Basic Metallurgy



Objective of this Lecture:

 The trainees should be able to understand: Basics of crystal structure What is solid solution Phase, Phase rule & Phase diagrams Iron Carbon Phase Diagram



Solids : the Atomic arrangement



Crystal Structure

• Arrangement of atoms , ions , molecules in a crystalline solid is called crystal structure.

- Is also called space lattice
- Crystal is also called grain.







DIFFERENT TYPES OF UNIT CELLS:

- Depending upon the lattice parameters, there are seven types of unit cells.
 1) Triclinic in which a≠b≠c and α≠β≠γ;
 - **2) Monoclinic** in which $a \neq b \neq c$ and $\alpha = \gamma = 90^{\circ} \neq \beta$
 - **3) Orthorhombic** in which $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^{\circ}$
 - **4)** Hexagonal in which $a=b\neq c$ and $\alpha = \beta = 90^{\circ}$, and $\gamma \neq 90^{\circ}$
 - **5) Rhombohedral** in which a=b=c and; $\alpha = \beta = \gamma \neq 90^{\circ}$
 - **6)** Tetragonal in which $a=b\neq c$ and $\alpha = \beta = \gamma = 90^{\circ}$
 - **7)** Cubic in which a=b=c and and $\alpha = \beta = \gamma = 90^{\circ}$
- Some geometrical patterns can have more than one way of arranging atoms.
- Total 14 different types of crystals are found in nature.
- Most metals and many other solids have unit cell structures described as Body Center Cubic (BCC), Face Centered Cubic (FCC) & Hexagonal Close Packed (HCP).

Metallic Crystal Structures

- Tend to be densely packed.
- Reasons for dense packing:
 - Typically, only one element is present, so all atomic radii are the same.
 - Metallic bonding is not directional.
 - Nearest neighbor distances tend to be small in order to lower bond energy.
 - Electron cloud shields cores from each other
- Have the simplest crystal structures.

We will examine three such structures...

Introduction

- Various solution in our common life
- Namely two types:
 - Same solvent volume after mixing solute/ solutions of limited miscibility at given temperature: Sugar-Water
 - Increased solvent volume after mixing solute / solutions miscible in all proportions with increase in volume Alcohol-Water
- Where really the solute atoms go in the matrix of solvent atoms?

Solid Solution

- Solutions can happen in solid state also: SOLID SOLUTIONS
 What is Solid Solution?
- A solid mixture containing a minor solid component distributed within the crystal lattice of the major solid component without disturbing its crystal structure.
- Major solid component is called solvent whereas minor solid component is solute.
- Solvent matrix has void space within atoms.

Introduction

- If solute atoms are very small, they occupy the void spaces Interstitial solutions - Limited Solubility!
- If not, they dislodge some solvent atoms and occupy the location Substitution solution - Can be of unlimited solubility , however at the cost of increase in overall volume.
- Substitution : it can be of limited proportion or unlimited solubility depending upon the compatibility of the elements via crystal structure, valency etc. of the phases.

Interstitial Solid Solution



SUBSTITUTIONAL SOLID SOLUTION



Hume Rothery Principles

- Some parameters which decides type of solid solutions
- Most important is relative size of solute & solvent atoms
 - Solute \pm 15% of Solvent \rightarrow Substitution
 - − Solute \leq 0.515% of Solvent →Interstitial
- Other parameters being Valence, Position in Periodic Table etc.

System & Phase

- A specific body of material under consideration is called system. For example : a ladle of molten steel
- That portion of a system which is homogeneous due to its uniform physical and chemical characteristics is called phase.
- Phases are defined by conditions of state composition, temperature, pressure, magnetic field, electrostatic field, gravitational field etc.
- Every pure material is considered as one phase.
- solid , liquid and gaseous solutions are considered as one phase.
- Single phase system termed as Homogeneous.
- Two or more phases termed as Heterogeneous.
- Metallic alloys, ceramics, polymeric, composite systems are two phases.

