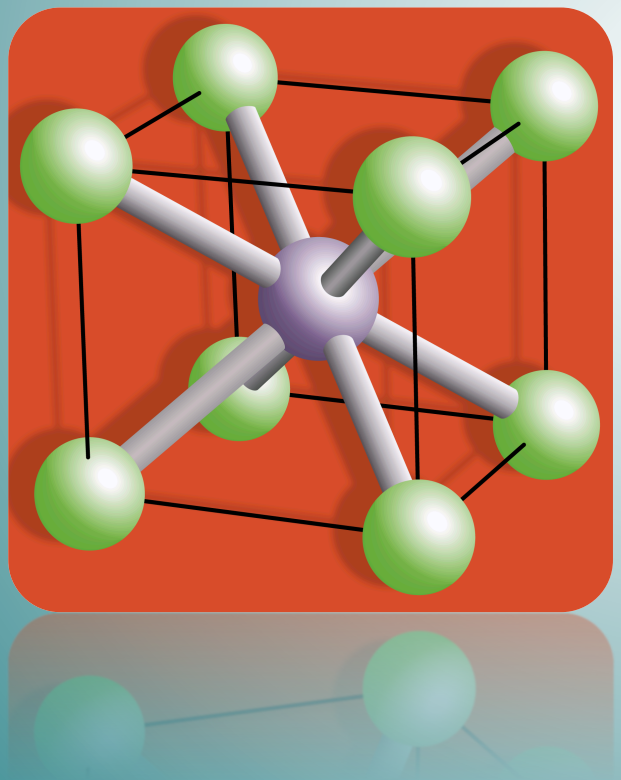
Materials

Topic 9. Oxidation and corrosion



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9.1. INTRODUCTION

- **Deterioration of a material by chemical interaction with its environment:**
  - **Oxidation: reaction of the material with atmospheric oxygen (dry corrosion).**
  - **Corrosion: electrochemical process that is verified in aqueous solutions.**

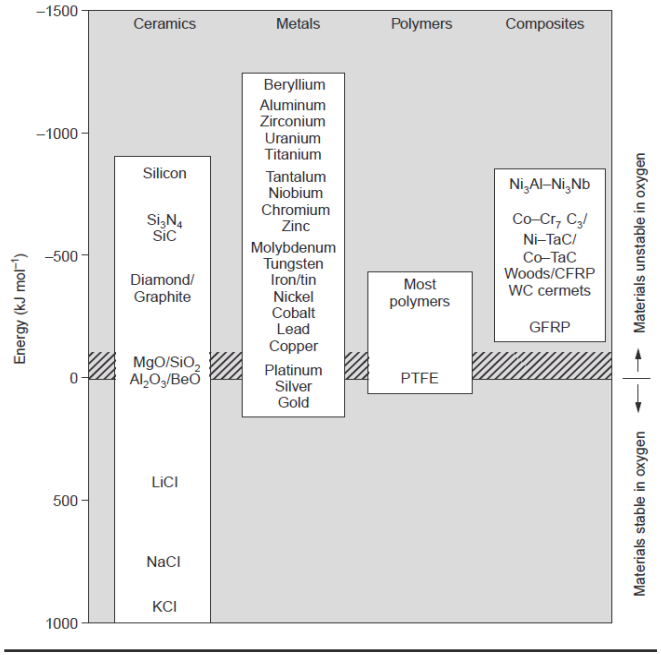
9.2. OXIDATION

- **The energy of oxidation:**

$$\text{Material (M)} + \text{Oxygen } (O_2) \underset{E>0}{\overset{E<0}{\rightleftharpoons}} \text{Oxide of material.}$$

Energy needed for the reaction

- **Positive (E > 0)** ➡ **Stable material.**
- **Negative (E < 0)** ➡ **Oxidizable material.**



Energies of formation of oxides at 273 K in kJ mol^{-1} of oxygen O_2.

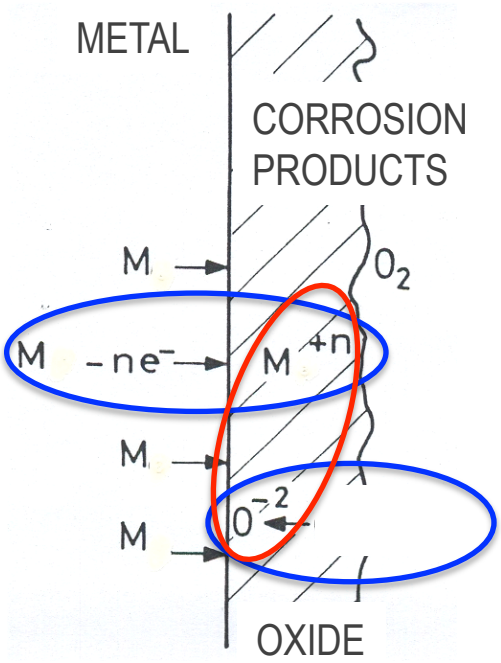
Energies of formation of oxides at 273 K

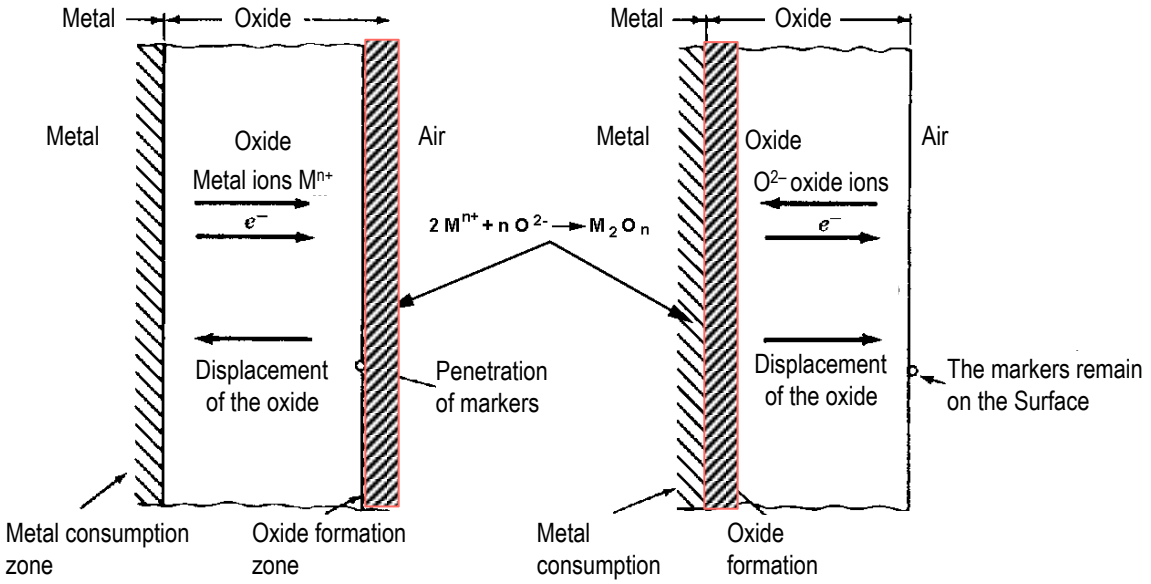
Material (oxide)		*Energy (kJ mol^{-1} of oxygen, O_2)*	*Material (oxide)*		*Energy (kJ mol^{-1} of oxygen, O_2)*
Beryllium	(BeO)	−1182	Woods, most polymers, CFRP		≈−400
Magnesium	(MgO)	−1162			
Aluminium	(Al_2O_3)	−1045	Diamond, graphite	(CO_2)	−389
Zirconium	(ZrO_2)	−1028	Tungsten carbide cermet (mainly WC)	(WO_3+ CO_2)	−349
Uranium	(U_3O_8)	≈−1000			
Titanium	(TiO)	−848	Lead	(Pb_3O_4)	−309
Silicon	(SiO_2)	−836	Copper	(CuO)	−254
Tantalum	(Ta_2O_5)	−764	GFRP		≈−200
Niobium	(Nb_2O_5	−757	Platinum	(PtO_2)	≈−160
Chromium	(Cr_2O_3)	−701	Silver	(Ag_2O)	−5
Zinc	(ZnO)	−636	PTFE		≈zero
Silicon nitride, Si_3N_4	($3SiO_2$+$2N_2$)	≈−629	Gold	(Au_2O_3)	+80
Silicon carbide, SiC	(SiO_2+CO_2)	≈−580	Alkali halides		≈+400 to ≈+1400
Molybdenum	(MoO_2)	−534			
Tungsten	(WO_3)	−510	Magnesia, MgO	Higher oxides	Large and positive
Iron	(Fe_3O_4)	−508	Silica, SiO_2		
Tin	(SnO)	−500	Alumina, Al_2O_3		
Nickel	(NiO)	−439	Beryllia, BeO		
Cobalt	(CoO)	−422			

9.3. OXIDATION MICROMECHANISMS

- The reaction M + O → MO really goes in two steps:
  1) First M forms an ion, releasing electrons, e: $M \rightarrow M^{n+} + ne^-$
  2) These electrons are then absorbed by oxygen to give an oxygen ion: $1/2O_2 + 2e^- \rightarrow O^{2-}$

$$2 \cdot M^{n+} + n \cdot O^{2-} \rightarrow M_2O_n$$





Oxidation forms an oxide layer that increases in thickness and covers the material.

