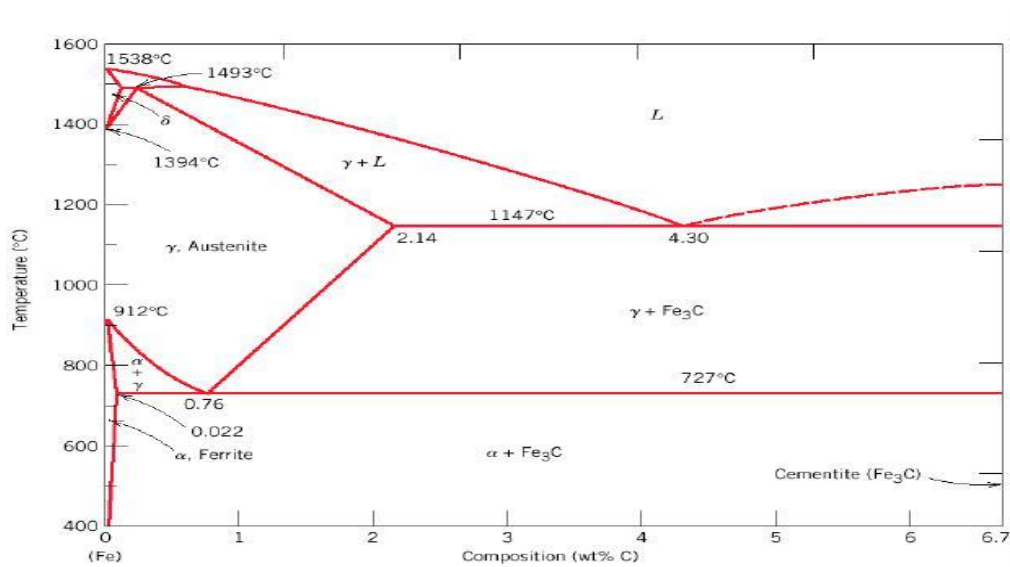
The solidification of alloy takes place not at a specific temperature but over a range of temperatures. While the alloy is in this range, it has a pasty form that consists of solid, tree like structures called dendrites and liquid metals. Formation of substitutional solid solutions between two metals is governed by a set of rules known as **Hume-Rothery rules**. The relative fractions of the phases at a given temperature for an alloy composition are obtained by the lever rule. A eutectic reaction is defined as the one which generates two solids from the liquid at a given temperature and composition, $L \rightarrow \alpha + \beta$. Peritectic is Liquid + Solid 1 \rightarrow Solid 2 ($L + \alpha \rightarrow \beta$)

In both the cases three phases (two solids and a liquid) coexist and the degrees of freedom $F = 2 - 3 + 1 = 0$. This is known as invariant ($F = 0$) reaction or transformation.

Self assessment questions

1. Define nucleation. Derive an expression for the critical size of the nucleus for homogeneous nucleation.
2. State and explain Gibb's phase rule. How it can be applied to a unary phase diagram? Show that degrees of freedom at triple point are zero.
3. Describe the solidification mechanism in pure metal. Distinguish between homogeneous and heterogeneous nucleation.
4. Discuss the factors worked out by Hume-Rothery that governs the formation of an ideal solid solution.
5. What are the different types of solidification
6. Explain with neat sketches the different stages of mechanisms of solidification.
7. Define solid solution. Explain substitutional and interstitial solid solution.
8. Explain the factors governing the formation of substitutional solid solution.
9. With the help of cooling curves explain the solidification of pure metal and binary eutectic alloy
10. A binary alloy A-50% B contains at a particular temperature two solid phases α and β are 5% B and 95% B respectively. calculate the amount of α and β in the alloy.

IRON CARBON DIAGRAM



OBJECTIVES:

- To construct equilibrium diagrams involving complete and partial solubility,
- To understand lever rule
- To understand Iron carbon equilibrium diagram description of phases,
- To know solidification of steels and cast irons invariant reactions.

