الجامعة التكنولوجية

قسم الهندسة الكيمياوية

المرحلة الرابعة

هندسة التاكل

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Corrosion :-

Corrosion can be define as the destructive attack of a metal by chemical or electrochemical reaction with its environment.

SIGNIFICANCE AND COST OF CORROSION

Corrosion compromises structure safety and is a leading factor in the catastrophic failure in bridges, nuclear facilities, airplane components, and equipment used in chemical, petrochemical, transportation, and construction industries. Corrosion is a spontaneous, slow-progressing phenomenon. The rate is mainly governed by the environment, metal composition, and metallurgical, chemical, and electrochemical properties. Because it takes a long time to evaluate the extent of corrosion, it is often underestimated in industrial equipment and structure design.

Corrosion is a major expense in estimating production cost and investments in any industry. According to a recent study, the direct cost of corrosion is estimated to be approximately $276 billion in the United States . These losses are sustained by industry and government and constitute 3.2% of the gross domestic product (GDP). The direct cost of corrosion is considered the cost of replacing corroded structures and labor. Indirect losses add billions of dollars. The following losses are considered indirect costs:

product loss, shutdown, efficiency loss, product contamination, metal and food and structure and equipment over design, for example, using more expensive, overqualified materials.

Why metal corrode?

The corrosion occurs because of the natural tendency for most metals return to their natural state; e.g. , iron in the presence of moist air will revert to its natural state , iron oxide.

Metals can be corroded by the direct reaction of metal to a chemical;e.g. , zinc will react with dilute sulfuric acid, and magnesium will react with alcohols.

The driving force that makes metals corrode is a natural sequence of their temporary existence in the metallic form.

Thermodenamically: corrosion is the ability of the metal to revert to compounds which are more stable, i.e. , present in the nature initially.

Metal atoms in nature are present in chemical compounds (i.e. minerals). The same amounts of energy needed to extract metals from their minerals are emitted during the chemical reactions that produce corrosion. Corrosion returns the metal to its combined state in chemical compounds that are similar or even identical to the minerals from which the metals were extracted. Thus corrosion has been called extractive metallurgy in reverse .

Corrosion science and engineering

Corrosion science is the study of the chemical and metallurgical processes that occur during corrosion.

Corrosion engineering is the design and application of methods to prevent corrosion. Ideally , science should be associated with engineering so as to invent new and better methods of prevention and apply existing methods more intelligently and effectively .

Position of some metals in order of energy required to convert their ores to metals.

Least energy required ↑ Au
Pt
Ag
Cu
Pb
Ni
Co
Cd
Fe
Cr
Zn
Al
Mg
Na
Most energy required ↓ K

Basic Causes of Corrosion

Electro chemical corrosion is the most important classification of corrosion. Four conditions must be exist before electrochemical corrosion can be proceed:-

1- There must be something that corrodes (the metal anode).

2- There must be a cathode.

3- There must be a continuous conductive liquid path (electrolyte, usually liquid , condensate , salts , other contaminations).

4- There must be a conductor to carry the flow of electrons from anode to cathode. This conductor is usually in the form of metal –to – metal contact as in bolted or riveted joints.

The elimination of any one of the four conditions will stop corrosion .An unbroken (perfect) coating on the surface of the metal will prevent the electrolyte from connecting the cathode and anode so the current cannot flow.

Therefore, no corrosion will occur as long as the coating is unbroken.

Definition of Anode and Cathode

Anode :-as the electrode at which current leaves to return to the electrolyte (oxidation reaction).

$Zn \longrightarrow Zn^{2+} + 2e$ Oxidation reaction anodic reaction

Cathode : as the electrode at which current enters from the electrolyte .

