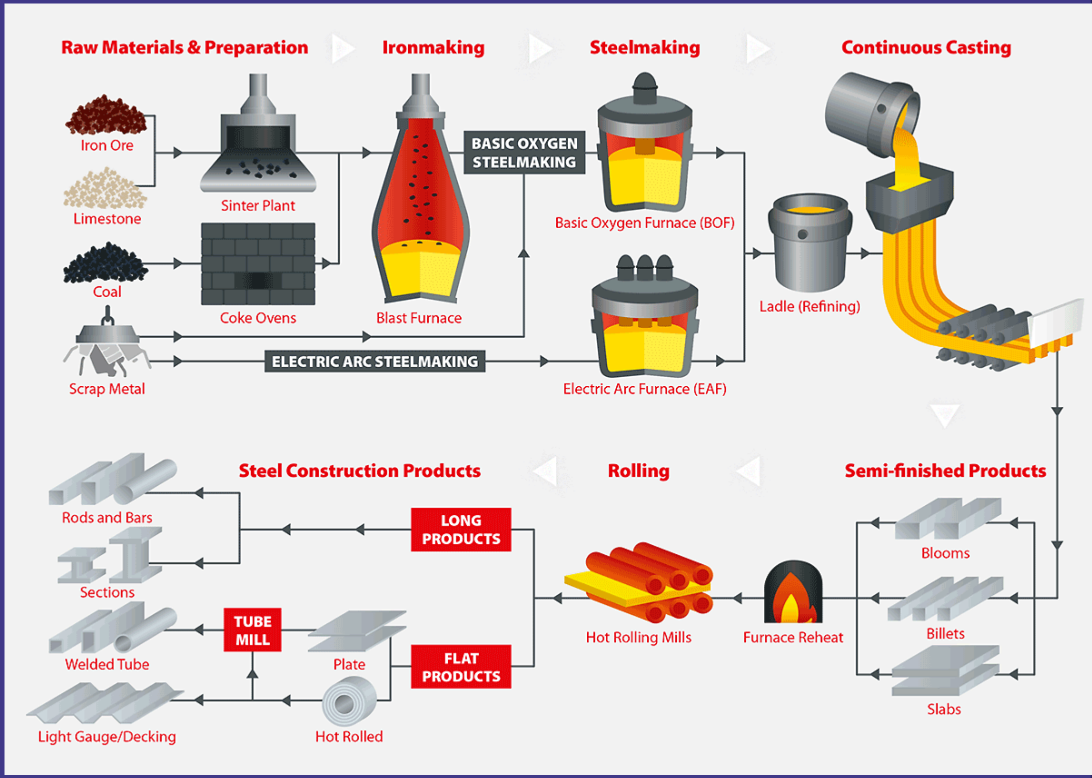
Imperial College London

Materials and Manufacturing



Corrosion

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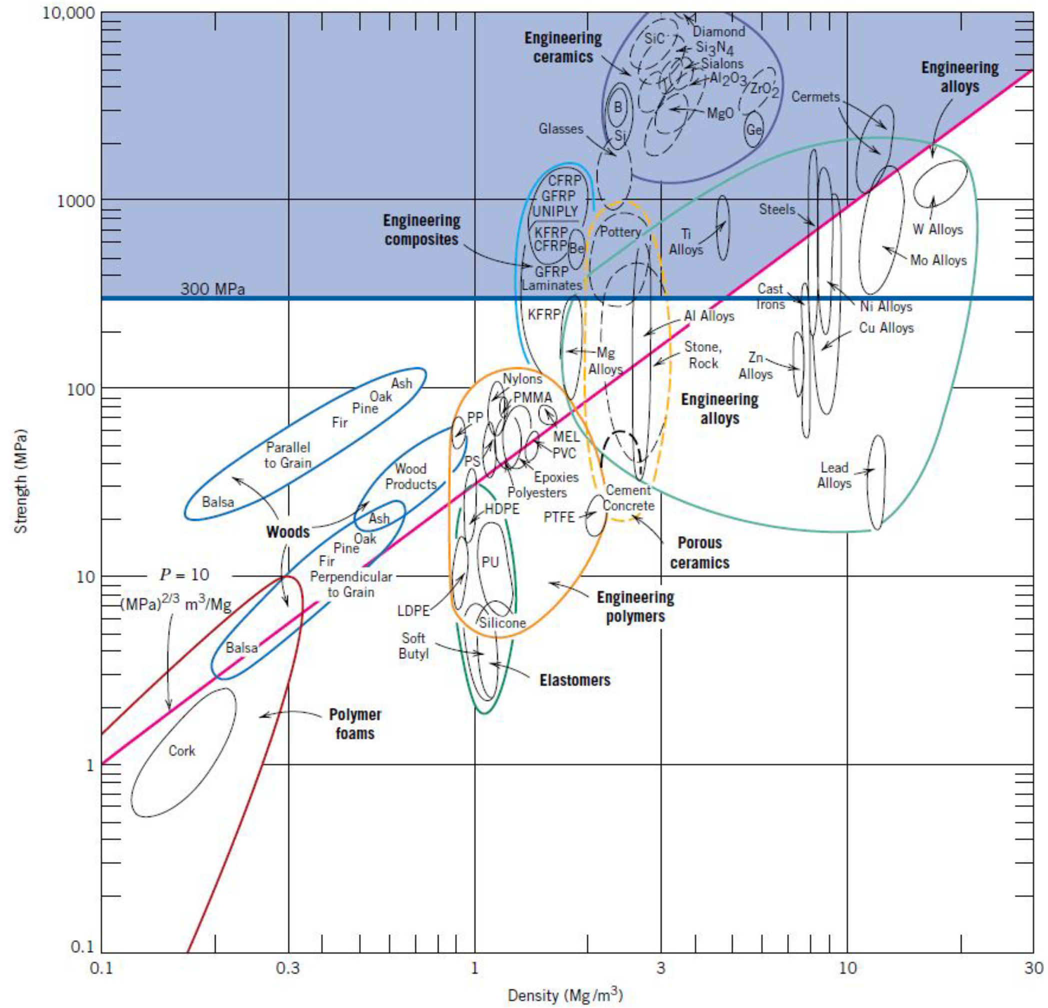
Dyson School of Design Engineering

Last time on M&M…

Recycling, selection and design

- Recycling
    - Metals
    - Glasses
    - Plastics and rubbers
    - Composites
- Combining your knowledge
- Torsionally stressed shaft
- Performance index
- Ashby plot



Learning objectives

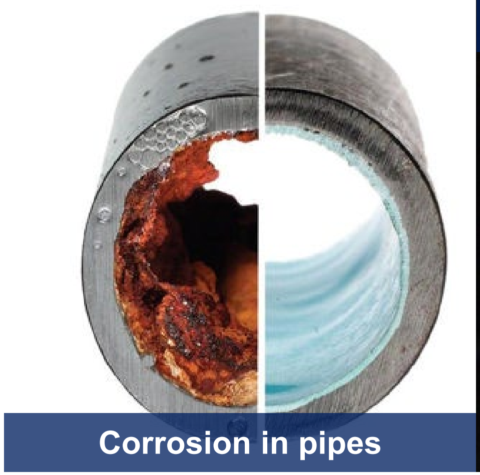
- Understand how materials corrode
- Define the measures commonly taken to prevent corrosion
- Explain why ceramics are typically resistant to corrosion
- Understand why polymers are vulnerable to liquid solvents and explain the cause of molecular chain bond rupture

Why is it important?

