Semester: 5th Subject: Corrosion Engineering

LECTURE - 1

Corrosion: Introduction – Definitions and Types

INTRODUCTION:

Corrosion can be viewed as a universal phenomenon. It is there everywhere, air, water, soil and in every environment, we encounter.

Corrosion costs manifest in the form of premature deterioration or failure necessitating maintenance, repairs and replacement of damaged parts.

Corrosion has a huge economic and environmental impact on all facets of national infrastructure; from highways, bridges, buildings, oil and gas, chemical processing, water and waste water treatment and virtually on all metallic objects in use.

Other than material loss, corrosion interferes with human safety, disrupts industrial operations and poses danger to environment. Awareness to corrosion and adaptation of timely and appropriate control measures hold the key in the abatement of corrosion failures.

Definition: The word **Corrosion** stands for material or metal deterioration or surface damage in an aggressive environment by chemical or electrochemical means.
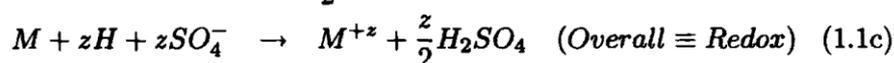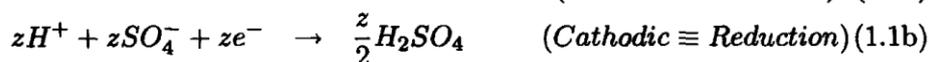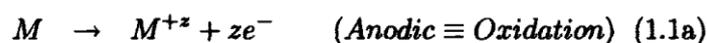In simple terminology, corrosion processes involve reaction of metals with environmental species.

Corrosion is a chemical or electrochemical oxidation process, in which the metal transfers electrons to the environment and undergoes a valence change from zero to a positive value z. The environment may be a liquid, gas or hybrid soil-liquid. These environments are called electrolytes since they have their own conductivity for electron transfer.

An electrolyte is analogous to a conductive solution, which contains positively and negatively charged ions called cations and anions, respectively.

An ion is an atom that has lost or gained one or more outer electron (s) and carries an electrical charge. Thus, the corrosion process which can be chemical in nature or electrochemical due to a current flow, requires at least two reactions that must occur in a particular corrosive environment.

These reactions are classified as anodic and cathodic reactions and are defined below for a metal *M* immersed in sulfuric acid solution as an example. Hence, metal oxidation occurs through an anodic reaction and reduction is through a cathodic reaction as shown below

$$M \; \rightarrow \; M^{+z} + ze^- \qquad (Anodic \equiv Oxidation) \; (1.1a)$$

$$zH^+ + zSO_4^- + ze^- \; \rightarrow \; \frac{z}{2}H_2SO_4 \qquad (Cathodic \equiv Reduction)\,(1.1b)$$

$$M + zH + zSO_4^- \; \rightarrow \; M^{+z} + \frac{z}{2}H_2SO_4 \quad (Overall \equiv Redox) \;\; (1.1c)$$

where M = Metal $\qquad$ M^{+z} = Metal cation

H^+ = Hydrogen cation $\qquad$ SO_4^- = Sulfate anion

z = Valence or oxidation state

The interpretation of the above equations indicate that an anodic reaction, which is equivalent to what is known as oxidation, loses ze^- metal electrons and the cathodic reaction accepts or gains ze^- electrons for reducing pertinent ions.

Consequently, both anodic and cathodic reactions are coupled in a corrosion process. Adding eqs. (1.1a) and (1.1b) yields eq. (1.1c). Thus, REDOX (RED = reduction and OX = oxidation) is the resultant reaction equation, eq. (1.1c), and represents the overall reaction at equilibrium where the anodic and cathodic reaction rates are equal.

Observe that the anodic reaction is also referred to as an oxidation reaction since it has lost ze^- electrons, which has been gained by the cathodic reaction for producing sulfuric acid. Thus, a cathodic reaction is equivalent to a reduction reaction.

