Degradation

Introduction

Ceramics are resistive to degradation. That’s why glass is often used to contain liquids.

Degradation of metals and polymers are discussed in this section.

Degradation of Metals

Corrosion

Deterioration of metals due to the reaction with the environment.

All corrosion reactions are electrochemical in nature.

> ⓘ **Note**
>
> If the water contained salt(s), metal chloride(s) will be formed. All metal chlorides other than $\mathrm{NaCl}, \mathrm{KCl}$ hydrolize in water, and produces acid. Acids increase the rate of corrosion.

Electrochemical reactions

Pair of reactions in which electron transfer occurs from one reaction to another.

Oxidation

The reaction where an electron is released. Aka. anodic reaction.

Reduction

The reaction where an electron is consumed. Aka. cathodic reaction.

Electrodes

Anode

The site at which oxidation takes place.

Cathode

The site at which reduction takes place.

Standard Electrode Potential

Measure of a metal’s ability to work as a anode or cathode. Measured in reference to hydrogen. Denoted by E^θ.

Electrochemical series

A series of pure metals in the order of their standard electrode potential. Alloys and other materials are not listed.

Cell

When 2 electrodes are electrically connected. The metal with the least E^0 becomes the anode.

Cell potential

Absolute difference between the 2 electrode’s standard electrode potentials. Denoted by ΔE^0.

For a corrosion reaction to occur spontaneously, $\Delta E^0 > 0$. Cell potential is an approximate indication of the rate of corrosion.

Common reactions

Hydrogen evolution reaction (HER)

$$2\,\mathrm{H}^+ + 2\,\mathrm{e}^- \longrightarrow \mathrm{H}_2$$

Oxygen reduction reaction (ORR)

$$\mathrm{O}_2 + \mathrm{H}_2\mathrm{O} + 4\,\mathrm{e}^- \longrightarrow 4\,\mathrm{OH}^-$$

Examples

Zn in acid

$$\mathrm{Anodic:Zn} \longrightarrow \mathrm{Zn}^{2+} + 2\,\mathrm{e}$$

$$\text{Cathodic} : 2\,\mathrm{H}^+ + 2\,\mathrm{e} \longrightarrow \mathrm{H}_2$$

Fe rusting in atmosphere

$$\text{Anodic} : \mathrm{Fe} \longrightarrow \mathrm{Fe}^{2+} + 2\,\mathrm{e}$$

$$\text{Cathodic} : \tfrac{1}{2}\,\mathrm{O}_2 + \mathrm{H}_2\mathrm{O} + 2\,\mathrm{e} \longrightarrow 2\,\mathrm{OH}^-$$

Note

Al doesn't corrode in atmosphere because Al_2O_3 is stable and works as a barrier between the metal and the atmosphere.

Steel corrodes but stainless steel doesn't. The reason is: stainless steel contains Cr and Cr_2O_3 is stable and it acts as a barrier.

Forms of Corrosion

8 main forms:

1. Uniform / General corrosion
2. Galvanic corrosion
3. Crevice corrosion
4. Pitting corrosion
5. Inter-granular corrosion
6. Erosion corrosion
7. Stress corrosion
8. Selective leaching

Only the first 3 forms are discussed in s1.

Uniform corrosion

Occurs uniformly over the entire exposed area of the metal. Rust forms all over the surface. Leads to 30% of corrosion failures.

All other forms of corrosion happen on selected areas of a metal.

Galvanic corrosion

When 2 metals are in contact (electrically) and placed in a corrosive environment, only one metal — the element with most negative potential— corrodes. Aka. two metal corrosion. Corrosion happens in the anode near the junction.

Area effect

Smaller the anode, severe will be the corrosion. To reduce the corrosion when 2 metals are in contact, bigger anode is used to reduce the area effect.

Galvanic series

Designed to be an extension of electrochemical series that includes alloys and non-metals. Materials are ordered in ascending order of reactivity. Only a ranking order and not a measure. Materials in the lower position becomes the anode. Specific for a particular environment.

In a single metal

Galvanic corrosion can happen in a single metal. One part of the metal becomes anodic to the rest.

