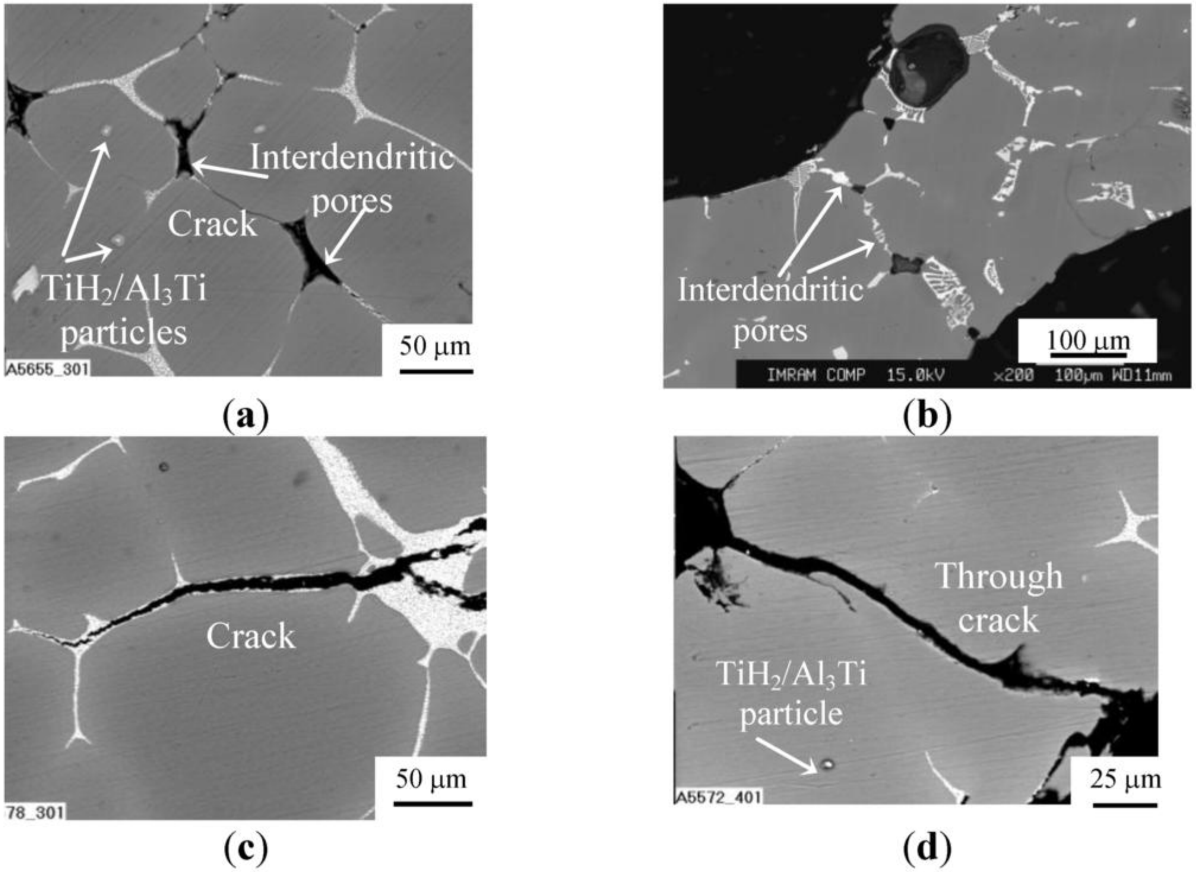
Chapter (5-B)

FORMS OF CORROSION-Part B

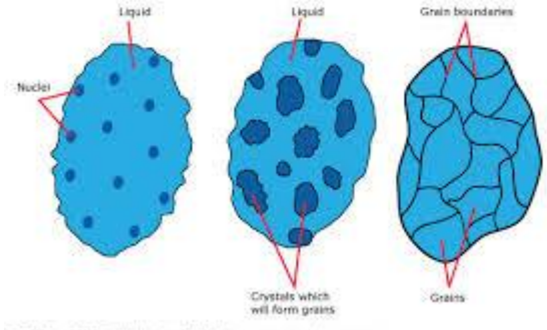


Sept.7th , 2017

5. INTER-GRANULAR ATTACK (IGA)

- Inter-granular attack **(IGA)** refers to preferential corrosion along the grain boundaries:
  - **Grains are 'crystals' usually on a microscopic scale, that constitute the microstructure of the metal and alloys.**
  - **By analogy, they are like the grains of sand which constitute a sandstone.**

Description of IGA



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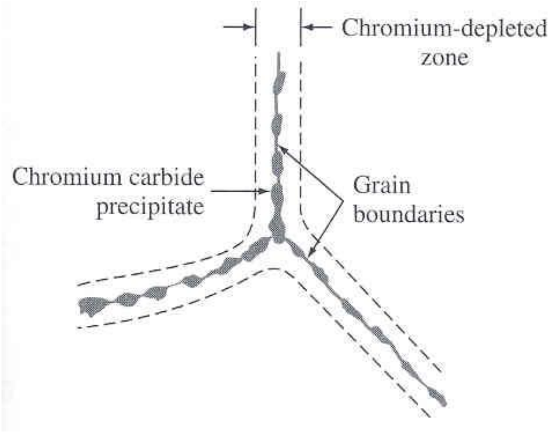
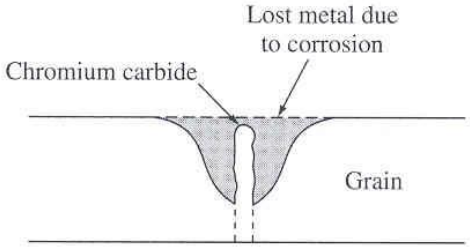
- Metals are crystalline materials. They consist of grains.

