

Engineering Materials

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Chapter One Fundamentals of Engineering Materials

1.1. Introduction

Materials are substance of which something is composed or made. Since civilization began, materials along with energy have been used by people to improve their standard living. Materials are everywhere about us since products are made of materials. Some of the commonly encountered materials are wood, concrete, steel, glass, rubber, iron etc. the production and processing of materials into finished products constitute a large part of our present economy. Engineers design most manufactured products and the processing systems required for their production. Since products are requiring materials, engineers should be knowledgeable about the internal structure and properties of materials so that they will be able to select the most suitable ones for each application and should be able to develop the best processing methods.

1.2. Material science and engineering

Material sciences is primarily concerned with the search of for basic knowledge about the internal structure, properties, and processing of materials. Whereas, Engineering material is concerned the use of the fundamental and applied knowledge of materials so that materials can be converted into products necessary or desired by society.

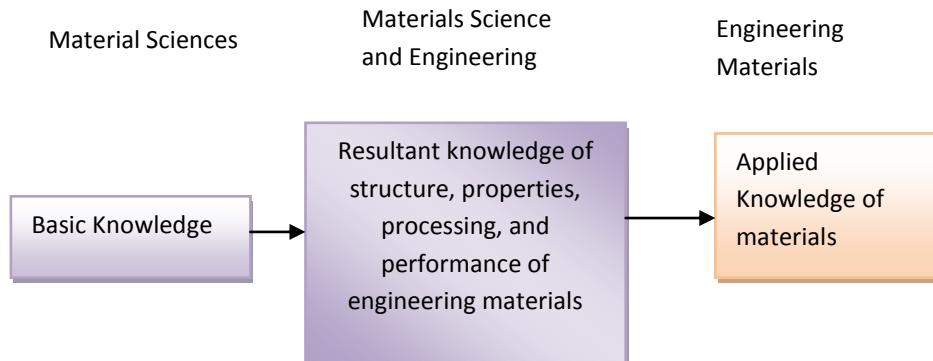


Figure 1.1. Materials knowledge Spectrum

Material sciences is at the basic knowledge end of the materials knowledge spectrum and engineering materials is at applied knowledge end, and there is no clear demarcation between them (Fig 1.1).

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Figure 1.1. Shows three-ringed diagrams which indicates the relationship among basic sciences (and mathematics), material sciences, and engineering, and the other engineering disciplines. The basic sciences are located within the first ring or core of the diagrams, while the various engineering disciplines (Mechanical, electrical, civil, chemical, etc) are located in the out most third ring. The applied sciences, metallurgy, ceramics, and polymer sciences are located in the middle or the second ring. Material sciences and engineering is shown to form a bridge of material knowledge from the basic science to engineering disciplines.

1.3. Engineering materials classification

For Convenience engineering materials are divided into three main classes: Metallic, polymeric (Plastics), and ceramics materials. In addation of three main classes of material, we shall consider two more types, composite materials and electronic materials because of recently fastly developed and great engineering materials.

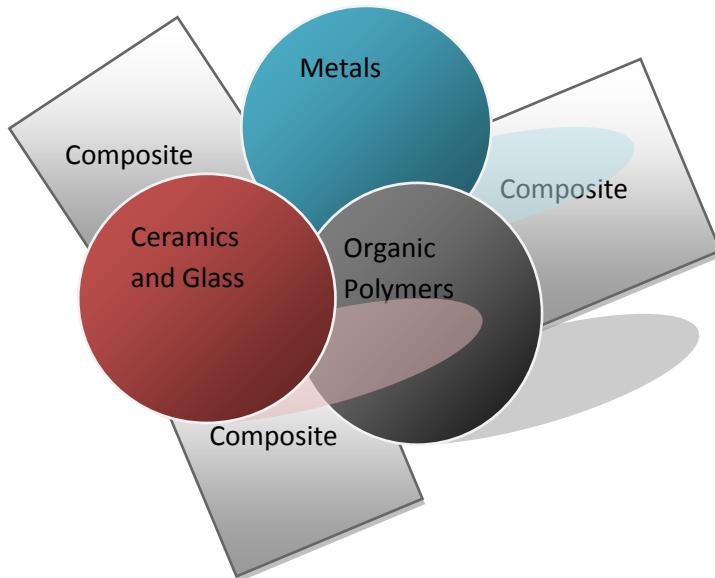
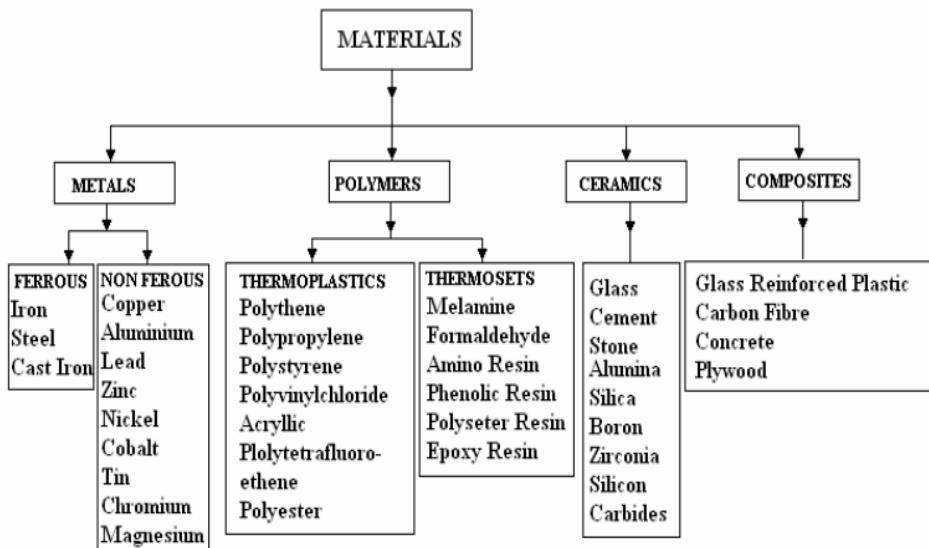


Figure 1.2. Diagram representation of engineering material classification

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1.3. Engineering Material Classification

1.3.1. Metal

These materials are inorganic substances which are composed one or more metallic elements and may also contain some non-metallic elements. Examples of metallic elements such as iron, copper, aluminum, nickel, etc. Non-metallic elements such as carbon, nitrogen, and oxygen and may also be contained in metallic minerals. Metals in general are good thermal and electrical conductors. Many metals relatively strong and ductile at room temperatures.

Metals and alloys are commonly divided in to two classes: Ferrous metals and alloys that contain a large percentage of iron such as the steel and cast irons and non-ferrous metals and alloys that do not contain iron or only a relatively small amount of iron. Eg. Aluminum, copper, zinc, titanium, and nickel.

1.3.2. Polymeric Materials

Most polymeric materials consist of organic (Carbon-containing) long molecular chain or networks. Structurally, most polymeric materials are non-crystalline but some consists of mixture of crystalline and non-crystalline regions. The strength and ductility of polymeric materials vary greatly. Most polymeric materials are poor

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conductors of electricity. Some of these materials are good insulators and are used for electrical insulative applications.

In general, polymeric materials have low density and relatively low softening decomposition temperature.

1.3.3. Ceramic materials

Ceramic materials are inorganic materials which consist of metallic and non-metallic elements chemically bonded together. Ceramic materials can be crystalline, non-crystalline, or mixture of both. Most ceramic materials high hardness and high-temperature strength but tend to have mechanically brittleness. Advantage of ceramic materials are light weight, high strength, and hardness, good heat and wear resistance, reduced friction, insulative properties.

The insulative property along with the high heat and wear resistance of many ceramics make them useful for furnaces lining for high temperature of liquid metals such as steel.

1.3.4. Composite Materials

Composite materials are a mixture of two or more materials. Most composite materials consist of a selected filler or reinforced material and a compatible risen binder to obtain the specific characteristics and properties desired. Usually, the components do not dissolve in each other and can be physically identified by an interface between the components. Composites can be of many types. Some of the predominant types are fibrous (composed of fibers in a matrix) and particulate (composed of particle in a matrix). It can be used widely for transport equipments due to light weight and excellent corrosion resistant.

1.3.5. Electronic Materials

Electronic materials are not major type of materials by volume but are an extremely important type of materials for advanced engineering technology. The most important electronic materials is pure silicon which is modified in various ways to change its electrical characteristics.

1.3. 6. Smart Materials

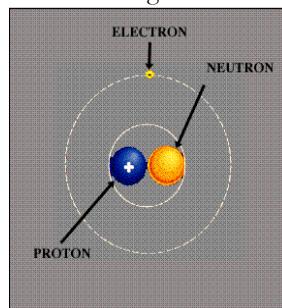
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Chapter Two

Atomic Structure and Interatomic Bonding

2.1. Atomic structure

Atom is the basic and smallest unit of an element that can undergo chemical change. They are the basis for everything in the Universe. You should start by remembering that matter is composed of atoms. We're going to cover basics like atomic structure and bonding between atoms. Are there pieces of matter that are smaller than atoms? Sure there are. You'll soon be learning that atoms are composed of pieces like neutrons, electrons, and protons. The parts of atoms are the electrons, protons, and neutrons. What are electrons, protons, and neutrons? There are three pieces to an atom. There are electrons, protons, and neutrons. That's all you have to remember. Three things! As you know, there are over 100 elements in the periodic table. The thing that makes each of those elements different is the number of electrons, protons, and neutrons. The protons and neutrons are always in the center of the atom. Scientists call the center of the atom the nucleus. The electrons are always found whizzing around the center in areas called orbital. You can also see that each piece has either a "+", "-", or a "0." That symbol refers to the charge of the particle. You know when you get a shock from a socket, static electricity, or lightning? Those are all different types of electric charges. There are even charges in tiny particles of matter like atoms. The electron always has a "-" or negative charge. The proton always has a "+" or positive charge. If the charge of an entire atom is "0", that means there are equal numbers of positive and negative pieces, equal numbers of electrons and protons. The third particle is the neutron. It has a neutral charge (a charge of zero).



Particle	Symbol	Location	Relative electrical charge	Approximate relative mass in amu	Actual mass in grams
Electron	e ⁻	orbits the nucleus	1-	1/1840	9.11×10^{-28}
Proton	p ⁺	nucleus	1+	1	1.66×10^{-24}
Neutron	n ⁰	nucleus	0	1	1.66×10^{-24}

amu (atomic mass unit = 1.66×10^{-24} grams)

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	I	II	Transition elements														III	IV	V	VI	VII	VIII
1	1 H																5 B	6 C	7 N	8 O	9 F	2 He
2	3 Li	4 Be															13 Al	14 Si	15 P	16 S	17 Cl	10 Ne
3	11 Na	12 Mg															14 Si	15 P	16 S	17 Cl	18 Ar	
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr				
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe				
6	55 Cs	56 Ba															85 At	86 Rn				

Metals
Metalloids
Nonmetals

2.2. Atomic Bonds

Chemical bonds between atoms occur since there is a net decrease in the potential energy of an atom in bonded state. This is, atoms in the bonded state are more stable energy condition than when they are unbounded. In general, chemical bonds between an atom can be divided into two groups: primary and secondary or weak bonds.

2.2.1. Primary Bonds

Primary bonds are the strongest bonds which hold atoms together. The three types of primary bonds are: Covalent Bonds, Ionic Bonds, and Metallic Bonds

a. Ionic Bonds

Atoms like to have a filled outer shell of electrons. Sometimes, by transferring electrons from one atom to another, electron shells are filled. The donor atom will take a positive charge, and the acceptor will have a negative charge. The charged atoms or ions will be attracted to each other, and form bonds. The compound NaCl is a good example.

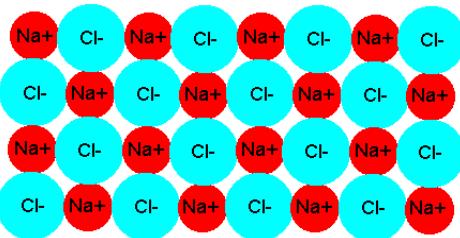


Figure 2.1. ionic bond between Na and Cl

The electron structure of atoms is relatively stable when the outer shells contain eight electrons (or two in the case of the first shell). An element like sodium with **one excess electron will give it up** so that it has a **completely filled outer shell**. It will then have more protons than electrons and become a positive ion (charged atom) with a +1 charge. An atom of chlorine, on the other hand, with **seven electrons in its outer shell would like to accept one electron**. When it does, it

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will have one more electron than protons and become a negative **ion with a -1 charge**. When sodium and chlorine atoms are placed together, there is a **transfer of electrons from the sodium to the chlorine atoms**, resulting in a strong **electrostatic attraction between the positive sodium ions and the negative chlorine ions**. This explains the strong attraction between paired ions typical of the gas or liquid state. Ionic bond is **non-direction bond** because of ions attracted by cations in any direction.

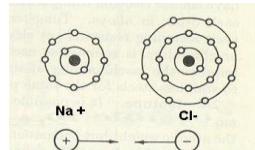
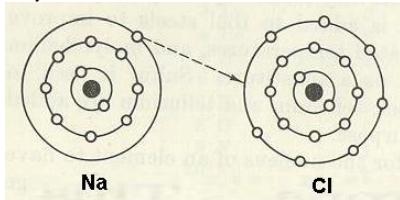
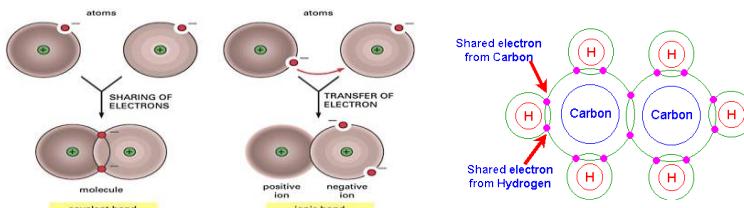


Figure 4a. Formation of ionic bond in NaCl. Figure 4b. Na⁺ and Cl⁻ ions formed by ionic bonding mechanism.

Covalent Bonds: Some atoms like to share electrons to complete their outer shells.



Each pair of shared atoms is called **a covalent bond**. Covalent bonds are called directional because the atoms tend to remain in fixed positions with respect to each other. Covalent bonds are also very strong. Examples include diamond, and the O-O and N-N bonds in oxygen and nitrogen gases.

Metallic Bonds

In metals, the metal atoms lose their outer electrons to form metal cations. The electrons from all the metal atoms form a "sea" of electrons that can flow around these metal cations. These electrons are often described as **delocalized electrons** - delocalized means "not fixed in one place" or "free to move".

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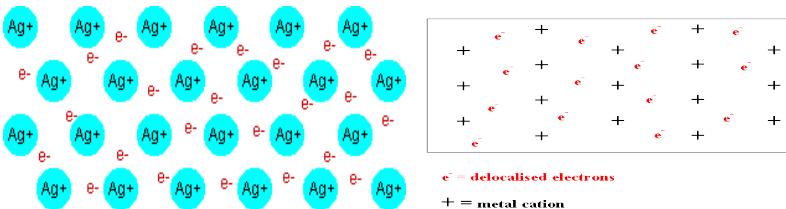
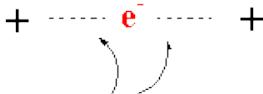


Figure 1. Metallic bond of Silver

AS THE METAL CATIONS AND THE ELECTRONS ARE OPPositely CHARGED, THEY WILL BE ATTRACTED TO EACH OTHER, AND ALSO TO OTHER METAL CATIONS. THESE ELECTROSTATIC FORCES ARE CALLED METALLIC BONDS, AND THESE ARE WHAT HOLD THE PARTICLES TOGETHER IN METALS.

e^- = delocalised electrons



$+$ = metal cation

Electrostatic forces of attraction

The lack of oppositely charged ions in the metallic structure and lack of sufficient valence electrons to form a true covalent bond necessitate the sharing of valence electrons by more than two atoms. Each of the atoms of the metal contributes its valence electrons to the formation of the negative "electron cloud". These electrons are not associated with a particular ion but are free to move among the positive metallic ions in definite energy levels. The metallic ions are held together by virtue of their mutual attraction for the negative electron cloud.

A result of the sharing of electrons is the cations arrange themselves in a regular pattern. This regular pattern of atoms is the crystalline structure of metals. In the crystal lattice, atoms are packed closely together to maximize the strength of the bonds. An actual piece of metal consists of many tiny crystals called grains that touch at grain boundaries.

The metallic bond yields three physical characteristics typical of solid metals:

- Metals are good conductors of electricity.
- Metals are good conductors of heat.
- Metals have a lustrous appearance. In addition, most metals are malleable, ductile, and generally denser than other elemental substance.

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2.2.2. Secondary Bonds

Secondary bonds are much weaker than primary bonds. They often provide a "weak link" for deformation or fracture. Examples for secondary bonds are:

Hydrogen Bonds

Van der Waals Bonds

a. Hydrogen Bonds

Hydrogen bonds are common in covalently bonded molecules which contain hydrogen, such as water (H_2O). Since the bonds are primarily covalent, the electrons are shared between the hydrogen and oxygen atoms. However, the electrons tend to spend more time around the oxygen atom. This leads to a small positive charge around the hydrogen atoms, and a negative charge around the oxygen atom. When other molecules with this type of charge transfer are nearby, the negatively charged end of one molecule will be weakly attracted to the positively charged end of the other molecule. The attraction is weak because the charge transfer is small.

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Chapter Three

Crystal structure of Metals

3.1. Introduction

3.2. Crystal structure

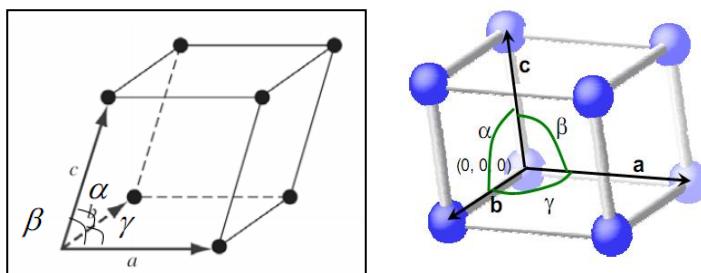
Crystal: a solid composed of atoms, ions, or molecules arranged in a pattern that is repeated in three dimensions.

The unit cell: is a structural unit or building block that can describe the crystal structure. Repetition of the unit cell generates the entire crystal.

Crystalline structure: a regular three dimensional patterns of atoms or ions in space.

Space lattice: a three dimensional array of points each of which has identical surroundings.

Lattice point: one point in an array in which all the points of each has identical surroundings. When discussing crystal structure, it is usually assumed that the space lattice continues to infinity in all directions. The intersections of the lines, called **lattice points**, represent locations in space with the same kind of atom or group of atoms of identical composition, arrangement, and orientation. The geometry of a space lattice is completely specified by **the lattice constants** a , b , and c and the **interaxial angles α , β , and γ** . The **unit cell** of a crystal is the smallest pattern of arrangement that can be contained in a parallelepiped, the edges of which form a , b , and c axes of the crystal.



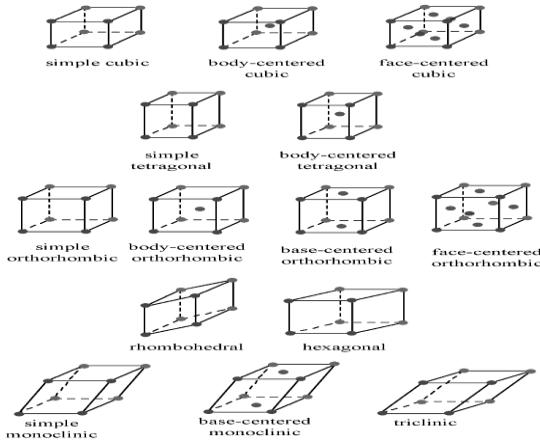
All crystal systems can be grouped into one of seven basic systems, which can be arranged in 14 different ways, called Brava's. It should be noted that the unit cell edge lengths and axial angles are unique for each crystalline substance. The unique edge lengths are parameters. other than 90°

Crystal system	Edge length	Interaxial angle
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$

called lattice
Axial angles
or 120° can

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also change slightly with changes in composition. When the edges of the unit cell are not equal in all three directions, all unequal lengths must be stated to completely define the crystal. The same is true if all axial angles are not equal.



3.3. Major Metallic Crystalline Structures

Almost all structural metals crystallize into one of three crystalline patterns: face centered cubic, hexagonal close-packed or body-centered cubic (Fig.1.7.1)

Primary Metallic Crystalline Structures (BCC, FCC, HCP)

As pointed out on the previous page, there are 14 different types of crystal unit cell structures or lattices found in nature. However most metals and many other solids have unit cell structures described as body center cubic (BCC), face centered cubic (FCC) or Hexagonal Close Packed (HCP). Since these structures are most common, they will be discussed in more detail.

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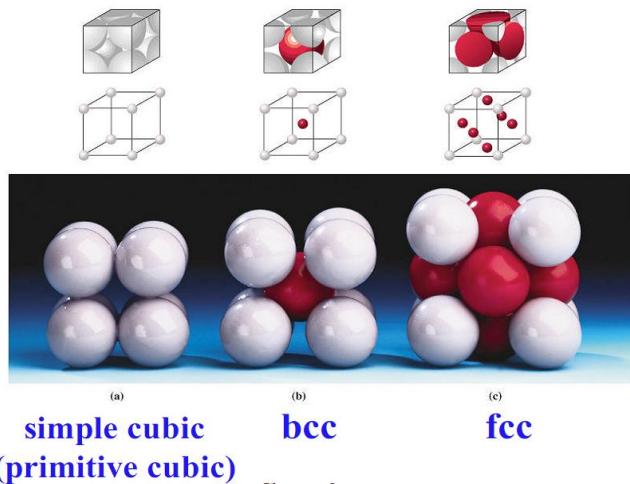
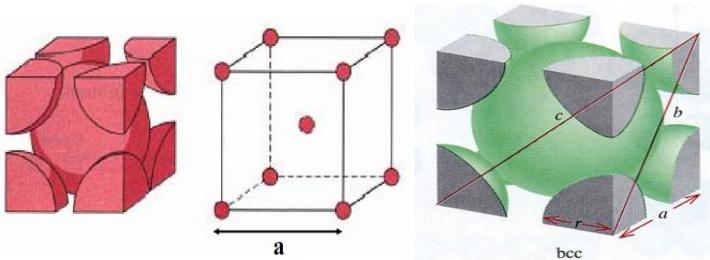


Figure 1.7.Cubic crystal structure

3.3.1 Body-Centered Cubic (BCC) Structure

The body-centered cubic unit cell has atoms at each of the eight corners of a cube (like the cubic unit cell) plus one atom in the center of the cube. Each of the corner atoms is the corner of another cube so the corner atoms are shared among eight unit cells. It is said to have a coordination number of 8. The BCC unit cell consists of a net total of two atoms; one in the center and eight eighths from corners atoms as shown in the middle image below (middle image below). The image below highlights a unit cell in a larger section of the lattice.

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The hard spheres touch one another along cube diagonal
⇒ the cube edge length, $a = 4R/\sqrt{3}$

The coordination number, CN = 8

Number of atoms per unit cell, n = 2

Center atom (1) shared by no other cells: $1 \times 1 = 1$

8 corner atoms shared by eight cells: $8 \times 1/8 = 1$

Atomic packing factor, APF = 0.68

Corner and center atoms are equivalent

Body-centered cubic: $a = 4r/(3)^{1/2}$

2 atom/unit cell

$$\text{occupancy} = 2 \times [4/3(\pi r^3)]/a^3 = 2 \times [4/3(\pi r^3)]/[4r/(3)^{1/2}]^3 \\ = 0.68 = 68\%$$

The BCC arrangement does not allow the atoms to pack together as closely as the FCC or HCP arrangements. The BCC structure is often the high temperature form of metals that are close-packed at lower temperatures. The volume of atoms in a cell per the total volume of a cell is called the **packing factor**. The BCC unit cell has a packing factor of 0.68.

Some of the materials that have a BCC structure include lithium, sodium, potassium, chromium, barium, vanadium, alpha-iron and tungsten. Metals which

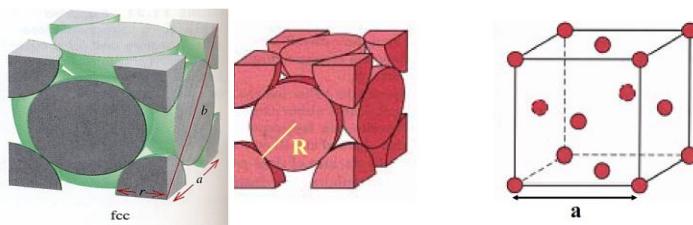
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have a BCC structure are usually **harder and less malleable than close-packed metals such as gold**. When the metal is deformed, the planes of atoms must slip over each other, and this is more difficult in the BCC structure. It should be noted that there are other important mechanisms for hardening materials, such as introducing impurities or defects which make slipping more difficult.

3.3.2. Face Centered Cubic (FCC) Structure

The face centered cubic structure has atoms located at each of the corners and the centers of all the cubic faces (left image below). Each of the corner atoms is the corner of another cube so the corner atoms are shared among eight unit cells. Additionally, each of its six face centered atoms is shared with an adjacent atom. Since 12 of its atoms are shared, it is said to have a coordination number of 12. The FCC unit cell consists of a net total of four atoms; eight eighths from corners atoms and six halves of the face atoms as shown in the middle image below. The image below highlights a unit cell in a larger section of the lattice.

In the FCC structure (and the HCP structure) the atoms can pack closer together than they can in the BCC structure. The atoms from one layer nest themselves in the empty space between the atoms of the adjacent layer. To picture packing arrangement, imagine a box filled with a layer of balls that are aligned in columns and rows. When a few additional balls are tossed in the box, they will not balance directly on top of the balls in the first layer but instead will come to rest in the pocket created between four balls of the bottom layer. As more balls are added they will pack together to fill up all the pockets. The packing factor (the volume of atoms in a cell per the total volume of a cell) is 0.74 for FCC crystals. Some of the metals that have the FCC structure include aluminum, copper, gold, iridium, lead, nickel, platinum and silver.



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The hard spheres touch one another across a face diagonal \Rightarrow the cube edge length, $a = 2r\sqrt{2}$

The coordination number, CN = the number of closest neighbors to which an atom is bonded = number of touching atoms, CN = 12

Number of atoms per unit cell, n = 4. (For an atom that is shared with m adjacent unit cells, we only count a fraction of the atom, 1/m). In FCC unit cell we have:
6 face atoms shared by two cells: $6 \times 1/2 = 3$

8 corner atoms shared by eight cells: $8 \times 1/8 = 1$

$$\text{APF} = (\text{Sum of atomic volumes}) / (\text{Volume of unit cell})$$

$$\text{Volume of 4 hard spheres in the unit cell: } 4 \times \frac{4}{3} \pi R^3$$

$$\text{Volume of the unit cell: } a^3 = 16R^3\sqrt{2}$$

$$APF = \frac{16}{3} \pi R^3 / 16R^3\sqrt{2} = \pi/3\sqrt{2} = 0.74$$

maximum possible packing of hard spheres

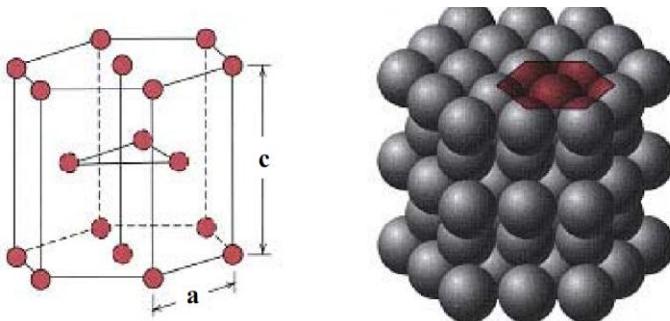
3.3.3. Hexagonal Close Packed (HPC) Structure

Another common close packed structure is the hexagonal close pack. The hexagonal structure of alternating layers is shifted so its atoms are aligned to the gaps of the preceding layer. The atoms from one layer nest themselves in the empty space between the atoms of the adjacent layer just like in the FCC structure. However, instead of being a cubic structure, the pattern is hexagonal. (See image below.) The difference between the HPC and FCC structure is discussed later in this section.

The HCP structure has three layers of atoms. In each the top and bottom layer, there are six atoms that arrange themselves in the shape of a hexagon and a seventh atom that sits in the middle of the hexagon. The middle layer has three atoms nestled in the triangular "grooves" of the top and bottom plane. Note that there are six of these "groove" surrounding each atom in the hexagonal plane, but only three of them can be filled by atoms. As shown in the middle image above, there are six atoms in the HCP unit cell. Each of the 12 atoms in the corners of the top and bottom layers contribute 1/6 atom to the unit cell, the two atoms in the center of the hexagon of both the top and bottom layers each contribute 1/2 atom and each of

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the three atoms in the middle layer contribute 1 atom. The image on the right above attempts to show several HCP unit cells in a larger lattice.



Unit cell has two lattice parameters a and c . Ideal ratio $c/a = 1.633$

The coordination number, CN = 12 (same as in FCC)

Number of atoms per unit cell, n = 6.

3 mid-plane atoms shared by no other cells: $3 \times 1 = 3$

12 hexagonal corner atoms shared by 6 cells: $12 \times 1/6 = 2$

2 top/bottom plane center atoms shared by 2 cells: $2 \times 1/2 = 1$

Atomic packing factor, APF = 0.74 (same as in FCC)

All atoms are equivalent

The coordination number of the atoms in this structure is 12. There are six nearest neighbors in the same close packed layer, three in the layer above and three in the layer below. The packing factor is 0.74, which is the same as the FCC unit cell. The HCP structure is very common for elemental metals and some examples include beryllium, Cadmium, Magnesium, Titanium, Zinc and Zirconium.

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Chapter Four

Metal Solid solution

4.1. Introduction

Alloy is a metal, composed of a mixture of elements. Most of alloys are composed of a base metal with small amounts of additives or alloying elements. The typical examples of alloys are steel/cast iron (iron base alloys), bronze/brass (copper base alloys), aluminum alloys, nickel base alloys, magnesium base alloys, titanium alloys.

Alloys may be prepared by different technological methods: melting, sintering of a powders mixture, high temperature diffusion of an alloying element into the base metal, plasma and vapor deposition of different elements, electroplating etc.

Alloy structure may be a single phase or a multi phase.

Phase is a uniform part of an alloy, having a certain chemical composition and structure, and which is separated from other alloy constituents by a phase boundary.

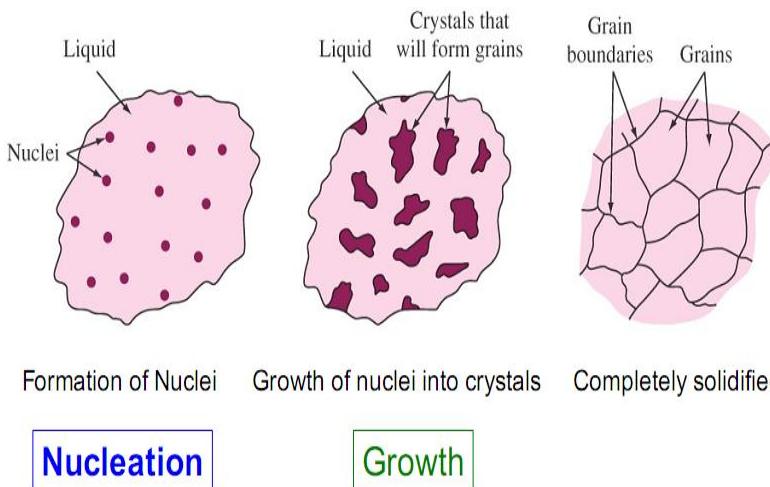
An alloy phase may be in form of **valence compound** (substance formed from two or more elements), with a fixed ratio determining the composition) or in form of solid solution.

4. 2. Solidification of metals

The solidification of metal and alloy is an important industrial process since most metal and are melted and then casted into a semi finished or finished shape.

In general solidification of metals or alloy can be dividing into the following steps: the formation of stable nuclei in the melt (nucleation), the growth of nuclei into crystals and the formation of grain structure.

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The formation of stable nuclei in liquid metals

The two mechanism by which nucleation of the solid particles in a liquid metals occurs are homogeneous nucleation and heterogeneous nucleation.

Homogeneous nucleation: it is considered first since it is the simplest case of nucleation. It a liquid melt occurs when the metal itself provides the atoms to form nuclei. Let us consider the case of pure metal solidifying. When a pure metal liquid is cooled below its equilibrium freezing temperature to a sufficient degree, numerous homogeneous nuclei are created by slow-moving atoms bonding together. Homogeneous nucleation usually requires a considerable amount of under cooling which may be as much as several hundred degrees Celsius for some metals. For a nucleus to be stable so that it can grow into a crystal, it must reach a critical size. A cluster of atoms bonded together which is less than the critical size is called embryo, and one which is larger than the critical size is called a nucleus. Because of their instability, embryos are continuously being formed and redissolved in the molten metal due to the agitation of the atoms.

Heterogeneous nucleation: it is a nucleation that occurs in a liquid on the surface of the container, insoluble impurities, or other structural material

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which lowers the critical free energy required to form a stable nucleus. Since large amount of under cooling do not occur during industrial casting operation.

4.3. Metallic Solid solution

A Solid solution is mixture of two crystalline solids that coexist as a new crystalline solids or crystal lattice. The mixing can be accomplished by combining the two solids when they have been melted into liquids at high temperatures and then cooling the result to form the new solids. In other words, when homogeneous mixtures of two or more kinds of atoms (of metals) occur in the solid state, they are known as **solid solutions**. *The more abundant atomic form is referred as solvent and the less abundant atomic form is referred as solute.* For example sterling silver (92.5 percent silver and the remainder copper) is a solid solution of silver and copper. In this case silver atoms are solvent atoms whereas copper atoms are solute atoms. Another example is brass. Brasses are a solid solution of copper (64 percent) and zinc (36 percent). In this case copper atoms are solvent atoms whereas zinc atoms are solute atoms.

Although very few metals are used in pure or nearly pure state, a few are used in the nearly pure form. Metal alloy is a mixture of two or more metals and non-metals for the purpose of improving mechanical properties of metals (to get better property than parent metals).

4.3.1 Type of Solid Solutions

Solid solutions are of two types. They are

a. *Substitution Solid Solutions*

If the atoms of the solvent or parent metal are replaced in the crystal lattice by atoms of the solute metal then the solid solution is known as substitution solid solution.