Most materials experience some type of interaction with the environment and over time their properties can change (often worse)

If this is not designed for, material corrosion can have catastrophic implications

It has been estimated that approximately 5% of an industrialized nation's income is spent on corrosion protection and maintenance


Corrosion in pipes


Corrosion on exposed metal


Rusty fence

Corrosion in different materials

- Deteriorative mechanisms are different for the three material types
- **Metals** - Material loss either by dissolution (**corrosion**), or by the formation of a non-metallic scale of film (**oxidation**)
- **Ceramics** - Relatively resistance to deterioration, which normally occurs at elevated temperatures or in extreme environments
- **Polymers** - Mechanisms and consequences differ from those for metals and ceramics and the term **degradation** is often used instead
  - May dissolve when exposed to a liquid solvent
  - May absorb the solvent and swell
  - Electromagnetic radiation (primarily ultraviolet) and heat may cause changes in their molecular structures

Rusty metal chain and bolt

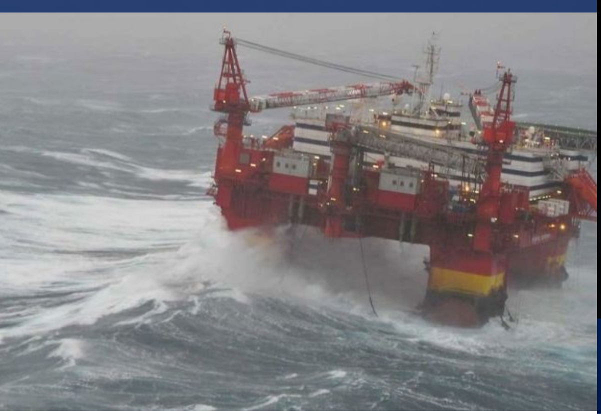
Aqua Regia dissolving platinum in a glass container

Plastic chairs can react with UV radiation

Corrosive environments

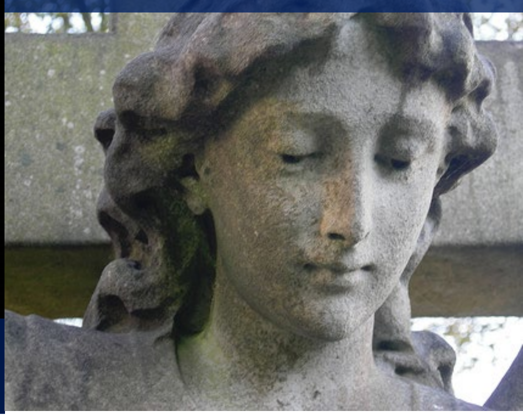
- Corrosive environments include:
  - Atmosphere, aqueous solutions, soils, acids, bases, inorganic solvents, liquid metals and the human body
- **Atmospheric corrosion** accounts for the greatest losses
  - Moisture containing dissolved oxygen is the primary corrosive agent
- Marine atmospheres are extremely corrosive since they contain sodium chloride (salt)
- Dilute sulphuric acid solutions (acid rain) can cause corrosion problems
- Water environments can also have a variety of compositions and corrosion characteristics
  - Freshwater normally contains dissolved oxygen
  - Seawater is generally more corrosive than freshwater

Oil rigs sit in very aggressive conditions



The human mouth is very warm and moist requiring dental implants to be extremely corrosion resistant

Acid rain can corrode statues

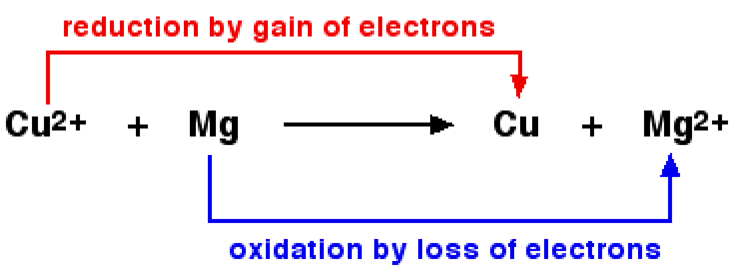


Corrosion in metals

- Corrosion is defined as the destructive and unintentional attack of a metal
  - It is electrochemical and ordinarily begins at the surface
- **Electrochemical** processes involve a chemical reaction where there is a transfer of electrons from one chemical species to another
- Metal atoms characteristically give up electrons (**oxidation**)