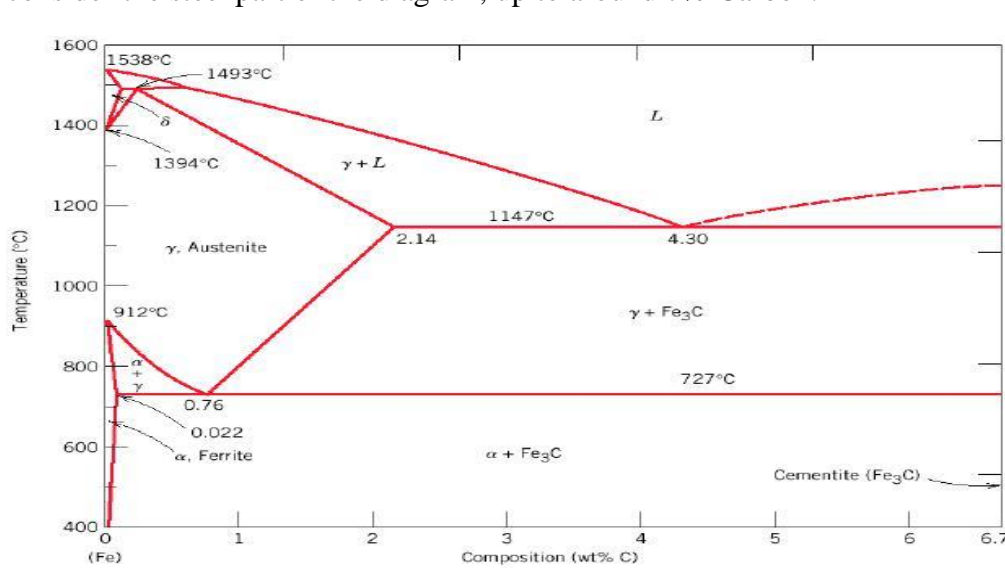
Outcomes:

1. Student can better understand the phase diagrams those are important to design and control of heat treating process and to obtain desirable microstructures.

Introduction

A phase in a material is a region that differs in its microstructure and /or composition from another region. Phase diagrams are graphical representations of what phases are present in a materials system at various temperatures and pressures and compositions. Most phase diagrams are constructed by using equilibrium conditions and used by engineers and scientists to understand and predict many aspects of the behaviour of materials.

The Iron–Iron Carbide (Fe–Fe₃C) Phase Diagram In their simplest form, steels are alloys of Iron (Fe) and Carbon (C). The Fe-C phase diagram is a fairly complex one, but we will only consider the steel part of the diagram, up to around 7% Carbon.



Phases in Fe–Fe₃C Phase Diagram

α-ferrite - solid solution of C in BCC Fe

- Stable form of iron at room temperature.
- The maximum solubility of C is 0.022 wt%
- Transforms to FCC γ-austenite at 912 °C

γ-austenite - solid solution of C in FCC Fe

- The maximum solubility of C is 2.14 wt %.
- Transforms to BCC δ-ferrite at 1395 °C
- Is not stable below the eutectic temperature (727 °C) unless cooled rapidly (Chapter 10)

δ-ferrite solid solution of C in BCC Fe

- The same structure as α-ferrite
- Stable only at high T, above 1394 °C
- Melts at 1538 °C

Fe₃C (iron carbide or cementite)

- This intermetallic compound is metastable, it remains as a compound indefinitely at room T, but decomposes (very slowly, within several years) into α-Fe and C (graphite) at 650 - 700 °C

Fe-C liquid solution

A few comments on Fe–Fe₃C system

C is an interstitial impurity in Fe. It forms a solid solution with α, γ, δ phases of iron. Maximum solubility in BCC α-ferrite is limited (max. 0.022 wt% at 727 °C) - BCC has relatively small

interstitial positions. Maximum solubility in FCC austenite is 2.14 wt% at 1147 °C - FCC has larger interstitial positions.

Mechanical properties: Cementite is very hard and brittle - can strengthen steels. Mechanical properties also depend on the microstructure, that is, how ferrite and cementite are mixed.

