

# 10

## Corrosion of Metal And Alloys

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## 10.1 Introduction

- ▶ Corrosion is a natural process that converts a refined metal into a more chemically-stable form such as oxide, hydroxide, or sulphide.
- ▶ It is the gradual destruction of materials (usual metals) by chemical and/or electrochemical reaction with their environment. Corrosion engineering is the field dedicated to controlling and stopping corrosion.
- ▶ In the most common use of the word, this means electrochemical oxidation of metal in reaction with an oxidant such as oxygen or sulfates. Rusting, the formation of iron oxides is a well-known example of electrochemical corrosion.
- ▶ This type of damage typically produces oxide(s) or salt(s) of the original metal and results in distinctive orange coloration.
- ▶ Corrosion can also occur in materials other than metals, such as ceramics or polymers, although in this context, the term "degradation" is more common. Corrosion degrades the useful properties of materials and structures including strength, appearance, and permeability to liquids and gases.

## 10.2 Mechanism of Corrosion

- ▶ The bulk of the metallic corrosion is due to the electrolytic action (i.e.,) when two different metals or alloys [or the same metal having different compositions (heterogeneity) at two or more surface areas] are in electrical contact with each other and are also in common contact with an electrolyte.
- ▶ One metal becomes anodic towards the other and naturally, the second metal will work as a cathode. For example, zinc is anodic towards copper.
- ▶ The anodic reaction is always associated with the dissolution of (anode) metal in the form of ions going into solution.
- ▶ The cathodic reaction involves two different processes, namely
  - (a) Hydrogen evolution, or
  - (b) Oxygen absorption.

### (a) Hydrogen Evolution

- ▶ The hydrogen evolution type of corrosion usually occurs in acid environments such as acid industrial waters and the solutions of non-oxidising acids.
- ▶ The hydrogen evolution type of corrosion has been explained under section 48.3.

### (b) Oxygen Absorption Mechanism

- ▶ Iron is corroded by a neutral aqueous solution of electrolytes in the presence of oxygen, thereby giving rise to rusting of (mild) steel.

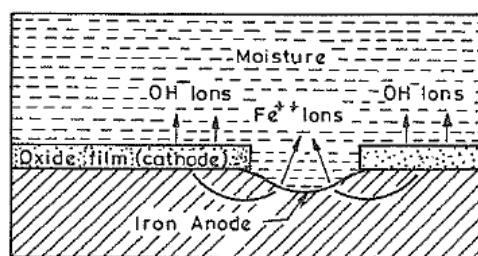


Fig.10.1 – Oxygen absorption mechanism

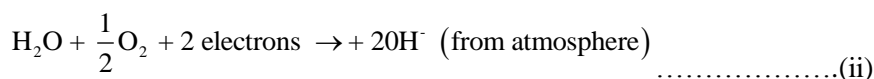
- ▶ Refer Fig. 10.1 that explains the mechanism of corrosion by means of oxygen absorption.

- ▶ Assume that due to some reasons (such as loading or improper handling) the oxide film on the steel surface breaks and the iron exposes to damp atmosphere, (or electrolyte).

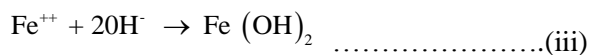
- ▶ Since iron is anodic to its oxide, it will go into solution in the form of ferrous ions



- ▶ Thus released electrons travel to the cathode (i.e., the unbroken oxide film



- ▶ The hydroxyl (OH-) ions dissolve at the cathode. When Fe++ and OH- ions meet away from the region of electrolytic action, the following reaction takes place:



- ▶ This ferrous hydroxide, Fe(OH)<sub>2</sub>, is quickly oxidized by atmospheric oxygen to ferric hydroxide, Fe(OH)<sub>3</sub>, which is precipitated as a reddish-brown substance, the main constituent of rust.
- ▶ Because of reaction (iii) above, the concentration polarization effect near the cathode is absent and the corrosion may proceed as long as there is an available supply of fresh oxygen.

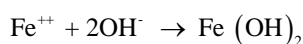
### 10.3 Types of Corrosion

- ▶ It is customary to classify the multitude of possible corrosion reactions into a few broad types such as

- 1 Direct corrosion.
- 2 Electrochemical and galvanic corrosion (Room Temperature).
- 3 Liquid-Metal corrosion (High Temperature).
- 4 Corrosion of a metal by a gas.
- 5 Special corrosion types.

