

UNIT-1

Introduction

Materials science, also commonly known as materials science and engineering, is an interdisciplinary field which deals with the discovery and design of new materials. This relatively new scientific field involves studying materials through the materials paradigm (synthesis, structure, properties and performance). It incorporates elements of physics and chemistry, and is at the forefront of nano science and nanotechnology research. In recent years, materials science has become more widely known as a specific field of science and engineering.

Importance of Materials

A material is defined as a substance (most often a solid, but other condensed phases can be included) that is intended to be used for certain applications. There are a myriad of materials around us—they can be found in anything from buildings to spacecrafts. Materials can generally be divided into two classes: crystalline and non-crystalline. The traditional examples of materials are metals, ceramics and polymers. New and advanced materials that are being developed include semiconductors, nanomaterials, biomaterials etc.

The material of choice of a given era is often a defining point. Phrases such as Stone Age, Bronze Age, Iron Age, and Steel Age are great examples. Originally deriving from the manufacture of ceramics and its putative derivative metallurgy, materials science is one of the oldest forms of engineering and applied science. Modern materials science evolved directly from metallurgy, which itself evolved from mining and (likely) ceramics and the use of fire. A major breakthrough in the understanding of materials occurred in the late 19th century, when the American scientist Josiah Willard Gibbs demonstrated that the thermodynamic properties related to atomic structure in various phases are related to the physical properties of a material. Important elements of modern materials science are a product of the space race: the understanding and engineering of the metallic alloys, and silica and carbon materials, used in the construction of space vehicles enabling the exploration of space. Materials science has driven, and been driven by, the development of revolutionary technologies such as plastics, semiconductors, and biomaterials.

Before the 1960s (and in some cases decades after), many materials science departments were named metallurgy departments, reflecting the 19th and early 20th century emphasis on

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metals. The field has since broadened to include every class of materials, including ceramics, polymers, semiconductors, magnetic materials, medical implant materials, biological materials and nanomaterials (materiomics).

Historical Perspective

Materials are so important in the development of civilization that we associate ages with them. In the origin of human life on earth, the Stone Age, people used only natural materials like stone, clay, skins, and wood. When people found copper and how to make it harder by alloying, the Bronze Age started about 3000 BC. The use of iron and steel, stronger materials that gave advantage in wars started at about 1200 BC. The next big step was the discovery of a cheap process to make steel around 1850, which enabled the railroads and the building of the modern infrastructure of the industrial world.

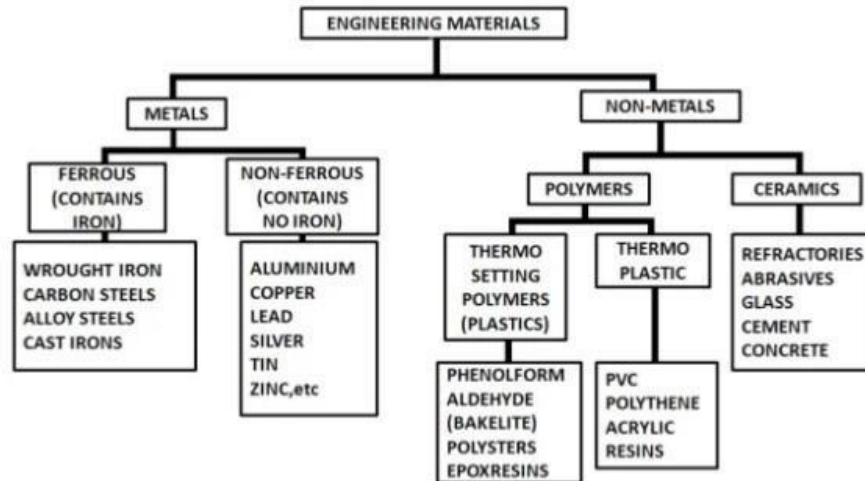
Why Study Materials Science and Engineering?

- To be able to select a material for a given use based on considerations of cost and performance.
- To understand the limits of materials and the change of their properties with use.
- To be able to create a new material that will have some desirable properties.

All engineering disciplines need to know about materials. Even the most immaterial like software or system engineering depend on the development of new materials, which in turn alter the economics, like software-hardware trade-offs. Increasing applications of system engineering are in materials manufacturing (industrial engineering) and complex environmental systems.

Classification of Materials

Classification of Engineering Materials



Like many other things, materials are classified in groups, so that our brain can handle the complexity. One could classify them according to structure, or properties, or use. The one that we will use is according to the way the atoms are bound together:

Metals: The valence electrons are detached from atoms, and spread in an 'electron sea' that "glues" the ions together. Metals are usually strong, conduct electricity and heat well and are opaque to light (shiny if polished). Examples: aluminum, steel, brass, gold.

Semiconductors: The bonding is covalent (electrons are shared between atoms). Their electrical properties depend extremely strongly on minute proportions of contaminants. They are opaque to visible light but transparent to the infrared. Examples: Si, Ge, GaAs.

Ceramics: Atoms behave mostly like either positive or negative ions, and are bound by Coulomb forces between them. They are usually combinations of metals or semiconductors with oxygen, nitrogen or carbon (oxides, nitrides, and carbides). Examples: glass, porcelain, many minerals.

Polymers: are bound by covalent forces and also by weak van der Waals forces, and usually based on H, C and other non-metallic elements. They decompose at moderate temperatures (100 – 400 C), and are lightweight. Other properties vary greatly. Examples: plastics (nylon,

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teflon, polyester) and rubber. Other categories are not based on bonding. A particular microstructure identifies

Composites: Composites made of different materials in intimate contact (example: fiberglass, concrete, wood) to achieve specific properties. **Biomaterials** can be any type of material that is biocompatible and used, for instance, to replace human body parts.

Advanced Materials

Materials used in "High-Tec" applications, usually designed for maximum performance, and normally expensive. Examples are titanium alloys for supersonic airplanes, magnetic alloys for computer disks, special ceramics for the heat shield of the space shuttle, etc.

Modern Material's Needs

- Engine efficiency increases at high temperatures: requires high temperature withstanding materials
- Use of nuclear energy requires solving problem with residues, or advances in nuclear wasteprocessing.
- Hypersonic flight requires materials that are light, strong and resist high temperatures.
- Optical communications require optical fibers that absorb light negligibly.
- Civil construction – materials for unbreakable windows.

Structures: materials that are strong like metals and resist corrosion like plastics.

Crystallography

Crystal Structures:

Atoms self-organize in *crystals*, most of the time. The crystalline lattice is a periodic array of the atoms. When the solid is not crystalline, it is called amorphous. Examples of crystalline solids are metals, diamond and other precious stones, ice, graphite. Examples of amorphous solids are glass, amorphous carbon (a-C), amorphous Si, most plastics To discuss crystalline structures it is useful to consider atoms as being hard spheres, with well-defined radii. In this scheme, the shortest distance between two like atoms is one diameter.

Crystal Lattice is used to represent a three-dimensional periodic array of points coinciding

with atom positions.

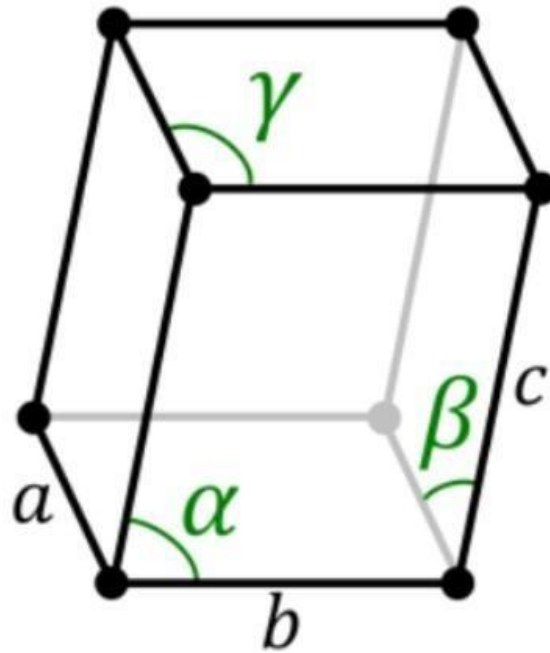
Unit cell is smallest repeatable entity that can be used to completely represent a crystal structure. It is the building block of crystal structure.

Crystal Structure is obtained by attaching atoms, groups of atoms or molecules. This structure occurs from the intrinsic nature of the constituent particles to produce symmetric patterns. A small group of a repeating pattern of the atomic structure is known as the unit cell of the structure. A unit cell is the building block of the crystal structure and it also explains in detail the entire crystal structure and symmetry with the atom positions along with its principal axes. The length, edges of principal axes and the angle between the unit cells are called lattice constants or lattice parameters.

The Seven Crystal Systems is an approach for classification depending upon their lattice and atomic structure. The atomic lattice is a series of atoms that are organized in a symmetrical pattern. With the help of the lattice, it is possible to determine the appearance and physical properties of the stone. It is possible to identify which crystal system they belong to. In a Cubic System crystals are said to represent the element earth. They are Seven Crystal Systems and are stated below with illustrated examples.

Triclinic System:

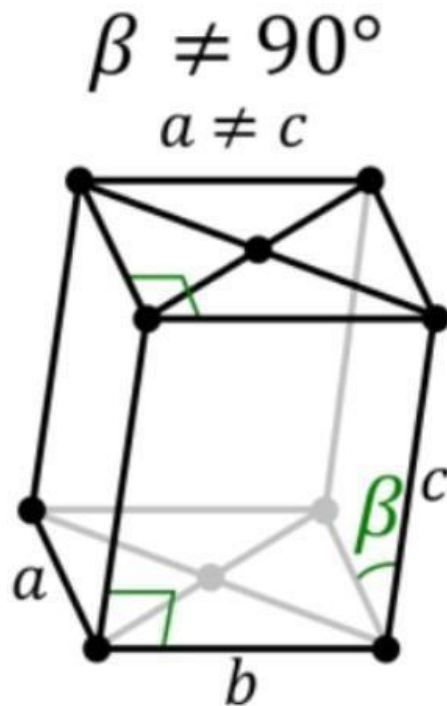
It is the most unsymmetrical crystal system. All three axes are inclined towards each other, and they are of the same length. Based on the three inclined angles the various forms of crystals are in the paired faces. Some standard Triclinic Systems include Labradorite, Amazonite, Kyanite, Rhodonite, Aventurine Feldspar, and Turquoise.



Monoclinic System:

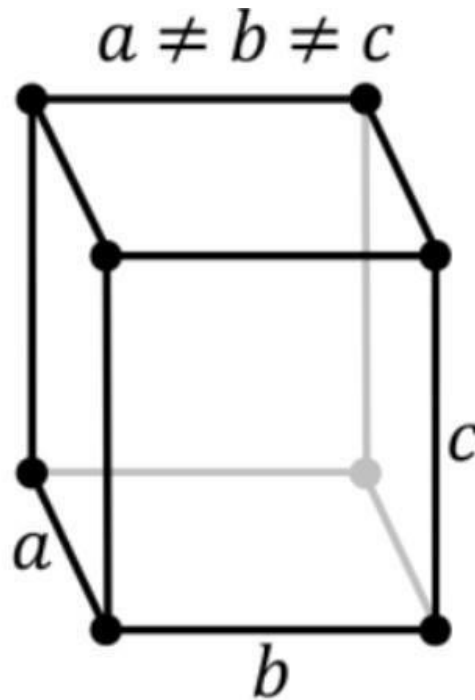
It comprises three axes where two are at right angles to each other, and the third axis is inclined. All three axes are of different length. Based on the inner structure the monoclinic system includes Basal pinacoids and prisms with inclined end faces. Some examples include Diopside, Petalite, Kunzite, Gypsum, Hiddenite, Howlite, Vivianite and more.





Orthorhombic System:

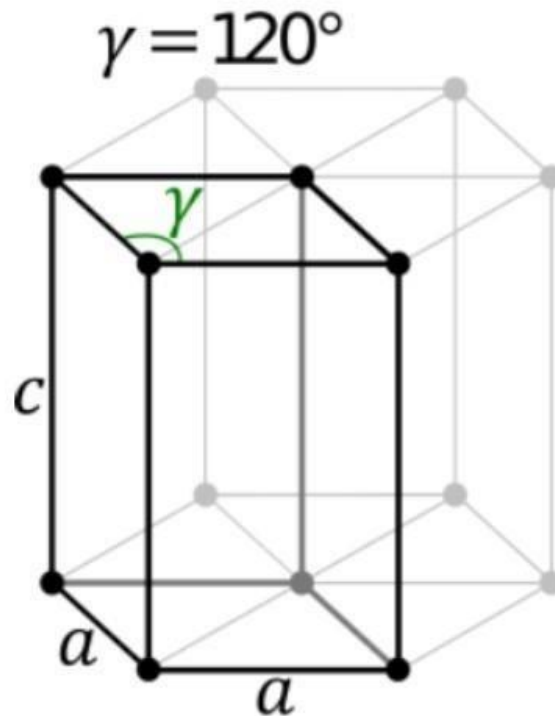
It comprises three axes and is at right angles to each other. There are different lengths. Based on their Rhombic structure the orthorhombic system includes various crystal shapes namely pyramids, double pyramids, rhombic pyramids, and pinacoids. Some common orthorhombic crystals include Topaz, Tanzanite, Iolite, Zoisite, Danburite and more.



Hexagonal System:

It comprises four axes. The three a_1 , a_2 and a_3 axes are all contained within a single plane (called the basal plane) and are at 120° . They intersect each other at an angle of sixty degrees. The fourth axis intersects other axes at right angles. Crystal shapes of hexagonal systems include Double Pyramids, Double-Sided Pyramids, and Four-Sided Pyramids.

Example: Beryl, Cancrinite, Apatite, Sugilite, etc.

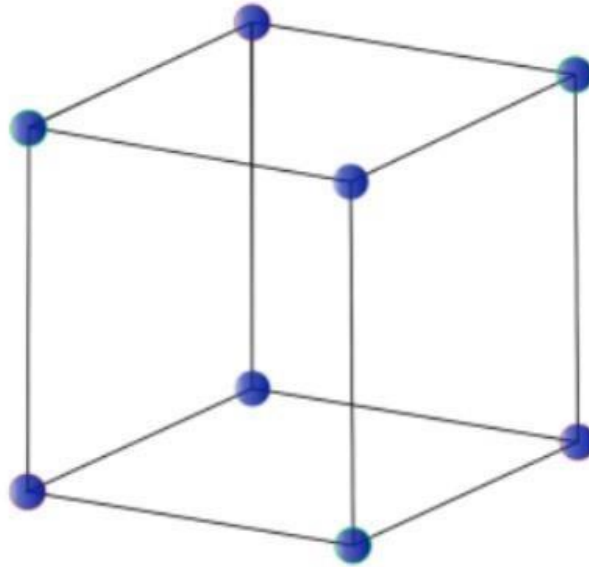


Tetragonal Systems:

It consists of three axes. The main axis varies in length; it can either be short or long. The two-axis lie in the same plane and are of the same length. Based on the rectangular inner structure the shapes of crystal in tetragonal include double and eight-sided pyramids, four-sided prism, trapezohedrons, and pyrite.