Magnetic properties: α -ferrite is magnetic below 768 °C, austenite is non-magnetic

Classification.

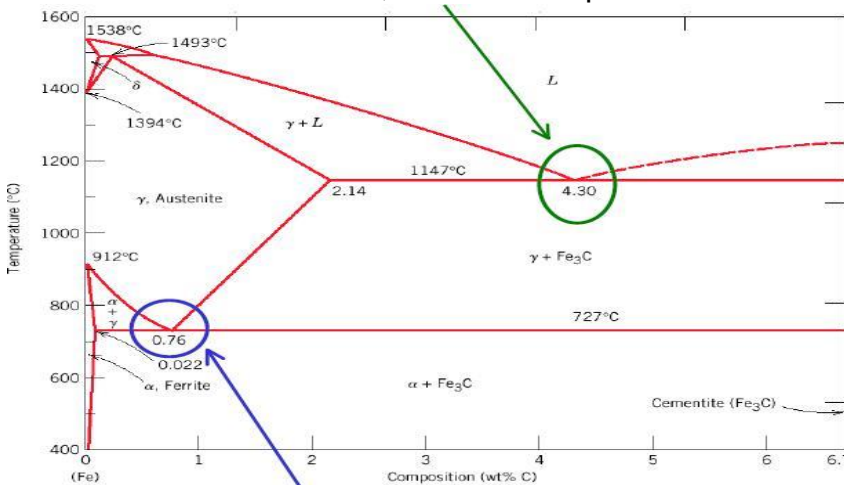
Three types of ferrous alloys:

- Iron: less than 0.008 wt % C in α -ferrite at room T
- Steels: 0.008 - 2.14 wt % C (usually < 1 wt %) α -ferrite + Fe₃C at room T
- Cast iron: 2.14 - 6.7 wt % (usually < 4.5 wt %)

Eutectic and eutectoid reactions in Fe-Fe₃C

Eutectoid: 0.76 wt % C, 727 °C $\gamma(0.76 \text{ wt\% C}) \leftrightarrow \alpha(0.022 \text{ wt\% C}) + \text{Fe}_3\text{C}$

Eutectic: 4.30 wt % C, 1147 °C $L \leftrightarrow \gamma + \text{Fe}_3\text{C}$



Eutectoid: 0.76 wt % C, 727 °C

$\gamma(0.76 \text{ wt\% C}) \leftrightarrow \alpha(0.022 \text{ wt\% C}) + \text{Fe}_3\text{C}$

Fe₃C Eutectic: 4.30 wt% C, 1147 °C

$L \leftrightarrow \gamma + \text{Fe}_3\text{C}$

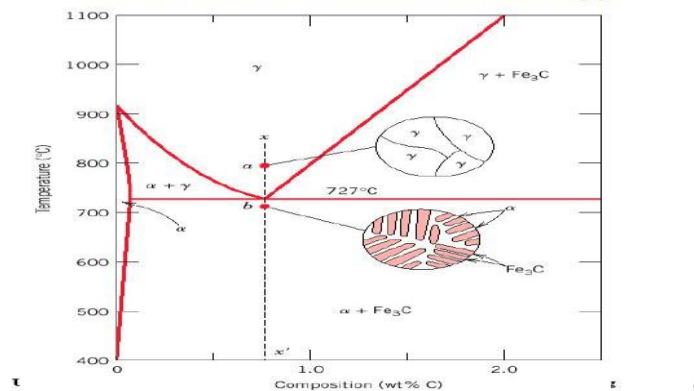
Eutectic and eutectoid reactions are very important in heat treatment of steels

Development of Microstructure in Iron - Carbon alloys

Microstructure depends on composition (carbon content) and heat treatment.

In the discussion below we consider slow cooling in which equilibrium is maintained.