9.4. TYPES OF OXIDE LAYERS

- **There are 3 behaviors depending on the relative volumes of oxide and metal.**

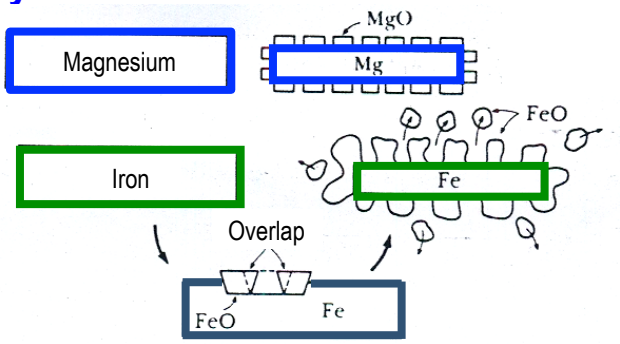
Pilling – Bedworth ratio (P – B)

$$P\text{-}B = \frac{volume\ of\ oxide\ produced}{volume\ of\ metal\ consumed}$$

$$P\text{-}B = \frac{M_{oxide} \cdot \rho_{metal}}{n \cdot M_{metal} \cdot \rho_{oxide}}$$

Metal and oxide	Oxide density (g/cm^3)	P – B ratio
Mg-MgO	3.6	0.8
Al-Al_2O_3	4.0	1.3
Ti-TiO_2	5.1	1.5
Zr-ZrO_2	5.6	1.5
Fe-Fe_2O_3	5.3	2.1
Cr-Cr_2O_3	5.1	2.1
Cu-Cu_2O	6.2	1.6
Ni-NiO	6.9	1.6
Si-SiO_2	2.7	1.9
U-UO_2	11.1	1.9
W-WO_3	7.3	3.3

P – B < 1 ➡ **Porous oxide and low protective capacity**



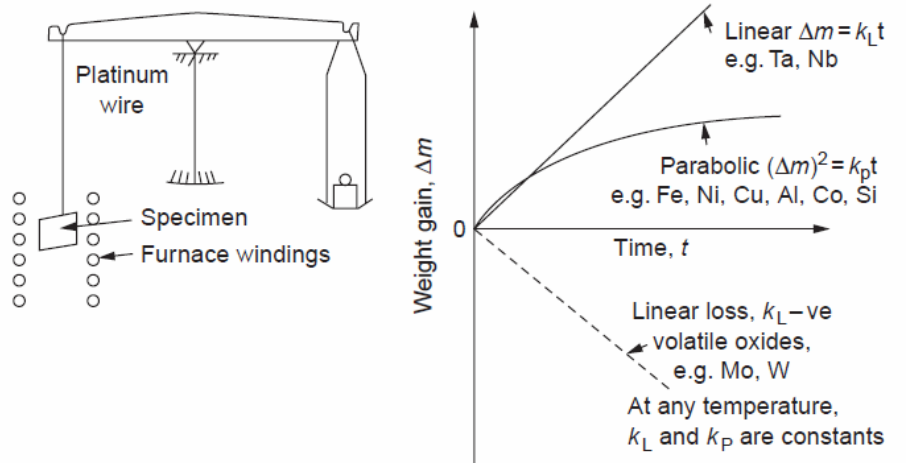
P – B > 2 ➡ **Excess oxide generates cracking**

1 < P – B < 2 ➡ **Protective oxide**

9.5. KINETICS OF OXIDATION

- **The oxidation rate in metals is expressed as the weight increase per unit area.**

Measurement of oxidation rates



- **If the oxide is porous:**
  Linear oxidation: $\Delta m = K_L \cdot t$
  O_2 has continuous access to metal.

- **If the layer is not porous and there is ion diffusion:**
  Parabolic oxidation: $(\Delta m)^2 = K_P \cdot t$

- **If the layer is not porous and there is no electronic diffusion:**
  Logarithmic oxidation: $\Delta m = K_e \cdot \ln(c \cdot t + a)$ (c, a = constants).

Oxidation is a thermally activated phenomenon

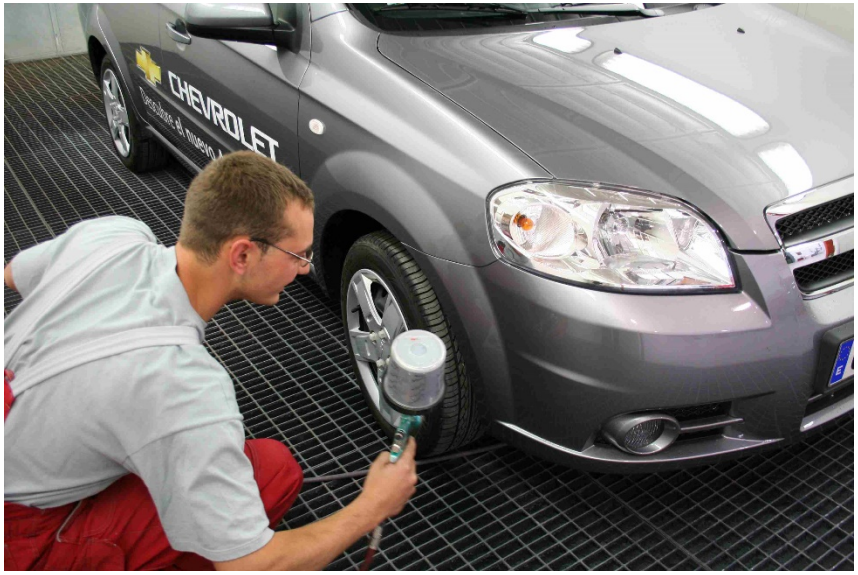
$$K_L = A_L e^{-Q_L/RT}$$

$$K_P = A_P e^{-Q_P/RT}$$

$$K_e = A_e e^{-Q_e/RT}$$

9.6. PROTECTION AGAINST OXIDATION

- Action of the **oxide itself** (except for non-protective or very brittle oxides).
- Addition of certain **alloying elements** (Ni, Cr and Co added to Fe).
- **Coatings** with protective layers (paints, plastics, ceramics...).
  - **Metal** coatings: galvanized steel, tin...
  - **Inorganic** coatings: glazed steel, blued steel...
  - **Organic** coatings: paints, primers, varnishes...



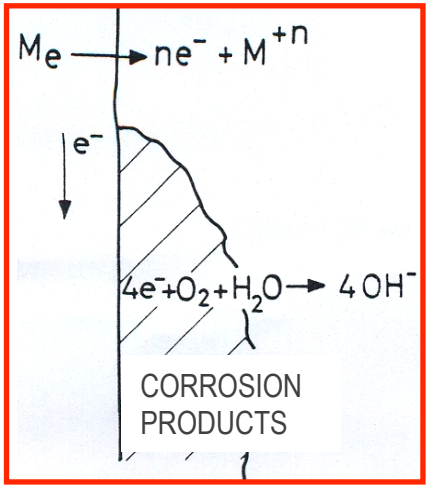
9.7. CORROSION

- Oxidation at room temperature in dry conditions is very light and increases rapidly with temperature
- In wet conditions, the situation changes and steel, for example, quickly corrodes at room temperature.

ELECTROCHEMICAL CORROSION

Material (M) + Oxigen (O_2) + water (H_2O) → Hydroxide $M(OH)_n$

- Great economic importance (3.5% Gross Domestic Product).



9.8. ELECTROCHEMICAL CONSIDERATIONS

- Corrosion is an electrochemical process ➔ There is electron transfer between species.

OXIDATION: $M \rightarrow M^{n+} + ne^-$

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

Anodic reaction (anode): production of electrons.