Cubic System:

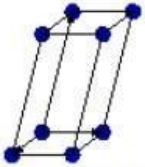
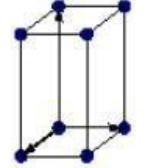
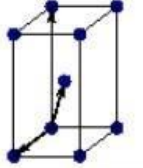
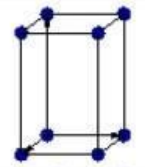
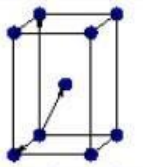
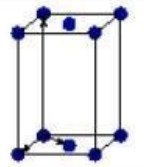
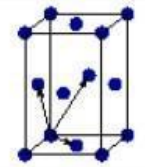
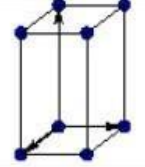
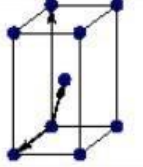
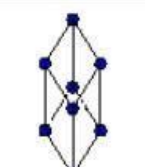
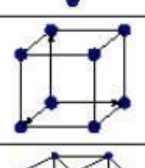
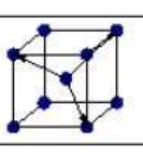
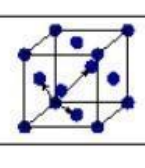
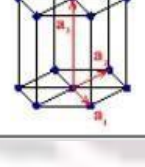
Cubic system is the most symmetrical one out of the seven crystal system. All three angles intersect at right angles and are of equal length. Crystal shapes of a cubic system based on inner structure (square) include octahedron, cube, and Hexaciscoherdron. Example: Silver, Garnet, Gold, and Diamond.



Bravais lattices

When the crystal systems are combined with the various possible lattice centerings, we arrive at the Bravais lattices. They describe the geometric arrangement of the lattice points, and thereby the translational symmetry of the crystal. In three dimensions, there are 14 unique Bravais lattices that are distinct from one another in the translational symmetry they contain.

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Bravais lattice	Parameters	Simple (P)	Volume centered (I)	Base centered (C)	Face centered (F)
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$				
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90^\circ$ $\alpha_{12} \neq 90^\circ$				
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$				
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$				
Trigonal	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120^\circ$				
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$				
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120^\circ$ $\alpha_{23} = \alpha_{31} = 90^\circ$				

All crystalline materials recognized until now (not including quasicrystals) fit in one of these arrangements. The fourteen three-dimensional lattices, classified by crystal system, are shown above. The Bravais lattices are sometimes referred to as space lattices.

The crystal structure consists of the same group of atoms, the basis, positioned around each and every lattice point. This group of atoms therefore repeats indefinitely in three dimensions according to the arrangement of one of the 14 Bravais lattices. The characteristic rotation and mirror symmetries of the group of atoms, or unit cell, is described by its crystallographic

point group.

Metallic Crystal Structures

Important properties of the unit cells are

- The type of atoms and their radii R .
- Cell dimensions (side a in cubic cells, side of base a and height c in HCP) in terms of R .
- n , number of atoms per unit cell. For an atom that is shared with m adjacent unit cells, we only count a fraction of the atom, $1/m$.
- **CN**, the coordination number, which is the number of closest neighbors to which an atom is bonded.
- **APF**, the atomic packing factor, which is the fraction of the volume of the cell actually occupied by the hard spheres. $APF = \text{Sum of atomic volumes} / \text{Volume of cell}$.

Crystalline and Non-crystalline materials:

Single Crystals

Crystals can be *single crystals* where the whole solid is one crystal. Then it has a regular geometric structure with flat faces.

Polycrystalline Materials

A solid can be composed of many crystalline grains, not aligned with each other. It is called *polycrystalline*. The grains can be more or less aligned with respect to each other. Where they meet is called a *grain boundary*.

Non-Crystalline Solids

In amorphous solids, there is no long-range order. But amorphous does not mean random, since the distance between atoms cannot be smaller than the size of the hard spheres. Also, in many cases there is some form of short-range order. For instance, the tetragonal order of crystalline SiO_2 (quartz) is still apparent in amorphous SiO_2 (silica glass.)

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Unit Cell	n	CN	a/R	APF
SC	1	6	2	0.52
BCC	2	8	$4\sqrt{3}$	0.68
FCC	4	12	$2\sqrt{2}$	0.74
HCP	6	12		0.74

Principal Metal Crystal Structures

Simple Cubic Lattice Structure

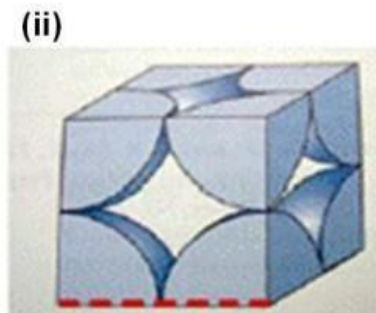
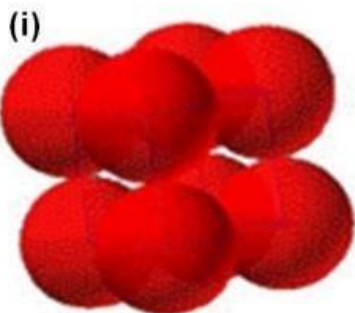
Body Centered Cubic (BCC) Structure

Face Centered Cubic (FCC) Structure

Simple Cubic Lattice

Most elementary crystal structure with three mutually perpendicular axes arbitrarily placed through one of the corners of a cell.

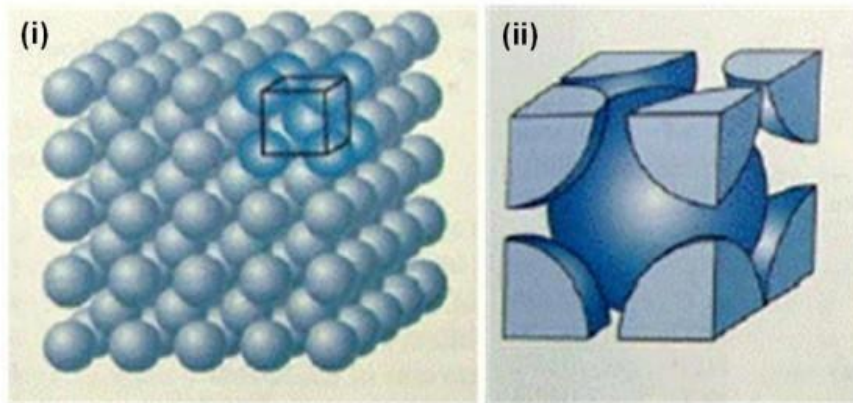
Each corners occupied with one atom. Example: alpha polonium



Body Centered Cubic (BCC) Structure:

BCC cell has an atom at each corner and another atom at body center of cube. Each atom at corner is surrounded by eight adjacent atoms. Example: alpha iron, chromium, molybdenum & tungsten

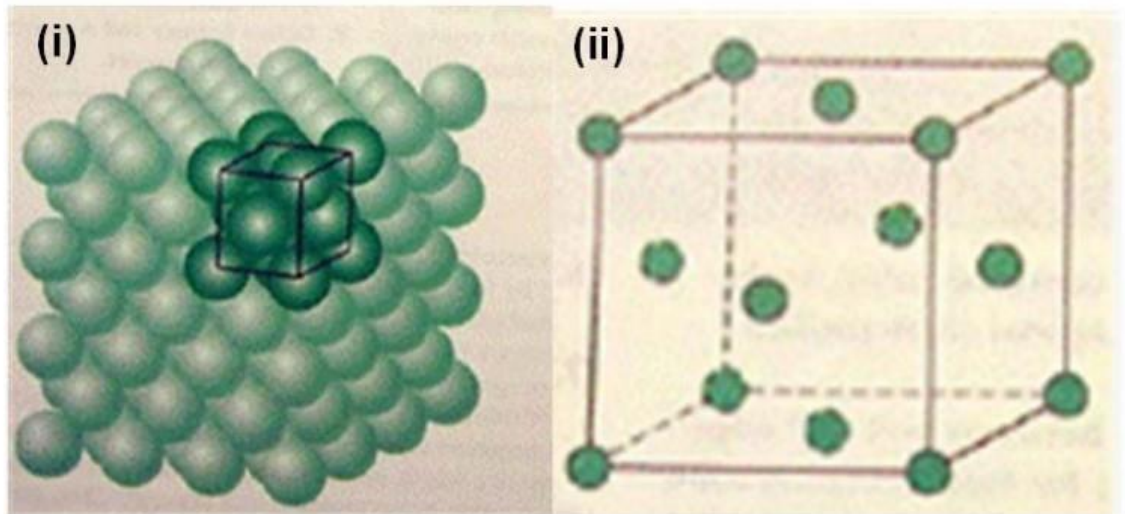
BCC Structure



i). Aggregate of atoms (ii). Hard Sphere Unit Cell

Face Centered Cubic (FCC) Structure:

Atoms at each corner of cube, and in addition there is an atom at the center of each cube's face. Example: aluminium, copper, gold, lead, silver and nickel



(i). Aggregate of atoms

(ii). Hard Sphere Unit Cell

Imperfections in Solids

Point Defects

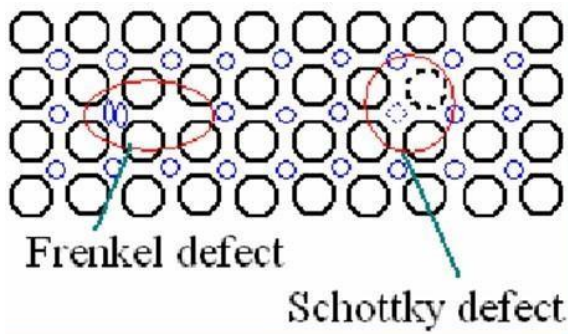
Vacancies and Self-Interstitials

A **vacancy** is a lattice position that is vacant because the atom is missing. It is created when the solid is formed. There are other ways of making a vacancy, but they also occur naturally as a result of thermal vibrations.

An **interstitial** is an atom that occupies a place outside the normal lattice position. It may be the same type of atom as the others (self interstitial) or an impurity atom. In the case of vacancies and interstitials, there is a change in the coordination of atoms around the defect. This means that the forces are not balanced in the same way as for other atoms in the solid, which results in lattice distortion around the defect. A high temperature is needed to have a high *thermal* concentration of vacancies.

Frenkel-defect is a vacancy-interstitial pair of cations

Schottky-defect is a pair of nearby cation and anion vacancies



Theoretical yield point

Theoretical yield is the maximum quantity of a product that could be formed in a chemical reaction if all the limiting reactant reacted to form products (distinguished from actual yield).

Dislocations—Linear Defects

Dislocations are abrupt changes in the regular ordering of atoms, along a line (dislocation line) in the solid. They occur in high density and are very important in mechanical properties of material. They are characterized by the Burgers vector, found by doing a loop around the dislocation line and noticing the extra inter atomic spacing needed to close the loop. The Burgers vector in metals points in a close packed direction.

Line Defects

- Line defects or Dislocations are abrupt change in atomic order along a line.
- They occur if an incomplete plane inserted between perfect planes of atoms or when vacancies are aligned in a line.
- A dislocation is the defect responsible for the phenomenon of slip, by which most metals deform plastically.

Dislocations occur in high densities (10^8 - 10^{10} m^{-2}), and are intimately connected to almost all mechanical properties which are in fact structure-sensitive.

- Dislocation form during plastic deformation, solidification or due to thermal stresses arising from rapid cooling.

Line Defects – Burger's Vector

- A dislocation is characterized by Burger's vector, b .

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- It is unique to a dislocation, and usually has the direction of close packed lattice direction. It is also the slip direction of a dislocation.
- It represents the magnitude and direction of distortion associated with that particular dislocation.
- Two limiting cases of dislocations, edge and screw, are characterized by Burger's vector perpendicular to the dislocation line (t) and Burger's vector parallel to the dislocation line respectively. Ordinary dislocation is of mixed character of edge and screw type.

Edge dislocations occur when an extra plane is inserted. The dislocation line is at the end of the plane. In an edge dislocation, the Burgers vector is perpendicular to the dislocation line.

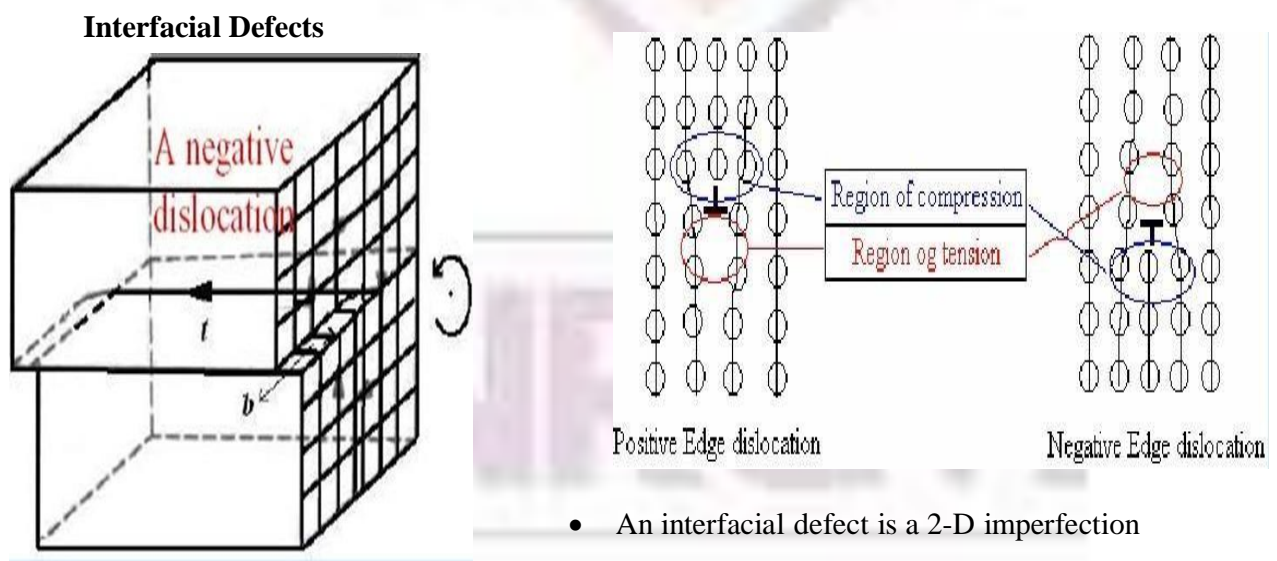
Line Defects – Edge Dislocation

- It is also called as Taylor-Orowan dislocation.
- It will have regions of compressive and tensile stresses on either side of the plane containing dislocation.

Screw dislocations result when displacing planes relative to each other through shear. In this case, the Burgers vector is parallel to the dislocation line.

Line Defects – Screw Dislocation

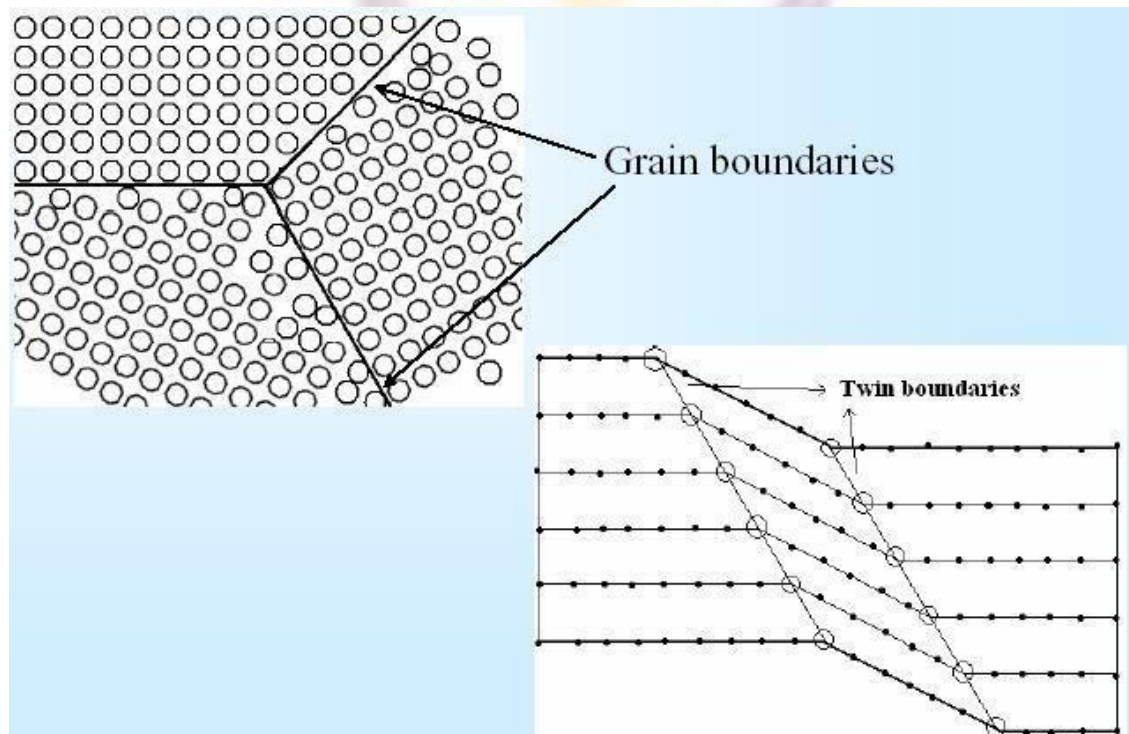
- It is also called as Burger's dislocation.
- It will have regions of shear stress around the dislocation line
- For positive screw dislocation, dislocation line direction is parallel to Burger's vector, and vice versa.



crystallographic orientations on either side of it.