For example, copper atoms may substitute for nickel atoms without disturbing the F.C.C. structure of nickel (Fig. 3.2.1). In the substitution solid solutions, the substitution can be either disordered or ordered. Figure 5.1b shows disordered substitution solid solution. Here the solute atoms have substituted disorderly for the solvent atoms on their lattice site. Fig. 5.1c shows an

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ordered substitution solid solution. Here the solute atoms have substituted in an orderly manner for the solvent atoms on their lattice site.

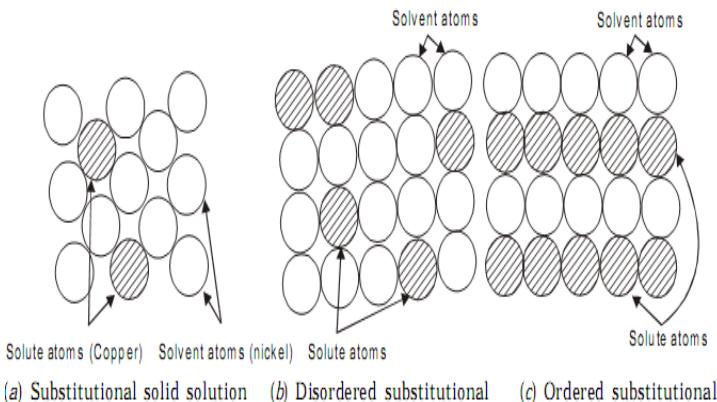


Figure 3.1 substitutional solid solution

Hume Rothery rules for the formation of substitutional solid solutions

By studying a number of alloy systems, Hume Rothery formulated certain rules which govern the formation of substitution solid solutions. These are:

(a) Crystal structure factor: For complete solid solubility, the two elements should have the same type of crystal structure i.e., both elements should have either F.C.C. or B.C.C. or H.C.P. structure.

(b) Relative size factor: As the size (atomic radii) difference between two elements increases, the solid solubility becomes more restricted. For extensive solid solubility the difference in atomic radii of two elements should be less than about 15 percent. If the relative size factor is more than 15 percent, solid solubility is limited. For example, both silver and lead have F.C.C. structure and the relative size factor is about 20 percent. Therefore the solubility of lead in solid silver is about 1.5 percent and the solubility of silver in solid lead is about 0.1 percent. Copper and nickel are completely soluble in each other in all proportions. They have the same type of crystal structure (F.C.C.) and differ in atomic radii by about 2 percent.

(c) Chemical affinity factor: Solid solubility is favored when the two metals have lesser chemical affinity. If the chemical affinity of the two metals is

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greater than the tendency towards compound formation. Generally, if the two metals are separated in the periodic table widely then they possess greater chemical affinity and are very likely to form some type of compound instead of solid solution.

(d) Relative valence factor: It is found that a metal of lower valence tends to dissolve more of a metal of higher valence than vice versa. For example in aluminum-nickel alloy system, nickel (lower valance) dissolves 5 percent aluminum but aluminum (higher valence) dissolves only 0.04 percent nickel

Shortly Factors for high solubility should fulfill the following points

(Solubility limit → maximum that can dissolve)

- Atomic size: need to “fit” \Rightarrow solute and solvent atomic radii should be within $\sim 15\%$
- Crystal structure: solute and solvent the same
- Electro negativities: should be comparable (otherwise new intermetallic phases favored)
- Valency: If solute has higher valence than solvent, generally more goes into solution.

Example: Using the data in table below, predict the relative degree of solid solubility of the following elements in copper. (a) Zinc, (b) lead, (Silicon), (d) Nickel, (e) Aluminum, (f) Beryllium.

Element	Atom radius, nm	Crystal Structure	Electro-negativity	Valance
Copper	0.128	FCC	1.8	+2
Zinc	0.133	HCP	1.7	+2
Lead	0.175	FCC	1.6	+2,+4
Silicon	0.117	Diamond Cubic	1.8	+4
Nickel	0.125	FCC	1.8	+2
Aluminum	0.143	FCC	1.5	+3
Beryllium	0.114	HCP	1.5	+2

Q. Which one form better solution with copper? Nickel, why?

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b. Interstitial solid solutions

In interstitial solid solutions, the solute atom does not displace a solvent atom, but rather it enters one of the holes or interstices between the solvent atoms. An excellent example is iron-carbon system which is shown in Fig. 3.2.2.

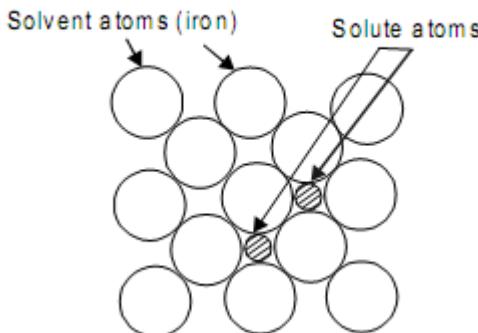


Figure 3.2. Interstitial solid solutions

In this system the carbon (solute atom) atom occupies an interstitial position between iron (solvent atom) atoms. Normally, atoms which have atomic radii less than one angstrom are likely to form interstitial solid solutions. Examples are atoms of carbon (0.77 \AA), nitrogen (0.71 \AA), hydrogen (0.46 \AA), Oxygen (0.60 \AA) etc.

b. Intermetallic compounds

Intermetallic compounds are generally formed when one metal (for example magnesium) has chemical properties which are strongly metallic and the other metal (for example antimony, tin or bismuth) has chemical properties which are only weakly metallic. Examples of intermetallic compounds are Mg_2Sn , Mg_2Pb , Mg_3Sb_2 and Mg_3Bi_2 . These Intermetallic compounds have higher melting point than either of the parent metal. This higher melting point indicates the high strength of the chemical bond in intermetallic compounds.

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Chapter Five Solid Diffusion

5.1. Introduction

The

5.2. Type of Solid Diffusion

There

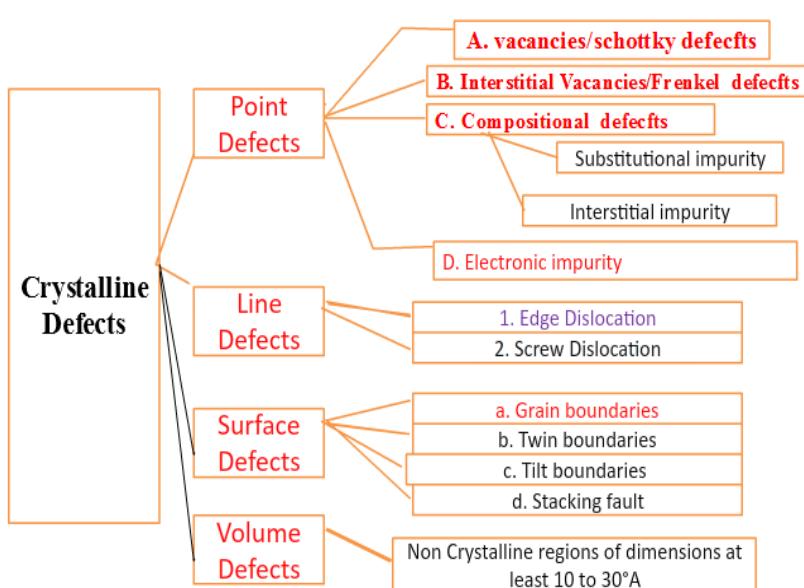
5.3. Application of solid Diffusion

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Chapter Six Crystal Imperfection

6.1. Introduction

A perfect crystal, with every atom of the same type in the correct position, does not exist. All crystals have some defects. Defects contribute to the mechanical properties of metals. In fact, using the term "defect" is sort of misnomers since these features are commonly intentionally used to manipulate the mechanical properties of a material. Adding alloying elements to a metal ilal



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one way of introducing a crystal defect. Nevertheless, the term “defect” will be used, just keep in mind that crystalline defects are not always bad.

6.2. Crystal imperfections

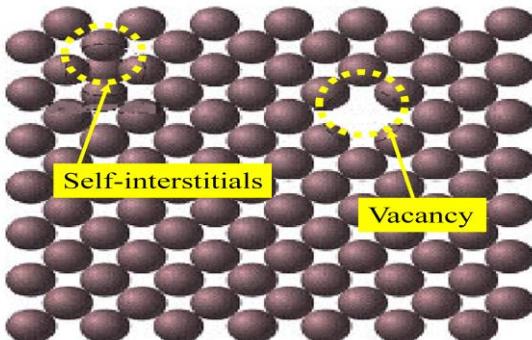
- Point defects, which are places where an atom is missing or irregularly placed in the lattice structure. Point defects include lattice vacancies, self-interstitial atoms, substitution impurity atoms, and interstitial impurity atoms
- **Linear/planer called dislocations.**
- Planar defects, which are interfaces between homogeneous regions of the material. Planar defects include grain boundaries, stacking faults and external surfaces.

It is important to note at this point that plastic deformation in a material occurs due to the movement of dislocations (linear defects). Millions of dislocations result for plastic forming operations such as rolling and extruding. It is also important to note that any defect in the regular lattice structure disrupts the motion of dislocation, which makes slip or plastic deformation more difficult. These defects not only include the point and planer defects mentioned above, and also other dislocations. Dislocation movement produces additional dislocations, and when dislocations run into each other it often impedes movement of the dislocations. This drives up the force needed to move the dislocation or, in other words, strengthens the material. Each of the crystal defects will be discussed in more detail in the following pages.

1. Point Defects

Point defects are where an atom is missing or is in an irregular place in the lattice structure. Point defects include self interstitial atoms, interstitial impurity atoms, substitution atoms and vacancies.

a. A self

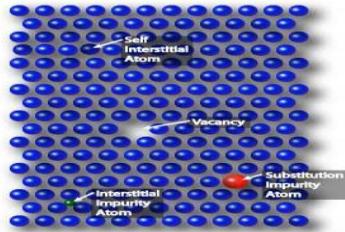


interstitial atom is an extra atom that has crowded its way into an interstitial void in the crystal structure. Self interstitial atoms occur

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only in low concentrations in metals because they distort and highly stress the tightly packed lattice structure.

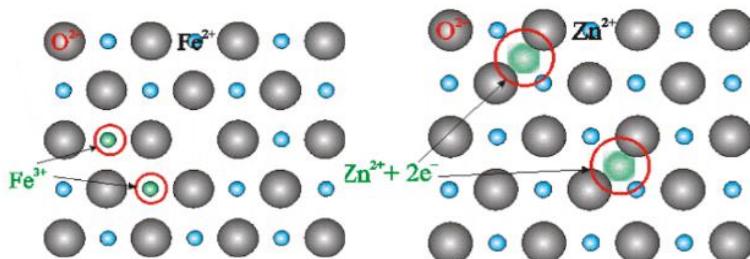
- b. Vacancies are empty spaces where an atom should be, but is missing. They are common, especially at high temperatures when atoms are frequently and randomly change their positions leaving behind empty lattice sites. In most cases diffusion (mass transport by atomic motion) can only occur because of vacancies.



c. Compositional Defects

1. A substitution impurity atom is an atom of a different type than the bulk atoms, which has replaced one of the bulk atoms in the lattice. Substitution impurity atoms are usually close in size (within approximately 15%) to the bulk atom. An example of substitution impurity atoms is the zinc atoms in brass. In brass, zinc atoms with a radius of 0.133 nm have replaced some of the copper atoms, which have a radius of 0.128 nm.
2. Interstitial impurity atoms are much smaller than the atoms in the bulk matrix. Interstitial impurity atoms fit into the open space between the bulk atoms of the lattice structure. An example of interstitial impurity atoms is the carbon atoms that are added to iron to make steel. Carbon atoms, with a radius of 0.071 nm, fit nicely in the open spaces between the larger (0.124 nm) iron atoms.

- d. Electronic defects: errors in charge distribution in solid are called electronic defects. These defects are produced when the composition of an ionic crystal does not correspond to the exact stoichiometric formula.



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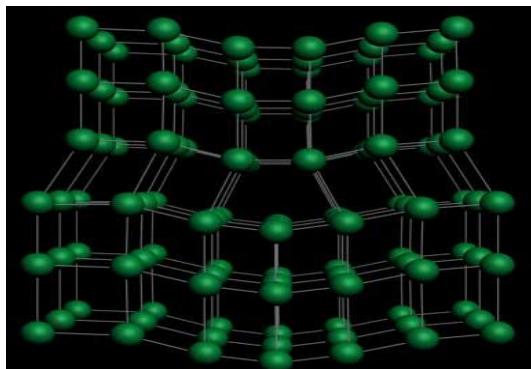
2. Linear Defects /Dislocations/

Dislocations are another type of defect in crystals. Dislocations are areas where the atoms are out of position in the crystal structure. Dislocations are generated and move when a stress is applied. The motion of dislocations allows slip – plastic deformation to occur.

There are two basic types of dislocations, the edge dislocation and the screw dislocation. Actually, edge and screw dislocations are just extreme forms of the possible dislocation structures that can occur. Most dislocations are probably a hybrid of the edge and screw forms but this discussion will be limited to these two types.

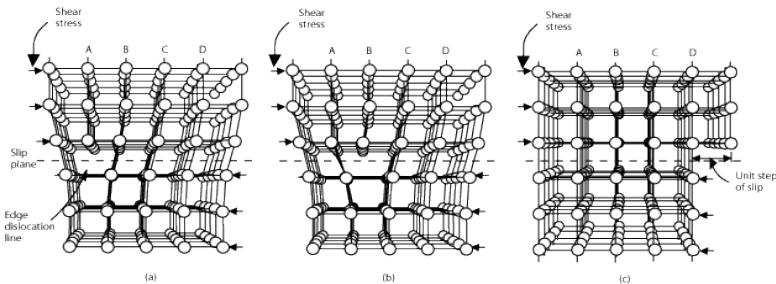
a. Edge Dislocations

The edge defect can be easily visualized as an extra half-plane of atoms in a lattice. The dislocation is called a line defect because the locus of defective points produced in the lattice by the dislocation lie along a line. This line runs along the top of the extra half-plane. The inter-atomic bonds are significantly distorted only in the immediate vicinity of the dislocation line. In perfect crystal atoms are arranged in both vertical and horizontal planes parallel to side faces. If one of these planes does not extend to the full length but ends in between within crystal it is called edge dislocations. Edge locations are caused by the termination of a plane of atoms in the middle crystal.



Understanding the movement of a dislocation is key to understanding why dislocations allow deformation to occur at much lower stress than in a perfect crystal. Dislocation motion is analogous to movement of a caterpillar.

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As shown in the set of images above, the dislocation moves similarly moves a small amount at a time. The dislocation in the top half of the crystal is slipping one plane at a time as it moves to the right from its position in image (a) to its position in image (b) and finally image (c). In the process of slipping one plane at a time the dislocation propagates across the crystal. The movement of the dislocation across the plane eventually causes the top half of the crystal to move with respect to the bottom half. However, only a small fraction of the bonds are broken at any given time. Movement in this manner requires a much smaller force than breaking all the bonds across the middle plane simultaneously.

line of the dislocation



Fig. 5.20 Edge dislocation in projection

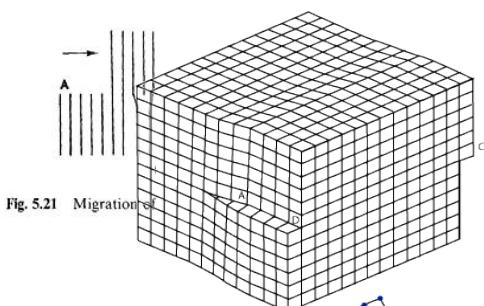
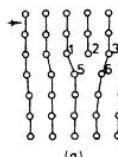
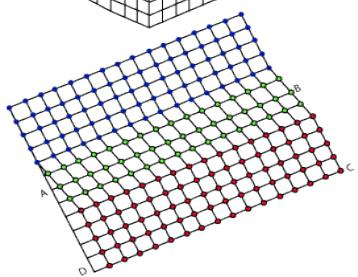


Fig. 5.21 Migration of

b. Screw Dislocations

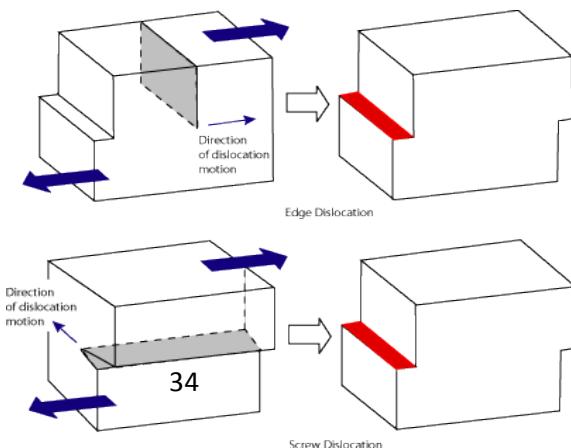


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There is a second basic type of dislocation, called screw dislocation. The screw dislocation is slightly more difficult to visualize. The motion of a screw dislocation is also a result of shear stress, but the defect line movement is perpendicular to direction of the stress and the atom displacement, rather than parallel. To visualize a screw dislocation, imagine a block of metal with a shear stress applied across one end so that the metal begins to rip. This is shown in the upper right image. The lower right image shows the plane of atoms just above the rip. The atoms represented by the blue circles have not yet moved from their original position. The atoms represented by the red circles have moved to their new position in the lattice and have reestablished metallic bonds. The atoms represented by the green circles are in the process of moving. It can be seen that only a portion of the bonds are broke at any given time. As was the case with the edge dislocation, movement in this manner requires a much smaller force than breaking all the bonds across the middle plane simultaneously.

If the sheer force is increased, the atoms will continue to slip to the right. A row of the green atoms will find their way back into a proper spot in the lattice (and become red) and a row of the blue atoms will slip out of position (and become green). In this way, the screw dislocation will move upward in the image, which is perpendicular to direction of the stress. Recall that the edge dislocation moves parallel to the direction of stress. As shown in the image below, the net plastic deformation of both edge and screw dislocations are the same, however.

The dislocations move along the densest planes of atoms in a material, because the stress needed to move the dislocation increases with the spacing between the planes. FCC and BCC metals have many dense planes, so dislocations move relatively easy and these materials have high ductility. Metals are strengthened by making it more difficult for dislocations to move. This may involve the



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introduction of obstacles, such as interstitial atoms or grain boundaries, to “pin” the dislocations. Also, as a material plastically deforms, more dislocations are produced and they will get into each other’s way and impede movement. This is why strain or work hardening occurs.

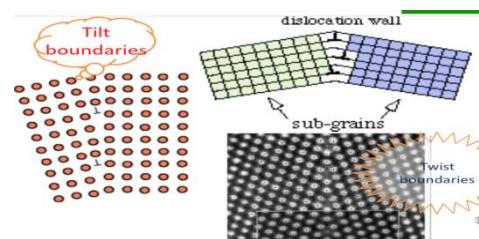
In ironically bonded materials, the ion must move past an area with a repulsive charge in order to get to the next location of the same charge. Therefore, slip is difficult and the materials are brittle. Likewise, the low density packing of covalent materials makes them generally more brittle than metals.

3. Planar Defects/Surface imperfections

Grain boundaries (or) crystal imperfections

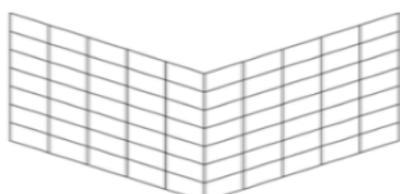
At the interface between two crystals randomly oriented the atom held in between are attracted by crystals on either side and depending on the forces the atoms either side and depending on the forces the atoms occupy equilibrium positions. This distorted region of a few atomic diameter thicknesses is called grain boundary. The orientation difference is usually greater than $10\text{--}15^\circ$. For this reason the grain boundaries are also known as high angle boundaries. When the orientation difference between the two crystals is less than 10° the distortion in the boundary is no so drastic. They are called low angle boundaries. The sub grain boundaries are of two types:

1. Tilt boundaries: an array of edge dislocation is called tilt boundary.
2. Twist boundaries: A cross grid of screw dislocation is called twist.



Twin Boundaries

Twin boundaries happen when the crystals on either side of a plane are mirror image of each other. Two crystal sections are miss oriented but



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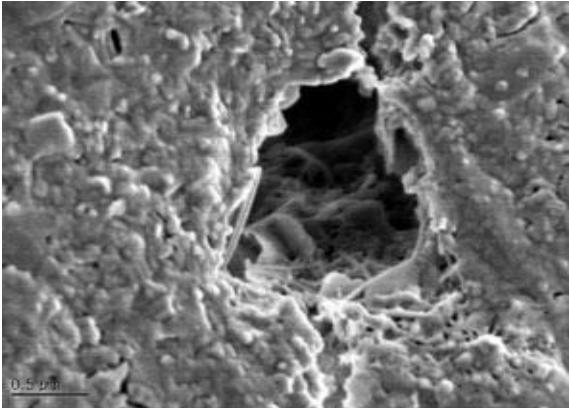
joined together such that one plane is a mirror image of the other. The two boundary common to the two planes is a twin boundary. They are formed during the growth of crystals. The boundary between the two twinned crystals will be a single plane of atoms.

Stacking Fault Boundaries.

A change in the stacking sequence over a few atomic spacing produces a stacking fault whereas a changeover much atomic spacing produces a twin region.

A stacking fault is a one or two layer interruption in the stacking sequence of atom planes. Stacking faults occur in a number

of crystal structures, but it is easiest to see how they occur in close packed structures. For example, it is known from a previous discussion that face centered cubic (fcc) structures differ from hexagonal close packed (hcp) structures only in their stacking order.



4. Bulk Defects/Bulk defects

Bulk defects occur on a much bigger scale than the rest of the crystal defects discussed in this section. However, for the sake of completeness and since they do affect the movement of dislocations, a few of the more common bulk defects will be mentioned. **Voids** are regions where there are a large number of atoms missing from the lattice. The image to the right is a void in a piece of metal. The image was acquired using a Scanning Electron Microscope (SEM). Voids can occur for a number of reasons. When **voids** occur due to air bubbles becoming trapped when a material solidifies, it is commonly called porosity. When a void occurs due to the shrinkage of a material as it solidifies,

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it is called capitation. Another type of bulk defect occurs when ***impurity/inclusions, cracks atoms*** cluster together to form small regions of a different phase. The term 'phase' refers to that region of space occupied by a physically homogeneous material.

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Chapter Seven

Mechanical Properties of metals

7.1. Mechanical Properties of Materials

The mechanical properties of a material are those properties that involve a reaction to an applied load. The mechanical properties of metals determine the range of usefulness of a material and establish the service life that can be expected. Mechanical properties are also used to help classify and identify material. The most common properties considered are strength, ductility, hardness, impact resistance, and fracture toughness. Most structural materials are anisotropic, which means that their material properties vary with orientation. The variation in properties can be due to directionality in the microstructure (texture) from forming or cold working operation, the controlled alignment of fiber reinforcement and a variety of other causes. Mechanical properties are generally specific to product form such as sheet, plate, extrusion, casting, forging, and etc. When studying materials and especially when selecting materials for a project / design, it is important to understand key properties. The most important properties are outlined below.

1. Strength

Strength is the property that enables a metal to resist deformation under load. The ultimate strength is the maximum strain a material can withstand. Tensile strength is a measurement of the resistance to being pulled apart when placed in a tension load.

2. **Fatigue strength** is the ability of material to resist various kinds of rapidly changing stresses and is expressed by the magnitude of alternating stress for a specified number of cycles.
3. **Impact strength** is the ability of a metal to resist suddenly applied loads and is measured in foot-pounds of force.
4. **Hardness** is the property of a material to resist permanent indentation.
5. **Toughness** is the property that enables a material to withstand shock and to be deformed without rupturing. Toughness may be considered as a combination of strength and plasticity
6. **Elasticity** is the ability of a material to return to its original shape after the load is removed. Theoretically, the elastic limit of a material is the limit to which a material can be loaded and still recover its original shape after the load is removed.
7. **Plasticity** is the ability of a material to deform permanently without breaking or rupturing. This property is the opposite of strength. By careful alloying of metals, the combination of plasticity and strength is used to manufacture large structural members.
8. **Brittleness** is the opposite of the property of plasticity. A brittle metal is one that breaks or shatters before it deforms. White cast iron and glass are good examples

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of brittle material. Generally, brittle metals are high in compressive strength but low in tensile strength.

9. **Ductility** is the property that enables a material to stretch, bend, or twist without cracking or breaking. This property makes it possible for a material to be drawn out into a thin wire.
10. **Malleability** is the property that enables a material to deform by compressive forces without developing defects. A malleable material is one that can be stamped, hammered, forged, pressed, or rolled into thin sheets.
11. **Machinability:** It is the property of materials which refers to relative ease of with which a material can be cut.
12. **Creep:** when a part is subjected to a constant stress at high temperature for a long period of time.
13. **Resilience:** It is property of a material to absorbed energy and resistant shock and impact loads.

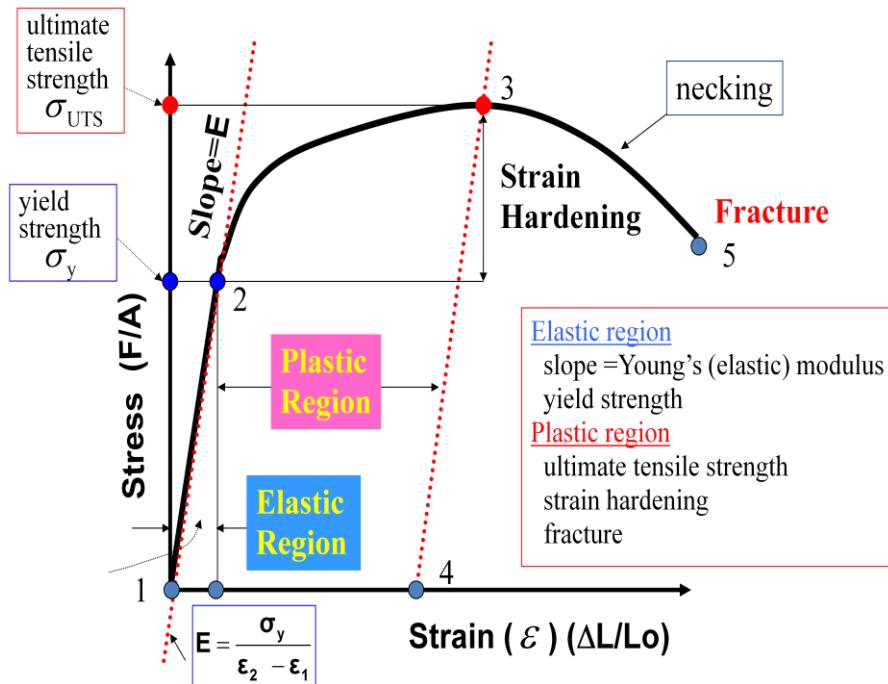
7.2. Elastic and Plastic deformation Graphical representation

$$\text{stress}(\sigma) = \frac{\text{Force}(F)}{\text{Orginal Cross Sectional are } (A_0)} \quad --- \text{1}$$

$$\begin{aligned}\text{strain}(\varepsilon) &= \frac{\text{change in length}}{\text{orginal length}} \\ &= \frac{l_f - l_0}{l_0} \quad --- \text{2}\end{aligned}$$

$$\text{Modulus of Elasticity}(\epsilon) = \frac{\sigma}{\varepsilon}$$

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A mechanical testing program from Element can include:

- **Hardness and Microhardness Testing** is the measure of how resistant solid matter is to various kinds of permanent shape change when a force is applied. Methods include: Rockwell standard testing, Rockwell superficial testing, Knoop & Vickers microhardness testing, and Brinell hardness testing.

Measurement of Hardness:

Hardness is not an intrinsic material property dictated by precise definitions in terms of fundamental units of mass, length and time. A hardness property value is the result of a defined measurement procedure. Hardness of materials has probably long been assessed by resistance to scratching or cutting. An example would be material B scratches material C, but not material A. Alternatively, material A scratches material B slightly and scratches material C heavily. Relative

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hardness of minerals can be assessed by reference to the Mohs scale that ranks the ability of materials to resist scratching by another material. Similar methods of relative hardness assessment are still commonly used today. An example is the file test where a file tempered to a desired hardness is rubbed on the test material surface. If the file slides without biting or marking the surface, the test material would be considered harder than the file. If the file bites or marks the surface, the test material would be considered softer than the file.

The above relative hardness tests are limited in practical use and do not provide accurate numeric data or scales particularly for modern day metals and materials. The usual method to achieve a hardness value is to measure the depth or area of an indentation left by an indenter of a specific shape, with a specific force applied for a specific time. There are three principal standard test methods for expressing the relationship between hardness and the size of the impression, these being Brinell, Vickers, and Rockwell. For practical and calibration reasons, each of these methods is divided into a range of scales, defined by a combination of applied load and indenter geometry.

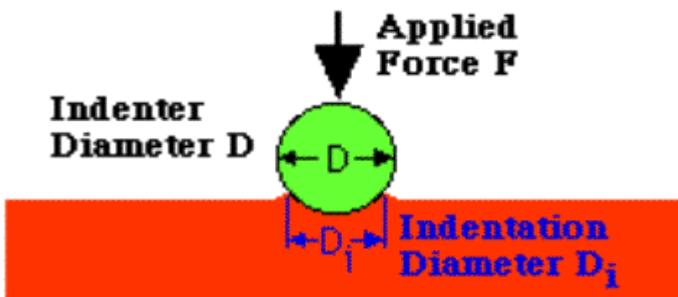
Hardness Testing Methods:

Rockwell Hardness Test

Rockwell	Superficial	Hardness	Test
Brinell		Hardness	Test
Vickers		Hardness	Test
Microhardness			Test
Mohs		Hardness	Test
Scleroscope and other hardness testing methods			

Brinell hardness Test

Brinell hardness is determined by forcing a hard steel or carbide sphere of a specified diameter under a specified load into the surface of a material and measuring the diameter of the indentation left after the test. The Brinell hardness number, or simply the Brinell number, is obtained by dividing the load used, in kilograms, by the actual surface area of the indentation, in square millimeters. The result is a pressure measurement, but the units are rarely stated.



$$BHN = \frac{F}{\frac{\pi}{2} D \cdot (D - \sqrt{D^2 - D_i^2})}$$

where

BHN = the Brinell hardness number
F = the imposed load in kg

D = the diameter of the spherical indenter in mm

D_i = diameter of the resulting indenter impression in mm

Several BHN tests are usually carried out over an area of armour plate. On a typical plate each test would result in a slightly different number. This is due not only to minor variations in quality of the armour plate (even homogenous armour is not absolutely uniform) but also because the test relies on careful measurement of the diameter of the depression. Small errors in this measurement will lead to small variations in BHN values. As a result, BHN is usually quoted as a range of values (e.g. 210 to 245, or 210-245) rather than as a single value.

Tensile Testing subjects a sample to uniaxial tension until it fails. Element tensile testing capabilities include: wedge tensile testing, axial tensile testing, weld tensile testing, castings tensile testing, elevated temperature tensile, tensile testing for machined specimens, full-size tensile testing and yield tensile, plus heat treatment capabilities.

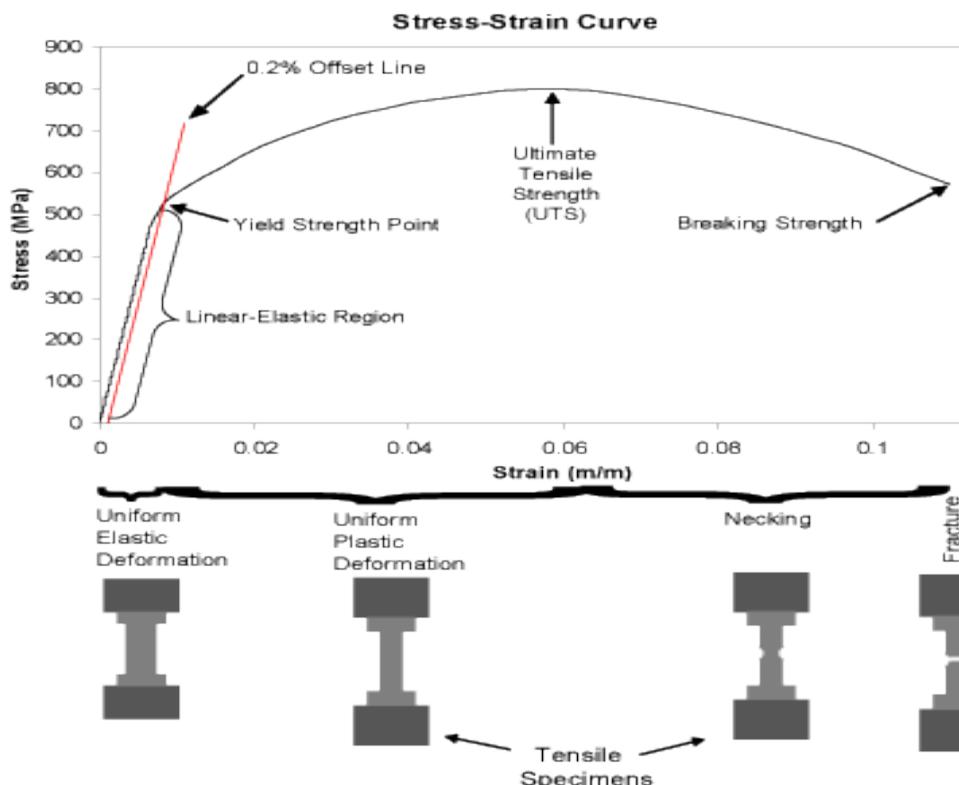
Tensile Properties

Tensile properties indicate how the material will react to forces being applied in tension. A tensile test is a fundamental mechanical test where a carefully prepared specimen is loaded in a very controlled manner while measuring the applied load and the elongation of the specimen over some distance. Tensile tests are used to

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determine the modulus of elasticity, elastic limit, elongation, proportional limit, and reduction in area, tensile strength, yield point, yield strength and other tensile properties.

The main product of a tensile test is a load versus elongation curve which is then converted into a stress versus strain curve. Since both the engineering stress and the engineering strain are obtained by dividing the load and elongation by constant values (specimen geometry information), the load-elongation curve will have the same shape as the engineering stress-strain curve. The stress-strain curve relates the applied stress to the resulting strain and each material has its own unique stress-strain curve. A typical engineering stress-strain curve is shown below. If the true stress, based on the actual cross-sectional area of the specimen, is used, it is found that the stress-strain curve increases continuously up to fracture.



