

DIFFERENT FORMS OF CORROSION IN INDUSTRIES

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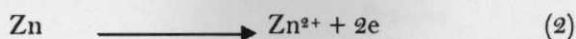
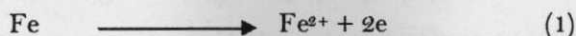
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Abstract

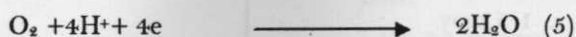
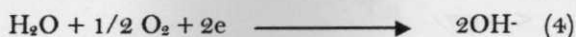
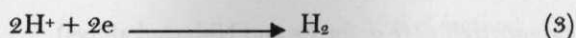
Corrosion is an inevitable process which causes degradation of metals/ alloys when exposed to the environment. It causes huge economic losses in terms of maintenance and repair cost, unplanned shutdowns of plant, loss of costly products due to leakage. Besides this, aesthetic loss, contamination of the product, safety and human loss are important. According to a survey conducted by federal highway authority (FHWA) of USA and NACE, direct corrosion costs were estimated to be about 137 billion dollars annually due to all sectors in United States of America. Corrosion losses are roughly approximated to be about 1.5 lakhs crore due to various sectors in India.

Corrosion involves electrochemical reaction that results oxidation of metal atom into the metal ions leaving electrons at anode; the electrons are consumed at cathode during simultaneous reduction reaction. This can be understood from below given reactions

Anodic (corrosion) reactions



Cathodic reactions



In electrochemical convention, the site where metal atoms lose electrons is called the anode (release of electron) and the site where electrons are transferred to the reducing species is called the cathode (consumption of electron). In most practical situations, more than one reduction reactions may occur simultaneously to cause metal corrosion.

FORMS OF CORROSION

Classification of corrosion is made by the appearance of corroded surface. Corrosion marks are often identifiable with naked eyes but sometimes careful examinations using more advance equipment such as optical and scanning electron microscopes are necessary to describe the corrosion types. In most industrial situations, components are suffered from more than one form of corrosion and are interrelated. Corrosion is categorized into eight different forms namely uniform/general, galvanic/

bimetallic, crevice, pitting, inter-granular, selective leaching/ dealloying, stress corrosion cracking, and erosion corrosion. A few of these are further subdivided or linked to others such as filiform, corrosion fatigue, fretting, exfoliation corrosion and microbiologically induced corrosion (MIC). Most prevalent types of corrosion are discussed in more details in the forthcoming sections.

Uniform or general corrosion

Corrosion occurs uniformly over a wide area of the metal surface leading to overall thinning is manifested by the uniform or general corrosion. The rate of general corrosion is easily predictable and therefore corrosion allowance at the time of component fabrication/ design can be given to achieve desired service life. Equipment, machineries and industrial structures made of carbon steel are frequently suffered from uniform corrosion. The losses due to uniform corrosion may be reduced by using appropriate maintenance and repair strategies. Application of paint, coating, inhibitor, and cathodic protection is helpful to minimize uniform corrosion. The corrosion rate can be determined by employing weight-loss measurement and electrochemical polarization technique (tafel extrapolation and linear polarization). In weight-loss method, clean specimens is weighed before and after exposure to corroding solution for preset duration; the weight-loss obtained may be used to calculate corrosion rate using following formula

$$\text{Corrosion Rate (mils/year)} = (534 \times W) / A \times T \times D$$

Where W-mass is loss (g), A is area, cm^2 , T is time in hours, and D is Density g/cm^3 .

The Tafel extrapolation, an accelerated method, can be used to obtain the corrosion current density (i_{corr}) which can be converted into corrosion rate (mils/year) by using following formula

$$\text{Corrosion rate} = (0.129 \times i_{\text{corr}} \times E) / d$$

where i_{corr} is corrosion current density in $\mu\text{A/cm}^2$, E is equivalent weight in g, and d is density in g/cm^3 .

Relative corrosion resistance can be categorized as (e.g. for Fe and Ni-based alloys)

Outstanding	<1 mpy
Excellent	1-5 mpy
Good	5-20 mpy
Unsatisfactory	>50 mpy

Galvanic or bimetallic corrosion

When two dissimilar metals are put in contact and exposed to corrosive electrolyte, a galvanic corrosion occurs. The one which corrode at relatively higher rate than the other, in dissimilar metals joint, is known as anode and the other which remains protected or corrodes at a lesser rate is known as cathode. The potential difference between the two metals/ alloys is the driving force for current and corrosion reaction to occur. To minimize the galvanic corrosion, constituent materials of the

joints should be as close as possible in the galvanic series, shown in Table-1. The galvanic series is based on the potential measurements and galvanic corrosion tests in unpolluted seawater conducted by the International Nickel company at Harbour Island, NC. The galvanic series (Table 1) indicates relative position of alloys rather than their potential, as done in the electromotive force (EMF) series. The galvanic corrosion may further be prevented by insulating the contact between dissimilar metals (by placing a non metallic washer). Unfavorable area effect such as large cathode to small anode area must be avoided to enhance the service life of joints.

