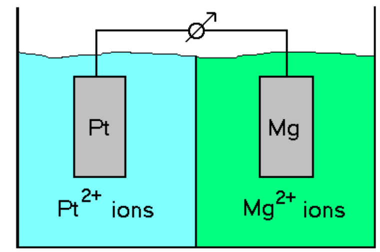
Outline

- Brief Review: *EMF*
- Environmental Effects
- Forms of Corrosion
  - *Galvanic*
  - *Crevice*
  - *Pitting*
  - *Intergranular*
  - *SCC*
  - *Erosion Corrosion*
  - *Hydrogen Embrittlement*
- Corrosion Environments
- Corrosion Prevention
- Example

Calculation of Cell Potential



Table

$Pt^{2+} + 2e^{-} \rightarrow Pt$ +1.2V

$Mg^{2+} + 2e^{-} \rightarrow Mg$ -2.363V

Actual — Actual

$Mg \rightarrow Mg^{2+} + 2e^{-}$ (oxidation) ……...V

$Pt^{2+} + 2e^{-} \rightarrow Pt$ +1.2V

Total — Total

$Mg + Pt^{2+} \rightarrow Mg^{2+} + Pt$ ………V

- (+) Potential means rxn will proceed as written.
- (-) Potential means opposite rxn occurs.
- The more positive rxn will proceed as written

Environmental Effects

- As we saw; concentration affects corrosion rate.
- Other variables can also affect the corrosion rate:

✓ Fluid velocity: usually corrosion rate↑ as velocity ↑ due to ……...

✓ Temperature: most chemical reaction rates ↑ as T ↑ hence so do most corrosion rates.

✓ Composition: increasing concentration of corrosive species (e.g.. H^{+} ions) usually increases corrosion rate (*except in passivation*).

✓ Microstructure: cold-worked regions of a metal are more susceptible to corrosion than the annealed regions.

✓ Alloying: Alloys tend to have higher corrosion rates than their pure metals (*except when passive films form - stainless steels*).

Forms of Corrosion

Uniform / General Attack

Uniform chemical reaction across entire metal surface. Some areas anodic some cathodic but these change with time giving uniform overall corrosion. Usually produces a scale or deposit.

- General rusting of steel
- Tarnishing of silver,.

Can have ……… weight loss but relatively ……. to prevent.

Galvanic corrosion

- Occurs when certain areas always act as anodes and others only as cathodes.
- Less noble metal (*more reactive*) will corrode. E.g
  - Steel screws in contact with brass in marine environment will rust preferentially.
  - If steel & copper tubing is joined in a water heater, the steel pipe corrodes.
- Rate of corrosion depends on **surface areas** of anode and cathode (*small anode will corrode faster than larger anode for similar cathode size – current density is ………*) - e.g. steel nail in copper sheet.
- Also within steel - two phases (***ferrite** and **cementite***) ferrite is anodic to cementite so cell set up and corrodes.

most commonly when dissimilar metals (*different electrochemical potentials*) are in electrical contact and exposed to an electrolyte.

Stainless screw and cadmium plated steel washer

Galvanic corrosion

Use galvanic series to show tendencies to corrode - when two metals coupled in seawater, lower one in series will tend to corrode. (**Brackets indicate similar base metal - unlikely to cause problems if joined**)

Table 18.2 The Galvanic Series

↑ Increasingly inert (cathodic)	Platinum
	Gold
	Graphite
	Titanium
	Silver
	[316 Stainless steel (passive)
	[304 Stainless steel (passive)
	[Inconel (80Ni–13Cr–7Fe) (passive)
	[Nickel (passive)
	[Monel (70Ni–30Cu)
	[Copper–nickel alloys
	[Bronzes (Cu–Sn alloys)
	[Copper
	[Brasses (Cu–Zn alloys)
	[Inconel (active)
	[Nickel (active)
	Tin
	Lead
Increasingly active (anodic) ↓	[316 Stainless steel (active)
	[304 Stainless steel (active)
	[Cast iron
	[Iron and steel
	Aluminum alloys
	Cadmium
	Commercially pure aluminum
	Zinc
	Magnesium and magnesium alloys