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- **Torque Testing** is the tendency of a force to rotate an object about an axis. Element can perform torque testing on most hardware and fastener products.
- **Fatigue Testing** is performed on parts and materials to simulate the progressive and localized structural damage that occurs when a material is subjected to cyclic loading. Element's fatigue testing methods include: fracture toughness testing, a measure of the fracture resistance of a material containing a crack; rotating beam fatigue testing; strain controlled axial fatigue testing; stress controlled axial fatigue testing, and da/dN testing (crack propagation rate).
- **Charpy Impact Testing:** The Charpy impact test, also known as the Charpy v-notch test, is a standardized high strain-rate test which determines the amount of energy absorbed by a material during fracture. Element conducts sub-size Charpy impact testing and standard Charpy impact testing.
- **Bend Testing** determines the ductility or the strength of a material by bending the material over a given radius. Element performs bolt bend testing, weld bend testing, and raw materials bend testing.
- **Proof Load Testing** is often used interchangeably with yield strength; it refers to the tension-applied load that a test sample must support without evidence of deformation. Proof load testing can be done on nuts, bolts, components, and assembled products. Methods include: tension testing, compression testing.
- **Shear Testing:** Shear strength measures a material's response to shear loading, a force that tends to produce a sliding failure on a material along a plane that is parallel to the direction of the force. Element performs shear testing on bolts, rivets, pins, and other products: single shear testing, double shear testing, and washer testing and other testing.
- **Other mechanical testing capabilities** include mechanical durability, experimental stress analysis, flow measurement, fatigue analysis, structural testing, and pressure cycling.

Assignment

What are the differences between plastic and elastic deformation with graphical representation.

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Chapter Eight

Iron Carbon Diagrams

8.1. Iron-carbon phase diagram

A phase in a material is a region that differs in its microstructure and/or composition from another region. A phase diagram is graphical representation of what phases are present in a material system at various temperature, pressure, and composition.

Iron-carbon phase diagram describes the iron-carbon system of alloys containing up to 6.67% of carbon, discloses the phase's compositions and their transformations occurring with the alloys during their cooling or heating. Carbon content 6.67% corresponds to the fixed composition of the iron carbide Fe_3C .

Constituent in steels

There are a number of special names that are used to denote the various phases and type of structure that occur in steels

- **L** - Liquid solution of carbon in iron;
- **δ -ferrite** – Solid solution of carbon in iron. Maximum concentration of carbon in δ -ferrite is 0.09% at 2719 °F (1493°C) – temperature of the peritectic transformation.

The crystal structure of δ -ferrite is BCC (cubic body centered).

- **Austenite** – interstitial solid solution of carbon in γ -iron.

Austenite has FCC (cubic face centered) crystal structure, permitting high solubility of carbon – **up to 2.06%** at 2097 °F (1148 °C).

Austenite does not exist below 1333 °F (723°C) and maximum carbon concentration at this temperature is **0.83%**.

- **α -ferrite** – 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** – iron carbide, intermetallic compound, having fixed composition Fe_3C .

Cementite is a **hard and brittle** substance, influencing on the properties of steels and cast irons.

- **Pearlite:** Pearlite is eutectoid mixture of ferrite and cementite, and is formed when austenite decompose during cooling from austenite state.

The following phase transformations occur with **iron-carbon alloys**:

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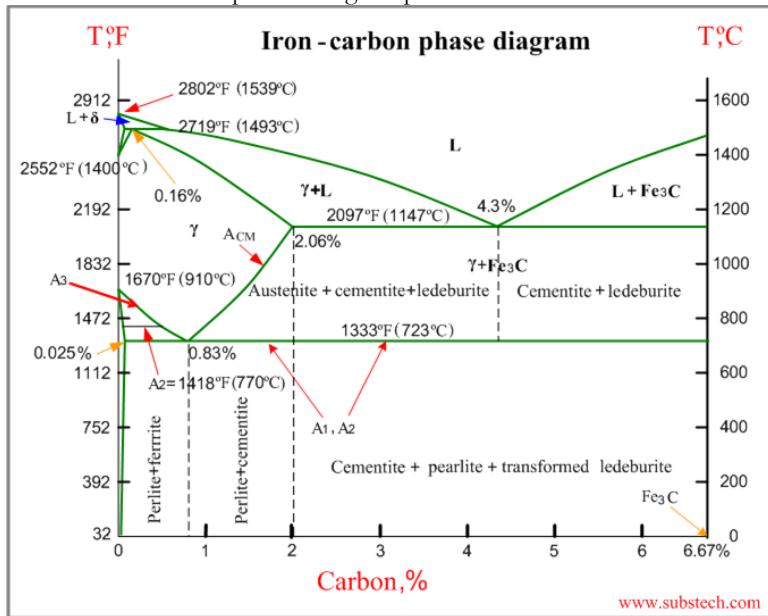
Reaction in the Fe-Fe₃C

a. Peritectic Reaction

- ✓ Alloys, containing up to **0.51%** of carbon, start solidification with formation of crystals of δ -ferrite. Carbon content in δ -ferrite increases up to **0.09%** in course solidification, and at 2719 °F (1493°C) remaining liquid phase and δ -ferrite perform **peritectic transformation**, resulting in formation of austenite.



As mentioned so far, iron is allotropic. The crystal structure of pure iron at ordinary temperature is body center cubic. This form is known as α iron. α Iron is stable at all temperature up to 908°C. On heating through 908°C, the crystal structure of iron changes to face centered cubic. This form is known as γ iron. Γ iron changes into δ when heated through 1400°C, and this high temperature form possesses a body center cubic structure and it is stable up to melting temperature of 1553°C.



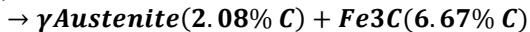
- ✓ Alloys, containing carbon more than **0.51%**, but less than **2.06%**, form primary austenite crystals in the beginning of solidification and when the temperature reaches the curve ACM primary cementite stars to form.
- ✓ Iron-carbon alloys, containing up to **2.06%** of carbon, are called **steels**.

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b. Eutectic Reaction

- ✓ Alloys, containing from 2.06 to 6.67% of carbon, experience eutectic transformation at 2097 °F (1148 °C). The eutectic concentration of carbon is 4.3%.

Liquid (4.3% c)at 1148°C



- ✓ In practice only hypoeutectic alloys are used. These alloys (carbon content from 2.06% to 4.3%) are called cast irons. When temperature of an alloy from this range reaches 2097 °F (1147 °C), it contains primary austenite crystals and some amount of the liquid phase. The latter decomposes by eutectic mechanism to a fine mixture of austenite and cementite, called **ledeburite**.

c. Eutectoid reaction

γ Austenite (4.3% c)at 723°C



- ✓ All iron-carbon alloys (steels and cast irons) experience eutectoid transformation at 1333 °F (723°C). The eutectoid concentration of carbon is 0.83%.
- ✓ When the temperature of an alloy reaches 1333 °F (723°C), **austenite transforms to pearlite** (fine ferrite-cementite structure, forming as a result of decomposition of austenite at slow cooling conditions).

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 A₃) 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 proeutectoid cementite C₂ ejected from austenite according to the curve A_{CM}, pearlite and transformed ledeburite (ledeburite in which austenite transformed to pearlite).

Critical temperatures

- **Upper critical temperature (point) A₃** is the temperature, below which ferrite starts to form as a result of ejection from austenite in the hypoeutectoid 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 hypereutectoid alloys.
- **Lower critical temperature (point) A₁** is the temperature of the austenite-to-pearlite eutectoid transformation. Below this temperature austenite does not exist.
- **Magnetic transformation temperature A₂** is the temperature below which α -ferrite is ferromagnetic.

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Chapter Nine Production of iron and Steel

9.1 Introduction

Metals and alloys have many useful engineering properties and so have wide spread application. Iron and its alloy account for 90% of the world's production of metals mainly because of their combination of good strength, toughness, and ductility at relatively low cost.

9.2. Production of pig-iron

Most iron is extracted from iron ore in large blast furnaces. In the blast furnaces coke (Carbon) acts as reducing agent to reduce iron oxide (mainly Fe_2O_3) to produce raw pig iron, which contains 4% carbon along with some other impurities according to typical reactions. The purpose of a blast furnace is to reduce and convert iron oxides into liquid iron called "hot metal".

The blast furnace is a huge, steel stack lined with refractory brick. Iron ore, coke and limestone are put into the top, and preheated air is blown into the bottom.

Raw Materials for production of pig iron in blast furnaces

Three substances are needed to enable extraction of iron from its ore. The combined mixture is called the **charge**:

- 1 Iron Ore e.g. haematite ore (iron(III) oxide) the source of iron (Fe_2O_3) or magnetite ore (Fe_3O_4)



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- 2 Coke (carbon, C) used for fuel and reducing agent.



- 3 Limestone (calcium carbonate = CaCO_3) to remove certain impurities like silica.



- **hot air** (for the oxygen in it) to burn the coke

The charge is placed in a giant chimney called a blast furnace. The blast furnace is around 30 metres high and lined with fireproof bricks. Hot air is blasted through the bottom.

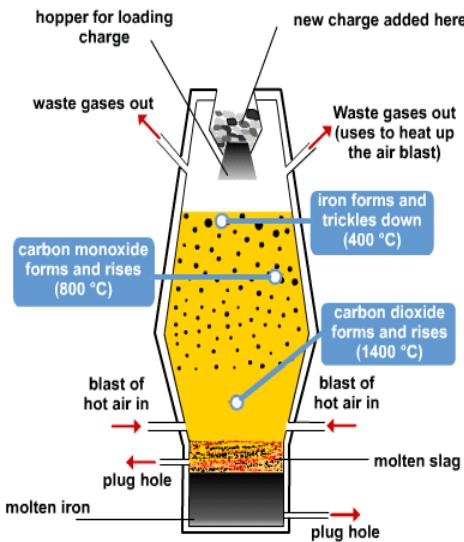


Figure 1.1. Blast Furnace

The heat source

The air blown into the bottom of the furnace is heated using the hot waste gases from the top. Heat energy is valuable, and it is important not to waste any.

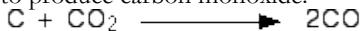
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The coke (essentially impure carbon) burns in the blast of hot air to form carbon dioxide - a strongly exothermic reaction. This reaction is the main source of heat in the furnace.



The reduction of the ore

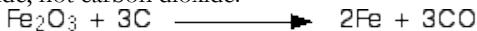
At the high temperature at the bottom of the furnace, carbon dioxide reacts with carbon to produce carbon monoxide.



It is the carbon monoxide which is the main reducing agent in the furnace.



In the hotter parts of the furnace, the carbon itself also acts as a reducing agent. Notice that at these temperatures, the other product of the reaction is carbon monoxide, not carbon dioxide.

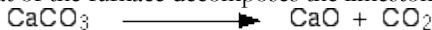


The temperature of the furnace is hot enough to melt the iron which trickles down to the bottom where it can be tapped off.

The function of the limestone

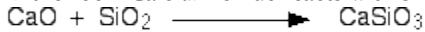
Iron ore isn't pure iron oxide - it also contains an assortment of rocky material. This wouldn't melt at the temperature of the furnace, and would eventually clog it up. The limestone is added to convert this into *slag* which melts and runs to the bottom.

The heat of the furnace decomposes the limestone to give calcium oxide.



This is an endothermic reaction, absorbing heat from the furnace. It is therefore important not to add too much limestone because it would otherwise cool the furnace.

Calcium oxide is a basic oxide and reacts with acidic oxides such as silicon dioxide present in the rock. Calcium oxide reacts with silicon dioxide to give calcium silicate.



The calcium silicate melts and runs down through the furnace to form a layer on top of the molten iron. It can be tapped off from time to time as slag.

Slag is used in road making and as "slag cement" - a final ground slag which can be used in cement, often mixed with Portland cement.

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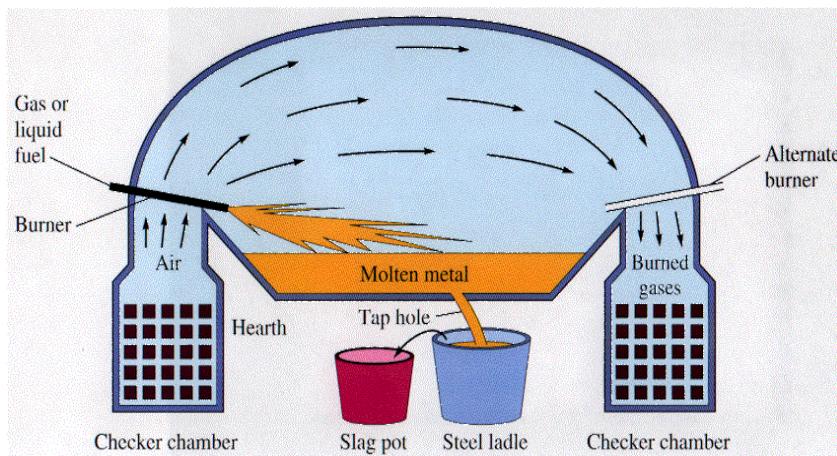
9.3. Steel Production Process

To make steel you are simply removing more impurities, such as, manganese, silicon, carbon..., from the pig iron. Impurities are removed by re-melting the metal and adding carbon, steel scrap, and more limestone.

The steels can be melted using one of three methods.

1. Open-Hearth furnace
2. Electric furnace
3. Basic Oxygen furnace. (BOF)

Open-hearth Furnaces



Uses a fuel to generate heat, and melt the metal

Basic-Oxygen Furnace

The Basic Oxygen Steelmaking process differs from the EAF in that it is autogenous, or self-sufficient in energy. The primary raw materials for the BOP are 70-80% liquid hot metal from the blast furnace and the balance is steel scrap. These are charged into the Basic Oxygen Furnace (BOF) vessel. Oxygen (>99.5% pure) is "blown" into the BOF at supersonic velocities. It oxidizes the carbon and silicon contained in the hot metal liberating great quantities of heat which melts the scrap. There are lesser energy contributions from the oxidation of iron, manganese, and phosphorus. The post combustion of carbon monoxide as it exits the vessel also transmits heat back to the bath.

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The product of the BOS is molten steel with a specified chemical analysis at 2900°F-3000°F. From here it may undergo further refining in a secondary refining process or be sent directly to the continuous caster where it is solidified into semi finished shapes: blooms, billets, or slabs.

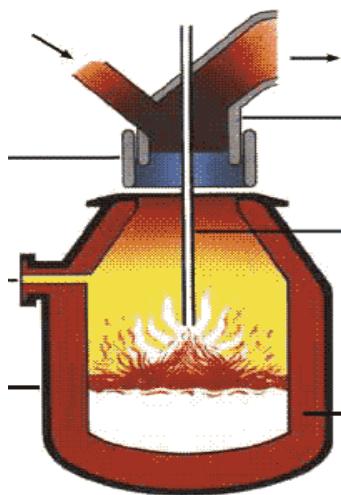
Basic refers to the magnesia (MgO) refractory lining which wears through contact with hot, basic slag. These slags are required to remove phosphorus and sulfur from the molten charge.

This rate of production made the process compatible with the continuous casting of slabs, which in turn had an enormous beneficial impact on yields from crude steel to shipped product, and on downstream flat-rolled quality.

II BASIC OPERATION

BOS process replaced open hearth steelmaking. The process predated continuous casting. As a consequence, ladle sizes remained unchanged in the renovated open hearth shops and ingot pouring aisles were built in the new shops. Six-story buildings are needed to house the Basic Oxygen Furnace (BOF) vessels to accommodate the long oxygen lances that are lowered and raised from the BOF vessel and the elevated alloy and flux bins. Since the BOS process increases productivity by almost an order of magnitude, generally only two BOFs were required to replace a dozen open hearth furnaces.

- Fastest steelmaking process – can make 250 tons of steel / hour
- Melted pig iron and scrap are poured (charged) into a vessel.
- Fluxing agents are added, like limestone.
- The molten metal is blasted with pure oxygen. This produces iron oxide which then reacts with carbon to produce CO and CO₂. The slag floats to the top of the metal.
- Higher steel quality than open hearth. Used to make plate, sheet, I-beam, tubing and channel.



Electric Furnace

Electric Arc Furnaces operation

The electric arc furnace operates as a batch melting process producing batches of molten steel known "heats". The electric arc furnace operating cycle is called the tap-to-tap cycle and is made up of the following operations:

- [Furnace charging](#)
- [Melting](#)
- [Refining](#)
- [De-slagging](#)
- [Tapping](#)
- [Furnace turn-around](#)

Modern operations aim for a tap-to-tap time of less than 60 minutes. Some twin shell furnace operations are achieving tap-to-tap times of 35 to 40 minutes.

Furnace Charging

The first step in the production of any heat is to select the grade of steel to be made. Preparation of the charge bucket is an important operation, not only to ensure proper melt-in chemistry but also to ensure good melting conditions. The scrap must be layered according to size and density to promote the rapid formation of a liquid pool

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of steel in the hearth while providing protection for the sidewalls and roof from electric arc radiation. Other considerations include minimization of scrap cave-ins which can break electrodes and ensuring that large heavy pieces of scrap do not lie directly in front of burner ports which would result in blow-back of the flame onto the water cooled panels. The charge can include lime and carbon or these can be injected into the furnace during the heat.

The number of charge buckets of scrap required to produce a heat of steel is dependent primarily on the volume of the furnace and the scrap density. Most modern furnaces are designed to operate with a minimum of back-charges. This is advantageous because charging is a dead-time where the furnace does not have power on and therefore is not melting. Minimizing these dead-times helps to maximize the productivity of the furnace. In addition, energy is lost every time the furnace roof is opened.

Melting

The melting period is the heart of EAF operations. The EAF has evolved into a highly efficient melting apparatus and modern designs are focused on maximizing the melting capacity of the EAF. Melting is accomplished by supplying energy to the furnace interior. This energy can be electrical or chemical. Electrical energy is supplied via the graphite electrodes and is usually the largest contributor in melting operations. Initially, an intermediate voltage tap is selected until the electrodes bore into the scrap. Usually, light scrap is placed on top of the charge to accelerate bore-in. Approximately 15 % of the scrap is melted during the initial bore-in period. After a few minutes, the electrodes will have penetrated the scrap sufficiently so that a long arc (high voltage) tap can be used without fear of radiation damage to the roof. The long arc maximizes the transfer of power to the scrap and a liquid pool of metal will form in the furnace hearth. At the start of melting the arc is erratic and unstable. Wide swings in current are observed accompanied by rapid movement of the electrodes. As the furnace atmosphere heats up the arc stabilizes and once the molten pool is formed, the arc becomes quite stable and the average power input increases.

Chemical energy is being supplied via several sources including oxy-fuel burners and oxygen lances. Oxy-fuel burner's burn natural gas using oxygen or a blend of oxygen and air. Heat is transferred to the scrap by flame radiation and convection by the hot products of combustion. Heat is transferred within the scrap by conduction. Large pieces of scrap take longer to melt into the bath than smaller pieces. In some operations, oxygen is injected via a consumable pipe lance to "cut" the scrap. The oxygen reacts with the hot scrap and burns iron to produce intense heat for cutting the scrap. Once a molten pool of steel is generated in the furnace, oxygen can be

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lanced directly into the bath. This oxygen will react with several components in the bath including, aluminum, silicon, manganese, phosphorus, carbon and iron. All of these reactions are exothermic (i.e. they generate heat) and supply additional energy to aid in the melting of the scrap. The metallic oxides that are formed will end up in the slag. The reaction of oxygen with carbon in the bath produces carbon monoxide, which either burns in the furnace if there is sufficient oxygen, and/or is exhausted through the direct evacuation system where it is burned and conveyed to the pollution control system.

Refining

Refining operations in the electric arc furnace have traditionally involved the removal of phosphorus, sulfur, aluminum, silicon, manganese and carbon from the steel. In recent times, dissolved gases, especially hydrogen and nitrogen, been recognized as a concern. These refining reactions are all dependent on the availability of oxygen. Oxygen was lanced at the end of meltdown to lower the bath carbon content to the desired level for tapping. Most of the compounds which are to be removed during refining have a higher affinity for oxygen than the carbon. Thus the oxygen will preferentially react with these elements to form oxides which float out of the steel and into the slag.

In modern EAF operations, especially those operating with a "hot heel" of molten steel and slag retained from the prior heat, oxygen may be blown into the bath throughout most of the heat. As a result, some of the smelting and refining operations occur simultaneously.

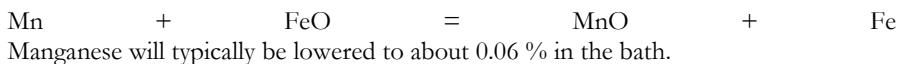
Phosphorus and sulfur occur normally in the furnace charge in higher concentrations than are generally permitted in steel and must be removed. Unfortunately the conditions favorable for removing phosphorus are the opposite of those promoting the removal of sulfur. Therefore once these materials are pushed into the slag phase they may revert back into the steel. Phosphorus retention in the slag is a function of the bath temperature, the slag basicity and FeO levels in the slag. At higher temperature or low FeO levels, the phosphorus will revert from the slag back into the bath. Phosphorus removal is usually carried out as early as possible in the heat. Hot heel practice is very beneficial for phosphorus removal because oxygen can be lanced into the bath while its temperature is quite low. Early in the heat the slag will contain high FeO levels carried over from the previous heat thus aiding in phosphorus removal. High slag basicity (i.e. high lime content) is also beneficial for phosphorus removal but care must be taken not to saturate the slag with lime. This will lead to an increase in slag viscosity, which will make the slag less effective. Sometimes fluorspar is added to help fluidize the slag. Stirring the bath with inert gas is also beneficial because it renews the slag/metal interface thus improving the reaction kinetics.

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In general, if low phosphorus levels are a requirement for a particular steel grade, the scrap is selected to give a low level at melt-in. The partition of phosphorus in the slag to phosphorus in the bath ranges from 5 to 15. Usually the phosphorus is reduced by 20 to 50 % in the EAF.

Sulfur is removed mainly as a sulfide dissolved in the slag. The sulfur partition between the slag and metal is dependent on slag chemistry and is favored at low steel oxidation levels. Removal of sulfur in the EAF is difficult especially given modern practices where the oxidation level of the bath is quite high. Generally the partition ratio is between 3 and 5 for EAF operations. Most operations find it more effective to carry out desulfurization during the reducing phase of steelmaking. This means that desulfurization is performed during tapping (where a calcium aluminate slag is built) and during ladle furnace operations. For reducing conditions where the bath has a much lower oxygen activity, distribution ratios for sulfur of between 20 and 100 can be achieved.

Control of the metallic constituents in the bath is important as it determines the properties of the final product. Usually, the melter will aim at lower levels in the bath than are specified for the final product. Oxygen reacts with aluminum, silicon and manganese to form metallic oxides, which are slag components. These metallics tend to react with oxygen before the carbon. They will also react with FeO resulting in a recovery of iron units to the bath. For example:



The reaction of carbon with oxygen in the bath to produce CO is important as it supplies a less expensive form of energy to the bath, and performs several important refining reactions. In modern EAF operations, the combination of oxygen with carbon can supply between 30 and 40 % of the net heat input to the furnace. Evolution of carbon monoxide is very important for slag foaming. Coupled with a basic slag, CO bubbles are tapped in the slag causing it to "foam" and helping to bury the arc. This gives greatly improved thermal efficiency and allows the furnace to operate at high arc voltages even after a flat bath has been achieved. Burying the arc also helps to prevent nitrogen from being exposed to the arc where it can dissociate and enter into the steel.

If the CO is evolved within the steel bath, it helps to strip nitrogen and hydrogen from the steel. Nitrogen levels in steel as low. Bottom tapping is beneficial for maintaining low nitrogen levels because tapping is fast and a tight tap stream is maintained. A high oxygen potential in the steel is beneficial for low nitrogen levels

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and the heat should be tapped open as opposed to blocking the heat.

Decarburization is also beneficial for the removal of hydrogen. It has been demonstrated that decarburizing at a rate of 1 % per hour can lower hydrogen levels in the steel from 8 ppm down to 2 ppm in 10 minutes. At the end of refining, a bath temperature measurement and a bath sample are taken. If the temperature is too low, power may be applied to the bath. This is not a big concern in modern meltshops where temperature adjustment is carried out in the ladle furnace.

De-Slagging

De-slagging operations are carried out to remove impurities from the furnace. During melting and refining operations, some of the undesirable materials within the bath are oxidized and enter the slag phase. It is advantageous to remove as much phosphorus into the slag as early in the heat as possible (i.e. while the bath temperature is still low). The furnace is tilted backwards and slag is poured out of the furnace through the slag door. Removal of the slag eliminates the possibility of phosphorus reversion. During slag foaming operations, carbon may be injected into the slag where it will reduce FeO to metallic iron and in the process produce carbon monoxide which helps foam the slag. If the high phosphorus slag has not been removed prior to this operation, phosphorus reversion will occur. During slag foaming, slag may overflow the sill level in the EAF and flow out of the slag door.

The following table shows the typical constituents of an EAF slag:

Component	Source	Composition Range
CaO	Charged	40 - 60 %
SiO ₂	Oxidation product	5 - 15 %
FeO	Oxidation product	10 - 30 %
MgO	Charged as dolomite	3 - 8 %
CaF ₂	Charged - slag fluidizer	
MnO	Oxidation product	2 - 5%
S	Absorbed from steel	
P	Oxidation product	

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Tapping

Once the desired steel composition and temperature are achieved in the furnace, the tap-hole is opened, the furnace is tilted, and the steel pours into a ladle for transfer to the next batch operation (usually a ladle furnace or ladle station). During the tapping process bulk alloy additions are made based on the bath analysis and the desired steel grade. De-oxidizers may be added to the steel to lower the oxygen content prior to further processing. This is commonly referred to as "blocking the heat" or "killing the steel". Common de-oxidizers are aluminum or silicon in the form of ferrosilicon or silicomanganese. Most carbon steel operations aim for minimal slag carry-over. A new slag cover is "built" during tapping. For ladle furnace operations, a calcium aluminate slag is a good choice for sulfur control. Slag forming compounds are added in the ladle at tap so that a slag cover is formed prior to transfer to the ladle furnace. Additional slag materials may be added at the ladle furnace if the slag cover is insufficient.

Furnace Turn-around

Furnace turn-around is the period following completion of tapping until the furnace is recharged for the next heat. During this period, the electrodes and roof are raised and the furnace lining is inspected for refractory damage. If necessary, repairs are made to the hearth, slag-line, tap-hole and spout. In the case of a bottom-tapping furnace, the tap hole is filled with sand. Repairs to the furnace are made using gunned refractories or mud slingers. In most modern furnaces, the increased use of water-cooled panels has reduced the amount of patching or "fettling" required between heats. Many operations now switch out the furnace bottom on a regular basis (2 to 6 weeks) and perform the hearth maintenance off-line. This reduces the power-off time for the EAF and maximizes furnace productivity. Furnace turn-around time is generally the largest dead time (i.e. power off) period in the tap-to-tap cycle. With advances in furnace practices this has been reduced from 20 minutes to less than 5 minutes in some newer operations.

Vacuum Furnaces

- Uses induction furnaces.

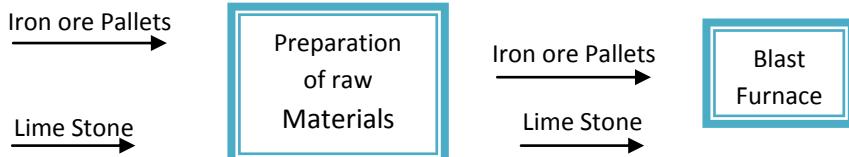
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- Air is removed from the furnace; this removes the gaseous impurities from the molten metal.
- Produces very high-quality steel.

Steel

made-I

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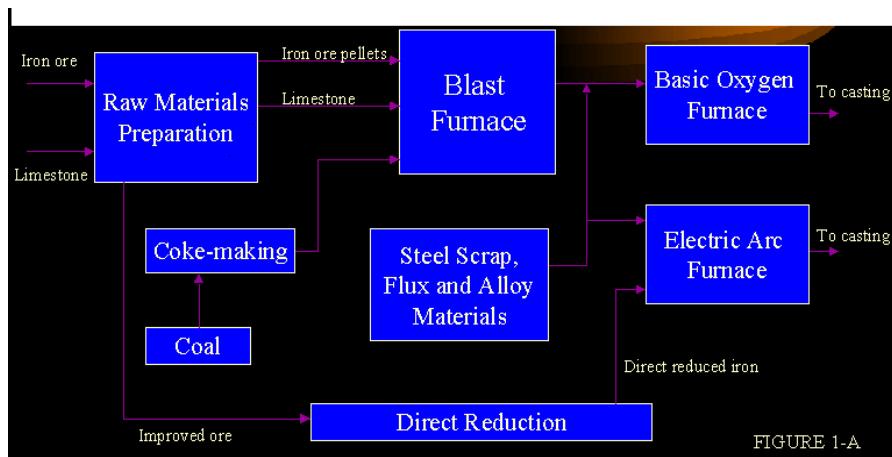


FIGURE 1-A

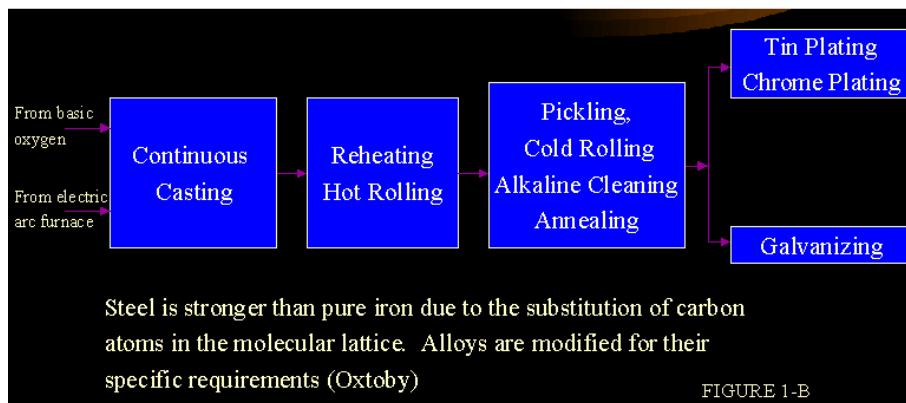
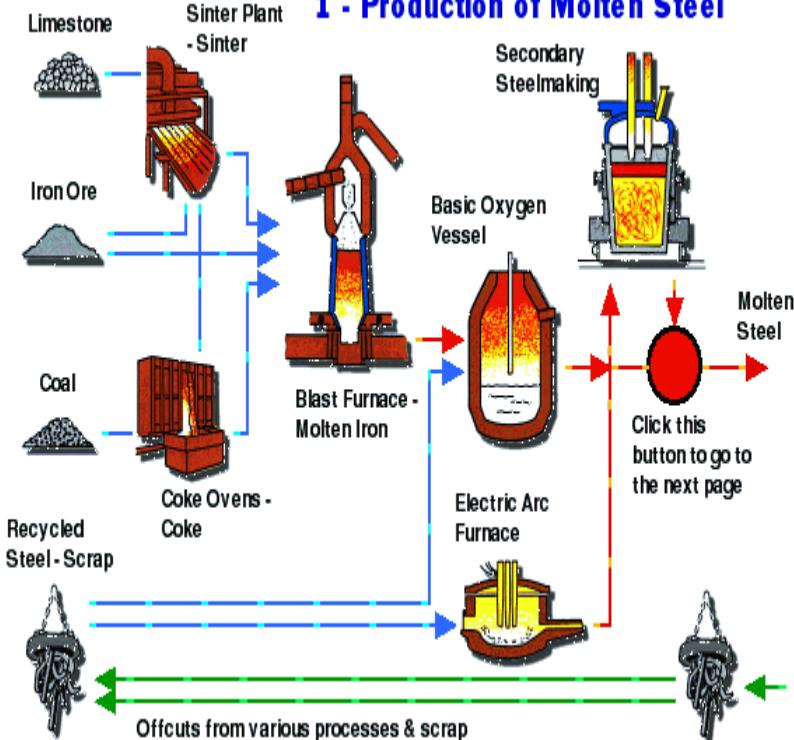
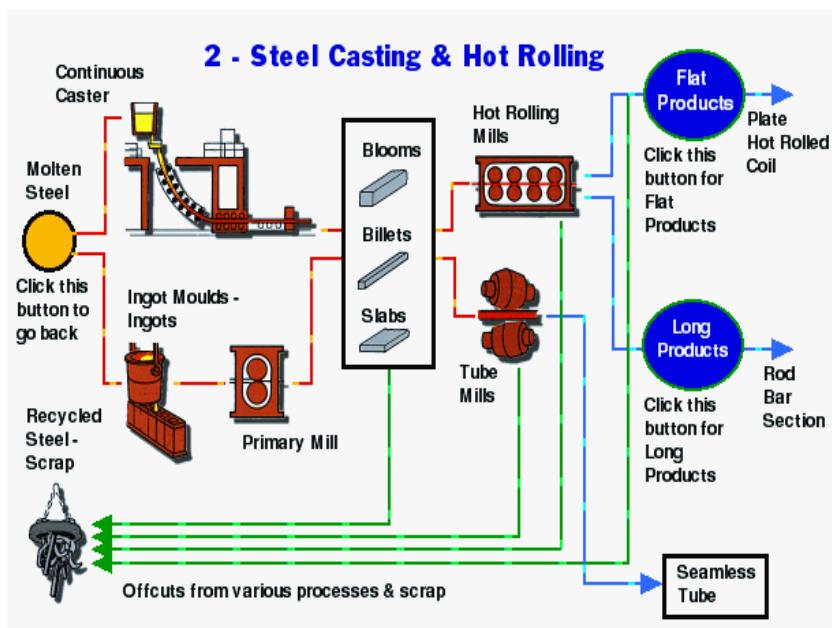
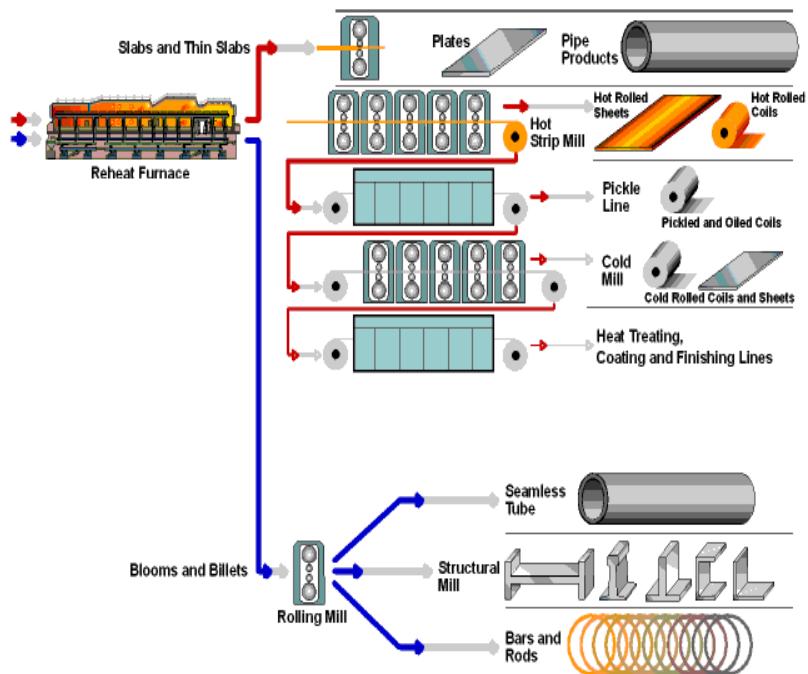


FIGURE 1-B

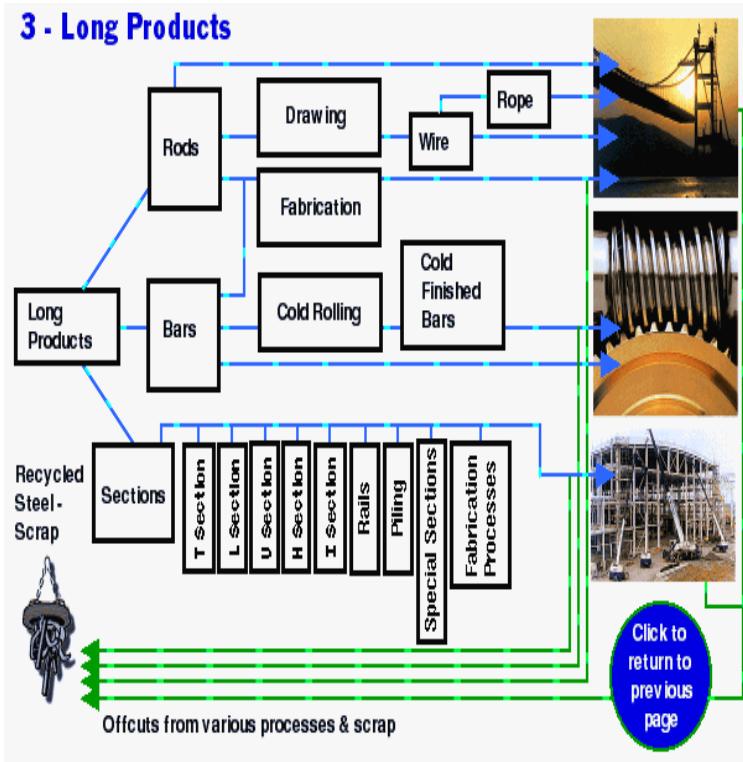
1 - Production of Molten Steel

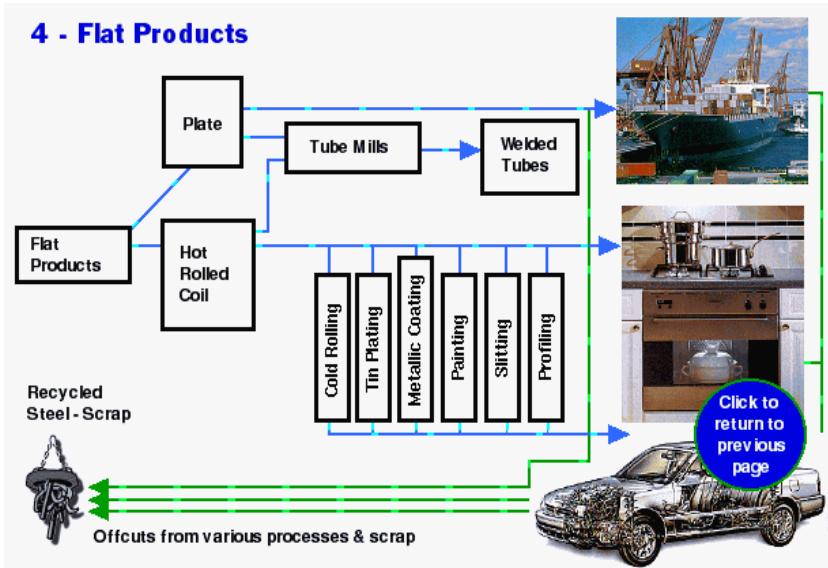






3 - Long Products





■ Killed – Semi-Killed – Rimmed Steel

Killed Steel – This is fully deoxidized steel, and thus, has no porosity.