Furthermore, the arrows in eq. (1.1) indicate the reaction directions as written and they represent irreversible reactions. On the other hand, a reversible reaction is represented with an equal sign. Thus, the metal reaction can proceed to the right for oxidation or to the left for reduction as indicated by eq. (1.2)

$$M = M^{+z} + ze^-$$

This expression means that the reaction proceeds from left to right or vice versa under specific chemical or electrochemical conditions.

The concepts of metal oxidation and metal reduction or electrodeposition are schematically shown in Figure 1.1. The dark thick line on the metal electrode is a representation of metal deposition as a result of metal ion reduction and metal oxidation is shown on the left-hand side of the electrode.
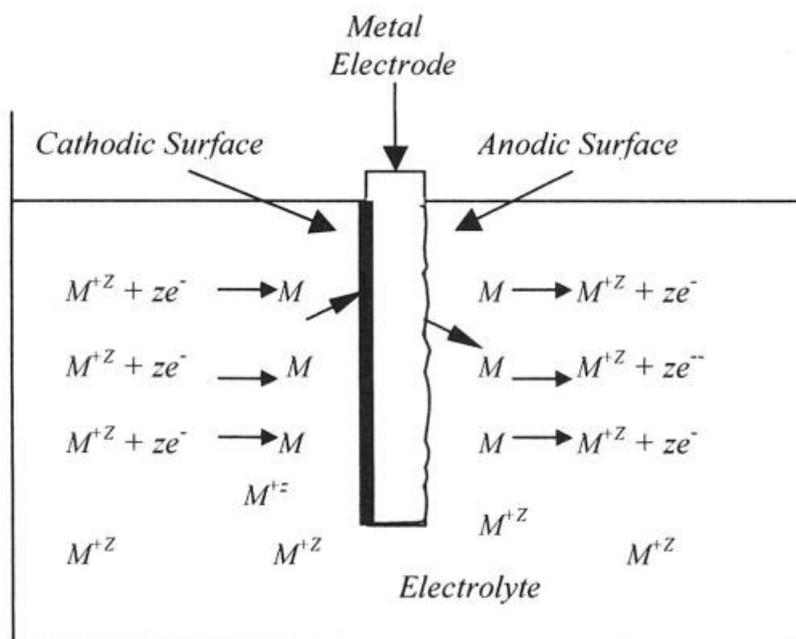

Figure 1.1 Schematic electrochemical cell.

CLASSIFICATION OF CORROSION

There is not a unique classification of the types of corrosion.

Table 1.1 ASM classifications of corrosion types

General Corrosion:	Localized Corrosion:	Metallurgically Influenced Corrosion:	Mechanically Assisted Degradation:	Environmentally Induced Cracking:
Corrosive attack dominated by uniform thinning • Atmospheric corrosion • Galvanic corrosion • Stray-current corrosion • General biological corrosion • Molten salt corrosion • Corrosion in liquid metals • High – temperature corrosion	High rates of metal penetration at specific sites • Crevice corrosion • Filiform corrosion • Pitting corrosion • Localized biological corrosion	Affected by alloy chemistry & heat treatment • Intergranular corrosion • Dealloying corrosion	Corrosion with a mechanical component • Erosion corrosion • Fretting corrosion • Cavitation and water drop impingement • Corrosion fatigue	Cracking produced by corrosion, in the presence of stress. • Stress – Corrosion Cracking (SCC) • Hydrogen Damage • Liquid metal embrittlement • Solid metal induced embrittlement

Uniform corrosion:
This is the case when the exposed metal/alloy surface area is entirely corroded in an environment such as a liquid electrolyte (chemical solution, liquid metal), gaseous electrolyte (air, etc.), or a hybrid electrolyte (solid and water, biological organisms, etc.).

Uniform corrosion is a very common form found in ferrous metals and alloys that are not protected by surface coating or inhibitors. A uniform layer of rust on the surface is formed when exposed to corrosive environments. Atmospheric corrosion is a typical example of this type.

Galvanic corrosion:
Galvanic corrosion often referred to as dissimilar metal corrosion occurs in galvanic couples where the active one corrodes.