Galvanic corrosion

***FIGURE 18.14** Galvanic corrosion of a magnesium shell that was cast around a steel core.*

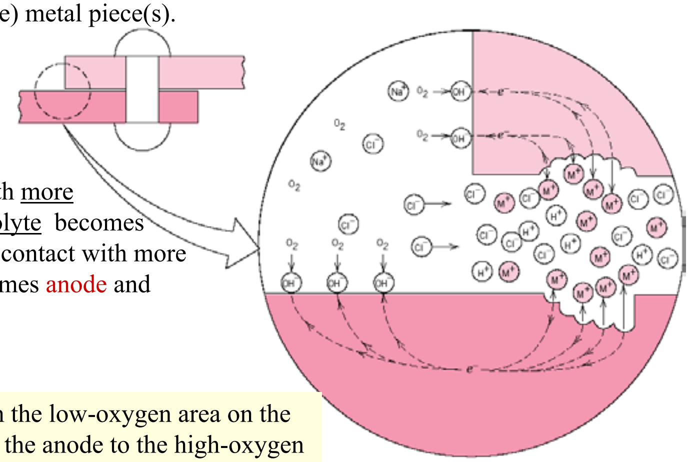
To reduce galvanic corrosion:

- If dissimilar metals must be coupled, use metals close to each other in galvanic series.
- Avoid a large cathode-to-anode surface area ratio (*use …… anode*).
- Electrically insulate dissimilar metals from each other
- Electrically connect a third, more anodic metal to the other two (…………. *Protection*).

Crevice Corrosion

Concentration cells form due to **differences in metal (or dissolved gases) ion concentration** in the electrolyte between two regions of (same) metal piece(s).

Metal in contact with more concentrated electrolyte becomes "cathode", metal in contact with more dilute solution becomes anode and corrodes.



Electrons flow from the low-oxygen area on the metal which acts as the anode to the high-oxygen area on the metal which acts as the cathode.

Crevice Corrosion

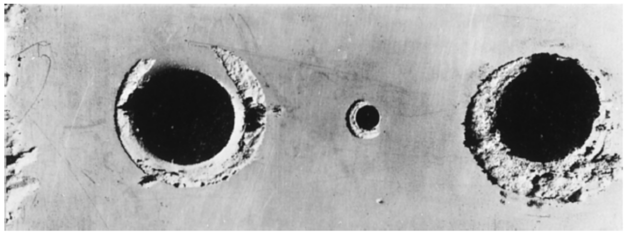


FIGURE 18.15 On this plate, which was immersed in seawater, crevice corrosion has occurred at the regions that were covered by washers.

• Eg. Localised electrochemical attack in crevices etc. where stagnant solutions exist. (Cracks, crevices, under paint, under gaskets, rivets, bolts, porous deposits.)

• Liquid gets into crevice but does not flow in/out. (i.e. gaps of ~ mm's or less) stagnant.

Deposits such as rust or water droplets shield the metal from oxygen so the metal underneath is anodic and corrodes.
Occurs in many alloys: stainless steels, cu-alloys, titanium, aluminium alloys.
e.g. s/s in seawater. Salt increases conductivity of solution so increases corrosion.

Crevice Corrosion

To reduce crevice corrosion:

• Use ………. rather than bolted or riveted joints;

• Use non-absorbing gaskets

• Remove accumulated deposits

• Design vessels with …………….. without stagnant areas

Pitting Corrosion

Localized attack which forms small holes or pits. Can be very deep and penetrate through sheet without much warning/indication. *Similar to crevice corrosion.*

• Pits usually grow downwards due to gravity.

• Initiation may be at surface scratches, defects etc.

• Polishing helps reduce pitting.

• Stainless steels are susceptible but alloying with 2% molybdenum greatly increases resistance.

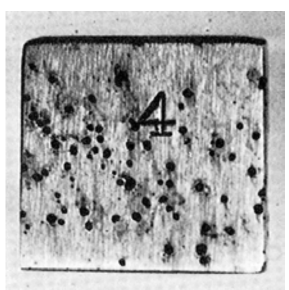


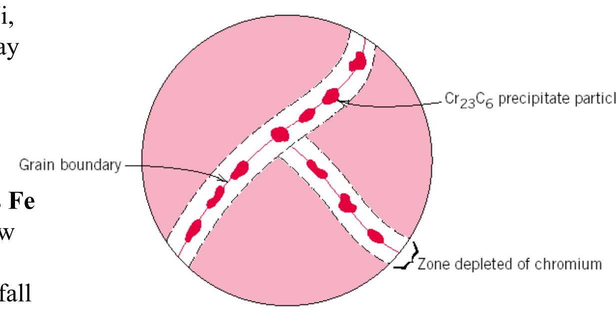
FIGURE 18.17 *The pitting of a 304 stainless steel plate by an acid-chloride solution.*

Intergranular Corrosion

Localised attack at/near to grain boundaries of alloys. Makes specimen disintegrate along grain boundaries. Very common in some stainless steels.