- Region of distortion is about few atomic distances.
- They usually arise from clustering of line defects into a plane.
- These imperfections are not thermodynamically stable, but meta-stable in nature.
- E.g.: External surface, Grain boundaries, Stacking faults, Twin boundaries, Phaseboundaries.

Volume defects are three-dimensional in nature. These defects are introduced, usually, during processing and fabrication operations like casting, forming etc. E.g.: Pores, Cracks, Foreign particles. These defects act like stress raisers, thus deleterious to mechanical properties of parent solids. In some instances, foreign particles are added to strengthen the solid – dispersion hardening. Particles added are hindrances to movement of dislocations which have to cut through or bypass the particles thus increasing the strength.



Dislocation Strengthening Mechanism:

Strain Hardening:

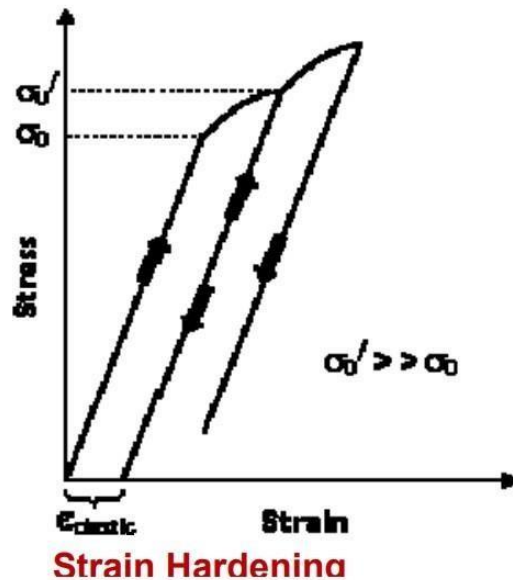
Increase in yield stress of material when loaded subsequently in same direction again and again below recrystallization temperature.

When material is loaded in any direction (say tensile direction), it experiences linear elastic deformation till elastic limit. If load is removed, material comes back to its original shape and size and curve will retrace back loading path.

If material is further loaded (beyond yield stress σ_0'), slight plastic deformation occurs leading to small permanent deformation. Now, if load is removed, material will retain this small plastic /

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permanent deformation and curve will not retrace original path, but will follow path parallel to



original loading path.

If same material is loaded in same (tensile) direction again, it will start yielding at new yield stress σ_0' , which will be higher than initial yield stress of material σ_0 .

This is because material becomes harder during plastic deformation by storing strain energy (some % of total deformation energy)

Reduces ductility and plasticity of material. At micro level, dislocation piles up during plastic deformation at slip planes, which interact with each other and create barriers to further motion / movement of dislocations through crystal lattice.

Bauschinger Effect / Elastic Hysteresis:

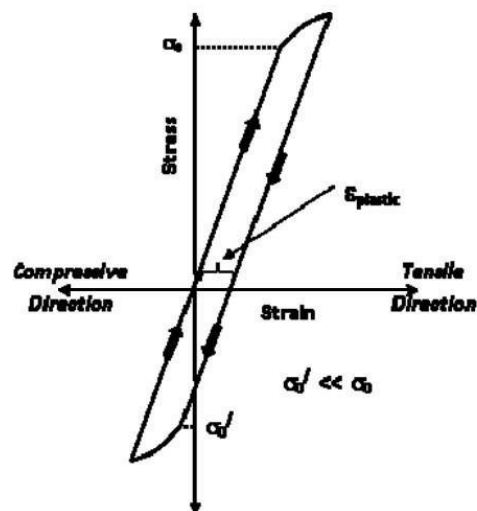
Decrease in yield stress of material when loaded initially in one direction (tensile) and then subsequently in opposite direction (compressive) below recrystallization temperature.

When a material is loaded in any direction (say tensile direction), it experiences linear elastic deformation till elastic limit. If it is further loaded (beyond yield stress σ_0), slight plastic deformation will occur leading to small permanent deformation.

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Now, even if load is removed, material will retain this small plastic / permanent deformation and curve will not retrace original path, but will follow path parallel to original loading path

Further, loaded in opposite direction (compressive), it will start yielding at new yield stress σ_0' , which will be very less than initial yield stress of material σ_0 . This is because residual tensile stress stored in material during tensile loading need to be removed / compensated before elastic deformation in reversal (compressive) direction starts. At micro level, dislocations piles up during tensile loading along at slip planes, which can be easily moved in opposite direction (compressive loading) by residual stresses.

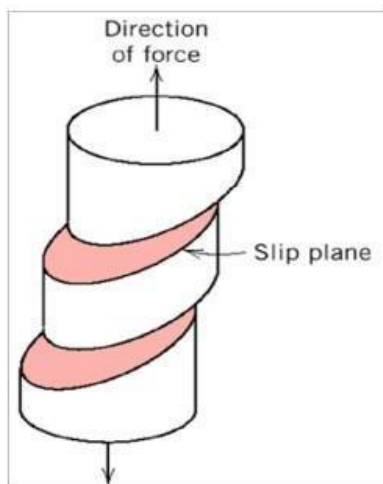


Bauschinger Effect

slip in single crystal:

If a single crystal of a metal is stressed in tension beyond its elastic limit, it elongates slightly and a step appears on the surface due to the relative displacement of one part of the crystal with respect to the others and the elongation stops.

- Further increase in the load causes movement of another parallel plane, resulting in another step. Similarly numbers of small steps are formed on the surface of the single crystal that are parallel to one another and loop around the circumference of the specimen.
- Each step (shear band) results from the movement of a large number of dislocations and their propagation in the slip system.

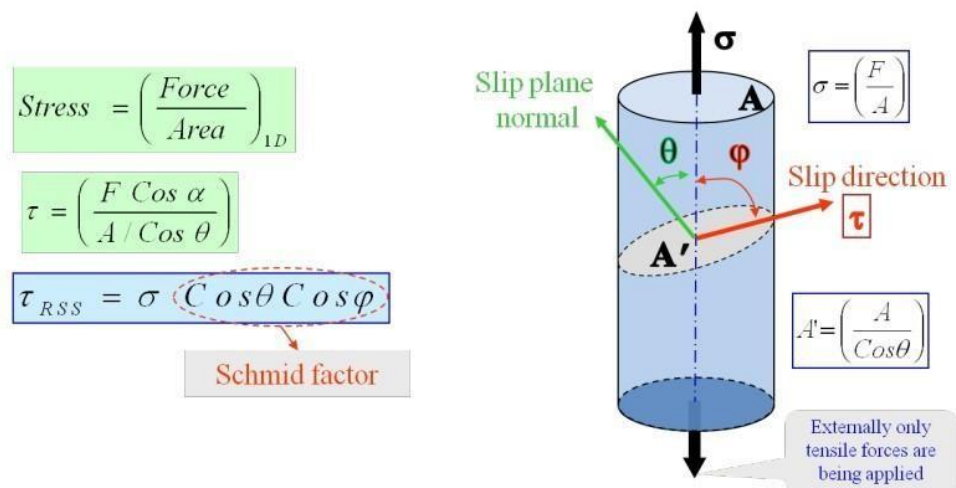


Macroscopic slip in single crystal

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Extent of slip in a single crystal depends on the magnitude of shearing stress produced by external loads, geometry of the crystal structure and the orientation of the active slip planes with respect to the shearing stress.

- Slip begins when the shearing stress on slip plane in the slip direction/Resolved Shear Stress (RSS) reaches a critical value called the Critical Resolved Shear Stress (CRSS) and plastic deformation starts (The actual Schmid's law)
- Even if we apply a tensile force on the specimen → the shear stress resolved onto the slip plane is responsible for slip.



- τ_{RSS} is maximum (P/2A) when $\phi = \lambda = 45^\circ$
- If the tension axis is normal to slip plane i.e. $\lambda = 90^\circ$ or if it is parallel to the slip plane i.e. $\phi = 90^\circ$ then $\tau_{RSS} = 0$ and slip will not occur as per Schmid's law.

Schmid's law

Slip is initiated when

$$\tau_{RSS} \geq \tau_{CRSS}$$



UNIT – II

NIRCM

Phase Diagrams

Equilibrium Phase Diagrams

Give the relationship of composition of a solution as a function of temperatures and the quantities of phases in equilibrium. These diagrams do not indicate the dynamics when one phase transforms into another. Sometimes diagrams are given with pressure as one of the variables. In the phase diagrams we will discuss, pressure is assumed to be constant at one atmosphere.

Binary Isomorphous Systems

This very simple case is one complete liquid and solid solubility, an *isomorphous* system. The example is the Cu-Ni alloy of Fig. 9.2a. The complete solubility occurs because both Cu and Ni have the same crystal structure (FCC), near the same radii, electronegativity and valence. The *liquidus line* separates the liquid phase from solid or solid + liquid phases. That is, the solution is liquid above the liquidus line. The *solidus line* is that below which the solution is completely solid (does not contain a liquid phase.)

Interpretation of phase diagrams

Concentrations: Tie-line method

- locate composition and temperature in diagram
- In two phase region draw tie line or isotherm
- note intersection with phase boundaries. Read compositions.

Fractions: lever rule

- construct tie line (isotherm)
- obtain ratios of line segments lengths.

Development of microstructure in isomorphous alloys

a) Equilibrium cooling

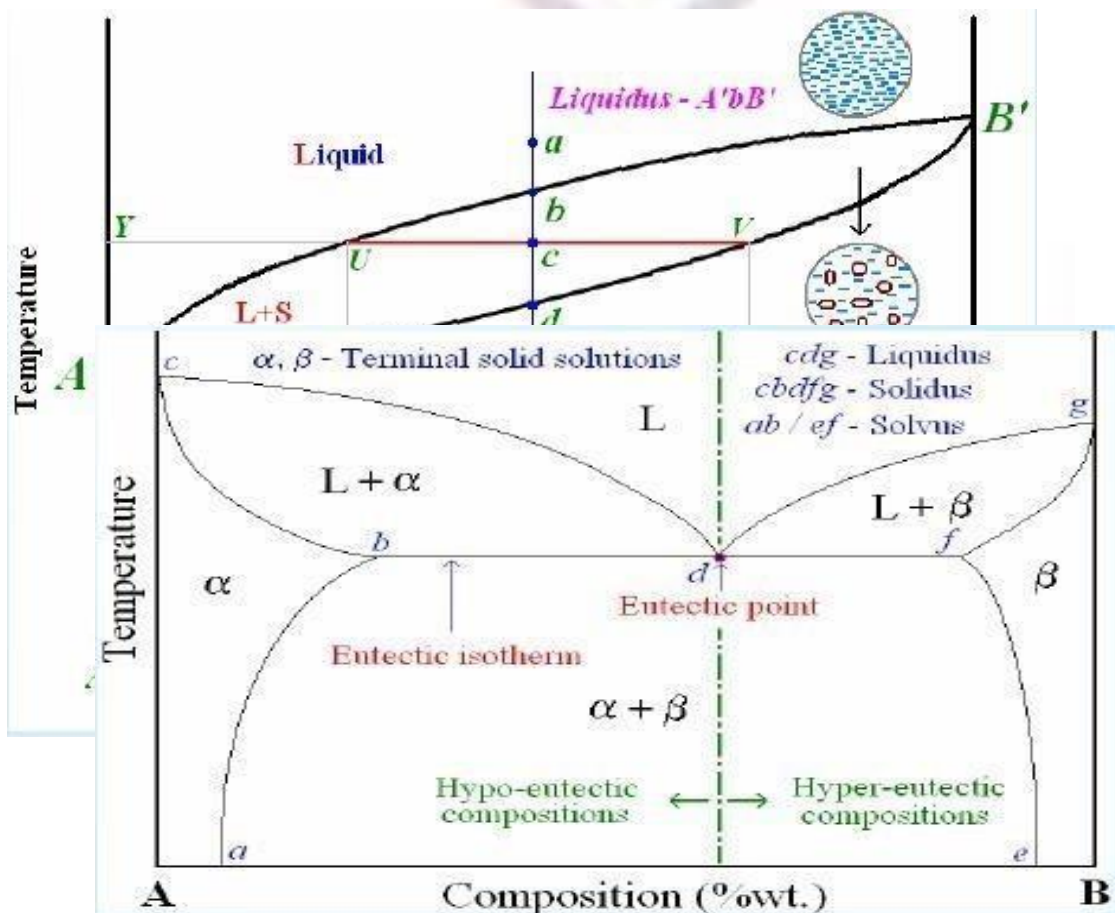
Solidification in the solid + liquid phase occurs gradually upon cooling from the liquidus line. The composition of the solid and the liquid change gradually during cooling (as can be determined by the tie-line method.) Nuclei of the solid phase form and they grow to consume all the liquid at the solidus line.