EMF series (thermodynamic) and galvanic series (kinetic) could be used for prediction of this type of corrosion. Galvanic corrosion can occur in multiphase alloys.

Different metals and alloys have different electrochemical potentials (or corrosion potentials) in the same electrolyte. When the corrosion potentials of various metals and alloys are

measured in a common electrolyte (e.g. natural seawater) and are listed in an orderly manner (descending or ascending) in a tabular form, a Galvanic Series is created.

Table 3-2 Galvanic series of some commercial metals and alloys in seawater

Noble or cathodic ↑

- Platinum
- Gold
- Graphite
- Titanium
- Silver
- [Chlorimet 3 (62 Ni, 18 Cr, 18 Mo
  [Hastelloy C (62 Ni, 17 Cr, 15 Mo)
- [18-8 Mo stainless steel (passive)
  [18-8 stainless steel (passive)
  [Chromium stainless steel 11-30% Cr (passive)
- [Inconel (passive) (80 Ni, 13 Cr, 7 Fe)
  [Nickel (passive)
- Silver solder
- [Monel (70 Ni, 30 Cu)
  [Cupronickels (60-90 Cu, 40-10 Ni)
  [Bronzes (Cu-Sn)
  [Copper
  [Brasses (Cu-Zn)
- [Chlorimet 2 (66 Ni, 32 Mo, 1 Fe)
  [Hastelloy B (60 Ni, 30 Mo, 6 Fe, 1 Mn)
- [Inconel (active)
  [Nickel (active)
- Tin
- Lead
- Lead-tin solders
- [18-8 Mo stainless steel (active)
  [18-8 stainless steel (active)
- Ni-Resist (high Ni cast iron)
- Chromium stainless steel, 13% Cr (active)
- [Cast iron
  [Steel or iron
- 2024 aluminum (4.5 Cu, 1.5 Mg, 0.6 Mn)

Active or anodic ↓

- Cadmium
- Commercially pure aluminum (1100)
- Zinc
- Magnesium and magnesium alloys

From Fontana (1986).

It should be emphasized that the corrosion potentials must be measured for all metals and alloys in the same electrolyte under the same environmental conditions (temperature, pH, flow rate etc.), otherwise, the potentials are not comparable.

The potential difference (i.e., the voltage) between two dissimilar metals is the driving force for the destructive attack on the active metal (anode).

Current flows through the electrolyte to the more noble metal (cathode) and the less noble (anode) metal will corrode.

The conductivity of electrolyte will also affect the degree of attack. The cathode to anode area ratio is directly proportional to the acceleration factor.

Crevice Corrosion:

It is associated with a stagnant electrolyte such as dirt, corrosion product, sand, etc. It occurs on a metal/alloy surface holes, underneath a gasket, lap joints under bolts, under rivet heads.
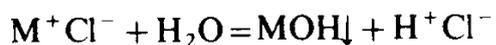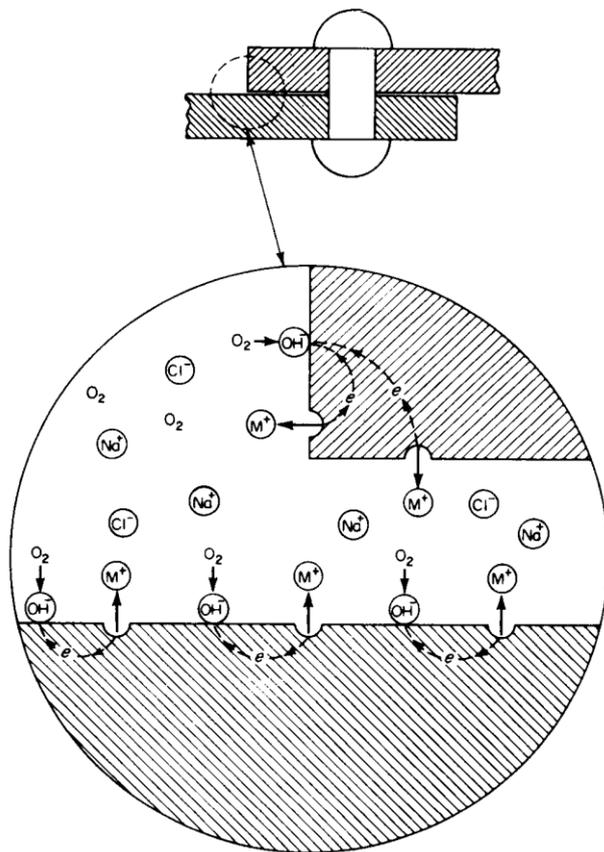

