

Local and Other Corrosion Mechanisms;

* Local corrosion can be due to;

- Differences in metal composition. (e.g. more than one metal present)
- Differences in local solution conc. (e.g. presence of liquid droplets)
- Microstructural defects in the metal. (e.g. grain boundaries)

Bimetallic (Galvanic) Corrosion;

* When two metals are in electrical contact the less reactive of them will act as the cathode and the more reactive will be an anode and corrode rapidly.

* e.g. Zn and Fe \Rightarrow conservation of charge applies;



* To prevent; - Use the same metal, or metals with the same reactivity according to a galvanic series, if possible.

- Insulate dissimilar metals from one another.

Relative Leaching;

* This is the removal of one element from an alloy to reduce the strength of a material. Usually as a result of the bimetallic effect.

Crevice Corrosion;

* Initially metal is both anode ($M \rightarrow M^{2+}$) and cathode ($H_2O + \frac{1}{2}O_2 \rightarrow 2OH^-$).

* However in crevice the liquid is trapped so oxygen is eventually used up due to poor diffusion.

* Now the cathodic reaction will be at the larger metal surface whilst the anodic reaction is still in the crevice; here $A_a \ll A_c$ so rapid corrosion occurs.

* Also, Cl^- ions can migrate into the crevice to preserve charge neutrality.

(OH^- ions are less mobile). Also $M^{2+} + H_2O \rightarrow M(OH)_2 + 2H^+$ occurs when $[OH^-]$ is low. So the liquid in a crevice can become acidic!

* High $[Cl^-]$ and acidity equals rapid corrosion!

* This corrosion is autocatalytic; once it starts it gets worse faster!

Pitting;

- * Similar to crevice corrosion but a "pit" is formed first;
- * Pit initiation depends on local surface defects;
 - dislocations emerging from the surface.
 - heterogeneities in composition (e.g. inclusions / segregates / precipitates).

or;



- * Once a pit is formed crevice corrosion can take over. Not all crevice corrosion is a result of pitting though.

Intergranular Corrosion; (Weld Decay)

- * Most metals are prepared by quenching. Crystallites form in a melt and grow, linking up to form grains. Intergranular corrosion occurs when precipitates form at grain boundaries, affecting the corrosion properties of the metal.

- * e.g. Weld Decay; - If steel is heated to around 700°C, near where welding occurs, chromium carbide can precipitate.
 - This reduces [Cr] in the area. If [Cr] < 11% the region is not stainless!

- * Avoiding Weld Decay; - use low-carbon steel to avoid carbide formation.
 - beware of oily rags!
 - have Ti or Nb in the steel as their carbide will form in preference to Cr carbide.
 - post-weld treatment dissolves the precipitates by heating to 1000°C and quenching.

Erosion Corrosion;

- * Due to motion between the fluid and the metal.
- * Increased mass transfer can remove diffusional limitations and promote corrosion reactions.
- * Particles in the liquid can scour away protective layers + cause mechanical wear.
- * Avoid \rightarrow sudden changes in pipe diameter / direction.
 \rightarrow gaskets / joints which leave discontinuities in smooth surfaces.
- * Cavitation \rightarrow formation + collapse of vapour bubbles on a metal surface breaks protective layers and deforms the surface. Smooth surfaces avoid this as they have fewer nucleation sites.