The common cathodic reaction are:-

$2H^+ + 2e \longrightarrow H_2\uparrow$ Hydrogen evolution(H ER)

$O_2 + 4H^+ + 4e \longrightarrow 2H_2O$ O_2 reduction(acid solution)

$O_2 + 2H_2O + 4e \longrightarrow 4OH^-$ O_2 reduction(or basic solution)

$M^{+3} + e \longrightarrow M^{+2}$ Metal ion reduction

$M^+ + e \longrightarrow M$ Metal deposition

Classification of Corrosion

Corrosion has been classified in many different ways. One method divides corrosion into low- temperature and high – temperature corrosion. Another separates corrosion into direct combination (or oxidation) and electrochemical corrosion. The preferred classification here is (1) Wet corrosion and (2) Dry Corrosion.

(1) Wet Corrosion: Occurs when a liquid is present. This usually involves aqueous solutions or electrolytes and accounts for the greatest amount of corrosion by far. A common example is corrosion of steel by water.

(2) Dry Corrosion: occurs in the absence of a liquid phase or above the dew point of the environment. Vapors and gases are usually the corrodents. Dry corrosion is most often associated with high temperatures. An example is attack on steel by furnace gases.

The presence of even small amounts of moisture could change the corrosion picture completely. For example, dry chlorine is practically non corrosive to ordinary steel, but moist chlorine, or chlorine dissolved in water, is extremely corrosive and attacks of the common metals and alloys.

The reverse is true for titanium – dry chlorine.

Forms of Corrosion

It is convenient to classify corrosion by the forms in which it manifests itself, the basis for classification being the appearance of corroded metal. Each form can be identified by mere visual observation. In most cases the naked eye is sufficient but sometimes magnification is helpful or required. Valuable information for the solution of a corrosion problem can often be obtained through careful observation of the corroded test specimens or failed equipment. Examination before cleaning is particularly desirable.

Some of the eight forms of corrosion are unique, but all of them are more or less interrelated. The eight forms are:

1- Uniform (or General) attack.
2- Galvanic (or Tow- metal) .
3- Crevice corrosion .
4- Pitting.
5- Filiform corrosion
6- Intergranular corrosion .
7- Erosion corrosion
8- stress corrosion.
9- Corrosion fatigue cracking

Uniform corrosion

It is the uniform thinning of a metal without any localized attack. Corrosion dose not penetrate very deep inside. The most familiar example is the rusting of steel in air.

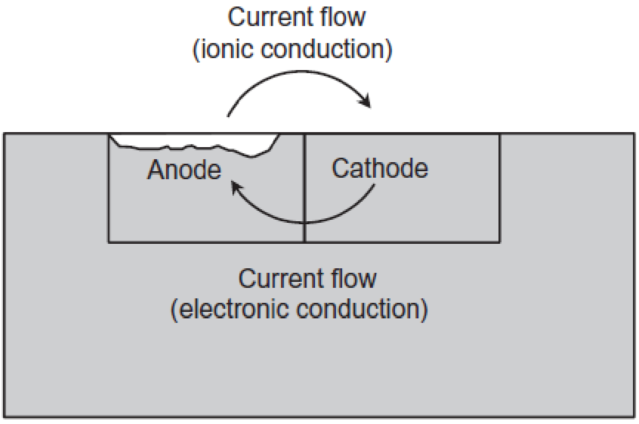
A uniform, regular removal of metal from the surface is the usually expected mode of corrosion. For uniform corrosion, the corrosion environment must have the same access to all parts of the metal surface, and the metal itself must be metallurgically and compositionally uniform. These requirements are not prevalent in operating equipment, and some degree of nonuniformity is tolerated within the definition of uniform corrosion.

Atmospheric corrosion is probably the most prevalent example of uniform corrosion at a visually apparent rate. The other frequently cited example of steel in an acid solution. A properly specifies alloy must corrode uniformly at a low rate in service. The other localized forms of corrosion are much less predictable and are to be avoided whenever possible. Thus, uniform corrosion is preferred from a technical view point because it is predictable and thus acceptable for design.

Galvanic Corrosion

Galvanic Corrosion occurs when two metals with different electrochemical potentials or with different tendencies to corrode are in metal-to-metal contact in a corrosive electrolyte, i.e. when two dissimilar alloys are coupled in the presence of a corrosive electrolyte one of them is preferentially corroded while the other is protected from corrosion.