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

- Electrons generated from oxidation are transferred become part of another chemical species (**reduction**)
- Oxidation takes place on the **anode** | Reduction happens at the **cathode**
- The 2 happen together in what is termed a **redox reaction** (reduction-oxidation)



OIL RIG

oxidation is loss   reduction is gain

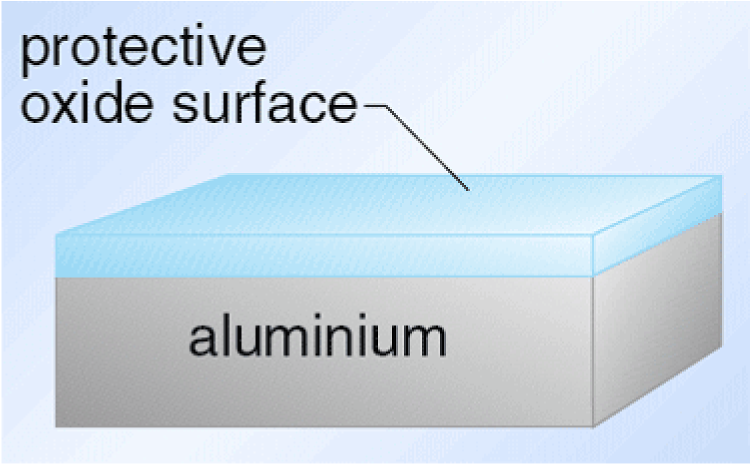
Galvanic series

- Galvanic series represents the relative reactivities
- Metals and alloys near the top are cathodic and unreactive
- Metals and alloys near the bottom are anodic and relatively reactive
- Most metals and alloys are subject to oxidation or corrosion
  - They are more stable in an ionic state than as metals
- Thermodynamically, there is a net decrease in free energy going from metallic to oxidized states
  - Most metals occur in nature as compounds
  - Two exceptions are gold and platinum
  - For them, oxidation in most environments is not favorable, and therefore, they may exist in nature in the metallic state
- Gold and platinium can actually be dissolved but needs extremely strong acid
  - Aqua regia

	Platinium
	Gold
	Graphite
	Titanium
↑	Silver
Increasingly inert (cathodic)	Stainless steel (Passive)
	Nickel (Passive)
	Bronzes
	Copper
	Brasses
	Nickel (Active)
	Tin
Increasingly active (anodic)	Lead
↓	Stainless steel (Active)
	Iron and steels
	Aluminium and aluminium alloys
	Zinc
	Magnesium and magnesium alloys

Passivity

- Some metals appear twice on the Galvanic series because they become inert
- This is called **passivity**
- Normally displayed in chromium, iron, nickel, titanium and their alloys
- Arises due to thin oxide film on the surface which prevents further reaction
- Stainless steel (11% Chromium)
- Aluminium forms an oxide layer



	Platinium
	Gold
	Graphite
	Titanium
↑	Silver
Increasingly inert (cathodic)	Stainless steel (Passive)
	Nickel (Passive)
	Bronzes
	Copper
	Brasses
	Nickel (Active)
	Tin
Increasingly active (anodic)	Lead
↓	Stainless steel (Active)
	Iron and steels
	Aluminium and aluminium alloys
	Zinc
	Magnesium and magnesium alloys

Environmental effects

- Factors which affect corrosion include:

