Corrosion and oxidation corrosion and protect of materials

بارم بندی کلاس

فعالیت کلاسی

کوییزهای مستمر

پایان ترم

references

1-Corrosion Engineering: Mars, G. Fontana

2-Fundamentals of Corrosion, Philip A. Schweitzer

3- Introduction to Corrosion, Edward Mc-Cafferty

content

content

content

content

content

content

Why Study Corrosion?

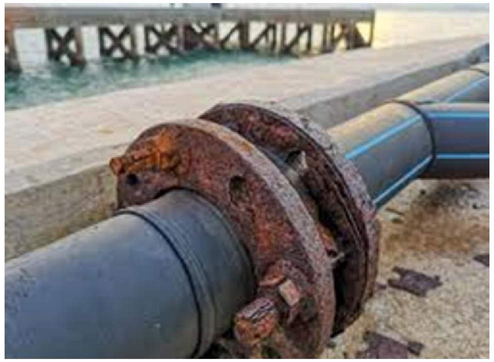
- There are four main reasons to study corrosion. Three of these reasons are based on societal issues

regarding (i) human life and safety, (ii) the cost of corrosion, and (iii) protection of materials. The fourth reason is that corrosion is inherently a difficult phenomenon to understand, and its study is in itself a challenging and interesting pursuit.

On December 15, 1967, the Silver Bridge connecting Ohio and West Virginia over the Ohio River collapsed, and 46 people lost their lives. The cause of the collapse was stress-corrosion cracking

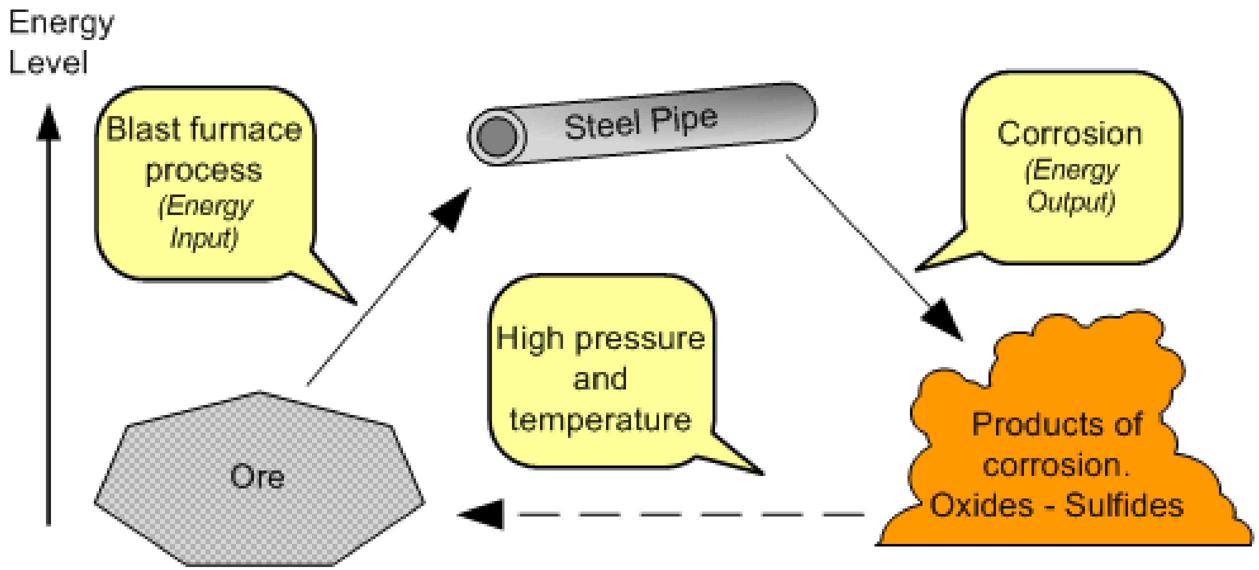






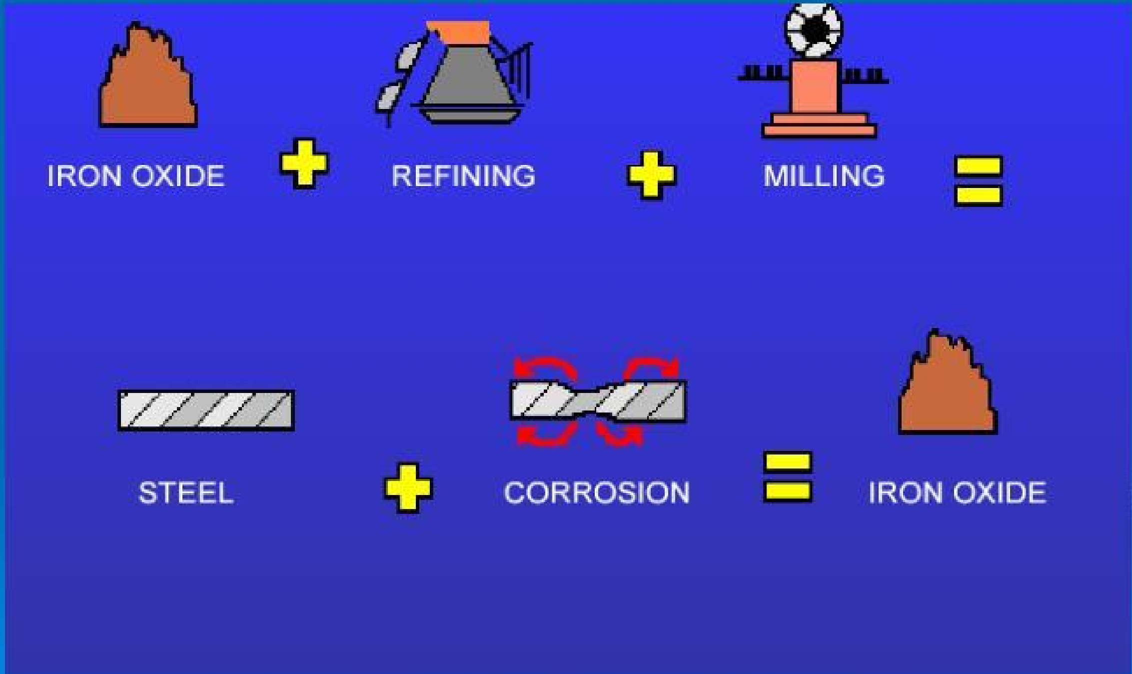
Definitions

- Carrosion - is the changing of the surface of a metal element into a compound (oxide)
  - Silver + oxygen ⟶ silver oxide
- Rusting - is the special name given to the corrosion of iron
  - Iron + oxygen ⟶ iron (III) oxide



Energy Level
Blast furnace process (Energy Input)
Steel Pipe
Corrosion (Energy Output)
High pressure and temperature
Ore
Products of corrosion. Oxides - Sulfides

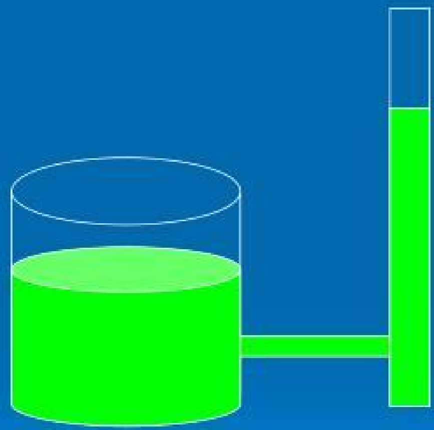
Corrosion

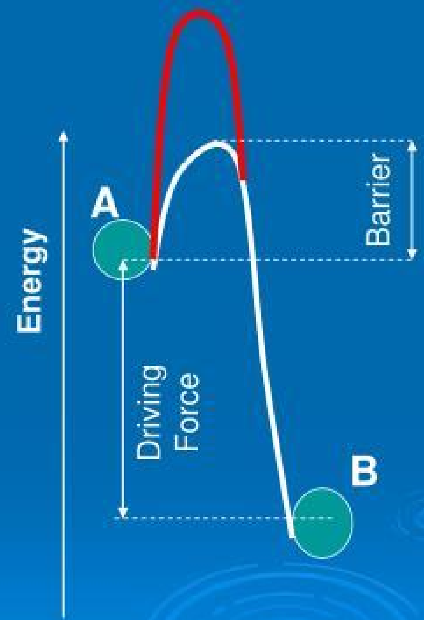


Driving force

- Every Process to take place, we should have some driving force.
- The driving force depends on the energy of the first state and that of the final state.

Driving force





Dr. Eng. Hamid A. Nagy

Thermodynamics

- Every material has two sources of its energy
  - Heat content, Enthalpy
  - Content depending on its randomness, Entropy.
- We can not measure this energy directly.
- So we have a reference zero value which is the hydrogen molecule formation.

Thermodynamics

- Now consider the reaction between two materials a and B to produce C.
- The same law applies.

$$\Delta G_A + \Delta G_B > \Delta G_C$$

For the reaction to proceed in the direction

$$A + B \rightarrow C$$

And vice versa.

Kinetics

- Rate of reaction depends on what is called mechanism.
- There should be some energy done to activate the first stage.
- This is called the energy barrier.
- This energy barrier could be high or low depending on the mechanism.

Dr. Eng. Hamid A. Nagy

Kinetics

- Overcoming energy barrier may consist of several steps.
- The rate of occurrence of this reaction depends on the interaction of steps to overcome energy barrier.
- There is usually what is called rate determining step.
- Determining the rate of the reaction is what is called KINETICS.

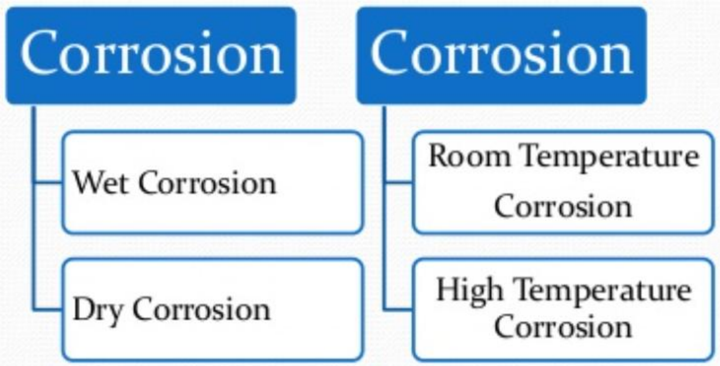
EFFECTS OF CORROSION

- *Reduces Strength*
- *Life time is reduced*
- *Metallic properties are lost*
- *Wastage of metal*

FORMS OF CORROSION

Corrosion may be classified in different ways:

- Wet / Aqueous corrosion & Dry Corrosion
- Room Temperature/ High Temperature Corrosion



WET & DRY CORROSION

- ***Wet / aqueous corrosion*** is the major form of corrosion which occurs at or near room temperature and in the presence of water

- ***Dry / gaseous corrosion*** is significant mainly at high temperatures

Differences between dry and wet corrosion

Dry corrosion	Wet corrosion
• Corrosion occurs in the absence of moisture.	• Corrosion occurs in presence of conducting medium.
• It involves direct attack of chemicals on the metal surface.	• It involves formation of electrochemical cells.
• The process is slow.	• It is a rapid process.
• Corrosion products are produced at the site of corrosion.	• Corrosion occurs at anode but rust is deposited at cathode.
• The process of corrosion is uniform.	• It depends on the size of the anodic part of metal.

