

Material Science

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Chapter 13. Corrosion and Degradation of Materials

All engineering materials are subjected to numerous external mechanical and environmental factors during their service. Those factors include temperature, chemical attack, mechanical vibration, applied mechanical loads, etc. Under the influence of these factors, engineering materials gets degraded i.e. they loss their potential to perform the task. The degradation is inevitable, and may lead to catastrophes! Hence, degradation of materials not only be monitored but also be factored into the design of different components by engineers.

Mechanism of degradation is different for each engineering material group. Material loss either by dissolution or by formation of nonmetallic scale/film occurs in metals, while ceramics are relatively resistant to degradation. However, ceramics also gets deteriorated at extreme temperatures. Polymers, on the other hand, may dissolve/distort in presence of a liquid solvent or even when exposed to electromagnetic radiation. Degradation due to chemical/electro-chemical factors is termed as corrosion, while oxidation refers to formation of nonmetallic scales in metals.

13.1 Corrosion of Metals

Corrosion can be defined as unintentional deterioration of materials due to electrochemical factors. It usually starts at the external material surface. The corrosion resistance of metals and alloys is a basic property related to the easiness with which these materials react with a given environment. Corrosion is a natural process that seeks to reduce the binding energy in metals, and is of electrochemical in nature. The end result of corrosion involves a metal atom being oxidized, whereby it loses one or more electrons and leaves the bulk metal. The process is called oxidation, some times also called anodic reaction. The lost electrons are conducted through the bulk metal to another site where they are reduced, the process called reduction. The site where metal atoms lose electrons is called the anode, and the site where electrons are transferred to the reducing species is called the cathode. As a consequence of these electrochemical reactions, metal ions either go into the corroding solution as ions, or they may form an insoluble compound with nonmetallic elements.

Corrosion tendencies for different metals are measured in terms of electromotive force (EMF). A series of metals are arranged according to their potential to get corroded with respect to hydrogen electrode. Table 13.1 presents EMF series, and those at top are noble, while those metals at bottom are more prone to corrosion than the metals above them in the series.

As corrosion is electrochemical in nature, temperature and concentration of chemical does have an important role to play. In general, with increase of either or both temperature and concentration, corrosion rate increases. The electrode potential depends on the concentration of the electrolyte. At 25°C, the following equation, known as Nernst equation, gives the electrode potential:

$$E = E_0 + \frac{0.0592}{n} \log(C_{ion})$$

where E is the electrode potential in a solution containing a concentration C_{ion} (in moles) of metals, n is the valence of the metallic ion, E_0 is the standard electrode potential in a 1-M solution.

Faraday's equation gives the amount (w , weight in gms.) of metal plated on the cathode, or removed from the metal by corrosion:

$$w = \frac{ItM}{nF}$$

where I is the current (A), M is the atomic mass of the metal, n is the valence of the metal ion, t is the time (secs), and F is the Faraday's constant (96,500 C).

Table 13.1: Standard EMF series of metals.

	Metal	Electrode potential, E_0 (V)
Increasingly inert ↑	$\text{Au} \rightarrow \text{Au}^{3+} + 3\text{e}^-$	+1.420
	$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$	+1.229
	$\text{Pt} \rightarrow \text{Pt}^{2+} + 2\text{e}^-$	+1.200
	$\text{Ag} \rightarrow \text{Ag}^+ + \text{e}^-$	+0.800
	$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$	+0.771
	$4(\text{OH})^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$	+0.401
	$\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$	+0.340
	$\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$	0.000
	$\text{Pb} \rightarrow \text{Pb}^{2+} + 2\text{e}^-$	-0.126
	$\text{Sn} \rightarrow \text{Sn}^{2+} + 2\text{e}^-$	-0.136
	$\text{Ni} \rightarrow \text{Ni}^{2+} + 2\text{e}^-$	-0.250
	$\text{Co} \rightarrow \text{Co}^{2+} + 2\text{e}^-$	-0.277
	$\text{Cd} \rightarrow \text{Cd}^{2+} + 2\text{e}^-$	-0.403
	$\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$	-0.440