#### 1 Direct Corrosion

- ▶ It is essentially an ordinary chemical attack by a corrosive solution on a metal.
- ▶ Acid pickling used to clean steel surfaces is another example of direct corrosion



- ▶ The reaction describes the direct attack of iron by hydrogen ions in the (e.g; 5-10% H<sub>2</sub>SO<sub>4</sub>) acid pickling of steel. In acid solution, the metal surface dissolves uniformly and can be measured in milligrams per square decimeter per day.
- ▶ The direct corroded surface has an etched appearance and may look clean as though it were ground or it may look darkened by the appearance of the non-metallic compounds which are formed.
- ▶ The rate of direct corrosion tends to be relatively high as compared with that of other corrosion mechanisms.
- ▶ Direct corrosion may be controlled by suitable addition (of an inhibiting chemical) to the corroding medium to cause to form a protective layer of the corrosion reaction product to alter the process by which corrosion occurs.

#### 2 Electrochemical Corrosion

- ▶ Probably the most serious corrosion takes the form of chemical reaction in conjunction with electrolysis

The factor governing electrochemical corrosion is.

- Existing potential difference, between a metal and its surrounding medium or between different parts of the same metal (owing to a difference in microstructure or composition).
  - The presence of an electrolyte. An electrolyte is any solution that contains ions. Ions are electrically charged atoms (or groups of atoms).
  - The electrolyte can be plain water, saltwater, or acid or alkaline solutions of any concentration.
  - The completion of a closed circuit; because corrosion requires a flow of electricity between certain areas of a metal surface, through an electrolyte.
  - To complete the electric circuit, there must be (two electrodes) an anode and a cathode [which may be two different kinds of metals (e.g., Fe and Cu) or they may be different areas on the same piece of metal.
- ▶ The connection between the anode and the cathode may be by a metallic bridge, but in corrosion, it is usually achieved simply by contact.
  - ▶ Electricity flows because of the potential difference between one metal (i.e; cathode) and another metal (i.e; anode).
  - ▶ The maintenance of current through the circuit. Current flow may stop if hydrogen evolved in the electrolytic circuit tends to concentrate on the cathode surface and thus forms an insulating layer that slows down or stops the electro-chemical action. This is known as cathodic polarization.
  - ▶ If this hydrogen layer gets broken down or swept away by some other reaction at the surface or by virtue of convection currents in the electrolyte, the initial conditions will have resorted, current will begin to flow and corrosion will start once again.
  - ▶ Fig.10.2 shows the action of a hydrochloric acid solution on a piece of iron.
  - ▶ Numerous tiny anode and ..cathode areas get formed on the surface of iron, owing to surface imperfections, localized stresses, grain orientations, inclusions in the metal or perhaps due to variations in the environment.
  - ▶ At the anode, positive charged iron atoms detach themselves from the solid surface and enter the solution (electrolyte) as positive ions; while the negative charges (electrons) that are released pass round the external circuit to the cathode, thus constituting the current.

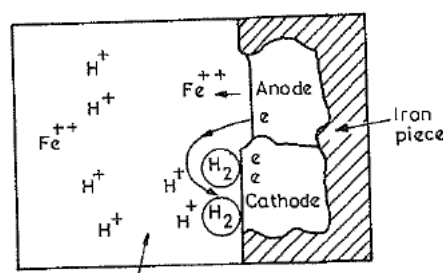
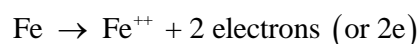
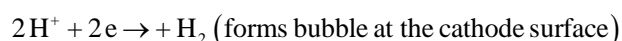


Fig.10.2 – Electrochemical Corrosion

- ▶ Iron passes and thus dissolves into solution, whereas the free electrons on reaching the cathode, meet and neutralize some positively charged hydrogen ions which have arrived at the (cathode) surface through the electrolyte. In losing their charge, the positive hydrogen ions become neutral atoms and these atoms combine to form (molecular) hydrogen gas



- ▶ The amount of metal (iron) which dissolves in the electrolyte is proportional to the number of electrons flowing, which in turn is dependent upon the potential and resistance of the metal.
- ▶ The (corrosion process) continues, till, in some cases where the evolution of the hydrogen gas at the cathode is very slow and the accumulation of a layer of hydrogen on the cathode surface slows down the electrochemical reaction. This is called cathodic polarization.
- ▶ However, oxygen dissolved in the electrolyte can react with accumulated hydrogen to form water and thus permitting corrosion to proceed. The effective concentration of oxygen in water adjacent to cathode depends upon the degree of aeration, temperature, degree of agitation (motion), presence of dissolved salts, etc.