REDUCTION: (It depends on the environment)

- $2H^+ + 2e^- \rightarrow H_2\uparrow$ (acid solution)
- $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ (acid solution with O_2)
- $O_2 + 2H_2O + 4e^- \rightarrow 4(OH)^-$ (aqueous with air)
- $M^{n+} + ne^- \rightarrow M$ (in the presence of metal ions)

Cathodic reaction (cathode): consumption of electrons.

- The total electrochemical reactions are obtained by combining the oxidation and reduction half-reactions.

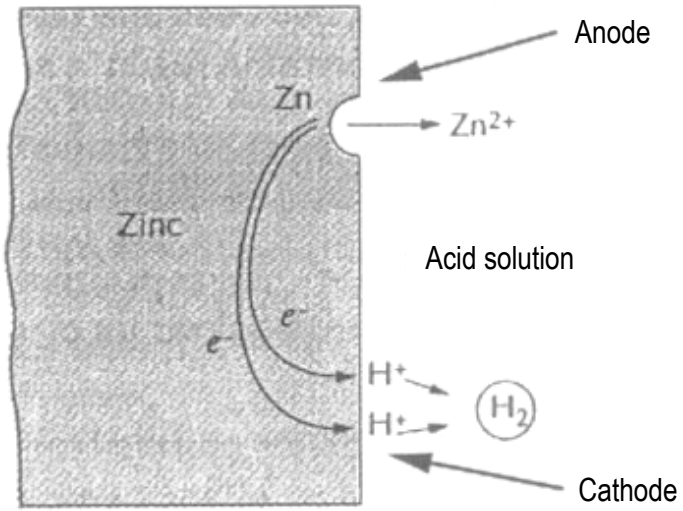
- **In aqueous media without air:**

$$M\,(s) + n\,H_2O\,(l) \longleftrightarrow M(OH)_n\,(s) + n/2\,H_2\,(g)$$

- **In aqueous media with air:**

$$M\,(s) + n/4\,O_2\,(g) + n/2\,H_2O\,(l) \longleftrightarrow M(OH)_n\,(s)$$

- **Example: Zn submerged in an acid solution.**



Anodic reaction: $Zn \longrightarrow Zn^{2+} + 2e^-$

Cathodic reaction: $2H^+ + 2e^- \longrightarrow H_2\,(g)\uparrow$

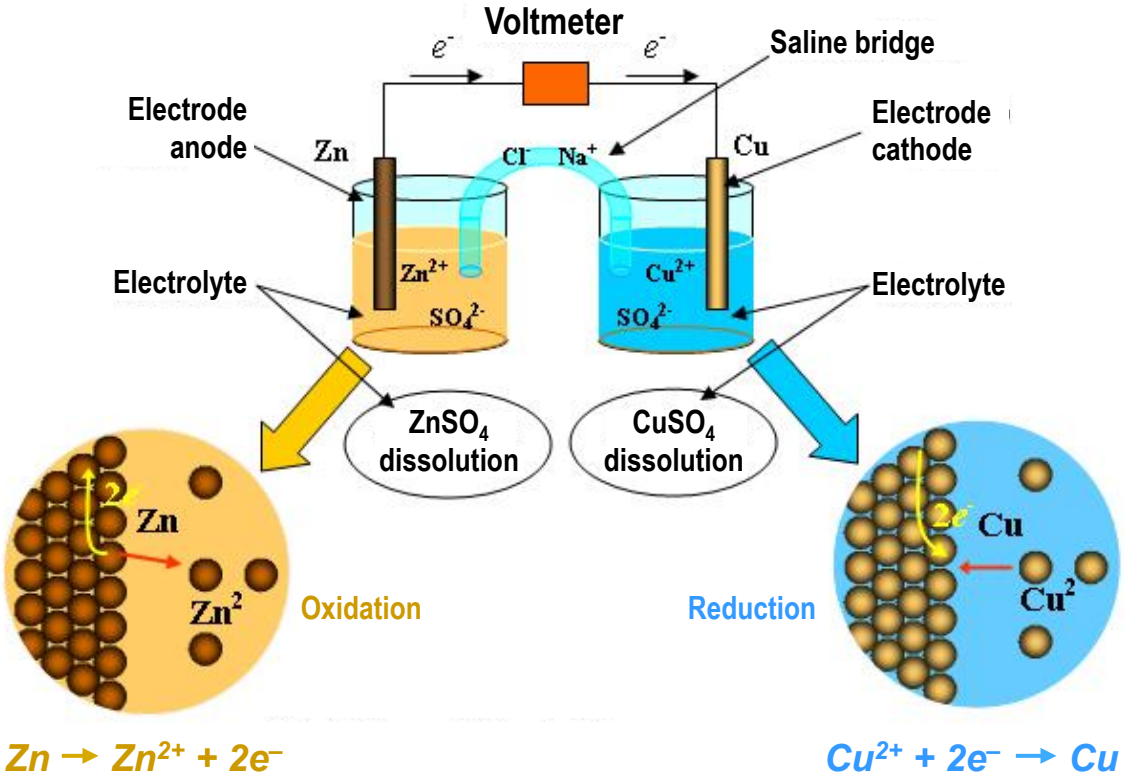
Global electrochemical reaction:

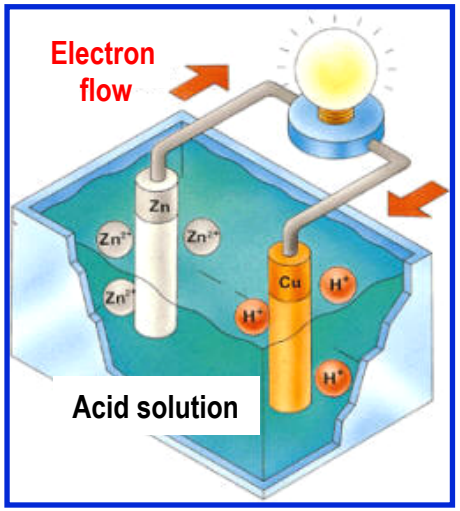
$$Zn \longrightarrow Zn^{2+} + 2e^-$$
$$2H^+ + 2e^- \longrightarrow H_2\,(g)$$

$$Zn + 2H^+ \longrightarrow Zn^{2+} + H_2\,(g)$$

9.9. ELECTROCHEMICAL SERIES

- In electrochemical corrosion there are electronic flows ➡ **Possibility of measuring voltages.**





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

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

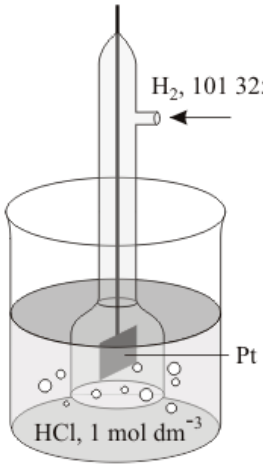
$$Zn + Cu^{2+} \longrightarrow Zn^{2+} Cu$$

$$\Delta G < 0$$

- **Standard half-cells** ⟹ **Electrode of a pure metal submerged in a 1 M solution of its own ions at 25°C and 1 atm.**