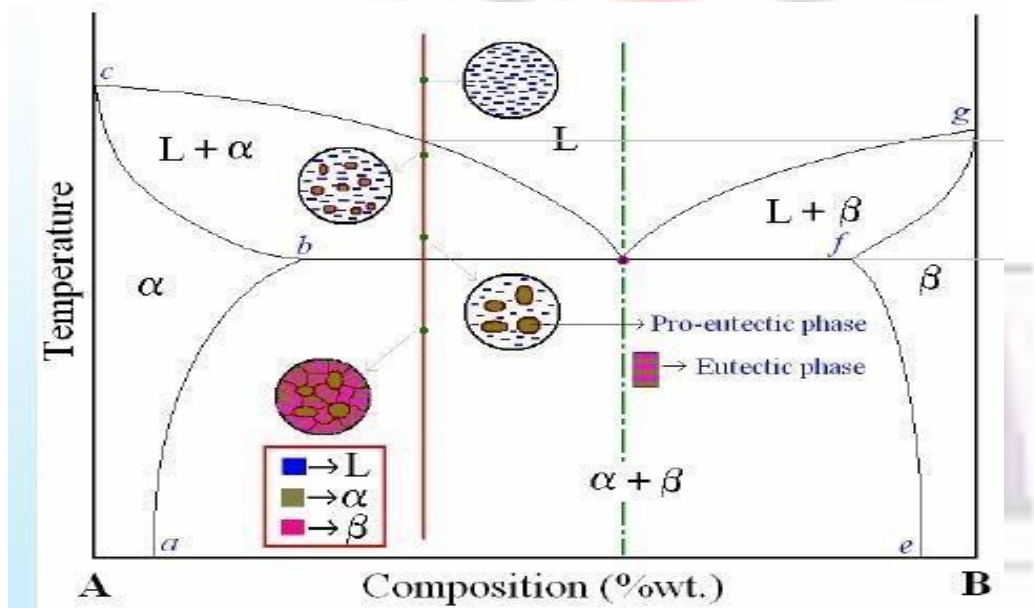
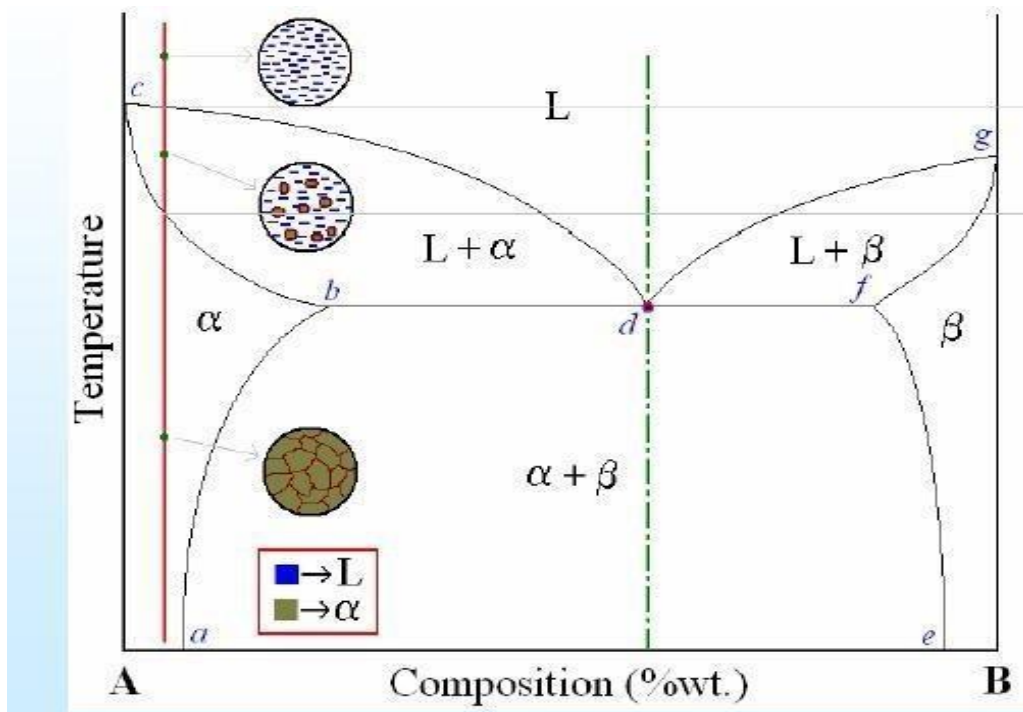
b) Non-equilibrium cooling

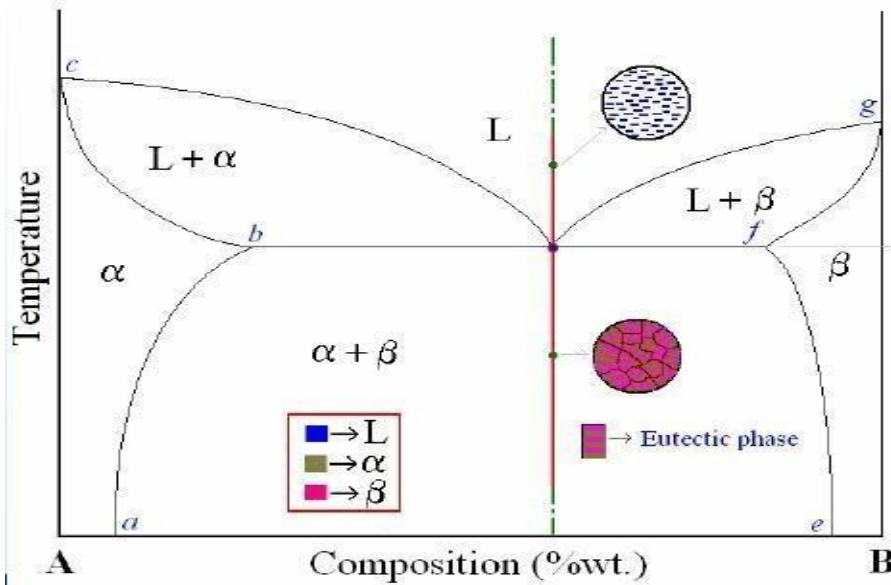
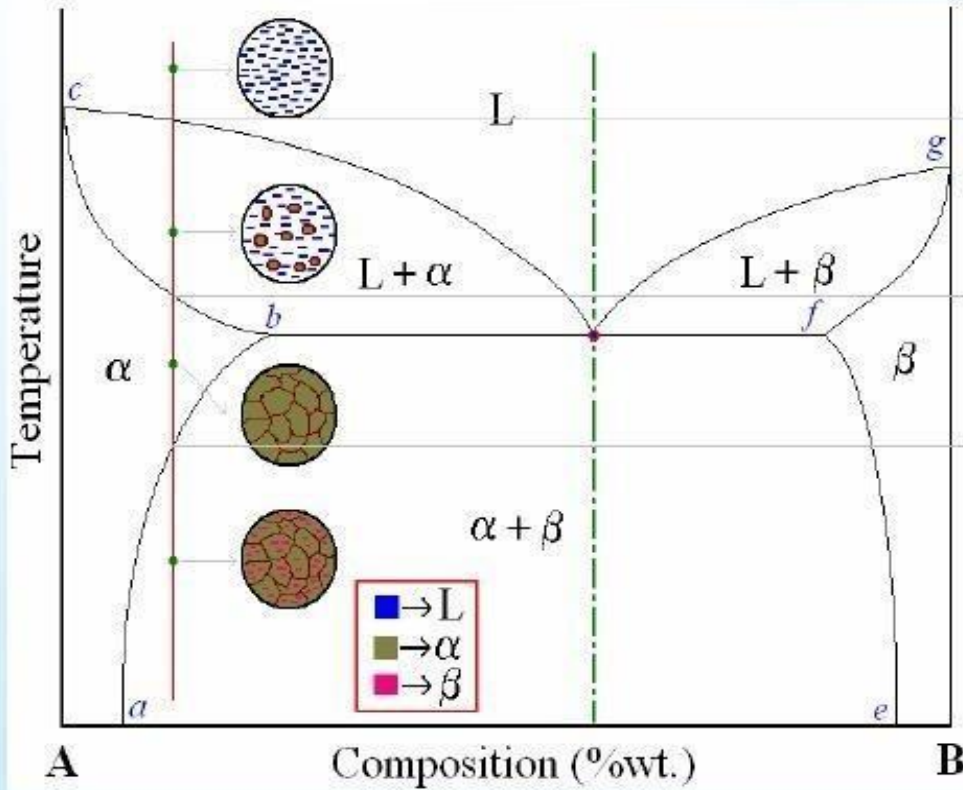
Solidification in the solid + liquid phase also occurs gradually. The composition of the liquid phase evolves by diffusion, following the equilibrium values that can be derived from the tie-line method. However, diffusion in the solid state is very slow. Hence, the new layers that solidify on top of the grains have the equilibrium composition at that temperature but once they are solid their composition does not change. This lead to the formation of layered (cored) grains (Fig. 9.14) and to the invalidity of the tie-line method to determine the composition of the solid phase (it still works for the liquid phase, where diffusion is fast.)

Binary Eutectic Systems

Interpretation: Obtain phases present, concentration of phases and their fraction (%). *Solvus line*: limit of solubility **Eutectic** or invariant point. Liquid and two solid phases exist in equilibrium at the *eutectic composition* and the *eutectic temperature*. The melting point of the eutectic alloy is lower than that of the components (eutectic = easy to melt in Greek).• At most two phases can be in equilibrium within a phase field. • Single-phase regions are separated by 2-phase regions.







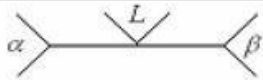
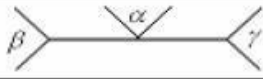
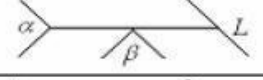

Development of microstructure in eutectic alloys

Case of lead-tin alloys, A layered, eutectic structure develops when cooling below the eutectic temperature. Alloys which are to the left of the eutectic concentration (*hipoeutectic*) or to the right (*hypereutectic*) form a *proeutectic* phase before reaching the eutectic temperature, while in the solid + liquid region. The eutectic structure then adds when the remaining liquid is solidified when cooling further. The eutectic microstructure is lamellar (layered) due to the reduced diffusion distances in the solid state. To obtain the concentration of the eutectic microstructure in the final solid solution, one draws a vertical line at the eutectic concentration and applies the lever rule treating the eutectic as a separate phase.

Eutectoid and Peritectic Reactions

The *eutectoid* (eutectic-like) reaction is similar to the eutectic reaction but occurs from one solid phase to two *new* solid phases. It also shows as V on top of a horizontal line in the phase diagram. There are associated eutectoid temperature (or temperature), eutectoid phase, eutectoid and proeutectoid microstructures.

The *peritectic* reaction also involves three solid in equilibrium, the transition is from a solid + liquid phase to a *different* solid phase when cooling. The inverse reaction occurs when heating.

Reaction	Symbolic equation	Schematic presentation	Example
Eutectic	$L \rightarrow \alpha + \beta$		Fe-C, 4.27% C, 1147 C
Eutectoid	$\alpha \rightarrow \beta + \gamma$		Fe-C, 0.80% C, 723 C
Peritectic	$L + \alpha \rightarrow \beta$		Fe-C, 0.16% C, 1495 C
Peritectoid	$\alpha + \beta \rightarrow \gamma$		

Particle strengthening by precipitation

The strength and hardness of some metal and alloys may be enhanced by the formation of

extremely small uniformly dispersed particles of a second phase within the original phase matrix; this must be accomplished by phase transformations that are induced by appropriate heat

treatments. The process is called **precipitation hardening** because the small particles of the new phase are termed –precipitates. Precipitation hardening and the treating of steel to form tempered martensite are totally different phenomena, even though the heat treatment procedures are similar.

Precipitation reactions

A precipitation reaction is a reaction in which soluble ions in separate solutions are mixed together to form an insoluble compound that settles out of solution as a solid. That insoluble compound is called a precipitate

Kinetics of nucleation and growth

From a micro structural standpoint, the first process to accompany a phase transformation is **nucleation**- the formation of very small particles or nuclei, of the new phase which are capable of growing. The second stage is **growth**, in which the nuclei increase in size; during this process, some volume of the parent phase disappears. The transformation reaches completion if growth of these new phase particles is allowed to proceed until the equilibrium fraction is attained.

As would be expected, the time dependence of the transformations rate (which is often termed the **kinetics** of a transformation) is an important consideration in the heat treatment of materials. With many investigations, the fraction of reaction that has occurred is measured as a function of time, while the temperature is maintained constant. Transformation progress is usually ascertained by either microscopic examination or measurement of some physical property. Data are plotted as the fraction of transformed material versus the logarithm of time; an S-shaped curve, represents the typical kinetic behavior for most solid state reactions.

Solid Solutions

A solid solution may be formed when impurity atoms are added to a solid, in which case the original crystal structure is retained and no new phases are formed.

- **Substitutional solid solutions:** impurity atoms substitute for host atoms, and appreciable

solubility is possible only when atomic diameters and electronegativities for both atom types are similar, when both elements have the same crystal structure, and when the impurity atoms have a valence that is the same as or less than the host material.

- **Interstitial solid solutions:** These form for relatively small impurity atoms that occupy interstitial sites among the host atoms

The Iron–Carbon Diagram

The Iron–Iron Carbide (Fe–Fe₃C) Phase Diagram

This is one of the most important alloys for structural applications. The diagram Fe–C is simplified at low carbon concentrations by assuming it is the Fe–Fe₃C diagram.

Concentrations are usually given in weight percent. The possible phases are:

- α -ferrite (BCC) Fe-C solution
- γ -austenite (FCC) Fe-C solution
- δ -ferrite (BCC) Fe-C solution
- liquid Fe-C solution
- Fe₃C (iron carbide) or cementite. An intermetallic compound.

The maximum solubility of C in α -ferrite is 0.022 wt%. δ -ferrite is only stable at high temperatures. It is not important in practice. Austenite has a maximum C concentration of 2.14 wt %. It is not stable below the eutectic temperature (727 C) unless cooled rapidly (Chapter 10). Cementite is in reality metastable, decomposing into α -Fe and C when heated for several years between 650 and 770 C.

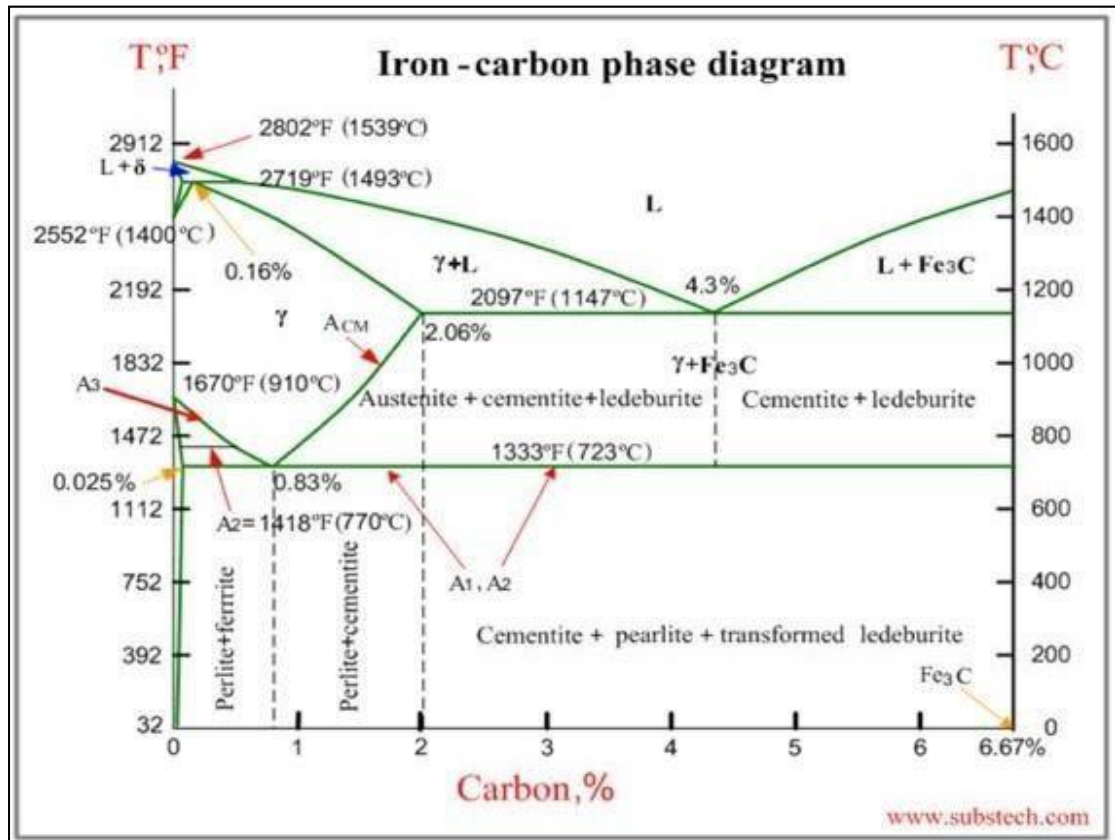
- **δ -ferrite:** – It is solid solution of carbon in δ -iron. Maximum concentration of carbon in δ -ferrite is 0.09% at 2719 °F (1493°C) which is the temperature of the peritectic transformation. The crystal structure of δ -ferrite is BCC (cubic body centered).
- **Austenite:** – Austenite is interstitial solid solution of carbon in γ -iron.