Mechanism of crevice corrosion.
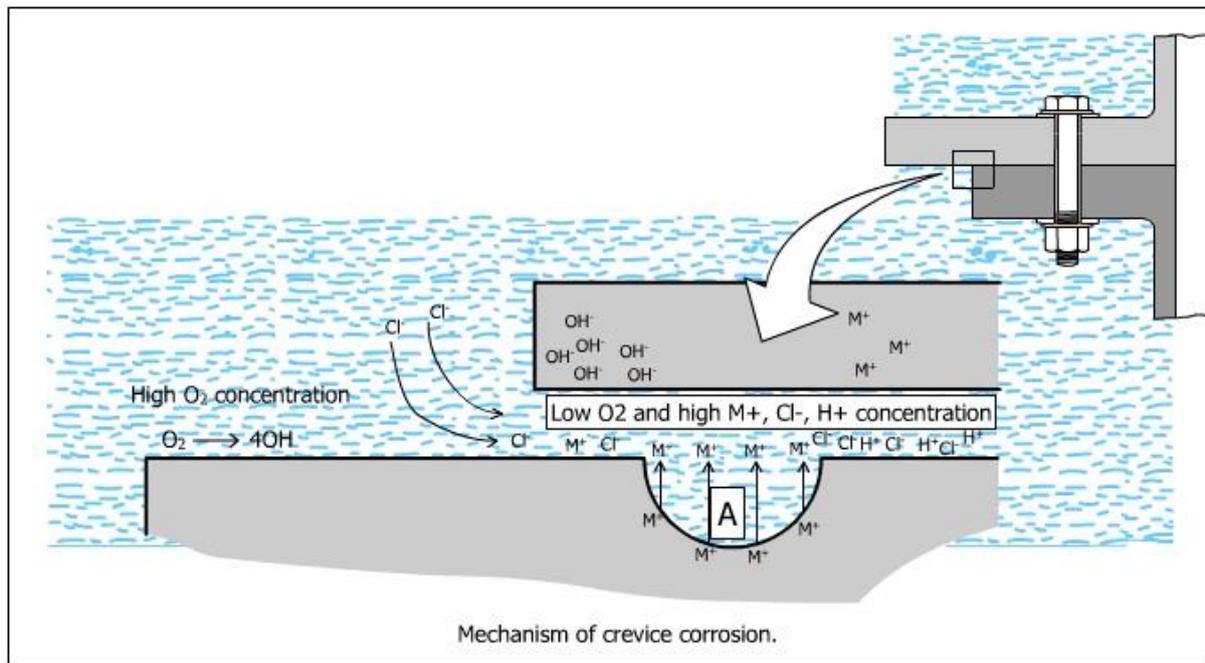
Mechanism: To illustrate the basic mechanism of crevice corrosion, consider a reverted plate section of metal M (e.g., iron or steel) immersed in aerated sea water. The overall reaction involves the dissolution of metal M and the reduction of oxygen to hydroxide ions.

Oxidation $\quad M \rightarrow M^+ + e$

Reduction $\quad O_2 + 2H_2O + 4e \rightarrow 4OH^-$
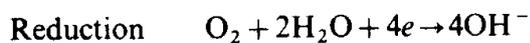
Initially, these reaction occur uniformly over the entire surface. Every electron produced during the formation of a metal ion is immediately consumed by the oxygen reduction reaction. After a short interval, the oxygen reduction ceases in this area.