  As corrosion proceeds along the grain boundaries, the grains become weaker particularly at the grain boundaries and they eventually disintegrate.
- It is a form of localized attack on the grain boundaries of a metal or alloy in corrosive media, which results in the loss of strength and ductility.

Intergranular corrosion

- Localized corrosion at and/or adjacent to highly reactive grain boundaries resulting in disintegration.
- When stainless steels are heated to or cooled through sensitizing temperature range (500-800°C) chromium carbide precipitate along grain boundaries.
- When exposed to corrosive environment, the region next to grain boundaries become anodic and corrode.





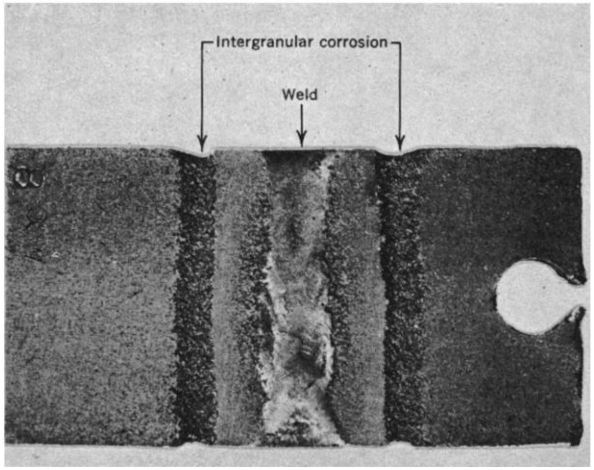
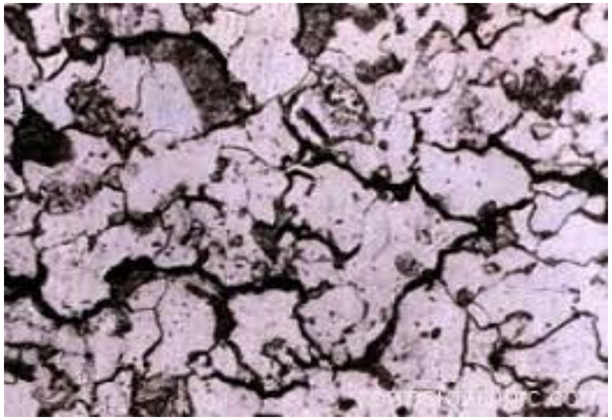


Figure 17.10 Weld decay in a stainless steel. The regions along which the grooves have formed were sensitized as the weld cooled. (From H. H. Uhlig and R. W. Revie, *Corrosion and Corrosion Control*, 3rd edition, Fig. 2, p. 307. Copyright © 1985 by John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.)