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Austenite has FCC (cubic face centered) crystal structure, permitting high solubility of carbon i.e. up to 2.06% at 2097 °F (1147 °C). Austenite does not exist below 1333 °F (723°C) and maximum carbon concentration at this temperature is 0.83%.

- **α -ferrite:** – It is solid solution of carbon in α -iron. α -ferrite has BCC crystal structure and low solubility of carbon – up to 0.025% at 1333 °F (723°C). α -ferrite exists at room temperature.
- **Cementite** – Cementite is also known as iron carbide, is an intermetallic compound of iron and carbon, having fixed composition Fe_3C . Cementite is a hard and brittle substance, influencing the properties of steels and cast irons.

The logo for NIRCM (National Institute of Research in Composite Materials) features a stylized tree with colorful leaves in shades of purple, red, and yellow. Below the tree, the acronym 'NIRCM' is written in large, bold, purple capital letters. Underneath the acronym, the full name 'National Institute of Research in Composite Materials' is written in a smaller, lighter purple font.



Critical temperatures

- **Upper critical temperature (point) A_3** is the temperature, below which ferrite starts to form as a result of ejection from austenite in the hypo-eutectoid alloys.
- **Upper critical temperature (point) A_{CM}** is the temperature, below which cementite starts to form as a result of ejection from austenite in the hyper-eutectoid alloys.
- **Lower critical temperature (point) A_1** is the temperature of the austenite-to-Pearlite eutectoid transformation. Below this temperature austenite does not exist.
- **Magnetic transformation temperature A_2** is the temperature below which α -ferrite is ferromagnetic.

Phase compositions of the iron-carbon alloys at room temperature

- **Hypoeutectoid steels** (carbon content from 0 to 0.83%) consist of primary (proeutectoid) ferrite (according to the curve A_3) and Pearlite.
- **Eutectoid steel** (carbon content 0.83%) entirely consists of Pearlite.
- **Hypereutectoid steels** (carbon content from 0.83 to 2.06%) consist of primary

(proeutectoid)cementite (according to the curve A_{CM}) and Pearlite.

- **Cast irons** (carbon content from 2.06% to 4.3%) consist of cementite ejected from austenite according to the curve A_{CM} , Pearlite and transformed ledeburite (ledeburite in which austenite transformed to pearlite).

When the liquid of eutectic composition is cooled, at or below eutectic temperature this liquid transforms simultaneously into two solid phases (two terminal solid solutions, represented by α and β). This transformation is known as eutectic reaction and is written symbolically as:

Liquid (L) \leftrightarrow solid solution-1 (α) + solid solution-2 (β)

In the solid state analog of a eutectic reaction, called a eutectoid reaction, one solid phase having eutectoid composition transforms into two different solid phases. Another set of invariant reactions that occur often in binary systems are - peritectic reaction where a solid phase reacts with a liquid phase to produce a new solid phase.

For their role in mechanical properties of the alloy, it is important to note that: ***Ferrite is soft and ductile Cementite is hard and brittle.*** Thus, combining these two phases in solution an alloy can be obtained with intermediate properties. (Mechanical properties also depend on the microstructure, that is, how ferrite and cementite are mixed.)

Development of Microstructures in Iron—Carbon Alloys

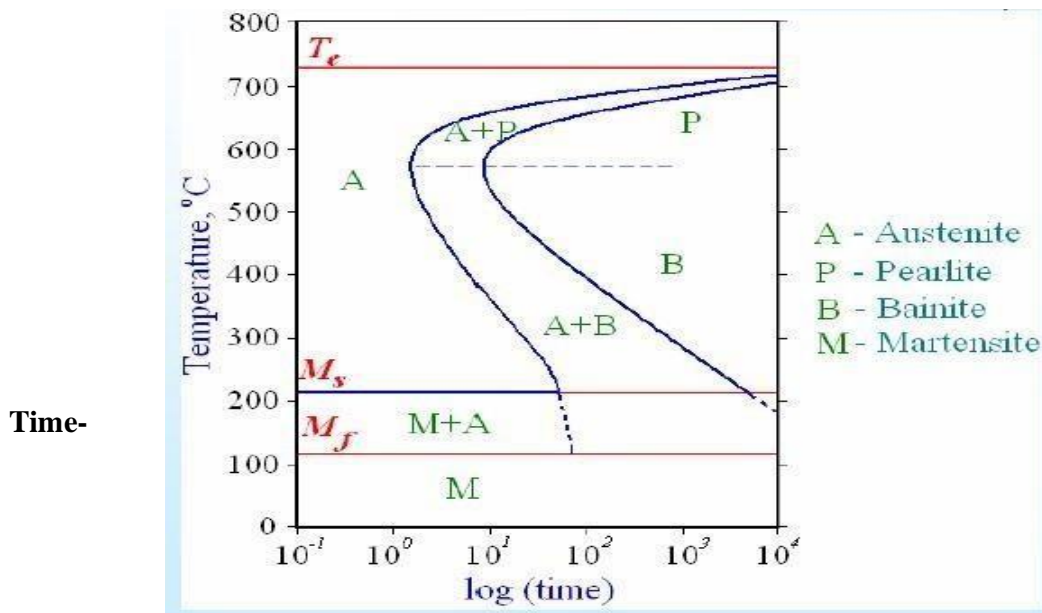
The eutectoid composition of austenite is 0.8 wt %. When it cools *slowly* it forms *pearlite*, a lamellar or layered structure of two phases: α -ferrite and cementite (Fe_3C). Hypoeutectoid alloys contain *proeutectoid ferrite* plus the eutectoid pearlite. Hypereutectoid alloys contain *proeutectoid cementite* plus pearlite. Since reactions below the eutectoid temperature are in the solid phase, the equilibrium is not achieved by usual cooling from austenite.

The Influence of Other Alloying Elements

Alloying strengthens metals by hindering the motion of dislocations. Thus, the strength of Fe–C alloys increase with C content and also with the addition of other elements.

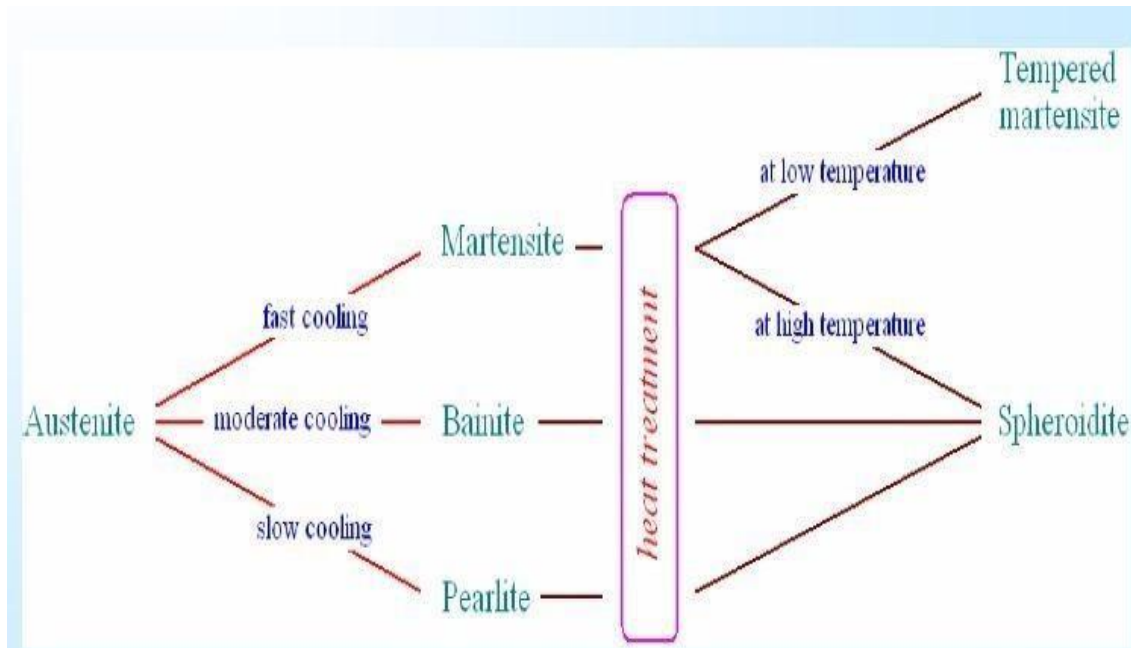
The logo of NRCM (National Research Center for Metallurgy) is centered in the background. It features a stylized tree with a purple trunk and branches, and leaves in shades of yellow, orange, and red. Below the tree, the letters 'NRCM' are written in a large, purple, serif font.

UNIT – III



temperature transformation (TTT) diagrams measure the rate of transformation at a constant temperature. In other words a sample is austenitised and then cooled rapidly to a lower temperature and held at that temperature whilst the rate of transformation is measured, for example by dilatometry. Obviously a large number of experiments is required to build up a complete TTT diagram.

- An increase in carbon content shifts the TTT curve to the right (this corresponds to an increase in hardenability as it increases the ease of forming martensite - i.e. the cooling rate required to attain martensite is less severe).
- An increase in carbon content decreases the martensite start temperature.
- An increase in Mo content shifts the TTT curve to the right and also separates the ferrite + pearlite region from the bainite region making the attainment of a bainitic structure more controllable.



Microstructure and Property Changes in Fe-C Alloys

Isothermal Transformation Diagrams

We use as an example the cooling of an eutectoid alloy (0.8 % C) from the austenite (γ -phase) to pearlite, that contains ferrite (α) plus cementite (Fe_3C or iron carbide). When cooling proceeds below the eutectoid temperature (727°C) nucleation of pearlite starts. The S-shaped curves (fraction of pearlite vs. log. time, fig. 10.3) are displaced to longer times at higher temperatures showing that the transformation is dominated by nucleation (the nucleation period is longer at higher temperatures) and not by diffusion (which occurs faster at higher temperatures).

The family of S-shaped curves at different temperatures can be used to construct the TTT (Time- Temperature-Transformation) diagrams For these diagrams to apply, one needs to cool the material quickly to a given temperature T_0 before the transformation occurs, and keep it at that temperature over time. The horizontal line that indicates constant temperature T_0 intercepts the TTT curves on the left (beginning of the transformation) and the right (end of the transformation); thus one can read from the diagrams when the transformation occurs. The formation of pearlite indicates that the transformation occurs sooner at low temperatures, which is an indication that it is controlled by the rate of nucleation. At low temperatures, nucleation occurs fast and grain growth is reduced (since it occurs by diffusion, which is hindered at low

temperatures). This reduced grain growth leads to fine-grained microstructure (**fine pearlite**). At higher temperatures, diffusion allows for larger grain growth, thus leading to **coarse pearlite**.

At lower temperatures nucleation starts to become slower, and a new phase is formed, **bainite**. Since diffusion is low at low temperatures, this phase has a very fine (microscopic) microstructure.

Spheroidite is a coarse phase that forms at temperatures close to the eutectoid temperature. The relatively high temperatures caused a slow nucleation but enhances the growth of the nuclei leading to large grains.

A very important structure is **martensite**, which forms when cooling austenite very fast (**quenching**) to below a maximum temperature that is required for the transformation. It forms nearly instantaneously when the required low temperature is reached; since no thermal activation is needed, this is called an *athermal transformation*. Martensite is a different phase, a body-centered tetragonal (BCT) structure with interstitial C atoms. Martensite is *metastable* and decomposes into ferrite and pearlite but this is extremely slow (and not noticeable) at room temperature.

In the examples, we used an eutectoid composition. For hypo- and hypereutectoid alloys, the analysis is the same, but the proeutectoid phase that forms before cooling through the eutectoid temperature is also part of the final microstructure

Heat Treatment

Heat Treatment is the controlled heating and cooling of metals to alter their physical and mechanical properties without changing the product shape. Heat treatment is sometimes done inadvertently due to manufacturing processes that either heat or cool the metal such as welding or forming. Heat Treatment is often associated with increasing the strength of material, but it can also be used to alter certain manufacturability objectives such as improve machining, improve formability, restore ductility after a cold working operation. Thus it is a very enabling manufacturing process that can not only help other manufacturing process, but can also improve product performance by increasing strength or other desirable characteristics.

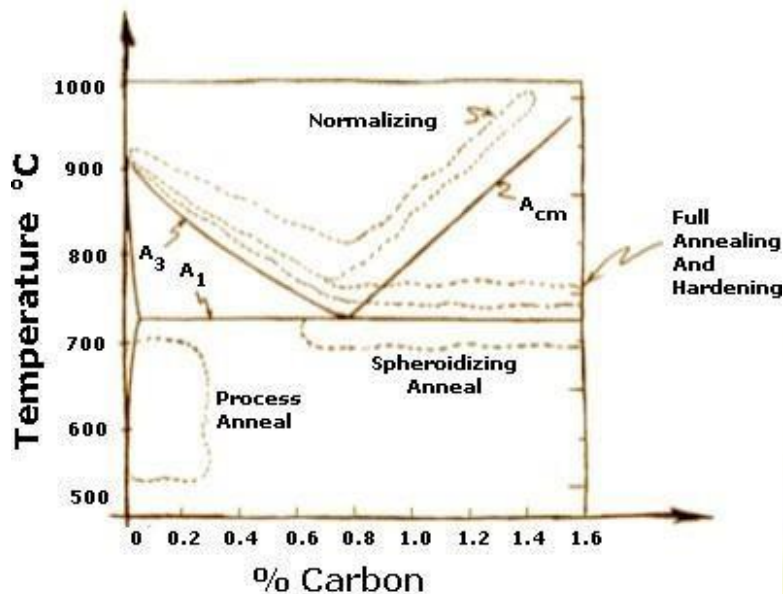
Steels are particularly suitable for heat treatment, since they respond well to heat treatment and the commercial use of steels exceeds that of any other material. Steels are heat treated for one of the following reasons:

1. Softening
2. Hardening
3. Material modification

Softening: Softening is done to reduce strength or hardness, remove residual stresses, improve toughness, restore ductility, refine grain size or change the electromagnetic properties of the steel. Restoring ductility or removing residual stresses is a necessary operation when a large amount of cold working is to be performed, such as in a cold-rolling operation or wire drawing. Annealing — full Process, spheroidizing, normalizing and tempering austempering, martempering are the principal ways by which steel is softened.

Hardening: Hardening of steels is done to increase the strength and wear properties. One of the pre-requisites for hardening is sufficient carbon and alloy content. If there is sufficient Carbon content then the steel can be directly hardened. Otherwise the surface of the part has to be Carbon enriched using some diffusion treatment hardening techniques.

Material Modification: Heat treatment is used to modify properties of materials in addition to hardening and softening. These processes modify the behavior of the steels in a beneficial manner to maximize service life, e.g., stress relieving, or strength properties, e.g., cryogenic treatment, or some other desirable properties



HEAT TREATMENT PROCESS

Full annealing is the process of slowly raising the temperature about 50 °C (90 °F) above the *Austenitic temperature* line A₃ or line A_{CM} in the case of Hypoeutectoid steels (steels with < 0.77% Carbon) and 50 °C (90 °F) into the Austenite-Cementite region in the case of Hypereutectoid steels (steels with > 0.77% Carbon).

It is held at this temperature for sufficient time for all the material to transform into Austenite or Austenite-Cementite as the case may be. It is then slowly cooled at the rate of about 20 °C/hr (36 °F/hr) in a furnace to about 50 °C (90 °F) into the Ferrite-Cementite range. At this point, it can be cooled in room temperature air with natural convection. The grain structure has coarse Pearlite

with ferrite or Cementite (depending on whether hypo or hyper eutectoid). The steel becomes soft and ductile.