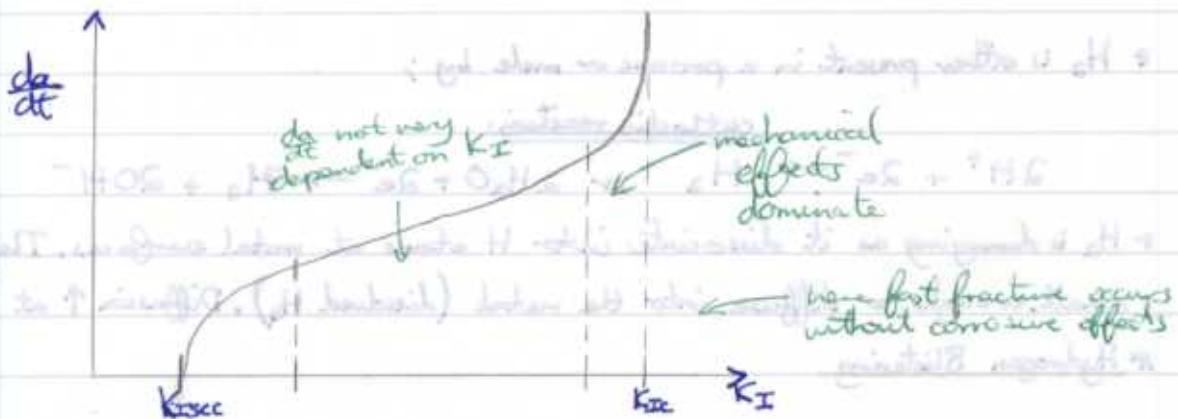
Environment Sensitive Cracking (ESC); Stress-Corrosion Cracking (SCC)

- * Occurs when both of the following happen; a static tensile stress is applied to the material AND there is a corrosive environment.
- * KEY POINT; CRACKS GROW FASTER IN CORROSIVE ENVIRONMENTS AT LOWER STRESSES.
- * Causes ductile materials to fail in a brittle way.

$$K_{Ic} = \propto \sigma_{APP} \sqrt{\pi a}$$

fracture toughness \uparrow applied stress \uparrow crack length \leftarrow geometric factor ≈ 1

Cracks appear when $K_I > K_{Isc}$



- * Initiation; formation of defects at surface (e.g. pitting, rupture of passivating film)
- * Propagation; crack may grow along grain boundaries. If the passivating film is ruptured propagation depends on relative rates of corrosion + passivation.

Environment Sensitive Cracking (ESC); Corrosion Fatigue

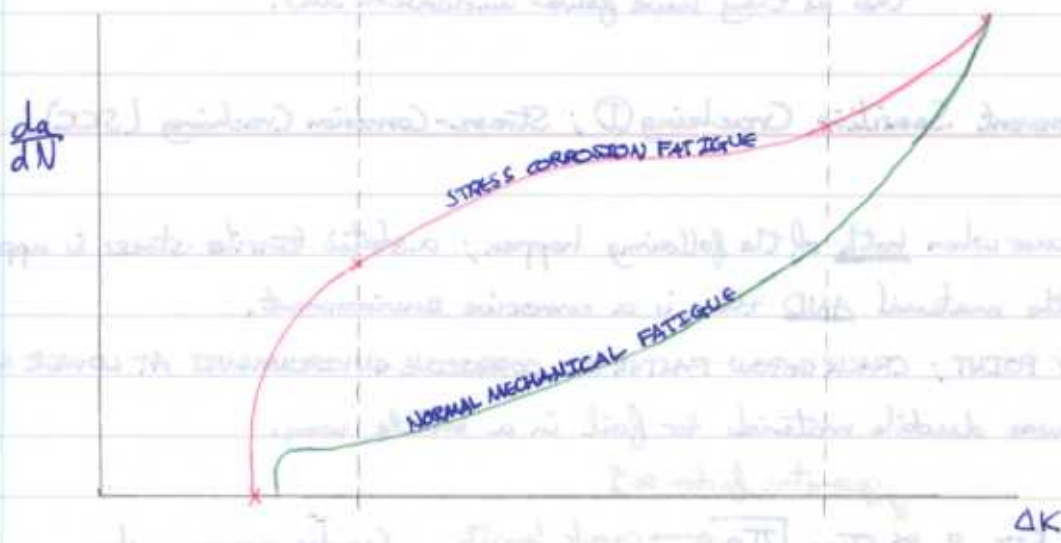
* This is a combination of both; a VARYING applied stress and a corrosive environment.