Increasingly active ↓	$\text{Cr} \rightarrow \text{Cr}^{3+} + 3\text{e}^{-}$	-0.744
	$\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^{-}$	-0.763
	$\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^{-}$	-1.662
	$\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^{-}$	-2.363
	$\text{Na} \rightarrow \text{Na}^{+} + \text{e}^{-}$	-2.714
	$\text{K} \rightarrow \text{K}^{+} + \text{e}^{-}$	-2.924
	$\text{Li} \rightarrow \text{Li}^{+} + \text{e}^{-}$	-3.050

Galvanic Series
Anodic or Least Noble end
Magnesium Magnesium Alloys Zinc Aluminum 5052, 3004, 3003, 1100, 6053 Cadmium Aluminum 2117, 2017, 2024 Mild Steel (1018), Wrought Iron Cast Iron, Low Alloy High Strength Steel Chrome Iron (Active) Stainless Steel, 430 Series (Active) 302, 303, 321, 347, 410, 416, Stainless Steel (Active) Ni - Resist 316, 317, Stainless Steel (Active) Carpenter 20cb-3 Stainless (Active) Aluminum Bronze (Ca 687) Hastelloy C (Active) Inconel 625 (Active) Titanium (Active) Lead - Tin Solders Lead Tin Inconel 600 (Active) Nickel (Active) 60 Ni-15 Cr (Active) 80 Ni-20 Cr (Active) Hastelloy B (Active) Brasses Copper (Ca102) Manganese Bronze (Ca 675), Tin Bronze (Ca903, 905) Silicone Bronze Nickel Silver Copper - Nickel Alloy 90-10 Copper - Nickel Alloy 80-20 430 Stainless Steel Nickel, Aluminum, Bronze (Ca 630, 632) Monel 400, K500

Silver Solder Nickel (Passive) 60 Ni- 15 Cr (Passive) Inconel 600 (Passive) 80 Ni- 20 Cr (Passive) Chrome Iron (Passive) 302, 303, 304, 321, 347, Stainless Steel (Passive) 316, 317, Stainless Steel (Passive) Carpenter 20 Cb-3 Stainless (Passive), Incoloy 825nickel - Molybdeum - Chromium - Iron Alloy (Passive) Silver Titanium (Pass.) Hastelloy C & C276 (Passive), Inconel 625(Pass.) Graphite Zirconium Gold Platinum Cathode Or Most Noble end
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Passivity: Under particular environments, some active metals and alloys may turn inert, known as passivity. It is usually observed in metals such as Cr, Fe, Ni, Ti and their alloys. Passivity is inherited as a result of formation of a thin and highly adherent oxide film on the metal surface. For example: stainless steels are highly resistant to corrosion in many environments, except in hard sea water. For steels, Cr forms a protective layer. Aluminium is also observed to passive in many environments. This is due to formation thin oxide layer.

Corrosion in metals is classified based on the manner in which it is manifest into eight forms, namely: uniform, galvanic, crevice, pitting, inter-granular, selective leaching, erosion-corrosion, and stress corrosion.

Uniform corrosion: As the name suggests, electrochemical corrosion occurs over entire exposed surface with equal intensity. It usually results in formation of a scale/film. This form of corrosion is most common, easy to monitor, and less damaging than the other forms. Painting the surface is best counter measure for it.

Galvanic corrosion: This occurs when two metals with different compositions i.e. EMF are electrically connected in presence of an electrolyte. Out-of-these two metals, less inert metal will corrode, while the other will be protected from the corrosion. Corrosion rate depends on the relative anode-to-cathode surface areas that are exposed to the electrolyte. the following measures are observed to reduce the damage due to this form of corrosion: when coupling of two different metals is unavoidable, choose that are close together in EMF series; tailor the anode-to-cathode area ratio; metals may be electrically insulated form each other; or use a third metal to protect the both, known as cathodic protection.