- This is accomplished by using elements like aluminum to de-oxidize the metal. The impurities rise and mix with the slag.
- It is called killed because when the metal is poured it has no bubbles, it is quiet.
- Because it is so solid, not porous, the ingot shrinks considerably when it cools, and a “pipe” or “shrinkage cavity” forms. This must be cut off and scrapped.

Semi-Killed Steel: This is practically the same as killed steel, with some minor differences.

- It is only partially de-oxidized, and therefore, is a little more porous than killed steel.
- Semi-Killed does not shrink as much as it cools, so the pipe is much smaller and scrap is reduced.
- It is much more economical and efficient to produce.

- Rimmed Steel: This is produced by adding elements like aluminum to the molten metal to remove unwanted gases. The gasses then form blowholes around the rim.
- Results in little or no piping.
- Impurities also tend to collect in the center of the ingot, so products or rimmed steel need to be inspected and tested.

Chapter Ten

Ferous Metals

10.1 Introduction

10.1. Ferrous metals and Classification

Ferrous metal contains their major constituent are iron and small proportion of other elements such as molybdenum, carbon etc. ferrous metals can be classified into two: steel and cast irons. Steels contain carbon up to 2.06% and cast iron contains a carbon 2.06%-4.3% in real application.

10.1.1. Plain carbon steel

Carbon steel is by far the most widely used kind of steel. The properties of carbon steel depend primarily on the amount of carbon it contains. Most carbon steel has a carbon content of less than 1%. Carbon steel is made into a wide range of products, including structural beams, car bodies, kitchen appliances, and cans. In fact, there are 3 types of plain carbon steel and they are low carbon steel, medium carbon steel, high carbon steel, and as their names suggest all these types of plain carbon steel differ in the amount of carbon they contain. Indeed, it is good to precise that plain carbon steel is a type of steel having a maximum carbon content of 1.5% along with small percentages of silica, sulphur, phosphorus and manganese.

Low carbon steel or mild steel

It containing carbon up to 0.25% responds to heat treatment as improvement in the ductility is concerned but has no effect in respect of its Strength properties. The largest category of this class of steel is flat-rolled products (sheet or strip), usually in the cold-rolled and annealed condition. The carbon content for these high-formability steels is very low, less than 0.10% C, with up to 0.4% Mn. Typical uses are in automobile body panels, tin plate, and wire products. These materials may be used for stampings, forgings, seamless tubes, and boiler plate.

Medium carbon steels

Having carbon content ranging from 0.25 to 0.70% improves in the machinability by heat treatment. It must also be noted that this steel is especially adaptable for machining or forging and where surface hardness is desirable. These steels are similar to low-carbon steels except that the carbon ranges from 0.25 to 0.60% and the manganese from 0.60 to 1.65%. Increasing the carbon content to approximately 0.5% with an accompanying increase in manganese allows medium carbon steels to be used in the quenched and tempered condition. The uses of medium carbon-manganese steels include shafts, axles, gears, crankshafts, couplings and forgings. Steels in the 0.25 to 0.70% C range are also used for rails, railway wheels and rail axles.

High carbon steels

It is steel-containing carbon in the range of 0.70 to 1.05% and is especially classed as high carbon steel. In the fully heat-treated condition it is very hard and it will withstand high shear and wear and will thus be subjected to little deformation.

Moreover, at maximum hardness, the steel is brittle and if some toughness is desired it must be obtained at the expense of hardness. Depth hardening ability (normally termed as hardenability) is poor, limiting the use of this steel.

Furthermore, as it has been seen that hardness, brittleness and ductility are very important properties as they determine mainly the way these different carbon content steels are used. Considering the microstructure of slowly cooled steel; for mild steel, for instance, with 0.2% carbon. Such steel consists of about 75% of proeutectoid ferrite that forms above the eutectoid temperature and about 25% of pearlite (pearlite and ferrite being microstructure components of steel). When the carbon content in the steel is increased, the amount of pearlite increases until we get the fully pearlitic structure of a composition of 0.8% carbon. Beyond 0.8%, high carbon steel contain proeutectoid cementite in addition to pearlite. However, in slowly cooled carbon steels, the overall hardness and ductility of the steel are determined by the relative proportions of the soft, ductile ferrite and the hard, brittle cementite. The cementite content increases with increasing carbon content, resulting in an increase of hardness and a decrease of ductility, as we go from **low carbon** to **high carbon** steels.

10.2. Designation system

American Iron and Steel Institute (AISI) together with Society of Automotive Engineers (SAE) have established four-digit (with additional letter prefixes) designation system:

SAE 1XXX

First digit 1 indicates carbon steel (2-9 are used for alloy steels);

Second digit indicates modification of the steel.

0 - Plain carbon, non-modified

1 - Resulfurized

2 - Resulfurized and rephosphorized

5 - Non-resulfurized, Mn over 1.0%

Last two digits indicate carbon concentration in 0.01%.

Example: SAE 1030 means non modified carbon steel, containing 0.30% of carbon.

A letter prefix before the four-digit number indicates the steel making technology:

A - Alloy, basic open hearth.

B - Carbon, acid Bessemer.

C - Carbon, basic open hearth.

D - Carbon, acid open hearth.

E - Electric furnace.

Example: AISI B1020 means non modified carbon steel, produced in acid Bessemer and containing 0.20% of carbon.

Alloy steels

- Low alloy steels (alloying elements $\leq 8\%$);
- High alloy steels (alloying elements $> 8\%$).

According to the four-digit classification SAE-AISI system:

First digit indicates the class of the alloy steel:

2- Nickel steels; 3- Nickel-chromium steels; 4- Molybdenum steels; 5- Chromium steels; 6- Chromium-vanadium steels; 7- Tungsten-chromium steels; 9- Silicon-manganese steels.

Second digit indicates concentration of the major element in percents (1 means 1%).

Last two digits indicate carbon concentration in 0, 01%.

Example: SAE 5130 means alloy chromium steel, containing 1% of chromium and 0.30% of carbon.

Stainless Steel

Stainless Steel is a common name for metal alloys that consist of 10.5% or more Chromium (Cr) and more than 50% Iron (Fe). Although it is called "stainless", a better term for it is "highly stain resistant". A somewhat dark metal, it looks bright because it reflects light.

What are the main benefits of stainless steel in kitchen utensils?

- ◆ It is one of the most hygienic surfaces for the preparation of foods and very easy to clean, as its unique surface has no pores or cracks to harbor dirt, grime or bacteria.
- ◆ It is very attractive and requires minimal care, since it won't chip or easily rust and it takes little seasoning.

- ◆ It will not affect flavor, as it does not react with acidic foods during food preparation or cooking.

- ◆ With proper care, it has a useful life expectancy of over 100 years, and it is totally recyclable.

What gives stainless steel its properties?

The chromium content in stainless steel alloys is what generally prevents corrosion. Pure iron, the primary element of stainless steel, is extracted from its natural state as iron ore; it is unstable by itself, and naturally wants to corrode (rust). The chromium helps to procrastinate nature's attempts to combine the pure iron with oxygen and water to form rust. The chromium works by reacting with oxygen to form a tough, adherent, invisible, passive layer of chromium oxide film on the steel surface. Generally, an increase of chromium content improves the corrosion resistance of stainless steels. The addition of nickel is used to raise the general corrosion resistance required in more aggressive usage or conditions. The presence of molybdenum (Mo) improves the localized corrosion resistance, such as against pitting (scarring).

Other alloying metals are also used to improve the structure and properties of stainless steels, such as Titanium, Vanadium and Copper. Non metal additions typically include

natural elements such as Carbon & Nitrogen, as well as Silicon. High-carbon stainless steel contains a minimum of 0.3% carbon. The higher the carbon content, the less formable and the tougher the steel becomes. Its hardness makes it suitable for things such as cutting edges, and other high-wear applications like plow blades. Carbon thus helps makes the edge easier to sharpen, and helps retain a sharp edge longer.

The three major classes of stainless steel are:

◆ Austenitic: Chromium-nickel-iron alloys with 16-26% chromium, 6-22% nickel (Ni), and low carbon content, with non-magnetic properties (if annealed - working it at low temperatures, then heated and cooled). Nickel increases corrosion resistance. Hardenable by cold-working (worked at low temperatures) as well as tempering (heated then cooled). Type 304 (S30400) or "18/8" (18% chromium 8% nickel), is the most commonly used grade or composition.

◆ Martensitic: Chromium-iron alloys with 10.5-17% chromium and carefully controlled carbon content, hardenable by quenching (quickly cooled in water or oil) and tempering (heated then cooled). It has magnetic properties. Commonly used in knives. Martensitic grades are strong and hard, but are brittle and difficult to form and weld. Type 420 (S42000) is a typical example.

◆ Ferritic: Chromium-iron alloys with 17-27% chromium and low carbon content, with magnetic properties. Cooking utensils made of this type contain the higher chromium levels. Type 430 is the most commonly used ferritic.

10.4. Effect of alloying elements on steel properties

Alloying is changing chemical composition of steel by adding elements with purpose to improve its properties as compared to the plain carbon steel.

- The properties, which may be improved.
- Characteristics of alloying elements.

The properties, which may be improved

• **Stabilizing austenite** – increasing the temperature range, in which austenite exists. The elements, having the same crystal structure as that of austenite (cubic face centered – FCC), raise the A_4 point (the temperature of formation of austenite from liquid phase) and decrease the A_3 temperature. These elements are nickel (Ni), manganese (Mn), cobalt (Co) and copper (Cu).

Examples of austenitic steels: austenitic stainless steels, Hadfield steel (1% C, 13% Mn, 1.2% Cr).

• **Stabilizing ferrite** – decreasing the temperature range, in which austenite exists.

The elements, having the same crystal structure as that of ferrite (cubic body centered – BCC), lower the A_4 point and increase the A_3 temperature.

These elements lower the solubility of carbon in austenite, causing increase of amount of carbides in the steel. The following elements have ferrite stabilizing effect: Chromium (Cr), tungsten (W), Molybdenum (Mo), vanadium (V), aluminum (Al) and silicon (Si). Examples of ferritic steels: transformer sheets steel (3% Si), F-Cr alloys.

- **Carbide forming** – elements forming hard carbides in steels.

The elements like chromium (Cr), tungsten (W), molybdenum (Mo), vanadium (V), titanium (Ti), niobium (Nb), tantalum (Ta), zirconium (Zr) form hard (often complex) carbides, increasing steel hardness and strength. Examples of steels containing relatively high concentration of carbides: hot work tool steels, high speed steels. Carbide forming elements also form nitrides reacting with Nitrogen in steels.

- **Graphitizing** – decreasing stability of carbides, promoting their breaking and formation of free Graphite. The following elements have graphitizing effect: silicon (Si), nickel (Ni), cobalt (Co), aluminum (Al).

- **Decrease of the eutectoid concentration.**

The following elements lower eutectoid concentration of carbon: titanium (Ti), molybdenum (Mo), tungsten (W), silicon (Si), chromium (Cr), nickel (Ni).

- **Increase of corrosion resistance.** Aluminum (Al), silicon (Si), and chromium (Cr) form thin a strong oxide film on the steel surface, protecting it from chemical attacks.

10.5. Characteristics of alloying elements

Manganese (Mn) – improves hardenability, ductility and wears resistance. Mn eliminates formation of harmful iron sulfides, increasing strength at high temperatures.

Nickel (Ni) – increases strength, impact strength and toughness, impart corrosion resistance in combination with other elements.

Chromium (Cr) – improves hardenability, strength and wear resistance, sharply increases corrosion resistance at high concentrations ($> 12\%$).

Tungsten (W) – increases hardness particularly at elevated temperatures due to stable carbides, refines grain size.

Vanadium (V) – increases strength, hardness, creep resistance and impact resistance due to formation of hard vanadium carbides, limits grain size.

Molybdenum (Mo) – increases hardenability and strength particularly at high temperatures and under dynamic condition.

Silicon (Si) – improves strength, elasticity, acid resistance and promotes large grain sizes, which cause increasing magnetic permeability.

Titanium (Ti) – improves strength and corrosion resistance, limits austenite grain size.

Cobalt (Co) – improves strength at high temperatures and magnetic permeability.

Zirconium (Zr) – increases strength and limits grain sizes.

Boron (B) – highly effective hardenability agent improves deformability and machinability.

Copper (Cu) – improves corrosion resistance.

Aluminum (Al) – deoxidizer, limits austenite grains growth.

10.6. Stainless steels

Classification of steels by application

Stainless steels:

AISI has established three-digit system for the stainless steels:

- 2XX series – chromium-nickel-manganese austenitic stainless steels;
- 3XX series – chromium-nickel austenitic stainless steels;
- 4XX series – chromium martensitic stainless steels or ferritic stainless steels;
- 5XX series – low chromium martensitic stainless steels;

10.7 Tool and die steels

Designation system of one-letter in combination with a number is accepted for tool steels.

The letter means:

- W - Water hardened plain carbon tool steels;
- O - Oil hardening cold work alloy steels;
- A - Air hardening cold work alloy steels;
- D -Diffused hardening cold work alloy steels;
- S – Shock resistant low carbon tool steels;
- T – High speed tungsten tool steels;
- M - High speed molybdenum tool steels;
- H – Hot work tool steels;
- P – Plastic mold tool steels.

Stainless steels are steels possessing high corrosion resistance due to the presence of substantial amount of **chromium**. **Chromium forms a thin film of chromium oxide on the steel surface. This film protects the steel from further oxidation, making it stainlesss.**

Most of the stainless steels contain **12% - 18%** of chromium. Other alloying elements of the stainless steels are nickel, molybdenum, Nitrogen, titanium and manganese.

According to the AISI classification Stainless steels are divided onto groups:

- Austenitic stainless steels
- Ferritic stainless steels
- Martensitic stainless steels
- Austenitic-ferritic (Duplex) stainless steels
- Precipitation hardening stainless steels

Chemical compositions of some stainless steels: Properties of some stainless steels.

Austenitic stainless steels

Austenitic stainless steels (200 and 300 series) contain chromium and nickel (7% or more) as major alloying elements.

- The crystallographic structure of the steels is austenitic with FCC crystal lattice.

- ▶ The steels from this group have the highest corrosion resistance, weldability and ductility.
- ▶ Austenitic stainless steels retain their properties at elevated temperatures.
- ▶ At the temperatures 900-1400°F (482-760°C) chromium carbides form along the austenite grains. This causes depletion of chromium from the grains resulting in decreasing the corrosion protective passive film.
- ▶ This effect is called sensitization. It is particularly important in welding of austenitic stainless steels.
- ▶ Sensitization is depressed in low carbon steels (0.03%) designated with suffix L (304L, 316L). Formation of chromium carbides is also avoided in stabilized austenitic stainless steels containing carbide forming elements like titanium, niobium, tantalum, zirconium. Stabilization heat treatment of such steels results in preferred formation of carbides of the stabilizing elements instead of chromium carbides.
- ▶ These steel are not heat treatable and may be hardened only by cold work.
- ▶ *Applications of austenitic stainless steels:* chemical equipment, food equipment, kitchen sinks, medical devices, heat exchangers, parts of furnaces and ovens.

Ferritic stainless steels

- ▶ Ferritic stainless steels (400 series) contain chromium only as alloying element.
- ▶ The crystallographic structure of the steels is ferritic (BCC crystal lattice) at all temperatures.
- ▶ The steels from this group are low cost and have the best machinability. The steels are ferromagnetic. Ductility and formability of ferritic steels are low. Corrosion resistance and weldability are moderate. Resistance to the stress corrosion cracking is high.
 - ▶ Ferritic steels are not heat treatable because of low carbon concentration and they are commonly used in annealed state.
- ▶ *Applications of ferritic steels:* decorative and architectural parts, automotive trims and exhausting systems, computer floppy disc hubs, hot water tanks.

Martensitic stainless steels

- ▶ Martensitic stainless steels (400 and 500 series) contain chromium as alloying element and increased (as compared to ferritic grade) amount of carbon.
- ▶ Due to increased concentration of carbon the steels from this group are heat treatable. The steels have austenitic structure (FCC) at high temperature, which transforms to martensitic structure (BCC) as a result of quenching .
- ▶ Martensitic steels have poor weldability and ductility. Corrosion resistance of these steels is moderate (slightly better than in ferritic steels).
- ▶ *Applications of martensitic stainless steels:* turbine blades, knife blades, surgical instruments, shafts, pins, springs.

Austenitic-ferritic (Duplex) stainless steels

- Austenitic-ferritic (Duplex) stainless steels contain increased amount of chromium (18% -28%) and decreased (as compared to austenitic steels) amount of nickel (4.5% - 8%) as major alloying elements. As additional alloying element molybdenum is used in some of Duplex steels.
- Since the quantity of nickel is insufficient for formation of fully austenitic structure, the structure of Duplex steels is mixed: austenitic-ferritic. The properties of Duplex steels are somewhere between the properties of austenitic and ferritic steels. Duplex steels have high resistance to the stress corrosion cracking and to chloride ions attack. These steels are weldable and formable and possess high strength.
- Applications of austenitic-ferritic stainless steels: desalination equipment, marine equipment, petrochemical plants, heat exchangers.

Precipitation hardening stainless steels

- Precipitation hardening stainless steels contain chromium, nickel as major alloying elements.
- Precipitation hardening steels are supplied in solution treated condition. These steels may be either austenitic or martensitic and they are hardened by heat treatment (aging). The heat treatment is conducted after machining, however low temperature of the treatment does not cause distortions.
- Precipitation hardening steels have very high strength, good weldability and fair corrosion resistance. They are magnetic.
- Applications of precipitation hardening stainless steels: pump shafts and valves, turbine blades, paper industry equipment, aerospace equipment.

Chemical compositions of some stainless steels

No.	Grade	C max, %	Mn max,%	Cr,%	Ni,%	Mo,%	N,%	Cu,%	Cb+Ta, %
AISI 201	Austenite	0.15	6.0	17.0	4.5		.25 max		
AISI 304	Austenite	0.08	2.0	19.0	9.5		-		
AISI 316	Austenite	0.08	2.0	17.0	12.0		-		
						.5			
AISI 430	Ferritic	0.12	1.0	17.0	-		-	-	
AISI 410	Martensitic	0.15	1.0	12.5	-		-	-	
2205	Duplex	0.30	2.0	22.0	5.0		-	-	
						.14			
17-4PH	Precipit. hardening	0.07	1.0	16.5	4.0	-	-	4.0	0.30

10.8. Cast Iron

10.8.1. General Properties

Cast irons are a family of ferrous alloys with a wide range of properties, and as their name implies, they are intended to be cast into desired shape instead of being worked in the solid state.

Cast iron make excellent casting alloys since they are easily melted, are very fluid in the liquid state, do not form undesirable surface films when poured. Cast iron solidifies with slight to moderate shrinkage during casting and cooling. These alloys have a wide range of strengths and hardness and in most cases are easy to machine. They can alloy to produce superior wear, abrasion, and corrosion resistance. However, cast irons have relatively low impact resistance and ductility which limits their use for applications. The wide industrial use of cast irons is due mainly to their comparatively low cost and versatile engineering properties.

Cast irons – iron alloys containing between 2.06 to 4.3% of carbon.

9.8. 2. Type of cast irons

Four different kinds of cast iron can be differentiated from each other by distribution of carbon in their microstructures: **White, gray, Malleable, and ductile iron.**

a. **White cast irons:** it is formed when much of the carbon in a molten cast iron forms iron carbide instead of graphite upon solidification. The microstructure of as – cast unalloyed white cast iron contains large amount of iron carbides in a pearlitic matrix. White cast irons are so called because they fracture to produce a white or bright crystalline fractured surface. To retain the carbon in the form of iron carbide in white cast irons, their carbon and silicon contents must be kept relatively low (that is 2.5-3.0% c and 0.5-1.5% si) and the solidification rate must be high.

Hard and brittle highly wear resistant cast irons consisting of pearlite and cementite. White cast irons are produced by **chilling** some surfaces of the cast mold. **Chilling** prevents formation of Graphite during solidification of the cast iron.

Properties of cast iron

- Hard, brittle
- Shows a “white” crystalline fractured surface
- Excellent wear resistance
- High compressive stress

Applications of white cast irons

- Brake shoes

- Shot blasting nozzles
- Mill liners
- Crushers
- Pump impellers
- Abrasion resistant parts.
- Raw materials for malleable cast irons

b. Grey cast irons:

Gray cast iron is formed when the carbon in the alloy exceeds the amount that can dissolve in the austenite and precipitates as graphite flakes. When a pieces of solidified gray iron is fractured, the fracture surface appears gray because of the exposed graphite.

Composition and microstructure: unalloyed gray cast irons usually contain 2.5 to 4% C and 1 to 3% Si. Since silicon is graphite stabilizing elements in cast irons, relatively high silicon content is used to promote the formation of graphite forms. The solidification rate also slow cooling rate favor the formation of graphite. Moderate and slow cooling rates favor the formation of graphite. The solidification rate also affects the type of matrix formed in gray cast iron. Moderate cooling rate favor the formation of a pearlitic matrix, whereas slow cooling rate favor the favor of ferritic matrix. To produce a fully ferritic matrix in unalloyed gray cast iron, the iron usually annealed to allow the carbon remaining in the matrix to deposit on graphite flakes. Leaving the matrix completely ferritic.

General characteristics/advantages of gray cast iron

- Cheap
- Low melting point
- Fluid – easy to cast, especially advantageous into large complex shapes
- Excellent machinability
- Excellent bearing properties
- Excellent damping properties
- Excellent wear resistance (hi C)
- Can be heat treated (surface hardened etc.)
- Can be alloyed etc.

Applications of grey cast irons:

- Gears
- Flywheels
- water pipes
- engine cylinders
- brake discs

c. Malleable cast iron:

Malleable cast irons are first cast as white cast iron that contains large amount of iron carbide and no graphite. The chemical compositions of malleable casts are therefore restricted to compositions that form white cast iron as shown in the table 10.8.1. The carbon and silicon contents of malleable cast irons are 2 to 2.6% C and 1.1 to 1.6% Si respectively.

To produce a malleable iron structure, cold white iron castings are heated in a malleablizing furnace to dissociate the iron carbide of white iron to graphite and iron. The graphite in the malleable cast iron is in the form of irregular nodular aggregates called *temper carbon*.

Malleable cast irons are important engineering materials since they have the desirable properties of castability, machinability, moderate strength, toughness, corrosion resistance for certain applications and uniformity since all castings heated-treated.

Heat Treatment: the heat treatment of white cast iron produce malleable irons consists of two stages:

1. Graphitization. In this stage the white iron castings are heated above eutectoid temperature, usually 940°C, and held for about 3 to 20 hour depending on the composition and structure, and size of casting. In this stage the iron carbide of white cast iron is transformed to temper carbon and austenite.
2. Cooling. In this stage the austenite of iron can be transformed to the three basic types of matrixes: ferrite, pearlite, or martensite.
 - a. Ferritic malleable iron: to produce a ferritic matrix, the casting, after first stage heating, is fast cooled to 740 to 760°C and then slowly cooled at the rate of 3 to 11°C per hour. During cooling austenite transformed to ferrite and graphite, with the graphite depositing on existing particles of temper carbon.
 - b. Pearlitic malleable iron: to produce this iron, the castings are slowly cooled to about 870°C and are air cooled. The rapid cooling in this transforms the austenite to pearlite; as a result pearlitic malleable iron is formed, which consists of temper carbon nodules in a pearlite matrix.
 - c. Tempered martensitic malleable iron: this type of malleable iron is produced by cooling the castings in the furnace to a quenching temperature of 845°C to 870°C, holding for 15 to 30min to allow them to homogenize, and quenching in agitated oil to develop a martensitic matrix. Finally, the casting are tempered between 590 to 725°C to develop the specified mechanical properties.

Properties of malleable cast iron

- Malleable cast irons have good ductility and machinability.
- Ferritic malleable cast irons are more ductile and less strong and hard, than pearlitic malleable cast irons.

Applications of malleable cast irons:

- Parts of power train of vehicles
- Bearing caps
- Steering gear housings
- Agricultural equipment
- Railroad equipment.

d. Nodular (ductile) cast irons

Ductile cast iron combines the processing advantage of gray cast iron with the engineering advantages of steel. Ductile iron has good fluidity and castability, excellent machinability and good wear resistance. In addation, ductile cast iron has a number of

properties similar to those of steel such as high strength, toughness, ductility, hot workability, and hardenability.

Composition and microstructure: the exceptional engineering properties of ductile iron are due to the spherical nodules of graphite in its internal structure. The relative ductile matrix region between the nodular allows significant amounts of deformation to take place without fracture.

The compositional of unalloyed ductile iron is similar to that of gray iron with respect to carbon and silicon content. The carbon content of unalloyed ductile iron ranges from 3.0 to 4.0% C and the silicon content from 1.8 to 2.8% Si. The sulfur and phosphorus levels of high-quality ductile iron, however, must be kept very low at 0.03% S maximum and 0.1%P maximum, which are about 10 times lower than the maximum levels for gray cast iron.

The spherical nodules in ductile cast iron are formed during solidification of the molten iron because the sulfur and oxygen levels in the iron are reduced to very low levels by adding magnesium to the metal just before it is cast. The magnesium reacts with sulfur and oxygen so that these elements cannot interfere with the formation of the sphere-like nodules.

Ductile cast irons possess high ductility, good fatigue strength; wear resistance, shock resistance and high modulus of elasticity.

Applications of nodular (ductile) cast irons:

- Automotive engine crankshafts
- Heavy duty gears.
- Military and railroad vehicles.

Table 10.8.1: Chemical compositions of some cast irons

Element	Gray iron (%)	White iron (%)	Malleable iron Cast (%)	Ductile iron (%)
Carbon	2.5-4.0	1.8-3.6	2.0-2.6	3.0-4.0
Silicon	1.0-3.0	0.50-1.90	1.1-1.6	1.8-2.8
Manganese	0.25-1.0	0.25-0.08	0.2-1.0	0.10-1.0
sulfur	0.02-0.25	0.06-0.20	0.04-0.18	0.03 max
Phosphorus	0.05-0.18	0.06-0.18	0.18 max	0.1 max

Source: C.F Walton (ed.) iron casting hand book, iron carbon society, 1981.

Chapter Eleven

Heat Treatment

11.1. Introduction

Heat treatment is an important operation in the final fabrication process of many engineering components. Only by heat treatment is it possible to impart high mechanical properties components.

Heat treatment is considered to be a very important tool of metallurgies by range mechanical and properties if subjected to different heat treatment. Today, when science and technology are advancing very rapidly in pursuit of higher and higher properties in materials, heat treatment plays a very important role.

11.2. Principle of heat treatment

Heat treatment may be defined as a sequence of heating and cooling designed of steel to get the desired combination of properties in the steel. The changes in properties of steel after heat treatment are due to phase transformation and structural changes that occur during the heat treatment. The factors which determine and control these structural changes are called the principle of heat treatment. The important principle of heat treatment area as follows:

1. Phase transformation during heating
2. Effect of cooling rate on structural changes during cooling
3. Effect of carbon content and alloying element.

11.4. Phase Transformations in steel during heating

Before heating, microstructure of steel consists of ferrite, pearlite and carbides in widely different amounts depending upon the carbon content and alloying elements in the steel. During heating the first structure change in the steel begins when its temperature reaches lower critical temperature. AC₁ at this temperature pearlite changes austenite. The phase transformation occurs by nucleation of austenite phase at the interfaces between ferrite and carbide (Cementite) crystals. The rate of nucleation increases with increase ferrite-Cementite interfacial area. As the temperature increase, more and more ferrite and Cementite are dissolved in austenite and the structure becomes completely austenite after reaching upper critical temperature. However, some undissolved carbides are still present and formation of homogenous austenite occurs after holding the steel at this temperature. The homogenous austenite is dependant upon time and temperature of heating as shown in the figure below.

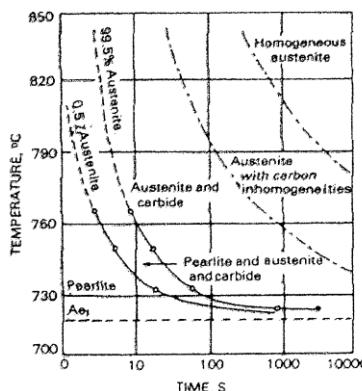


Fig. 3.1 Pearlite to austenite transformation on heating in a eutectoid steel as a function of time and temperature

The figure shows that the formation of homogenous austenite takes places in four stages, namely nucleation austenite from pearlite, transformation of ferrite and Cementite, dislocations carbide carbides and finally the formation of homogenous austenite.

Transformation of Austenite during Cooling

After the formation of homogenous austenite, the steel is allowed tool. Depending upon the rate of cooling, austenite can be made to transform, to different phase. Ferrite, pearlite and Cementite are obtained during slow cooling, while binate and martensitic are formed when the steel is cooled rapidly.

In eutectoid steel contained 0.8% carbon, transformation of austenite to pearlite occurs when austenite reaches the lower critical (AC₁) during slow cooling. The transformation begins by the nucleation and growth of alternate plates of Cementite and ferrite at several points along the austenite the austenite grain has been boundaries. These form pearlite colonies, which grow until the entire austenite grain has been consumed and has become a pearlite module.

When Hypoeutectoid and hypereutectoid steels are cooled from the austenite region, precipitation of ferrite and Cementite is formed between the upper and lower critical temperatures. Ferrite and Cementite takes places between upper and lower critical temperature. Ferrite or Cementite is formed at the grain boundaries of austenite, if sufficient time is allowed for the diffusion to takes place. The proeutectoid phase forms at the region boundaries while the pearlite occupies the center of the grain, thus forming a network structure.

Transformation of austenite to proeutectoid ferrite and Cementite, and eutectoid pearlite, can be avoided by cooling the steel at a sufficient fast rate. When austenite is cooled at a rate greater than critical cooling rate (as given by time-temperature-transformation diagrams), it transforms instantly to a new

phase called martensit. High hardness and strength are obtained due to the formation of martensite.