Microstructure of eutectoid steel (D)

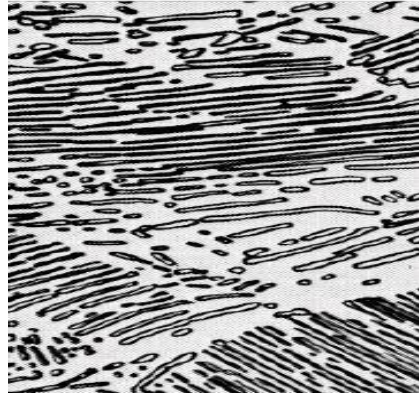


Microstructure of eutectoid steel (II)

When alloy of eutectoid composition (0.76 wt % C) is cooled slowly it forms **pearlite**, a lamellar or layered structure of two phases: α -ferrite and cementite (Fe_3C). The layers of alternating phases in pearlite are formed for the same reason as layered structure of eutectic structures: redistribution C atoms between ferrite (0.022 wt%) and cementite (6.7 wt%) by atomic diffusion. Mechanically, pearlite has properties intermediate to soft, ductile ferrite and hard, brittle cementite.

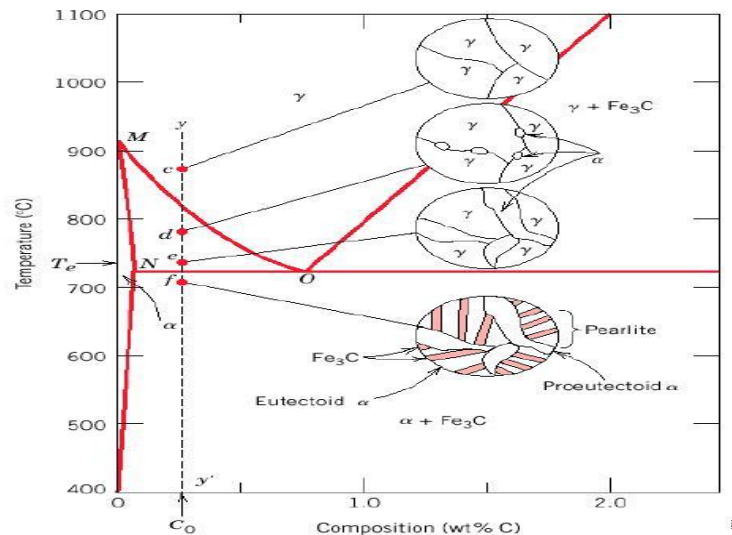
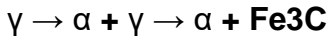
Microstructure of eutectoid steel (II)

In the micrograph, the dark areas are Fe_3C layers, the light phase is α -ferrite



Microstructure of hypo eutectoid steel (I)

Compositions to the left of eutectoid (0.022 - 0.76 wt % C) **hypo eutectoid** alloys.