### 3 Corrosion of Metal by a Liquid Galvanic Cells

- ▶ Galvanic corrosion is the mechanism of nearly all corrosion of metals by liquids, in which anode metal is made to dissolve or corrode continuously.
- ▶ Zn and Cu form the two electrodes and their potentials are referred to as electrode potentials. The combination of electrodes and electrolyte is called a galvanic cell.
- ▶ Depending upon the nature of the corrosive environment, the cathodic reaction may involve hydrogen evolution or oxygen adsorption.
- ▶ As the two electrodes are joined by a conductor, the electronic current flows from the anode (Zn) through a conductor to the cathode (Cu). At the anode, some of the excess electrons are removed, permitting more (anode) metal atoms to be oxidized and go into solution. At the cathode, more electrons are added that are intercepted by the positive ions deposited there.
- ▶ The corrosion current flows at the expense of anode metal, which is corroded continuously, whereas the cathode metal is protected from the attack.

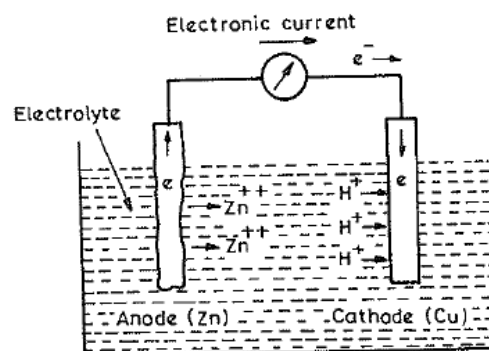


Fig.10.3 – Galvanic Corrosion

### 4 Liquid-Metal Corrosion

- ▶ Whereas electrochemical and galvanic corrossions take place at or near room temperature, the liquid-metal corrosion discussed under occurs at high temperatures. Usually, the driving force for this form of corrosion is the tendency of the solid to dissolve in the liquid up to the solubility limit at the given temperature.
- ▶ Serious damage by liquid-metal attack occurs in heat exchangers carrying liquid-metal (Bi and Na) coolants. As the solid container (e.g; copper tubing) approaches equilibrium with the liquid-metal coolant in the hot zone of the heat exchanger, a portion of the solid goes into solution in the liquid.
- ▶ As the liquid (containing this solid) moves to a cooler part of the heat exchanger, the solid tends to deposit on the walls of the exchanger tubes.
- ▶ This way the hot zone of the heat exchanger is continuously corroded and the cold zone becomes plugged with the deposited corrosion products.

## 5 Corrosion of Metal by a Gas

- ▶ In this type of corrosion, the gas molecules are absorbed on the surface of the metal and they react with surface atoms of metal.

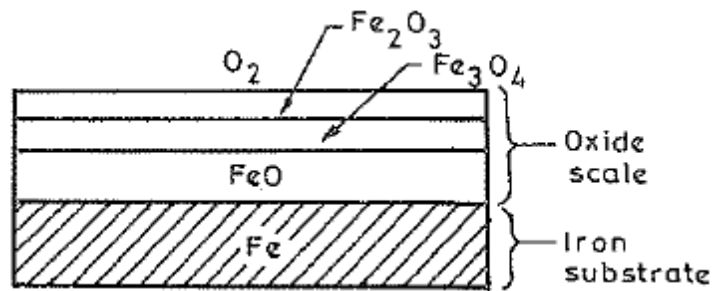
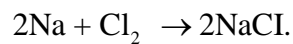
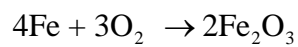
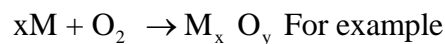


Fig.10.4 – Oxide scale formed iron  $>600^{\circ}\text{C}$

- ▶ Most metals (M) react with air, oxygen or other gases to produce corrosion products



- ▶ If the volume of corrosion product is greater than that of the metal consumed in the reaction, the layer must be compressed to fit the surface on which it is formed; and the result is a nonporous (protective) shield over the metal surface.
- ▶ In case, the volume of corrosion products is lesser than that of the metal consumed, the result is a porous film that offers little or no protection against further corrosion; because the porous layer will allow the corroding gas to come in direct contact with metal.