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Normalizing is the process of raising the temperature to over $60\text{ }^{\circ}\text{C}$ ($108\text{ }^{\circ}\text{F}$), above line A_3 or line A_{CM} fully into the Austenite range. It is held at this temperature to fully convert the structure into Austenite, and then removed from the furnace and cooled at room temperature under natural convection. This results in a grain structure of fine Pearlite with excess of Ferrite or Cementite. The resulting material is soft; the degree of softness depends on the actual ambient conditions of cooling. This process is considerably cheaper than full annealing since there is not the added cost of controlled furnace cooling.

Process Annealing is used to treat work-hardened parts made out of low-Carbon steels ($< 0.25\%$ Carbon). This allows the parts to be soft enough to undergo further cold working without fracturing. Process annealing is done by raising the temperature to just below the Ferrite- Austenite region, line A_1 on the diagram. This temperature is about $727\text{ }^{\circ}\text{C}$ ($1341\text{ }^{\circ}\text{F}$) so heating it to about $700\text{ }^{\circ}\text{C}$ ($1292\text{ }^{\circ}\text{F}$) should suffice. This is held long enough to allow recrystallization of the ferrite phase, and then cooled in still air. Since the material stays in the same phase through out the process, the only change that occurs is the size, shape and distribution of the grain structure. This process is cheaper than either full annealing or normalizing since the material is not heated to a very high temperature or cooled in a furnace.

Stress Relief Anneal is used to reduce residual stresses in large castings, welded parts and cold- formed parts. Such parts tend to have stresses due to thermal cycling or work hardening. Parts are heated to temperatures of up to $600 - 650\text{ }^{\circ}\text{C}$ ($1112 - 1202\text{ }^{\circ}\text{F}$), and held for an extended time (about 1 hour or more) and then slowly cooled in still air.

Spheroidization is an annealing process used for high carbon steels (Carbon $> 0.6\%$) that will be machined or cold formed subsequently. This is done by one of the following ways:

Heat the part to a temperature just below the Ferrite-Austenite line, line A_1 or below the Austenite-Cementite line, essentially below the $727\text{ }^{\circ}\text{C}$ ($1340\text{ }^{\circ}\text{F}$) line. Hold the temperature for a prolonged time and follow by fairly slow cooling. **Or**

Cycle multiple times between temperatures slightly above and slightly below the $727\text{ }^{\circ}\text{C}$ ($1340\text{ }^{\circ}\text{F}$) line, say for example between 700 and $750\text{ }^{\circ}\text{C}$ ($1292 - 1382\text{ }^{\circ}\text{F}$), and slow cool. **Or**

For tool and alloy steels heat to 750 to $800\text{ }^{\circ}\text{C}$ ($1382-1472\text{ }^{\circ}\text{F}$) and hold for several hours followed by slow cooling.

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All these methods result in a structure in which all the Cementite is in the form of small globules (spheroids) dispersed throughout the ferrite matrix. This structure allows for improved machining in continuous cutting operations such as lathes and screw machines. Spheroidization also improves resistance to abrasion.

Tempering is a process done subsequent to quench hardening. Quench-hardened parts are often too brittle. This brittleness is caused by a predominance of Martensite. This brittleness is removed by tempering. Tempering results in a desired combination of hardness, ductility, toughness, strength, and structural stability. Tempering is not to be confused with tempers on rolled stock—these tempers are an indication of the degree of cold work performed.

The mechanism of tempering depends on the steel and the tempering temperature. The prevalent Martensite is a somewhat unstable structure. When heated, the Carbon atoms diffuse from Martensite to form a carbide precipitate and the concurrent formation of Ferrite and Cementite, which is the stable form. Tool steels for example, lose about 2 to 4 points of hardness on the Rockwell C scale. Even though a little strength is sacrificed, toughness (as measured by impact strength) is increased substantially. Springs and such parts need to be much tougher — these are tempered to a much lower hardness.

Tempering is done immediately after quench hardening. When the steel cools to about 40 °C (104 °F) after quenching, it is ready to be tempered. The part is reheated to a temperature of 150 to 400 °C (302 to 752 °F). In this region a softer and tougher structure Troostite is formed. Alternatively, the steel can be heated to a temperature of 400 to 700 °C (752 to 1292 °F) that results in a softer structure known as Sorbite. This has less strength than Troostite but more ductility and toughness.

The heating for tempering is best done by immersing the parts in oil, for tempering up to 350 °C (662 °F) and then heating the oil with the parts to the appropriate temperature. Heating in a bath also ensures that the entire part has the same temperature and will undergo the same tempering. For temperatures above 350 °C (662 °F) it is best to use a bath of nitrate salts. The salt baths can be heated up to 625 °C (1157 °F). Regardless of the bath, gradual heating is important to avoid cracking the steel. After reaching the desired temperature, the parts are



CEMENTITE



FERRITE

held at that temperature for about 2 hours, then removed from the bath and cooled in still air.

Hardening

Hardness is a function of the Carbon content of the steel. Hardening of a steel requires a change in structure from the body-centered cubic structure found at room temperature to the face-centered cubic structure found in the Austenitic region. The steel is heated to Austenitic region. When suddenly quenched, the Martensite is formed. This is a very strong and brittle structure. When slowly quenched it would form Austenite and Pearlite which is a partly hard and partly soft structure. When the cooling rate is extremely slow then it would be mostly Pearlite which is extremely soft.

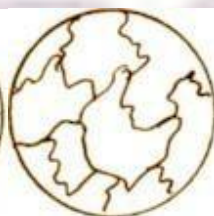
Usually when hot steel is quenched, most of the cooling happens at the surface, as does the hardening. This propagates into the depth of the material. Alloying helps in the hardening and by determining the right alloy one can achieve the desired properties for the particular application.



AUSTENITE



MARTENSITE



PEARLITE
COARSE



PEARLITE
FINE

Quench Media

Water: Quenching can be done by plunging the hot steel in water. The water adjacent to the hot steel vaporizes, and there is no direct contact of the water with the steel. This slows down cooling until the bubbles break and allow water contact with the hot steel. As the water contacts and boils, a great amount of heat is removed from the steel. With good agitation, bubbles can be prevented from sticking to the steel, and thereby prevent soft spots.

Water is a good rapid quenching medium, provided good agitation is done. However, water is corrosive with steel, and the rapid cooling can sometimes cause distortion or cracking.

Salt Water: Salt water is a more rapid quench medium than plain water because the bubbles are broken easily and allow for rapid cooling of the part. However, salt water is even more corrosive than plain water, and hence must be rinsed off immediately.

Oil: Oil is used when a slower cooling rate is desired. Since oil has a very high boiling point, the transition from start of Martensite formation to the finish is slow and this reduces the likelihood of cracking. Oil quenching results in fumes, spills, and sometimes a fire hazard.



UNIT IV

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is removed by tempering. Tempering results in a desired combination of hardness, ductility, toughness, strength, and structural stability. Tempering is not to be confused with tempering on rolled stock—these tempers are an indication of the degree of cold work performed.

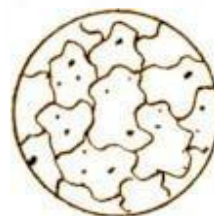
The mechanism of tempering depends on the steel and the tempering temperature. The prevalent Martensite is a somewhat unstable structure. When heated, the Carbon atoms diffuse from Martensite to form a carbide precipitate and the concurrent formation of Ferrite and Cementite, which is the stable form. Tool steels for example, lose about 2 to 4 points of hardness on the Rockwell C scale. Even though a little strength is sacrificed, toughness (as measured by impact strength) is increased substantially. Springs and such parts need to be much tougher — these are tempered to a much lower hardness.

Tempering is done immediately after quench hardening. When the steel cools to about 40 °C (104 °F) after quenching, it is ready to be tempered. The part is reheated to a temperature of 150 to 400 °C (302 to 752 °F). In this region a softer and tougher structure Troostite is formed. Alternatively, the steel can be heated to a temperature of 400 to 700 °C (752 to 1292 °F) that results in a softer structure known as Sorbite. This has less strength than Troostite but more ductility and toughness.

The heating for tempering is best done by immersing the parts in oil, for tempering up to 350 °C (662 °F) and then heating the oil with the parts to the appropriate temperature. Heating in a bath also ensures that the entire part has the same temperature and will undergo the same tempering. For temperatures above 350 °C (662 °F) it is best to use a bath of nitrate salts. The salt baths can be heated up to 625 °C (1157 °F). Regardless of the bath, gradual heating is important to avoid cracking the steel. After reaching the desired temperature, the parts are held at that temperature for about 2 hours, then removed from the bath and cooled in still air.



CEMENTITE



FERRITE

Hardening

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Hardness is a function of the Carbon content of the steel. Hardening of a steel requires a change in structure from the body-centered cubic structure found at room temperature to the face-centered cubic structure found in the Austenitic region. The steel is heated to Austenitic region. When suddenly quenched, the Martensite is formed. This is a very strong and brittle structure. When slowly quenched it would form Austenite and Pearlite which is a partly hard and partly soft structure. When the cooling rate is extremely slow then it would be mostly Pearlite which is extremely soft.

Usually when hot steel is quenched, most of the cooling happens at the surface, as does the hardening. This propagates into the depth of the material. Alloying helps in the hardening and by determining the right alloy one can achieve the desired properties for the particular application.



AUSTENITE



MARTENSITE



CEMENTITE



PEARLITE
COARSE



PEARLITE
FINE

Quench Media

Water: Quenching can be done by plunging the hot steel in water. The water adjacent to the hot steel vaporizes, and there is no direct contact of the water with the steel. This slows down cooling until the bubbles break and allow water contact with the hot steel. As the water contacts and boils, a great amount of heat is removed from the steel. With good agitation, bubbles can be prevented from sticking to the steel, and thereby prevent soft spots.

Water is a good rapid quenching medium, provided good agitation is done. However, water

is corrosive with steel, and the rapid cooling can sometimes cause distortion or cracking.

Salt Water: Salt water is a more rapid quench medium than plain water because the bubbles are broken easily and allow for rapid cooling of the part. However, salt water is even more corrosive than plain water, and hence must be rinsed off immediately.

Oil: Oil is used when a slower cooling rate is desired. Since oil has a very high boiling point, the transition from start of Martensite formation to the finish is slow and this reduces the likelihood of cracking. Oil quenching results in fumes, spills, and sometimes a fire hazard.

Precipitation hardening is achieved by:

1. solution heat treatment where all the solute atoms are dissolved to form a single-phase solution.
2. rapid cooling across the solvus line to exceed the solubility limit. This leads to a supersaturated solid solution that remains stable (metastable) due to the low temperatures, which prevent diffusion.
3. precipitation heat treatment where the supersaturated solution is heated to an intermediate temperature to induce precipitation and kept there for some time (aging). If the process is continued for a very long time, eventually the hardness decreases. This is called over aging.

The requirements for precipitation hardening are:

- appreciable maximum solubility
- solubility curve that falls fast with temperature
- composition of the alloy that is less than the maximum solubility

Precipitation Hardening

Hardening can be enhanced by extremely small precipitates that hinder dislocation motion. The precipitates form when the solubility limit is exceeded. Precipitation hardening is also called age hardening because it involves the hardening of the material over a prolonged time.

Case Hardening

Case hardening produces a hard, wear-resistant surface or case over a strong, tough core.

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The principal forms of casehardening are carburizing, cyaniding, and nitriding. Only ferrous metals are case-hardened. Case hardening is ideal for parts that require a wear-resistant surface and must be tough enough internally to withstand heavy loading. The steels best suited for case hardening are the low-carbon and low-alloy series. When high-carbon steels are case hardened, the hardness penetrates the core and causes brittleness. In case hardening, you change the surface of the metal chemically by introducing a high carbide or nitride content. The core remains chemically unaffected. When heat-treated, the high-carbon surface responds to hardening, and the core toughens.

Carburizing

Carburizing is a case-hardening process by which carbon is added to the surface of low-carbon steel. This results in a carburized steel that has a high-carbon surface and a low-carbon interior. When the carburized steel is heat-treated, the case becomes hardened and the core remains soft and tough. Two methods are used for carburizing steel. One method consists of heating the steel in a furnace containing a carbon monoxide atmosphere. The other method has the steel placed in a container packed with charcoal or some other carbon-rich material and then heated in a furnace. To cool the parts, you can leave the container in the furnace to cool or remove it and let it air cool. In both cases, the parts become annealed during the slow cooling. The depth of the carbon penetration depends on the length of the soaking period. With today's methods, carburizing is almost exclusively done by gas atmospheres.

Cyaniding

This process is a type of case hardening that is fast and efficient. Preheated steel is dipped into a heated cyanide bath and allowed to soak. Upon removal, it is quenched and then rinsed to remove any residual cyanide. This process produces a thin, hard shell that is harder than the one produced by carburizing and can be completed in 20 to 30 minutes vice several hours. The major drawback is that cyanide salts are a deadly poison.

Nitriding

This case-hardening method produces the hardest surface of any of the hardening processes. It differs from the other methods in that the individual parts have been heat-treated and tempered before nitriding. The parts are then heated in a furnace that has an ammonia gas

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atmosphere. No quenching is required so there is no worry about warping or other types of distortion. This process is used to case harden items, such as gears, cylinder sleeves, camshafts and other engine parts, that need to be wear resistant and operate in high-heat areas.

Flame Hardening

Flame hardening is another procedure that is used to harden the surface of metal parts. When you use an oxyacetylene flame, a thin layer at the surface of the part is rapidly heated to its critical temperature and then immediately quenched by a combination of a water spray and the cold base metal. This process produces a thin, hardened surface, and at the same time, the internal parts

retain their original properties. Whether the process is manual or mechanical, a close watch must be maintained, since the torches heat the metal rapidly and the temperatures are usually determined visually. Flame hardening may be either manual or automatic. Automatic equipment produces uniform results and is more desirable. Most automatic machines have variable travel speeds and can be adapted to parts of various sizes and shapes. The size and shape of the torch depends on the part. The torch consists of a mixing head, straight extension tube, 90-degree extension head, an adjustable yoke, and a water-cooled tip. Practically any shape or size flame-hardening tip is available. Tips are produced that can be used for hardening flats, rounds, gears, cams, cylinders, and other regular or irregular shapes. In hardening localized areas, you should heat the metal with a standard hand-held welding torch. Adjust the torch flame to neutral for normal heating; however, in corners and grooves, use a slightly oxidizing flame to keep the torch from sputtering. You also should particularly guard against overheating in corners and grooves. If dark streaks appear on the metal surface, this is a sign of overheating, and you need to increase the distance between the flame and the metal. For the best heating results, hold the torch with the tip of the inner cone about an eighth of an inch from the surface and direct the flame at right angles to the metal. Sometimes it is necessary to change this angle to obtain better results; however, you rarely find a deviation of more than 30 degrees. Regulate the speed of torch travel according to the type of metal, the mass and shape of the part, and the depth of hardness desired. In addition, you must select the steel according to the properties desired. Select carbon steel when surface hardness is the primary factor and alloy steel when the

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physical properties of the core are also factors. Plain carbon steels should contain more than 0.35% carbon for good results in flame hardening. For water quenching, the effective carbon range is from 0.40% to 0.70%. Parts with a carbon content of more than 0.70% are likely to surface crack unless the heating and quenching rate are carefully controlled. The surface hardness of a flame-hardened section is equal to a section that was hardened by furnace heating and quenching. The decrease in hardness between the case and the core is gradual. Since the core is not affected by flame hardening, there is little danger of spalling or flaking while the part is in use. Thus flame hardening produces a hard case that is highly resistant to wear and a core that retains its original properties. Flame hardening can be divided into five general methods: stationary, circular band progressive, straight-line progressive, spiral band progressive, and circular band spinning.



