Intergranular Corrosion (IGC)

- Microstructure of metals and alloys is made up of grains (separated by grain boundaries)
- Intergranular corrosion is a localized attack along the grain boundaries, or immediately adjacent to grain boundaries, while the bulk of the grains remain largely unaffected
- IGC is associated:
  1. With chemical segregation effects (impurities segregate at grain boundaries)
  2. Precipitate of compounds (e.g.; carbides) at grain boundaries
- IGC then occurs at the GB phase that has lost an element necessary for adequate corrosion resistance: the GB becomes more anodic relative to the rest of the metal surface (which is cathodic).

Example: Weld Decay

- When stainless steel (SS) is heated to about 650 °C, Cr₂₃C₆ carbides form at the GB and the metal is said to be "sensitised"
- Cr-rich GB precipitates lead to a local depletion of Cr immediately adjacent to these precipitates, leaving these areas vulnerable to corrosive attack in certain electrolytes.
- If the Cr concentration falls low enough (<9%), SS will no longer remain passive and corrosion occurs.

Prevention of weld decay:

1. Use low carbon content grade stainless steel, e.g: 316L, 304L ~ 0.03 wt%, so carbide formation is minimal.
2. Use a stabilised grade of SS, which contain strong carbide-forming elements such as Nb or Ti
3. Heat treatment to redissolve the carbides (post welding heat treatment)
4. Weak corrosive conditions do not cause IGC
5. Low acidity (high pH) will generally reduce the susceptibility to IGC
Exfoliation Corrosion

- Exfoliation corrosion is a form of IGC found in high strength aluminium alloys (especially alloys that have been extruded or worked heavily, with a microstructure of elongated grains).
- Corrosion products building up along the GB exert pressure between the grains and the end result is a lifting or leafing effect.

Example of a guardrail showing exfoliation of aluminium

Localised Corrosion (Dealloying (leaching))

- Dealloying is the removal of one element from the alloy the electrolyte.
- The entire exposed surface of the metal may be attacked
- The cause of dealloying is a “galvanic effect”
  - One element of an alloy is more anodic than the rest, and as a result, this element can dissolve leaving a matrix of the noble element.

Type of Dealloying:
1. is the removal of zinc in chloride waters from brass (Cu-Zn alloy) called “dezincification”
2. Graphitisation of grey cast iron
3. Dealloying causes loss in mechanical strength without changes in shape of structure or component.

Dezincification of brass

Typical example of dealloying:

Localised Corrosion (Flow Induced Corrosion)

- Many engineering structures operate with electrolytes flowing either through or around them. Flow can:
  1. Increase transport of oxygen to the metal surface (may help to passivate)
  2. Increase the rate of dissolution of corrosion product films
  3. Mechanically remove oxides

Types of flow-induced corrosion include:
- Erosion-corrosion
- Cavitation corrosion
- Fretting corrosion
Erosion – Corrosion

- Erosion - corrosion attack in metals occurs due to the relative motion of a corrosive fluid and a metal surface.
- Corrosion is accelerated by impact of solid particles.
- These particles may remove metal, or they may just remove oxide and allow metal to corrode more quickly.
- For example, burrs left at cut tube ends can upset smooth water flow, causing localized turbulence and high flow velocities, which in turn results in erosion corrosion.

Prevention of Erosion - Corrosion

- Materials selection plays an important role in minimizing erosion corrosion damage.
- Design is also important:
  - It is generally desirable to reduce the fluid velocity and promote laminar flow; increased pipe diameters are useful.
  - Rough surfaces are generally undesirable.
  - Designs creating turbulence, flow restrictions and obstructions are undesirable.
  - Abrupt changes in flow direction should be avoided.

Cavitation Corrosion

- Cavitation corrosion occurs in valves, heat exchanger tubes, pumps and at elbows and tees in pipelines and any structural features that change the flow direction or velocity and increases turbulence.
- Cavitation corrosion is a form of erosion – corrosion and is caused by formation and collapse of bubbles of vapour.
- Vapour bubbles form because of pressure changes (which falls < 0) across surfaces exposed to high velocity liquid flow.
- When the pressure increases again the collapse of the vapour bubbles creates an intense shockwave that removes metal or oxide from the metal surface.
Prevention of Cavitation Corrosion

- Careful design to minimise pressure drops across the metal surface
- Optimum material selection
- Environmental modifications:
  - Abrasive particles in fluids can be removed (filtering or settling)
  - Deaeration (removal of air). A deaerator is a device that is widely used for the removal of air and other dissolved gases from the feedwater to steam-generating boilers.
- Cathodic protection
- Use protective coating (rubber can absorb shock waves)

Deaerator

Deaerator is a device that is widely used for the removal of air and other dissolved gases from the feedwater to steam-generating boilers.

Fretting Corrosion

- Fretting corrosion is a damage that occurs at the asperities (unevenness) of contact metal surfaces.
- It occurs at the interface of two highly stressed surfaces in the presence of repeated relative surface motion, for example vibration. (The surfaces are not designed to move against each other).
- The most common type of fretting is caused by vibration. The protective film on the metal surfaces is removed by the rubbing action and exposes fresh, active metal to the corrosive action of the atmosphere.