## 6 Uniform Corrosion

- ▶ When the entire surface of the metal is attacked to the same degree, it is known as uniform corrosion. One type of uniform corrosion may be the uniform dezincification that proceeds through a brass water pipe.
- ▶ Dezincification does not necessarily mean that only zinc is removed; this term is now applied to any condition of corrosion in which a specific element is removed from an alloy.
- ▶ Dezincification is associated with galvanic action. Mostly, the uniform corrosion is unusual in metals, since they (i.e., metals) are rarely so homogeneous that the surface will be evenly corroded.

## 7 Atmospheric Corrosion

- ▶ Atmospheric corrosion is very frequent in ferrous materials.
- ▶ A humid atmosphere is mainly responsible for this type of corrosion.
- ▶ Atmospheric corrosion generally follows an oxygen absorption mechanism.
- ▶ A layer of corrosion products forms; cracks in this layer expose the fresh metal to a corrosive atmosphere.

## 8 Pitting Corrosion

- ▶ It is non-uniform corrosion that results from inhomogeneities in metal due to inclusions, coring, and distorted zones which set up the difference of potential at localized spots to cause deep isolated holes or pits.
- ▶ Pitting corrosion results from an electrochemical reaction.

- ▶ Pitting of the metal occurs when there is a break in the protecting layer; for example, when the chromium plate (film) in a steel auto bumper breaks, the point of film breakage becomes anode while the surrounding unbroken film works as a cathode and thus the pitting of the exposed steel begins.

## 9 Intergranular Corrosion

- ▶ It is a non-uniform corrosion.
- ▶ From the solid solution, when a phase precipitates at the grain boundaries, the material in the vicinity of the grain boundary becomes depleted of the dissolved element, thus creating a potential difference between the grain boundaries and the rest of the alloy.
- ▶ When this situation exists and the alloy is placed in contact with a corrosive agent, the attack begins at the surface in the region of this grain boundary material and then penetrates into the body of the alloy, following the boundaries. - Intergranular corrosion is detrimental to the strength of the alloy.
- ▶ Microscopic examination can reveal clearly the intergranular corrosion.
- ▶ 18/8 stainless steel, aluminum alloys, and copper alloys are susceptible to this type of corrosion

## 10 Stress Corrosion

- ▶ In cold-worked stressed metals, the pile-Up of dislocations at grain boundaries and other points increases the energy in those regions so that they become sufficiently anodic to the rest of the structure (under certain environments).
- ▶ Therefore, corrosion takes place in these regions of high energy and the stresses locked up (in the metal), give rise to the formation of cracks which grow progressively with the continuance of corrosion. The cracks may be trans granular (i.e., in the grains) or intergranular (i.e., along the grain boundaries) or a combination of both.
- ▶ It has been observed that most commercial alloys (such as those of aluminum, brasses, stainless steels, and low carbon steels) are susceptible to stress-corrosion cracking when subjected to high tensile stresses and exposed to certain specific corrosive environments. Pure metals are relatively immune to stress corrosion cracking. For instance, aluminum alloys and low carbon steels stress corrode in seawater.
- ▶ Well, known examples of stress corrosion are season cracking that occurs in brasses, especially in the presence of moisture and traces of ammonia, and caustic embrittlement of steel exposed to solutions containing NaOH. An effective control against stress corrosion is the elimination of tensile stresses from the component part.

## 11 Erosion Corrosion (or Impingement Corrosion)

This type of corrosion refers to the combined effects of

- (i) Mechanical abrasion on the metal surface caused by the impingement of entrained air bubbles, abrasive particles suspended in the liquid or turbulent flow of liquids, and
  - (ii) Chemical corrosion, on a metallic surface. Erosion corrosion is caused by the breakdown of the protective film at the spot of impingement, which contributes, to the formation of differential cells in such areas and causes localized pitting at the anodic points of the cells.
- ▶ The place where the scale has been broken forms anode whereas the unbroken protective layer (e.g., oxide film) surrounding that place (of a removed layer) acts as a cathode. - This type of corrosion is encountered in
    - Pump mechanisms,
    - Turbines,
    - Condenser tubes and pipings, and
    - Tubes carrying seawater.