Noble	
↑	Platinum
	Gold
	Graphite
	Titanium
	Silver
	Hastelloy C
	18-8 Mo stainless steel (passive)
	18-8 stainless steel (passive)
	Inconel (passive)
	Nickel (passive)
	Silver solder
	Bronzes
	Copper
	Brasses
	Hastelloy B
	Inconel (active)
	Nickel (active)
	Tin
	Lead
	Lead-tin solders
	18-8 Mo stainless steel (active)
	18-8 stainless steel (active)
	Cast iron
	Steel or iron
	2024 aluminum
	Commercially pure aluminum
	Zinc
	Magnesium and its alloys
↓	
Anodic	

Table-1: Galvanic series of some alloys

Crevice corrosion

It generally occurs in shielded or occluded geometries such as crevices, joints, bolted, and threaded parts and under the deposits including corrosion product. The surface between metal and non-metal such as under the gasket or spacers also forms crevice as shown in the Fig 1. Creviced area acts as anode while the remaining surface in the bulk solution (relatively larger area) acts as a cathode; this accelerates the corrosion reaction under the crevice. Electrochemical reactions produce extremely acidic condition ($\text{pH} \sim 2-3$) with chloride concentration as high as 3-10 times the concentration in bulk solution within the crevice as shown in Fig. 2. Such solution chemistry is very corrosive and degrades the material within the crevice at accelerated rate. Filiform corrosion is a type of crevice corrosion that occurs under the protective film e.g. enameled and lacquered surfaces.

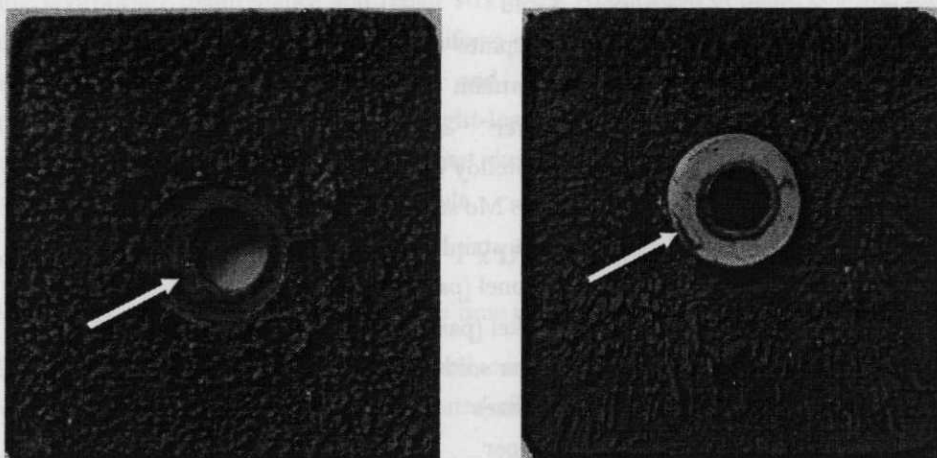


Figure 1: Crevice corrosion in mild steel coupons below Teflon spacer

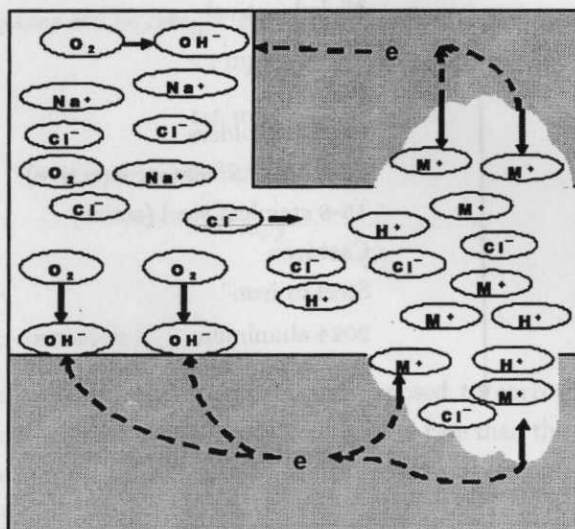


Figure 2: Mechanism of crevice corrosion

Crevice corrosion can be prevented by careful design and by avoiding sharp corners. Butt weld instead of riveted or bolted joints may be useful. Frequent cleaning of deposits and non-stagnant solution condition shall also be helpful to minimize crevice corrosion.