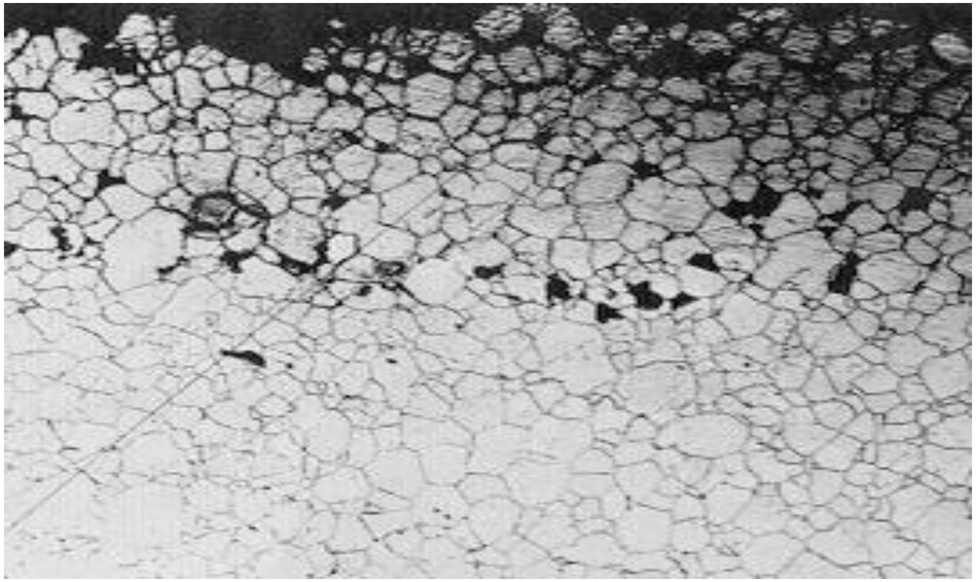
INTER-GRANULAR ATTACK



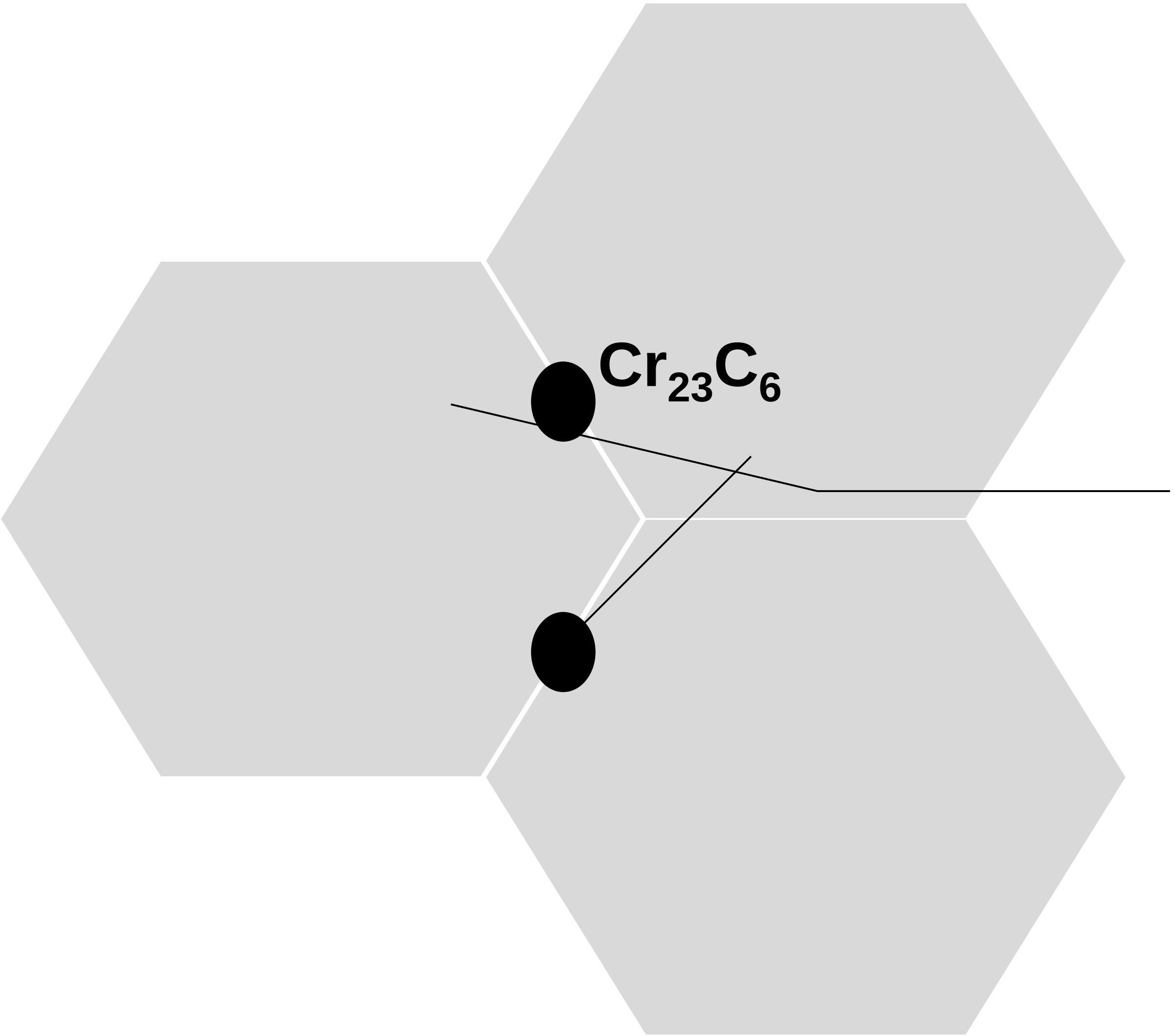
1. It works inwards between the grains and causes more loss of strength than the same total destruction of metal uniformly distributed over the whole surface.
2. The attack is distributed over all the grain boundaries cutting the surface.
3. There are many materials which are susceptible to intergranular corrosion and not to stress corrosion cracking.
4. The attack is very common on: stainless steel, nickel and aluminum alloys.

Intergranular / Grain Boundary

- The material undergoing IGA is said to be sensitized
- Most significant problem:
  - *Weld decay* of austenitic SS
  - Metal becomes susceptible to IGA corrosion



- Depletion (loss) of Cr, precipitates as Chromium carbide, $Cr_{23}C_6$.



Concentration of Cr decreases near the precipitates

Grain boundaries will be depleted in Cr and will corrode

6. Selective Leaching or Dealloying

1. Corrosion in which one constituent of an alloy is preferentially removed, leaving behind an altered (weakened) residual structure.
2. Selective etching
   - Net removal of one element from an alloy
   - Whole of exposed surface may be attacked
   - Leaving the overall geometry unchanged (compare with uniform attack & pitting)
3. Prime cause of dealloying is **galvanic effect.**
4. Alloy containing one noble element and one base element (e.g. brass, Cu + Zn)
5. Base element can dissolve leaving a matrix of the noble element
   - dezincification of brass (Zn loss)
   - graphitization of grey cast iron (Fe loss)
6. May be reduced by addition of Tin.

Combinations of alloys and environments subject to dealloying and elements preferentially removed

Alloy	Environment	Element removed
Brasses	Many waters, especially under stagnant conditions	Zn (dezincification)
Grey iron Aluminum bronzes	Soils, many waters HCl, acids containing Chloride	Fe (graphitic corrosion) Al (dealuminification)
Silicon bronzes	High-temperature steam and acidic species	Si (desiliconification)
Tin bronzes Copper-nickels	Hot brine or steam High heat flux and low water velocity (in refinery condenser tubes)	Sn (destannification) Ni (denickelification)
Copper-gold single crystals Monels	Ferric chloride Hydrofluoric and other acids	Cu Cu in some acids, and Ni in others
Gold alloys with copper or silver High-nickel alloys	Sulfide solutions, human saliva Molten salts	Cu, Ag, Cr, Fe, Mo and T
Medium- and high-carbon steels	Oxidizing atmospheres, hydrogen at high temperatures	C (decarburization)
Iron-chromium alloys	High-temperature oxidizing atmospheres	Cr, which forms a protective film
Nickel-molybdenum alloys	Oxygen at high temperature	Mo

DEZINCIFICATION: a known de-alloying case

1. It is a form of corrosion in which zinc is selectively attacked in zinc-containing alloys, like brasses.
2. It mainly occurs in alloys containing less than 85% copper.
3. De-alloying and selective leaching are broader terms which refer to the corrosion of one or more constituent of a solid solution alloy.
4. Dezincification is a form of de-alloying.
   - **As the phenomenon was first observed in brass in which zinc separated by dissolution from copper, the term dezincification is still used.**
5. Ordinary brass consists of about 30% zinc and 70% copper.
6. Dezincification can be observed by naked eyes, because the alloy changes in colour from yellow to red.