Sometimes precipitates form in/near GB's which make GB very sensitive or prone to attack.

e.g.: in 304 (18/8) stainless steel, (0.08C, 19Cr, 9Ni, 2.0Mn), Cr carbides may form if heated at 500-800°C for some time (*sensitisation*).
$Cr \rightarrow Cr_{23}C_6$ (ppts)
(Cr normally protects Fe from corrosion) so now get corrosion of Cr-depleted zones- grains fall out or cracks run down GB's.



Intergranular corrosion

✓ Can occur during welding of stainless steels – known as **weld decay.**

✓ Protect by:

1) proper heat treatment, (re-dissolve carbides at high T),

2) ……… carbon content (to < 0.03wt%C - 304L) so minimal carbides form,or

3) add Nb, (347) Ti (321) to form stable carbides instead of chromium carbides.

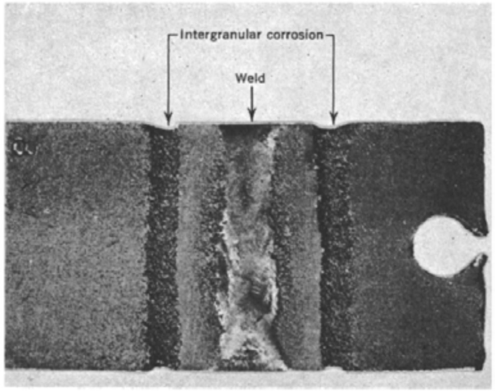


FIGURE 18.19 *Weld decay in a stainless steel. The regions along which the grooves have formed were sensitized as the weld cooled.*

Selective leaching

• Found in solid solutions; when one element is preferentially removed by corrosion.

• E.g.. Dezincification of brass (Cu-Zn) – Zinc is removed leaving weak, porous copper mass.(often with colour change from yellow to orange/red)

Erosion-Corrosion

• Combined effect of chemical attack and mechanical abrasion (slurry).

• All metals are affected;

-Very bad for metals that are normally protected by passive layer – stainless steels, aluminum. Erosion removes protective film exposing metal.

- Soft metals also more susceptible - Cu and Al alloys.

• More prevalent in piping, elbows, bends etc when flow changes direction or becomes turbulent.

• Cavitation and bubbles can also cause problems.

• Reduce impingement, turbulence and any particulates.

FIGURE 18.20 *Impingement failure of an elbow that was part of a steam condensate line.*

Stress corrosion: *(stress corrosion cracking)*

• Combined effect of tensile stress on metals **and** a particular corrosive environment. Only when both together and only on certain metals.

• E.g. stainless steels and chloride ions, brass and ammonia.

• Small cracks form and propagate perpendicular to tensile stress, failure is brittle - no or little plastic deformation.

• Stress may be external OR internal residual stress.

• To avoid check combinations of metal and environment, keep stresses low and if necessary, stress-relieve.

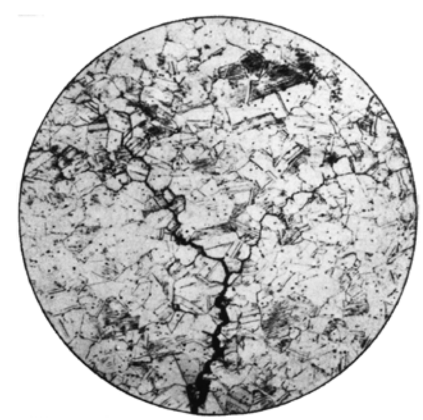


FIGURE 18.21 Photomicrograph showing intergranular stress corrosion cracking in brass.