Fluid velocity

- Increasing fluid velocity enhances corrosion rates due to mass transport

Temperature

- Increasing temperature increases the rates of reaction

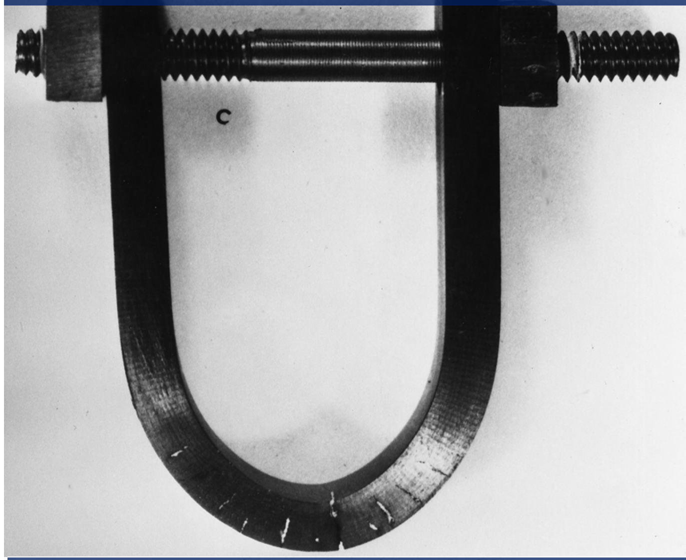
Composition

- Increasing concentration of species (H^+) typically increases the corrosion rate

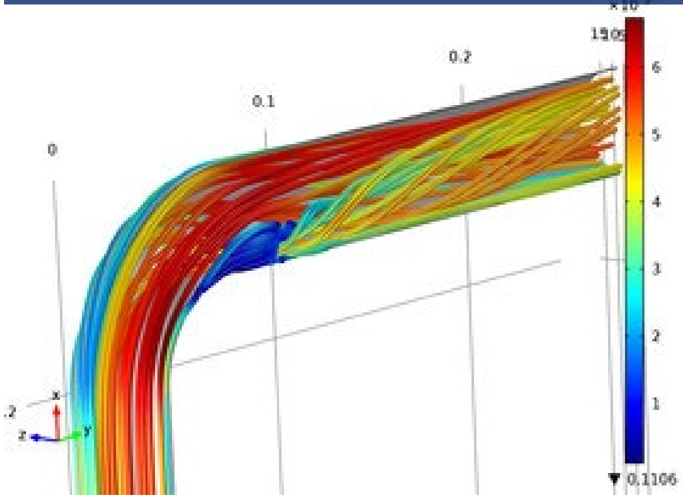
Cold working

- Plastic deformation typically makes it more susceptible to corrosion

Stress corrosion cracks in steel



CFD flow through pipe



Forms of corrosion

- Metallic corrosion is sometimes classified into eight forms:
- **Uniform**
- **Galvanic**
- **Crevice**
- **Pitting**
- **Intergranular**
- **Selective leaching**
- **Erosion-corrosion**
- **Stress corrosion**

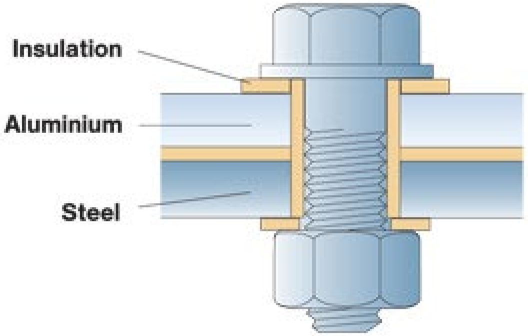



Uniform attack

- **Uniform attack** occurs with equivalent intensity over the entire exposed surface and often leaves behind scale or deposit
- The oxidation and reduction reactions occur over randomly over the surface
- Common forms include rusting of iron and tarnishing of silverware
- Generally most common and lease objectionable
  - Can be predicted and designed for
  - Painting of fence