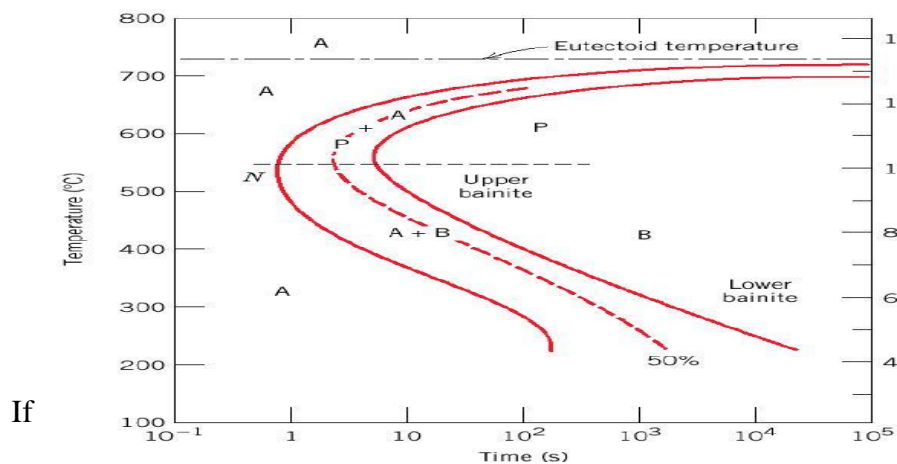


TTT Diagrams

- The family of S-shaped curves at different T is used to construct the TTT diagrams. The TTT diagrams are for the **isothermal** (constant T) transformations (material is cooled quickly to a given temperature before the transformation occurs, and then keep it at that temperature).
- At low temperatures, the transformation occurs sooner (it is controlled by the rate of nucleation) and grain growth (that is controlled by diffusion) is reduced.
- Slow diffusion at low temperatures leads to fine-grained microstructure with thin-layered structure of pearlite (**fine pearlite**).

- At higher temperatures, high diffusion rates allow for larger grain growth and formation of thick layered structure of pearlite (**coarse pearlite**).
- At compositions other than eutectoid, a proeutectoid phase (ferrite or cementite) coexist with pearlite.
- Additional curves for proeutectoid transformation must be included on TTT diagrams.

Formation of Bainite Microstructure (I)

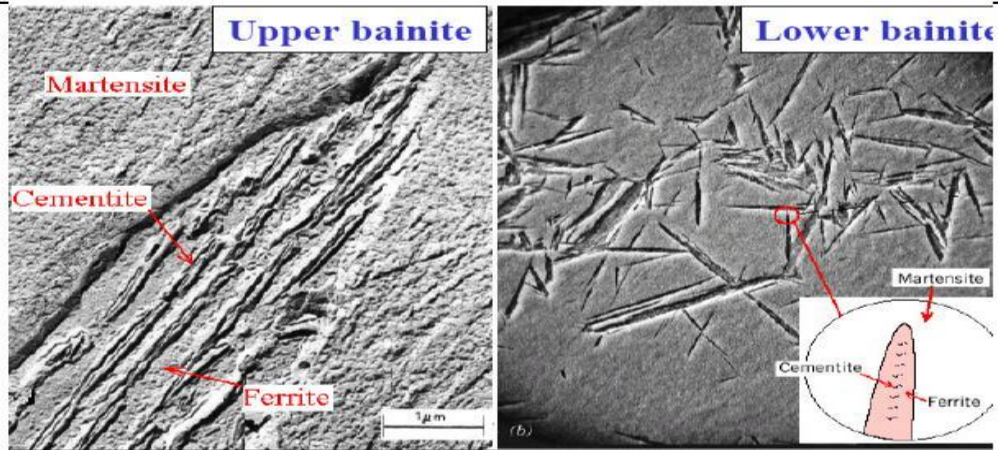


Formation of Bainite Microstructure (II)

- For $T \sim 300\text{-}540^\circ\text{C}$, **upper bainite** consists of needles of ferrite separated by long cementite particles
- For $T \sim 200\text{-}300^\circ\text{C}$, **lower bainite** consists of thin plates of ferrite containing very fine rods or blades of cementite
- In the bainite region, transformation rate is controlled by microstructure growth (diffusion) rather than nucleation.
- Since diffusion is slow at low temperatures, this phase has a very fine (microscopic) microstructure.
- Pearlite and bainite transformations are competitive; transformation between pearlite and bainite not possible without first reheating to form austenite