خوردگی:

۱- خوردگی در دمای بالا (اکسیداسیون و خوردگی داغ)

۲- خوردگی در دماهای پایین (خوردگی)

خوردگی:
۱- الکتروشیمیایی

۲- شیمیایی

$$Fe + 1/2\ O = FeO$$

$$Zn + 2H^{+} = Zn^{2+} + H_2$$

$$Cu + H_2SO_4\ (conc.) = CuSO_4 + H_2$$

$$2Cu = 2\ Cu^{2+} + 4e^{-}$$

$$2H_2O + O_2 + 4e^{-} = 4\ OH^{-}$$

$$2Cu + 2\ H_2O + O_2 = 2\ Cu\ (OH)_2$$

خوردگی:
۱- موضعی

۲- یکنواخت

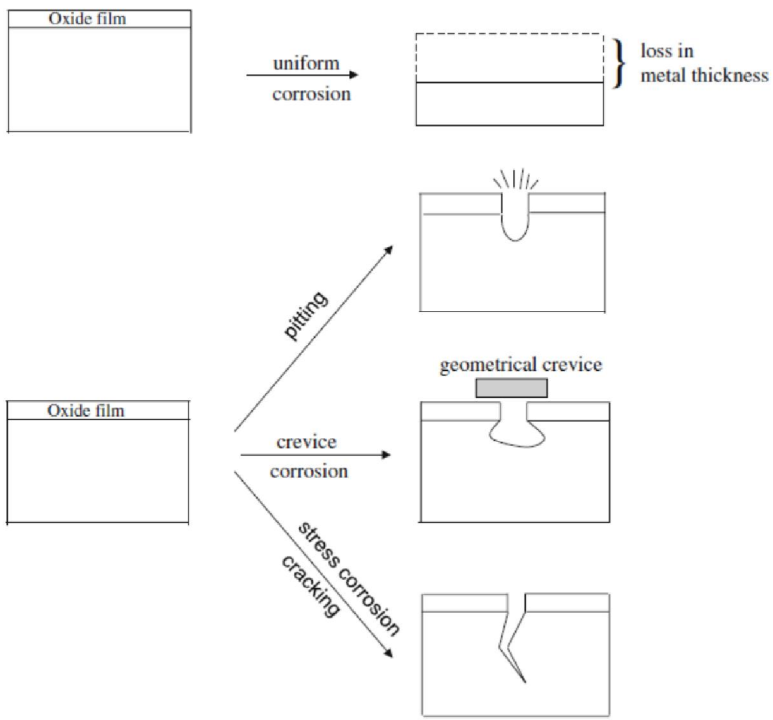


Fig. 2.12 Schematic representation of uniform corrosion (*top*) and three different forms of localized corrosion

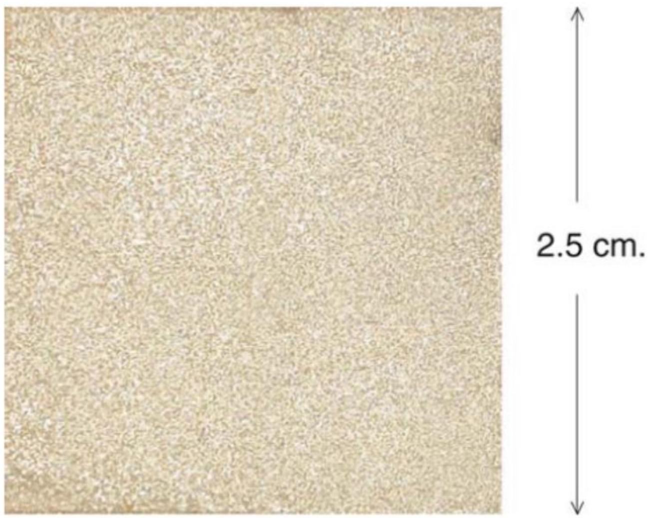


Fig. 2.13 The uniform corrosion of zinc after immersion in hydrochloric acid

فصل دوم

Corrosion rate expression

1- weight loss/time

g/s

mg/h

microgram/year

2- weight loss/time. area

$g/s.cm^2$

$mg/h.in^2$

$microgram/year.mm^2$

3- Thickness/time

Mpy: mil per year

Mils per year (MPY) is a unit of measurement equal to one thousandth of an inch. Mils penetration per year is commonly known as mil in the U.S. measurement system.

$$\text{mpy} = \frac{534W}{DAT}$$

where W = weight loss, mg

D = density of specimen, g/cm^3

A = area of specimen, sq. in.

T = exposure time, hr

This corrosion rate calculation involves whole numbers, which are easily handled.

$$\frac{\mu m}{year} = 87600 \frac{W}{DAT}$$

W → mg

D → g/cm^3

A → cm^2

T → hr

$$mpy = 0.0254 \frac{mm}{year} = 25400 \frac{nm}{ye\ldots}$$

$$= 25.4 \frac{\mu m}{year}$$

mpy = (mil per yeal)

ipy = (inch per year)

$$1 \text{ mil} = \frac{1}{1000} \text{ inch}$$

mdd (naillgram , $decimeter^2$, day)

$$mdd = ipy \times 696 \times D$$

D → gr/cm^3

IMPORTANCE OF CORROSION DATA

5 mpy	Good corrosion resistant material
5 to 50 mpy	Low corrosion resistant material
50 mpy	Unsuitable as constructional material

$M = I \cdot t \cdot e$ کاهش وزن

M → gr

I → A

t → (s)

e → اکی والان شیمیایی

$$e = \frac{M/n}{F}$$

M → جرم اتمی عنصر

M/n → اکی والان وزنی

n → تعداد الکترون ظرفیت

F → فاراده 96494 C/mole

میزان بار الکتریکی در یک مول الکترون

$F = N_A \times q$

N_A → عدد آووگادرو 6.022×10^{23}

q → بار الکترون 1.602×10^{-19} C

کولن

پولاریزاسیون:

۱- کاتدی شامل

اکتیواسیون

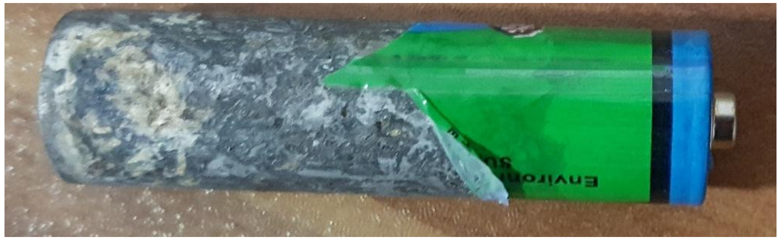
غلظتی

۲- آندی شامل

اکتیواسیون

پسیواسیون

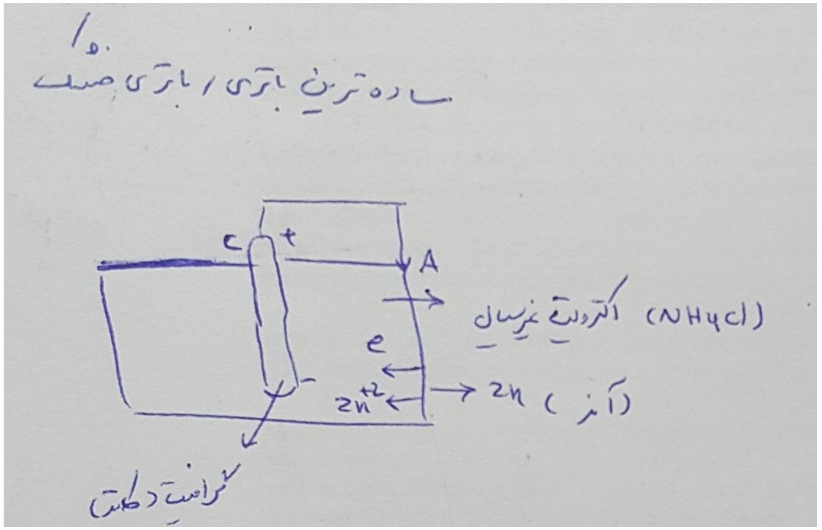
Peel	انگلیسی
Cell	فرانسه
battery	آلمانی



$$Zn \rightarrow Zn^{+2} + 2e$$

$$NH_4Cl \rightarrow NH_4^{+} + Cl^{-}$$

$$H^{+} + e^{-} \rightarrow \tfrac{1}{2} H_2$$



Overall chemical reaction

$$Fe + 2H^+ \rightarrow Fe^{2+} + H_2$$

Oxidation half reaction

$$Fe \rightarrow Fe^{2+} + 2e^-$$

Reduction half reaction

$$2H^+ + 2e^- \rightarrow H_2$$

Neutral or basic conditions w/ oxygen contamination

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_{2,(s)}$$

Carbon dioxide
"Sweet" corrosion

$$Fe + CO_2 + H_2O \rightarrow FeCO_{3,(s)} + H_2$$

Hydrogen sulfide
"Sour" corrosion

$$Fe + H_2S \rightarrow FeS_{(s)} + H_2$$

General corrosion

Galvanic corrosion

$$M^{n+} + ne = M$$

$$\Delta G = -nF\Delta E$$

$$\Delta E = E_c - E_a$$

$\Delta E > 0 \rightarrow$ واکنش صورت می گیرد

$\Delta E < 0 \rightarrow$ واکنش در آن جهت انجام نمی شود

H^+ , Fe

$$\Delta E = E_c - E_a = 0 - (-0.44) = 0.44 > 0$$

volt

E_c: $2H^+ + 2e \rightarrow H_2$

E_a: $Fe \rightarrow Fe^{+2} + 2e$

H^+ , Zn

$$\Delta E = 0 - (-0.763) = 0.763 > 0$$

volt

Cu^{+2} , H^+

$$\Delta E = 0 - (+0.337) = -0.337 < 0$$

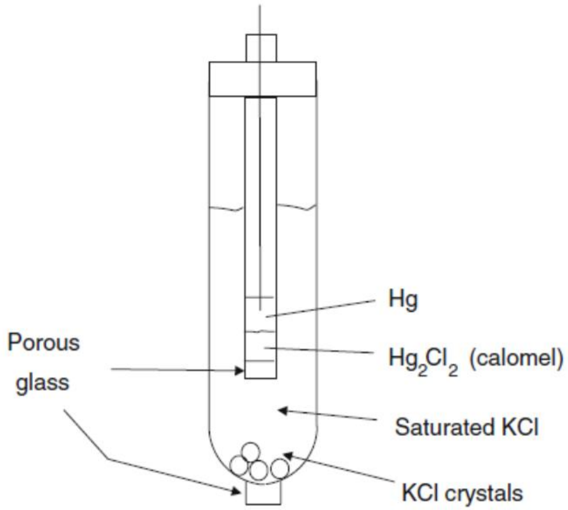


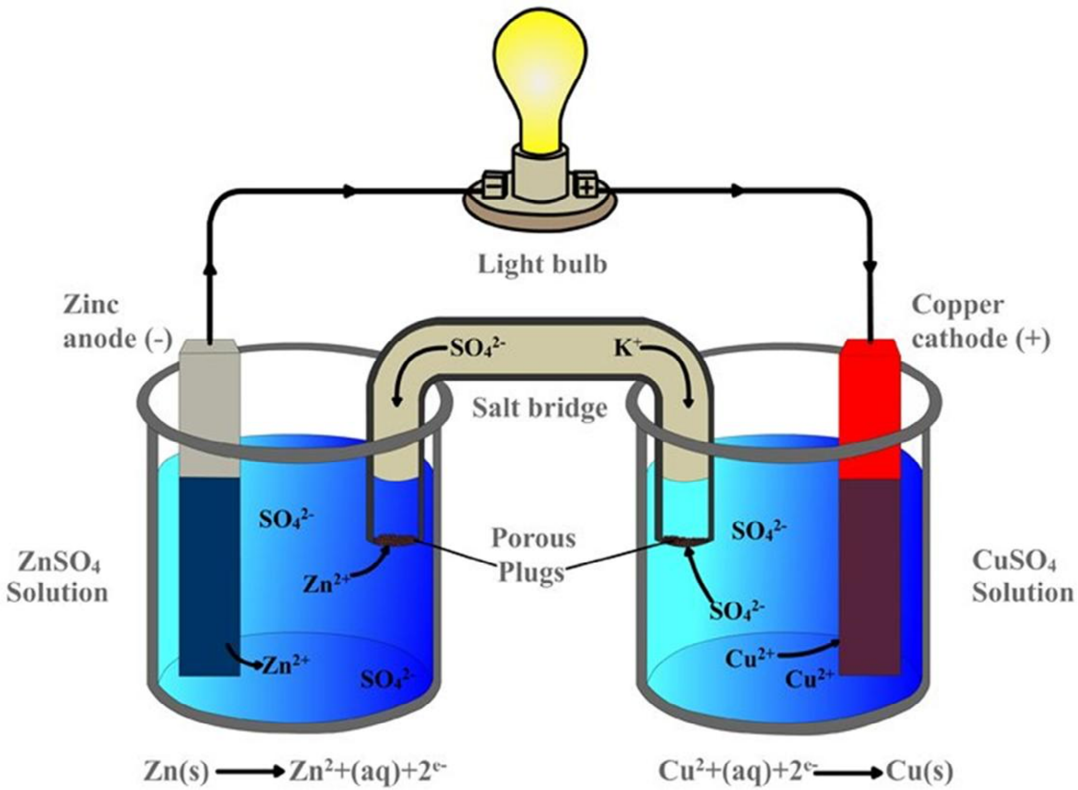
Fig. 3.18 A saturated calomel reference electrode

Types of Local Cell Formations

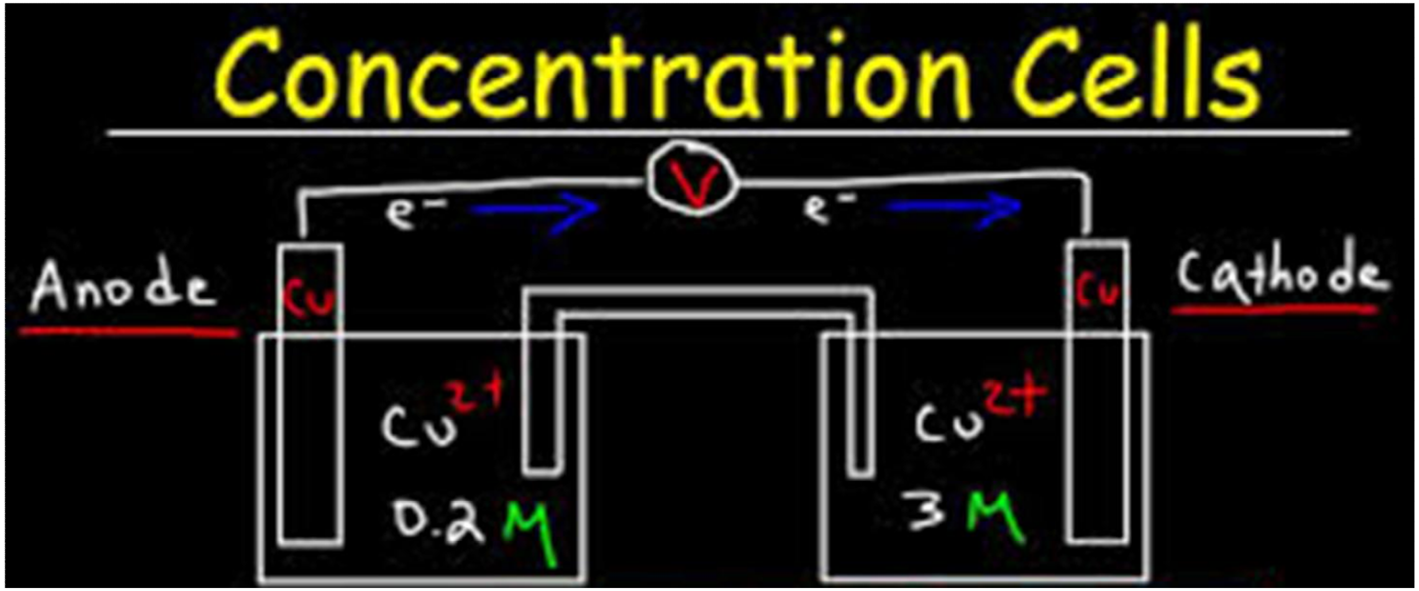
- Three main types of local cell formations leading to corrosion are encountered in practice:

- Dissimilar electrode cells Or Galvanic cell
- Concentration cells:
  - Salt concentration cell
  - Differential aeration cell
- Differential temperature cells

Galvanic cell

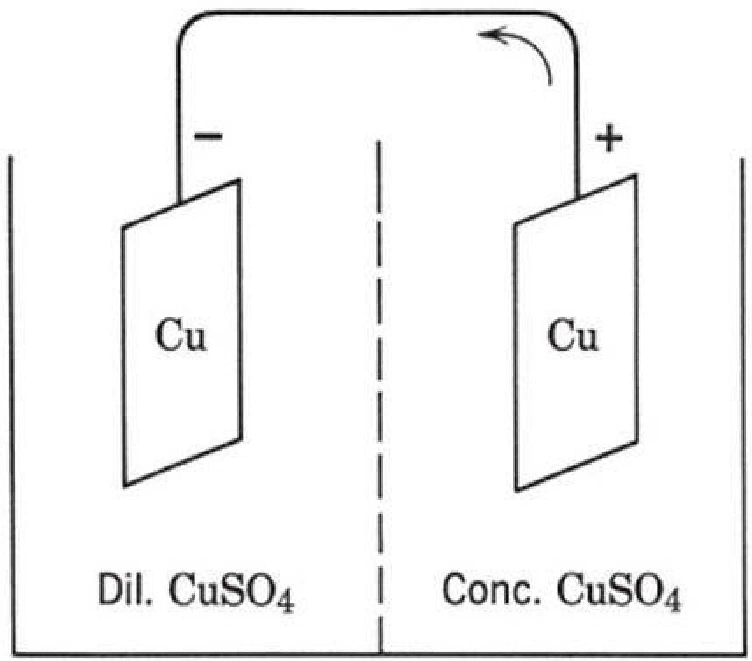


Salt concentration cell



Salt concentration cell

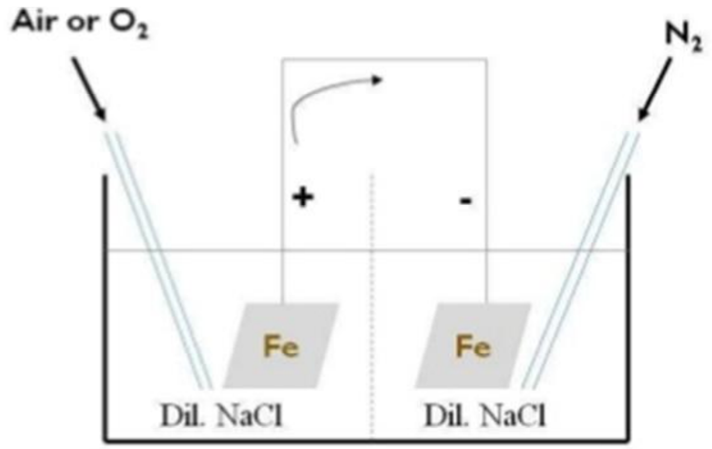
anode



cathode

Differential Aeration Corrosion Cells

cathode

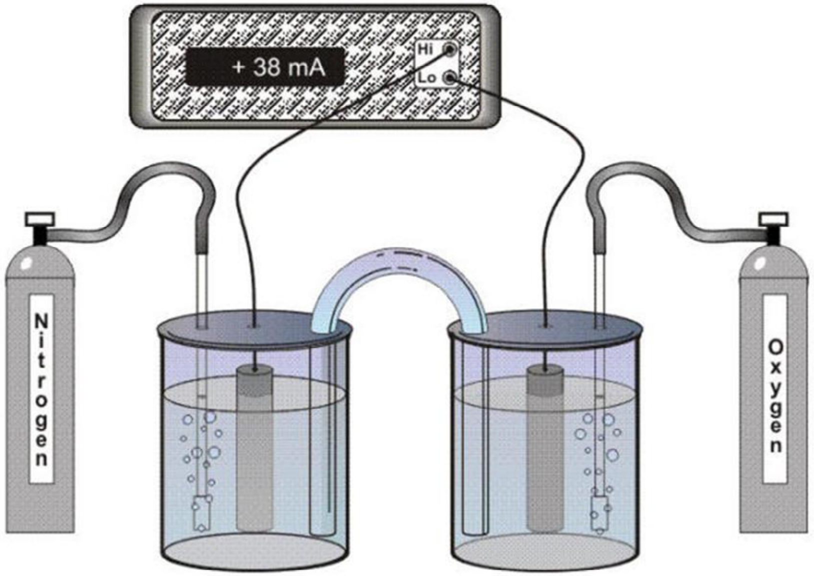


anode

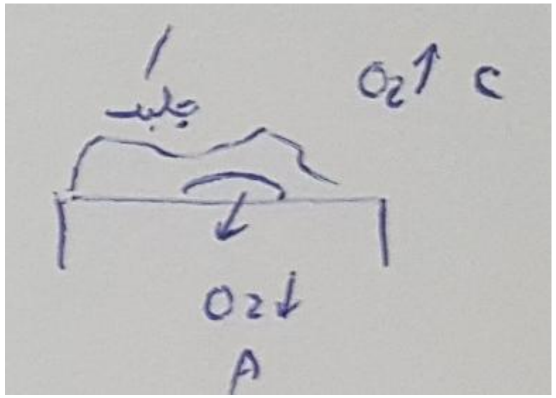
Differential aeration cell

- *Same electrode material*
- *Same electrolyte*
- *Only difference is O_2 concentration (causes potential difference)*