11.4. Heat treatment Process

A heat treatment process consists of the following steps:

- i. Firstly, the steel is heated to a high temperature called the austenitizing temperature. During heating, the previous structure of steel is converted into austenite phase.
- ii. After reaching the austenitic temperature, the steel is held at this temperature for some period of time, called soaking period. Soaking results in the formation of homogenous austenite throughout the entire cross section.
- iii. Steel having a homogenous austenite structure is cooled back to the room temperature, at particular cooling rate depending up on the properties required.
- iv. If necessary, steel may be reheated to a higher temperature (but lower than AC1) and cooled again.

The above sequence of heating and cooling may vary from a most simple form of heating in a closed furnace and cooling in the air to a more form which requires preheating, soaking in a controlled atmosphere and two-step cooling.

11.5. Type of heat treatment

Depending upon the method of heating, the furnaces atmosphere, the heating temperature, the cooling medium used, and the properties desired, heat treatment processes may be divided into the following basic types.

1. Annealing
2. Normalizing
3. Hardening
4. Tempering
5. Surface Hardening

The basic types of heat treatment are widely in industry depending upon the properties required. Details of these processes, their purposes, phase transformations and the resulting properties shall be discussed in the following sections.

11.5.1. Annealing

Annealing may be defined as heating the steel to austenite phase and then cooling slowly through the transformation range. Slow cooling is generally achieved in closed furnace by switching-off the following process:

Steel is annealed for the following purpose:

- ✓ To reduce hardness
- ✓ To relieve internal stress
- ✓ To improve machinability
- ✓ To facilitate further cold working by restoring ductility

- ✓ To produce the necessary microstructure having desired mechanical, physical, or other process.

The important characteristics of annealing treatment are the slow cooling of steel during the critical transformation range. These slow cooling results in the formation of spheroids carbides and coarse lamellar perlite. These products of transformation are very soft and result in the softening of steel.

In practice steels are generally annealed by simple switching of the furnace after the formation of austenite, there is nothing further of consequence that can occur in the steel during further cooling up to the room temperature. Therefore, after complete transformation of austenite, i.e below 600°C the steel may cool rapidly in air without affecting the structure or properties.

The cooling rate during annealing varies from 50°C/hour to 30°C/hour depending upon the allowing elements in the steel. Lower rates of cooling are used for alloy steel as compared to plain carbon steel.

Annealed Temperature and Soaking Times

The final heating or austeninting temprature for annealing for the given steeel depends on the percentage of carbon in the steel. Generally the follwing guid liune are used.

Type of Steel	Annealeing tempratiure in C
Hypo-eucteciod	AC3 +50
Hyper-eucteciod	AC3 +50

After heating up to austenitzing temprature, the steel is held at this temprature for a minimum of one hour for sections upto 25mm thick. For larger sections, soaking or holding time is increased at the rate of 30 minutes for each additional 25mm of thickness.

The holding time for hypereuctiod and alloy steel can be increased if low hardness values are required. Lower austenizing temprature and longer holding time pruduce spheroidized structure.

Properties After Annealing

Annealing reslts in the formation of ferrite, spheroidal cementite and coarse perlite. All these phases and micro-constitutents are relatively soft. Therefore, annealing is called as softening treatment, and produce relativly lower hardness calues. After hardness of steel can vary fromm 110BHN (Brinell hardness number) to 230 BHN, depending up on the carbon and the alloying elements. Variation of hardness with carbon content in the steel is shown in the table blow.

Table 10.1 Variation of annealing temperature the resulting hardness with carbon content in the steel .

s.n	Carbon content in steel in %	Annealing Temperature in °C	Hardness BHN
1	0.18-0.22	860-900	110-149
2	0.23-0.28	850-890	130-180
3	0.29-0.38	840-880	140-206
4	0.39-0.55	820-870	150-217
5	0.56-0.80	790-840	160-230
6	0.81-0.99	790-830	170-230

Type of Annealing

Annealing is as mention above, is a softening process achieved by heating and slow cooling of materials. In practice, materials require different degree of softening for different applications. The different degrees of softening in steel can be achieved by slight variation in the annealing parameters, such as heating temperature and cooling temperature rate. The variation in these parameters results in what is known as different type of annealing, isothermal annealing, etc. These different types of annealing processes are widely used in commercial practices to achieve a proper combination of structures and hardness required for applications. Important characteristics of different type of annealing process are as follows.

1. **Full Annealing.** Full annealing is defined as heating the steel to austenite phase and then cooling slowly through transformation range. When applied to steel, full annealing is called as annealing.

2. **Box Annealing.** Annealing a metal or alloy in a sealed container under conditions that minimize oxidation, called box annealing. The material is packed with cast iron chips, burnt charcoal, or washed sand. It is called black annealed, close annealing or pot annealing.

3. **Bright Annealing.** Annealing in a protective medium to prevent surface discoloration is called bright annealing. The protective medium is obtained by the use of an inert gas, such as argon, or nitrogen or by using reducing gas.

atmosphere. Typical reducing atmosphere may consist of 15% H₂, 10%CO, 5% CO₂, 1.5%CH₄ and the remainder N₂.

4. Stress Relieve. All process of annealing usually reduce stress, but if the treatment is applied for sole purpose of stress relieve, it is called stress relieving. It may be categorized as finish annealing. It is a low temperature annealing treatment applied to cold worked steels. It results in lowering of the residual stresses, thereby lessening the risk of distortion in machining. Tool steels are generally stress relieved after rough machining.

5. Process Annealing. In sheet and wire industry, steel is heated to a temperature below AC₁ and cooled slowly, in order to soften the alloy for further cold working. It is called process annealing or intermediate annealing.

Application of Annealing

Different type of annealing treatments are widely used in commercial practice. Some typical applications are as follows.

a. Annealing steel casting. The structure of cast steel is characterized by dendritic nature and non-uniformity in composition, due to this process of dendritic formation and chemical segregation which take place during solidification. The microstructure of a cast steel consisting of dendrites of the ferrite phase is shown in the fig 3.2. The undesirable cast structure can be modified by annealing. The cast structures are usually annealed at higher temperatures, and for longer time as compared to wrought steels of similar composition. Cored structures are homogenized by annealing.

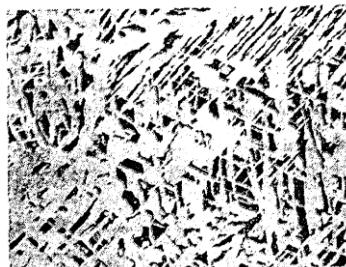


Fig. 3.2 Microstructure of a 0.28 per cent carbon steel in cast condition showing dendritic structure of ferrite (white) and pearlite (black). Etched with Nital, 150 X.

b. Annealing of steel sheet and strip. The hot rolled and the cold rolled steel sheet and strip are annealed to relieve the stresses induced during rolling, and soften the material for subsequent fabrications. Annealing is done at subcritical temperature. It results in recrystallization of the elongated and distorted grain structure developed during cold working and improves ductility.

c. Annealing of steel forging. Forging are generally annealed to improve their machinability and to obtain the desired microstructure. Forgings are annealed as per conventional annealing cycles.

d. Annealing for machinability. Machinability depends upon the microstructure and hardness of steel. A suitable combination of microstructure

and hardness results in good machinability. Presence of coarse lamellar pearlite in medium carbon steel results in high machinability. This type of microstructure can be obtained by annealing as follows:

- a. Medium carbon steels-full annealing
- b. High carbon steels spheroidizing.

Microstructure of high carbon steel after spheroidizing is shown in fig 3.3. The structure shows that cementite is present in the globular form of to impart good machinability.

11.5.2. Normalizing

Normalizing may be defined as heating the steel to Austenite phase and cooling in air. It is done to achieve any one of the following purpose:

- To eliminate coarse-grain structure obtained in previous working operations such as rolling, forging etc.

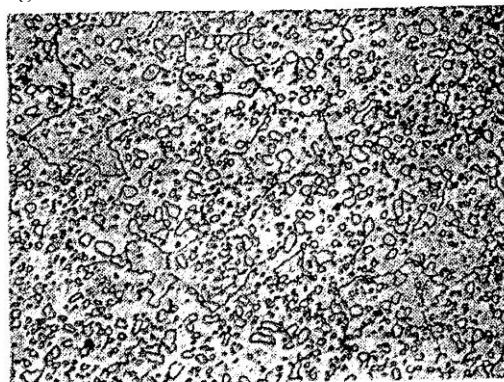


Fig. 3.3 Microstructure of a 1.0 per cent carbon steel after spheroidizing showing globular form of cementite in a ferrite matrix. Etched with Nital, 500 X.

- To modify and improve cast dendrite structure and reduce segregation by homogenizing structure.
- To obtain desired microstructure and mechanical properties. To improve machinability of low carbon steel.

In normalizing steel is uniformly heated to a temperature when cause complete transformation to austenite. The steel is held at this temperature for sufficient time for the formation of homogenous structure throughout its mass. It is then allowed to cool in still air a uniform manner. Air cooling results in faster cooling rate than furnace cooling. Thus, the cooling time is normalizing is drastically reduced as compared to annealing.

Normalizing Temperatures and Soaking Times

Depending up on the carbon content of the steel, the following normalizing temperatures are recommended:

Hypoeutectoid steels- $AC_3 + 50\text{ }^{\circ}\text{C}$

Hypereutectoid steels- $AC_M + 50\text{ }^{\circ}\text{C}$

Normalizing temperature generally varies from 810 to 930 $^{\circ}\text{C}$. after reaching normalizing temperature, it is held at this temperature at the rate of 1hour/25mm thickness. Higher temperatures and longer soaking time may be given alloy steels and heavy cross sections.

Properties after Normalizing

Similar to annealing, normalizing also results the formation of ferrite, cementite and lamellar pearlite. But in normalizing due to higher cooling rate, transformation of austenite takes place at much lower temperature than in annealing. Therefore, the transformation product, pearlite, is finer the interlamellar distance between two neighboring cementite plates.

Normalizing steel will have higher hardness and strength than annealed steel due to the following reasons:

- i. The amount of pearlite in the normalizing steel is much more than annealed steel having the same carbon content, due to the shifting of eutectoid compositions into a lower value.
- ii. The dispersion of pearlite and ferrite is finer.
- iii. The pearlite of normalized steel is finer and has lower interlamellar spacing than that of annealed steel.

Microstructure of a 0.3% carbon steel in annealed and normalizing generally varies from 120 to 300BHN depending up on the carbon content and the thickness. Variation of normalizing temperature and the resulting hardness values with the carbon content in the steel is shown in the table3.2.

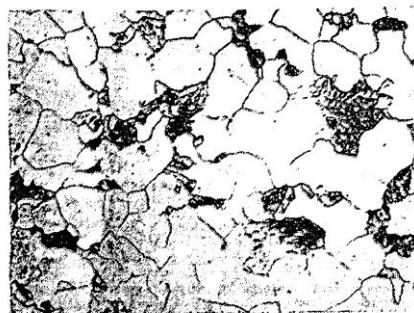


Fig. 3.4 Microstructure of a 0.3 per cent carbon after annealing , showing coarse pearlite (black) and ferrite (white). Etched with Nital, 150 X

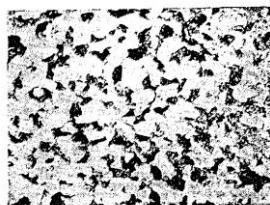


Fig. 3.5 Microstructure of a 0.3 per cent carbon steel after normalizing showing finely dispersed pearlite (black) and ferrite (white). Etched with Nital, 150 X.

Table 3.2 Variation of Normalizing temperature and the resulting hardness with carbon content in steel

SN	Carbon content in steel (%)	Normalizing Temperature (°c)	Resulting hardness (BHN)
1	10.18-0.22	900-925	120-160
2	0.23-0.28	890-910	140-190
3	0.29-0.38	1880-900	150-220
4	0.39-0.55	840-870	180-230
5	0.56-0.80	810-840	210-270
6	0.81-0.99	810-840	260-300

Application of normalizing

Normalizing extensively used in industries because it is much more economical to normalize steel as against annealing. In normalizing, cooling takes place in air and the furnace is ready for other charge, but in annealing cooling takes place inside the furnace, which may take about 8 to 20hrs depending upon the quantity of the charge. In many cases annealing may be replaced by normalizing to reduce the cost of heat treatment. It could be done only if the properties requirements are not very critical. Some typical examples of normalizing in commercial practice are homogenizing of cast and wrought structures, improvements of machinability, grain size refinement of cast and structure and stress relieving of casting.

1. Cast metals are characterized by segregation cored and dendrite structure and non-uniform mechanical properties. Similarly, wrought alloys after forging, rolling, extrusion, etc are non-uniform in structure and properties. These structure and properties are made homogenous by normalizing.

2. Machinability of steel depends on the microstructure, which can be controlled by heat treatment. For example, low carbon steels would have better machinability if the structure is fine and possess higher hardness: medium carbon steels should possess spheroidized structure and lower hardness. The above structure and hardness values can be obtained by different treatment process as given table 3.3 for different steels.

3. The structure of casting is characterized by cause dendrite or equiaxed grains, due to higher temperatures used during melting, slow cooling rates during sand casting. The coarse grain structure undesirable and possess poorer mechanical and properties. It can be improved or refined by annealing or normalizing.

4. The casting also characterized by the presence of high internal stresses developed due to differences in the cooling rates at the core during solidification and subsequent cooling. These internal stresses are undesirable because they may cause cracking during subsequent fabrication, handling or service period.

These internal stresses can be relieved by normalizing or annealing the castings.

Table 3.3 Variation of microstructure for high machinability for different carbon steels

Carbon content in steel, 1%	Desirable microstructure for high machinability
0.06 to 0.20	As cooled rolled
0.20 to 0.30	Normalized
0.30 to 0.40	Annealed to give coarse pearlite
0.40 to 0.60	Annealed to give coarse pearlite and coarse spheroidized
0.60 to 1.20	100% Spheroidized, coarse to fine.

11.5.3. Hardening of steel

Hardening may be defined as rapid cooling of steel from austenite phase. The rapid cooling is obtained by immersion of steel in a liquid bath such as water or oil. Sometimes forced air can be used. The fast cooling of steel from austenite phase results in the formation of a meta-stable phase called martensit. Hardening is also called quenching, because steel is quenched from a high temperature to a liquid bath at room temperature.

The main purpose of hardening of steel is, to increase hardness, strength and wear resistance, and to obtain a suitable microstructure will have desired mechanical properties after tempering.

Successful hardening of steel requires two conditions to be met. Firstly, the formation of homogenous austenite and secondly, rapid cooling of austenite, which will results in the transformation to martensit. The formation of homogeneous austenite takes places when steel is heated to the correct austenitizing temperature, and held at this temperature for sufficient time. After

the formation of homogenous austenite, steel is cooled rapidly by immersion into water or oil bath. This results in the formation of martensite. The transformations of austenite to martensite are very critical and greatly depend upon the cooling rate and other variables.

The process of Quenching

When a piece of heated steel is dropped into a liquid quenching medium the outer surface will cool more rapidly than the core as indicated by two cooling curves in the figure 3.6. Each cooling curve can be divided into three parts called stages of quenching. These stages are the vapor-blanket stage, the vapor transport or boiling stage as shown in figure 3.6.

As soon as the hot metal is dropped into the bath, it is cooled rapidly and becomes surrounding by a blanket of vapor film of quenching medium. After formation of the vapor film the cooling rate drops, because the hot specimen is prevented from coming in contact with liquid medium, and further cooling occurs only through the vapor film by conduction and radiation. The first stage of quenching is called vapor blanket stage. The vapor film is stable, generally at temperatures upto 400°C. when the temperature of the specimen falls below this temperature, the upper film breaks away and the liquid comes into contact with hot metal. Due to this vigorous boiling occurs and the metal cooled rapidly. This second stage of quenching is called boiling stage due to continuous formation of bubbles at the metal surface. Martensite occurs during this stage.

When the metal cools to approximately the boiling point of quenching medium, the boiling ceases and the second stage of boiling ends cooling during the third stage, i.e liquid cooling stages begins by conventional and conditions through the liquid. The cooling rate in this stage is much slower than the other stages. It is advantages if austenite to martensite transformation occurs during this stage. It will result in much lower residual stresses, distortion and quench cracks.

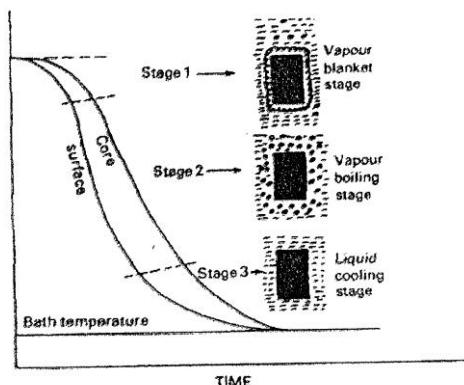


Fig. 3.6 Cooling curves for surface and core and various stages of quenching in a liquid bath

Hardening Temperatures and Soaking Times

Austenitizing temperature prior to hardening depends upon the carbon content of the steel. Hypoeutectoid steels are heated to completely austenite phase, while hypereutectoid steels are heated to obtain a phase mixture of austenite and cementite.

The austenitizing temperature is determined as follows.

- Hypereutectoid steels- $AC_3 + 50^{\circ}C$
- Hypereutectoid steels- $AC_3 + 50^{\circ}C$

The temperatures are generally unaffected by the presence of small amount of alloying elements. Care must be taken to obtain temperature uniformly through the entire cross-section and not to exceed the recommended temperatures. Optimum hardening temperatures for different carbon steels are given in the table 3.4. After reaching the austenitizing temperature, steel is held at this temperature at the rate of 1hr/25mm thickness.

Table 3.4 Variation of Hardening Temperature and the Resulting hardness with carbon content in the steel.

No	Carbon Content in steel	Hardening Temperature($^{\circ}C$)	Resulting hardness (BHN)
1	0.18-0.22	Not Hardening	-
2	0.23-0.28	850-890	370-440
3	0.29-0.38	840-880	420-570
4	0.39-0.55	820-870	550-615
5	0.56-0.80	790-840	-
6	0.81-0.99	90-840	-

Hardening methods

Hardening methods of steel can be slightly varied depending upon the temperature of quenching medium. Sometimes higher temperatures of quenching medium are advantageous and give lower cooling rate, less danger of cracking, and minimum distortion. Steel from austenitizing temperatures is quenched in a liquid bath having high temperatures, and then it may be transferred to a bath having a lower temperature. Thus, depending upon the temperature and type of quenching media used the hardening methods can be divided into three groups:

1. Conventional hardening

When steel is quenched in a single medium, such as water, oil, or air, it is called conventional hardening. It is the most widely used method of hardening steels. Temperature of quenching medium in conventional hardening is generally less than 100°C and well below M_s Temperature of steel.

Main disadvantage of conventional hardening method is that it produces internal stress in the steel after quenching. These high internal stresses in steel are after quenching. These high internal stresses may result in high distortion, warpage and quench cracks.

2. Martempering

After heating the steel to the austenizing temperature, it is quenching in medium having a temperature slightly above the M_s temperature (usually from 200 to 350°C). The article is held in the bath until it reaches the temperature of the medium and then it is cooled further to room temperature in air, or sometimes in oil. The holding time in quenching bath should be sufficient to enable a uniform temperature to be reached throughout the cross-section but not long enough to cause austenite decomposition. Austenite is transformed into martensite during the subsequent period of cooling to room temperature. This treatment produces of martensite and retained austenite in the hardened steel.

Martempering has the following advantages over conventional hardening:

- i. It results reducing warpage and distortion, since the transformation of austenite occurs almost simultaneously in all parts of the articles.
- ii. There is less danger of quenching cracks appearing in the article
- iii. Less volume changes occur in the article due to the presence of larger amount of retained austenite.
- iv. Martempering is used for low-alloy steels having adequate hardenability and articles of smaller sections.

3. Austempering

It is very similar to Martempering. Steel is austenizing and then quenching in a salt bath maintained at a constant temperature in the range of 260 to 400°C . The part is held at this temperature for long enough to allow isothermal transformation to be complete. After the complete transformation of austenite to bainite, steel is cooled to room temperature in air.

Microstructure and Properties after Hardening

When steel is quenched from the austenitizing temperature, austenite is transformed to martensite. This transformation of austenite to martensite is temperature dependant, and some amount of austenite remains untransformed even at room temperature. The untransformed austenite is called retained

austenite. Retained austenite is always present in steels after quenching, unless steel has been quenched at subzero temperatures less than room temperature.

In addition to retained austenite and retained austenite, hardened steel may contain carbides which are not dissolved in austenite during austenitizing. Therefore, microstructure of hardened steel may consist of martensite, retained austenite and carbides. Relative amount of these phases will vary depending upon the composition of steel, austenitizing temperature, soaking time and temperature of quenching medium. If the cooling rate during quenching is low and less than the critical cooling rate, formation of ferrite, pearlite and bainite may result before the formation of martensite from austenite.

The hardness of steel after quenching depends upon the hardness of martensite. Hardness of martensite is a function of its carbon content. It increases with increase in the carbon content and attains the saturation at carbon content of about 0.6%. The figure shows that steels containing less than 0.2% carbon give low hardness values after hardening. Hardness greater than $50R_c$ can be obtained only after hardening steels containing 0.3% carbon.

Variables affecting hardening of steel

The process of hardening of steel is widely used in industry. Most of the engineering components are hardened and tempered before they are put into service. The hardening process of steel looks to be very simple. It requires heating the steel to austenitizing temperature and then quenching it in a liquid bath. But it may not give you the expected hardness in steel. The reason is, that the kinetics of formation of variables which may reduce hardness to an appreciable extent. Some of these variables are austenitizing temperature, holding time, type and temperature of quenching medium, mass and size of the object, etc.

d. Austenitizing temperature. The steel should be heated to the optimum austenitizing temperature will result in lower hardness due to one of the following defects.

- ✓ A coarse-grain structure.
- ✓ Higher amount of retained austenite after quenching.
- ✓ Decarburizing and oxidation at the surface

In addition to lower hardness, higher austenitizing temperature gives increased distortion and danger of cracks in specimen.

e. Soaking time. After heating the steel to the correct austenitizing temperature, it should be held at this temperature for long enough to allow for the formation of homogeneous austenite. As a rule, steel is held at the austenitizing temperature at the rate of 1 hour for every 25mm thickness. If carbides and alloying elements are not fully dissolved in austenite, one may not get the required hardness after quenching.

Soaking time increases with increase in the section thickness and the amount of alloying elements.

f. Delay in quenching. After heating and soaking the steel at the austenitizing temperature, it should be quenched immediately due to the partial transformation of austenite to other phases such as ferrite, pearlite, etc.

g. Type of quenching Medium. As soon as the hot specimen is dropped into liquid bath, extraction of heat from the specimen by liquid begins. Transformation of austenite takes place when the surface of the specimen reaches the martensitic transformation temperature, called M_s temperature. For plain carbon steels this temperature lies between 210 to 230°C. at this temperature a large amount of martensite instantly forms. But if the reaching of this temperature is delayed, some amount of austenite may transform to ferrite, pearlite and bainite. Therefore, temperature of the specimen should be decreased below the M_s Temperature as quickly as possible by the liquid bath to suppress the transformation of austenite to other products. The degree of the lowering of the specimen temperature by the liquid will depend on the heat transfer characteristics of the liquid. The rate of heat extraction will depend upon the heat transfer characteristics of the liquid. The following baths provide different rates of heat extraction:

- i. Water +5% salts, such as sodium chloride, sodium hydroxide, calcium chloride etc. it is called as brine bath.
- ii. Water
- iii. Water +oil
- iv. Oil
- v. Molten salt bath

The higher the heat transfer characteristics of the liquid, higher will be the rate of cooling the specimen, and earlier will be the M_s temperature obtained at the surface of the specimen. The effect of type of quenching medium on the hardness of a 5% of plain carbon steel is shown in table 3.5. Brine quenching gives only about 28 R_c. The lower hardness after oil quenching is due to the formation of some amount of ferrite and pearlite in addition to martensite.

In industry, water and oil are widely used as quenching media. Water is recommended for plain carbon steels for simple shapes, and when the section thickness is not too large. It is a dangerous quenchant, and generally results in higher distortion and quenches cracking. Oil is universally used for quenching of alloy steels, large sections, and for complex shapes parts.

h. Temperature of quenching medium affects the heat transfer characteristics of the liquid and hence changes the cooling rate at the surface of specimen. It gives different hardness values at the surface of the specimen. The effect of temperature of quenching medium on the hardness of 0.5% carbon steel is shown in the table 3.5. The table shows that on one hand the hardness is decreased by increasing the temperature of the water bath; and on the other hand, hardness is first increased by increasing the temperature of the oil bath (due to an appreciable decrease in the viscosity of oil) and then decreased with further increasing the temperature of the bath.

Table 3.5. Effect of Type and Temperature of the Quenching Medium on the hardness of A 0.5% Carbon Steel After Hardening. (Specimens were austenitized at 850°C and quenched in the liquid bath without agitation)

S.N	Type of quenching media	Temperature of the media in C	Hardness obtained after hardening in R
1	Brine	20	60
2	Water	20	59
3	Water	70	56
4	Oil	20	28
5	Oil	60	36
6	Oil	120	24

i. Agitation and circulation of liquid bath. The cooling power of the liquid is greatly improved by agitation and circulation of the liquid bath hence; it results in obtaining higher hardness values agitation. In practice, either the object is strongly agitated in the liquid bath or the liquid is circulated in the tank at high speed to get the best results.

j. Alloy Elements in steel. Alloying elements (such as manganese, Chromium, nickel, molybdenum, etc) have no effect on the hardness of martensite obtained after hardening. Hardness after hardening is mainly determined by the carbon content in the steel.

In spite of the fact that alloying elements do not affect the hardness of martensite all the important engineering steels used after hardening contain an appreciable amount of alloying element. It is because of the fact that alloying elements help to achieve the expected hardness values in larger cross-sections and quenching in oil or even in air other words. Alloying elements suppress the transformation of austenite to pearlite, kainite etc, and allow uniform hardness to be obtained throughout the cross sections for larger size specimens.

The effect of alloying elements on hardness of steel at the surface and at the center, for different diameter bars, is shown in table 3.6.

Table3.6 Effect of Alloying Elements on the Hardness After Hardening Different Diameter Bars
(Specimens were quenched 1 oil from the recommended austenitizing temperatures)

Sl. No.	Composition of steel Percent	Diameter of the bar Mm	Hardness at the surface		Hardness at the centre R_c
			R_c	R_c	
1	C - 0.4	50	38	26	
		100	28	18	
2	C - 0.4	50	50	46	
	Cr-1.0	100	48	43	
	Mo-0.25	150	44	38	
		200	40	30	
3	Cr-0.4	50	57	55	

11.5.4. Tempering

After the hardening treatment is applied, steel is often harder than needed and is too brittle for most practical uses. Also, severe internal stresses are set up during the rapid cooling from the hardening temperature. To relieve the internal stresses and reduce brittleness, you should temper the steel after it is hardened. Tempering consists of heating the steel to a specific temperature (below its hardening temperature), holding it at that temperature for the required length of time, and then cooling it, usually instill air. The resultant strength, hardness, and ductility depend on the temperature to which the steel is heated during the tempering process.

The purpose of tempering is to reduce the brittleness imparted by hardening and to produce definite physical properties within the steel. Tempering always follows, never precedes, the hardening operation. Besides reducing brittleness, tempering softens the steel. That is unavoidable, and the amount of hardness that is lost depends on the temperature that the steel is heated to during the tempering process. That is true of all steels except high-speed steel. Tempering increases the hardness of high-speed steel.

Tempering is always conducted at temperatures below the low-critical point of the steel. In this respect, tempering differs from annealing, normalizing, and hardening in which the temperatures are above the upper critical point. When hardened steel is reheated, tempering begins at 212°F and continues as

the temperature increases toward the low-critical point. By selecting a definite tempering temperature, you can predetermine the resulting hardness and strength. The minimum temperature time for tempering should be 1 hour. If the part is more than 1 inch thick, increase the time by 1 hour for each additional inch of thickness.

Normally, the rate of cooling from the tempering temperature has no effect on the steel. Steel parts are usually cooled in still air after being removed from the tempering furnace; however, there are a few types of steel that must be quenched from the tempering temperature to prevent brittleness. These blue brittle steels can become brittle if heated in certain temperature ranges and allowed to cool slowly. Some of the nickel chromium steels are subject to this temper brittleness. Steel may be tempered after being normalized, providing there is any hardness to temper. Annealed steel is impossible to temper. Tempering relieves quenching stresses and reduces hardness and brittleness. Actually, the tensile strength of hardened steel may increase as the steel is tempered up to a temperature of about 450°F. Above this temperature it starts to decrease. Tempering increases softness, ductility, malleability, and impact resistance. Again, high-speed steel is an exception to the rule. High-speed steel increases in hardness on tempering, provided it is tempered at a high temperature (about 1550°F). Remember, all steel should be removed from the quenching bath and tempered before it is completely cold. Failure to temper correctly results in a quick failure of the hardened part.

Permanent steel magnets are made of special alloys and are heat-treated by hardening and tempering. Hardness and stability are the most important properties in permanent magnets. Magnets are tempered at the minimum tempering temperature of 212°F by placing them in boiling water for 2 to 4 hours. Because of this low tempering temperature, magnets are very hard.

Case-hardened parts should not be tempered at too high a temperature or they may lose some of their hardness. Usually, a temperature range from 212°F to 400°F is high enough to relieve quenching stresses. Some metals require no tempering. The design of the part helps determine the tempering temperature.

Color tempering is based on the oxide colors that appear on the surface of steel, as it is heated. When you slowly heat a piece of polished hardened steel, you can see the surface turn various colors as the temperature changes. These colors indicate structural changes are taking place within the metal. Once the proper color appears, the part is rapidly quenched to prevent further structural change. In color tempering, the surface of the steel must be smooth and free of

oil. The part may be heated by a torch, in a furnace, over a hot plate, or by radiation.

Table 2.3.—Oxide Colors for Tempering Steel

Color	Temperature	
	°F	°C
Pale yellow	428	220
Straw	446	230
Golden yellow	469	243
Brown	491	255
Brown dappled with purple	509	265
Purple	531	277
Dark blue	550	288
Bright blue	567	297
Pale blue	610	321

Cold chisels and similar tools must have hard cut- cutting edge. When you have completed the above dating edges and softer bodies and heads. The head must be tough enough to prevent shattering when struck with shammer. The cutting edge must be more than twice as hard as the head, and the zone separating the two must be carefully blended to prevent a line of demarcation. A method of color tempering frequently used for chisels and similar tools is one in which the cutting end is heated by the residual heat of the opposite end of the same tool.

To harden and temper a cold chisel by this method, you heat the tool to the proper hardening temperature and then quench the cutting end only. Bob the chisel up and down in the bath, always keeping the cutting edge below the surface. This method air-cools the head while rapidly quenching the cutting edge. The result is a tough head, fully hardened cutting edge, and a properly blended structure.

When the cutting end has cooled, remove the chisel from the bath and quickly polish the cutting end with a buff stick (emery). Watch the polished surface, as the heat from the opposite end feeds back into the quenched end. As the temperature of the hardened end increases, oxide colors appear. These oxide colors progress from pale yellow, to a straw color, and end in blue colors. As soon as the correct shade of blue appears, quench the entire chisel to prevent further softening of the cutting edge. The metal is tempered as soon as the proper oxide color appears and quenching merely prevents further tempering by freezing the process. This final quench has no effect on the body and the head of the chisel, because their temperature will have dropped below the critical point by the time the proper oxide color appears on the scribed process, the chisel will be hardened and tempered and only needs grinding.

During the tempering, the oxide color at which you quench the steel varies with the properties desired in the part. Table 2-3 lists the different colors and their corresponding temperatures. To see the colors clearly, you must turn the part from side to side and have good lighting. While hand tempering produces the same result as furnace tempering, there is a greater possibility for error. The slower the operation is performed, the more accurate are the results obtained.

11.6. Quenching Media

The cooling rate of an object depends on many things. The size, composition, and initial temperature of the part and final properties are the deciding factors in selecting the quenching medium. A quenching medium must cool the metal at a rate rapid enough to produce the desired results. Mass affects quenching in that as the mass increases, the time required for complete cooling also increases. Even though parts are the same size, those containing holes or recesses cool more rapidly than solid objects. The composition of the metal determines the maximum cooling rate possible without the danger of cracking or warping. This critical cooling rate, in turn, influences the choice of the quenching medium. The cooling rate of any quenching medium varies with its temperature; therefore, to get uniform results, you must keep the temperature within prescribed limits. The absorption of heat by the quenching medium also depends, to a large extent, on the circulation of the quenching medium or the movement of the part. Agitation of the liquid or the part breaks up the gas that forms an insulating blanket between the part and the liquid.

Normally, hardening takes place when you quench a metal. The composition of the metal usually determines the type of quench to use to produce the desired hardness. For example, shallow-hardened low-alloy and carbon steels require severer quenching than deep-hardened alloy steels that contain large quantities of nickel, manganese, or other elements. Therefore, shallow-hardening steels are usually quenched in water or brine, and the deep-hardening steels are quenched in oil. Sometimes it is necessary to use a combination quench, starting with brine or water and finishing with oil. In addition to producing the desired hardness, the quench must keep cracking, warping, and soft spots to a minimum.

The volume of quenching liquid should be large enough to absorb all the heat during a normal quenching operation without the use of additional cooling. As more metals are quenched, the liquid absorbs the heat and this temperature rise causes a decrease in the cooling rate. Since quenching liquids

must be maintained within definite temperature ranges, mechanical means are used to keep the temperature at prescribed levels during continuous operations.

11.6.1 Liquid Quenching

The two methods used for liquid quenching are called still-bath and flush quenching.

In still-bath quenching, you cool the metal in a tank of liquid. The only movement of the liquid is that caused by the movement of the hot metal, as it is being quenched.

For flush quenching, the liquid is sprayed onto the surface and into every cavity of the part at the same time to ensure uniform cooling. Flush quenching is used for parts having recesses or cavities that would not be properly quenched by ordinary methods. That assures a thorough and uniform quench and reduces the possibilities of distortion.

Quenching liquids must be maintained at uniform temperatures for satisfactory results. That is particularly true for oil. To keep the liquids at their proper temperature, they are usually circulated through water-cooled.

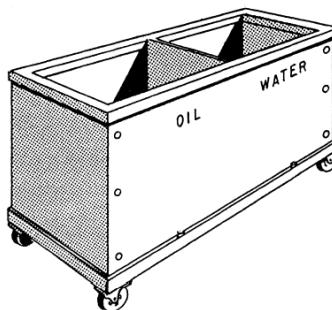


Figure 2-3.—Portable quench tank.