Pitting corrosion

It is extremely localized and commonly evident in the form of small pin holes as shown in Fig. 3. Severe perforation of the components leading to leakage is often found due to pitting corrosion. In general, the material-environment combination that forms a protective passive film on the specimens suffers from pitting corrosion. Presence of halide anions particularly chlorides and thiosulfate ions enters the defective areas and damage the passive layer; this results in the pin hole corrosion. The solution chemistry of pit is such that it becomes extremely acidic having high concentration of chloride as compared to the bulk solution. The mechanism of pitting corrosion is similar to as for crevice. By selecting the pitting resistant alloys, one can minimize the failure and increase the useful service life of component. Pitting resistance equivalent (PRE) index ($= 1 \times \%Cr + 3.3 \times \%Mo + 16 \times \%N$) can be used to compare various alloys while selecting material for pitting corrosion service. For instance PRE of AISI 316 stainless steel is ~ 25.6 shows higher pitting resistance than that of AISI 304 with lower PRE ~ 18 . The pitting resistance of a few commonly used engineering alloys is found in the decreasing order as Ti > Hastelloy C or Chlorimet > Hastelloy F, Durimet 20 > Type 316 stainless steel > Type 304 stainless steel.



Figure 3: Pitting on stainless steel surface exposed to chemical industry

Intergranular corrosion (IGC)

Intergranular or intercrystalline corrosion is preferential attack on alloys exposed to certain environment from along the grain boundaries. This is mainly caused by microsegregation of impurities and alloying elements in the grain boundaries. The driving force for intergranular corrosion is the potential difference between grain boundary and the grain matrix, which forms a galvanic cell in presence of an electrolyte. Dissolution of anodic grain boundaries starts from the surface and advances towards the thickness direction along the grain interfaces as shown in Fig. 4. The process results in deterioration of the bonding between the grains and metal thus disintegrates losing the strength.

Austenitic stainless steels, nickel and aluminum alloys frequently suffer from intergranular corrosion. Heat treatment of austenitic stainless steels performed at temperature ranging from 482-

760°C forms chromium carbides Cr_{23}C_6 along grain boundaries. This causes depletion of chromium from the near grain boundary regions that results in decrease of corrosion resistance. This phenomenon is known as sensitization; it may occur during stress relieving and solution annealing processes and welding operations. IGC is often called weld decay as sensitization occurs in heat affected zones (HAZ) produced in the weld joints. IGC of stainless steels can be prevented by suitable solution annealing heat treatment, by adding strong carbide formers (stainless steel 321, 347) and reducing the carbon content in stainless steel to $<0.03\%$ (e.g. 304L/ 316L)

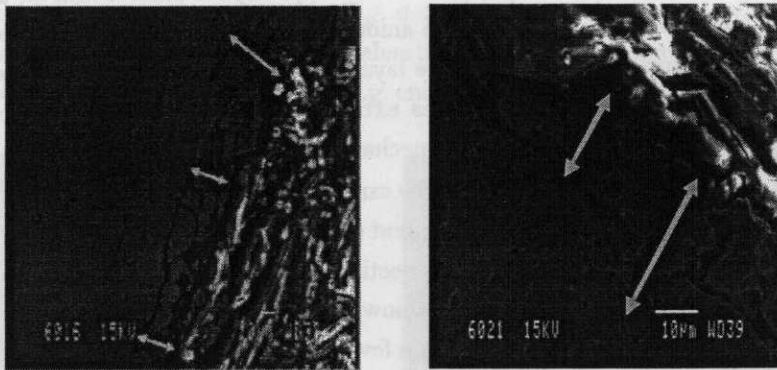


Figure 4: Intergranular corrosion of stainless steel 304LN

STRESS CORROSION CRACKING (SCC)

SCC is brittle cracking of alloys caused by the simultaneous presence of tensile stresses and specific environment, following three factors needed to initiate SCC:

Tensile stress: this can be either operational or residual stresses in the materials occurring as a result of the metal forming, fabrication and welding processes.

Susceptible materials: Not all materials are susceptible to stress corrosion cracking. Pure metal are resistant to SCC. Austenitic stainless steels are resistant SCC in amoniacal environment whereas brass are susceptible to SCC in such environment.

Susceptible environment: It needs specific environment to cause SCC. For example stainless steels are cracking prone in chloride containing environment but not in sulfuric acid, nitric acid, acetic acid or pure water.