Differential Aeration cell

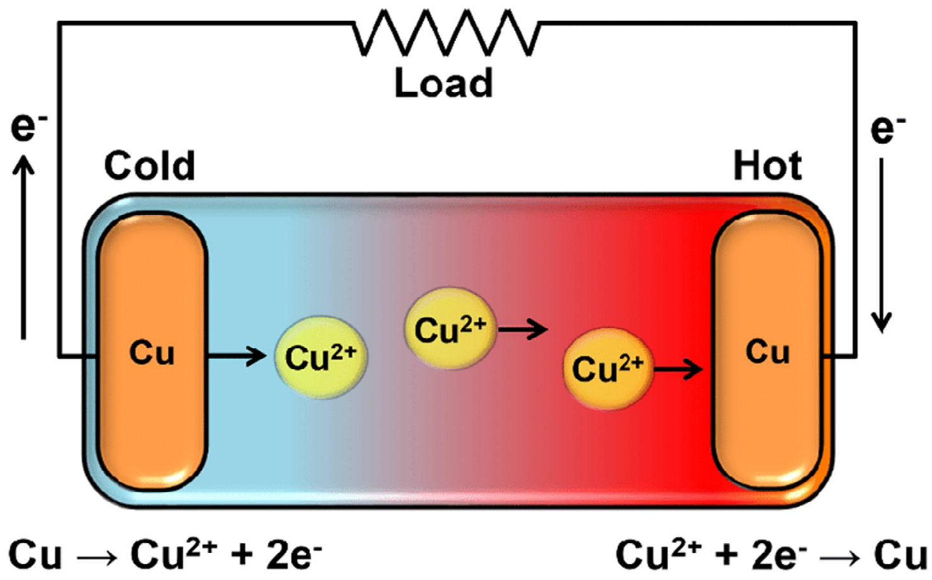


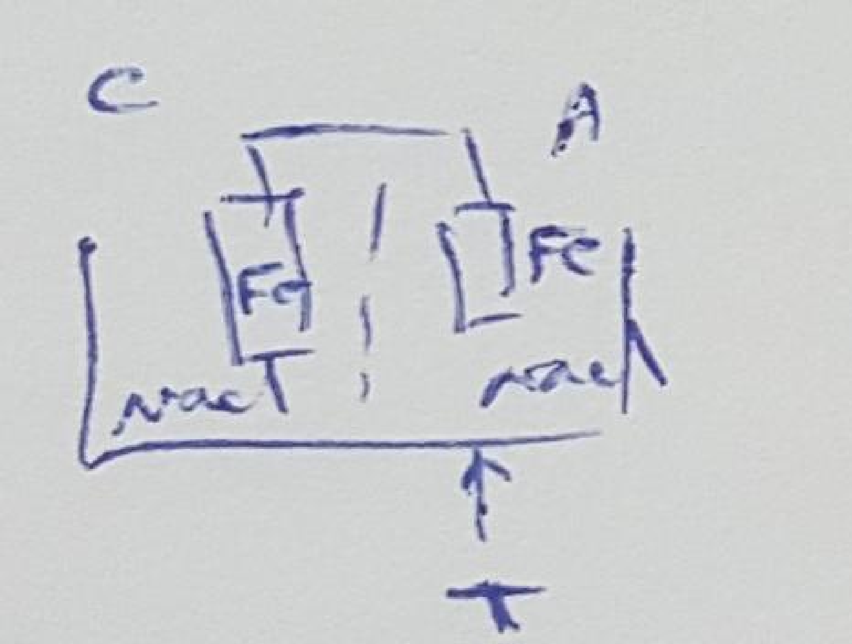
$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$



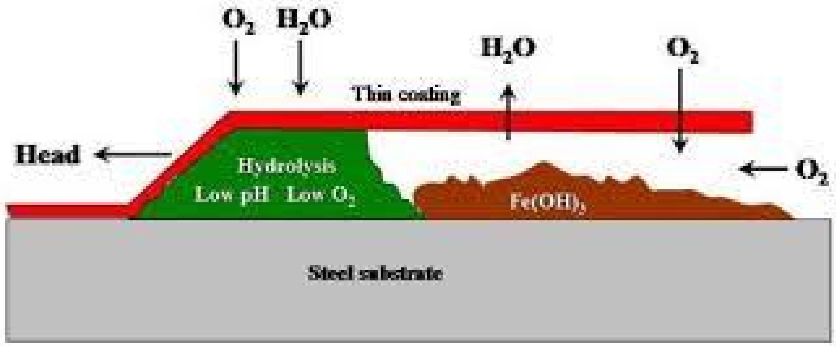
Differential temperature cell

Environment: $CuSO_4$




C
A
Fe
Fe
nacl
nacl

Crevice corrosion



Cross sectional view of a corrosion filament on a steel substrate

Filiform corrosion

ماده ای که مستعد به خوردگی شیاری است مستعد به خوردگی حفره ای نیز هست.

ماده ای که مستعد به خوردگی حفره ای است مستعد به خوردگی شیاری نیز هست.

فولاد زنگ نزن

۱- مارتنزیتی 4xx

۲- فریتی 4xx

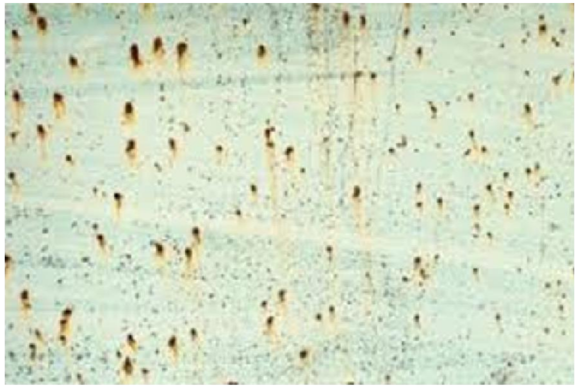
۳- آستنیتی 3xx و 2xx

۴- دو فازی

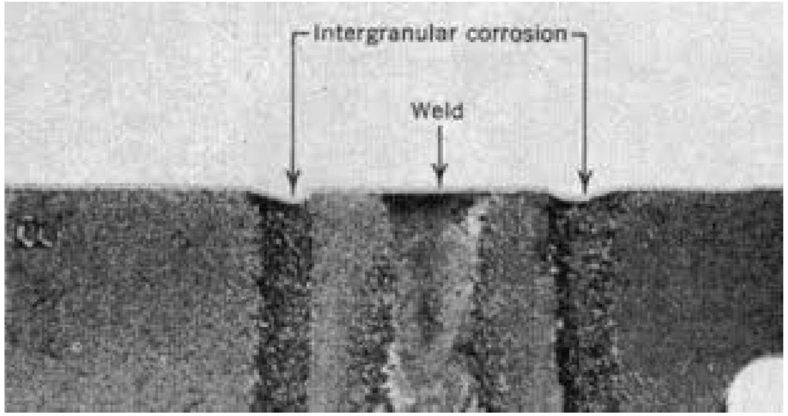
الف- فریتی- استنیتی (Duplex)

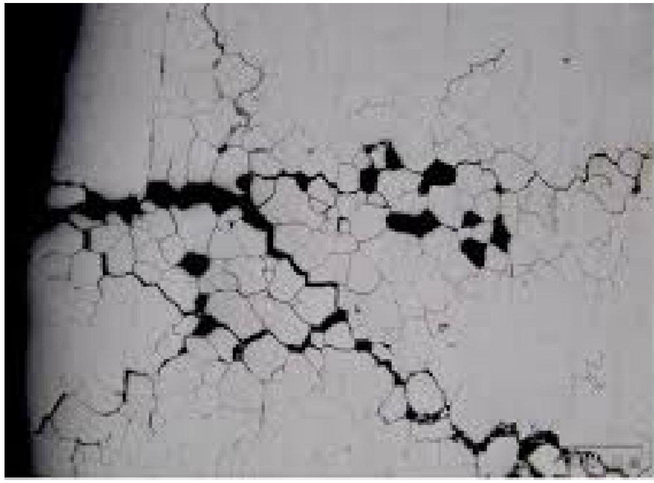
ب- فریتی-مارتنزیتی (Dual)

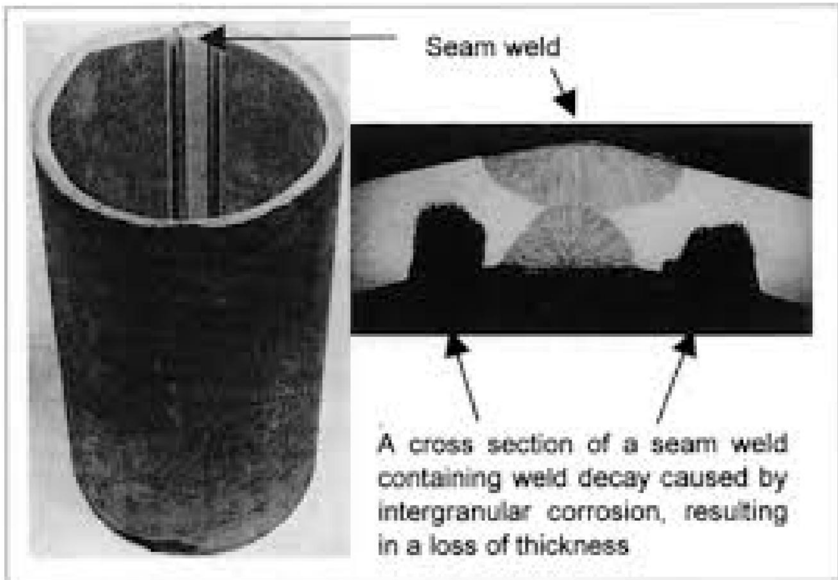
۵- رسوب سختی



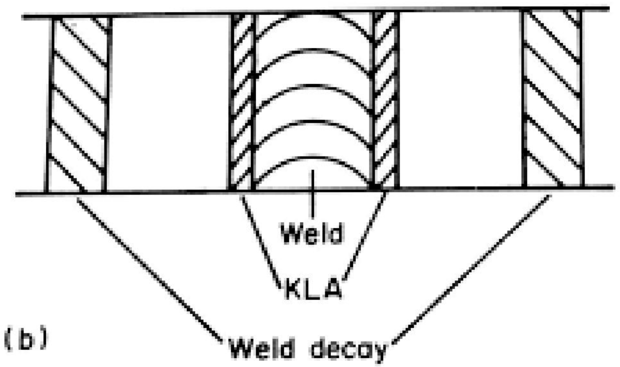
Pitting corrosion


Intergranular corrosion
Weld



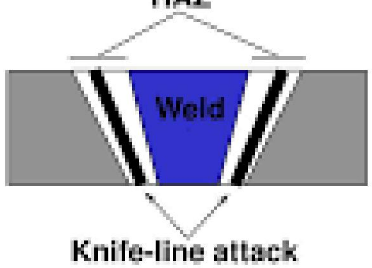

Seam weld
A cross section of a seam weld containing weld decay caused by intergranular corrosion, resulting in a loss of thickness