For example, a piece of iron immersed in water. Initially iron goes under uniform corrosion. Once the oxygen in the water is depleted, the iron inside the water will become the anode. Iron just above the water surface becomes the cathode. Severe corrosion occurs just below the water level.

Crevice corrosion

When a crevice is in contact with a liquid, the crevice undergoes corrosion. Corrosion is limited to the crevice.

> **Note**
>
> A crevice is a crack forming a narrow opening.

Crevice becomes anodic becuase of low oxygen supply. Exposed area has high oxygen supply and works as a cathode.

Mechanism of CC

Consider a riveted metal-plate section in contact with domestic water.

Initially it will corrode uniformly. After some time, crevice becomes depleted with oxygen due to restricted convection. Now the crevice becomes the anode. Becasue of area effect, corrosion will be severe.

Prevention of Corrosion

Corrosion results in loss of materials and money. It must be minimized or controlled.

To avoid corrosion

- Use noble metals $(\mathrm{Au}, \mathrm{Pt})$
- Use purest possible metal - not possible in real life
- Use corrosion resistant alloys
- Use non-metals (like polymers or ceramics)

Cathodic protection

Corrosion can be prevented by making the metallic structure as cathode.

2 types of cathodic protection is available.

Galvanic protection

Metal to be protected is made cathode by connecting it to an anodic metal (which is called the sacrificial anode). Zn and Mg are commonly used as anodic metals. Aka. sacrificial anodic protection.

Uses

- Protection from soil corrosion of buried pipelines, underground cables
- Protection from marine corrosion of cables, ship hulls, piers
- Prevention of rust in water boilers by inserting Mg
- Minimizing engine corrosion using Ca

Impressed current cathodic protection

Suppressing corrosion by supplying external current (opposite to corrosion). The applied current converts corroding metal from anode to cathode.

Usually current is derived from DC sources with an inert anode.

Modifying the environment

Corrosion can be prevented by adding inhibitors to the environment.

Examples:

- Hydrogen evolution poisons - used when cathodic reactions are HER.
- Oxygen scavengers - eliminates oxygen from the corroding medium. used when cathodic reactions are ORR.

Protective coatings

Preventing corrosion by covering the surface by means of protective coatings.

The coating acts as a physical barrier between the coated metal surface and the environment.

2 types:

- Inorganic
  - Metallic
  - Non-metallic
- Organic
  - Paints

> **Note**
>
> Stainless steel is usually protected from corrosion by Cr_2O_3 layer.

Galvanizing

The process of coating steel sheets with a thin coat of Zn to prevent them from rusting.

The process steps are, Steel article is:

1. cleaned with diluted H_2SO_4
2. washed with distilled water
3. dried
4. dipped in a bath of molten Zn

And now the Zn coating will have been applied.

Paints

Paint is a viscous, opaque mechanical dispersion mixture of one or more pigments (dye) in a vehicle (drying oil).

Corrosion inhabitors are added to paints.

Note

Coating is enough to prevent corrosion. But in steel, Zn coating is preferred instead of Sb coating. The reason for this is, when Sb coating is used, when the coating is damaged (even a little), the corrosion of steel will not be prevented. When Zn is used, it will work as an anode and steel will be protected from corrosion.

Degradation of Polymers

Change in the chemical and/or physical structure of the polymer chain.

Degradation is undesirable during use but desirable after use (as in biodegradation).

Types of degradations

Type of degradation	Agent
Thermal degradation	Heat
Chemical degradation	Chemical
Photo-degradation	UV & other radiations
Mechanical degradation	Stress
Biodegradation	Bacteria and other organisms

Note

UV stablized - the polymer is protected from UV degradation.

Susceptibility to degradation

Depends on its structure and the type of degradation.

- Chains containing aromatic functionality are suspectible to ultraviolet degradation
- Hydrocarbon-based polymers are susceptible to thermal degradation

Bond rupture or scission

Breaking into smaller polymer chains. Molecular weight of the polymer decreases.

Swelling & dissolution

Main form of degradation when a polymer is exposed to liquids.

Swelling

The liquid or solute diffuses into the polymer. Polymer absorbs the liquid or solute. Chain separation increases. Secondary inter-molecular bonding forces decreases.

Dissolution

Extreme state of swelling. Occurs when the polymer is completely soluable.