Oxygen depletion has an important indirect influence, which becomes more pronounced with increasing exposure. After oxygen is depleted no further oxygen reduction occurs, although dissolution of metal M continues. This tends to produce an excess of positive charge in the solution (M^+), which is necessarily balanced by the migration of other chloride ions into the crevice.

$$M^+Cl^- + H_2O = MOH\downarrow + H^+Cl^-$$

Initial stage
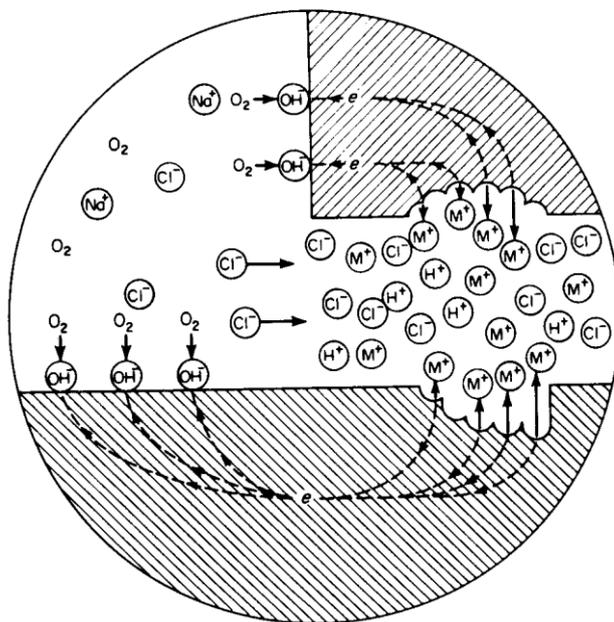
Later stage.

Filiform Corrosion:

It is basically a special type of crevice corrosion, which occurs under a protective film. It is common on food and beverage cans being exposed to the atmosphere.

Pitting Corrosion:

It is an extremely localized corrosion mechanism that causes destructive pits. Pits are sometimes isolated or so close together that they look like a rough surface. Generally a pit may be described as a cavity or hole with the surface diameter about the same as or less than the depth. Pits usually grow in the direction of gravity.

Consider a piece of metal M devoid of holes or pits, immersed in aerated sodium chloride solution. If, for any reason, the rate of metal dissolution is momentarily high at one particular point, chloride ions will migrate to this point. Since chloride stimulates metal dissolution, this change tends to produce conditions that are favourable to further rapid dissolution at this point.
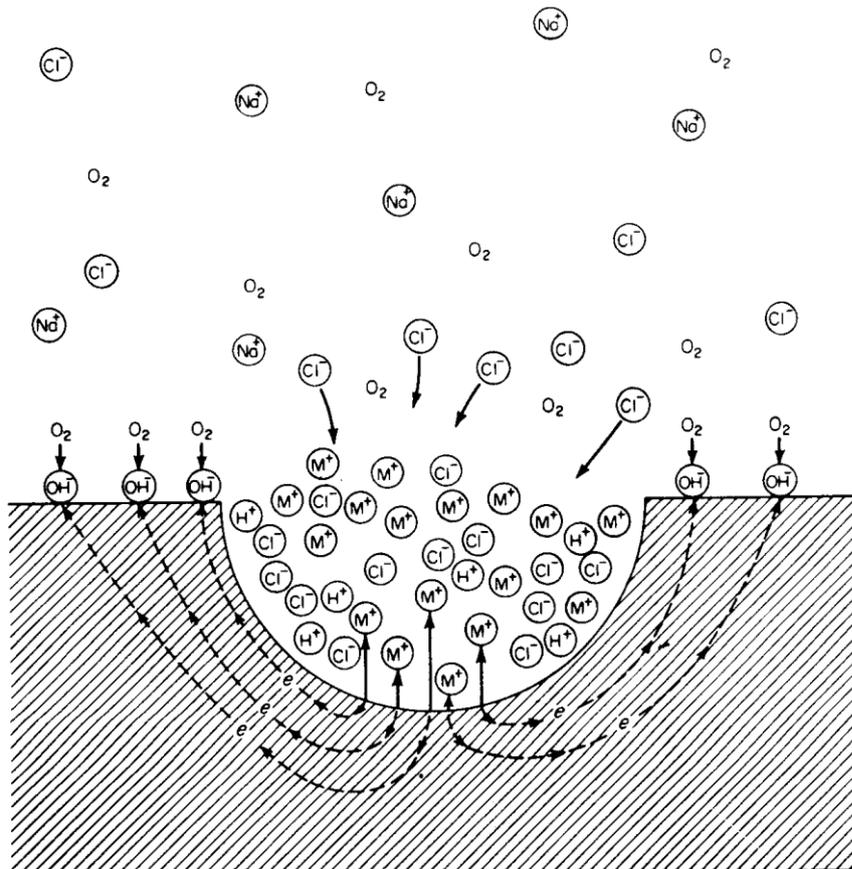