## 10.4 Corrosion Control

### Introduction

- ▶ The types of corrosion are many and the conditions under which corrosion takes place are extremely varied. For this reason, many ways have been found out to control and prevent the corrosion of metals and alloys.
- ▶ Broadly the methods to control corrosion base upon:
  - (a) Proper design of structures (i.e., Design against corrosion).
  - (b) Control of corrosion mechanism.
  - (c) Insulation of the material from the corrosive environment.
- ▶ Different techniques of corrosion control are:
  1. Design against corrosion.
  2. Use of high purity metals.
  3. Use of alloy additions.
  4. Use of special heat-treatments.
  5. Cathodic protection.
  6. Use of inhibitors.
  7. Environment control.
  8. Use of protective surface coatings

### 1 Design against corrosion

- ▶ Proper design should permit the least contact between the structure and the corroding agent.
- ▶ Joints should be such that the liquid does not get a chance to enter and be retained.
- ▶ The use of dissimilar-metal contacts should be avoided where the presence of an electrolyte may result in galvanic corrosion.
- ▶ If two different metals have to be used, they should be as close as possible to each other in the galvanic series.
- ▶ If this is not possible, they (i.e., metals) should be separated (i.e., insulated) by rubber or plastic to reduce the possibility of galvanic corrosion, Fig.10.5

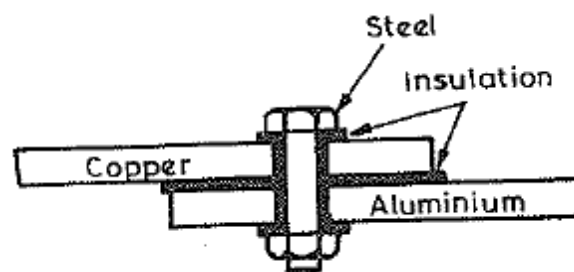


Fig.10.5 – Practice of insulating to avoid galvanic Corrosion

- ▶ The anodic material should have as large an area as possible, whereas the cathodic material should be of much smaller area.- Crevices, recesses, pockets and sharp corners should be avoided.
- ▶ The structure should be stress-free and possess good surface finish Welded joints, rather than brazed, soldered or bolted joints, may be used in order to avoid crevices, etc.



- ▶ Proper design should avoid conditions that may subject some area of the structure to cold working in service.- All equipment should be kept clean and free from sediments.-' Lastly, the proper design should select corrosion-resistant materials for the fabrication of structures.

## 2 Use of high purity metals

- ▶ The corrosion resistance of a given metal may be improved by increasing its purity. In most cases, the use of high purity metals tends to reduce pitting corrosion; for example, pure aluminum suffers much less from pitting corrosion as compared to aluminum alloys. Impurities in metals reduce corrosion resistance. However, pure metals possess low strength as compared to their alloys.

## 3 Use of alloy additions (Corrosion-resistant alloys)

- ▶ It is common to increase both strength and corrosion resistance by the use of suitable alloying elements.

For example

- (i) Small amounts of phosphorous and copper improve the resistance of structural steels to atmospheric corrosion.
- (ii) About 10% aluminum renders iron extremely resistant to high-temperature oxidation (but also makes it brittle). Intergranular corrosion in stainless steels may be avoided either by reducing carbon to a low value (below 0.03%) or by the addition of titanium or columbium.

## 4 Use of Heat-Treatments

- ▶ Heat treatment that leads to the homogenization of solid solutions,
- ▶ especially in cast alloys that are subject to coring, tends to improve corrosion resistance. Stress-relief treatments following cold working are widely used to improve the resistance of alloys susceptible to stress corrosion.