TYPES OF ATTACK

Brass Alloy (sieves)

Two types of dezincification are commonly observed:

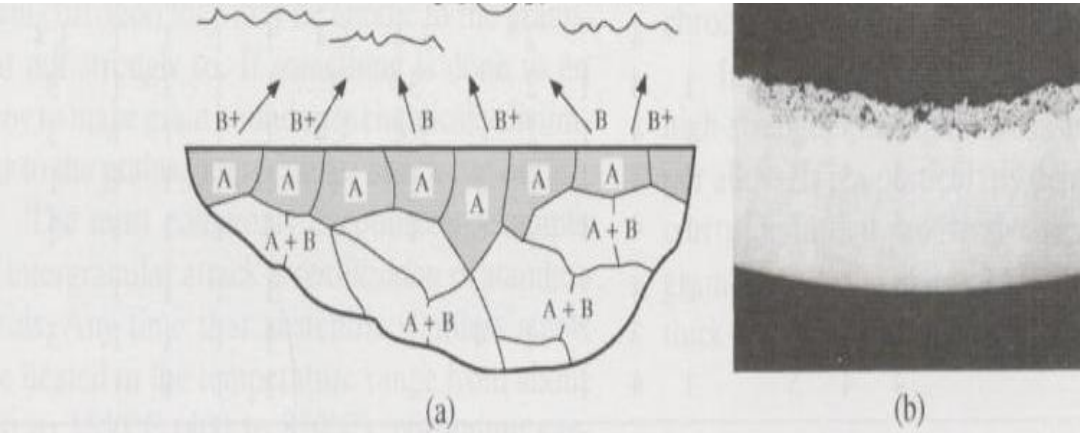
1. Uniform (layer) type:

- **The active area is leached out over a *broad area of the surface* and it is not localized to a certain point of the surface.**
- **Usually found in high brasses (high Zn content) and acid environments.**

2. Plug type:

- **This attack is *localized, at a certain point on the surface* and the surrounding area remains unaffected.**
- **Usually found in low brasses, alkaline, neutral or slightly acid environments.**

(See graphs on next slide………).



igure 13–18
) Dealloying in the form of dezincification of a brass part; zinc has been removed from
e surface, which leaves weak copper. (b) (×40)

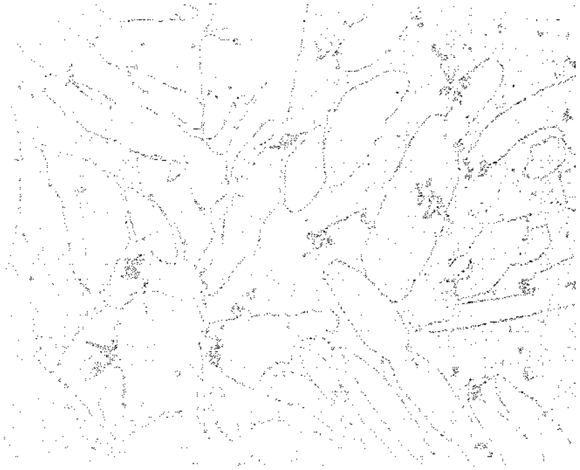
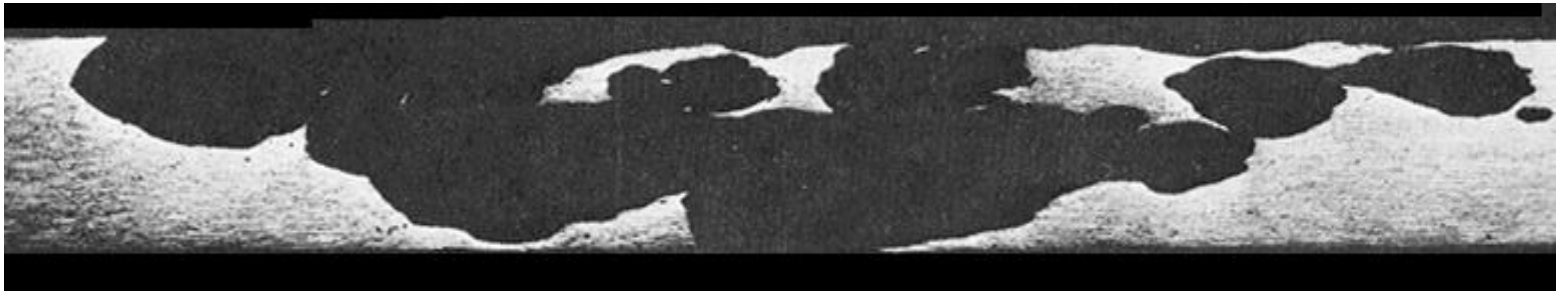


Figure 4.9 Dezincification of α β brass (500 x 300)

Uniform or “Broad” Layer Type



Plug Type (localized)

ENVIRONMENT:

- ➢ Dezincification generally takes place in water under *stagnant conditions.*

- ➢ Copper-zinc alloys containing more than 15% zinc are susceptible to dezincification (less than 85% copper).

Remarks on Dezincification:

- ❑ Overall dimensions of original material tend to be retained. The residual is spongy and porous, often brittle.