Autocatalytic process occurring in corrosion pit.

It is apparent that during the initiation or early growth stages of a pit, conditions are rather unstable. The gravity effect mentioned before is a direct result of the autocatalytic nature of pitting. Pits are more stable when growing in the direction of gravity. Also, pits are generally initiated on the upper surfaces of specimens because chloride ions are more easily retained under these conditions.

Intergranular Corrosion:

Grain interfaces are very reactive and intergranular corrosion results. Localized attack at and adjacent to grain boundaries, with relatively little corrosion of the grains is intergranular corrosion.

Intergranular corrosion can be caused by impurities at the grain boundaries, enrichment of one of the alloying elements, or depletion of one of these elements in the grain boundary areas.

Small amount of iron in aluminium, wherein the solubility of iron is low, have been shown to segregate in the grain boundaries and cause intergranular corrosion. Depletion of chromium in the grain boundary regions results in intergranular corrosion of stainless steels.
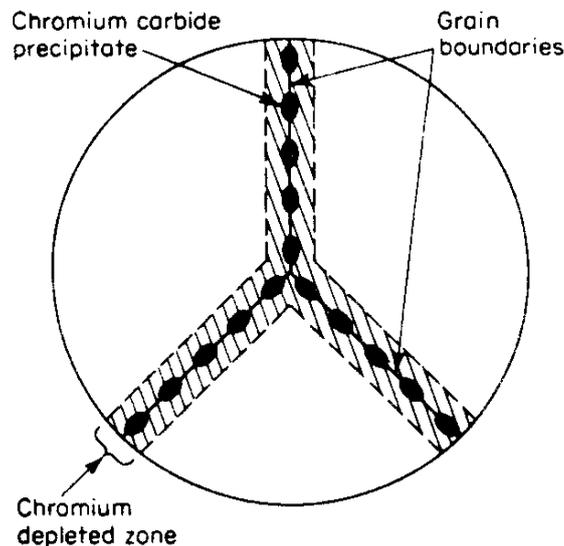
Diagrammatic representation of a grain boundary in sensitized type 304 stainless steel.

Selective leaching:

It is a metal removal process from the base alloy matrix by corrosion process, such as dezincification (Zn is removed) in Cu-Zn alloys and graphitization (*Fe* is removed) in cast irons.

Decarburization is the selective loss of carbon from the surface layer of a carbon-containing alloy due to reaction with one or more chemical substances in a medium that contacts the surface.

Decobaltification is selective leaching of cobalt from cobalt-base alloys, such as Stellite, or from cemented carbides.

Denickelification is the selective leaching of nickel from nickel-containing alloys. Most commonly observed in copper-nickel alloys after extended service in fresh water.

Dezincification is the selective leaching of zinc from zinc-containing alloys. Most commonly found in copper-zinc alloys containing less than 85% copper after extended service in water containing dissolved oxygen.