Standard Hydrogen Electrode (SHE): $H_2 \rightarrow 2H^+ + 2e^-$ $(E^0 = 0)$

ELECTROCHEMICAL SERIES



Cathodic
Ease of oxidation decreases

Anodic
Ease of oxidation increases

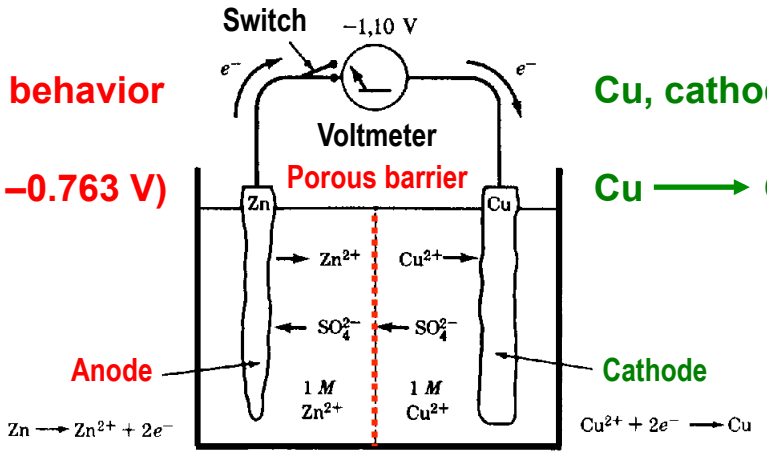
(Oxidation) Half-Reaction	Standard oxidation potentials at 25°C E^0 (volts)
$Au \rightarrow Au^{3+} + 3e^-$	+1,498
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	+1,229
$Pt \rightarrow Pt^{2+} + 2e^-$	+1,200
$Ag \rightarrow Ag^+ + e^-$	+0,799
$2Hg \rightarrow Hg_2^{2+} + 2e^-$	+0,788
$Fe^{2+} \rightarrow Fe^{3+} + e^-$	+0,771
$4(OH)^- \rightarrow O_2 + 2H_2O + 4e^-$	+0,401
$Cu \rightarrow Cu^{2+} + 2e^-$	+0,337
$Sn^{2+} \rightarrow Sn^{4+} + 2e^-$	+0,150
$H_2 \rightarrow 2H^+ + 2e^-$	0,000
$Pb \rightarrow Pb^{2+} + 2e^-$	−0,126
$Sn \rightarrow Sn^{2+} + 2e^-$	−0,136
$Ni \rightarrow Ni^{2+} + 2e^-$	−0,250
$Co \rightarrow Co^{2+} + 2e^-$	−0,277
$Cd \rightarrow Cd^{2+} + 2e^-$	−0,403
$Fe \rightarrow Fe^{2+} + 2e^-$	−0,440
$Cr \rightarrow Cr^{3+} 3e^-$	−0,744
$Zn \rightarrow Zn^{2+} + 2e^-$	−0,763
$Al \rightarrow Al^{3+} + 3e^-$	−1,662
$Mg \rightarrow Mg^{2+} + 2e^-$	−2,363
$Na \rightarrow Na^+ + e^-$	−2,714

- **The reactions are described as anodic half cells. The most negative half-cell reaction, the most anodic, has a greater tendency to appear corrosion or oxidation.**

- **Example: electrochemical cell Zn – Cu**

Zn, anodic behavior

$Zn \longrightarrow Zn^{2+} + 2e^-$ $(E^0 = -0.763\ V)$



Cu, cathodic behavior

$Cu \longrightarrow Cu^{2+} + 2e^-$ $(E^0 = 0.337\ V)$

- **Cell Electromotive Force, or cell EMF, E^0_{cell}** net voltage between the oxidation and reduction half-reactions.

Oxidation: $Zn \longrightarrow Zn^{2+} + 2e^-$ $E^0 = -0.763\ V$

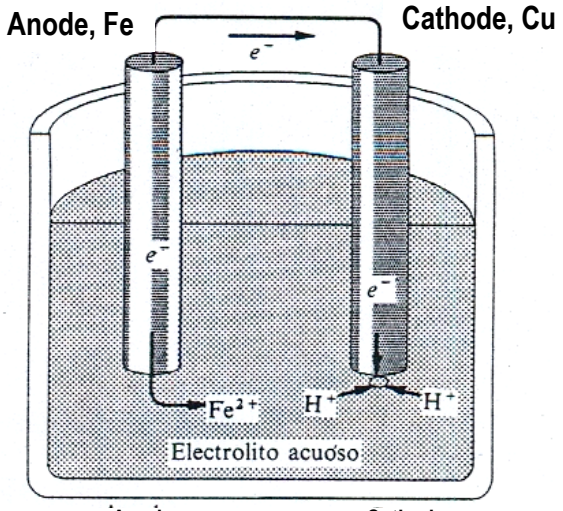
Reductión: $Cu^{2+} + 2e^- \longrightarrow Cu$ $E^0 = -0.337\ V$

Reaction: $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$ $E^0_{cell} = -1.100\ V$

9.10. GALVANIC SERIES

- **When electrodes are not found in solutions of their own salts, other corrosion situations appear.**

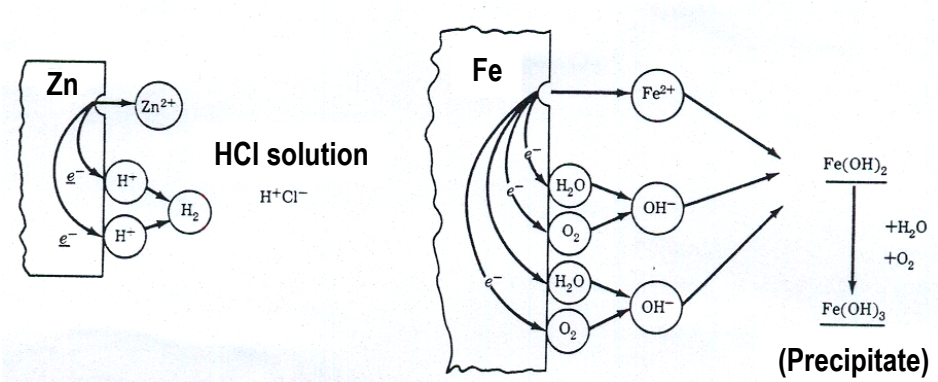
Two different metals in electrolyte where initially there are no metal ions (galvanic couple).



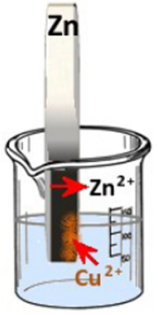
Neutral or basic

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

A metal with differences in structure and / or microscopic composition.



A metal in an electrolyte with ions of a different metal.

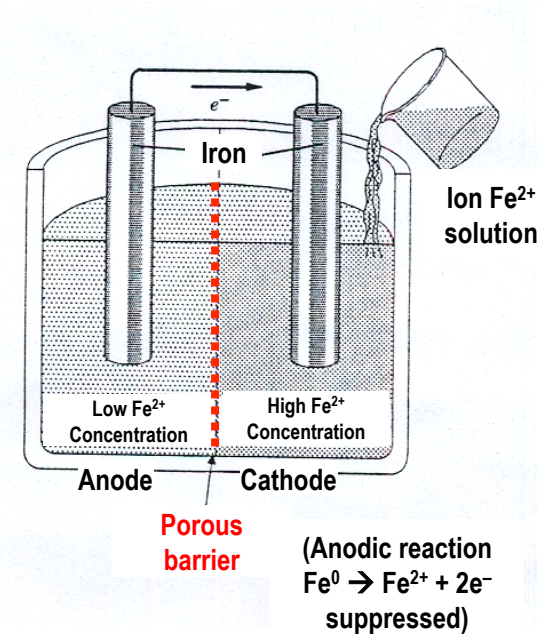


$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

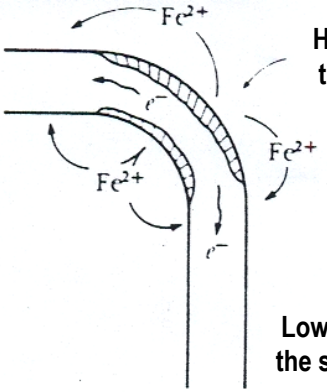
Reduction: $Cu^{2+} + 2e^- \rightarrow Cu$

Oxidation: $Zn \rightarrow Zn^{2+} + 2e^-$

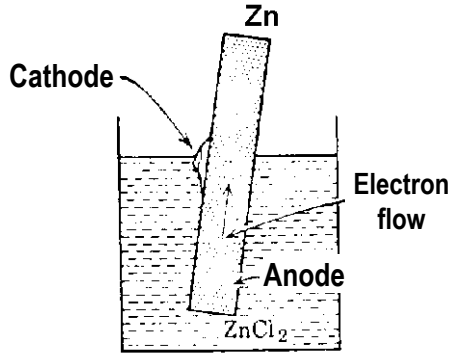
A metal in an electrolyte with different concentration (differential concentration).

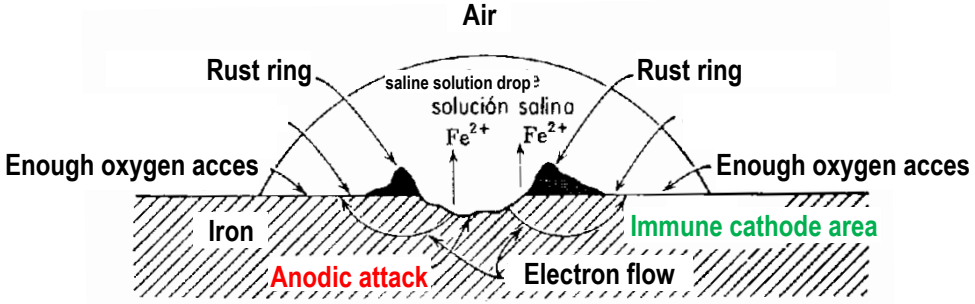


A metal containing regions with different local stresses



A metal in contact with an electrolyte when there is a difference in O_2 concentration (differential aeration).