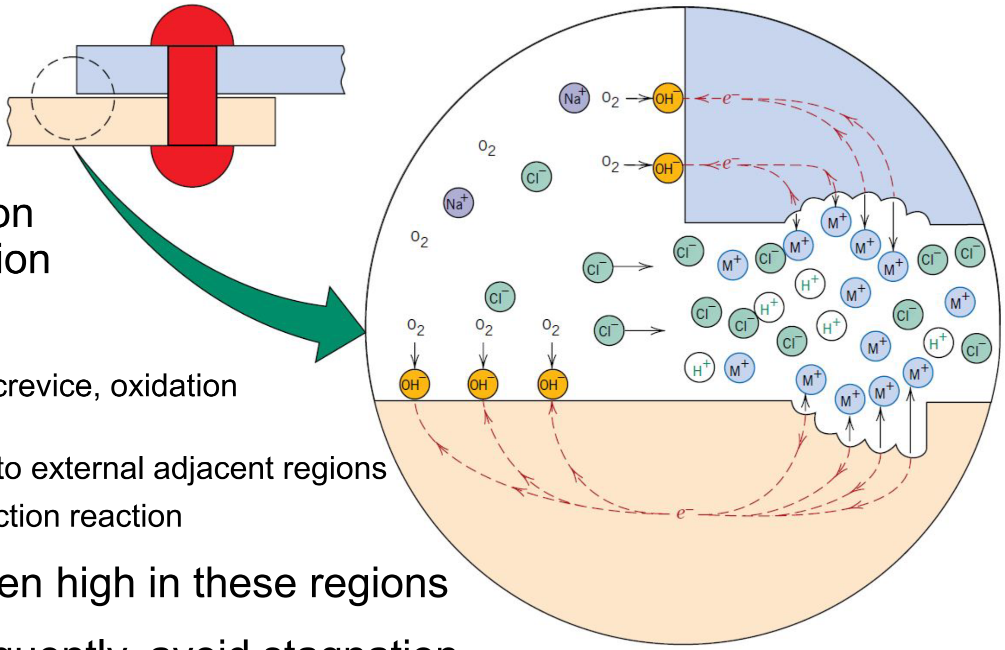
Galvanic corrosion

- **Galvanic corrosion** occurs when two metals or alloys having different compositions are electrically coupled while exposed to an **electrolyte**
- **Electrolyte** - A liquid which contains anions and cations. When an electric potential is applied the charged ions moves
- Typically, the most reactive metal will corrode before the more inert one
- The rate of galvanic attack depends on the relative anode-to-cathode surface areas that are exposed to the electrolyte
- To reduce this effect
  1. Choose two close in the galvanic series
  2. Avoid an unfavorable anode-to-cathode surface area ratio; use a large anode area
  3. Electrically insulate dissimilar metals from each other
  4. Electrically connect a third, anodic metal to the other two (cathodic protection)
- E.g. steel screws corrode when in contact with brass in an marine environment.



Crevice corrosion

- Corrosion occurs as a consequence of **concentration differences of ions**
- **Crevice corrosion** happens in small gaps where solution can become stagnant and locally deplete the oxygen
- Gap has to be wide enough for solution to get in but small enough for stagnation



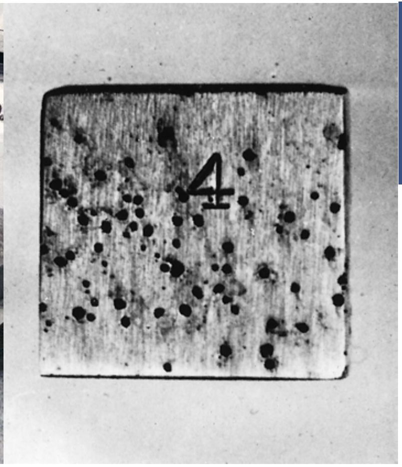
Mechanism

- After oxygen has been depleted within the crevice, oxidation of the metal occurs
- Electrons from this reaction are conducted to external adjacent regions
- Here the electrons are consumed in a reduction reaction

- H^+ and Cl^- ions concentrations are often high in these regions
- Avoided by welding, removing dirt frequently, avoid stagnation