Description:- when two metals with different potentials are joined ,such as copper(+0.334 v) and iron (-0.44 v) , a galvanic cell is formed. a cell in which the chemical change is the source of energy is called a "galvanic cell". The corrosion which is caused due to the formation of the galvanic cell, therefore, called "galvanic corrosion" . The driving force for corrosion is a potential different between different materials. Between two different materials connected through the electrolyte, the less noble will became the anode and tend to corrode. For example a galvanic corrosion between welded steel and stainless steel. The carbon steel pipe flange is active to the stainless steel pipe, and is corroded preferentially near the weld. Preferential corrosion near the junction between dissimilar alloys is characteristic of galvanic corrosion. the corrosion decreases at points farther from the junction due to higher resistance through a longer electrolyte path.



Factors affecting galvanic corrosion

A- Position of metals in the galvanic series as mentioned earlier, the further apart the metals are in the galvanic series, the greater is the chance for galvanic corrosion. The magnitude of galvanic corrosion primarily depends on how much potential difference exists between two metals. For a particular environment, the metals selected should be close to each other in the galvanic series to minimize galvanic corrosion. Active metals should not be joined with passive metals.

B- The nature of environment

For instance, water containing copper iron, like seawater, is likely to form galvanic cells on a steel surface of the tank. If the water in contact with steel is either acidic or contains salt, the galvanic reaction is accelerated because of the increased ionization of the electrolyte.

C- Area, Distance and Geometric effects. The anode to cathode area ratio is extremely important as the magnitude of galvanic corrosion is seriously affected by it. For a given amount of current, the metal with smallest area has the largest current density, and hence is more damage if corrosion occurs at it. The rate of corrosion increase with the ratio of cathode to anode area.

CREVICE CORROSION

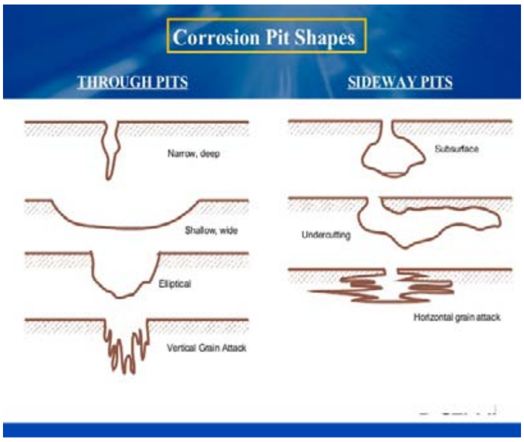
Crevices are formed at welds, in condensers, and between metal surfaces and valves. This type of corrosion is initiated by small volumes of solution captured in crevices under bolt gasket rivets or surface deposits. It destroys mechanical joint integrity in structures constructed from stainless steel, aluminum, titanium, and copper. For corrosion to occur, the aggressive solution must permeate the crevice and be sufficiently narrow to keep corrosion products inside the crevice. In the case of corrosion by dissolved oxygen, activepassive short circuits are formed between the aggressive solution in the crevice, which becomes oxygen depleted (anode), and the external metal surface (cathode). The initiation of crevice corrosion is based on pH decrease in the bottom of the crevice.

Several steps can be taken to prevent and/or control crevice corrosion:

1. Proper design, avoiding crevices, will control crevice corrosion. If lap joints are used, the crevices caused by such joints should be closed by either welding or caulking. Welded butt joints are preferable to bolted or riveted joints.
2. Porous gaskets should be avoided. Use an impervious gasket material. During long shutdown periods, wet packing materials should be removed.
3. The use of alloys resistant to crevice corrosion should be considered. The resistance of stainless steels to crevice corrosion can be improved by increasing the chromium, nickel, molybdenum,
4. Reduction of crevice corrosion can be accomplished, when possible, by reducing the temperature, decreasing the chloride content, or decreasing the acidity.
6. Regular inspections and removal of deposits should be scheduled.