Hydrogen Embrittlement

- For some metal alloys (specifically steels) σ_{TS} ↓ and %El ↓ if atomic hydrogen (H) gets into structure. (*hydrogen stress cracking, hydrogen induced cracking*).
- Cracking and brittle fracture occur under tensile stress. (*similar to* ……….. ……………).
- Requires source of atomic hydrogen, e.g.
  - Acid solutions (*sulphuric acid in steel pickling, electroplating of parts*)
  - Water vapour presence at high temps (*welding, heat-treating*)
  - "Poisons" - (H_2S) such as in petroleum industry
- Higher strength steels more susceptible (*especially* ………….. *steels*)
- Reduce likelihood of Hydrogen Embrittlement by:
  - Annealing alloy (*softening*)
  - removing hydrogen source
  - "baking" component to remove dissolved hydrogen
  - substitute more resistant alloy (*FCC*)

Corrosion Environments

- Includes: atmosphere, aqueous solutions, soils, acids, bases, solvents, molten salts, liquid metals, body fluids…
- Most prevalent is moist air containing dissolved oxygen. (+ salt - "sea air", + acid - "acid rain")
  - *Aluminum, copper alloys and galvanized steel used for atmospheric applications.*
- Sea water (3.5% salt) is more corrosive than fresh water (including pitting & crevice corrosion)
  - Cast iron, steel, aluminum, copper, brass, stainless steels used for fresh water.
  - Titanium, bronze, Cu-Ni alloys, Ni-Cr-Mo alloys good resistance in sea-water.
  - Have to match material to environment (*solutions, temperatures, erosion, etc*)

Corrosion Prevention

✓ Select appropriate material for conditions (usually too …………!)

✓ Change environment (reduce temp, fluid velocity, change concentration etc).

✓ Use inhibitors - chemical which when added to electrolyte migrates to electrodes and reduces reactions (polarisation). Specific inhibitor for alloy and electrolyte.

- *E.g.. Chromate salts in car radiators.*

✓ Design to allow complete drainage, and easy washing, (& exclude air).

✓ Coatings - *used to isolate anodes and cathodes.*

- *E.g. Grease/oil temporary coatings,*
- *paints, enamels, metals etc more permanent.*

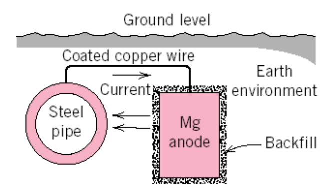
BUT if coating damaged then anode forms and corrosion occurs.

- *With tin coatings, the steel is* ……… *to tin so a scratch through to the steel causes a small anode which corrodes rapidly.*

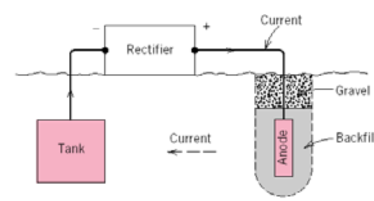
Cathodic Protection

- Corrosion occurs by: $M_1 \rightarrow M_1^{n+} + ne^-$

  So protect metal (from most types of corrosion) by supplying it with electrons and making it a cathode rather than an anode.
- Use a sacrificial anode or an impressed voltage to supply electrons.
- Sacrificial anode - make a galvanic couple with more reactive metal which corrodes away first (*eg. Zinc or magnesium*)
  - *Anode is consumed and may need to be replaced. E.g. ships, pipelines etc.*
- Impressed voltage.
  - *Supply a current to make a circuit between metal and scrap metal making the scrap the anode.*



Cathodic protection of an underground pipeline using a ………………………… *anode*



Cathodic protection of an underground tank using an ………………………….

Cathodic protection

E.g. galvanised steel - (zinc-plated). When scratched, zinc still protects steel because zinc is anodic to steel in most aqueous solutions and corrodes preferentially (but slowly because of **.......** area).

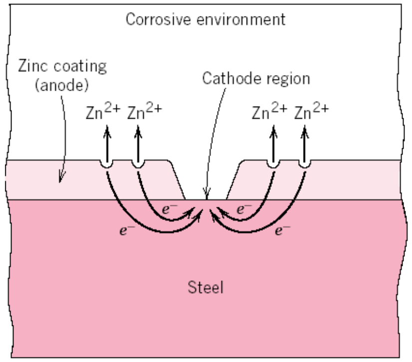


FIGURE 18.23 *Galvanic protection of steel as provided by a coating of zinc.*

Example

Consider a copper-zinc corrosion couple. If the current density at the copper cathode is 0.05 A/cm^2, calculate the weight loss of zinc per hour if (1) the copper cathode area is 100 cm^2 and the zinc anode area is 1 cm^2 and (2) the copper cathode area is 1 cm^2 and the zinc anode area is 100 cm^2.

Next time:

Wear