Weld decay



(b)

Knife-Line Attack in the HAZ



- $Cr_{23}C_6$ precipitate in HAZ
  - Band where peak temperature is 800-1600°F
- Can occur even in stabilized grades
  - Peak temperature dissolves titanium carbides
  - Cooling rate doesn't allow them to form again

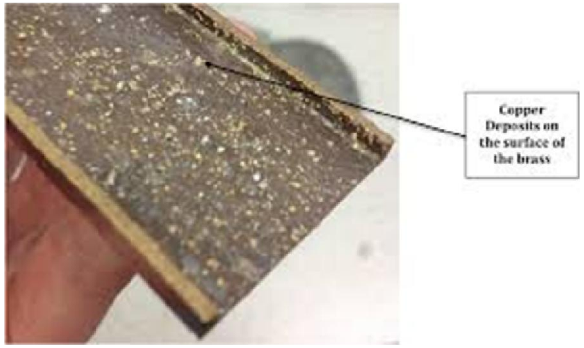
Types of brass

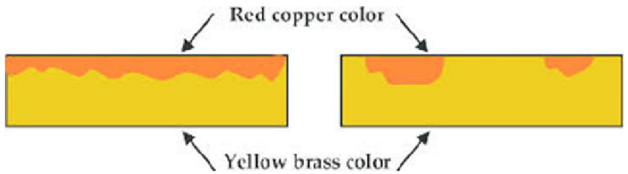
1- 40 % Zn, 60% Cu: muntz brass

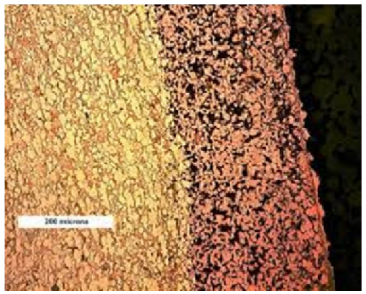
2-35 % Zn, 65% Cu: naval brass

3- 30 % Zn, 70% Cu: yellow brass

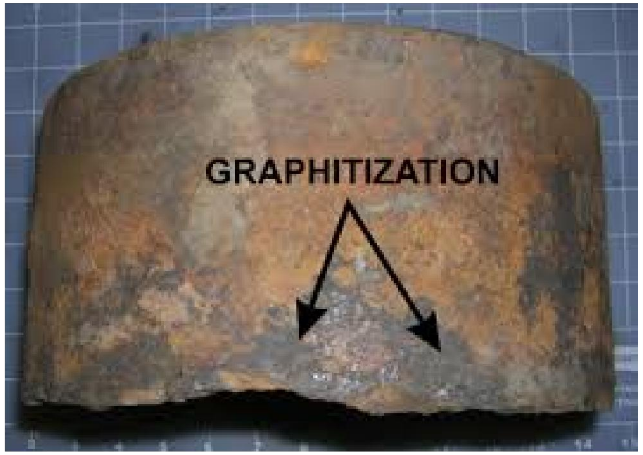
4- 15% Zn, 85% Cu: red brass

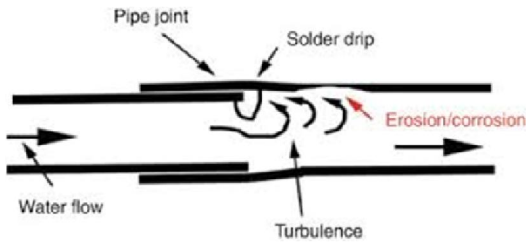




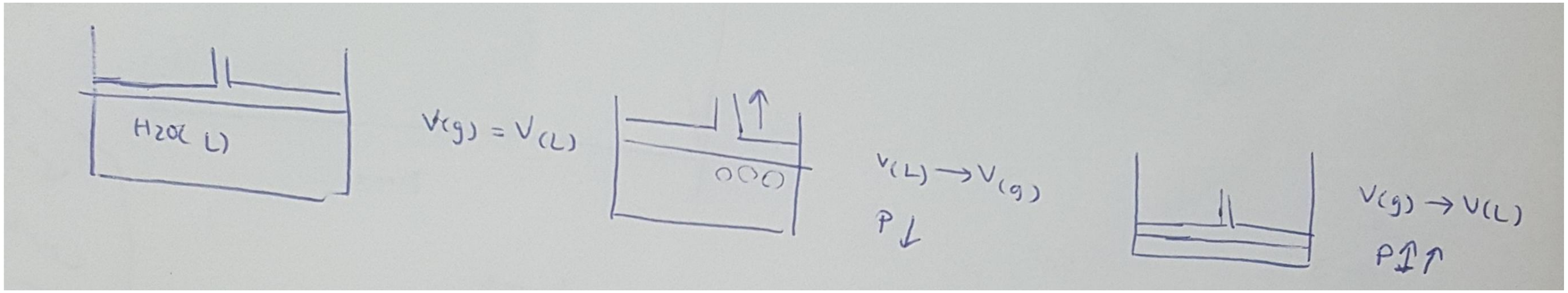


Dealloying corrosion

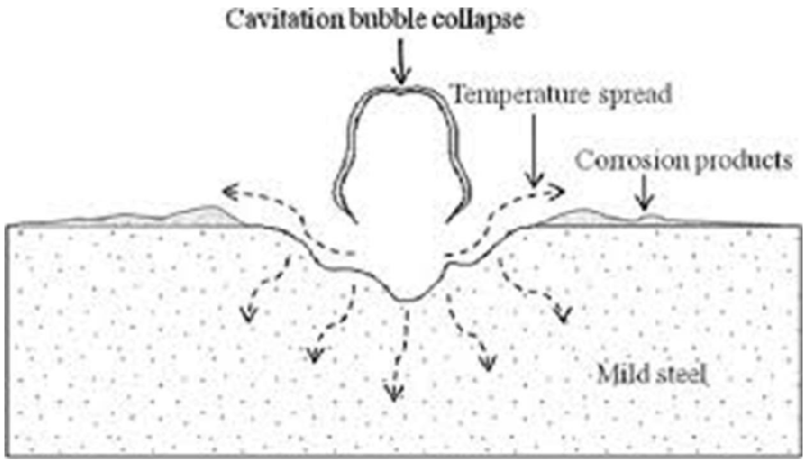

GRAPHITIZATION

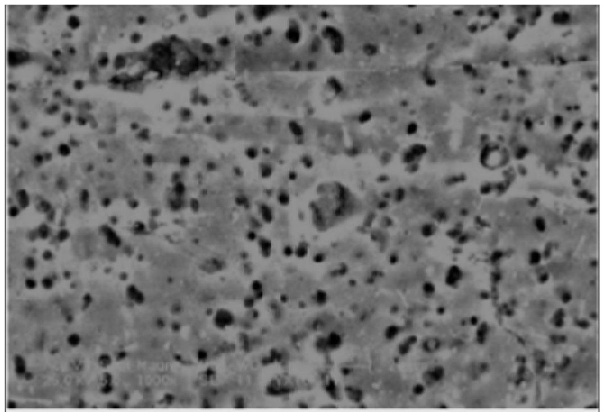


Erosion corrosion

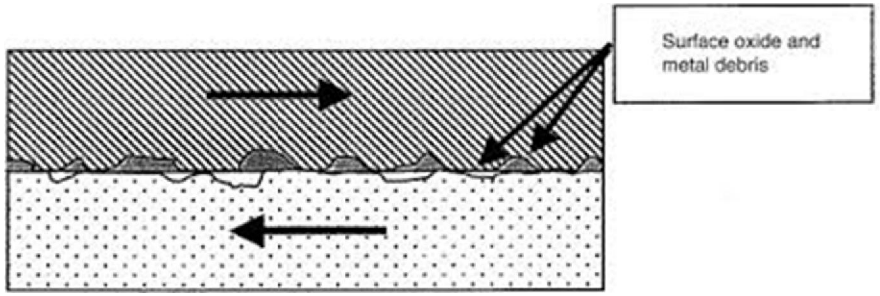


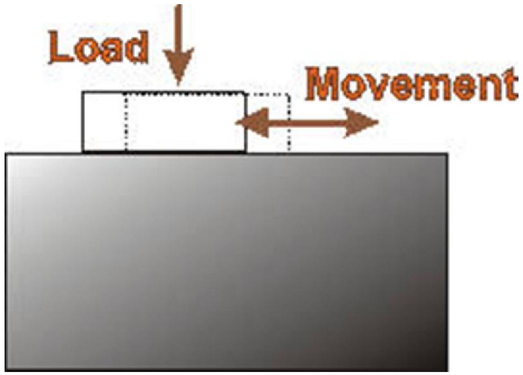
bobble production



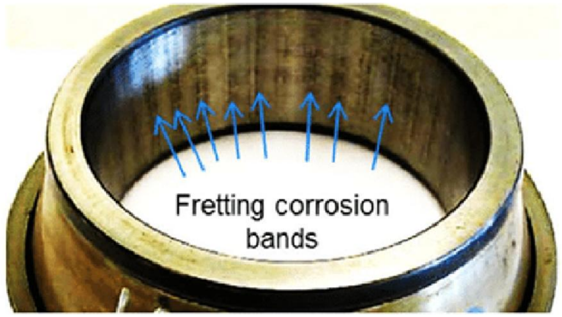


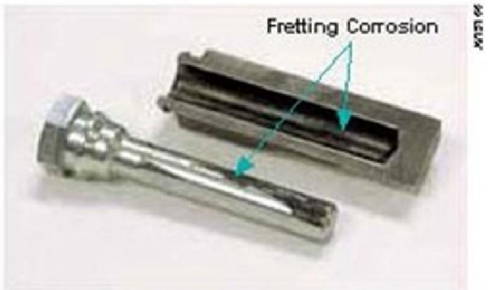