## 5 Cathodic Protection

- ▶ Cathodic protection is the most effective method of corrosion control; in fact, it is the only one capable of completely preventing corrosion.
- ▶ This is accomplished by placing a metal that is higher in the electro potential series (e.g; zinc) in contact with metal (e.g., steel) to be protected. In this manner, the inserted metal (Zn, Al or Mg), the anode, which should not form a functional part of the structure, will establish a potential with the metal to be protected and will prevent corrosion. Of course, from time to time it is necessary to replace the anode because it itself gets corroded and cathodically protects the other (less active) metal. This protecting metal (e.g., Zn) is known as a sacrificial anode.
- ▶ An example of cathodic protection is Galvanized iron, in which zinc coating itself gets consumed under working conditions but protects the iron from being corroded.
- ▶ Structures most frequently protected by this method (i.e., cathodically) are underground pipelines, hulls of ships and boilers. For the protection of the underground pipe, anodes are buried some 2 to 3 meters from the pipe. The depth of the hole should be sufficient to locate the anode in permanently moist soil.
- ▶ Individual anodes are connected to a collector wire which in turn is brazed to the pipeline. The current discharges from the anode to the soil collects on the pipeline and returns to the anode through the connecting wire.
- ▶ To protect ship hulls cathodically, Zinc or Magnesium anodes are fastened to the rudder and to the hull itself-in the region around the propeller.
- ▶ For cathodic protection of domestic and industrial water heaters and elevated water storage tanks, Magnesium anodes have been widely employed.

- ▶ Care should be exercised in cathodic protection that Polarization'
- ▶ Care should be exercised in cathodic protection that Polarization'
- ▶ moreover, the' an odd area should be small as compared with the cathode area to secure expected protection against corrosion.

## 6 Use of Inhibitors

- ▶ Inhibitors are (chemical) compounds added to an electrolyte that protectively coats the anode or cathode and stops corrosion.
- ▶ Inhibitors are added to antifreeze mixtures used in automobile radiators.
- ▶ The oxidizing agent, when added to the corrosive solution, will produce oxide film on aluminum, chromium, and manganese.
- ▶ Anodic and cathodic inhibitors
  - Anod, inhibitor suppresses the anodic reaction or metal dissolution. Examples of anodic' Inhibitors are' oxidizing substances such as phosphates, chromates, etc., used for the protection of iron and steel.
  - Cathodic inhibitor either prevents the evolution of hydrogen-oxygen absorption at the cathodic areas. Examples of cathodic inhibitors are calcium bicarbonates in hard water, Magnesium, Nickel.

### Inorganic and organic inhibitors

- ▶ Inorganic inhibitors such as chromates and nitrates, phosphates, and silicate and hydroxide, etc., are generally protective in neutral and alkaline solutions but they offer little or no protection in the presence of acids, acid brines, reducing conditions and microbiological action.
- ▶ For such conditions, polar organic compounds and colloidal organic materials are mostly used as inhibitors.
- ▶ The inhibitive action of an organic compound and colloidal is the result of physical adsorption and chemisorption of the molecule at the metal surface.
- ▶ Example of organic is various amines mercaptans, a heterocyclic nitrogen compound, substituted ureas and thioureas, sulphides and heavy metal soap.

## 7 Environmental Control

- ▶ One method of corrosion prevention is to modify the environment.
- ▶ This may involve removing the corrosion constitute (e.g. use of vacuum instead of a corrosive atmosphere) or by using inhibitor (as explained above).
- ▶ A slight decrease in the temperature of the corroding medium may cause a pronounced decrease in the amount of corrosion.
- ▶ Corrosion rate can usually be lowered by reducing the velocity of the corroding medium. - Changes in the chemical composition of the corroding medium (by introducing inhibitors or otherwise, e.g., by removing the dissolved oxygen from the corroding medium such as water) may have a great effect on corrosion behavior.
- ▶ Protective atmosphere such as an inert gas like helium, hydrogen and the mixture of hydrogen and nitrogen produced by dissociating ammonia (NH<sub>3</sub>) has been successfully employed to stop high temperature (oxidation) corrosion of ferrous metals and alloys.
- ▶ An example of a gaseous controlled atmosphere, employed to prevent both high-temperature oxidations of steel and change in its surface carbon content, is a mixture of carbon monoxide and carbon dioxide.
- ▶ Purified and .dehumidified atmosphere around the structure decidedly reduces corrosion.

### Use of Protective Surface Coatings

- Protective surface coatings include.
- Salt (phosphate films) and oxide (Anodising on Al) films.
- Metallic coatings (Zn, Cu, Cr, etc.)
- Organic coatings. (Paints)
- Ceramic (vitreous enamel) coatings.- Protective surface coatings have been discussed under the section.

### 10.5 References

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O. P. Khanna “Material Science and Metallurgy” Dhanpat Rai Publications.