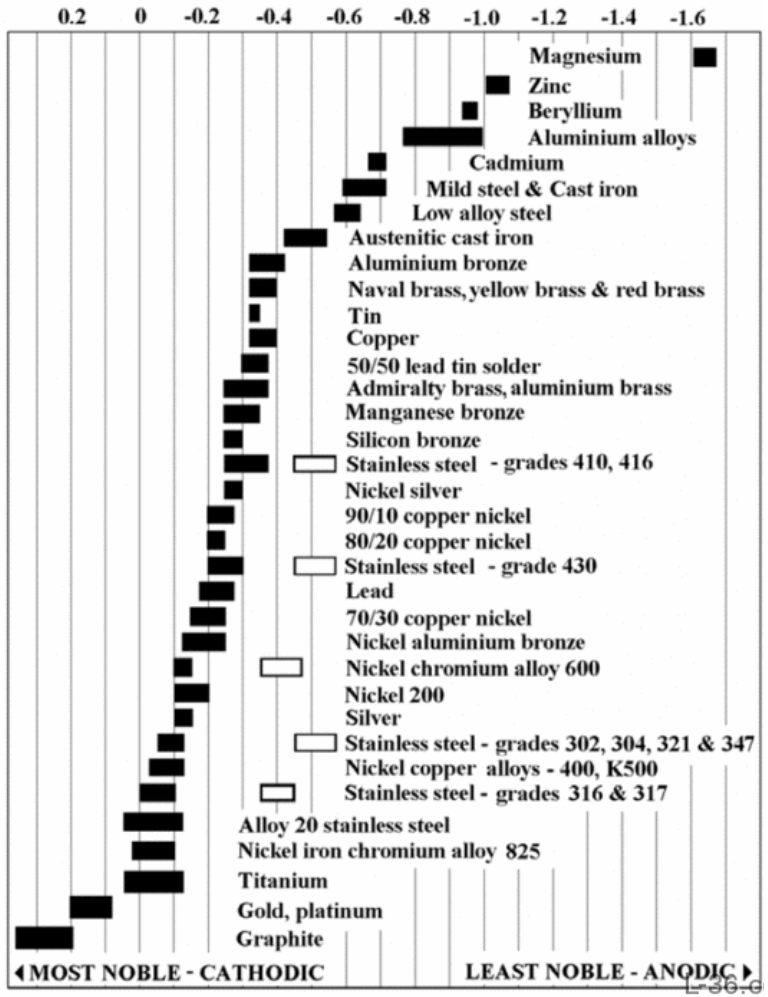
- The tendency to corrosion of a metal shown by the **electrochemical series** can be altered due to the non-fulfillment of the conditions imposed for its definition.

GALVANIC SERIES

- Relative reactivities of metal pairs in a given medium and under specific conditions.

- **Example**:

  Galvanic series of metals and metal alloys exposed to **seawater**.



9.11. PASSIVATION

- Formation of a relatively inert film on the surface of a material (often a metal) that protects it from the action of external agents.
- Although the reaction between the metal and the external agent is thermodynamically feasible at the macroscopic level, the passivating layer or film does not allow them to interact, in such a way that the chemical or electrochemical reaction is reduced or completely prevented.
- Passivation should not be confused with immunity, in which the base metal is itself resistant to the action of corrosive media, for example gold and platinum, which do not oxidize easily and are therefore called noble metals.
- Examples: aluminum, stainless steel...

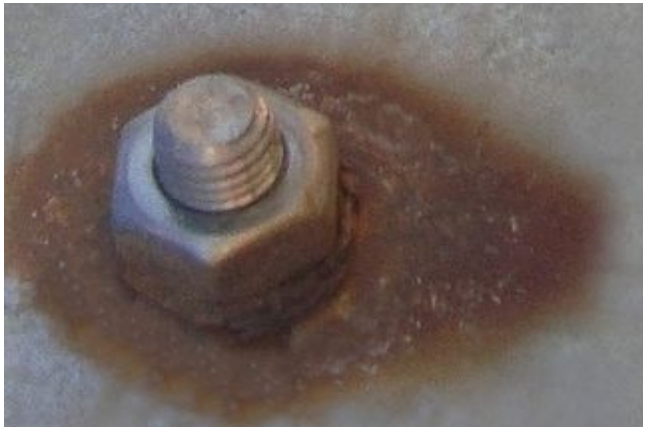
9.12. FORMS OF CORROSION

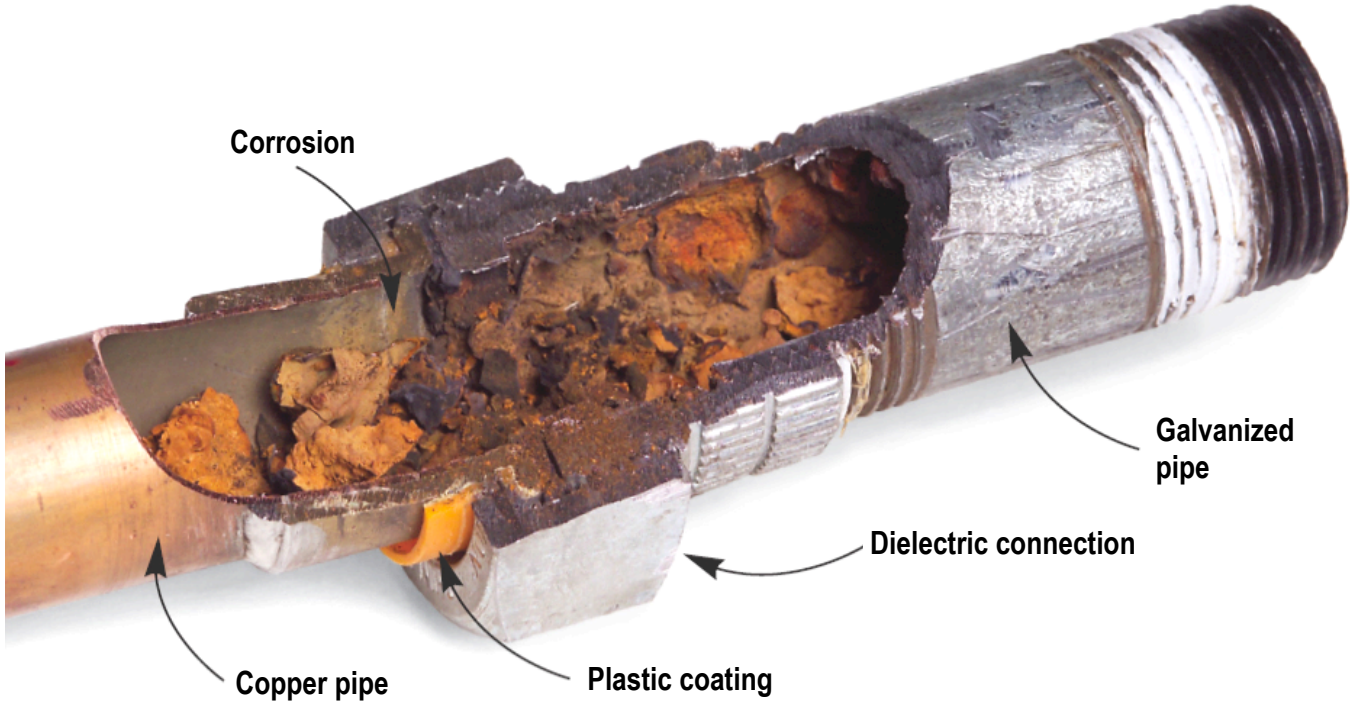
- **Uniform or generalized corrosion:**

  It is the most common form of corrosion but the least annoying and dangerous, because it can be predicted and mitigated with relative ease.