Cavitation damage





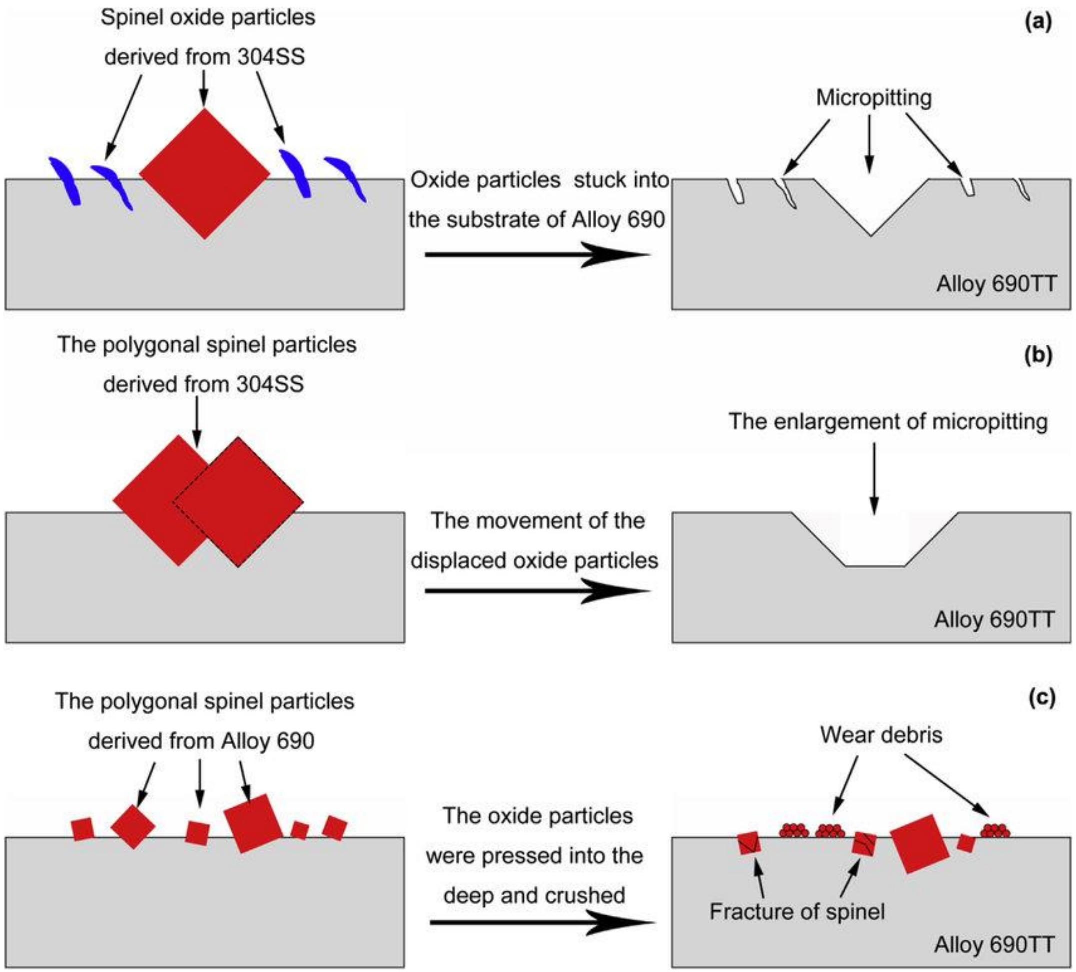
Fretting corrosion



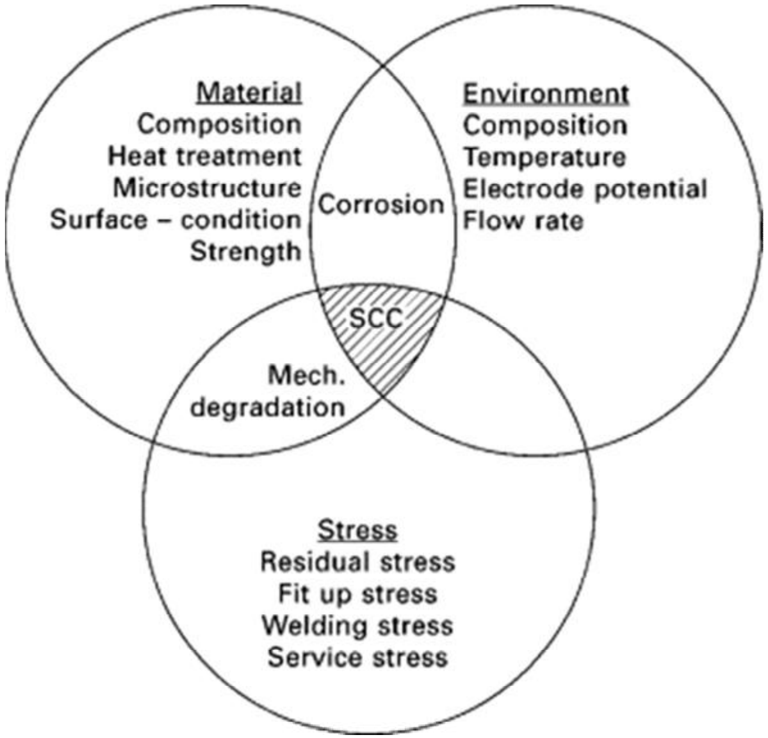


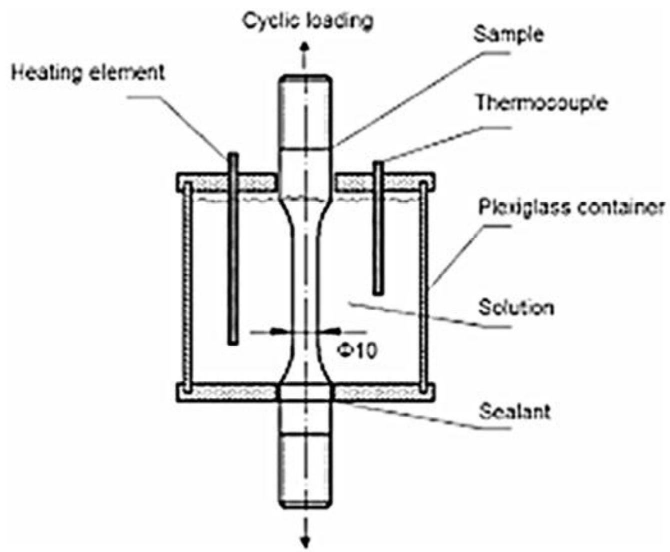
Excessive fretting corrosion and wear on caliper guide pins can result from using the improper guide pin lubricant.

Fretting corrosion

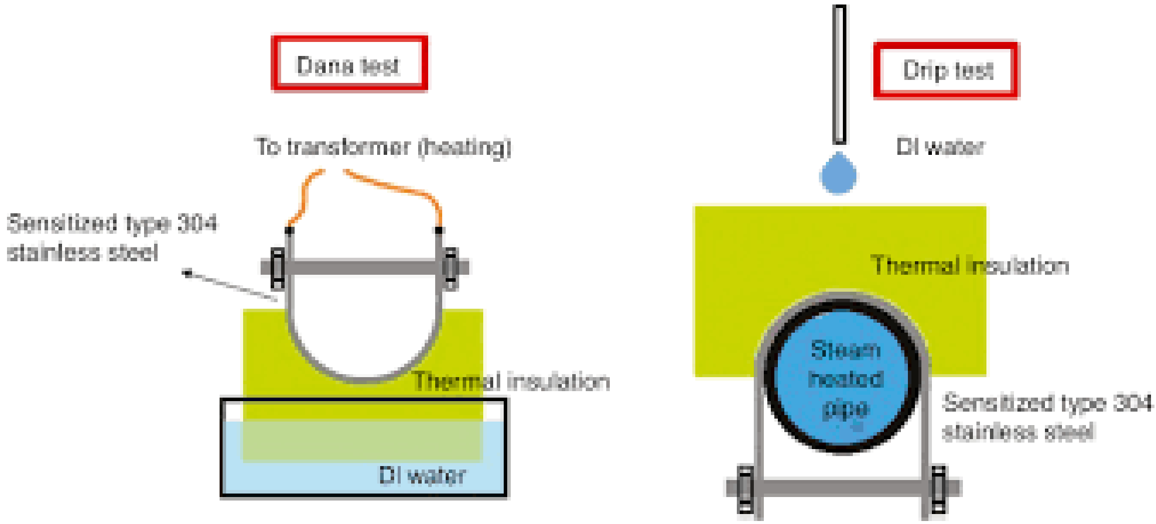


Fretting corrosion= False brinelling

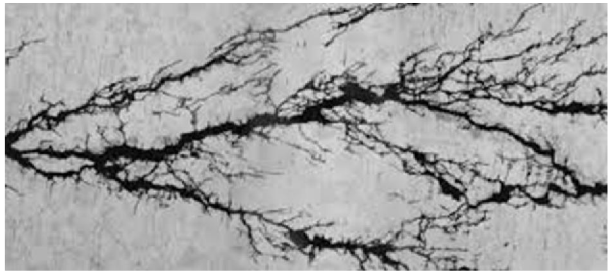

Material
Composition
Heat treatment
Microstructure
Surface – condition
Strength
Environment
Composition
Temperature
Electrode potential
Flow rate
Corrosion
SCC
Mech.
degradation
Stress
Residual stress
Fit up stress
Welding stress
Service stress


Cyclic loading
Sample
Heating element
Thermocouple
Plexiglass container
Solution
Φ10
Sealant

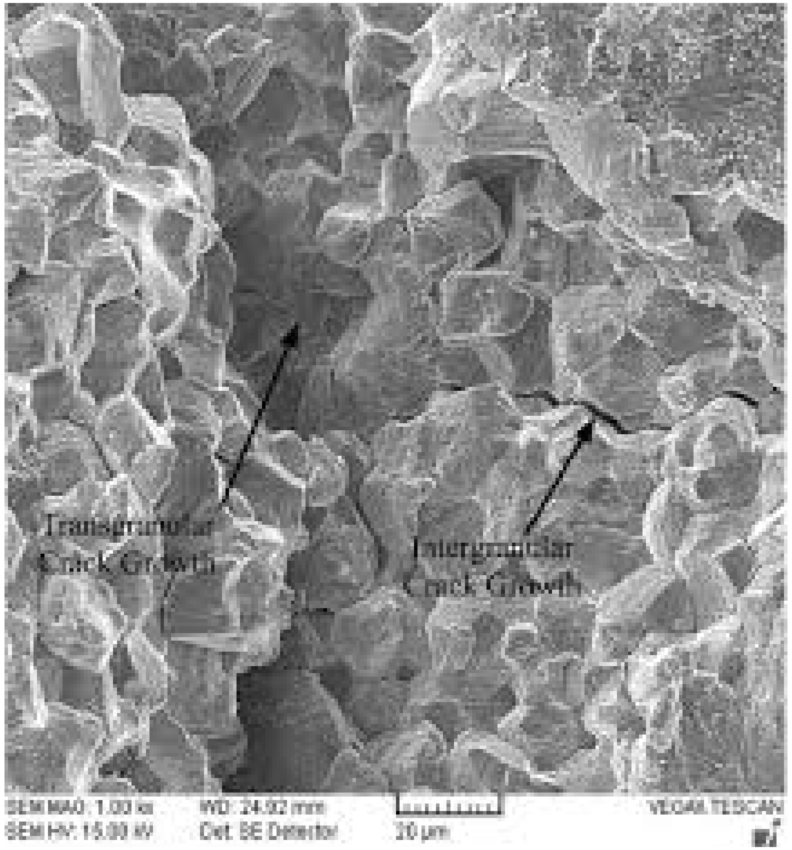
SCC


Dana test
To transformer (heating)
Sensitized type 304
stainless steel
Thermal insulation
DI water
Drip test
DI water
Thermal insulation
Steam
heated
pipe
Sensitized type 304
stainless steel