UNIT V



Various types of carbon steel

Carbon steel is steel in which the main interstitial alloying constituent is carbon in the range of 0.12–2.0%. The American Iron and Steel Institute (AISI) defines carbon steel as the following: "Steel is considered to be carbon steel when no minimum content is specified or required for chromium, cobalt, molybdenum, nickel, niobium, titanium, tungsten, vanadium or zirconium, or any other element to be added to obtain a desired alloying effect; when the specified minimum for copper does not exceed 0.40 percent; or when the maximum content specified for any of the following elements does not exceed the percentages noted:

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manganese 1.65, silicon 0.60, copper 0.60.

Types:

Carbon steel is broken down into four classes based on carbon content:

Mild and low-carbon steel

Mild steel also known as plain-carbon steel, is the most common form of steel because its price is relatively low while it provides material properties that are acceptable for many applications, more so than iron. Low-carbon steel contains approximately 0.05–0.320 % carbon making it malleable and ductile. Mild steel has a relatively low tensile strength, but it is cheap and malleable; surface hardness can be increased through carburizing.

It is often used when large quantities of steel are needed, for example as structural steel. The density of mild steel is approximately 7.85 g/cm^3 (7850 kg/m^3 or 0.284 lb/in^3) and the Young's modulus is 210 GPa (30,000,000 psi).

Low-carbon steels suffer from yield-point run out where the material has two yield points. The first yield point (or upper yield point) is higher than the second and the yield drops dramatically after the upper yield point. If low-carbon steel is only stressed to some point between the upper and lower yield point then the surface may develop louver bands. Low-carbon steels contain less carbon than other steels and are easier to cold-form, making them easier to handle.

Higher carbon steels

Carbon steels which can successfully undergo heat-treatment have carbon content in the range of 0.30–1.70% by weight. Trace impurities of various other elements can have a significant effect on the quality of the resulting steel. Trace amounts of sulfur in particular make the steel red-short, that is, brittle and crumbly at working temperatures. Low-alloy carbon steel, such as A36 grade, contains about 0.05% sulfur and melts around $1,426\text{--}1,53^\circ\text{C}$ ($2,599\text{--}2,800^\circ\text{F}$). Manganese is often added to improve the hardenability of low-carbon steels. These additions turn the material into low-alloy steel by some definitions, but AISI's definition of carbon steel allows up to 1.65% manganese by weight.

Low carbon steel

Less than 0.3% carbon content

Medium carbon steel

Approximately 0.30–0.59% carbon content. Balances ductility and strength and has good wear resistance; used for large parts, forging and automotive components.

High-carbon steel

Approximately 0.6–0.99% carbon content. Very strong, used for springs and high-strength wires.

Ultra-high-carbon steel

Approximately 1.0–2.0% carbon content. Steels that can be tempered to great hardness. Used for special purposes like (non-industrial-purpose) knives, axles or punches. Most steels with more than 1.2% carbon content are made using powder metallurgy. Note that steel with carbon content above 2.14% is considered cast iron.

Alloy steel

Alloy steel is steel that is alloyed with a variety of elements in total amounts between 1.0% and 50% by weight to improve its mechanical properties. Alloy steels are broken down into two groups: low-alloy steels and high-alloy steels. The difference between the two is somewhat

arbitrary: Smith and Hasemi define the difference at 4.0%, while Degarmo, et al., define it at 8.0%. Most commonly, the phrase "alloy steel" refers to low-alloy steels.

Types:

According to the World Steel Association, there are over 3,500 different grades of steel, encompassing unique physical, chemical and environmental properties.

In essence, steel is composed of iron and carbon, although it is the amount of carbon, as well as the level of impurities and additional alloying elements that determines the properties of each steel grade.

The carbon content in steel can range from 0.1-1.5%, but the most widely used grades of

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steel contain only 0.1-0.25% carbon. Elements such as manganese, phosphorus and sulphur are found in all grades of steel, but, whereas manganese provides beneficial effects, phosphorus and sulphur are deleterious to steel's strength and durability.

Different types of steel are produced according to the properties required for their application, and various grading systems are used to distinguish steels based on these properties. According to the American Iron and Steel Institute (AISI), steels can be broadly categorized into four groups based on their chemical compositions:

1. Carbon Steels
2. Alloy Steels
3. Stainless Steels
4. Tool Steels

1) Carbon Steels:

Carbon steels contain trace amounts of alloying elements and account for 90% of total steel production. Carbon steels can be further categorized into three groups depending on their carbon content:

- Low Carbon Steels/Mild Steels contain up to 0.3% carbon
- Medium Carbon Steels contain 0.3 – 0.6% carbon
- High Carbon Steels contain more than 0.6% carbon

2) Alloy Steels:

Alloy steels contain alloying elements (e.g. manganese, silicon, nickel, titanium, copper, chromium and aluminum) in varying proportions in order to manipulate the steel's properties, such as its hardenability, corrosion resistance, strength, formability, weldability or ductility. Applications for alloy steel include pipelines, auto parts, transformers, power generators and electric motors.

3) Stainless Steels:

Stainless steels generally contain between 10-20% chromium as the main alloying element

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and are valued for high corrosion resistance. With over 11% chromium, steel is about 200 times more resistant to corrosion than mild steel. These steels can be divided into three groups based on their crystalline structure:

- **Austenitic:** Austenitic steels are non-magnetic and non heat-treatable, and generally contain 18% chromium, 8% nickel and less than 0.8% carbon. Austenitic steels form the largest portion of the global stainless steel market and are often used in food processing equipment, kitchen utensils and piping.
- **Ferritic:** Ferritic steels contain trace amounts of nickel, 12-17% chromium, less than 0.1% carbon, along with other alloying elements, such as molybdenum, aluminum or titanium. These magnetic steels cannot be hardened with heat treatment, but can be strengthened by cold works.
- **Martensitic:** Martensitic steels contain 11-17% chromium, less than 0.4% nickel and up to 1.2% carbon. These magnetic and heat-treatable steels are used in knives, cutting tools, as well as dental and surgical equipment.

4) Tool Steels:

Tool steels contain tungsten, molybdenum, cobalt and vanadium in varying quantities to increase heat resistance and durability, making them ideal for cutting and drilling equipment.

Steel products can also be divided by their shapes and related applications:

- Long/Tubular Products include bars and rods, rails, wires, angles, pipes, and shapes and sections. These products are commonly used in the automotive and construction sectors.
- Flat Products include plates, sheets, coils and strips. These materials are mainly used in automotive parts, appliances, packaging, shipbuilding, and construction.
- Other Products include valves, fittings, and flanges and are mainly used as piping materials.

Cast iron

Cast iron is iron or a ferrous alloy which has been heated until it liquefies, and is then poured into a mould to solidify. It is usually made from pig iron. The alloy constituents affect

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its colour when fractured: white cast iron has carbide impurities which allow cracks to pass straight through. Grey cast iron has graphite flakes which deflect a passing crack and initiate countless new cracks as the material breaks.

Carbon (C) and silicon (Si) are the main alloying elements, with the amount ranging from 2.1–4 wt% and 1–3 wt%, respectively. Iron alloys with less carbon content are known as steel. While this technically makes these base alloys ternary Fe–C–Si alloys, the principle of cast iron solidification is understood from the binary iron–carbon phase diagram. Since the compositions of most cast irons are around the eutectic point of the iron–carbon system, the melting temperatures closely correlate, usually ranging from 1,150 to 1,200 °C (2,100 to 2,190 °F), which is about 300 °C (572 °F) lower than the melting point of pure iron.

Cast iron's properties are changed by adding various alloying elements, or alloyants. Next to carbon, silicon is the most important alloying because it forces carbon out of solution. Instead the carbon forms graphite which results in a softer iron, reduces shrinkage, lowers strength, and decreases density. Sulfur, when present, forms iron sulfide, which prevents the formation of graphite and increases hardness. The problem with sulfur is that it makes molten cast iron sluggish, which causes short run defects. To counter the effects of sulfur, manganese is added because the two form into manganese sulfide instead of iron sulfide. The manganese sulfide is lighter than the melt so it tends to float out of the melt and into the slag. The amount of manganese required to neutralize sulfur is $1.7 \times \text{sulfur content} + 0.3\%$. If more than this amount of manganese is added, then manganese carbide forms, which increases hardness and chilling, except in grey iron, where up to 1% of manganese increases strength and density.

Nickel is one of the most common alloying elements because it refines the pearlite and graphite structure, improves toughness, and evens out hardness differences between section thicknesses. Chromium is added in small amounts to the ladle to reduce free graphite, produce chill, and because it is a powerful carbide stabilizer; nickel is often added in conjunction. A small amount of tin can be added as a substitute for 0.5% chromium. Copper is added in the ladle or in the furnace, on the order of 0.5–2.5%, to decrease chill, refine graphite, and increase fluidity. Molybdenum is added on the order of 0.3–1% to increase chill and refine the graphite and pearlite structure; it is often added in conjunction with nickel, copper, and chromium to form high strength irons. Titanium is added as a degasser and

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deoxidizer, but it also increases fluidity. 0.15–0.5% vanadium is added to cast iron to stabilize cementite, increase hardness, and increase resistance to wear and heat. 0.1–0.3% zirconium helps to form graphite, deoxidize, and increase fluidity.

In malleable iron melts, bismuth is added, on the scale of 0.002–0.01%, to increase how much silicon can be added. In white iron, boron is added to aid in the production of malleable iron; it also reduces the coarsening effect of bismuth.

Grey cast iron

Grey cast iron is characterised by its graphitic microstructure, which causes fractures of the material to have a grey appearance. It is the most commonly used cast iron and the most widely used cast material based on weight. Most cast irons have a chemical composition of 2.5–4.0% carbon, 1–3% silicon, and the remainder is iron. Grey cast iron has less tensile strength and shock resistance than steel, but its compressive strength is comparable to low and medium carbon steel.

White cast iron

It is the cast iron that displays white fractured surface due to the presence of cementite. With a lower silicon content (graphitizing agent) and faster cooling rate, the carbon in white cast iron precipitates out of the melt as the metastable phase cementite, Fe_3C , rather than graphite. The cementite which precipitates from the melt forms as relatively large particles, usually in a eutectic mixture, where the other phase is austenite (which on cooling might transform to martensite). These eutectic carbides are much too large to provide precipitation hardening (as in some steels, where cementite precipitates might inhibit plastic deformation by impeding the movement of dislocations through the ferrite matrix). Rather, they increase the bulk hardness of the cast iron simply by virtue of their own very high hardness and their substantial volume fraction, such that the bulk hardness can be approximated by a rule of mixtures. In any case, they offer hardness at the expense of toughness. Since carbide makes up a large fraction of the material, white cast iron could reasonably be classified as a cermet. White iron is too brittle for use in many structural components, but with good hardness and abrasion resistance and relatively low cost, it finds use in such applications as the wear surfaces (impeller and volute) of slurry pumps, shell liners and lifter bars in ball mills and autogenous grinding mills, balls and rings in coal pulverisers, and the teeth of a backhoe's

digging bucket (although cast medium-carbon martensitic steel is more common for this application).

It is difficult to cool thick castings fast enough to solidify the melt as white cast iron all the way through. However, rapid cooling can be used to solidify a shell of white cast iron, after which the remainder cools more slowly to form a core of grey cast iron. The resulting casting, called a chilled casting, has the benefits of a hard surface and a somewhat tougher interior.

High-chromium white iron alloys allow massive castings (for example, a 10-tonne impeller) to be sand cast, i.e., a high cooling rate is not required, as well as providing impressive abrasion resistance. These high-chromium alloys attribute their superior hardness to the presence of chromium carbides. The main form of these carbides are the eutectic or primary M_7C_3 carbides, where "M" represents iron or chromium and can vary depending on the alloy's composition. The eutectic carbides form as bundles of hollow hexagonal rods and grow perpendicular to the hexagonal basal plane. The hardness of these carbides are within the range of 1500-1800HV

Malleable cast iron

Malleable iron starts as a white iron casting that is then heat treated at about 900 °C (1,650 °F). Graphite separates out much more slowly in this case, so that surface tension has time to form it into spheroidal particles rather than flakes. Due to their lower aspect ratio, spheroids are relatively short and far from one another, and have a lower cross section vis-a-vis a propagating crack or phonon. They also have blunt boundaries, as opposed to flakes, which alleviates the stress concentration problems faced by grey cast iron. In general, the properties of malleable cast iron are more like mild steel. There is a limit to how large a part can be cast in malleable iron, since it is made from white cast iron.

Ductile cast iron

A more recent development is nodular or ductile cast iron. Tiny amounts of magnesium or cerium added to these alloys slow down the growth of graphite precipitates by bonding to the edges of the graphite planes. Along with careful control of other elements and timing, this allows the carbon to separate as spheroidal particles as the material solidifies. The properties are similar to malleable iron, but parts can be cast with larger sections.

TYPICAL USES

Cast iron is used in a wide variety of structural and decorative applications, because it is relatively inexpensive, durable and easily cast into a variety of shapes. Most of the typical uses include:

- historic markers and plaques
- hardware: hinges, latches
- columns, balusters
- stairs
- structural connectors in buildings and monuments
- decorative features
- fences
- tools and utensils
- ordnance
- stoves and firebacks
- piping.

The basic cast iron material in all of these applications may appear to be the same, or very similar, however, the component size, composition, use, condition, relationship to adjacent materials, exposure and other factors may dictate that different treatments be used to correct similar problems. Any material in question should be evaluated as a part of a larger system and treatment plans should be based upon consideration of all relevant factors.

NON FERROUS METAL & ALLOYS

Copper

- ❖ Copper is one of the earliest metals discovered by man.
- ❖ The boilers on early steamboats were made from copper.
- ❖ The copper tubing used in water plumbing in Pyramids was found in serviceable condition after more than 5,000 years.
- ❖ Cu is a ductile metal. Pure Cu is soft and malleable, difficult to machine.
- ❖ Very high electrical conductivity – second only to silver.

- ❖ Copper is refined to high purity for many electrical

Applications

- Excellent thermal conductivity – Copper cookware most highly regarded – fast and uniform heating.
- Electrical and construction industries are the largest users of Cu.

Copper Alloys

- Brasses and Bronzes are most commonly used alloys of Cu. Brass is an alloy with Zn. Bronzes contain tin, aluminum, silicon or beryllium.
- Other copper alloy families include copper-nickels and nickel silvers. More than 400 copper-base alloys are recognized.

Applications

- Electrical wires,
- roofing, nails, rivets
- Automotive radiator
- core, lamp fixture,
- clutch disk,
- diaphragm, fuse clips,
- springs
- Furniture, radiator
- fittings, battery clamps,
- light fixtures
- Bearings, bushings,
- valve seats and guards
- Electrical, valves,
- pumps
- Condenser, heat exchanger
- piping,

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- valves
- Tin bronze Sn,
- Bearings, bushing,
- piston rings, gears

Aluminum

- Aluminum is a light metal & easily machinable; has wide variety of surface finishes; good electrical and thermal conductivities; highly reflective to heat and light.
- Versatile metal - can be cast, rolled, stamped, drawn, spun, roll-formed, hammered, extruded and forged into many shapes.
- Aluminum can be riveted, welded, brazed, or resin bonded.
- Corrosion resistant - no protective coating needed, however it is often anodized to improve surface finish, appearance.
- Al and its alloys - high strength-to-weight ratio (high specific strength) owing to low density.
- Such materials are widely used in aerospace and automotive applications where weight savings are needed for better fuel efficiency and performance.