* In non-corrosive environments, fluctuations in stress can cause metal fracture (even though σ_{TS} is not surpassed). This can be modeled by;

PARIS LAW $\frac{da}{dN} = C(\Delta K)^m$ where $\Delta K = (\alpha \cdot \Delta \sigma \sqrt{t_a})^m$

number of cycles *stress range*

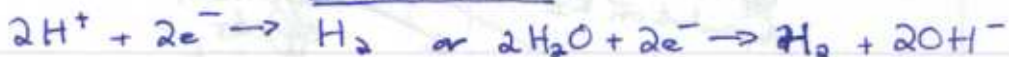
* Aqueous environments reduce "N" to failure. Corrosion fatigue affects all metals in an aqueous environment. The mechanisms are not well understood.



Hydrogen Damage;

* H_2 is either present in a process or made by;

cathodic reactions



* H_2 is damaging as it dissociates into H atoms at metal surfaces. They are small enough to diffuse into the metal (dissolved H_2). Diffusion \uparrow at \uparrow temp.

* Hydrogen Blistering



* pressure of H_2 in void increases causing a blister.

* Hydrogen Embrittlement → This is an example of stress-corrosion cracking by adsorption.

→ The cracking may be TRANSGRANULAR or INTERGRANULAR. ← high-temp.

→ ① Metal bonds weaken at crack tip.

② H_2 gas forms in local voids just ahead of the crack tip causing plastic deformation.

③ Metal hydrides form. e.g. Ti/Nb form hydrides at grain boundaries, making the material more brittle.

④ High T → decarburization, leading to loss of strength/ductility. (methane forms).

* Preventing H_2 damage

→ ① Choose alloy carefully. FCC < brittle than BCC, as has restricted slip capability for dislocations. Also FCC have lower diffusivity of H atoms. Mo/Cr reduce damage too.

② Sulphide ions slow down $H + H \rightarrow H_2$, so more dissolution of H into metal.

③ Mild heating ($150^\circ C$) in absence of H_2 , removes dissolved H atoms from steel.

④ Coat the metal to reduce contact of metal + H_2 . Also, H_2 formed at cathodes, so maybe reduce i_c ?

Microbially Induced Corrosion (MIC);

* Bio-organisms (fungi, bacteria, algae) affect the solution composition in the biofilm and cause pitting.

* Can get rid by ① cleaning surfaces regularly.

② Use biocides additives.

③ Protective coatings.

④ Some metals more resistant (e.g. Cu is toxic to many micro-organisms)

Specific Corrosion Environments;

Atmospheric Corrosion;

* There is moisture in the atmosphere, which coats surfaces. The conductivity of the water is crucial in corrosion and is affected by dissolved species in the water.

* NO_x , SO_x , H_2S (acidic) + NH_3 (basic) + Cl^- ions increase conductivity and change pH.

* Heavy rain can help by washing away pollutants.

* High ion conc. causes conc. polarization.

Soil Corrosion;

- * Dry soil - negligible corrosion
- * Rate depends on moisture / pH / conductivity / oxygen content / ions / microorganisms.

Sea Water Corrosion;

- * High ion conc. ∴ High conductivity. Easy to establish electrochemical cells
- * Dissolved O₂ present, but gets lower the deeper you go.
- * Chemical species (esp. Cl⁻) attack passivating oxide and facilitate SCC.
- * Waves and tides cause erosion corrosion + corrosion fatigue.
- * Lots of microorganisms.

Microbial Induced Corrosion (MIC)

- * Microorganisms (bacteria, fungi, algae) are the primary cause of MIC.
- * They produce corrosive byproducts.
- * They can penetrate protective coatings.
- * They can cause stress corrosion cracking.

Microbial Corrosion (MIC)

Microbial corrosion is a process where microorganisms (bacteria, fungi, algae) are the primary cause of corrosion. They produce corrosive byproducts that attack the metal surface. They can penetrate protective coatings and cause stress corrosion cracking.