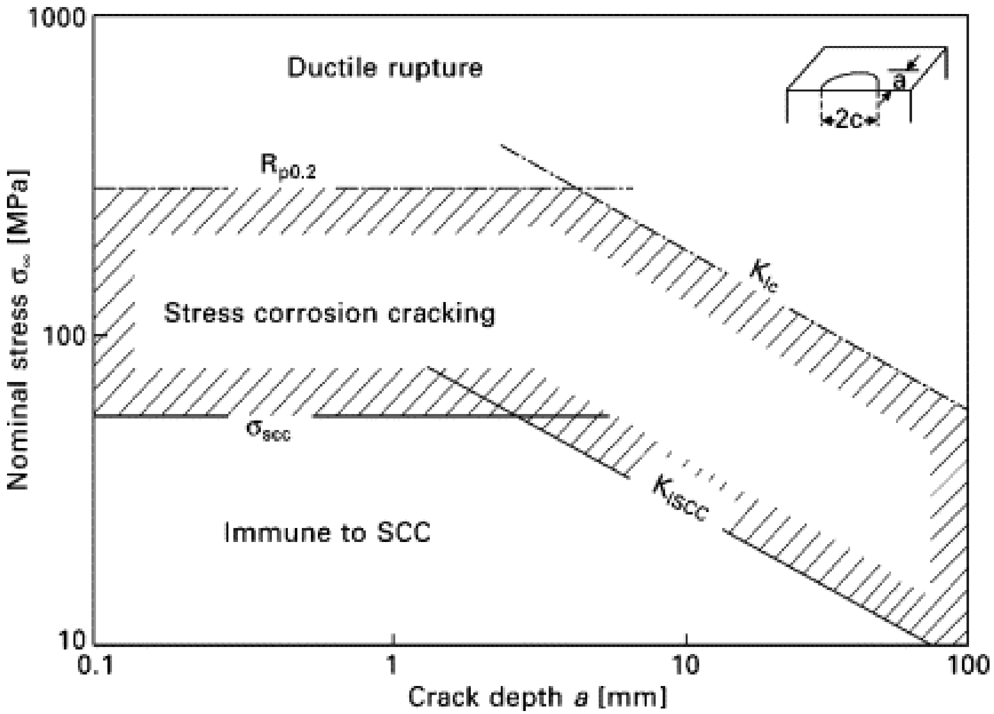
SCC



SCC

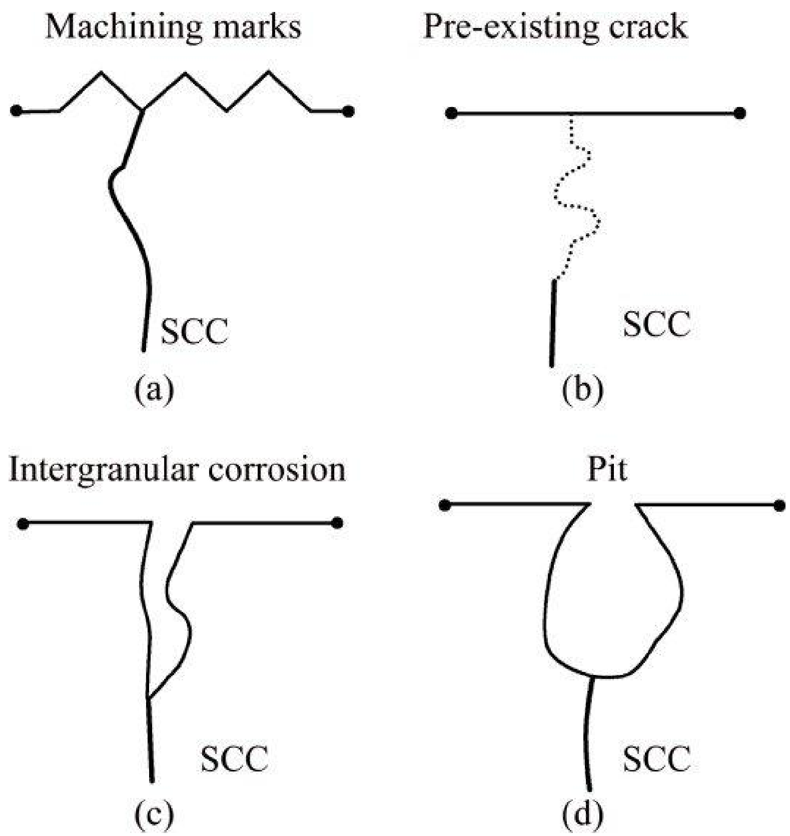

Transgranular
Crack Growth
Intergranular
Crack Growth
20 μm
VEGA\\ TESCAN

SCC

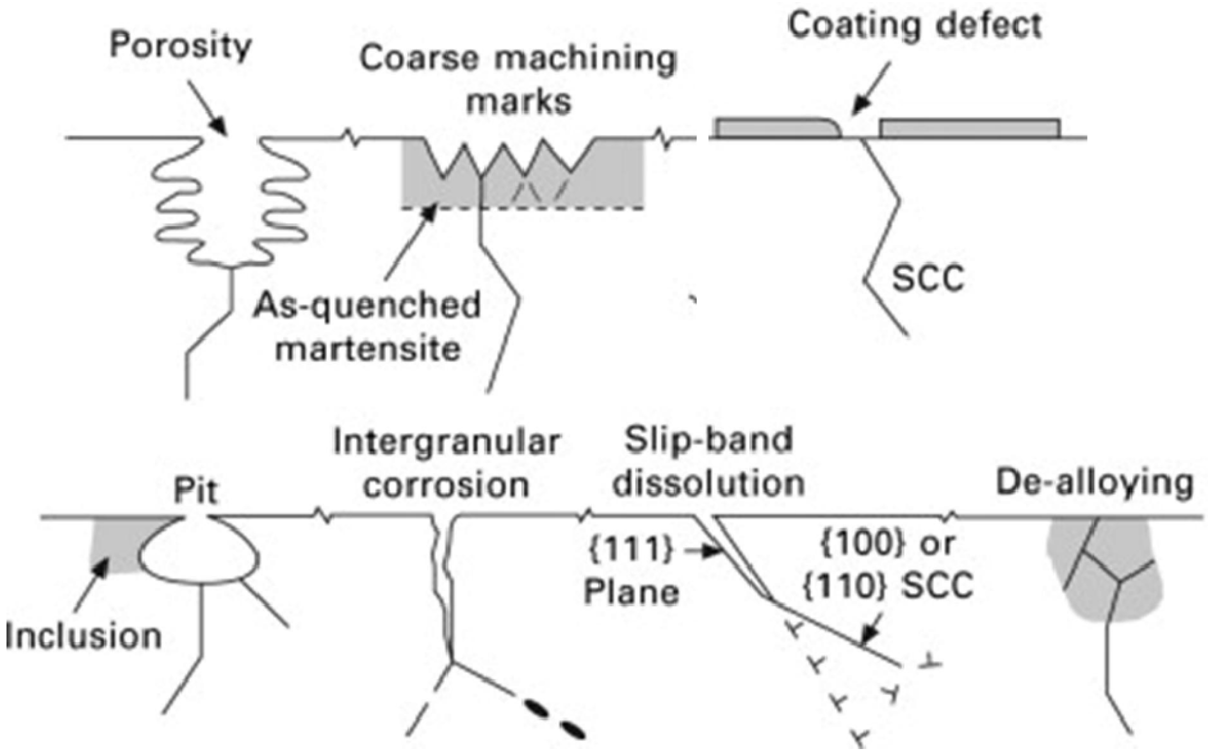


1000
100
10
0.1
1
10
100
Nominal stress σ∞ [MPa]
Crack depth a [mm]
Ductile rupture
Stress corrosion cracking
Immune to SCC
R p0.2
σ scc
K Ic
K ISCC
a
2c

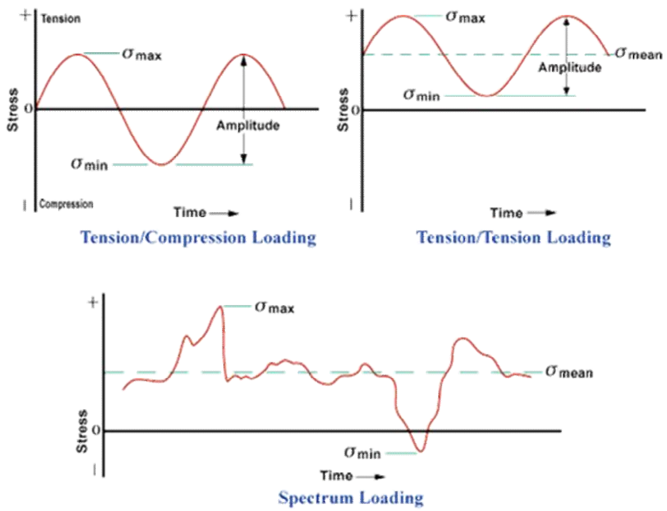
SCC

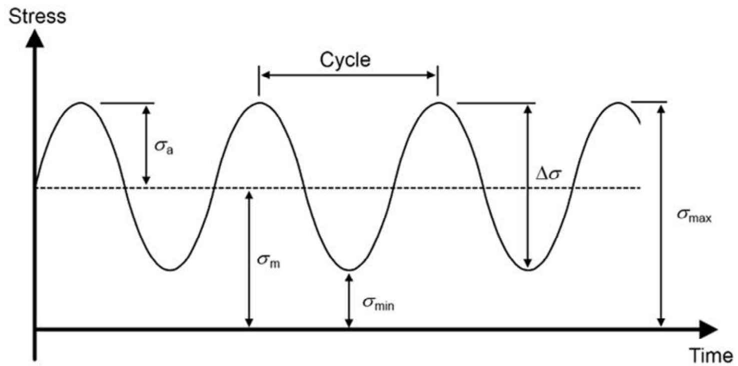


SCC mechanism

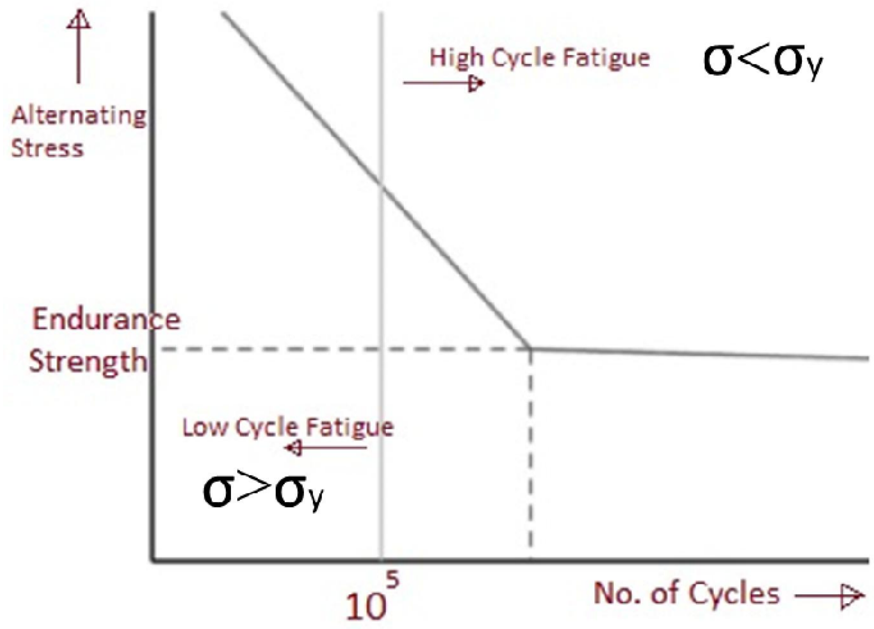


SCC mechanism


Tension
σ max
Stress
Amplitude
σ min
Compression
Time
Tension/Compression Loading
σ max
σ mean
Amplitude
σ min
Stress
Time
Tension/Tension Loading
σ max
σ mean
Stress
σ min
Time
Spectrum Loading