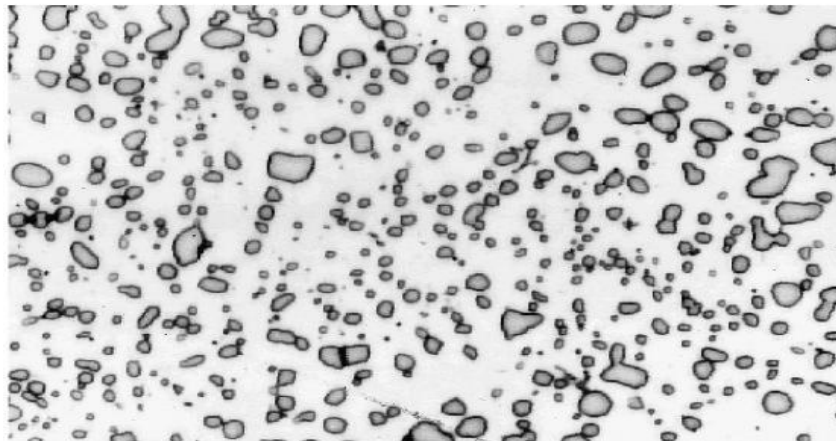
Upper bainite Lower bainite Spheroidite

- Annealing of pearlitic or bainitic microstructures at elevated temperatures just below eutectoid (e.g. 24 h at 700 C) leads to the formation of new microstructure – **spheroidite** - spheres of cementite in a ferrite matrix.
- Composition or relative amounts of ferrite and cementite are not changing in this transformation; **only shape of the cementite inclusions is changing**.
- Transformation proceeds by C diffusion – needs high T.
- Driving force for the transformation - reduction in total ferrite - cementite boundary area



Martensite (I)

- Martensite forms when austenite is rapidly cooled (quenched) to room T.
- It forms nearly instantaneously when the required low temperature is reached. The austenite-martensite does not involve diffusion → no thermal activation is needed, this is called a **thermal transformation**.
- Each atom displaces a small (sub-atomic) distance to transform FCC γ -Fe (austenite) to martensite which has a Body Centered Tetragonal (BCT) unit cell (like BCC, but one unit cell axis is longer than the other two).
- Martensite is metastable - can persist indefinitely at room temperature, but will transform to equilibrium phases on annealing at an elevated temperature.
- Martensite can coexist with other phases and/or microstructures in Fe-C system
- Since martensite is metastable non-equilibrium phase, it does not appear in phase Fe-C phase diagram



Summary

- A phase in a material is a region that differs in its microstructure and /or composition from another region. Phase diagrams are graphical representations of what phases are present in a materials system at various temperatures and pressures and compositions. Most phase diagrams are constructed by using equilibrium conditions and used by engineers and scientists to understand and predict many aspects of the behaviour of materials. The different forms of iron and carbon are α -ferrite, γ -austenite, δ -ferrite. TTT diagrams are

for the isothermal (constant T) transformations (material is cooled quickly to a given temperature before the transformation occurs, and then keep it at that temperature).

Self assessment questions

- 1) Draw iron carbon equilibrium diagram and mark on it all salient temperatures, composition and phases involved. Elaborate the invariant reactions.
- 2) Construct a phase diagram using the following data and label all the fields
Melting point of Ag = 961°C melting point of copper = 1083°C Eutectic temperature = 780°C
Eutectic composition = 28%Cu maximum solubility of Cu in Ag = 9% at 780°C
maximum solubility of Cu in Ag = 2% at 0°C. Determine the following. Solidification start and end of temperature for 30% Ag alloy, temperature at which a 15% Cu alloy has 50% liquid phase and 50% solid phase
- 3) What is a phase diagram?. Clearly explain the different predictions that can be made from phase diagram.
- 4) Draw the iron carbon equilibrium diagram and label all the parts.
- 5) With the help of a iron carbon diagram explain cooling of steel with 0.6% carbon showing the microstructure at different stages.
- 6) What is an invariant reaction? Write the following binary invariant reactions 1) Eutectoid 2) peritectic
- 7) Calculate the amount of proeutectoid ferrite, total ferrite and cementite in 0.6% C steel at room temperature.
- 8) Draw the TTT diagram for eutectoid steel and explain the different microstructures obtained at various cooling rates.
- 9) What is critical cooling rate?
- 10) Two metals A and B melt at 600°C and 400°C respectively. They do not form any intermediate phase. The maximum solid solubility in each other is 4% down to 0°C. an eutectic reaction takes place at a composition of 65%A-35%B at 300°C. Draw the phase diagram and label all regions. Find the temperature at which a 20% A-80%B alloy starts and completes solidification. Find the temperature at which the same alloy is 50% solid and 50% liquid.