Water: Water can be used to quench some forms of steel, but does not produce good results with tool or other alloy steels. Water absorbs large quantities of atmospheric gases, and when a hot piece of metal is quenched, these gases have a tendency to form bubbles on the surface of the metal. These bubbles tend to collect in holes or recesses and can cause soft spots that later lead to cracking or warping.

The water in the quench tank should be changed daily or more often if required. The quench tank should be large enough to hold the part being treated and should have adequate circulation and temperature control. The temperature of the water should not exceed 65°F. When aluminum alloys and other nonferrous metals require a liquid quench, you should quench them in clean

water. The volume of water in the quench tank should be large enough to prevent a temperature rise of more than 20°F during a single quenching operation. For heavy-sectioned parts, the temperature rise may exceed can cause cracking or stress in high-carbon or low-alloy

20°F, but should be kept as low as possible. For wrought steels that are uneven in cross section. Products, the temperature of the water should be about 65°F and should never exceed 100°F before the piece enters the liquid.

Table 2-4.—Properties and Average Cooling Abilities of Quenching Media

Quenching Medium	Cooling Rate Compared To Water	Flash Point (°F)	Fire Point (°F)
Sodium Hydroxide (10%)	2.06		
Brine (10%) at 65°F	1.96		
Caustic Soda (10%)	1.38		
Water at 65°F	1.00		
Prepared Oil	0.44	365	405
Fuel Oil	0.36	205	219
Cottonseed Oil	0.36	610	680
Neatsfoot Oil	0.33	500	621
Sperm Oil	0.33	500	581
Fish Oil	0.31	401	446
Castor Oil	0.29	565	640
Machine Oil	0.22	405	464
Lard Oil	0.19	565	685
Circulated Air	0.032		
Still Air	0.0152		

Brine: Brine is the result of dissolving common rock salt in water. This mixture reduces the absorption of atmospheric gases that, in turn, reduces the amount of bubbles. As a result, brine wets the metal surface and cools it more rapidly than water. In addition to rapid and uniform cooling, the brine removes a large percentage of any scale that may be present.

The brine solution should contain from 7% to 10% salt by weight or three-fourths pound of salt for each gallon of water. The correct temperature range for a brine solution is 65°F to 100°F.

Low-alloy and carbon steels can be quenched in brine solutions; however, the rapid cooling rate of brine can cause cracking or stress in high-carbon or low-alloy steels that are uneven in cross section.

Because of the corrosive action of salt on nonferrous metals, these metals are not quenched in brine.

Oil: Oil is used to quench high-speed and oil-hardened steels and is preferred for all other steels provided that the required hardness can be obtained. Practically any type of quenching oil is obtainable, including the various animal oils, fish oils, vegetable oils, and mineral oils. Oil is classed as an intermediate quench. It has a slower cooling rate than brine or water and a faster rate than air. The quenching oil temperature should be kept within a range of 80°F to 150°F. The properties and average cooling powers of various quenching oils are given in table 2-4. Water usually collects in the bottom of oil tanks but is not harmful in small amounts. In large quantities it can interfere with the quenching operations; for example, the end of a long piece may extend into the water at the bottom of the tank and crack as a result of the more rapid cooling.

Nonferrous metals are not routinely quenched in oil unless specifications call for oil quenching.

Caustic Soda: A solution of water and caustic soda, containing 10 percent caustic soda by weight, has a higher cooling rate than water. Caustic soda is used only for those types of steel that require extremely rapid cooling and is NEVER used as a quench for nonferrous metals.

WARNING

Caustic soda requires special handling because of its harmful effects on skin and clothing.

11.6.2. Dry Quenching

This type of quenching uses materials other than liquids. In most cases, this method is used only to slow the rate of cooling to prevent warping or cracking.

Air: Air quenching is used for cooling some highly alloyed steels. When you use still air, each tool or part should be placed on a suitable rack so the air can reach all sections of the piece. Parts cooled with circulated air are placed in the same manner and arranged for uniform cooling. Compressed air is used to concentrate the cooling on specific areas of a part. The airlines must be free of moisture to prevent cracking of the metal. Although nonferrous metals are usually quenched in water, pieces that are too large to fit into the quench tank can be cooled with forced-air drafts; however, an air quench should be used for nonferrous metal only when the part will not be subjected to severe corrosion conditions and the required strength and other physical properties can be developed by a mild quench.

11.6.2. Solids

The solids used for cooling steel parts include cast iron chips, lime, sand, and ashes. Solids are generally used to slow the rate of cooling; for example, a cast-iron part can be placed in a lime box after welding to prevent cracking and warping. All solids must be free of moisture to prevent uneven cooling.

11.7. Surface heat Treatment

Most of the load bearing components requires better properties at surface than the interior (core) of the part due the following reason:

- a. In actual service, a metal piece is never stressed uniformly through its section even in the laboratory; it is difficult to align a tensile specimen so accurately as to avoid higher stresses somewhere on the circumference than on other parts.
- b. Rotating shafts have maximum stress at the surface, and minimum at the center.
- c. Wear and fatigue start the surface.
- d. It is the surface where stress concentration appears from nicks, scratches, tool marks, poor fillets, etc.
- e. Wear, seizure, and galling also occur at the surface and produce stress raisers.

On the other hand, the core of the components should have rather contradictory properties. The core should be tough, in the sense that it should provide resistant to notch propagation. If a crack develops on the surface, it should stop when it reaches the core, instead of containing through the core.

The above example illustrates that for many engineering components it is desirable to have different properties at the surface and the core. By basic heat treatment processes, such as annealing, normalizing, hardening and tempering, it is possible to obtain steels in any condition soft, tough and hard. But question arises as to how to achieve different properties at the surface and at the core of the component. Such a combinations of proprieties at different places of the same component can be achieved by a special heat treatment called case-hardening or surface-hardening.

Case hardening may be defined as a process for hardening ferrous materials in such a manner that the surface layer, known as layer as the case, is substantially harder than the remain materials called core. Such a case-hardened

materials can be obtained by having different chemical composition and structures at the surface and at the core these can be achieved by two different methods:

- i. Firstly, without changing the chemical composition of the surface of the steel. It is called surface hardening.
- ii. Secondly, by changing the chemical composition of the steel. It is called case hardening.

11.7.1. Surface hardening of steel

This method is based on the fact that the properties of steel not only depend upon the chemical composition but also upon the presence of various phases and microconstituents. A steel having a definite chemical composition is soft when ferrite and pearlite are present, but it becomes hard when martensite is present. Such a distribution of various phases at the surface of various phases at the surface and the center is obtained by a special heat treatment, called surface hardening. In surface hardening, the aim is to obtain hard martensite phase at the surface and soft ferrite and pearlite microconstituents at the center of the steel. This could be achieved in a medium carbon steel by satisfying the following conditions:

- a. The steel should be heated in such a way that the austenite forms at the surface only and negligible pearlite to austenite forms at the center.
- b. After obtaining such a distribution of various phases across the specimen, it is cooled rapidly so that martensite forms at the surface.

Flame Hardening

Flame hardening is another procedure that is used to harden the surface of metal parts. When you use 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 (see chapter 4) 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 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 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.

Induction Hardening

An electrical conductor (such steel) can be heated by electromagnetic induction by passing an alternative current through an induction, or work coil. When alternating current is passed through the work coil, a rapidly alternating

magnetic field is established with in the coil. The magnetic field thus established induces an electric potential in the part to be heated, because of the part present in the closed circuit, the induced voltage causes the flow of current through the conductor. The resistance R offered by the coil to flow of induced current causes heating. The heat produced in the conductor is proportional to I^2R . the pattern of heating is determined by the shape and design of the induction coil, and the rate of heating, by strength of magnetic field.

Advantage of surface hardening

Flame and induction methods of surface hardening possess many advantages over other methods of hardening. Some of these advantages are:

1. The method are cheaper as compared to other methods of case hardening due to lower cost of energy used per piece, increased production rate, reduced labor cost and less fininsh grinding and machining operations.
2. The induction method can be made completely automatica by the use of heating coils, quenching nozzles, and temperting coils.
3. These methods could be easily applied for selective hardening, where a small area of the part require heat treatment.
4. These method can be used for hardening large parts which are difficult to heat and quench economically in conventiolnal furnaces. Typical examples include, large gears, machine ways, and large dies and rolls.
5. They result in small deformation and distortion because only a thin layer at the surface is heated.
6. Shorter heating times, results in lower degree of decarburization and increased production.

On other hand these methods of surface hardening have certain draw backs, which are:

1. Many times flame and induction heated parts result in cracking during quenching
2. Irrigular shaped parts are not suitable for induction hardening.
3. It is uneconomical to induction harden small quantities of the high intial costs of induction heating equipment and fixtures.
4. Both the methods results in poor surface properties as compared to other method of case hardening.

11.7.2. Case Hardening

Hardness of steel is mainly determined by the percentage of carbon present. As the percentage of carbon increase beyond 0.2%, hardness increase

rapidly after quenching. The same result can be achieved by increasing the nitrogen content at the surface which results in the formation of hard nitrides.

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

Chapter Eleven

Corrosion

12.1 Introduction

Corrosion is the destructive attack of a metal by chemical or electrochemical reaction with its environment. Since corrosion is caused by chemical reaction, the rate at which the corrosion takes place will depend up on to some extent on the temperature and the concentration of reactants and products. Other factors such as mechanical stress and erosion may also contribute.

When we deal about corrosion, we are typically referring to an electromechanical attack process on metals. Metals are susceptible to this attack because the possess free electrons and can setup electromechanical cells within their structures.

The corrosion of metals can be regarded in some ways as reverse of extractive metallurgy. Most metal exist in nature in the combined state, for example, as oxides, sulfides, carbonates or silicates.

12.2. Corrosion Science and Corrosion Engineering

Since corrosion involves chemical change, anyone must be familiar with principles of chemistry in order to understand corrosion reactions. Because corrosion processes are mostly electrochemical, an understanding of a metal often determine corrosion behavior, the student should be familiar with the fundamentals of physical metallurgy as well.

The **corrosion scientist** studies corrosion mechanisms to improve (a) the understanding of the causes of corrosion and (b) the ways to prevent or at least minimize damage caused by corrosion.

The **corrosion engineer**, on the other hand, applies scientific knowledge to control corrosion. For example, the corrosion engineer uses Cathodic protection on a large scale to prevent corrosion of buried pipelines, tests and develops new and better paints, prescribes proper dosage of corrosion inhibitors, or recommends the correct coating. The corrosion scientist, in turn, develops better criteria of cathodic protection, outlines the molecular structure of chemical compounds that behave best as inhibitors, synthesizes.

Why we need study corrosion?

1. To understand how material destroys by corrosion and how they must be protected by applying corrosion protection technology "keep material and precious resources"
2. Engineering knowledge is incomplete without understanding corrosion , areoplanes, ships automobiles and others cannot be designed without knowledge to corrosion behavior of material used in these structure
3. Corrosion is a treat to the environment i.e. water can become contaminated by corrosion products and unsuitable for consumption.

12.3. Importance of corrosion

The three main reasons for the importance of corrosion are: *economics, safety, and conservation*. To reduce the economic impact of corrosion, corrosion engineers, with the support of corrosion scientists, aim to reduce material losses, as well as the accompanying economic losses, that result from the corrosion of piping, tanks, metal components of machines, ships, bridges, marine structures, and so on. Corrosion can compromise the safety of operating equipment by causing failure (with catastrophic consequences) of, for example, pressure vessels, boilers, metallic containers for toxic chemicals, turbine blades and rotors, bridges, airplane components, and automotive steering mechanisms.

Safety is a critical consideration in the design of equipment for nuclear power plants and for disposal of nuclear wastes. Loss of metal by corrosion is a waste not only of the metal, but also of the energy, the water, and the human effort that was used to produce and fabricate the metal structures in the first place. In addition, rebuilding corroded equipment requires further investment of all these resources —metal, energy, water, and human.

Economic losses are divided into (1) direct losses and (2) indirect losses.

Direct losses include the costs of replacing corroded structures and machinery or their components, such as condenser tubes, mufflers, pipelines, and metal roofing, including necessary labor. Other examples are (a) repainting structures where prevention of rusting is the prime objective and (b) the capital costs plus maintenance of cathodic protection systems for underground pipelines. **Direct losses** include the extra cost of using corrosion - resistant metals and alloys\ instead of carbon. Steel where the latter has adequate mechanical properties but not sufficient corrosion resistance; there are also the costs of galvanizing or nickel plating of steel, of adding corrosion inhibitors to water, and of dehumidifying storage rooms for metal equipment.

Indirect losses are more difficult to assess, but a brief survey of typical losses of this kind compels the conclusion that they add several billion dollars to the direct losses already outlined. Examples of indirect losses are as follows:

1. **Shutdown.** The replacement of a corroded tube in an oil refinery may cost a few hundred dollars, but shutdown of the unit while repairs are underway may be high per hour in lost production.
2. **Loss of Product.** Losses of oil, gas, or water occur through a corroded pipe system until repairs are made. Antifreeze may be lost through a corroded auto radiator; or gas leaking from a corroded pipe may enter the basement of a building, causing an explosion.
3. **Loss of Efficiency.** Loss of efficiency may occur because of diminished heat transfer through accumulated corrosion products, or because of the clogging of pipes with rust necessitating increased pumping capacity.
4. **Contamination of Product.** A small amount of copper picked up by slight corrosion of copper piping or of brass equipment that is otherwise durable may damage an entire batch of soap. Copper salts accelerate rancidity of soaps and shorten the time that they can be stored before use.
5. **Overdesign.** Overdesign is common in the design of reaction vessels, boilers, condenser tubes, oil - well sucker rods, pipelines transporting oil and gas at high pressure, water tanks, and marine structures. Equipment is often designed many times heavier than normal operating pressures or applied stresses would require in order ensuring reasonable life. With adequate knowledge of corrosion, more reliable estimates of equipment life can be made, and design can be simplified in terms of materials and labor.

TYPES OF CORROSION

Corrosion is often thought of only in terms of rusting and tarnishing. However, corrosion damage occurs in other ways as well, resulting, for example, in failure by cracking or in loss of strength or ductility. In general, most types of corrosion, with some exceptions, occur by electrochemical mechanisms, but corrosion products are not necessarily observable and metal weight loss need not be appreciable to result in major damage. The main types of corrosion classified with respect to outward appearance or altered physical properties are as follows:

1. **General Corrosion or Uniform Attack.**

Uniform corrosion attack is characterized by an electromechanical or chemical reaction that proceeds uniformly on entire metals surface exposed to corrosive environment. On weight basis, uniform attack represents the greatest destruction of metals particularly steels. However, relatively it is easy to control by (1) protecting coating, (2) inhibitors, (3) Cathodic protection.

Uniform Corrosion



Or specifically Uniform corrosion can be slowed or stopped by using the five Basic facts;

- (1) Slow down or stop the movement of electrons

- a) Coat the surface with a non-conducting medium such as paint, lacquer or oil
 - b) Reduce the conductivity of the solution in contact with the metal an extreme case being to keep it dry. Wash away conductive pollutants regularly.
 - c) (Apply a current to the material (see cathodic protection).
- (2) Slow down or stop oxygen from reaching the surface. Difficult to do completely but coatings can help.
- (3) Prevent the metal from giving up electrons by using a more corrosion resistant metal higher in the electrochemical series. Use a sacrificial coating which gives up its electrons more easily than the metal being protected. Apply cathodic protection. Use inhibitors.
- (4) Select a metal that forms an oxide that is protective and stops the reaction.

2. Localized corrosion

The consequences of localised corrosion can be a great deal more severe than uniform corrosion generally because the failure occurs without warning and after a surprisingly short period of use or exposure. The following are localized corrosions:

Pitting, Galvanic, Crevices, Intergranular, selective attack, stray current corrosion, microbial, corrosion fatigue, fretting, Stress concentration, hydrogen Damage.

a. Pitting.

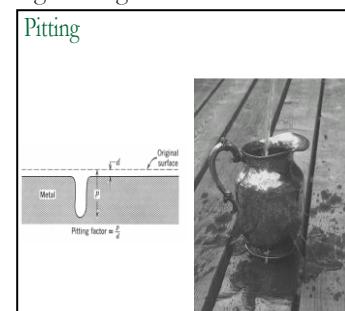
This is a localized type of attack that produces holes or pits in a metal. This form of corrosion is very destructive for engineering structure if its causes perforation of metals. However, if perforation does not occur, minimum pitting is sometimes acceptable in engineering equipment. Pitting is often difficult to detect because small pits may be covered by corrosion products.

As a result, pitting, because of its localized nature, pitting can often result in sudden, unexpected failures. Pitting usually requires an initiation period, but once started, the pit grows at an ever-increasing rate. Most pits develop and grow the direction of gravity and on the lower surface of engineering equipment.

Pits are initiated at places where local increases in corrosion rate occur. Inclusions, other structural heterogeneous on the metal surface are common place where pits initiate.

Control can be ensured by:

- Selecting a resistant material;



- Ensuring a high enough flow velocity of fluids in contact with the material or frequent washing;
- Control of the chemistry of fluids and use of inhibitors;
- Use of a protective coating;
- Maintaining the material's own protective film;

b. Galvanic Corrosion

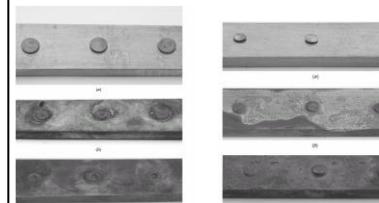
This can occur when two different metals are placed in contact with each other and is caused by the greater willingness of one to give up electrons than the other. Three special features of this mechanism need to operate for corrosion to occur:

- The metals need to be in contact electrically
- One metal needs to be significantly better at giving up electrons than the other
- An additional path for ion and electron movement is necessary.

Prevention of this problem is based on ensuring that one or more of the three features do not exist.

- Break the electrical contact using plastic insulators or coatings between the metals.
- Select metals close together in the galvanic series.
- Prevent ion movement by coating the junction with an impermeable material, or
- Ensure environment is dry and liquids cannot be trapped.

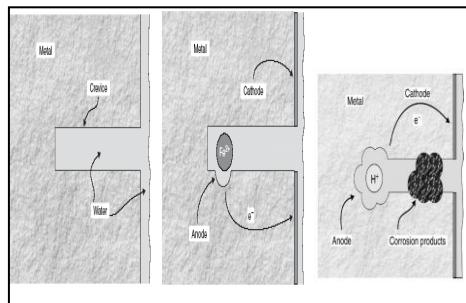
Galvanic Corrosion



Steel riveted in copper or Vis-versa

c. Concentration cell corrosion/Crevice

It is a form of localized electromechanical corrosion that can occur in crevices and under shielded surfaces where stagnant solution can exist. It occurs under gaskets, rivets, and bolts, between valve discs and seats, under porous deposits and in many other similar situations.



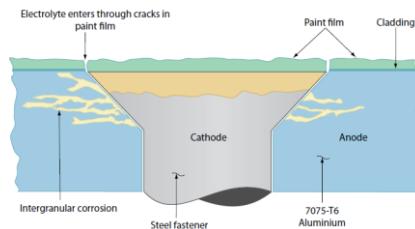
If two areas of a component in close proximity differ in the amount of reactive constituent available the reaction in one of the areas is speeded up. An example of this is crevice corrosion which occurs when oxygen cannot penetrate a crevice and a differential aeration cell is set up. Corrosion occurs rapidly in the area with less oxygen.

The potential for crevice corrosion can be reduced by:

- Avoiding sharp corners and designing out stagnant areas
- Use of sealants
- Use welds instead of bolts or rivets
- Selection of resistant materials

d. Intergranular Corrosion

This is preferential attack of the grain boundaries of the crystals that form the metal. It is caused by the physical and chemical differences between the centres and edges of the grain.



It can be avoided by:

- Selection of stabilised materials
- Control of heat treatments and processing to avoid susceptible temperature range.

e. Stress corrosion Cracking

The combined action of a static tensile stress and corrosion which forms cracks and eventually catastrophic failure of the component. This is specific to a metal material paired with a specific environment.

Prevention can be achieved by:

- Reducing the overall stress level and designing out stress concentrations
- Selection of a suitable material not susceptible to the environment
- Design to minimise thermal and residual stresses
- Developing compressive stresses in the surface the material
- Use of a suitable protective coating
-

Erosion Corrosion

It can define as the acceleration in the rate of corrosion attack in a metal due to the relative motion of a corrosive fluid and a metal surface. When the relative motion of fluid is rapid, the effects of mechanical wear and abrasion can be severe. Corrosion erosion is characterized by the appearance on the metal surface of grooves, Valleys, pits, round holes, and other metal surface damage configuration that usually occur in the direction of the flow of the corrosive fluid.

Cavitation Damage

This type of erosion is caused by the formation and collapse of air bubbles or vapour-filled cavities in a liquid near a metal surface. Cavitation damage occurs on metal surfaces where high-velocity liquid flow and pressure changes exist such as are encountered with pump impellers and ship propellers.

Fretting corrosion: it occurs at interfaces between materials under load subjected to vibration and slip. Fretting corrosion appears as grooves or pits surround by corrosion products. In the case of the fretting corrosion of metals, metal fragments between the rubbing surfaces are oxidized and some oxide films are torn loss by the wear action. As a result, there is an accumulation of oxides particles that act as abrasive between the rubbing surfaces such as those found between shafts and bearings or sleeves.

Prevention is possible by:

- Designing out vibrations
- Lubrication of metal surfaces
- Increasing the load between the surfaces to stop the motion
- Surface treatments to reduce wear and increase friction coefficient.



Selective Leaching/Dealloying

It is preferential removal of one element of a solid alloy by corrosion processes. The most common example of this type of corrosion, dezincification, in which the selective leaching of zinc from copper in brass is, occurs. Similar processes also occur in other alloy systems such as the loss of nickel, tin, and chromium from copper alloys, iron from cast iron, nickel from alloy steels, and cobalt from satellite.

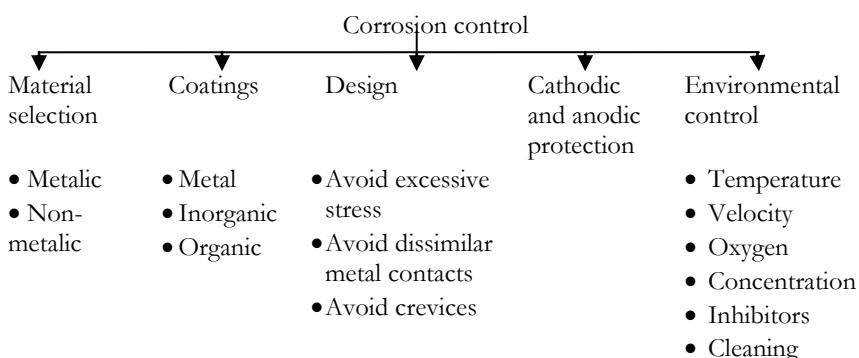
It is best avoided by selection of a resistant material but other means can be effective such as:

- Coating the material
- Reducing the aggressiveness of the environment
- Use of cathodic protection

Parting is similar to dezincification in that one or more reactive components of the alloy corrode preferentially, leaving a porous residue that may retain the original shape of the alloy. Parting is usually restricted to such noble metal alloys as gold – copper or gold – silver and is used in gold refining. For example, an alloy of Au – Ag containing more than 65% gold resists concentrated nitric acid as well as does gold itself. However, on addition of silver to form an alloy of approximately 25% Au – 75% Ag, reaction with concentrated HNO₃ forms silver nitrate and a porous residue or powder of pure gold. Copper - base alloys that contain aluminum are subject to a form of corrosion resembling dezincification, with aluminum corroding preferentially.

Corrosion control

Corrosion can be controlled or prevented by different ways. From an industrial point of view, the economics of the situation usually dictate the method used.



1. Material selection

Metallic materials: one of the most common methods of corrosion control is to use materials that are corrosion resistant for a particular environment.

Rules:

- For *reduced or non-oxidized* conditions such as *air-free acids* and aqueous solutions, *are often used.*
 - For *oxidized* conditions, chromium-alloys are used.
 - For extremely power full oxidizing conditions, *titanium and its alloy* are used.
- c. **Non-metallic material:** *polymeric materials* such as plastics and rubbers are weaker, softer and in general less resistant to strong inorganic acids than metals and alloys, and thus their use as primary materials for corrosion resistance is limited.
- d. **Ceramic materials** have excellent corrosion and high temperature resistance but have disadvantage of brittleness.

2. Coatings

Removing or separating the corrosive environment from the metal can prevent corrosion. This is the principle of coatings applied for corrosion protection. Paint and galvanizing are examples of coatings that have been used for many years.

Coatings can be divided into 3 general categories:

a. Metallic coatings

Most metal coatings are applied by dipping the article into a molten bath of the metal or by electroplating the coating from aqueous solution. Some coatings are also applied by metal spraying. Metal coatings can be classified as noble or sacrificial. A noble metal coating such as chrome plating protects by its own resistance to corrosion. Sacrificial coatings such as zinc and cadmium cathodically protect the base metal.

b. Inorganic coatings

Vitreous enamels, cement lining, phosphate coatings and oxide coatings represent inorganic coatings. Vitreous elements or glass coatings are very corrosion-resisted but somewhat brittle. Cement coatings are very popular for lining water flow lines.

c. Organic coatings

Organic coatings are the most widely used means of protecting against corrosion. These coatings represent a large variety of materials that can be classified as paint, enamel, lacquer, and plastic linings. In recent years, plastic linings have found frequent usage in protecting tubing, flow lines, and tanks from corrosion. The surface preparation and application of these coatings is very important in the success of the coating.

d. Use of plastics

Generally, plastics are used in applications where temperatures and pressures are low. Plastic pipe is frequently used for flow lines with particularly corrosive oilfield brines.

3. Design

The proper engineering design of equipment can be as important for corrosion prevention as the selection of proper materials. The engineer designer must be considering the materials along with the necessary mechanical, electrical and

thermal property requirements. All these considerations must be balanced with economic limitations

Important design rules

1. Allow for penetration action of corrosion along with the mechanical strength requirements when considering the thickness of the metal used.
2. Weld rather than rivet containers to reduce crevices corrosion.
3. If possible, use galvanically similar metals for the entire structure.
4. Avoid excessive stress and stress concentration in corrosive environment to prevent cross-section cracking.
5. Avoid sharp bends in piping systems where flow occurs to avoid erosion corrosion.
6. Design tanks and other containers for easy draining and cleaning.
7. Design system for easy removal and replacement of parts that are expected to fail rapidly in service.
8. Design heating systems so that the hot spot do not occur.

4. Alteration of Environment

Environmental conditions can be very important in determining the severity of corrosion. Important methods for reducing corrosion by environmental changes are:

1. Lowering the temperature

Lowering the temperatures of a system usually reduces corrosion because of the lower reactions rate at lower temperatures. However, there are some exceptions in which the reverse is the case. For example, boiling seawater is less corrosive than hot seawater because of decreasing in oxygen solubility with increasing temperature.

2. Decreasing velocity of liquids

Decreasing the velocity of a corrosive fluid reduce erosion corrosion. However, for metals and alloys that passivate, stagnant solutions should be avoided.

3. Removing oxygen liquids

Removing oxygen from water solutions is sometimes helpful for in reducing corrosion.

4. Reducing ion concentrations

Reducing the concentration of corrosive ions in the solutions that is corroding a metal can decrease the corrosion rate of the metal. For example reducing the chloride in water solution will reduce its corrosion attack of stainless steel.

5. Adding inhibitors to electrolytes

Adding inhibitors to a system can be decrease corrosion. Inhibitors are essentially retarding catalysts. Most inhibitors have been developed by emperical experiment and many are proprietors in the nature. Their actions also vary considerably.

Addition of inhibitors

Corrosion inhibitors are chemical substances that are added to the corrosive environment to reduce or eliminate corrosion. By the addition of corrosion

inhibitors to water a simple and inexpensive solution to the corrosion problem is often found. Otherwise, the solution to the corrosion problem may require extensive modification and replacement of equipment or installation of water treatment equipment.

Many commercially prepared corrosion inhibitors used in the oil field contain surface active agents. When these are added to a system for the first time, they remove loose deposits of corrosion products. Precautions should be taken to prevent these deposits from accumulating in equipment or in injection wells in order to prevent plugging.

Cathodic protection and Anodic

Cathodic protection consists of applying an electrical current to the surface of the metal to be protected in such a way that it will become a cathodic area. The current is applied externally, so that a net positive current enters all areas of the metal, including those that were previously anodic. Cathodic protection is applied to protect steel, brass, lead, copper and aluminium against corrosion when these metals are immersed in water.

Cathodic protection is particularly useful in protecting the submersed areas of water tanks and filters. Since only the areas below the water line are protected, other methods must be used to protect metal above the water line.

Cathodic protection has an advantage over coatings in protecting sand filters, since coatings will not stand sand abrasion during backwashing operations.

Anodic protections:

It is relatively new and based on the formation of protective passive films on metals and alloy surfaces by externally impressed anodic currents. Carefully controlled anodic currents by a device called a potentiostat can be applied to protect metals that passive, such as an austenite stainless steels, to make them passive and hence lower their corrosion rate in a corrosive environment. Advantages of anodic protection are that it can be applied in weak to very corrosive conditions and that it uses very small currents. A disadvantage of anodic protection is that it requires complex instrumentation and has a high installation cost.

Review Questions

1. Define corrosion
2. Describe the loss caused by corrosion
3. What are the factors affects corrossions.
4. Explain corrosion types and their causes.
5. Explain type of corrosion control methods.

Chapter Thirteen

Non-Ferrous metals

13.1 Introduction

Although there are many metallic elements, it is customary to divide metals and alloys into major categories, ferrous and non-ferrous. The former category covers the element iron and its alloy, while all the other metallic elements (70 in number) and their alloys are classified as non-ferrous. Iron occupies a very special position among metallic materials, owing to its availability, its comparatively low cost, and they are very useful range of alloys that are formed when iron is alloyed with carbon and other elements. 94% of world metallic consumption is in the form of steel and cast iron.

On other hand, out of all the non-ferrous metals, only a few, aluminum, copper, lead, magnesium, nickel, tin, titanium, and zinc, are produced moderately large quantities.

12.2. Aluminum and Aluminum Alloys

Pure aluminium is a silver-white metal characterized by a slightly bluish cast. It has a specific gravity of 2.70, resists the corrosive effects of many chemicals, and has a malleability approaching that of gold. When alloyed with other metals, numerous properties are obtained that make these alloys useful over a wide range of applications.

Aluminum alloys are light in weight compared with steel, brass, nickel, or copper; can be fabricated by all common processes; are available in a wide range of sizes, shapes, and forms; resist corrosion; readily accept a wide range of surface finishes; have good electrical and thermal conductivities; and are highly reflective to both heat and light.

Characteristics of Aluminum and Aluminum Alloys.—Aluminum and its alloys lose part of their strength at elevated temperatures, although some alloys retain good strength at temperatures from 400 to 500 degrees F. At subzero temperatures, however, their strength increases without loss of ductility so that aluminum is a particularly useful metal for low-temperature applications. Aluminum is a particularly useful metal for low-temperature applications.

When aluminum surfaces are exposed to the atmosphere, a thin invisible oxide skin forms immediately that protects the metal from further oxidation. This self-protecting characteristic gives aluminum its high resistance to corrosion. Unless exposed to some substance or condition that destroys this protective oxide coating, the metal remains protected against corrosion. Aluminum is highly resistant to weathering, even in industrial atmospheres. It is also corrosion resistant to many acids. Alkalies are among the few substances that attack the oxide skin and therefore are corrosive to aluminum. Although the metal can safely be used in the presence of certain mild alkalies with the aid of inhibitors, in general, direct contact with alkaline substances should be avoided. Direct contact with certain other metals should be avoided in the presence of an

electrolyte; otherwise, galvanic corrosion of the aluminum may take place in the contact area. Where other metals must be fastened to aluminum, the use of a bituminous paint coating or insulating tape is recommended.

Aluminum is one of the two common metals having an electrical conductivity high enough for use as an electric conductor. The conductivity of electric-conductor grade is about 62% that of the International Annealed Copper Standard. Because aluminum has less than one-third the specific gravity of copper, however, a pound of aluminium will go almost twice as far as a pound of copper when used as a conductor. Alloying lowers the conductivity somewhat so that wherever possible the EC grade is used in electric conductor applications. However, aluminum takes a set, which often results in loosening of screwed connectors, leading to arcing and fires. Special clamping designs are therefore required when aluminum is used for electrical wiring, especially in buildings.

Aluminium has nonspeaking and nonmagnetic characteristics that make the metal useful for electrical shielding purposes such as in bus bar housings or enclosures for other electrical equipment and for use around inflammable or explosive substances.

Heat-treatability of Wrought Aluminium Alloys.

In high-purity form, aluminium is soft and ductile. Most commercial uses, however, require greater strength than pure aluminium affords. This extra strength is achieved in aluminium first by the addition of other elements to produce various alloys, which singly or in combination impart strength to the metal. Further strengthening is possible by means that classify the alloys roughly into two categories, non-heat-treatable and heat-treatable.

Non-heat-treatable alloys

The initial strength of alloys in this group depends upon the hardening effect of elements such as manganese, silicon, iron and magnesium, singly or in various combinations. The non-heat-treatable alloys are usually designated, therefore, in the 1000, 3000, 4000, or 5000 series. These alloys are work-hardenable, so further strengthening is made possible by various degrees of cold working, denoted by the "H" series of tempers. Alloys containing appreciable amounts of magnesium when supplied in strain-hardened tempers are usually given a final elevated-temperature treatment called stabilizing for property stability.

Heat-treatable alloys:

The initial strength of alloys in this group is enhanced by the addition of alloying elements such as copper, magnesium, zinc, and silicon. These elements singly or in various combinations show increasing solid solubility in aluminium with increasing temperature, so it is possible to subject them to thermal treatments that will impart pronounced strengthening.

The first step, called heat-treatment or solution heat-treatment, is an elevated-temperature process designed to put the soluble element in solid solution. This step is followed by rapid quenching, usually in water, which momentarily "freezes" the structure and for a short time renders the alloy very workable. Some fabricators retain this more workable structure by storing the

alloys at below freezing temperatures until they can be formed. At room or elevated temperatures the alloys are not stable after quenching, however, and precipitation of the constituents from the supersaturated solution begins.