Polymorphism

- In stable equilibrium, solids are crystalline
- Crystal structure of each solid is unique
- However, for some solids, crystal structure transforms from one to another under application of temperature or pressure
- This is called polymorphism
- Allotropy is a result of polymorphism

Phase Rule

• Gibb's Phase Rule

 $\mathbf{F} = \mathbf{C} - \mathbf{P} + \mathbf{n}$

Where:

- F is the number of degree of freedom in the system.
- C is the number of components (pure elements) in the system.
- P is the number of phases in equilibrium.

n is the number of external factors (for example temperature and pressure) in the system.

Phase Rules

• In general, **n** =2 (Temp. & Pressure), so

$\mathbf{F}=\mathbf{C}-\mathbf{P}+\mathbf{2}$

• In metallic system, effect of Pressure is nil, so

 $\mathbf{F} = \mathbf{C} - \mathbf{P} + \mathbf{1}$

- The number of degree of freedom (F) is the number of ways through which variables such as (temperature, pressure & concentration) may be altered without causing disappearance or formation of a phase present in the system.
- Note: You will not be able to maintain all the phases at a time without deviating the no. of freedom ways.

Concept of Phase Equilibrium

- System where more than one phase Co- exist
- Constancy of time till changes in external factors take place increasing the free energy.

Invariant System

- The phase rule can be applied in any System or Phase Diagram
- At any point in Phase Diagram when degree of freedom become Zero, it is known as-

INVARIANT POINT

- There, any change in any external or internal variables (i.e. n) will cause disappearance of a phase
- At Triple point of water, Ice, Water & Steam co-exist.

Triple point of water



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 G_1 and G_2 are the Gibbs free energies of the initial and final states of the system

 $\Delta G = G_2 - G_1$ is the driving force for the transformation.

Phase Transformation

- Higher the degree of super cooling or heating, higher is the urge for transformation.
- But, the actual movement of atoms are through DIFFUSION
- Diffusion rate varies exponentially with temp.
- $K = Ae^{E\alpha/RT}$ (Arrhenius Equation), Diffusion occurs faster at high temperatures.
- The displacement of a given atom, *d*, is proportional to the square root of time, due to the tortuous path:
- $d = c(Dt)^{1/2}$ where c is a constant and D the diffusion constant.
- Extent diffused varies with time hence time is also a factor.

Types of Phase Transformation

• Primary Transformation:

- phase transformation from liquid solution to solid solution.
- Transformation is between two different phases i.e. liquid to solid and vice versa.
- Secondary Transformation: Solid Solution to Solid Solution. Transformation is within solid solution .

Phase Transformation



- Nucleation involves the formation of very small particles, or *nuclei* (e.g., grain boundaries, defects).
- During **growth**, the nuclei grow in size at the expense of the surrounding material.
- The nucleation phase is seen as an incubation period,
- The transformation rate has the form $r = A e^{-Q/RT}$ (similar to the temperature dependence of the diffusion constant), in which case it is said to be *thermally activated*.

Iron Carbon Diagram

Introduction

- By far, the most important alloy system in Engineering application – Mild steel & Cast Iron
- Carbon forms interstitial solid solution in Iron
- The phase diagram has many unique features
 - Limited solubility
 - Forms compound of Iron & Carbon Fe₃C
 - Shows Peritectic , Eutectic & Eutectoid reaction



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Introduction

- The melting point of pure iron is 1539°C approx.
- Two allotropic forms of iron- α -iron and ν iron
- Alloy systems of the iron and carbon include Steel and Cast iron.
- Extensive and versatile application in modern industry
- Alloys with carbon content up to 2.0% Steel.
- Carbon content from 2.1% Cast iron.



Free Energy concept

- Curves show the variation in free energy with temperature for αiron and μ – iron
- Lower FE, more stability
- Between 910°C & 1400° C ע -iron lower FE, so more stable
- Outside that interval, α-iron is more stable phase
- In interval of 1400°C to 1539° C, the phase is called δ iron, to distinguish from α -iron
- The crystal lattice of α -iron & δ -iron is of BCC type
- The crystal lattice of ע -iron is of FCC type



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Fig. 9.3—The austenite \rightarrow ferrite/cementite transformation in relation to the iron-carbon diagram.