Graphitic corrosion is the deterioration of gray cast iron in which the metallic constituents are selectively leached or converted to corrosion products leaving the graphite intact. It is sometimes also referred to as graphitization.
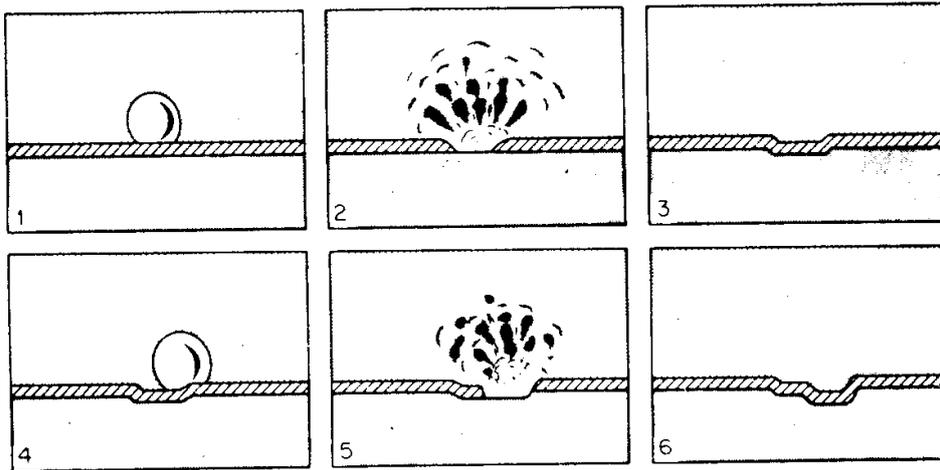
Erosion corrosion:

Erosion corrosion is the acceleration or increase in the rate of deterioration or attack on the metal because of relative movement between a corrosive fluid and the metal surface. Metal is removed from the surface as dissolved ions or it forms solid corrosion products that are mechanically swept from the metal surface.

Erosion corrosion is characterized in appearance by grooves, gullies, waves, rounded holes and valleys.

Cavitation damage:

A special form of erosion corrosion which is caused by the formation and collapse of vapour bubbles in a liquid near a metal surface. Cavitation damage occurs in hydraulic turbines, ship propellers, pump impellers and other surfaces where high-velocity liquid flow and pressure changes are encountered.

Mechanism: (1) A cavitation bubble forms on the protective film. (2) The bubble collapses and destroys the film. (3) The newly cavitaion bubble forms at the same spot (5) The bubble forms and destroys the film. (6) The exposed area corrodes and the film reforms. The repitation of this process results in deep holes.

Schematic representation of steps in cavitation.
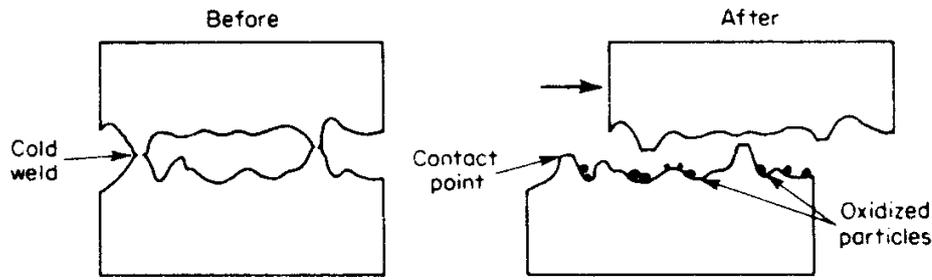
Fretting Corrosion:

Fretting describes corrosion occurring at contact areas between materials under load subjected to vibration and slip. It has been observed in engine components, automotive parts bolted parts and other machinery. Fretting occurs in atmosphere rather than under aqueous conditions.

In fretting corrosion destruction of metallic components and production of oxide debris, seizing and galling often occur, together with loss of tolerances and loosening of mating parts. Further, fretting causes fatigue fracture since the loosening of components permits excessive strain and the pits formed by fretting act as stress raisers.

The basic requirements for the occurrence of fretting corrosion are

1. The interface must be under load

2. Vibration or repeated relative motion between the two surfaces must occur

3. The load and the relative motion of the interface must be sufficient to produce slip or deformation on the surfaces.

   Two major mechanisms proposed for fretting corrosion.