Pitting

- Pitting is a form of very localized corrosion attack in which small pits or holes form
- They penetrate from the top of a horizontal surface downward in a nearly vertical direction
- Similar mechanism to crevice corrosion
  - Oxidation occurs in the pit and reduction at the surface
- Gravity causes pits to grow downwards
- Pits may be initiated by surface defect – scratch or compositional variation
- Polished surfaces can have a greater resistance to pitting



The pitting of a 304 stainless steel plate by an acid-chloride solution

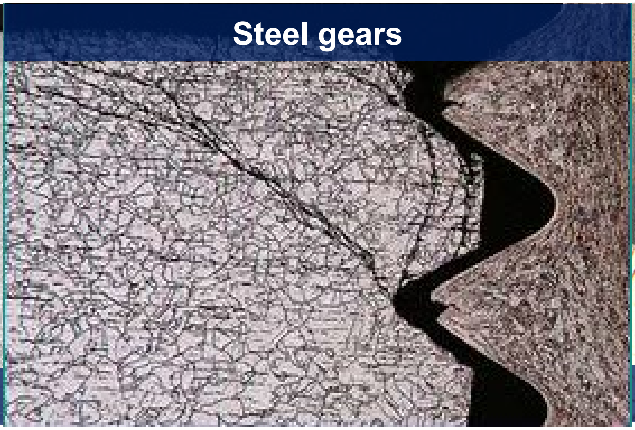
Erosion-corrosion

- **Erosion-corrosion** arises from the combined action of chemical attack and mechanical abrasion or wear as a consequence of fluid motion
- Especially harmful to alloys that passivate; the abrasive action may erode away the protective film, leaving exposed a bare metal surface
- If the coating is not capable of continuously and rapidly reforming as a protective barrier, corrosion may be severe
- Identified by surface grooves and waves having contours that are characteristic of the flow of the fluid
- Increasing fluid flow increases the rate of corrosion
- More corrosive if there are bubbles and particulates in suspension
- Commonly found in piping, especially at bends, elbows, and abrupt changes in pipe diameter-positions where the fluid changes direction/flow becomes turbulent

Stress corrosion

- **Stress corrosion** results from the combined action of an applied tensile stress and a corrosive environment
- Small cracks form and then propagate in a direction perpendicular to the stress, with the result that failure may eventually occur
- Failure behaviour is characteristic of that for a brittle material, even though the metal alloy is intrinsically ductile
- Cracks may form at relatively low stress levels, significantly below the tensile strength
- Stress doesn't have to be externally applied; may be a **residual** one that results from rapid temperature changes and uneven contraction, or for two phase alloys in which each phase has a different coefficient of expansion