How to read the Fe-C phase diagram



Fe – C Diagram



The horizontal axis shows % by weight of carbon in the mix. Fe – C Diagram



The vertical axis is calibrated in temperature – Celsius on the left and equivalent Fahrenheit on the right

Fe – C Diagram



This is Delta -ferrite zone.

Solid solution of C in BCC Fe

MP is 1538 C.

Unstable below 1394 C

Iron Carbon Diagram

- When steel is heated (or cooled), Phase transformation occur at definite temperatures.
- Associated with changes in crystal structure .
- Depends upon the composition of the steel .
- These temperatures are called critical points and designated as A1, A3 etc.
- Over the composition range, they form line.

Principal phases of steel and their Characteristics

Phase	Crystal structure	Characteristics
Ferrite	BCC	Soft, ductile, magnetic
Austenite	FCC	Soft, moderate strength, non- magnetic
Cementite	Compound of Iron & Carbon ,Fe ₃ C	Hard &brittle

Some Key Features

- The solid solution of carbon in α-iron is called Ferrite.
- The solid solution of carbon in y-iron is called Austenite
- Carbon solubility of y-iron at 1130°C reaches 2.0%.
- The maximum solubility of carbon in α-iron is 0.025% (723°C), at 20°C, the solubility is only 0.0025%.
- The solid solution of carbon in α-iron is called Ferrite.
- The solid solution of carbon in y-iron is called Austenite
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Delta region Transformation

- Line MPB Peritectic transformation at constant temperature.
- The result formation of Austenite.
- Solidification starts along the line AB (Liquidius).

Pearlite

- Average properties are:
 - Tensile strength = 120,000 psi;
 - Elongation = 20% in 2 in.;
 - Hardness = Rockwell C 20, Rockwell B 95-100, or BHN 250-300.

- Austenite is an interstitial solid solution of Carbon dissolved in γ (F.C.C.) iron.
- Maximum solubility is 2.0 % C at 1130°C.
- High formability, most of heat treatments begin with this single phase.
- It is normally not stable at room temperature. But, under certain conditions it is possible to obtain austenite at room temperature.

Austenite

• Average properties are:



- Tensile strength = 150,000 ps1;
- Elongation = 10 percent in 2 in.;
- Hardness = Rockwell C 40,

approx; and

 toughness = high



- **Cementite** or iron carbide, is very hard, brittle intermetallic compound of iron & carbon, as Fe₃C, contains fixed carbon content as 6.67 % C.
- It is the <u>hardest structure</u> that appears on the diagram, exact melting point unknown.
- Its crystal structure is orthorhombic.
- It has :
 - low tensile strength (approx. 5,000 psi), but
 - high compressive strength.

- Ledeburite is the eutectic mixture of austenite and cementite.
- It contains 4.3 percent C and is formed at 1130°C.

Martensite –

A super-saturated solid solution of carbon in ferrite.

It is formed when steel is cooled so rapidly that the change from austenite to pearlite is suppressed.

The interstitial carbon atoms distort the BCC ferrite into a BC-tetragonal structure (BCT).; responsible for the hardness of quenched steel.

The Iron-Iron Carbide Diagram

- A map of the temperature at which different phase changes occur on very slow heating and cooling in relation to Carbon, is called Iron- Carbon Diagram.
- Iron- Carbon diagram shows
 - the type of alloys formed under very slow cooling,
 - proper <u>heat-treatment temperature</u> and
 - how the properties of steels and cast irons can be radically changed by heat-treatment.