- ❑ Can go unnoticed, especially if covered with dirt or deposits.

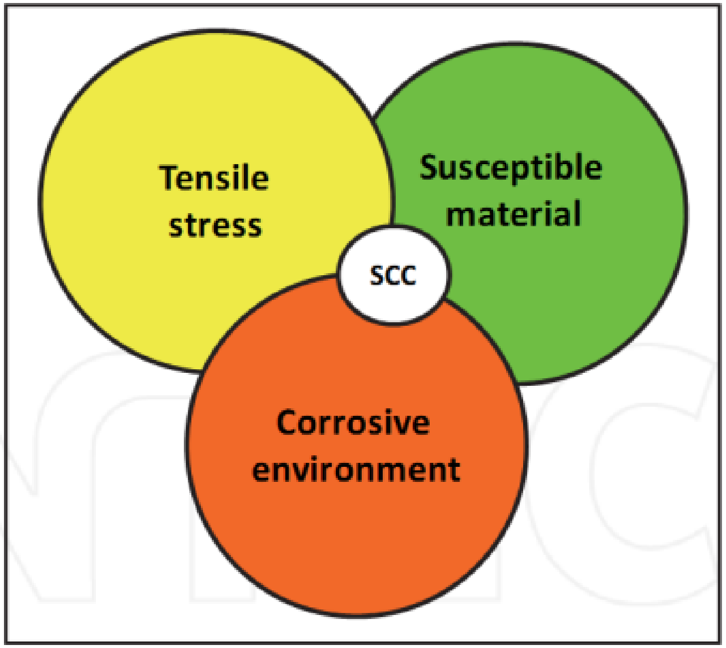
7. Stress Corrosion Cracking

- ❖ Combined action of applied tensile stress and a corrosive environment on susceptible material.

- ❖ Caused by either:

1. ***Residual internal stress in the metal*:**
   - **Unequal cooling from high temperature**
   - **Cold forming**
   - **Volume change**

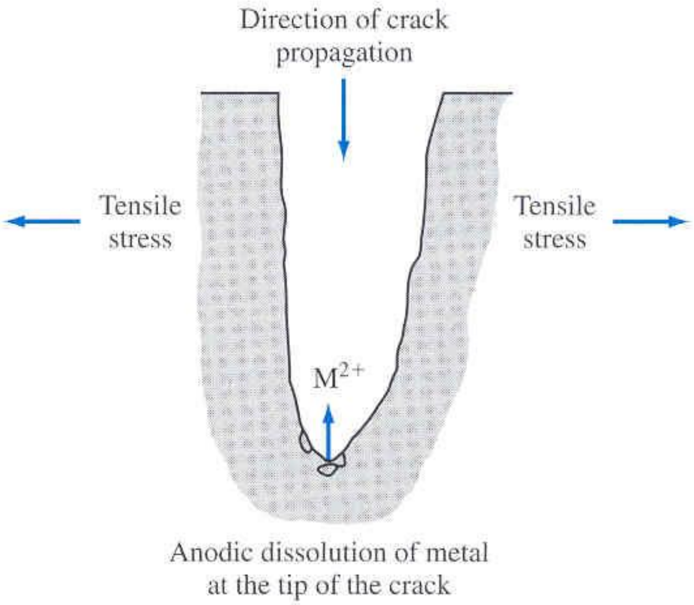
2. ***An externally applied stress:***
   - **Faulty design**
   - **Vibrations**
   - **Thermal effect (expansion or contraction)**

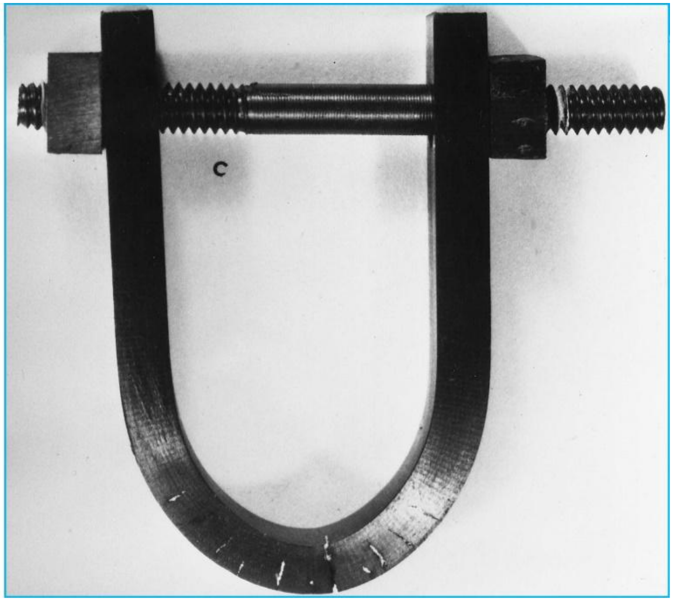


Conditions necessary for SCC occur.

Stress Corrosion Cracking (SCC)

- Cracking caused by combined effect of tensile stress and corrosive environment
- Stress might be residual and applied
- Only certain combination of alloy and environment causes SCC
- Crack initiates at pit or other discontinuity
- Crack propagates perpendicular to stress
- Crack growth stops if either stress or corrosive environment is removed.