Application of some Al Alloys

- Food/chemical handling
- equipment, heat exchangers
- light reflectors
- Utensils, pressure vessels and
- piping
- Strain-hardened.
- Bellows, clutch disk,
- diaphragm, fuse clips, springs
- Heat treated
- Aircraft structure, rivets, truck
- wheels, screw
- Trucks, canoes, railroad cars,

- furniture, pipelines
- Peak-aged
- Aircraft structures and other
- highly loaded applications
- Aircraft pump parts,
- automotive transmission
- cases, cylinder blocks

inc

Zinc (symbol Zn), in commerce also spelter, is a metallic chemical element. It has atomic number 30. It is the first element of group 12 of the periodic table. In some respects zinc is chemically similar to magnesium: its ion is of similar size and its only common oxidation state is

+2. Zinc is the 24th most abundant element in the Earth's crust and has five stable isotopes. The most common zinc ore is sphalerite (zinc blende), a zinc sulfide mineral. The largest mineable amounts are found in Australia, Asia, and the United States. Zinc production includes froth flotation of the ore, roasting, and final extraction using electricity (electrowinning).

Brass, which is an alloy of copper and zinc, has been used since at least the 10th century BC in Judea and by the 7th century BC in Ancient Greece. Zinc metal was not produced on a large scale until the 12th century in India and was unknown to Europe until the end of the 16th century. The mines of Rajasthan have given definite evidence of zinc production going back to 6th century BC. To date, the oldest evidence of pure zinc comes from Zawar, in Rajasthan, as early as the 9th century AD when a distillation process was employed to make pure zinc. Alchemists burned zinc in air to form what they called "philosopher's wool" or "white snow".

Applications

Major applications of zinc include

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- Galvanizing (55%)
- Alloys (21%)
- Brass and bronze (16%)
- Miscellaneous (8%)

The metal is most commonly used as an anti-corrosion agent. Galvanization, which is the coating of iron or steel to protect the metals against corrosion, is the most familiar form of using zinc in this way. In 2009 in the United States, 55% or 893 thousand tonnes of the zinc metal was used for galvanization.

Zinc is more reactive than iron or steel and thus will attract almost all local oxidation until it completely corrodes away. A protective surface layer of oxide and carbonate forms as the zinc corrodes. This protection lasts even after the zinc layer is scratched but degrades through time as

the zinc corrodes away. The zinc is applied electrochemically or as molten zinc by hot-dip galvanizing or spraying. Galvanization is used on chain-link fencing, guard rails, suspension bridges, light posts, metal roofs, heat exchangers, and car bodies.

The relative reactivity of zinc and its ability to attract oxidation to itself makes it an efficient sacrificial anode in cathodic protection (CP). For example, cathodic protection of a buried pipeline can be achieved by connecting anodes made from zinc to the pipe. Zinc acts as the anode (negative terminus) by slowly corroding away as it passes electric current to the steel pipeline. Zinc is also used to cathodically protect metals that are exposed to sea water from corrosion. A zinc disc attached to a ship's iron rudder will slowly corrode while the rudder stays unattacked. Other similar uses include a plug of zinc attached to a propeller or the metal protective guard for the keel of the ship.

With a standard electrode potential (SEP) of -0.76 volts, zinc is used as an anode material for batteries. (More reactive lithium (SEP -3.04 V) is used for anodes in lithium batteries). Powdered zinc is used in this way in alkaline batteries and sheets of zinc metal form the cases for and act as anodes in zinc-carbon batteries.[98][99] Zinc is used as the anode or fuel of the zinc-air battery/fuel cell. The zinc-cerium redox flow battery also relies on a zinc-based negative half-cell.

Alloys

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A widely used alloy which contains zinc is brass, in which copper is alloyed with anywhere from 3% to 45% zinc, depending upon the type of brass. Brass is generally more ductile and stronger than copper and has superior corrosion resistance. These properties make it useful in communication equipment, hardware, musical instruments, and water valves.

Other widely used alloys that contain zinc include nickel silver, typewriter metal, soft and aluminium solder, and commercial bronze. Zinc is also used in contemporary pipe organs as a substitute for the traditional lead/tin alloy in pipes.[104] Alloys of 85–88% zinc, 4–10% copper, and 2–8% aluminium find limited use in certain types of machine bearings. Zinc is the primary metal used in making American one cent coins since 1982. The zinc core is coated with a thin layer of copper to give the impression of a copper coin. In 1994, 33,200 tonnes (36,600 short tons) of zinc were used to produce 13.6 billion pennies in the United States. Alloys of primarily

zinc with small amounts of copper, aluminium, and magnesium are useful in die casting as well as spin casting, especially in the automotive, electrical, and hardware industries. These alloys are marketed under the name Zamak. An example of this is zinc aluminium. The low melting point together with the low viscosity of the alloy makes the production of small and intricate shapes possible. The low working temperature leads to rapid cooling of the cast products and therefore fast assembly is possible. Another alloy, marketed under the brand name Prestal, contains 78% zinc and 22% aluminium and is reported to be nearly as strong as steel but as malleable as plastic. This superplasticity of the alloy allows it to be molded using die casts made of ceramics and cement.

Similar alloys with the addition of a small amount of lead can be cold-rolled into sheets. An alloy of 96% zinc and 4% aluminium is used to make stamping dies for low production run applications for which ferrous metal dies would be too expensive. In building facades, roofs or other applications in which zinc is used as sheet metal and for methods such as deep drawing, roll forming or bending, zinc alloys with titanium and copper are used. Unalloyed zinc is too brittle for these kinds of manufacturing processes.

As a dense, inexpensive, easily worked material, zinc is used as a lead replacement. In the wake of lead concerns, zinc appears in weights for various applications ranging from fishing to tire balances and flywheels.

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Cadmium zinc telluride (CZT) is a semi conductive alloy that can be divided into an array of small sensing devices. These devices are similar to an integrated circuit and can detect the energy of incoming gamma ray photons. When placed behind an absorbing mask, the CZT sensor array can also be used to determine the direction of the rays.

Other industrial uses

Zinc oxide is used as a white pigment in paints. Roughly one quarter of all zinc output in the United States (2009), is consumed in the form of zinc compounds; a variety of which are used industrially. Zinc oxide is widely used as a white pigment in paints, and as a catalyst in the manufacture of rubber. It is also used as a heat disperser for the rubber and acts to protect its polymers from ultraviolet radiation (the same UV protection is conferred to plastics containing zinc oxide) The semiconductor properties of zinc oxide make it useful invaristors and photocopying products. The zinc zinc-oxide cycle is a two step thermochemical process based on zinc and zinc oxide for hydrogen production.

Zinc chloride is often added to lumber as a fire retardant and can be used as a wood preservative. It is also used to make other chemicals.

Crystals of ZnS are used in lasers that operate in the mid-infrared part of the spectrum. Zinc sulfate is a chemical in dyes and pigments. Zinc pyrithione is used in antifouling paints.

Zinc powder is sometimes used as a propellant in model rockets. When a compressed mixture of 70% zinc and 30% sulfur powder is ignited there is a violent chemical reaction. This produces zinc sulfide, together with large amounts of hot gas, heat, and light. Zinc sheet metal is used to make zinc bars.

Zn, the most abundant isotope of zinc, is very susceptible to neutron activation, being transmuted into the highly radioactive

Zn, which has a half-life of 244 days and produces intense gamma radiation. Because of this, Zinc Oxide used in nuclear reactors as an anti-corrosion agent is depleted of

Zn before use, this is called depleted zinc oxide. For the same reason, zinc has been proposed as a salting material for nuclear weapons (cobalt is another, better-known salting material). A jacket of isotopically enriched

Zn would be irradiated by the intense high-energy neutron flux from an exploding thermonuclear weapon, forming a large amount of

Zn significantly increasing the radioactivity of the weapon's fallout. Such a weapon is not known to have ever been built, tested, or used.

Zn is also used as a tracer to study how alloys that contain zinc wear out, or the path and the role of zinc in organisms.

Chromium

Chromium is a chemical element which has the symbol Cr and atomic number 24. It is the first element in Group 6. It is a steely-gray, lustrous, hard and brittle metal which takes a high polish,

resists tarnishing, and has a high melting point. Chromium oxide was used by the Chinese in the Qin dynasty over 2,000 years ago to coat metal weapons found with the Terracotta Army. Chromium was discovered as an element after it came to the attention of the western world in the red crystalline mineral crocoite (lead(II) chromate), discovered in 1761 and initially used as a pigment. Louis Nicolas Vauquelin first isolated chromium metal from this mineral in 1797. Since Vauquelin's first production of metallic chromium, small amounts of native (free) chromium metal have been discovered in rare minerals, but these are not used commercially. Instead, nearly all chromium is commercially extracted from the single commercially viable ore chromite, which is iron chromium oxide. Chromite is also now the chief source of chromium for chromium pigments.

Applications

The strengthening effect of forming stable metal carbides at the grain boundaries and the strong increase in corrosion resistance made chromium an important alloying material for steel. The high-speed tool steels contain between 3 and 5% chromium. Stainless steel, the main corrosion-proof metal alloy, is formed when chromium is added to iron in sufficient concentrations, usually above 11%. For its formation, ferrochromium is added to the molten iron. Also nickel-based alloys increase in strength due to the formation of discrete, stable metal carbide particles at the grain boundaries. For example, Inconel 718 contains 18.6% chromium. Because of the excellent high-temperature properties of these nickel superalloys,

they are used in jet engines and gas turbines in lieu of common structural materials.

The relative high hardness and corrosion resistance of unalloyed chromium makes it a good surface coating, being still the most "popular" metal coating with unparalleled combined durability. A thin layer of chromium is deposited on pretreated metallic surfaces by electroplating techniques. There are two deposition methods: Thin, below 1 μm thickness, layers are deposited by chrome plating, and are used for decorative surfaces. If wear-resistant surfaces are needed then thicker chromium layers are deposited. Both methods normally use acidic chromate or dichromate solutions. To prevent the energy-consuming change in oxidation state, the use of chromium(III) sulfate is under development, but for most applications, the established process is used.

In the chromate conversion coating process, the strong oxidative properties of chromates are used to deposit a protective oxide layer on metals like aluminium, zinc and cadmium. This passivation and the self-healing properties by the chromate stored in the chromate conversion coating, which is able to migrate to local defects, are the benefits of this coating method. Because of environmental and health regulations on chromates, alternative coating methods are under development.

Anodizing of aluminium is another electrochemical process, which does not lead to the deposition of chromium, but uses chromic acid as electrolyte in the solution. During anodization, an oxide layer is formed on the aluminium. The use of chromic acid, instead of the normally used sulfuric acid, leads to a slight difference of these oxide layers. The high toxicity of Cr(VI) compounds, used in the established chromium electroplating process, and the strengthening of safety and environmental regulations demand a search for substitutes for chromium or at least a change to less toxic chromium(III) compounds.

Dye and pigment

The mineral crocoite (lead chromate PbCrO_4) was used as a yellow pigment shortly after its discovery. After a synthesis method became available starting from the more abundant chromite, chrome yellow was, together with cadmium yellow, one of the most used yellow pigments. Chromium oxides are also used as a green color in glassmaking and as a glaze in ceramics. Green chromium oxide is extremely light-fast and as such is used in cladding coatings. It is also the main ingredient in IR reflecting paints, used by the armed forces, to

paint vehicles, to give them the same IR reflectance as green leaves.

Synthetic ruby and the first laser

Natural rubies are corundum (aluminum oxide) crystals that are colored red (the rarest type) due to chromium (III) ions (other colors of corundum gems are termed sapphires). A red-colored artificial ruby may also be achieved by doping chromium(III) into artificial corundum crystals, thus making chromium a requirement for making synthetic rubies

Wood preservative

Because of their toxicity, chromium(VI) salts are used for the preservation of wood. For example, chromated copper arsenate (CCA) is used in timber treatment to protect wood from decay fungi, wood attacking insects, including termites, and marine borers

Refractory material

The high heat resistivity and high melting point makes chromite and chromium(III) oxide a material for high temperature refractory applications, like blast furnaces, cement kilns, molds for the firing of bricks and as foundry sands for the casting of metals. In these applications, the refractory materials are made from mixtures of chromite and magnesite. The use is declining because of the environmental regulations due to the possibility of the formation of chromium(VI).

Brasses & Bronzes

Brass is an alloy made of copper and zinc; the proportions of zinc and copper can be varied to create a range of brasses with varying properties. Bronze is an alloy consisting primarily of copper, usually with tin as the main additive. It is hard and tough, and it was so significant in antiquity that the Bronze Age was named after the metal.

Admiralty brass contains 30% zinc, with 1% tin to inhibit dezincification in many environments. Alpha brasses with less than 35% zinc, are malleable, can be worked cold, and are used in pressing, forging, or similar applications. They contain only one phase, with face-centered cubic crystal structure. Alpha-beta brass (Muntz metal), also called duplex brass, is 35–45% zinc and is suited for hot working. It contains both α and β' phase; the β' -phase is body-centered cubic and is harder and stronger than α . Alpha-beta brasses are usually worked

hot. Aluminium brass contains aluminium, which improves its corrosion resistance. Red brass is both an American term for the copper-zinc-tin alloy known as gunmetal, and an alloy which is considered both a brass and a bronze. It typically contains 85% copper, 5% tin, 5% lead, and 5% zinc.

Aluminium Bronze

A type of BRONZE in which aluminium is the main alloying metal added to copper. Small amounts of other elements such as iron, manganese, nickel and silicon are added to impart

various properties such as corrosion resistance or malleability. It fares well in the marine environment.

Typical composition:

Copper 80%

Aluminium 10%

Nickel 5%

Iron 5%

Silicon Bronze

Has small amounts of silicon to allow it to be wrought or cold worked into a stronger alloy such as by rolling. It is also resistant to corrosion and therefore good for use in the marine environment. Typical composition:

Copper 96%

Silicon 3%

Manganese 1%

Phosphor bronze

Well this one is different! Rather than Phosphor being the main alloy metal, it is used during manufacture to purify the melt and create a purer stronger type of bronze. Usually not more than 0.2% of the Phosphur is left in the metal. It is very corrosion resistant and therefore good in the marine environment.

Typical composition:

Copper 94.8%

Tin 5%

Phosphorus 0.2%

Leaded Bronze

Leaded Gunmetal (LG2) Is a type of copper alloy that has a small amount of lead, tin and zinc added in similar quantities. It is not considered to be brass due to the amount of zinc being small. It has widespread use as a valve and through hull fitting material due to its good seawater resistance. It does not de-zincify in seawater despite having a zinc content. It is good for use in the marine environment.

Typical composition:

Copper 85%

Lead 5%

Tin 5%

Zinc 5%

Bronze was especially suitable for use in boat and ship fittings prior to the wide employment of stainless steel owing to its combination of toughness and resistance to salt water corrosion. Bronze is still commonly used in ship propellers and submerged bearings.

In the 20th century, silicon was introduced as the primary alloying element, creating an alloy with wide application in industry and the major form used in contemporary statuary. Sculptors may prefer silicon bronze because of the ready availability of silicon bronze brazing rod, which allows color-matched repair of defects in castings. Aluminium is also used for the structural metal aluminium bronze.

It is also widely used for cast bronze sculpture. Many common bronze alloys have the unusual and very desirable property of expanding slightly just before they set, thus filling in the finest details of a mold. Bronze parts are tough and typically used for bearings, clips, electrical connectors and springs.

Bronze also has very low metal-on-metal friction, which made it invaluable for the building of cannon where iron cannonballs would otherwise stick in the barrel. It is still widely used today for springs, bearings, bushings, automobile transmission pilot bearings, and similar fittings, and is particularly common in the bearings of small electric motors. Phosphor bronze is particularly suited to precision-grade bearings and springs. It is also used in guitar and

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piano strings.

Unlike steel, bronze struck against a hard surface will not generate sparks, so it (along with beryllium copper) is used to make hammers, mallets, wrenches and other durable tools to be used in explosive atmospheres or in the presence of flammable vapors.

Bronze is used to make bronze wool for woodworking applications where steel wool would discolor oak.