Stress corrosion crack in steel


Steel gears

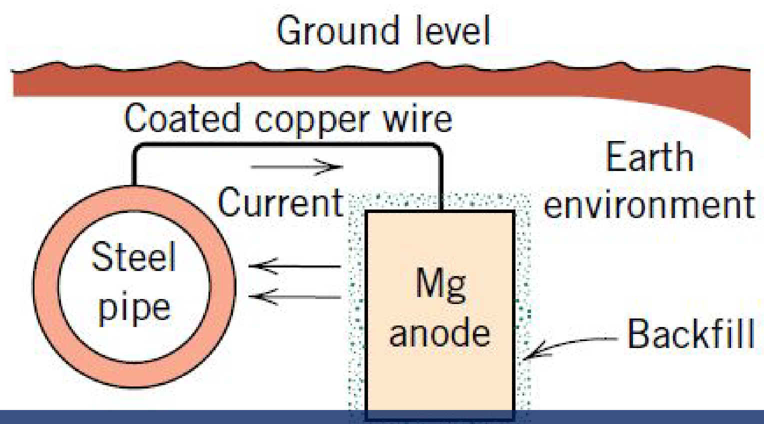

Stress corrosion crack in a pipe

Preventing corrosion

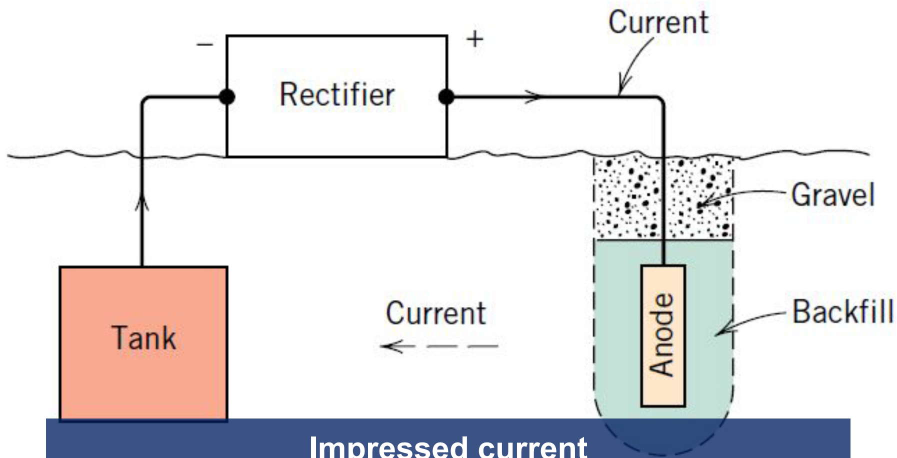
- **Choose the right material**
  - Pick one that doesn’t corrode!
- **Change the environment**
  - Reduce the temperature, stress, fluid flow etc
- **Inhibitors**
  - Eliminates the active component in the corrosion reaction
  - Interferes with redox reactions
  - Used in closed systems
- **Design of the system**
  - Being able to drain a liquid system and wash it
  - Designing it to prevent air (oxygen) coming in
- **Physical barriers**
  - Coatings and films
  - Needs good adhesion
  - Paint – prevent oxygen diffusion

Cathodic protection

- One of the most effective means of corrosion prevention is **cathodic protection**
- Involves supplying, from an external source, electrons to the metal to be protected, making it a cathode; the reaction above is thus forced in the reverse (or reduction) direction
- **Galvanic couple**
  - The metal to be protected is electrically connected to another metal that is more reactive
  - The latter experiences oxidation, and, upon giving up electrons, protects the first metal from corrosion
  - This is called a **sacrificial anode**
- **Impressed current**
  - Negative terminal connected to metal. Positive connected to an inert anode (typically graphite)



Galvanic couple



Impressed current

Corrosion in ceramics

- Ceramic materials (compounds of metallic and nonmetallic elements) may be thought of as having already been corroded
- They are exceedingly immune to corrosion by almost all environments, especially at room temperature
- Corrosion of ceramics generally involves simple chemical dissolution, in contrast to the electrochemical processes found in metals
- Ceramic materials are frequently utilized because of their resistance to corrosion



Degradation of polymers

- Polymers also deteriorate but we often call this **degradation** rather than corrosion
- Polymeric degradation is **physiochemical** vs electrochemical for metals
    - It involves physical as well as chemical phenomena

Swelling

- Liquid/solute diffuses into polymer and forces macromolecules apart weakening secondary bonds
- Polymer swells and becomes weaker

Dissolution

- Occurs when the polymer is completely soluble, may be thought of as just a continuation of swelling
- The greater the similarity between the solvent and polymer the more likely swelling/dissolution occurs
- For example, many hydrocarbon rubbers readily absorb hydrocarbon liquids such as gasoline

Bond rupture

- **Scission** is the severence or rupture of molecular chain bonds
- Reduced molecular weight and can be caused by radiation, chemical reaction and thermal effects

Acetone used to dissolve and smooth PLA 3D printed parts

Summary

- Understand how materials corrode
- Define the measures commonly taken to prevent corrosion
- Explain why ceramics are typically resistant to corrosion
- Understand why polymers are vulnerable to liquid solvents and explain the cause of molecular chain bond rupture

Next time on M&M…