Pitting corrosion

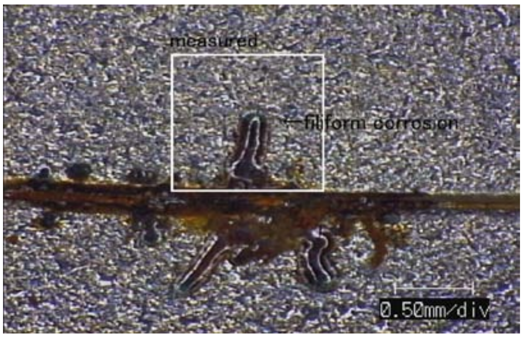
Pitting represents an extremely localized attack that produces holes in the metal or alloy. It is one of the most destructive, localized forms of corrosion. The pits are small cavities or holes with a depth greater than or equal to the surface diameter. They penetrate the metal, causing equipment failure due to preformation with minimal weight loss. The severity of pitting corrosion is controlled by environment, chloride concentration, electrolyte acidity, oxidizer concentration, temperature, structural characteristics, metal or alloy composition, dissolved oxygen concentration, potential, and potential scan rates. Surface pitting is proportional to the chloride concentration in the electrolyte. To initiate pitting corrosion, the electrolyte must act as a strong oxidizer to favor the passive state.



Pits on 304 stainless steel after exposure to simulated marine environment

Filiform corrosion

Filiform corrosion is observed under thin organic coatings on aluminum, steel, aircraft structures exposed to humid atmosphere, beverage cans, flanges, gaskets, dis-bonded underlying metals coated with organic coatings weld zones, and so forth.



Appearance of filiform corrosion tracks

The line in the center represents the knife-score. The filiform corrosion grew in both directions from the line and is composed of a head and the tail. The head and the tail are filled with a $FeCl_2$ solution and corrosion products, respectivel

Stress corrosion cracking

Stress corrosion cracking (SCC) is defined as crack growth due to simultaneous tensile stress and corrosive environments on active metals or alloys. In order for SCC to occur, the metal should be susceptible to SCC and be in a corrosive environment such as chloride ions, water, oxygen, pH, and so on. SCC leads to catastrophic failure in aircraft structures, nuclear facilities, boilers, and liquid or gas transmission pipes. Stress is induced by heat treatment, welding, machining, grinding, and cold work. The required tensile stresses may occur in the form of residual stress, applied load (directly applied stress), monotonic straining, or low amplitude cycling.

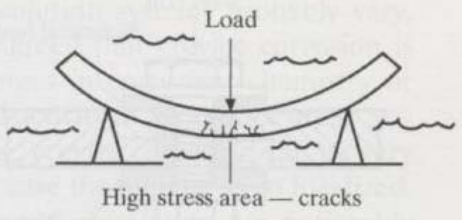


Figure 13–16
Stress corrosion cracking of stainless steel

Stress corrosion cracking of austenitic stainless steel

Corrosion fatigue cracking

High-strength material fatigue present in titanium alloys, aluminum alloys, and steel are susceptible to SCC when exposed to a corrosive environment. Fatigue cracking is mechanical degradation (brittle failure) when exposed to corrosion and cycling loading. Corrosion fatigue cracking (CFC) should not be confused with SCC, because the only requirement for CFC is exposure under tensile stress