Crack may propagate along preferential path such as along grain boundary, known as intergranular stress corrosion cracking (IGSCC) or across the grain boundary, transgranular stress corrosion cracking (TGSCC). A typical IGSCC failure may be seen in an austenitic stainless steel shown in Fig. 5. Several mechanisms have been postulated for SCC failures, these are grouped into anodic and cathodic. The most common anodic mechanisms are (i) active path dissolution and (ii) film induced cleavage; hydrogen embrittlement is caused by cathodic mechanism. Active path dissolution is accelerated through a specific path of high corrosion susceptibility such as grain boundary or specific crystal planes leaving the bulk material unaffected. Grain boundaries are most common active path

due to segregation of impurity elements or due to chromium depletion as a result of sensitization. The small crack initiates in the brittle passive film or coating that propagate into ductile material for small distance before being arrested by the ductile blunting (film induced cleavage). This cycle of crack propagation and blunting repeat itself to cause crack advancement. In contrast to anodic dissolution mechanism, hydrogen assisted cracking (hydrogen embrittlement/ hydrogen induced cracking) is enhanced by cathodic reaction: $H^+ + e = H$ occurring on the crack tip surface. The atomic hydrogen dissolves in the metal where it interacts with the dislocations of the crystal lattice causing decrease of the metal ductility (hydrogen embrittlement). High strength steels are well known for their susceptibility to hydrogen induced corrosion.

The SCC can be prevented by selection of suitable material e.g. replacement of austenitic stainless steels by austenitic-ferritic (duplex) stainless steels, which possess low susceptibility to stress corrosion cracking. Applying compressive stresses and coating would also help to reduce SCC failures. Stress relief heat treatment after cold work or welding operations are useful measures to minimize SCC.

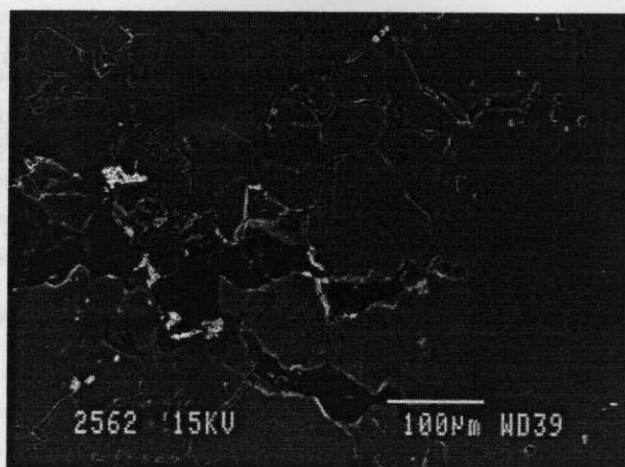


Figure 5: Intergranular stress corrosion cracking of stainless steel 304LN

CORROSION FATIGUE

Corrosion fatigue (CF) is tendency of engineering alloys to fracture due to synergistic effects of cyclic loading and corrosive environment. Failure occurs at stress levels far below the design or endurance limit of the alloys. It is an important failure mechanism responsible for damage of nuclear power systems, steam and gas turbines, aircraft, marine structures, pipelines, and bridges. CF damage accumulates with increasing load cycle count (N) in four stages: (i) cyclic plastic deformation, (ii) microcrack initiation, (iii) small crack growth to linkup and coalescence, and (iv) macrocrack propagation. Similar to SCC, the mechanism for CF may involve hydrogen embrittlement, film rupture, dissolution and repassivation, enhanced localized plasticity, interactions of dislocations with surface dissolution, films or adsorbed atoms, and complex combinations of these processes. The corrosion fatigue is strongly influenced by environmental composition, load frequency, stress intensity range, stress ratio, and electrode potential. Corrosion fatigue is generally

transgranular and does not show branching which is characteristics of stress corrosion cracking. This can be minimized by reducing the stress on the components; it may be accomplished by altering the design, stress relieving heat treatment.

Erosion corrosion

Erosion-corrosion is a general term that refers to a corrosion process enhanced by the relative motion of the flowing fluids and materials surface. The more usual effect of erosion-corrosion is localized attack, which appears as grooves, gullies, waves, rounded holes, etc., and usually exhibits a directional pattern that correlates well with the fluid flow. The erosion corrosion process is also manifested as pure cavitation, combined effect of solid particles and cavitation, impingement corrosion etc. Steam turbine blades, impellers, pump, underwater components, bends, tees, inlet pipes in tanks, and cyclones are a few examples of erosion corrosion. The metal destruction is accelerated as flowing fluid removes protective corrosion products from the surface; this exposes the fresh metal surface which corrodes at accelerated rate. The suspended corrosion products in the fluid cause abrasive action on the metal surface causing corrosion rate to increase.