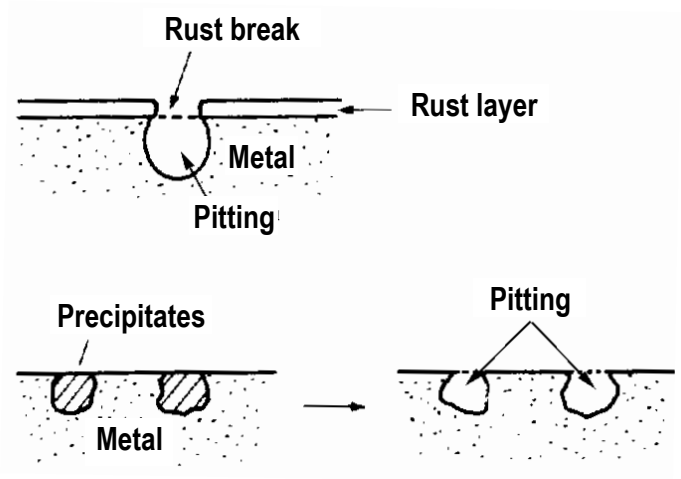
- **Examples: rust of steel and iron, tarnish of silverware, etc.**

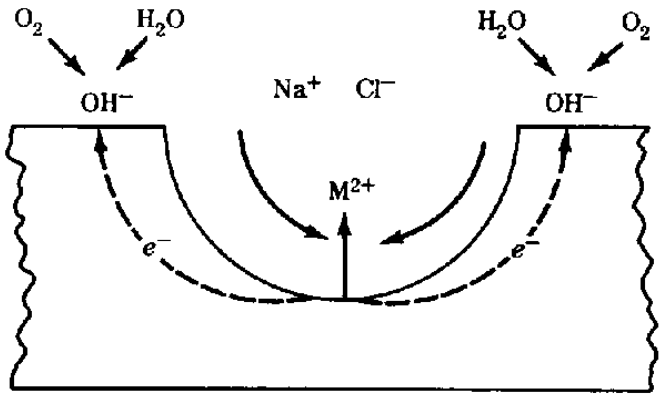
- **Galvanic or bimetallic corrosion:**
  It is produced by contact of two metals in the presence of an electrolyte. It is easily predictable and avoidable and can sometimes be used advantageously.
- **Examples: galvanized steel or tin.**

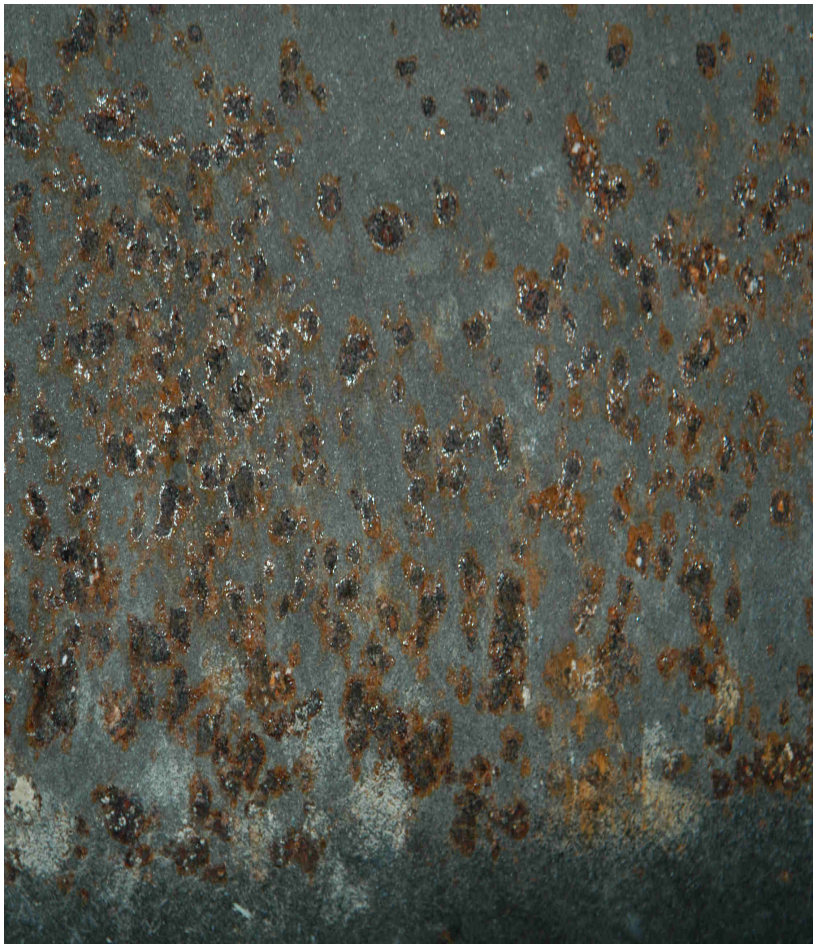




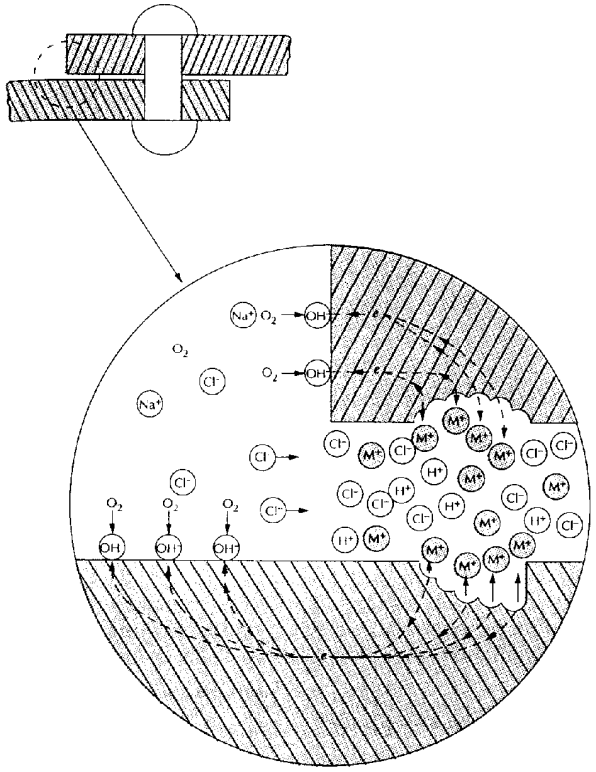
- **Pitting corrosion:**
  It is a localized and dangerous attack because it is difficult to detect.





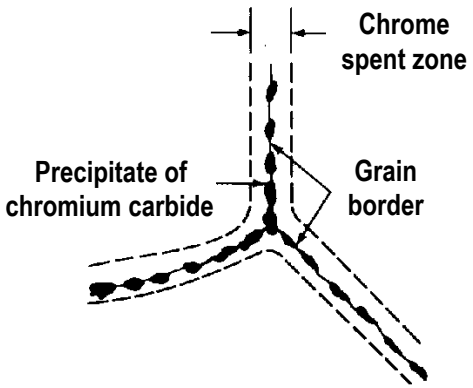


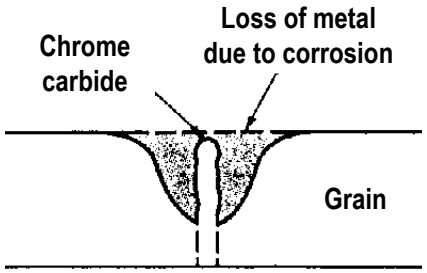
- **Crevice corrosion:**
  It is presented in holes, slits and under protected surfaces where there may be retained solutions with localized reduction of dissolved oxygen (differential aeration).

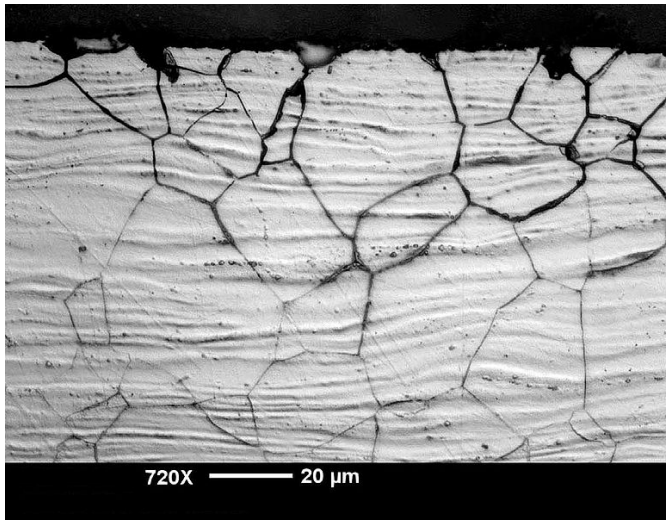


- **Intergranular corrosion:**
  Deterioration by localized corrosion and / or adjacent to the grain boundary of an alloy.
- **Predominates in some stainless steels heated to temperatures between 500°C and 800°C for long periods of time.**