Crevice corrosion: This occurs as a result of concentration difference between two regions of same metal component. Corrosion takes place in the locale that is of lower

concentration. Probable sites for this corrosion are: crevices and recesses, under scales of dirt/corrosion product. This form of corrosion may be avoided if enough care is taken to avoid concentration differences. E.g.: welding instead of riveting. Other measures include removing accumulated deposits; avoiding stagnant areas.

Pitting: It is another form of localized corrosion. As a consequence of this, small pits, and holes form, hence the name. This occurs in normal direction to the surface exposed, and so is difficult to monitor. Thus, it is extremely dangerous form of corrosion, as material loss is often undetectable till the component fails. Same measures as for crevice corrosion are part of care against this form of corrosion. In addition, polishing of surfaces could do good.



Uniform Corrosion



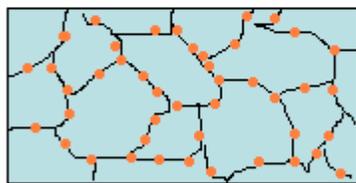
Galvanic corrosion



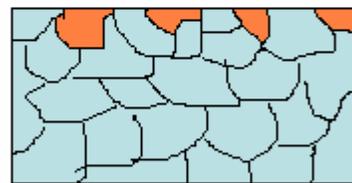
Crevice corrosion



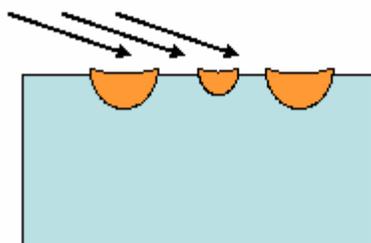
Pitting Corrosion



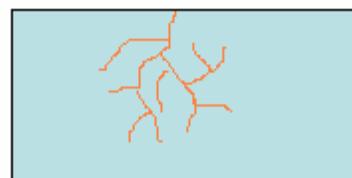
Inter-granular corrosion



Selective leaching



Erosion-corrosion



Stress corrosion

Inter-granular corrosion: This occurs again due to concentration difference, but now along grain boundaries, which are usually of different chemical composition compared with rest of the grains. Thus grain boundaries are highly susceptible to corrosion. This form of corrosion is very severe in stainless steels. These materials may be protected by suitable heat treatment; lowering carbon content; addition of alloying elements those readily forms of carbides.

Selective leaching: It is the preferential removal of a solid alloy by corrosion process. Best example can be dezincification of brass. It also occurs as the loss of Ni, Sn and Cr from Cu-alloys; Fe from cast iron; Ni from steel alloys, and Co from satellite. As a result of this corrosion, mechanical properties of the components are impaired as the component becomes porous. Measures of protection include change if composition; change of environment; use of cathodic protection.

Erosion-corrosion: It is defined as acceleration of corrosion attack in a metal due to relative motion of a corrosive fluid and a metal surface i.e. is result of combined action of chemical attack and mechanical abrasion/wear. Practically, all metals and alloys are prone to this corrosion form. It has more damaging influence on metals which passivate by forming a protective film and also on soft metals like Cu and Pb. Counter measures include: change of design; choosing different metal for the component; removal of particulates and bubbles form the fluid to lessen the erosive effects.

Stress corrosion: This form of corrosion, also known as stress corrosion cracking (SCC), occurs as a result of combined action of applied tensile stresses and corrosive environment. During SCC, the metal's surface is usually attacked very little while highly localized cracks propagate through the metal section. The stresses which cause SCC can be residual or applied. Only certain combinations of alloys and environments cause SCC. E.g.: Stainless steels crack in chloride environments but not in ammonia-containing ones. Best counter measure is elimination of external stress. Other measures are: to eliminate detrimental environment; change of the alloy if neither environment nor stress level can be changed; cathodic protection: addition of inhibitors.

Hydrogen embrittlement is more failure than a form of corrosion, but it is often results from the hydrogen, produced from corrosion. Atomic hydrogen produced during corrosion diffuses interstitially through crystal lattice, and interferes with dislocation motion, leading to failure. It is similar to stress corrosion in the sense that ductile materials experience brittle failures as a result. Counter measures to hydrogen embrittlement include: heat treatment to reduce strength of the alloy; removal of source of hydrogen; baking the component to drive out any dissolved hydrogen.

