

Module-13

Corrosion and Degradation of materials

Contents

- 1) Corrosion of metals
- 2) Corrosion of ceramics
- 3) Degradation of polymers

Deterioration of materials

- Conventional engineering materials are not able to serve at their full potential for long periods of time i.e. they get deteriorated during the service.
- There are many reasons for deterioration of engineering materials, like physical, chemical, mechanical, weather, etc.
- Chemical deterioration is most common in metals, and also observed to some extent in ceramics. It is known as corrosion.
- Physiochemical deterioration of polymers is known as degradation of polymers.

Corrosion of metals

- Corrosion of metals is mainly due to electrochemical reactions.
- It is also most influenced by temperature and concentration gradients.
- Relative tendency of a metal to get corroded is presented in terms of its electro-motive force (EMF).
- Standard EMF series is suitable for easy recognition of basic elements for their relative tendency towards corrosion.
- Another usefulness of the series is to pick material for cathodic protection.

Corrosion of metals (contd...)

- Effect of concentration on EMF is given by Nernst equation:

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

where E_0 – standard potential at 1M, n – valence, C_{ion} – concentration.

- Corrosion rate is presented in form of Faraday's equation:

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

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

Standard EMF series w.r.t Hydrogen

	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
Increasingly active ↓	$\text{Ni} \rightarrow \text{Ni}^{2+} + 2\text{e}^-$	-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
	$\text{Cr} \rightarrow \text{Cr}^{3+} + 3\text{e}^-$	-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

Forms of metal corrosion

- Corrosion of metals is classified based on the manner in which it is manifest into eight forms.
- Uniform corrosion: As name suggests, corrosion occurs over entire exposed surface. Less of detrimental. Easy to monitor and control. Is it also most common form. Painting is best counter measure for it.
- Galvanic corrosion: Occurs when two metal with different EMF are electrically connected, of which one gets corroded. Counter measures include: insulation; pairing metals with less difference between their EMF; altering the corrosive environment; tailoring the design of components *w.r.t.* their EMF.

Forms of metal corrosion (contd...)

- Crevice corrosion: This occurs as a result of concentration gradient within a component. Corrosion occurs at the site of lower concentration. Counter measures include: welding instead of riveting; removing scales, etc.
- Pitting: Other localized corrosion. Difficult monitor and very dangerous. Material removal is minimal, but occurs in normal to surfaces. Counter measures: polishing of surface, and other common methods.
- Inter-granular corrosion: This is due to concentration difference at micro-level. Grain boundaries are inferior to grains, and more prone to corrosion. Counter measures: suitable heat treatment; addition of alloying elements; low %C in steels.

Forms of metal corrosion (contd...)

- Selective leaching: Occurs in selective metals. It is selective removal of a particular metal from the component. Example – dezincification of brass. Counter measures: change of material; cathodic protection.
- Erosion-Corrosion: It is acceleration of corrosion due to mechanical actions. All metals and alloys are prone to this form of corrosion. More damaging in case of metals with passive scales. Counter measures: change of component design; clearing the fluids for particulates.
- Stress concentration: Also known as stress corrosion cracking (SCC). Result of combined action of tensile stresses and corrosive environment. Counter measures: change of environment; cathodic protection; addition of inhibitors.

H-embrittlement and Passivity

- Hydrogen embrittlement is a form of failure other than corrosion, but occurs as a result of hydrogen produced during corrosion. Atomic hydrogen diffuses into crystals and inhibits dislocation motion, causing failure. Counter measures: heat treatment; removal of hydrogen source.
- Passivity: It is a form of protection against corrosion. It results from a thin, strong adherent oxide layer formed over the surface. Usually observed in Al, Cr, Fe, Ni, Ti and their alloys. Passive layers may get damaged during mechanical vibrations, and so these metals are prone to erosion-corrosion.

Corrosion of ceramics

- As ceramics are made of metals and non-metals, they can be considered as already corroded!
- Ceramics do get deteriorated during their service under extreme temperatures and external loads.
- Factors effecting life of ceramic components include: temperature, external loads, vibrations, environment, etc.
- Life span of ceramics can be increased by controlling the environment they are exposed to; operational loads and temperatures; altering the component design.

Degradation of polymers

- As other engineering materials, polymers also deteriorated during their service. However, in contrast to electrochemical nature of metal corrosion, polymer degradation is of physiochemical in nature.
- As polymer structures are complex, so are the mechanisms involved in their deterioration.
- Many factors involved in degradation of polymers, like – temperature, radiation, environment, moisture, bacteria or external loads/stress.
- Polymers degrade mainly in three forms – swelling and dissolution, bond rupture, and weathering.

Forms of polymer degradation

- Swelling and Dissolution: When exposed to humid environment, polymers get swelling due to diffused and absorbed moisture. It may also involve dissolution of polymers, hence swelling is considered as partial dissolution. Dissolution involves complete solution of polymer in solvent.
- Weathering: When exposed to outdoor weather for long periods of time, polymer may get decolorized, distort from their original shape. This may be due to many actions including radiation of the sun, oxidation, etc.

Forms of polymer degradation (contd...)

- Bond rupture: This is main form of polymer failure. Bond rupture, also known as scission, may occur due to 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.