Cavitation, a form of erosion corrosion, is caused by the formation and sudden collapse of vapor bubbles in a liquid and resulting impact on the metal surface. The impact due to bubble collapse may be as high $>1500\text{MPa}$ which is sufficient to cause microstructural changes in the underlying surface. By continuous cavity implosions, passive film formation is difficult and hence metal dissolution increases. In industrial situations, process fluid contains hard solid particles which assist and accelerate corrosion process by their abrasive action. Fig. 6 shows a turbine blade which is severely corroded by the combination of solid particle and cavitation erosion and shows cavitation marks. Application of coatings and careful design of components are useful methods to prevent erosion and cavitation corrosion.



Figure 6: Cavitation erosion of turbine blade

Selective leaching

Selective leaching is corrosion of one constituent of an alloy in presence of electrolyte as a result of electrochemical reactions. It occurs due to the large difference in electrode potentials of components of alloy such as between Cu and Zn in brass alloy; and between iron and graphite in grey cast iron. The element with lower electrode potential corrodes preferentially and dissolves in the electrolyte

while the one which has higher electrode potential remains protected cathodically. Common alloys prone to selective corrosion are brasses (dezincification), Silicon bronze (desiliconification), Aluminum bronze (dealuminification), Tin bronze (destannification), Copper-nickels (denickelification), Grey cast irons (graphitic corrosion).

Dezincification occurs in brasses containing more than 15% of zinc. Zinc is chemically active element having very low standard electrode potential (-0.763) while electrode potential of copper is much higher $\sim +0.337$. The difference between the two potentials is the driving force for dezincification of brasses. Corrosion process starts with dissolution of zinc to zinc ion ($Zn = Zn^{2+} + 2e^-$) leaving behind the network of copper. Some researchers opined that the dissolution of both zinc and copper occurs followed by redeposition of copper by cathodic reaction while zinc remains in the solution.

Fretting corrosion

Fretting corrosion is an attack which is accelerated by the relative motion of contacting surfaces in corrosive medium. It is usually a combination of corrosion and abrasive wear. The relative motion between the surfaces removes protective films and results in accelerated corrosion. Also, most corrosion products are abrasive and their presence in the corrosive fluid increases the removal of protective films. Fretting is common in riveted joints in ships, aeroplane, and automobile assemblies where cyclic loading is experienced. Thermal expansion with frequent cycling can also result in fretting corrosion. Vibration in blade system can cause fretting in the blade roots and loosening. Bolted tie plates of rail roads rail also subjected to frequent fretting; the tightening of these plates must be done to avoid vibrations and fretting corrosion. Fretting also causes fatigue cracks formation in the components.

Microbiologically influenced corrosion (MIC)

Corrosion conditions are often aggravated by the microorganisms and thus indirectly influence the corrosion reaction. Process and sewage pipelines, buried structure, bridges, and seawater equipment are influenced by the MIC. Microorganisms are classified by their tendency to grow in oxygen containing or oxygen deficient environment and accordingly known as aerobic and anaerobic bacteria. Aerobic sulfur oxidizing bacteria such as thiobacillus thiooxidans oxidizes the elemental sulfur or sulfur bearing compound to sulfuric acid thus reduces the pH of the environment. Similarly Anaerobic or sulfate reducing bacteria such as Desulfuricans reduces sulfate to sulfide that influences the hydrogen evolution and accelerates metal oxidation (anodic reaction). MIC can be minimize by applying coating such as asphalt, enamel, and plastic tape on the structures prone to such corrosion. Corrosion inhibitors and germicides such as chlorine and chlorine containing compound may also be employed to the recirculating system to prevent microbiological corrosion.

Summary

Corrosion is an electrochemical reaction of metals/ alloys with environment in which they are exposed. Corrosion is classified into eight different forms according to their characteristics appearance produced by exposure to various environments. These are uniform/general, galvanic/ bimetallic, crevice/ underdeposit, pitting, intergranular, selective leaching/ dealloying, stress

corrosion cracking, and erosion corrosion. There are few more types such as corrosion fatigue, fretting, filiform and microbiologically induced corrosion which may be linked to the eight main forms with some peculiarities aroused from specific operational processes to which they belong. Various forms of corrosion need to be carefully inspected and categorized; accordingly appropriate preventive measures should be adopted. Appropriate materials selection and heat treatments, coatings, paints, inhibitors, suitable design, cathodic protection are the main preventive methodologies for corrosion protection.

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Wishing all success of the joint effort of HIT and IU for the 3-days workshop on "Industrial Corrosion and Protection in Coastal & Other Environments"



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