- Austenitic stainless steels, Ti and Al alloys (all have adherent protective films) are the most susceptible to fretting corrosion because they are relatively soft materials.
- Fretting corrosion can be minimised by:
  - Careful design: design the parts to exhibit less or relative motion
  - Use of lubrication on contacting surfaces
  - Use insulation material between surfaces
  - Reduce load between surfaces
  - Select a more resistant material
Localised Corrosion (Environmentally Induced Cracking (EIC))

- Engineering materials are frequently required to withstand loads (stresses).
- When these stresses are being applied in a corrosive environment, new types of corrosion may occur, classified as EIC.
- EIC results in brittle fracture.
- Many stress-related failures are associated with:
  1. Stress corrosion cracking (SCC) (tensile stress + corrosive environment)
  2. Hydrogen induced cracking (HIC)
  3. Corrosion fatigue (cyclic stress + corrosive environment)

Good engineering design should take into account stress levels and conditions that may arise at any time in the whole life cycle of a structure, including:

- Fabrication: residual and thermal stresses (SCC)
- Transport: shock, impact damage and vibration (fretting corrosion)
- Operation: fault conditions (SCC, corrosion fatigue, fretting corrosion)

Stress corrosion cracking (SCC)

- SCC is brittle failure of a metal under the combined effects of a static tensile stress and a specific chemical environment
- SCC is very common and is the cause of major industrial costs and safety hazards
- Three conditions must be present simultaneously for SCC to occur:
  - Specific environment
  - Susceptible alloy
  - Tensile stress (residual or applied)

SCC can proceed in either of two ways:

- Cracks may propagate along the grain boundaries (IGSCC - intergranular stress corrosion cracking) or
- May run through the individual grains (TGSCC – transgranular stress corrosion cracking).
Mechanisms of SCC

There are 3 possible mechanisms:

1. Anodic dissolution:
   - When there is no stress, the metal is not reactive to the environment because of the existing of a protective passive film at the crack tip.
   - The presence of stress leads to failure of this passive film by plastic strain and active corrosion occurs (by anodic dissolution).
   - The passivation rate is an important factor in this mechanism.

2. Hydrogen embrittlement:
   - H₂ atoms produced by the cathodic reaction diffuse to regions of tri-axial stress at the crack tip.
   - These H₂ atoms weaken the inter-atomic bonds at the crack tip.
   - Suggestions have been made that SCC can only be accounted for by a mechanism controlled by hydrogen induced cracking (HIC).
   - H₂ comes from welding, electroplating, corrosion.

3. Film - Induced Cleavage:
   - The sides and tip of the crack are covered by a brittle film (oxide film or de-alloyed layer).
   - The crack growing in the brittle film may propagate further into the metal.
   - The crack is then blunted by the plastic deformation.
   - For the crack to grow further, the surface film must reform at the crack tip surface.
Prevention of SCC
- Remove stress (often difficult, especially for residual stresses)
- Avoid the necessary environment
- Apply electrochemical protection where possible
- Use a different material

Prevention of Corrosion – fatigue
- Cathodic protection
- Inhibitors
- Select a more resistant material

Corrosion – fatigue is similar to SCC, except that the stresses are cyclic.
- A metal is said to have suffered corrosion – fatigue means when: in a corrosive environment the fatigue limit of a material is reduced and failure can occur at much lower stresses or in much shorter times than for non-corrosive environments.
- Unlike SCC, corrosion – fatigue is non-specific (it can occur in any environment)

Hydrogen attack (occurs at temperatures > 200°C)
1. Hydrogen attack
2. Hydrogen Embrittlement (HE)
3. Hydrogen Induced Cracking (HIC)
Hydrogen Embrittlement

- H₂ presence in steel reduces the tensile ductility and toughness and causes premature failure under static loads.
- Two types of HE:
  1. Internal HE, occurs when the hydrogen enters molten metal which becomes supersaturated with hydrogen immediately after solidification.
  2. Environmental HE, results from hydrogen being absorbed by solid metals.

Hydrogen Induced Cracking (HIC)

- HIC is a brittle failure caused by penetration and diffusion of H into the crystal structure of a metal.
- H normally recombines to form H₂ which bubbles off as hydrogen gas.

Prevention of HIC

- Two types of prevention:
  1. Minimising hydrogen content (Prevent trapping of H₂ within the metal)
  2. Reducing the residual (internal) stresses
- HIC can be reversed by heat treatment
- Other factors can be optimised to reduce HIC: Temperature, strength, Inhibitors and alloying elements (create traps which slow the diffusion rate of H₂)

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>SCC</th>
<th>Corrosion-Fatigue</th>
<th>HIC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stress</td>
<td>Static</td>
<td>Cyclic</td>
<td>Static</td>
</tr>
<tr>
<td>Aqueous corrosive</td>
<td>Specific</td>
<td>any</td>
<td>any</td>
</tr>
<tr>
<td>environment</td>
<td>to alloy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>accelerates</td>
<td>accelerates</td>
<td>Increases to RT, then decreases</td>
</tr>
<tr>
<td>Crack morphology</td>
<td>TG or IG, branched, sharp tip</td>
<td>TG, unbranched, blunt tip</td>
<td>TG or IG, unbranched, sharp tip</td>
</tr>
<tr>
<td>Corrosion product in</td>
<td>Absent (usually)</td>
<td>Present</td>
<td>Absent (usually)</td>
</tr>
<tr>
<td>crack</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crack surface appearance</td>
<td>Cleavage-like</td>
<td>Beach marks/striations</td>
<td>Cleavage-like</td>
</tr>
</tbody>
</table>