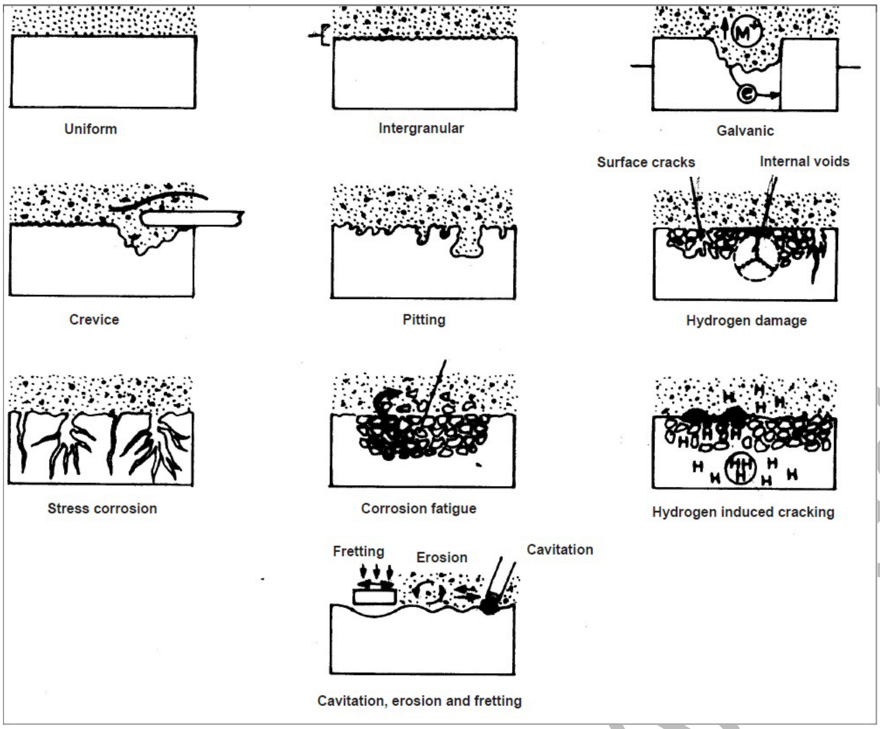
Intergranular Corrosion

Intergranular corrosion is a localized form of corrosion. It is a preferential attack on the grain boundary phases or the zones immediately adjacent to them. Little or no attack is observed on the main body of the grain. This results in the loss of strength and ductility. The attack is often rapid, penetrating deeply into the metal and causing failure.

The factors that contribute to the increased reactivity of the grain boundary area include:

1. Segregation of specific elements or compounds at the grain boundary, as in aluminum alloys or nickel–chromium alloys Fundamentals of Metallic Corrosion 7
2. Enrichment of one of the alloying elements at the grain boundary, as in brass
3. Depletion of the corrosion-resisting constituent at the grain boundary, as in stainless steel

All of these factors contributing to intergranular corrosion originate in the thermal processing of materials, such as welding, stress relief, and ther heat treatments.



Types of corrosion

Erosion Corrosion

The term “erosion” applies to deterioration due to mechanical force. When the factors contributing to erosion accelerate the rate of corrosion of a metal, the attack is called “erosion corrosion.” Erosion corrosion is usually caused by an aqueous or gaseous corrodent flowing over the metal surface or impinging on it. The mechanical deterioration may be aggravated by the presence of a corrodent, as in the case of fretting or corrosive wear.

Erosion corrosion is affected by velocity, turbulence, impingement, presence of suspended solids, temperature, and prevailing cavitation conditions. The acceleration of attack is due to the distribution or removal of the protective surface film by mechanical forces exposing fresh metal surfaces that are anodic to the uneroded neighboring film.

DEFINITION OF ANODE AND CATHODE

A combination of two electrical conductors (electrodes) immersed in an electrolyte is called a galvanic cell in honor of Luigi Galvani, a physician in Bologna, Italy, who published his studies of electrochemical action in 1791. A galvanic cell converts chemical energy into electrical energy.

The electrode at which chemical reduction occurs (or + current enters the electrode from the electrolyte) is called the ***cathode*** . Examples of cathodic reactions are

$$H^+ + e^- \longrightarrow 1/2\ H_2$$

$$Cu^{+2} + 2e^- \longrightarrow Cu$$

$$Fe^{+3} + e^- \longrightarrow Fe^{+2}$$

all of which represent reduction in the chemical sense.