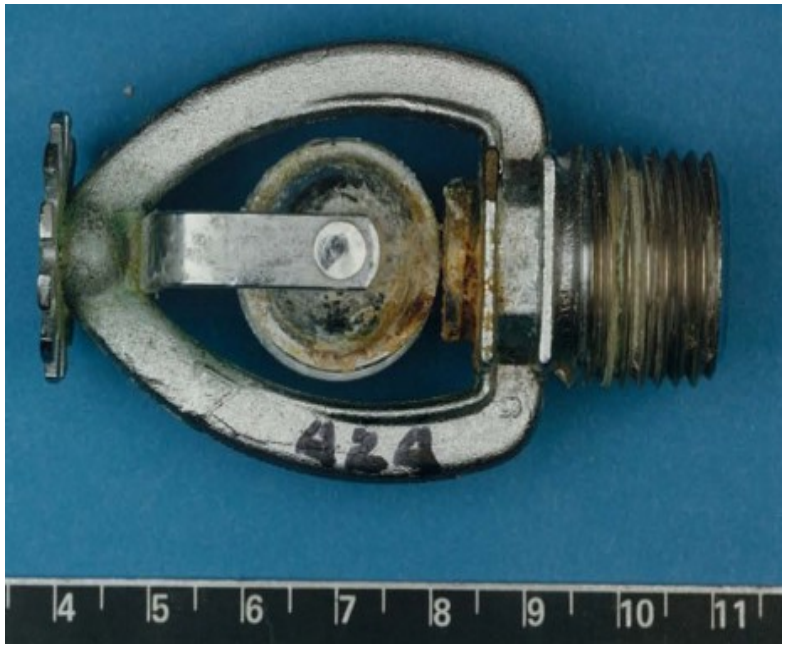
Sensitization by welding

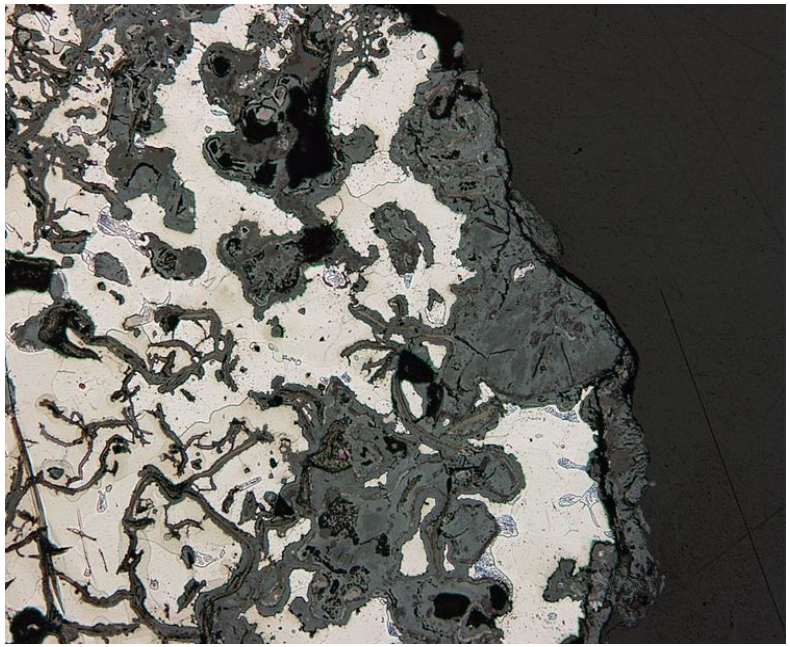




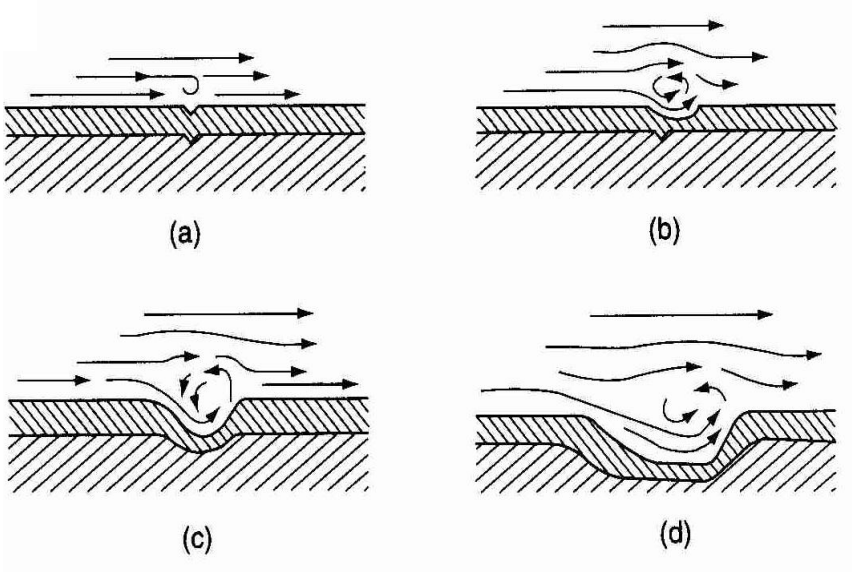


- **Selective elimination:**
  Preferential removal of an element from a solid alloy by corrosive processes.
- **Example: dezincification of the brass, graphitic corrosion of gray cast irons, etc.**

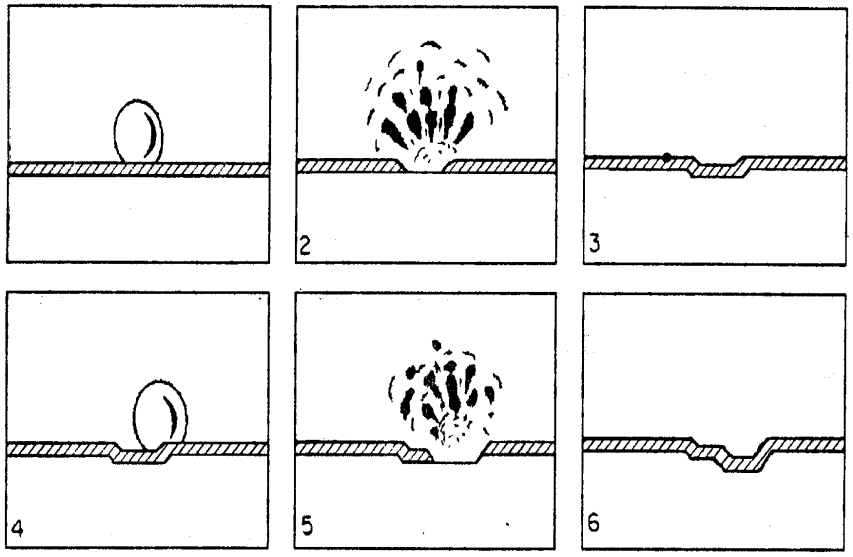


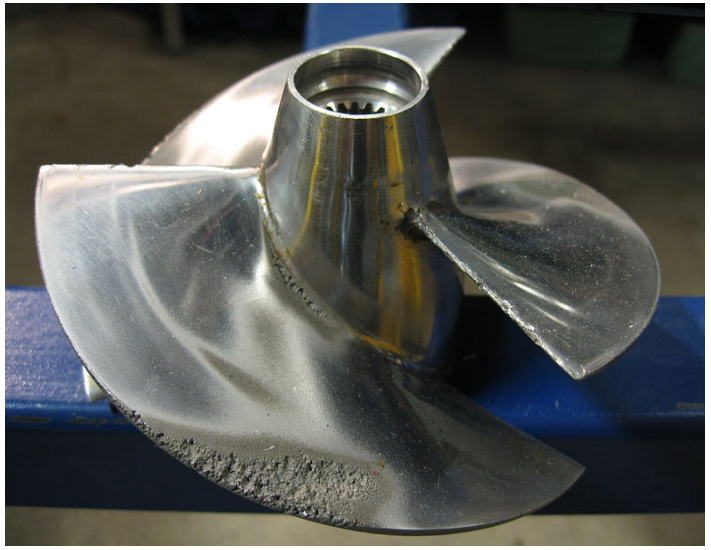


- **Corrosion by erosion:**
  Acceleration process in the speed of corrosive attack to a metal due to the relative movement of the corrosive fluid with respect to the metal surface.
- **It usually occurs in pipes, propellers, turbine blades, valves, pumps, etc.**



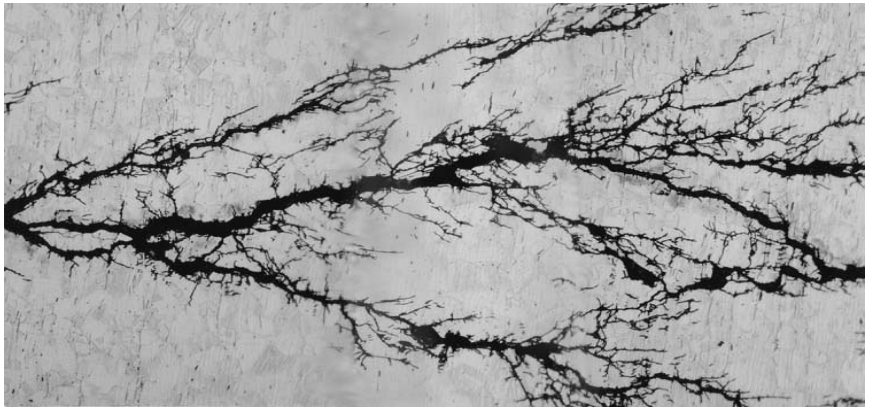
- **Cavitation damage:**
  It is caused by the formation and implosion of air bubbles or steam-filled cavities in a liquid that is in contact with a metal surface (booster pumps or boat propellers).