13.2 Corrosion of Ceramics

Ceramics, being compounds between metallic and nonmetallic elements, may be thought of as having already been corroded. It is often said that one of the biggest advantages which ceramics have over other engineering materials is their corrosion resistance, that is, their chemical inertness in corrosive environments.

Corrosion is generally understood as property degradation due to environmental attack. Ceramics corrode by simple chemical dissolution, in contrast to the electrochemical processes involved with corrosion of metals. There are a number of environments in which ceramics can degrade at a rapid rate. There exists a tremendous need for reliable and corrosion resistant structural ceramic or partly ceramic materials which can be used in aggressive environments such as:

- high energy battery systems (such as sodium-sulphur): beta-alumina is being investigated
- gas turbines: silicon nitride and/or carbide are being investigated
- heat exchangers: SiC, composites are being investigated

Ceramics are indeed much more environmentally stable, as compared to any other group of engineering materials, e.g. metals or plastics. Still, the potential for ceramics as corrosion resistant engineering structural materials are far from being fully realized, because of:

- mechanical non-reliability of structural ceramic components
- difficult design with brittle materials
- a shortage of information and standardization of ceramics
- human reluctance to use non-ductile materials

13.3 Degradation of polymers

While the plastics industry searches for solutions to the problem of plastics waste, there is, surprisingly, a growing band of people trying to save plastics. The crucial fact is that plastics are organic and can be prone to physiochemical attacks. Polymeric materials degrade by non-corrosive processes.

As all other engineering materials, plastics do indeed degrade during their service. However, degradation of plastics is not termed as corrosion, as it is of physiochemical in nature in contrast to electrochemical corrosion of metals. Degradation of polymers, thus, involves a wide variety of reactions and results like absorption and swelling, dissolution, bond rupture due to heat, chemical effects, or radiation; weathering, etc. Degradation of polymers might be due to exposure to light (especially UV), humidity, oxygen, heat, bacteria or external loads/stress. However, due to complex nature of chemical bonds in polymers, their degradation mechanisms are not well understood.

Swelling and dissolution: Polymers, when exposed to liquids, they get swelling as a result of solute diffusion and absorption of solute. Because of swelling i.e. separation of chains, secondary bonds become weaker. As a consequence, the material becomes softer and

more ductile. Swelling is considered as partial dissolution, while the dissolution or complete solubility is worse than the swelling. Swelling and dissolution effects are influenced by temperature because of their physiochemical nature.

Bond rupture: Bond rupture in polymers due to degradation is known as scission. Polymers bonds may get rupture due to many effects like radiation, heat energy, or chemical reactions. When polymers are exposed to certain types of radiation, which may result in broken bonds and rearrangement of atoms leads to degradation of polymers. At elevated temperatures, bonds in polymers may get weakened, leading to deterioration of polymers. Some chemical elements like oxygen, ozone can alter the chain scission rate as a result of chemical reactions. This is especially pronounced in vulcanized rubbers.

Weathering: Polymers are exposed to outdoor conditions in many instants of their service. Any degradation of polymer under these circumstances is termed as weathering, which in fact is a combination of several different processes. It primarily involves oxidation, which may be initiated by ultraviolet radiation from the Sun. polymer's resistance to weathering to very difficult to quantify and is very diverse.

Some examples of polymer degradation include:

- deterioration of acrylic paintings and pieces of art
- decomposition of photographic films
- decolorization of plastics pieces preserved in museums

Solutions to polymer degradation: As the recognition of polymer degradation improves, conservation guidelines are beginning to emerge. High-tech solutions which could help in theory are prohibitively expensive, but tailor made scavengers such as activated charcoal or Ageless help to create a low oxygen environment. Ageless is a reactive powdered iron and is normally used to prolong the shelf-life of dry foods by absorbing oxygen. Epoxidised soya bean oil (ESBO), has also been tested with encouraging results as an acid absorbing coating on degrading cellulose nitrate.

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