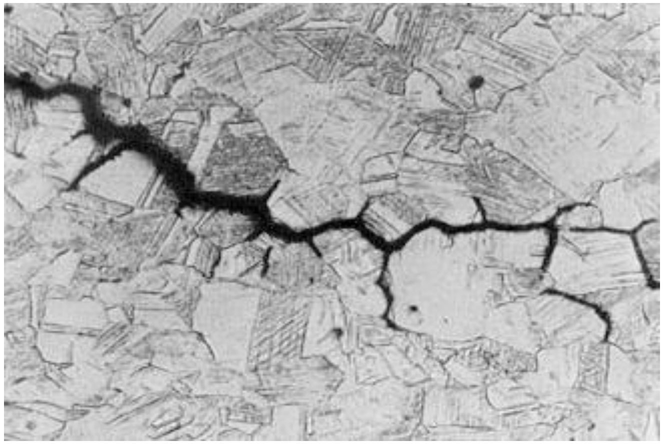


Photograph showing a bar of steel that has been bent into a "horseshoe" shape using a nut-and-bolt assembly. While immersed in seawater, stress corrosion cracks formed along the bend at those regions where the tensile stresses are the greatest. (Photograph courtesy of F. L. LaQue. From F. L. LaQue, *Marine Corrosion, Causes and Prevention.* Copyright © 1975 by John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.)

Stress Corrosion Cracking

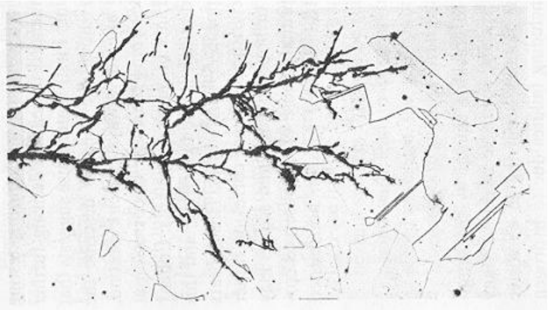
Mechanism:

1. Anodic dissolution
2. Hydrogen embrittlement
3. Film-induced cleavage



Example of Stress Corrosion
Aloha Flight 243
(28 APR 1988)

Stress Corrosion Cracking



1. Causes rupture of the film
2. Occurs in three stages:
    - Initiation: Slow attack which produces a pit
    - Slow crack growth plus corrosion enhances propagation
    - Rapid failure.
3. Cause of major industrial costs and safety hazards
4. stress corrosion is more dangerous than Intergranular corrosion.

Hydrogen Embrittlement:

1. When electrochemically generated, hydrogen *dissolves at the metal surface* then it migrates to stressed locations.
2. There, it can reduce the bond strength between metal atoms, so that they separate under applied stress.

Factors important in SCC:

a) Environmental Factors: No general pattern ….. SCC is common in:

1. aqueous solutions
2. liquid metals
3. fused salts
4. non-aqueous inorganic liquids . . .

e.g.

- **Brasses crack in NH_3, not in Cl^-**
- **Stainless Steels crack in Cl^-, not in NH_3**
- **Stainless Steels crack in caustic, not in acids (H_2SO_4, HNO_3, CH_3COOH, etc.)**
- **Inconel-600 cracked in pure water at 300°C.**

b) Stress:

1. The greater stress on material, the quicker it will crack.
2. In fabricated components, there are usually RESIDUAL STRESSES from cold working, welding, surface treatment such as grinding, etc.
3. APPLIED STRESSES from the service, such as hydrostatic, vapor pressure of contents, bending loads, etc.

SCC:

c) Temperature: Increasing temperature accelerates SCC:

- Most susceptible alloys crack ~ 100°C
- Mg alloys crack at *room temperature.*
- Alternate wetting and drying (due to ambient conditions) may aggravate SCC by accelerating crack growth;

  (*possibly because of increasing concentration of corrosive component as dryness is approached*).

d) Material composition and microstructure.

Environments that may cause stress corrosion of metals and alloys

Material	Environment
Aluminum alloys	$NaCl-H_2O_2$ solutions
	NaCl solutions
	Seawater
Copper alloys	NH_3 (g & aq)
	Amines
	Water, Water vapor
Gold alloys	$FeCl_3$ solutions
	Acetic-acid-salt solutions
Inconel	Caustic soda solutions
Lead	Lead acetate solutions
Magnesium alloys	$NaCl-K_2CrO_4$ solutions
	Rural and coastal atmospheres
	Distilled water
Monel	Fused caustic soda
	Hydrofluoric acid
	Hydrofluosilicic acid
Nickel	Fused caustic soda

Material	Environment
Ordinary steels	NaOH solutions
	$NaOH-Na_2SiO_2$ solutions
	Ca, NH_3, and $NaNO_3$ solutions
	Air, Water vapor
	Mixed acids ($H_2SO_4-HNO_3$)
	HCN solutions
	Acidic H_2S solutions
	Seawater
	Molten Na-Pb alloys
Stainless steels	Acid chloride solutions such as $MgCl_2$ and $BaCl_2$
	$NaCl-H_2O_2$ solutions
	Seawater
	H_2S
	$NaOH-H_2S$ solutions
	Condensing steam from chloride waters
Titanium alloys	Red fuming HNO_3, N_2O_4, seawater, methanol-HCl

SCC Systems : common examples

1. Brass and ammonia (often in local atmospheres).
2. Austenitic stainless steels (+16% Cr) and chloride solutions (70^{o}C)**.
3. Carbon steels in caustic, carbonate/ bicarbonate, nitrate and phosphate.
4. High-strength aluminium alloys in water or water vapour.

** 70% of all stainless steels produces (300 series).

8. Erosion (Velocity-Accelerated) Corrosion

- Corrosion accelerated by impact of solid particles carried by fluid. These particles may:
  1. remove metal, or
  2. remove oxide film and allow

     metal to corrode more quickly
- Also, the formation of protective film may be inhibited or slowed down.