Schematic illustration of the wear-oxidation theory of fretting corrosion
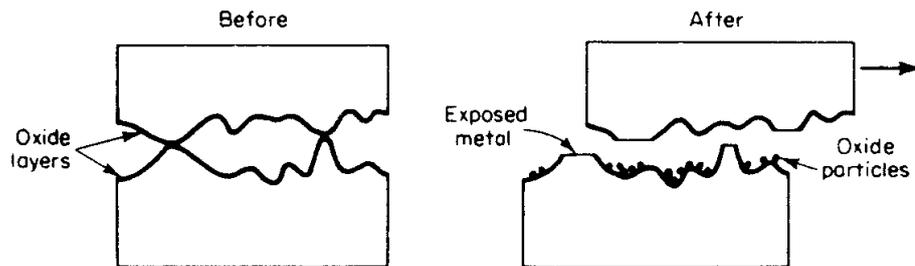
Schematic illustration of the oxidation-wear theory of fretting corrosion

Stress-corrosion cracking (SCC):

Stress-corrosion cracking (SCC) is a cracking process that requires the simultaneous action of a corrodent and sustained tensile stress. Stress-corrosion cracking may occur in combination with hydrogen embrittlement.

Mechanism:

Stress corrosion cracking results from the conjoint action of three components:

(1) a susceptible material;

(2) a specific chemical species (environment) and

(3) tensile stress.

For example, copper and its alloys are susceptible to ammonia compounds, mild steels are susceptible to alkalis and stainless steels are susceptible to chlorides. There is no unified mechanism for stress corrosion cracking in the literature. Various models have been proposed which include the following:

· Adsorption model: specific chemical species adsorbs on the crack surface and lowers the fracture stress.

· Film rupture model: stress ruptures the passive film locally and sets up an active-passive cell. Newly formed passive film is ruptured again under stress and the cycle continues until failure.

· Pre-existing active path model: Pre-existing path such as grain boundaries where intermetallic and compounds are formed.

· Embrittlement model: Hydrogen embrittlement is a major mechanism of SCC for steels and other alloys such as titanium. Hydrogen atoms diffuse to the crack tip and embrittle the metal.

Corrosion Fatigue:

Fatigue is defined as the tendency of a metal to fracture under repeated cyclic stressing. Usually fatigue failures occur at stress levels below the yield point and after many cyclic applications of this stress. Fatigue failures show a large smooth area and a smaller area which has a roughened and somewhat crystalline appearance.

Corrosion fatigue is defined as the reduction of fatigue resistance due to the appearance of a corrosive medium. Thus, corrosion fatigue is not defined in terms of the appearance of the failure, but in terms of mechanical properties. There is usually a large area covered with corrosion products and a smaller roughened area resulting from the final brittle fracture.

Hydrogen damage:
Hydrogen damage is a general term which refers to mechanical damage of a metal caused by the presence of, or interaction with hydrogen. Hydrogen damage may be classified into four distinct types:
1. Hydrogen blistering
2. Hydrogen embrittlement
3. Decarburization
4. Hydrogen attack

   Hydrogen blistering results from the penetration of hydrogen into a metal. Hydrogen embrittlement also is caused by penetration of hydrogen into a metal, which results in loss of ductility and tensile strength. Decarburization or removal of carbon from steel is often produced by moist hydrogen at high temperatures. Hydrogen attack refers to the interaction between hydrogen and a component of an alloy at high temperatures.

Corrosion rate expression:
Corrosion rates have been expressed in a variety of ways, such as percent weight loss, milligrams per square centimetre per day, and grams per square inch per hour. The expression **mills per year** is the most desirable way of expressing corrosion rates. This expression is readily calculated from the weight loss of the metal specimen during the corrosion test by the formula given below;

$$mpy = \frac{534W}{DAT}$$

where W = weight loss, mg
D = density of specimen, g/cm^3
A = area of specimen, sq. in.
T = exposure time, hr