After a period of several days at room temperature, termed aging or room-temperature precipitation, the alloy is considerably stronger. Many alloys approach a stable condition at room temperature, but some alloys, particularly those containing magnesium and silicon or magnesium and zinc, continue to age-harden for long periods of time at room temperature.

Heating for a controlled time at slightly elevated temperatures provides even further strengthening and properties are stabilized. This process is called artificial aging or precipitation hardening. By application of the proper combination of solution heat-treatment, quenching, cold working and artificial aging, the highest strengths are obtained.

Clad Aluminium Alloys.—The heat-treatable alloys in which copper or zinc are major alloying constituents are less resistant to corrosive attack than the majority of non-heat-treatable alloys. To increase the corrosion resistance of these alloys in sheet and plate form they are often clad with high-purity aluminium, a low magnesium-silicon alloy, or an alloy containing 1% zinc. The cladding, usually from 2.5 to 5% of the total thickness on each side, not only protects the composite due to its own inherently excellent corrosion resistance but also exerts a galvanic effect that further protects the core material.

Special composites may be obtained such as clad non-heat-treatable alloys for extra corrosion protection, for brazing purposes, or for special surface finishes. Some alloys in wire and tubular form are clad for similar reasons and on an experimental basis extrusions also have been clad.

Aluminum is one of the abundant elements in the earth crust, but, owing to its high affinity to oxygen, it cannot be reduced to metallic state by reduction with carbon or carbon mono-oxide.

12.3. Copper and copper alloys

Copper and copper alloys are widely used in a variety of products that enable and enhance our everyday lives. They have *excellent electrical and thermal conductivities, exhibit good strength and formability, have outstanding resistance to corrosion and fatigue, and are generally nonmagnetic*. They can be readily soldered and brazed, and many can be welded by various gas, arc and resistance methods. They can be polished and buffed to almost any desired texture and luster. Pure copper is used extensively for *electrical wire and cable, electrical contacts and various other parts that are required to pass electrical current*.

Copper in its pure, unalloyed state is *soft, provides high electrical and thermal conductivity and has excellent corrosion resistance*. There are various grades of unalloyed copper, which differ in the amount of impurities they contain.

Oxygen-free coppers are used specifically in applications requiring high conductivity and exceptional ductility.

Brasses are alloys made from *copper and zinc*; they exhibit good strength and ductility and are easily cold worked, properties which improve with *increased zinc content up to 35%*. Brass coloration ranges from red to golden yellow, depending on the amount of zinc the alloy contains. Gilding Metal, Commercial Bronze, Jewelry Bronze, Red Brass and Cartridge Brass are common names given to brass alloys with specific zinc contents. Brasses containing between 32% and 39% zinc exhibit excellent hot working characteristics but limited cold workability.

Brasses containing more than 39% zinc, such as Muntz Metal, have high strength and lower ductility at room temperature than alloys with less zinc. Brasses are known for their ease of fabrication by drawing, high cold-worked strength and corrosion resistance. Brasses are routinely blanked, coined, drawn and pierced to produce springs, fire extinguishers, jewelry, radiator cores, lamp fixtures, ammunition, flexible hose and the base for gold plate. Brasses have excellent castability. Cast brasses are used as plumbing fixtures, decorative hardware, architectural trim, low pressure valves, gears and bearings.

Tin Brasses are alloys made from copper, *zinc (2% to 40%) and tin (0.2% to 3%)*. This family of alloys includes admiralty brasses, naval brasses and free-machining tin brasses. These alloys are used to make high-strength fasteners, electrical connectors, springs, corrosion resistant mechanical products, marine hardware, pump shafts, and corrosion-resistant screw machine parts. They provide increased corrosion resistance, lower sensitivity to dezincification and higher strength compared with straight brasses. They possess good hot forgeability and good cold formability. These materials have moderate strength, high atmospheric and aqueous corrosion resistance and excellent electrical conductivity.

Silicon Bronzes are part of the subgroup of high-strength brasses. They contain less than 20% zinc and up to 6% silicon and are solid solution strengthened. Silicon red brasses are used for valve stems where corrosion resistance and high strength are critical. Included in this category are the silicon red bronzes, which are similar to silicon red brasses except for their very low concentrations of zinc. They are used to make bearings, gears and intricately shaped pump and valve components.

Nickel Silvers, also called nickel brasses, are alloys containing copper, nickel, and zinc. Though they do not contain silver, they have an attractive silver luster, moderately high strength and good corrosion resistance. They are used to make food and beverage handling equipment, decorative hardware, electroplated tableware, optical and photographic equipment and musical instruments.

Copper Nickel alloys contain anywhere from 2% to 30% nickel, are highly corrosion-resistant and thermally stable. The addition of iron, chromium, niobium and/or manganese can improve their strength and corrosion resistance. They are virtually immune to stress corrosion cracking and exhibit high oxidation resistance in steam and moist air. The higher nickel alloys are well known for their corrosion resistance in sea water as well as resistance to marine

biofouling. They are used to make electrical and electronic products, tubes for condensers in ships, on offshore platforms and in power plants, and various other marine products including valves, pumps, fittings and sheathing for ship hulls.

Phosphor Bronzes, or tin bronzes as they are sometimes called, contain between 0.5% and 11% tin and 0.01% to 0.35% phosphorous. Tin increases their corrosion resistance and tensile strength; phosphorous increases wear resistance and stiffness. Phosphor bronzes have super spring qualities, high fatigue resistance, excellent formability and solderability, and high corrosion resistance. They are used primarily for electrical products; other uses include corrosion resistant bellows, diaphragms and spring washers.

12.4. Lead

Lead is a metal that has been used by man for long years. It is soft and malleable and possesses an excellent resistant to corrosion. Because of these properties it has been used for water pipe work, and weather flashing on buildings. Because of its high density it can be radiation shielding materials.

Major application: Acid storage batteries. The soft solders are lead-tin alloys.

12.5. Tin

It exists in gray tin and white tin with body centered tetragonal structure. The attractive appearance of tin, its low melting point, good corrosion resistance and its lack of toxicity made tin an ideal metal for coating mild steel to make tin-plate for manufacture of cans.

12.6. Magnesium

Perhaps the most important property of magnesium is its very low density. Pure magnesium comparatively weak and is not unalloyed. Magnesium can be strengthening considerably by suitable alloy of adding aluminum, thorium, and zinc. Magnesium will improve corrosion resistance.

Applications: air craft construction, in the form of castings, forging and sheet materials for components of landing wheel, airscrew blades, fuel tanks, engine components and canning material for nuclear reactors.

12.7. Nickel

Nickel is one of the most important metals in these technology ages. It is used to large extent as an alloy addition in many steels and cast iron, and in a number of non-ferrous alloys.

Pure nickel possesses an excellent resistant to corrosion by alkalis and many acids and consequently, is used in chemical engineering plant, in food industries.

Chapter 13

Polymers

13.1 Introduction

The word polymer literally means many parts. A Polymer solid materials may be considered to be one that contains many chemically bonded parts or units that themselves are bonded together to form a solid. In this subtopic we shall study some aspects of structure, properties, processing an application of two important polymeric industrial materials: Plastic and Elastomers. Plastics are large and varied group of synthetic materials that are processing by forming or molding into shapes.

Plastics can be divided into two major groups' thermoplastic and thermosetting plastics, depending on how they are structurally bonded. Elastomers or rubbers can be elastically deformed a large amount when they a force is applied to them and can return to their original shape when the force released.

13.2. Thermoset Plastics vs Thermoplastics

When classified by chemical structure, there are two generally recognized classes of plastic materials: Thermoset, having cross-linked molecular chains and Thermoplastics, which are made up of linear molecular chains. Thermoset polymers require a two-stage polymerization process. The first is done by the material supplier which results in a linear chain polymer with partially reacted portions. The second is done by the molder, who controls final cross--linking. Short chains with many cross-links form rigid thermosets, while longer chains with fewer cross-links form more flexible thermosets. With all thermosets, the polymerization is permanent and irreversible.

Thermoplastic polymers require no further chemical processing before molding. There are two types of thermoplastic polymers: Crystalline and Amorphous. The pyramid graphic on page 5-3 identifies many of our common thermoplastic materials.

Crystalline Polymers:

- Have a relatively sharp melting point.
- Have an ordered arrangement of molecule chains.
- Generally require higher temperatures to flow well when compared to Amorphous.

- Reinforcement with fibers increases the load-bearing capabilities considerably.
- Shrink more than Amorphous, causing a greater tendency for warpage.
- Fiber reinforcement significantly decreases warpage.
- Usually produce opaque parts due to their molecular structure.

Amorphous Polymers

- Have no true melting point and soften gradually.
- Have a random orientation of molecules; chains can lie in any direction.
- Do not flow as easily in a mold as Crystalline Polymers.
- Shrink less than Crystalline Polymers.
- Generally yield transparent, water-clear parts.

Why plastics are important?

Plastics are important engineering materials for many reasons. They have wide range of properties, some of which are unattainable from any other materials:

- Most case relatively low in cost.
- The use of plastics in mechanical engineering design offers many advantage, which include
 - ✓ Elimination of parts through engineering design with plastics
 - ✓ Elimination of many finishing operations,
 - ✓ Simplified assembly
 - ✓ Weight saving
 - ✓ Noise reduction
 - ✓ And in some cases elimination of the need for lubrication of some parts.
- Plastics are also very usefull for electrical engineering for excellent insulative properties. Eg. Swith, TV turner componants, integrated circuit board etc.

13.3. Thermoplastic Materials

- ✓ Thermoplastic materials are composed of *long chains produced by joining together monomers; they typically behave in a plastic, ductile manner.*
- ✓ This chain may or may not have branches. Individual chains are intertwined. They are relatively weak bond between atoms.

- ✓ Thermoplastic require heat to make them formable and after cooling, retain the shape they were formed into.
- ✓ These materials can be reheated and reformed into new shapes a number of times without significant change in their properties.

Most thermoplastics are synthesized by the process of chain-growth polymerization. In these process many small molecules are covalently bonded together to form very long molecule chain. The simple molecules that are covalently bonded into long chains are called **monomers** (The long chain molecule formed mono, meaning "one", and "meros", meaning part).

Manufacturing Aids for Many Thermoplastic Processing Challenges

Thermoplastic processing operations involve the process of moving melted (viscous) materials with thermoplastic characteristics (soften when heated) into some form or mold and then cooling (solidifying) the materials for the purpose of making desired shapes. This material was the birth of many of the modern aesthetic and utility uses of plastics. Further development of new synthetic polymers goes hand in hand with the development of new processes to transform thermoplastic materials into desired shapes. Thermoplastic materials are melted and then solidified at lower temperatures, often a cooled mold is used to transform the polymer melt into a desired shape. Chem-Trend, with its over 50 years of experience working with molding, forming and casting operations, is a world leader in the development of manufacturing aids for thermoplastic processing.

Thermoplastic processes are constantly evolving, due to continuous innovation in materials. However, five major processes are most often employed. The common theme among all of the processes is the use of a thermoplastic polymer that's transformed by heat into a different shape, which can then be reversed.

The five major thermoplastic processes used to form thermoplastic materials are;

- Injection Molding
- Blow Molding
- Extrusion (also includes the sub-process of Calendering)
- Compounding
- Rotational Molding

Injection Molding

Injection molding can be used to economically produce formed parts in large quantities. A thermoplastic material is injected under pressure into a mold, with the cavity[†] of the mold determining the shape and surface texture of the finished part. Parts of these types can be found as small as a few tenths of a gram to as large as the two-digit kilogram range. The injection molding process can be further divided into multiple subcategories, all of which have their own specific parameters and challenges for efficient production.

With injection molding, objects can be produced with high accuracy, such as those produced for use in precision engineering, and can be mass-produced in a short time. With this process the surface of the component can be selected to match the particular need. As well, the injection molding process is (almost exclusively) the best economic choice for production of large quantities; however the cost of the tool is often a significant investment, even for relatively simple tools. Therefore, it is very important to protect the tooling both during the processing of the parts, as well as during shipment and storage periods. For these reasons Chem-Trend has developed multiple manufacturing aids focused on both making the injection molding process more efficient, such as mold release agents, as well as to protect molds and machinery such as our anti-corrosion and purge compound products.

Blow Molding

Blow molding is a collective term for the production of hollow vessels made of thermoplastic materials. There are several distinct blow molding processes, such as;

- Extrusion (Continuous or Intermittent), Stretch, Injection

Each type of blow molding process presents its own particular challenges to efficiency and scrap rates.

Extrusion

Extrusion is a broad category in which plastics are molded in one continuous process. Almost all processing of thermoplastics encompasses some type of extrusion, but the main extrusion process can be broken down into three main sub-categories;

- Pipe & Profile, Sheet, Film

Additionally, calendering is yet another, small sub-segment of thermoplastic extrusion. In the calendering process, melted plastic is passed through columns of these rollers to produce plastic films (PVC, PE, PS, etc.).

Compounding

Compounding is a process of refining plastics by the addition of additives (fillers, etc.) for the targeted optimization of the characteristic profiles required for the parts being made. Compounding takes place predominantly in extruders

and includes operations of; conveying, melting, dispersing, mixing, and degassing and pressure buildup.

Our expertise in the development of products to promote efficiency and lower scrap within thermoplastic processing operations allows us a unique position within the industry to support thermoplastics compounders.

Rotational Molding

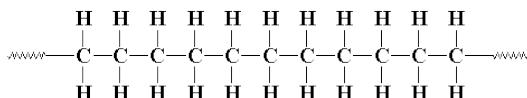
Rotational Molding is used to create thin-walled hollow forms by applying powdered thermoplastic layer by layer on the inner surfaces of a mold through biaxial rotation combined with heat. This method allows for relatively uniform, thin wall thickness. Rotomolding is a technique that suits products that need a good cosmetic outside appearance but do not require the inside surface to be as good looking.

The rotational molding process (rotomolding) enables relatively small volume part production for multitude applications, such as bulk fluid storage, children's toys and automotive components. The release agent plays a critical part in the correct formation of rotomolded parts. It needs to perform several tasks, some of which appear to be conflicting. Rotational molding provides a very different set of challenges than those found in thermoplastic extrusion processes. Chem-Trend has developed a strong array of products specifically designed for meeting the challenges found in rotational molding. To learn more about those products read our main rotational molding page or contact us to speak with one of our rotomolding experts.

13.3.1 General Purpose thermoplastics

1. Polyethylene

It is clear-to-whitish, translucent, thermoplastic materials and is often fabricated into clear thin films. Thick sections are translucent and have waxy appurtenance. With the use of colorants a wide variety of colored products is obtained. Polyethylene is the most popular plastic in the world.



Type of polyethylene

Low density (LDPE) or Branched it is relatively less strong than linear polyethylene. It is lower density materials and low density. High Density (HDPE) or unbranched or linear stronger than LDPE.

Properties PE

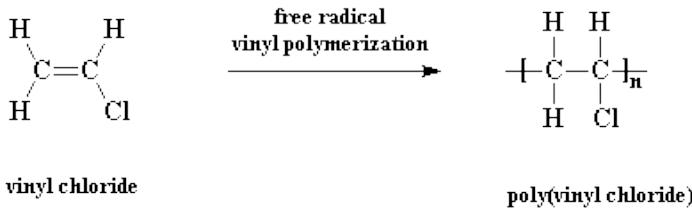
It is by far the most extensively used plastic materials. The main reason for its prime importance is low in cost and has many industrially important properties, which include toughness at room temperature and at low temperature with sufficient strength for many product applications, good flexibility over a wide range of temperature, excellent corrosion resistance, excellent insulative properties, colorlessness and tastelessness, and low water vapor transmission.

Application PE

Containers, electrical insulation, chemical tubing, housewares, blow-molded bottles, packaging, water pond liners.

2. Polyvinyl chloride /PVC/

- It is widely used synthetic plastics that have the second largest sales in tonnage in the world.
- Mainly due to chemical resistance and its unique ability to be mixed with additives to produce a large number of compounds with a wide range of physical and chemical properties.
- PVC is useful because it resists two things that hate each other: fire and water. Because of its water resistance it's used to make raincoats and shower curtains, and of course, water pipes.
- It has flame resistance, too, because it contains chlorine. When you try to burn PVC, chlorine atoms are released, and chlorine atoms inhibit combustion. Repeating chemical structural unite



Properties

PVC has relatively high strength along with brittleness. PVC has medium heat deflection, high solvent resistance.

PVC compounding

PVC can only be used for a few applications without the addition of a number of compounds to the basic materials so that it can be processed and converted into finished products. Compounds added to PVC include plasticizers, heat stabilizers, lubricants, fillers and pigments.

- Plasticizers impart flexibility to polymeric materials.
- Heat stabilizers are added to PVC to prevent thermal degradation during processing and may also help to extend the life of finished products.
- Lubricants aid the melt flow of PVC compounds during processing and preventing adhesion to metal surface.
- Waxes, fatty esters, and metallic soaps are commonly used lubricants.
- Fillers such as calcium carbonate are mainly added to lower the cost of PVC compounds.
- Pigments, both in organic and organic are used to give color, opacity, and wheatherability to PVC compounds.

Rigid PVC: it is used for some application but it is difficult to process due to low impact strength. Addition of rubbery risen can improve melt flow during processing of forming dispersion of small, soft rubbery particles for improving impact strength. Application: Pipe, siding, Windom frame, gutter, and interior molding and for electrical conduit.

Plasticized PVC: Plasticizers are added to PVC for producing softness, flexibility, and extensibility. It is used in much application where it outperforms in rubber, textile and Paper. It is used in furniture and automobile upholstery, interior wall coverings, rainwear, shoes, luggage,

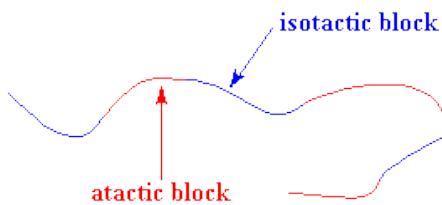
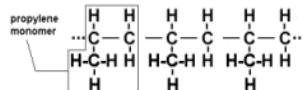
electrical wire insulation, and shower curtains. In transportation, it is used for auto top coverage, electrical wire insulation, flour mates, and interior and exterior trim. Other applications Garden hose, refrigerator gaskets, appliance components, and housewear.

3. Polypropylene

What is polypropylene?

Polypropylene (PP) is a thermoplastic.

It is a linear structure based on the monomer $CnH2n$. It is manufactured from propylene gas in presence of a catalyst such as titanium chloride. Beside PP is a by-product of oil refining processes.



Most polypropylene used is highly crystalline and geometrically regular (i.e. isotactic) opposite to amorphous thermoplastics, such as polystyrene, PVC, polyamide, etc., which radicals are placed randomly.

It is said that PP has an intermediate level of crystallinity between low density polyethylene (LDPE) and high density polyethylene (HDPE); On the other hand PP has higher working temperatures and tensile strength than polyethylene.

Properties of polypropylene

The properties of polypropylene that make the material popular include the non-toxic and non-staining nature of the plastic, and the relatively inexpensive cost of production. During the production phase, polypropylene can be combined with other materials, such as rubber, to alter its properties.

The properties of polypropylene that make the plastic a popular choice for products include the lightweight nature of the material and its high tensile strength. This makes the plastic a very useful for use in products like food packaging. Polypropylene also has a strong resistance to cracking when placed under stress and a high level of impact resistance.

Plastic product producers often make use of polypropylene as an alternative to other types of plastic because it usually does not contain bisphenol A (BPA). BPA is a chemical that is often used in the production of plastic products, but when used in food and drink packaging, BPA can leach into the contents of the containers. Although this chemical has not been proven to pose a health risk to children or adults in small amounts, many plastics manufacturers use BPA-free polypropylene to reduce the risks of health issues linked to the chemical.

Applications

Polypropylene plastic is usually broken down into three broad categories of usage. These include the automotive plastics industry, packaging plastics, and all other uses combined. The bulk of this at 54% went into use in the packaging industry, and the next top demand for polypropylene world supplies has been in automotive assembly, accounting for 15.6% of the total amount produced.

The low weight and good mechanical properties of polypropylene plastic have made it an ideal material in automotive construction. It reduces the total weight of cars where it is substituted for other interior materials in dashboards, door panels, and cushioning. Since polypropylene plastic has good corrosion and weather resistance, it is also used for exterior moldings and bumpers, and can be pre-colored so that some of the painting work on automobiles is eliminated.

The packaging industry's use of polypropylene plastic is divided up into flexible and rigid packaging.

a. **Flexible packaging:** Polypropylene bags and films use flexible designs of the plastic used in three main packaging industries:

- Food and confections,
- Tobacco, and
- Textiles.

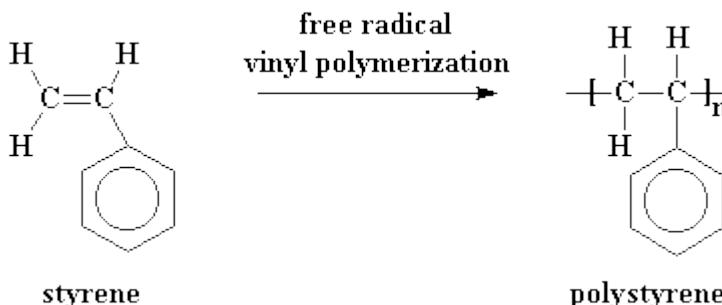
The food packaging industry dominates in its consumption of flexible polypropylene.

b. **Rigid polypropylene:** It is used to make food crates and pallets, as well as bottles for a wide range of uses and food containers for yogurt.

1. Polystyrene

Polystyrene is an inexpensive and hard plastic, and probably only polyethylene is more common in your everyday life. The outside housing of the computer you are using now is probably made of polystyrene. Model cars and airplanes are made from polystyrene, and it also is made in the form of foam packaging and insulation. Clear plastic drinking cups are made of polystyrene. So are a lot of the molded parts on the inside of your car, like the radio knobs. Polystyrene is also used in toys, and the housings of things like hairdryers, computers, and kitchen appliances.

Polystyrene is a vinyl polymer. Structurally, it is a long hydrocarbon chain, with a phenyl group attached to every other carbon atom. Polystyrene is produced by free radical vinyl polymerization, from the monomer styrene.



2. ABS

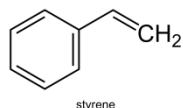
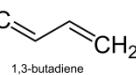
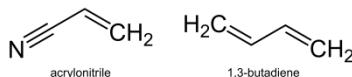
ABS driver from three monomers: Acrylonitrile, butadiene and styrene. ABS has good impact strength and mechanical strength combined with ease of processing. They are hard and durable through a broad range of temperatures.

Properties

- Acrylonitrile contributes heat and chemical resistance and toughness.
- Butadienes provide impact strength and low property retention.
- Styrene provides surface gloss, rigidity and ease of processing.

ABS plastics are highly versatile plastics. It bonds well using either adhesive or solvent cement. ABS plastics can be painted, screen-printed and chrome-plated.

ABS plastics extruded into sheets are used extensively for vacuum and pressure forming. Sheets are often extruded with surface texturing.



Typical ABS Plastics Application

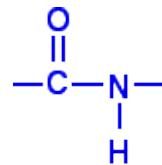
ABS Plastics are easily machined and in thinner gauges easily die cut. ABS plastics are used for such applications as: Panels for refrigerators, Musical instrument and equipment cases, luggage, food trays, belt guards, Covers, Storage bins. These include domestic appliances, telephone handsets computer and other office equipment housings, lawn mower covers, safety helmets, luggage shells, pipes and fittings. Because of the ability to tailor grades to the property requirements of the application and the availability of electroplatable grades ABS is often found as automotive interior and exterior trim components.

13.4. Engineering thermoplastic materials

These sections focus on the discussion of thermoplastic materials that can be used engineering applications.

1. Polyamides (Nylon)

Nylons are melt-processing thermoplastics whose main chain structure incorporates a repeating amide group. Nylons are members of engineering plastic families and offer superior load bearing capability at elevated temperature good toughness, low-frictional properties, and good chemical resistance.



Chemical repeating linkage

Polyamides are polymers where the repeating units are held together by amide links. An amide *group* has the formula -CONH₂. An amide *link* has this structure: In an amide itself, of course, the bond on the right is attached to a hydrogen atom.

Properties

Nylons are highly crystalline polymeric material because of the regular symmetric structure of their main polymer chains. The high strength of nylons is due to hydrogen bonding between the molecular chains. It has high strength, high heat-deflection temperatures, and good chemical resistance. The flexibility of the main carbon chains produces molecular flexibility, which leads to low melt viscosity and ease of processibility. The flexibility of carbon chains contributes to high lubricity, low surface friction, and good abrasion resistant.

Processing: Most nylons are processed by conventional injection-molding or extrusion methods.

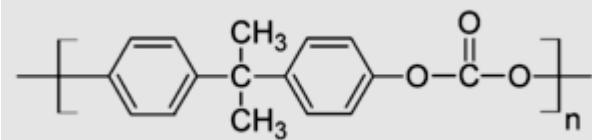
Application: Applications for nylons are found in almost all industries. Typically uses are for unlubricated gears, bearings, and antifriction parts, mechanical parts that must function at high temperature and resist hydrocarbons and solvents, electrical parts subjected to high temperature, and high-impact parts requiring strength and rigidity. Auto-mobile applications include speed meter and windshield

wipers gears. Glass-reinforced nylon is used for engine fan blades, brake and power steering fluid reservoirs, valve covers, and steering column housing. Electrical and/or electronics application includes connectors, plugs, hookup wire insulation, antenna mounts and terminals. It is also used in packaging and many general purpose applications.

2. Polycarbonate

Polycarbonate forms another class of engineering thermoplastics because some of their special high performance characteristics such as high strength, toughness, and dimensional stability are required for some engineering designs.

Basic repeating chemical unit



Structure and properties

The two phenyl and the two methyl groups attached to some carbon atom in the repeating structure produce considerable steric hindrance make a very stiff molecular structure. However, the carbon-oxygen single bonds in the carbonate linkage provide some molecular flexibility for the overall molecular structure, which produces high impact strength energy. High tensile strength at room temperature, high heat deflection temperature, good electrical insulating properties, and transparency. Good creep and resistance, resistance to variety of chemicals but are attacked by solvents. Their high dimensional stability enables them to be used in precision engineering components where close tolerance are required.

Application: Typical applications for polycarbonates include safety shields, cams, and gears, helmets, electrical relay cover, air craft components, boat propellers, traffic high housings and lens, glazing for windows and solar collectors, and housing for handheld power tools, small appliances and computer terminals.

3. Acetals

Acetals are a class of high-performance engineering thermoplastic materials. They are among the strongest and stiffest thermoplastics and have excellent fatigue life and dimensional stable. Other important characteristics include low friction coefficients, and good processibility, good solvent resistance, and high heat resistance. There are two types of acetals such as a homopolymer, and copolymer.

Structure and properties

The regularity, symmetry, and flexibility of acetals polymer molecule produce polymeric materials with high regularity, strength, and heat deflection temperature. Acetals have excellent long-term load-carrying properties and dimensional stability and thus can be used for precision parts such as gears bearings and cams. The homopolymer is harder and more rigid, thus higher tensile strength and flexural strength than the copolymer. The copolymer is more stable for long term, high temperature applications and has a higher elongation.

The low moisture absorption of unmodified acetals and homopolymer provides it with good dimensional stability. Also, the low wear and friction characteristics of acetal make it useful for moving parts. In all moving parts, acetals excellent fatigue resistance is an important property. However, acetals are flammable, and so their use in electrical and/or electronic application is limited.

Applications: acetals replace many metal casting of zinc, brass, and aluminium and stamping of steel because of low cost. Where the higher strength of the metals is not required, finishing and assembly operation costs can be reduced or eliminated by using acetals for many applications.

In automobile, acetals are used for components in fuel system, seat belts, and window handles. Machinery applications, for acetals include mechanical couplings, pump impeller, gears, cams, housings. Acetals are also used in a wide variety of consumers' products such as zippers, fishing reels, writing pens.

13.5. Thermosetting plastics

Thermosetting plastic are formed with a network molecular structure of primary covalent bonds. Some thermosets are cross-linked by heat or a combination of heat and pressure. Others may also cross linked by chemical reactions that occur at room temperature. Also cured parts made from thermosets can be softened by heat, their covalent –bonding cross-links them from being restored to the flowable state that existed before the plastic resin was cured. Thermoset, therefore, cannot be reheated and remelted as thermoplastic materials. This is the disadvantage of for thermosets since scrap produced during processing can not be recycled and reused.

In general, the advantage of thermosetting plastics for engineering design applications are one or more of the following:

1. High thermal stability.
2. High rigidity
3. High dimensional stability
4. Resistance to creep and deformation under load
5. Light weight
6. High electrical and thermal insulating properties

Thermosetting plastics are usually processed by using compression or transfer molding. However, in some cases thermosets injection-molding techniques have

been developed so that the processing cost is lowered. Many thermosets are used in the form of moulding compounds consisting of two major ingredients: (1) a resin containing curing agents, hardeners, and plasticizers and (2) fillers and or reinforcing materials that may be organic or inorganic materials.

1. Phenolics

Phenolics are used widely today because they are low in cost and have good electrical and heat insulating properties along with good mechanical properties. They are easily molded and but limited to in color (usually black or brown).

Properties: the high cross-linking of the aromatic structure produces high hardness, rigidity, strength combined with good heat and electrical insulating properties and chemical resistance.

Applications: It is widely used for in wiring device, electrical switch gear, connectors, and telephone relay systems. In automotive engineers used as power-assist brake components and transmission parts. Phenolics widely used for handles, knobs, and end panels for small appliance.

2. Epoxy resins

Epoxy resins are family of thermosetting polymeric materials that do not give off reactions products when they cure and so have low cur shrinkage. They also have good adhesion to other materials, good chemical and environmental resistance, good mechanical properties, good electrical insulating properties.

Property: low molecular weight of uncured epoxide resins in the liquid state gives them exceptionally high molecular mobility during processing.

Applications: widely used variety of protective and decorative coatings because of their good adhesion and good mechanical and chemical resistance. Typically uses are can and drum linings, automotive and appliance primers, and wire coatings, high voltage insulators, switchgear.

13.6. Elastomers or Rubbers

Elastomers are polymeric materials whose dimensional can be greatly changed when stressed and which return to their original dimensions when the deforming stress is removed. Natural rubber is produced commercially from the latex of Hevea brasiliensis tree. It has low tensile strength and extremely high elongations. Widely used tires and seals.

Chapter Fourteen

Ceramics Materials

14.1. Introduction

Ceramic materials are inorganic, non-metallic materials that consists of metallic and non-metallic elements bonded together primarily by ionic and/or covalent bonds. The chemical composition of ceramic materials is varying considerably, from simple compound to mixture of many complex phases bonded together.

The properties of ceramic materials also vary greatly due to the difference in bonding. In general ceramic materials are typically hard and brittle with low toughness and ductility. Ceramics are usually good electrical and thermal insulators because of the absence of conduction electrons. Ceramics materials normally have relatively high melting temperature and high chemical stability of their strong bonds. Because of their properties, ceramics materials are essential for many engineering designs.

In general, ceramic materials used for engineering applications can be divided into two groups:

14.2. Traditional Ceramic Materials

These are made from three basic components: *clay, silica and feldspar*. Traditional ceramics are made from minerals occurring in nature Products include pottery, porcelain, bricks, and cement. Example traditional ceramics are glasses, bricks, and tiles in used in construction industries and electrical porcelain in electrical industries.

The clay in traditional ceramics provides workability of the materials before firing hardens it and constitutes the major body materials. The silica (SiO_2), also called flint or quartz, has high melting temperature and is refractory components of traditional ceramics.

It is used as building brick, sewer pipe, drain tile, roofing tile, and floor tile are made of natural clay, which contains all three basic components.

Glasses: a glass is a ceramic material in that it is made from inorganic materials at high temperature. However, it is distinguished from other ceramic in that its constituents are heated to fusion and then cooled to a rigid state without crystallization. The characteristics of glass is amorphous structure that means their molecule do not arranged in a regular repetitive long range order as exists in crystalline solid. In a glass the molecules change their orientation in a random manner throughout the solid materials.

Glasses have special properties not found in other engineering materials. The combination of transparency and hardness at room temperature along with sufficient strength and excellent corrosion resistant to most normal environments makes glass indispensable for many engineering applications such as constructions and vehicle glazing. In electrical industries, glass is essential for various types of lamps because of insulative properties and ability to provide a vacuum tight enclosure. In the electronics industries electron tubes are also require the vacuum-tight enclosure provided by glass along with its insulative properties for lead-in connectors. The high chemical resistance of glass make it useful for laboratory apparatus and for corrosion resistance liners for pipe and reaction vessels in chemical industry.

14.3. Engineering ceramics

Typically consists of pure or nearly pure compounds such as aluminium oxide, silicon carbide, silicon nitride. Application area silicon carbide in high temperature areas, automotive gas turbine engines, and aluminium oxide in support base for integrated circuit chips in a thermal-conduction module and cutting tools.

Ceramics processing

Ceramic processing is used to produce commercial products that are very diverse in size, shape, detail, complexity, and material composition, structure, and cost. The purpose of ceramics processing to an applied science is the natural result of an increasing ability to refine, develop, and characterize ceramic materials.

Ceramics are typically produced by the application of heat upon processed clays and other natural raw materials to form a rigid product. Ceramic products that use naturally occurring rocks and minerals as a starting material must undergo special processing in order to control purity, particle size, particle size distribution, and heterogeneity. These attributes play a big role in the final properties of the finished ceramic. Chemically prepared powders also are used as starting materials for some ceramic products. These synthetic materials can be controlled to produce powders with precise chemical compositions and particle size.

The next step is to form the ceramic particles into a desired shape. This is accomplished by the addition of water and/or additives such as binders, followed by a shape forming process. Some of the most common forming methods for ceramics include extrusion, slip casting, pressing, tape casting and injection molding. After the particles are formed, these "green" ceramics undergo a heat-treatment (called firing or sintering) to produce a rigid, finished product. Some ceramic products such as electrical insulators, dinnerware and tile may then

undergo a glazing process. Some ceramics for advanced applications may undergo a machining and/or polishing step in order meet specific engineering design criteria.

Chapter Fifteen

Composite Materials

15.1 Introduction to composite Material

A composite material is a material made up of two or more materials that are combined in a way that allows the materials to stay distinct and identifiable. The purpose of composites is to allow the new material to have strengths from both materials, often times covering the original materials' weaknesses. Composites are different from alloys because alloys are combined in such a way that it is impossible to tell one particle, element, or substance from the other. Some common composite materials include concrete, fiberglass, mud bricks, and natural composites such as rock and wood.