The electrode at which chemical oxidation occurs (or + electricity leaves the electrode and enters the electrolyte) is called the ***anode.*** Examples of anodic reactions are:

$$\mathrm{Zn} \rightarrow \mathrm{Zn}^{2+} + 2e^-$$

$$\mathrm{Al} \rightarrow \mathrm{Al}^{3+} + 3e^-$$

$$\mathrm{Fe}^{2+} \rightarrow \mathrm{Fe}^{3+} + e^-$$

When current is impressed on a cell from a generator or an external battery — for example, as in electroplating — reduction occurs at the electrode connected to the negative pole of the external current source, and this electrode, consequently, is the cathode. Similarly, the electrode connected to the positive pole of the generator is the anode. It is perhaps best, therefore, not to

Cations are ions that migrate toward the cathode when electricity flows through the cell (e.g., H^+ , Fe^{2+}) and are always positively charged whether current is drawn from or supplied to the cell. Similarly, **anions** are always negatively Charged (e.g., Cl^- , OH^- , $SO4^{2-}$).

Table 1.5 *Standard potential series*

Electrode	Reaction	E°_{red} (V)
Li^+, Li	$Li^+ + e^- \rightarrow Li$	−3.024
K^+, K	$K^+ + e^- \rightarrow K$	−2.924
Ca^{2+}, Ca	$Ca^{2+} + 2\,e^- \rightarrow Ca$	−2.87
Na^+, Na	$Na^+e^- \rightarrow Na$	−2,714
Mg^{2+}, Mg	$Mg^{2+} + 2\,e^- \rightarrow Mg$	−2.34
Ti^{2+}, Ti	$Ti^{2+} + 2\,e^- \rightarrow Ti$	−1.75
Al^{3+}, Al	$Al^{3+} + 3\,e^- \rightarrow Al$	−1.67
Mn^{2+}, Mn	$Mn^{2+} + 2\,e^- \rightarrow Mn$	−1.05
Zn^{2+}, Zn	$Zn^{2+} + 2\,e^- \rightarrow Zn$	−0.761
Cr^{3+}, Cr	$Cr^{3+} + 3e^- \rightarrow Cr$	−0.71
Fe^{2+}, Fe	$Fe^{2+} + 2\,e^- \rightarrow Fe$	−0.441
Co^{2+}, Co	$Co^{2+} + 2\,e^- \rightarrow Co$	−0.277
Ni^{2+}, Ni	$Ni^{2+} + 2\,e^- \rightarrow Ni$	−0.250
Sn^{2+}, Sn	$Sn^{2+} + 2\,e^- \rightarrow Sn$	−0.140
Pb^{2+}, Pb	$Pb^{2+} + 2\,e^- \rightarrow Pb$	−0.126
Fe^{3+}, Fe	$Fe^{3+} + 3e^- \rightarrow Fe$	−0.036
H^+, H_2	$2\,H^+ + 2\,e^- \rightarrow H_2$	−0,000
Saturated calomel	$Hg_2Cl_2 + 2\,e^- \rightarrow 2\,Hg + 2\,Cl^-$ (Sat. KCl)	0.244
Cu^{2+},Cu	$Cu^{2+} + 2\,e^- \rightarrow Cu$	0.344
Cu^+,Cu	$Cu^+ + e^- \rightarrow Cu$	0.522
Hg_2^{2+}, Hg	$Hg_2^{2+} + 2\,e^- \rightarrow 2\,Hg$	0.798
Ag^+, Hg	$Ag^{2+} + 2\,e^- \rightarrow 2\,Hg$	0.799
Pd^+, Pd	$Pd^+ + 2\,e^- \rightarrow Pd$	0.83
Hg^+, Hg	$Hg^+ + e^- \rightarrow Hg$	0.854
Pt^{2+}, Pt	$Pt^{2+} + 2\,e^- \rightarrow Pt$	1.2 (ca)
Au^{3+}, Au	$Au^{3+} + 3e^- \rightarrow Au$	1.42
Au^+, Au	$Au^+ + e^- \rightarrow Au$	1.68