- **Corrosion due to friction or wear:**
  It takes place at the interfaces between materials under load subjected to vibration and sliding (axes and bearings).

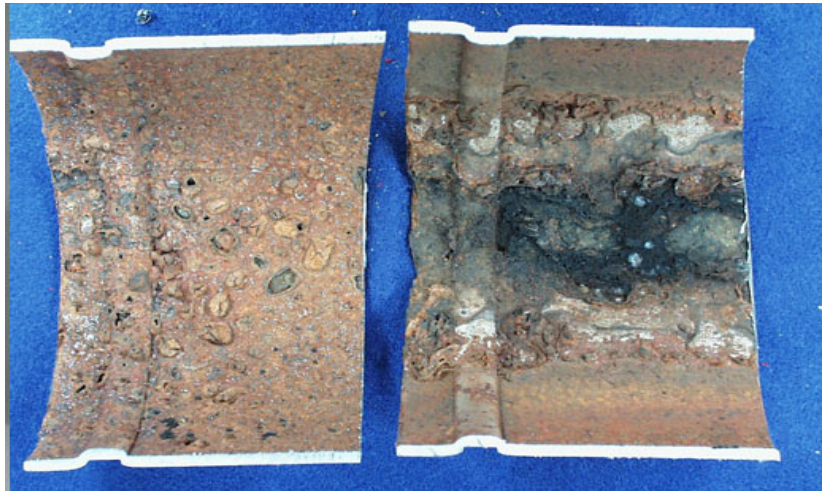
- **Stress corrosión (SC):**
  It is produced by the combined action of an applied tensile stress and an aggressive environment, the presence of both factors being necessary.
- **It appears on off-shore platforms, storage tanks, etc.**

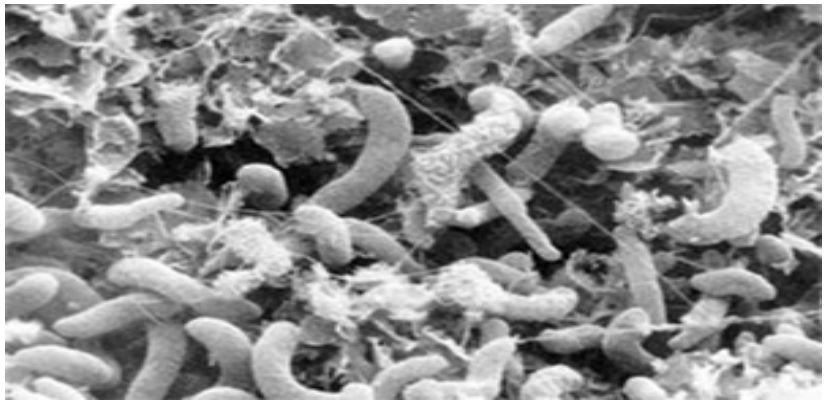


- **Fatigue corrosion (FC):**
  Damage that occurs due to the simultaneous action of a cyclic stress and an aggressive environment.

- **Corrosion in concrete:**
  Salts and other chemical agents penetrate the concrete through their network of pores and cause corrosion of the reinforcements. The corrosion of the metal generates expansive forces that cause the cracking of the concrete structure.

- **Microbial corrosion:**
  Caused by the presence and activities of living organisms (microbes, bacteria...).





9.13. PROTECTION AGAINST CORROSION

- **Material selection:**

  Adequate selection of the material according to the corrosive environment (Economic factors).

- **Design:**

  Avoid the joints, gaps and heterogeneities, facilitating cleaning operations and air extraction.

- **Inhibitors:**

  They are substances that, added to the medium in low concentrations, decrease their aggressiveness by eliminating the chemically active species from the solution or passivating the metal surfaces.

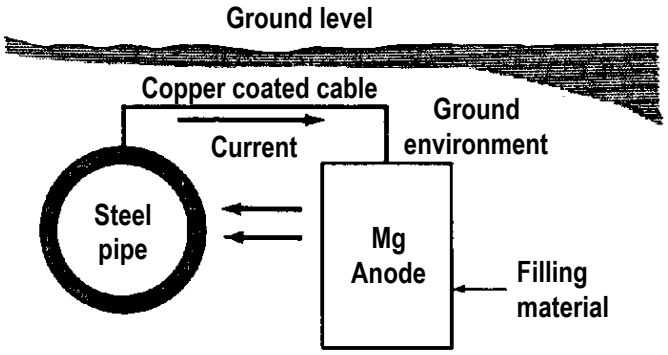
  They are used in closed systems such as heat exchangers or automobile radiators.

- **Protective coatings:**

  Application of physical barriers in the form of films and surface coatings that prevent direct access of the aggressive medium to the metal to be protected.

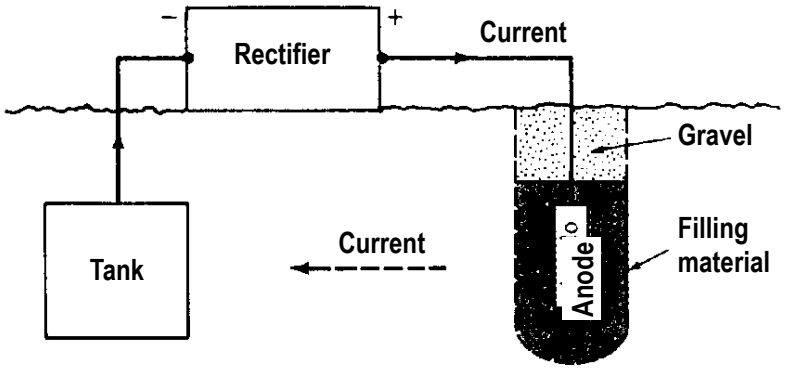
- **Cathodic protection:**

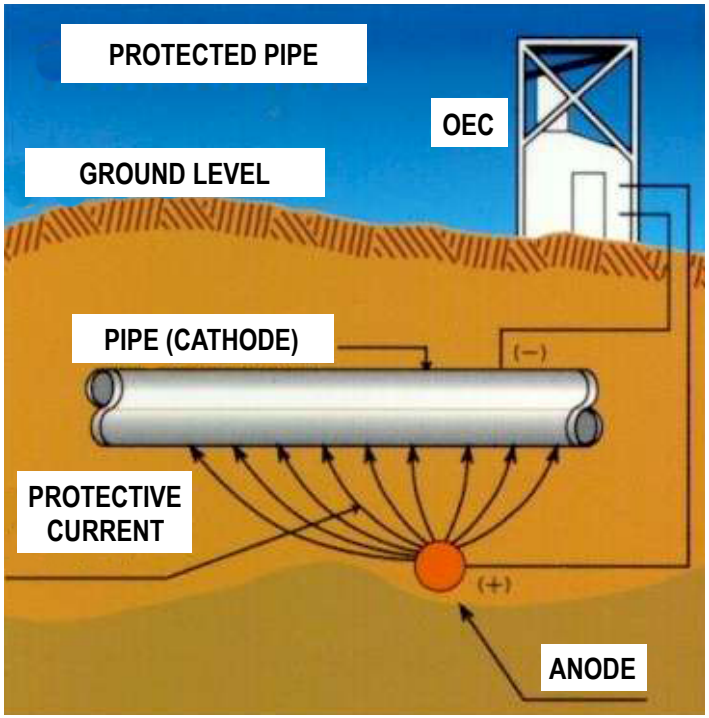
  It consists of reversing the sense of reaction $M \rightarrow M^{n+} + ne^-$ adding external electrons.



Sacrificial anodes

Printed current





- **Anodic protection:**

  It is based on the formation of protective passive films by the external application of anodic currents controlled by a potentiostat.