Erosion corrosion

- Acceleration in rate of corrosion due to relative motion between corrosive fluid and surface.
- Pits, grooves, valleys appear on surface in direction of flow.
- Corrosion is due to abrasive action and removal of protective film.

FIGURE 17.11 Impingement failure of an elbow that was part of a steam condensate line. (Photograph courtesy of Mars G. Fontana. From M. G. Fontana, *Corrosion Engineering*, 3rd edition. Copyright © 1986 by McGraw-Hill Book Company. Reproduced with permission.)

EROSION CORROSION

An increase in corrosion brought about by a high relative velocity between the corrosive environment and the surface.

Removal of the metal may be:

1. *as corrosion product* which “spalls off *as fragments*” the surface because of the high fluid shear and bares the metal beneath;
2. *as metal ions*, which are swept away by the fluid flow before they can deposit as corrosion product.

EROSION CORROSION

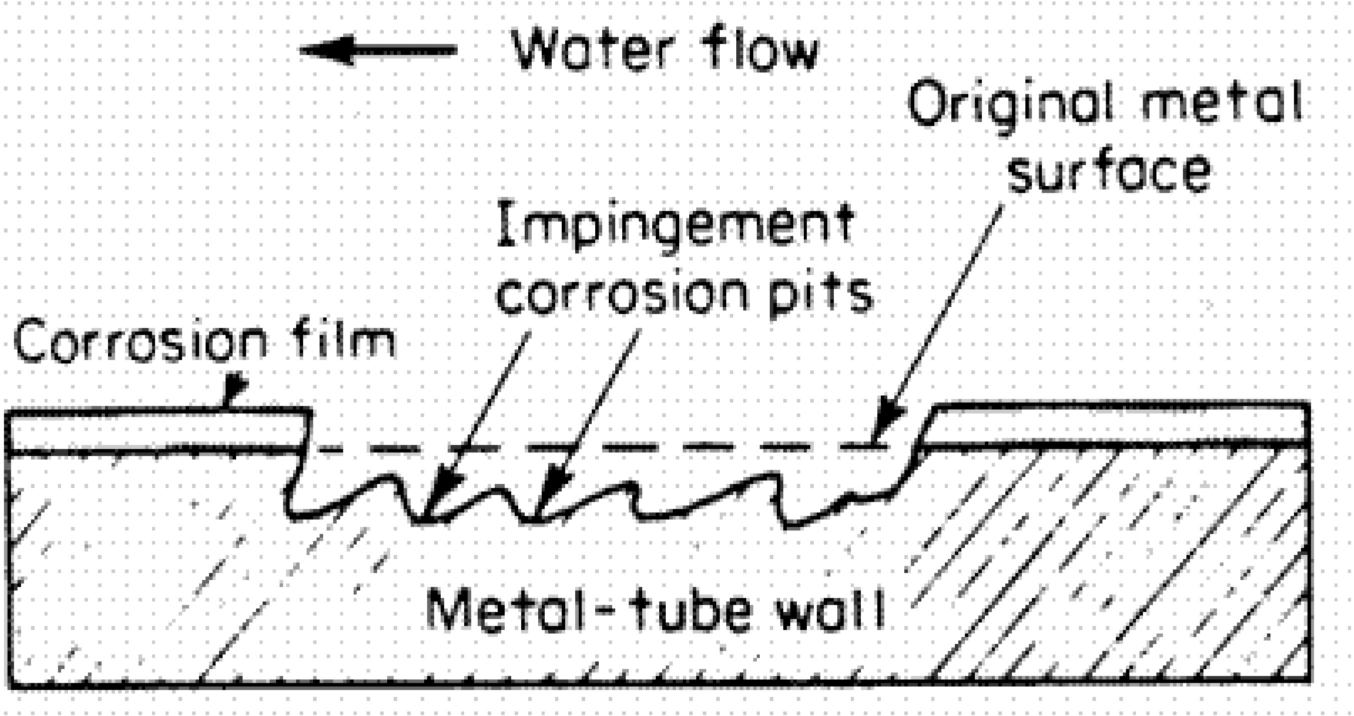
Distinction between Erosion-corrosion and Erosion:

Erosion is the straightforward wearing away by the mechanical abrasion caused by suspended particles,

- e.g., sand-blasting, erosion of turbine blades by droplets.

- ***Erosion-corrosion*** also involves a corrosive environment : The metal undergoes a chemical reaction.

Erosion-corrosion produces a distinctive surface finish: grooves, waves, holes, etc., all oriented with respect to the fluid flow pattern.