15.2. Types composites

Composite materials are usually classified by the type of reinforcement they use. This reinforcement is embedded into a matrix that holds it together. The reinforcement is used to strengthen the composite. For example, in a mud brick, the matrix is the mud and the reinforcement is the straw. Common composite types include random-fiber or short-fiber reinforcement, continuous-fiber or long-fiber reinforcement, particulate reinforcement, flake reinforcement, and filler reinforcement.

Reinforcements: Reinforcements for the composites can be fibers, fabrics particles or whiskers. Fibers are essentially characterized by one very long axis with other two axes either often circular or near circular. Particles have no preferred orientation and so does their shape. Whiskers have a preferred shape but are small both in diameter and length as compared to fibers.

Reinforcing constituents in composites, as the word indicates, provide the strength that makes the composite what it is. But they also serve certain additional purposes of heat resistance or conduction, resistance to corrosion and provide rigidity. Reinforcement can be made to perform all or one of these functions as per the requirements. A reinforcement that embellishes the matrix strength must be stronger and stiffer than the matrix and capable of changing failure mechanism to the advantage of the composite. This means that the ductility should be minimum or even nil the composite must behave as brittle as possible.

Fiber Reinforcement: Fibers are the important class of reinforcements, as they satisfy the desired conditions and transfer strength to the matrix constituent influencing and enhancing their properties as desired.

Glass fibers are the earliest known fibers used to reinforce materials. Ceramic and metal fibers were subsequently found out and put to extensive use, to render composites stiffer more resistant to heat. Fibers fall short of ideal performance due to several factors. The performance of a fiber composite is judged by its length, shape, orientation, composition of the fibers and the mechanical **properties of the matrix.**

The orientation of the fiber in the matrix is an indication of the strength of the composite and the strength is greatest along the longitudinal directional of fiber. This doesn't mean the longitudinal fibers can take the same quantum of load irrespective of the direction in which it is applied. Optimum performance from longitudinal fibers can be obtained if the load is applied along its direction. The slightest shift in the angle of loading may drastically reduce the strength of the composite.

Types of Fibers: Organic and inorganic fibers are used to reinforce composite materials. Almost all organic fibers have low density, flexibility, and elasticity. Inorganic fibers are of high modulus, high thermal stability and possess greater rigidity than organic fibers and notwithstanding the diverse advantages of organic fibers which render the composites in which they are used.

Mainly, the following different types of fibers namely, glass fibers, silicon carbide fibers, high silica and quartz fibers, aluminina fibers, metal fibers and wires, graphite fibers, boron fibers, aramid fibers and multiphase fibers are used. Among the glass fibers, it is again classified into E-glass, A-glass, R-glass etc. There is a greater marker and higher degree of commercial movement of organic fibers.

Glass fibers: Over 95% of the fibers used in reinforced plastics are glass fibers, as they are inexpensive, easy to manufacture and possess high strength and stiffness with respect to the plastics with which they are reinforced. Their low density, resistance to chemicals, insulation capacity are other bonus characteristics, although the one major disadvantage in glass is that it is prone to break when subjected to high tensile stress for a long time. However, it remains break-resistant at higher stress-levels in shorter time frames. This property mitigates the effective strength of glass especially when glass is expected to sustain loads for many months or years continuously.

Metals fibers: As reinforcement, metal fibers have many advantages. They are easily produced using several fabrication processes and are more ductile, apart from being not too sensitive to surface damage and possess high strengths and temperature resistance. However, their weight and the tendency to react each other through alloying mechanisms are major disadvantages.

Ceramic fibers improve vastly in performance when a fine metal outline is

incorporated with refractory ceramics by improving their thermal shock and impact resistance properties.

Metal wires, of the continuous version, also reinforce plastics like polyethylene and epoxy. Such combinations ensure high strength, light weight and good fatigue resistance.

15.3. Comparison of composites with metals

The requirements governing the choice of materials apply to both metals and reinforced plastics. It is, therefore, imperative to briefly compare main characteristics of the two.

- Composites offer significant weight saving over existing metals. Composites can provide structures that are 25-45% lighter than the conventional aluminium structures designed to meet the same functional requirements. This is due to the lower density of the composites.

Depending on material form, composite densities range from 1260 to 1820 kg/in³ (0.045 to 0.065 lb/in³) as compared to 2800 kg/in³ (0.10 lb/in³) for aluminium. Some applications may require thicker composite sections to meet strength/stiffness requirements, however, weight savings will still result.

- Unidirectional fibre composites have specific tensile strength (ratio of material strength to density) about 4 to 6 times greater than that of steel and aluminium.
- Unidirectional composites have specific modulus (ratio of the material stiffness to density) about 3 to 5 times greater than that of steel and aluminium.
- Fatigue endurance limit of composites may approach 60% of their ultimate tensile strength. For steel and aluminium, this value is considerably lower.
- Fibre composites are more versatile than metals, and can be tailored to meet performance needs and complex design requirements such as aero-elastic loading on the wings and the vertical & the horizontal stabilisers of aircraft.
- Fibre reinforced composites can be designed with excellent structural damping features. As such, they are less noisy and provide lower vibration transmission than metals.
- High corrosion resistance of fibre composites contributes to reduce life-cycle cost.
- Composites offer lower manufacturing cost principally by reducing significantly the number of detailed parts and expensive technical joints required to form large metal structural components. In other words, composite parts can eliminate joints/fasteners thereby providing parts simplification and integrated design.
- Long term service experience of composite material environment and

durability behaviour is limited in comparison with metals.

15.4. Advantages and disadvantage of composite

Advantage of composites

Summary of the advantages exhibited by composite materials, which are of significant use in aerospace industry are as follows:

- High resistance to fatigue and corrosion degradation.
- High ‘strength or stiffness to weight’ ratio. As enumerated above, weight savings are significant ranging from 25-45% of the weight of conventional metallic designs.
- Due to greater reliability, there are fewer inspections and structural repairs.
- Directional tailoring capabilities to meet the design requirements. The fibre pattern can be laid in a manner that will tailor the structure to efficiently sustain the applied loads.
- Fibre to fibre redundant load path.
- Improved dent resistance is normally achieved. Composite panels do not sustain damage as easily as thin gage sheet metals.
- It is easier to achieve smooth aerodynamic profiles for drag reduction. Complex double-curvature parts with a smooth surface finish can be made in one manufacturing operation.
- Composites offer improved torsional stiffness. This implies high whirling speeds, reduced number of intermediate bearings and supporting structural elements. The overall part count and manufacturing & assembly costs are thus reduced.
- High resistance to impact damage.
- Thermoplastics have rapid process cycles, making them attractive for high volume commercial applications that traditionally have been the domain of sheet metals. Moreover, thermoplastics can also be reformed.
- Like metals, thermoplastics have indefinite shelf life.
- Composites are dimensionally stable i.e. they have low thermal conductivity and low coefficient of thermal expansion. Composite materials can be tailored to comply with a broad range of thermal expansion design requirements and to minimise thermal stresses.
- Manufacture and assembly are simplified because of part integration (joint/fastener reduction) thereby reducing cost.
- The improved weatherability of composites in a marine environment as well as their corrosion resistance and durability reduce the down time for maintenance.
- Close tolerances can be achieved without machining.
- Material is reduced because composite parts and structures are

frequently built to shape rather than machined to the required configuration, as is common with metals.

- Excellent heat sink properties of composites, especially Carbon-Carbon, combined with their lightweight have extended their use for aircraft brakes.
- Improved friction and wear properties.
- The ability to tailor the basic material properties of a Laminate has allowed new approaches to the design of aeroelastic flight structures.

The above advantages translate not only into airplane, but also into common implements and equipment such as a graphite racquet that has inherent damping, and causes less fatigue and pain to the user.

Disadvantage of Composites

Some of the associated disadvantages of advanced composites are as follows:

- a) High cost of raw materials and fabrication.
- b) Composites are more brittle than wrought metals and thus are more easily damaged.
- c) Transverse properties may be weak.
- d) Matrix is weak, therefore, low toughness.
- e) Reuse and disposal may be difficult.
- f) Difficult to attach.
- g) Analysis is difficult.
- h) Matrix is subject to environmental degradation.
- i) Repair introduces new problems, for the following reasons:
 - Materials require refrigerated transport and storage and have limited shelf life.
 - Hot curing is necessary in many cases requiring special tooling.
 - Hot or cold curing takes time.

However, proper design and material selection can circumvent many of the above disadvantages.

New technology has provided a variety of reinforcing fibres and matrices those can be combined to form composites having a wide range of exceptional properties. Since the advanced composites are capable of providing structural efficiency at lower weights as compared to equivalent metallic structures, they have emerged as the primary materials for future use.

In aircraft application, advanced fibre reinforced composites are now being used in many structural applications, viz. floor beams, engine cowlings, flight control surfaces, landing gear doors, wing-to-body fairings, etc., and also major load carrying structures including the vertical and horizontal stabiliser main torque boxes.

Matrix Materials

Although it is undoubtedly true that the high strength of composites is largely due to the fibre reinforcement, the importance of matrix material cannot be

underestimated as it provides support for the fibres and assists the fibres in carrying the loads. It also provides stability to the composite material. Resin matrix system acts as a binding agent in a structural component in which the fibres are embedded. When too much resin is used, the part is classified as resin rich. On the other hand if there is too little resin, the part is called resin starved. A resin rich part is more susceptible to cracking due to lack of fibre support, whereas a resin starved part is weaker because of void areas and the fact that fibres are not held together and they are not well supported.

Functions of a Matrix

In a composite material, the matrix material serves the following functions:

- Holds the fibres together.
- Protects the fibres from environment.
- Distributes the loads evenly between fibres so that all fibres are subjected to the same amount of strain.
- Enhances transverse properties of a laminate.
- Improves impact and fracture resistance of a component.
- Helps to avoid propagation of crack growth through the fibres by providing alternate failure path along the interface between the fibres and the matrix.
- Carry interlaminar shear.

The matrix plays a minor role in the tensile load-carrying capacity of a composite structure. However, selection of a matrix has a major influence on the interlaminar shear as well as in-plane shear properties of the composite material. The interlaminar shear strength is an important design consideration for structures under bending loads, whereas the in-plane shear strength is important under torsion loads. The matrix provides lateral support against the possibility of fibre buckling under compression loading, thus influencing to some extent the compressive strength of the composite material. The interaction between fibres and matrix is also important in designing damage tolerant structures. Finally, the processability and defects

in a composite material depend strongly on the physical and thermal characteristics, such as viscosity, melting point, and curing temperature of the matrix.

Properties of a Matrix

The needs or desired properties of the matrix which are important for a composite structure are as follows:

- Reduced moisture absorption.
- Low shrinkage.
- Low coefficient of thermal expansion.
- Good flow characteristics so that it penetrates the fibre bundles completely

- and eliminates voids during the compacting/curing process.
- Reasonable strength, modulus and elongation (elongation should be greater than fibre).
 - Must be elastic to transfer load to fibres.
 - Strength at elevated temperature (depending on application).
 - Low temperature capability (depending on application).
 - Excellent chemical resistance (depending on application).
 - Should be easily processable into the final composite shape.
 - Dimensional stability (maintains its shape).

As stated above, the matrix causes the stress to be distributed more evenly between all fibres by causing the fibres to suffer the same strain. The stress is transmitted by shear process, which requires good bonding between fibre and matrix and also high shear strength and modulus for the matrix itself. One of the important properties of cured matrix system is its glass transition temperature (T_g) at which

the matrix begins to soften and exhibits a decrease in mechanical properties. The glass transition temperature is not only an important parameter for dimensional stability of a composite part under influence of heat, but it also has effect on most of the physical properties of the matrix system at ambient temperature.

Some of the *physical properties* of the matrix which influence the behaviour of composites are:

- Shrinkage during cure,
- Modulus of elasticity,
- Ultimate elongation,
- Strength (tensile, compressive and shear), and
- Fracture toughness.

Factors considered for Selection of Matrix

In selecting matrix material, following factors may be taken into consideration:

- The matrix must have a mechanical strength commensurate with that of the reinforcement i.e. both should be compatible. Thus, if a high strength fibre is used as the reinforcement, there is no point using a low strength matrix, which will not transmit stresses efficiently to the reinforcement.
- The matrix must stand up to the service conditions, viz., temperature, humidity, exposure to ultra-violet environment, exposure to chemicals, atmosphere, abrasion by dust particles, etc.
- The matrix must be easy to use in the selected fabrication process.
- Smoke requirements.
- Life expectancy.
- The resultant composite should be cost effective.

The fibres are saturated with a liquid resin before it cures to a solid. The solid resin

is then said to be the matrix for the fibres.

General types of Matrix Materials

In general, following general following types of matrix materials are available:

- Thermosetting material;
- Thermoplastic material;
- Carbon;
- Metals;
- Ceramics;
- Glass Matrix.

Thermosetting material is the one which when cured by heat or chemical reaction is changed into an infusible and insoluble material. Thermosetting resins undergo irreversible chemical cross-linking reaction upon application of heat. On the other hand, thermoplastics do not undergo a chemical reaction on application of heat. They simply melt on application of heat and pressure to form a component. Thermoplastics can be softened and they undergo large and rapid change in viscosity with variation in temperature. Thermoplastics can be repeatedly softened by heating and hardened by cooling.

Chapter Six

17. Metallurgy

17.1. Introduction

Metallurgy, art and science of extracting metals from their ores and modifying the metals for use. Metallurgy customarily refers to commercial as opposed to laboratory methods. It also concerns the chemical, physical, and atomic properties and structures of metals and the principles whereby metals are combined to form alloys.

17.2 Metallographic

The 20th century has seen metallurgy change progressively, from an art or craft to a scientific discipline and then to part of the wider discipline of materials science. In extractive metallurgy, there has been the application of chemical thermodynamics, kinetics, and chemical engineering, which has enabled a better understanding, control, and improvement of existing processes and the generation of new ones. In physical metallurgy, the study of relationships between macrostructure, microstructure, and atomic structure on the one hand and physical and mechanical properties on the other has broadened from metals to other materials such as ceramics, polymers, and composites.

This greater scientific understanding has come largely from a continuous improvement in microscopic techniques for metallographic, the examination of metal structure. The first true metallographer was Henry Clifton Sorby of Sheffield, Eng., who in the 1860s applied light microscopy to the polished surfaces of materials such as rocks and meteorites. Sorby eventually succeeded in making photomicrographic records, and by 1885 the value of metallography

was appreciated throughout Europe, with particular attention being paid to the structure of steel. For example, there was eventual acceptance, based on micrographic evidence and confirmed by the introduction of X-ray diffraction by William Henry and William Lawrence Bragg in 1913, of the allotropy of iron and its relationship to the hardening of steel. During subsequent years there were advances in the atomic theory of solids; this led to the concept that, in nonplastic materials such as glass, fracture takes place by the propagation of preexisting cracklike defects and that, in metals, deformation takes place by the movement of dislocations, or defects in the atomic arrangement, through the crystalline matrix. Proof of these concepts came with the invention and development of the electron microscope; even more powerful field ion microscopes and high-resolution electron microscopes now make it possible to detect the position of individual atoms.

Another example of the development of physical metallurgy is a discovery that revolutionized the use of aluminum in the 20th century. Originally, most aluminum was used in cast alloys, but the discovery of age hardening by Alfred Wilm in Berlin about 1906 yielded a material that was twice as strong with only a small change in weight. In Wilm's process, a solute such as magnesium or copper is trapped in supersaturated solid solution, without being allowed to precipitate out, by quenching the aluminum from a higher temperature rather than slowly cooling it. The relatively soft aluminum alloy that results can be mechanically formed, but, when left at room temperature or heated at low temperatures, it hardens and strengthens. With copper as the solute, this type of material came to be known by the trade name Duralumin. The advances in metallography described above eventually provided the understanding that age hardening is caused by the dispersion of very fine precipitates from the supersaturated solid solution; this restricts the movement of the dislocations that are essential to crystal deformation and thus raises the strength of the metal. The principles of precipitation hardening have been applied to the strengthening of a large number of alloys.

17.3. Extractive metallurgy

Following separation and concentration by mineral processing, metallic minerals are subjected to extractive metallurgy, in which their metallic elements are extracted from chemical compound form and refined of impurities.

Metallic compounds are frequently rather complex mixtures (those treated commercially are for the most part sulfides, oxides, carbonates, arsenides, or silicates), and they are not often types that permit extraction of the metal by

simple, economical processes. Consequently, before extractive metallurgy can effect the separation of metallic elements from the other constituents of a compound, it must often convert the compound into a type that can be more readily treated. Common practice is to convert metallic sulfides to oxides, sulfates, or chlorides; oxides to sulfates or chlorides; and carbonates to oxides. The processes that accomplish all this can be categorized as either pyrometallurgy or hydrometallurgy. Pyrometallurgy involves heating operations such as roasting, in which compounds are converted at temperatures just below their melting points, and smelting, in which all the constituents of an ore or concentrate are completely melted and separated into two liquid layers, one containing the valuable metals and the other the waste rock. Hydrometallurgy consists of such operations as leaching, in which metallic compounds are selectively dissolved from an ore by an aqueous solvent, and electrowinning, in which metallic ions are deposited onto an electrode by an electric current passed through the solution.

Extraction is often followed by refining, in which the level of impurities is brought lower or controlled by pyrometallurgical, electrolytic, or chemical means. Pyrometallurgical refining usually consists of the oxidizing of impurities in a high-temperature liquid bath. Electrolysis is the dissolving of metal from one electrode of an electrolytic cell and its deposition in a purer form onto the other electrode. Chemical refining involves either the condensation of metal from a vapour or the selective precipitation of metal from an aqueous solution.

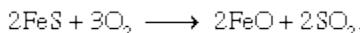
The processes to be used in extraction and refining are selected to fit into an overall pattern, with the product from the first process becoming the feed material of the second process, and so on. It is quite common for hydrometallurgical, pyrometallurgical, and electrolytic processes to be used one after another in the treatment of a single metal. The choices depend on several conditions. One of these is that certain types of metallic compounds lend themselves to easiest extraction by certain methods; for example, oxides and sulfates are readily dissolved in leach solutions, while sulfides are only slightly soluble. Another condition is the degree of purity, which can vary from one type of extraction to another.

17.4. Pyrometallurgy

Two of the most common pyrometallurgical processes, in both extraction and refining, are oxidation and reduction. In oxidation, metals having a great affinity for oxygen selectively combine with it to form metallic oxides; these can be treated further in order to obtain a pure metal or can be separated and

discarded as a waste product. Reduction can be viewed as the reverse of oxidation. In this process, a metallic oxide compound is fed into a furnace along with a reducing agent such as carbon. The metal releases its combined oxygen, which recombines with the carbon to form a new carbonaceous oxide and leaves the metal in an uncombined form.

Oxidation and reduction reactions are either exothermic (energy-releasing) or endothermic (energy-absorbing). One example of an exothermic reaction is the oxidation of iron sulfide (FeS) to form iron oxide (FeO) and sulfur dioxide (SO_2) gas:



This process gives off large quantities of heat beyond that required to initiate the reaction. One endothermic reaction is the smelting reduction of zinc oxide (ZnO) by carbon monoxide (CO) to yield zinc (Zn) metal and carbon dioxide (CO_2):



For this reaction to proceed at a reasonable rate, external heat must be supplied to maintain the temperature at $1,300^\circ$ to $1,350^\circ$ C ($2,375^\circ$ to $2,450^\circ$ F).

Roasting: As stated above, for those instances in which a metal-bearing compound is not in a chemical form that permits the metal to be easily and economically removed, it is necessary first to change it into some other compound. The preliminary treatment that is commonly used to do this is roasting.

Processes: There are several different types of roast, each one intended to produce a specific reaction and to yield a roasted product (or calcine) suitable for the particular processing operation to follow. The roasting procedures are:

1. Oxidizing roasts, which remove all or part of the sulfur from sulfide metal compounds, replacing the sulfides with oxides. (The sulfur removed goes off as sulfur dioxide gas.) Oxidizing roasts are exothermic.
2. Sulfatizing roasts, which convert certain metals from sulfides to sulfates. Sulfatizing roasts are exothermic.
3. Reducing roasts, which lower the oxide state or even completely reduce an oxide to a metal. Reducing roasts are exothermic.

4. Chloridizing roasts, or chlorination, which change metallic oxides to chlorides by heating with a chlorine source such as chlorine gas, hydrochloric acid gas, ammonium chloride, or sodium chloride. These reactions are exothermic.
5. Volatilizing roasts, which eliminate easily volatilized oxides by converting them to gases.
6. Calcination, in which solid material is heated to drive off either carbon dioxide or chemically combined water. Calcination is an endothermic reaction.

Roasters: Each of the above processes can be carried out in specialized roasters. The types most commonly in use are fluidized-bed, multiple-hearth, flash, chlorinator, rotary kiln, and sintering machine (or blast roaster).

Fluidized-bed roasters (see figure) have found wide acceptance because of their high capacity and efficiency. They can be used for oxidizing, sulfatizing, and volatilizing roasts. The roaster is a refractory-lined, upright cylindrical steel shell with a grate bottom through which air is blown in sufficient volume to keep fine, solid feed particles in suspension and give excellent gas-solid contact. The ore feed can be introduced dry or as a water suspension through a downpipe into the turbulent layer zone of the roaster. Discharge of the roasted calcines is through a side overflow pipe.

Multiple-hearth roasters also have found wide acceptance in that they can be used for oxidizing, sulfatizing, chloridizing, volatilizing, reducing, and calcining processes. The roaster is a refractory-lined, vertical cylindrical steel shell in which are placed a number of superimposed refractory hearths. A slowly rotating central shaft turns rabble arms on each hearth both to stir the roasting material and to push it into drop holes leading to the hearth below. Feed material is fed to the top hearth, and, as it follows a zig-zag path across the hearths and downward, it meets the rising gas stream that effects the roasting. The calcines are discharged from the bottom hearth.

Flash roasters are used only for oxidizing roasts and are, in effect, multiple-hearth roasters with the central hearths removed. This design came with the realization that much of the oxidizing takes place as the particles are actually dropping from hearth to hearth.

Chlorinators are used for roasting oxides to chlorides. They are tall, circular steel shells lined with refractory brick to prevent chlorine attack on the steel. The top of each chlorinator has a sealed hopper for periodic feed charging, and gaseous or liquid chlorine is added at the bottom of the unit. Heat is supplied by electrical resistance through the shell wall and by any exothermic reaction that

may occur. The product depends on the chloridizing reaction taking place, with magnesium dichloride, for example, forming as a watery liquid and titanium tetrachloride coming off as a gas.

Calcination of carbonates to oxides is done in a horizontal rotary kiln, which is a mild-steel circular shell lined with refractory material and having a length 10 to 12 times the diameter. Sloping slightly downward from feed to discharge ends, the kiln slowly rotates while fuel-fired burners located inside the kiln provide the required heat.

A sintering machine, or blast roaster, can conduct oxidizing or reducing roasts and then agglomerate the roasted calcines, or it can be used for agglomeration alone. (Agglomeration is the fusing of fine feed material into larger chunks that can be fed into a blast furnace or retort, eliminating the problem of losing the fine feed in the hot air blast.) The oxidizing or reducing reaction is exothermic, but in order for agglomeration alone to be conducted, a fuel such as fine coke must be mixed with the charge.

The sintering machine consists of an endless belt of moving metal pallets with grate bottoms on which a fine feed charge is spread and passed under a burner. As the charge ignites, the pallet passes over a suction wind box, so that air being drawn through the feed layer causes combustion (*i.e.*, oxidation) of sulfur or carbon to continue from top to bottom. Because the temperature is high and there is no agitation of the feed, a partial fusion takes place on the surface of the particles, leaving them adhering together in the form of a porous, cellular clinker known as sinter.

Smelting: Smelting is a process that liberates the metallic element from its compound as an impure molten metal and separates it from the waste rock part of the charge, which becomes a molten slag. There are two types of smelting, reduction smelting and matte smelting. In reduction smelting, both the metallic charge fed into the smelter and the slag formed from the process are oxides; in matte smelting, the slag is an oxide while the metallic charge is a combination of metallic sulfides that melt and recombine to give a homogeneous metallic sulfide called matte.

Reduction smelting: Many types of furnace are used for reduction smelting. The blast furnace is universally used in the reduction of such compounds as iron oxide, zinc oxide, and lead oxide, though there are great differences between the furnace designs used in each case. Iron, found naturally in the oxide ores hematite and magnetite, is smelted in a tall, circular, sealed blast furnace (A

sintered or pelletized feed consisting of coke (for fuel), limestone (as a flux for slag making), and iron oxide is charged into the top of the furnace through a double bell or rotating chute, and heated air is blown in through nozzles, or tuyeres, close to the furnace bottom. In the ensuing combustion reaction, oxygen in the air combines with carbon in the coke, generating enough heat to melt the furnace charge and forming carbon monoxide, which, in turn, reduces the iron oxide to metallic iron. The furnace is sealed to prevent the escape of carbon monoxide gas, which is recovered and burned as fuel to heat the tuyere air. In the hearth at the furnace bottom, molten slag and iron collect in two layers, the lighter slag on top. Both are periodically drawn off, with the slag being discarded and the iron going on to be refined into steel.

Refining: Refining is the final procedure for removing (and often recovering as by-products) the last small amounts of impurities left after the major extraction steps have been completed. It leaves the major metallic element in a practically pure state for commercial application. The procedure is accomplished in three ways: refining by fire, by electrolytic, or by chemical methods.

Fire refining: Iron, copper, and lead are fire-refined by selective oxidation. In this process, oxygen or air is added to the impure liquid metal; the impurities oxidize before the metal and are removed as an oxide slag or a volatile oxide gas.

The basic oxygen furnace (BOF) is a vessel used to convert pig iron, of about 94 percent iron and 6 percent combined impurities such as carbon, manganese, and silicon, into steel with as little as 1 percent combined impurities. The BOF is a large pear-shaped unit that can be tilted to charge and pour. Molten blast-furnace iron and steel scrap are charged into the furnace; then it is turned to an upright position and a lance inserted to blow high-tonnage oxygen gas into the bath. Oxidation reactions occur rapidly, with silicon and manganese oxidizing first and combining to form an oxide slag, then carbon oxidizing to carbon monoxide gas and burning to carbon dioxide as it leaves the furnace mouth. These reactions are strongly exothermic and keep the vessel up to its reaction temperature without any external heat or fuel being added.

Converter-produced blister copper and blast-furnace lead also are treated by fire refining, with both processes depending on the weaker affinity for oxygen of the metals than the impurities they contain. Molten copper in a small reverberatory-type furnace has compressed air blown into it through steel pipes below the surface. This oxidizes zinc, tin, iron, lead, arsenic, antimony, and sulfur; the sulfur goes off as sulfur dioxide gas, while the other impurities form an oxide slag that is skimmed off. Lead is refined in much the same way, with

compressed air blown into a molten lead bath and the major impurities of tin, antimony, and arsenic oxidizing in that order, rising to the surface as skims and being scraped off.

Other fire-refining operations use fractional distillation. By this method, zinc metal of 98-percent purity can be upgraded to 99.995-percent purity. The main impurities in blast-furnace zinc are lead and cadmium, with lead boiling at 1,744° C (3,171° F), zinc at 907° C (1,665° F), and cadmium at 765° C (1,409° F). In the first stage zinc and cadmium are boiled off, leaving liquid lead, and in the second stage cadmium is boiled off to leave special high-purity zinc metal.

Electrolytic refining: This method gives the highest-purity metal product as well as the best recovery of valuable impurities. It is used for copper, nickel, lead, gold, and silver. The metal to be refined is cast into a slab, which becomes the anode of an electrolytic cell; another sheet of metal is the cathode. Both electrodes are immersed in an aqueous electrolyte capable of conducting an electric current. As a direct current is impressed on the cell, metal ions dissolve from the anode and deposit at the cathode. The insoluble sludge left in the cell is treated to recover any valuable by-product metals.

Chemical refining: An example of chemical refining is the nickel carbonyl process, in which impure nickel metal is selectively reacted with carbon monoxide gas to form nickel carbonyl gas. This gas is then decomposed to give high-purity nickel metal.

17.5. Hydrometallurgy

Hydrometallurgy is concerned with the selective leaching of metallic compounds to form a solution from which the metals can be precipitated and recovered. Leaching processes are used when it is the simplest method or when the ore is of too low a grade for more expensive extractive procedures.

Conversion

Because not all ores and concentrates are found naturally in a form that is satisfactory for leaching, they must often be subjected to preliminary operations. For example, sulfide ores, which are relatively insoluble in sulfuric acid, can be converted to quite soluble forms by oxidizing or sulfatizing roasts. On the other hand, oxide ores and concentrates can be given a controlled reducing roast in order to produce a calcine containing a reduced metal that will dissolve easily in

the leaching solution. These treatments are described in more detail above (see Pyrometallurgy: Roasting). A second popular treatment for converting sulfides is pressure oxidation, in which the sulfides are oxidized to a porous structure that provides good access for the leaching solution. This treatment was developed for the recovery of gold from sulfide ores, which are not suitable for cyanide leaching without first being oxidized. A finely ground concentrate slurry is preheated to 175° C (350° F) and pumped into a four- or five-compartment autoclave, each compartment containing an agitator. Gaseous oxygen is added to each compartment, and retention time in the autoclave is two hours in order to achieve the desired oxidation.

Leaching

Oxides are leached with a sulfuric acid or sodium carbonate solvent, while sulfates can be leached with water or sulfuric acid. Ammonium hydroxide is used for native ores, carbonates, and sulfides, and sodium hydroxide is used for oxides. Cyanide solutions are a solvent for the precious metals, while a sodium chloride solution dissolves some chlorides. In all cases the leach solvent should be cheap and available, strong, and preferably selective for the values present.

Leaching is carried out by two main methods: simple leaching at ambient temperature and atmospheric pressure; and pressure leaching, in which pressure and temperature are increased in order to accelerate the operation. The method chosen depends on the grade of the feed material, with richer feed accommodating a costlier, more extensive treatment.

Leaching in-place, or in situ leaching, is practiced on ores that are too far underground and of too low a grade for surface treatment. A leach solution is circulated down through a fractured ore body to dissolve the values and is then pumped to the surface, where the values are precipitated.

17.6. Physical metallurgy

Physical metallurgy is the science of making useful products out of metals. Metal parts can be made in a variety of ways, depending on the shape, properties, and cost desired in the finished product. The desired properties may be electrical, mechanical, magnetic, or chemical in nature; all of them can be enhanced by alloying and heat treatment. The cost of a finished part is often determined

more by its ease of manufacture than by the cost of the material. This has led to a wide variety of ways to form metals and to an active competition among different forming methods, as well as among different materials. Large parts may be made by casting. Thin products such as automobile fenders are made by forming metal sheets, while small parts are often made by powder metallurgy (pressing powder into a die and sintering it). Usually a metal part has the same properties throughout. However, if only the surface needs to be hard or corrosion-resistant, the desired performance can be obtained through a treatment that changes only the composition and strength of the surface.

Structures and properties of metals

Metallic crystal structures

Metals are used in engineering structures (*e.g.*, automobiles, bridges, pressure vessels) because, in contrast to glass or ceramic, they can undergo appreciable plastic deformation before breaking. This plasticity stems from the simplicity of the arrangement of atoms in the crystals making up a piece of metal and the nondirectional nature of the bond between the atoms. Atoms can be arranged in many different ways in crystalline solids, but in metals the packing is in one of three simple forms. In the most ductile metals, atoms are arranged in a close-packed manner.

Alloying

Almost all metals are used as alloys—that is, mixtures of several elements—because these have properties superior to pure metals. Alloying is done for many reasons, typically to increase strength, increase corrosion resistance, or reduce costs.

Processes

In most cases, alloys are mixed from commercially pure elements. Mixing is relatively easy in the liquid state but slow and difficult in the solid state, so that most alloys are made by melting the base metal—for instance, iron, aluminum, or copper—and then adding the alloying agents. Care must be taken to avoid contamination, and in fact purification is often carried out at the same time, since this is also done more easily in the liquid state. Examples can be found in steelmaking, including the desulfurizing of liquid blast-furnace iron in a ladle, the decarburization of the iron during its conversion to steel, the removal of

oxygen from the liquid steel in a vacuum degasser, and finally the addition of tiny amounts of alloying agents to bring the steel to the desired composition.

The largest tonnages of alloys are melted in air, with the slag being used to protect the metal from oxidation. However, a large and increasing amount is melted and poured entirely in a vacuum chamber. This allows close control of the composition and minimizes oxidation. Most of the alloying elements needed are placed in the initial charge, and melting is done with electricity, either by induction heating or by arc melting. Induction melting is conducted in a crucible, while in arc melting the melted droplets drip from the arc onto a water-cooled pedestal and are immediately solidified.

Sometimes an inhomogeneous, composite structure is desired, as in cemented tungsten carbide cutting tools. In such cases, the alloy is not melted but is made by powder metallurgical techniques.

Increasing strength

The most common reason for alloying is to increase the strength of a metal. This requires that barriers to slip be distributed uniformly throughout the crystalline grains. On the finest scale, this is done by dissolving alloying agents in the metal matrix (a procedure known as solid solution hardening). The atoms of the alloying metals may substitute for matrix atoms on regular sites (in which case they are known as substitutional elements), or, if they are appreciably smaller than the matrix atoms, they may take up places between regular sites (where they are called interstitial elements).

Increasing corrosion resistance: Alloys can have much better high-temperature oxidation resistance than pure metals. The alloying elements most commonly used for this purpose are chromium and aluminum, both of which form an adherent film of stable oxide on the surface that protects the metal from further oxidation. Eleven percent or more chromium is added to iron to create a stainless steel, while 10 to 15 percent chromium and 3 to 5 percent aluminum are commonly added to the nickel- or cobalt-based superalloys used in the highest-temperature components of jet engines.

Inhibiting the corrosion of alloys in water is more varied and complex than inhibiting high-temperature oxidation. Nevertheless, one of the most common techniques is to add alloying elements that inhibit the corrosion.

Reducing costs: Gold and silver used in jewelry and coins are alloyed with other metals to increase strength and reduce cost.

Lowering melting points: Alloying can also be done to lower the melting point of a metal. For example, adding lead to tin lowers the melting point of the tin-rich alloy, and adding tin to lead lowers the melting point of the lead-rich alloy. A 62-percent-tin 38-percent-lead alloy, which is called the eutectic composition, has the lowest melting point of all, much lower than that of either metal. Eutectic lead-tin alloys are used for soldering.