Some Key Features

- Austenite is non-magnetic
- In normalised condition both form polyhedral equiaxed grains
- Iron and carbon forms a chemical compound, Iron carbide (Fe₃C), called Cementite.
- Cementite has fixed carbon content 6.67%.
- Crystal lattice Orthorhombic
- Hardest phase, generally seen as network

- **Ferrite** is known as *α* solid solution.
- It is an interstitial solid solution of a small amount of carbon dissolved in α (BCC) iron.
- stable form of iron below 912 deg.C
- The maximum solubility is 0.025 % C at 723°C and it dissolves only 0.008 % C at room temperature.
- It is the softest structure that appears on the diagram.

Microstructure of different phases of steel



Fig. 7-8 The microstructure of (a) austenite, 500X; (b) ferrite, 100X; (c) pearlite, 2,500X; (d) pearlite, electron micrograph, 17,000X; enlarged 3X in printing. (a, b, and c, Research Laboratory, U.S. Steel Corporation.)

In order to understand the transformation processes, consider a steel of the eutectoid composition. 0.8% carbon, being slow cooled along line *x*-*x*⁴.

- At the upper temperatures, only austenite is present, with the 0.8% carbon being dissolved in solid solution within the FCC. When the steel cools through 723°C, several changes occur simultaneously.
- The iron wants to change crystal structure from the FCC austenite to the BCC ferrite, but the ferrite can only contain 0.02% carbon in solid solution.
- The excess carbon is rejected and forms the carbon-rich intermetallic known as cementite.

Pearlitic structure

- The net reaction at the eutectoid is the formation of pearlitic structure.
- Since the chemical separation

 occurs entirely within
 crystalline solids, the resultant
 structure is a fine mixture of
 ferrite and cementite.



- Hypo-eutectoid steels: Steels having less than 0.8% carbon are called *hypo-eutectoid steels* (*hypo* means "less than").
- Consider the cooling of a typical hypo-eutectoid alloy along line y-y².
- At high temperatures the material is entirely austenite.
- Upon cooling it enters a region where the stable phases are ferrite and austenite.
- The low-carbon ferrite nucleates and grows, leaving the remaining austenite richer in carbon.

- Hypo-eutectoid steels- At 723°C, the remaining austenite will have assumed the eutectoid composition (0.8% carbon), and further cooling transforms it to pearlite.
- The resulting structure, is a mixture of *primary* or *pro-eutectoid ferrite* (ferrite that forms before the eutectoid reaction) and regions of pearlite.



- Hyper-eutectoid steels (hyper means "greater than") are those that contain more than the eutectoid amount of Carbon.
- When such a steel cools, as along line *z*-*z*', the process is similar to the hypo-eutectoid steel, except that the primary or pro-eutectoid phase is now cementite instead of ferrite.

- As the carbon-rich phase nucleates and grows, the remaining austenite decreases in carbon content, again reaching the eutectoid composition at 723°C.
- This austenite transforms to pearlite upon slow cooling through the eutectoid temperature.
- The resulting structure consists of primary cementite and pearlite.
- The continuous network of primary cementite will cause the material to be extremely brittle.



Hypo-eutectoid steel showing primary cementite along grain boundaries

- It should be noted that the transitions as discussed, are for equilibrium conditions, as a result of slow cooling.
- Upon slow heating the transitions will occur in the reverse manner.

- When the alloys are cooled rapidly, entirely different results are obtained, since sufficient time may not be provided for the normal phase reactions to occur.
- In these cases, the equilibrium phase diagram is no longer a valid tool for engineering analysis.
- Rapid-cool processes are important in the heat treatment of steels and other metals (to be discussed later in H/T of steels).

Cast Irons

- -Iron-Carbon alloys of 2.11%C or more are cast irons.
- -Typical composition:
 - 2.0-4.0%C,0.5-3.0% Si, less than 1.0% Mn and less than 0.2% S.
- -Si-substitutes partially for C and promotes formation of graphite as the carbon rich component instead Fe₃C.



Applications

- It is used tailor properties of steel and to heat treat them.
- It is also used for comparison of crystal structures for metallurgists in case of rupture or fatigue

Thank You