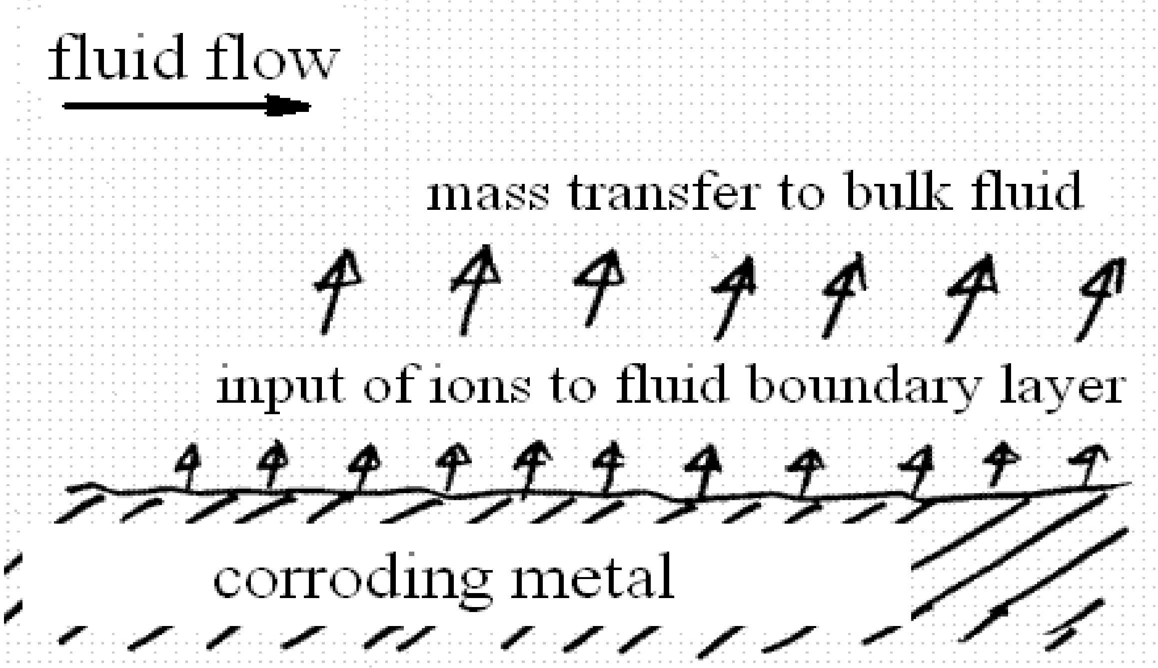
Erosion-corrosion of condenser tube wall

Most metals / alloys are susceptible to erosion-corrosion.

- Metals that rely on protective surface film for corrosion protection are particularly vulnerable, e.g.

  Al Pb SS CS

- **Attack occurs when:**
  - a protective film cannot be formed because of erosion caused by suspended particles (e.g.), or
  - rate of film formation is less than rate of dissolution and transfer to bulk fluid.



Vulnerable Equipment include:

- pipes (bends, elbows, tees);
- valves;
- pumps;
- blowers;
- propellers, impellers;
- stirrers;
- stirred vessels;
- H. Ex. tubing (heaters, condensers);
- flow-measuring orifice, venturis;
- turbine blades;
- nozzles;
- baffles;
- metal-working equipment (scrapers, cutters, grinders, mills);
- spray impingement components;
- etc…..

9. Fretting Corrosion

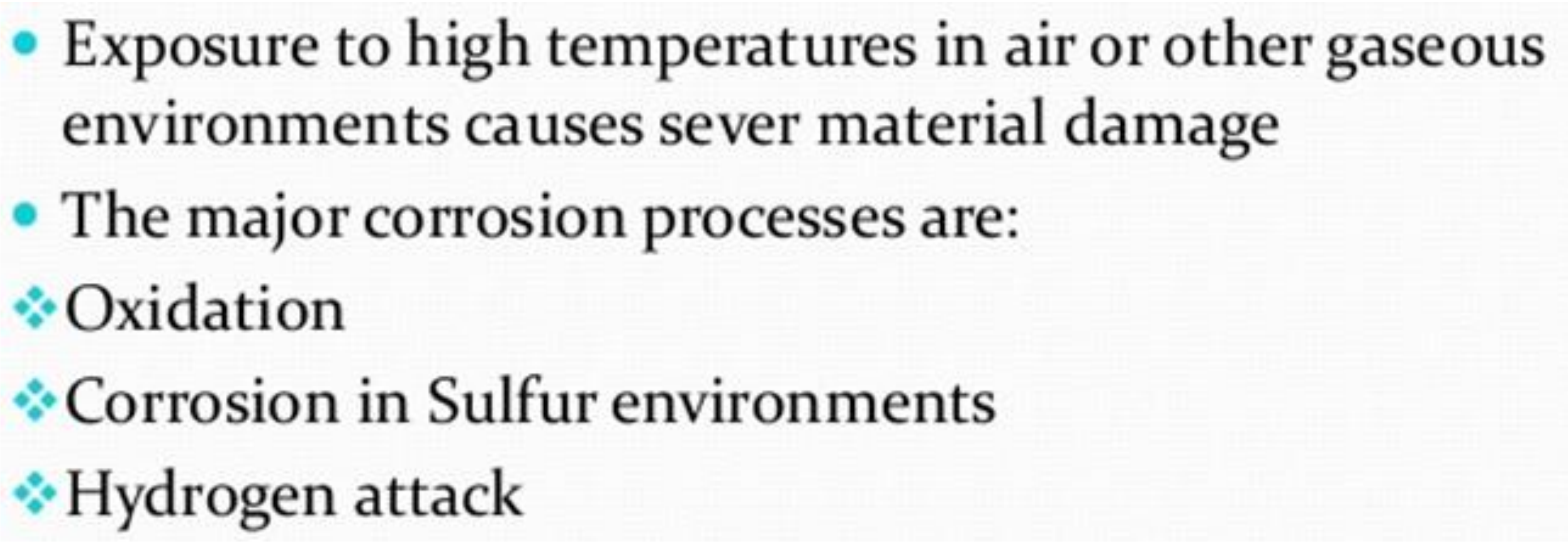
- Occurs at interface between materials under load subjected to vibration and sliding
- Metal fragments get oxidized and act as abrasives between the surfaces

Example of Fretting Corrosion

10. High Temperature Dry Corrosion

1. absence of liquid phase or above dew point of the environment.
2. vapors and gases are usually the corrosive materials.
3. often associated with high temp.

e.g: attack on steel by furnace gases.



- Exposure to high temperatures in air or other gaseous environments causes sever material damage
- The major corrosion processes are:

❖ Oxidation

❖ Corrosion in Sulfur environments

❖ Hydrogen attack