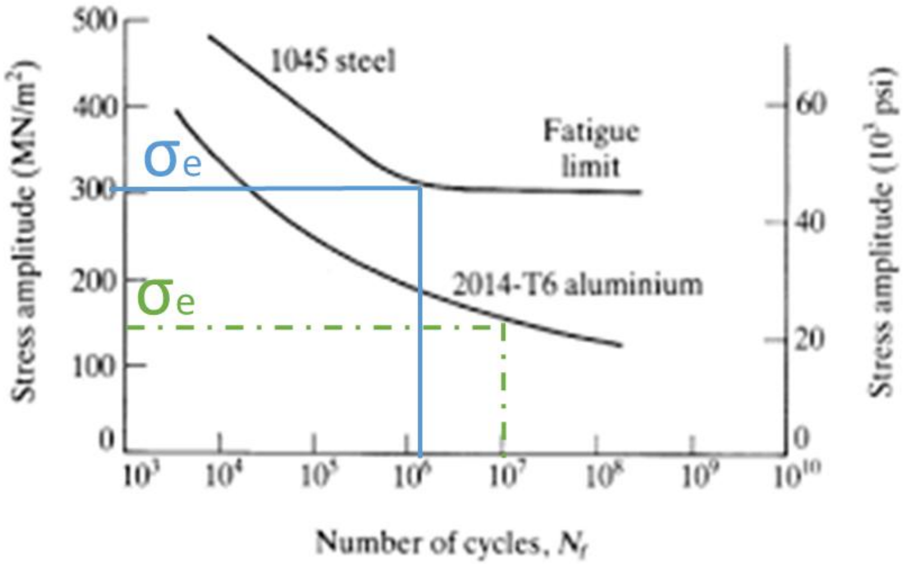

Stress
Cycle
σ_a
$\Delta\sigma$
σ_{max}
σ_m
σ_{min}
Time

Fatigue



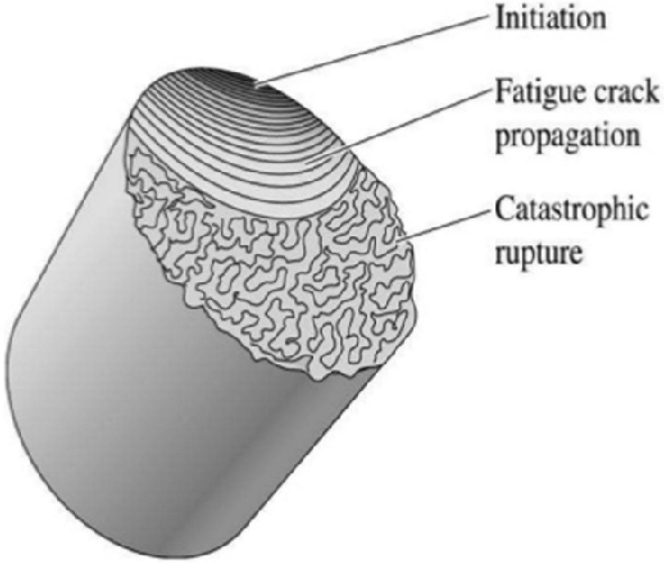
Alternating Stress
High Cycle Fatigue
σ<σy
Endurance Strength
Low Cycle Fatigue
σ>σy
10^5
No. of Cycles

Fatigue



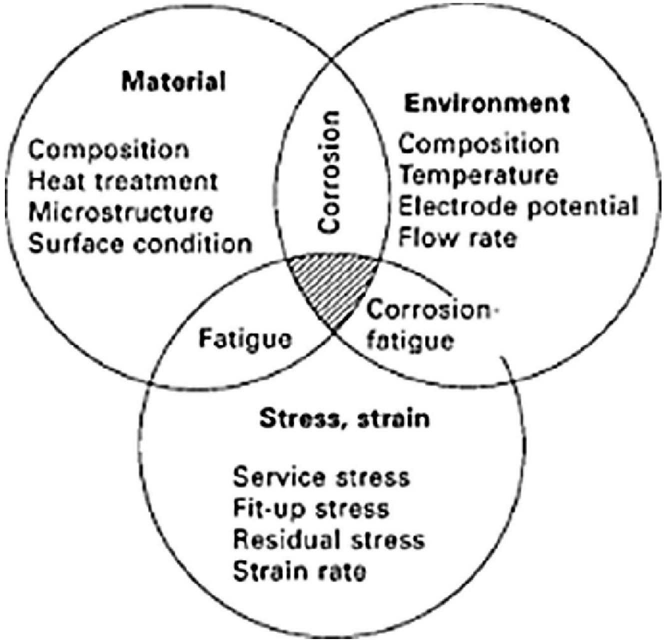
500
400
300
200
100
0
1045 steel
Fatigue
limit
2014-T6 aluminium
σe
σe
60
40
20
0
Stress amplitude (MN/m²)
Stress amplitude (10³ psi)
10³
10⁴
10⁵
10⁶
10⁷
10⁸
10⁹
10¹⁰
Number of cycles, Nf

Fatigue

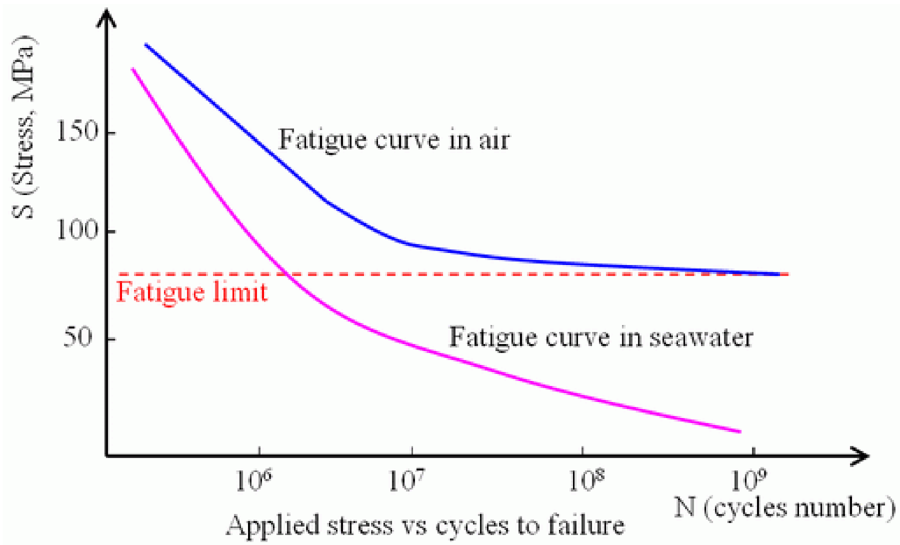


Initiation
Fatigue crack
propagation
Catastrophic
rupture

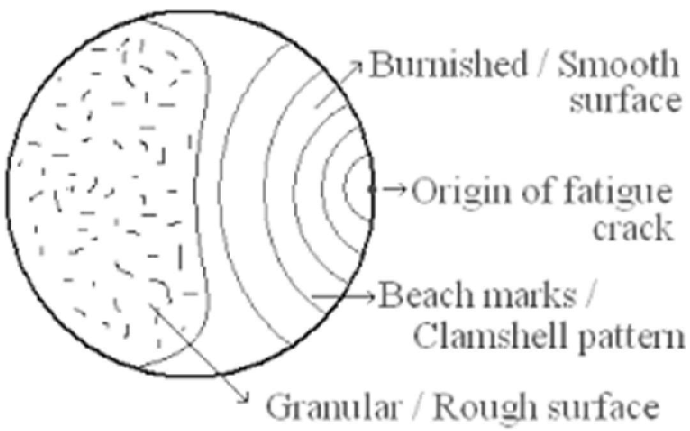
Fatigue



Fatigue corrosion



Fatigue corrosion



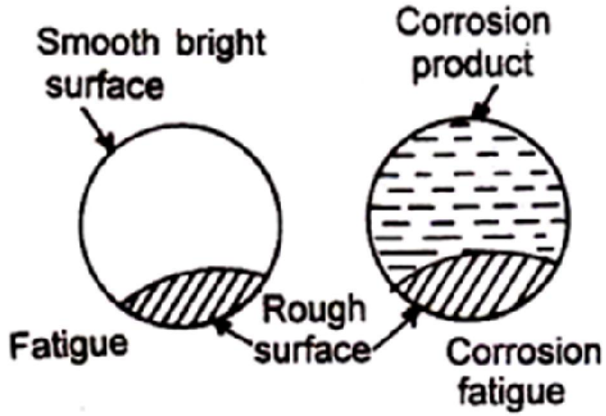
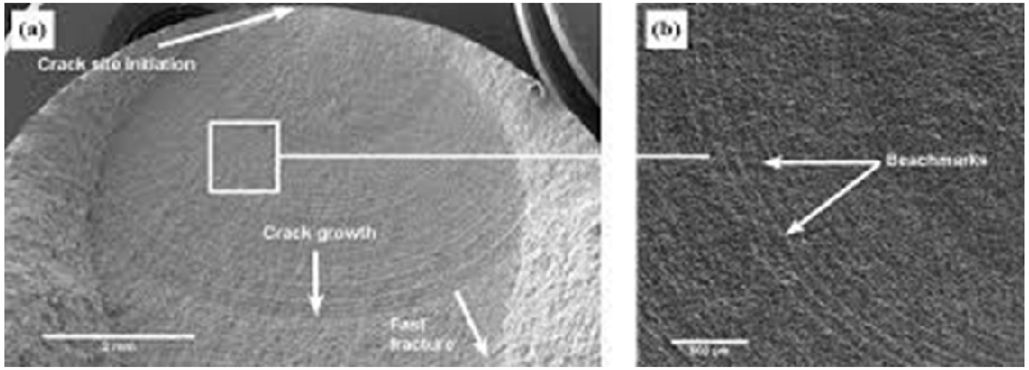
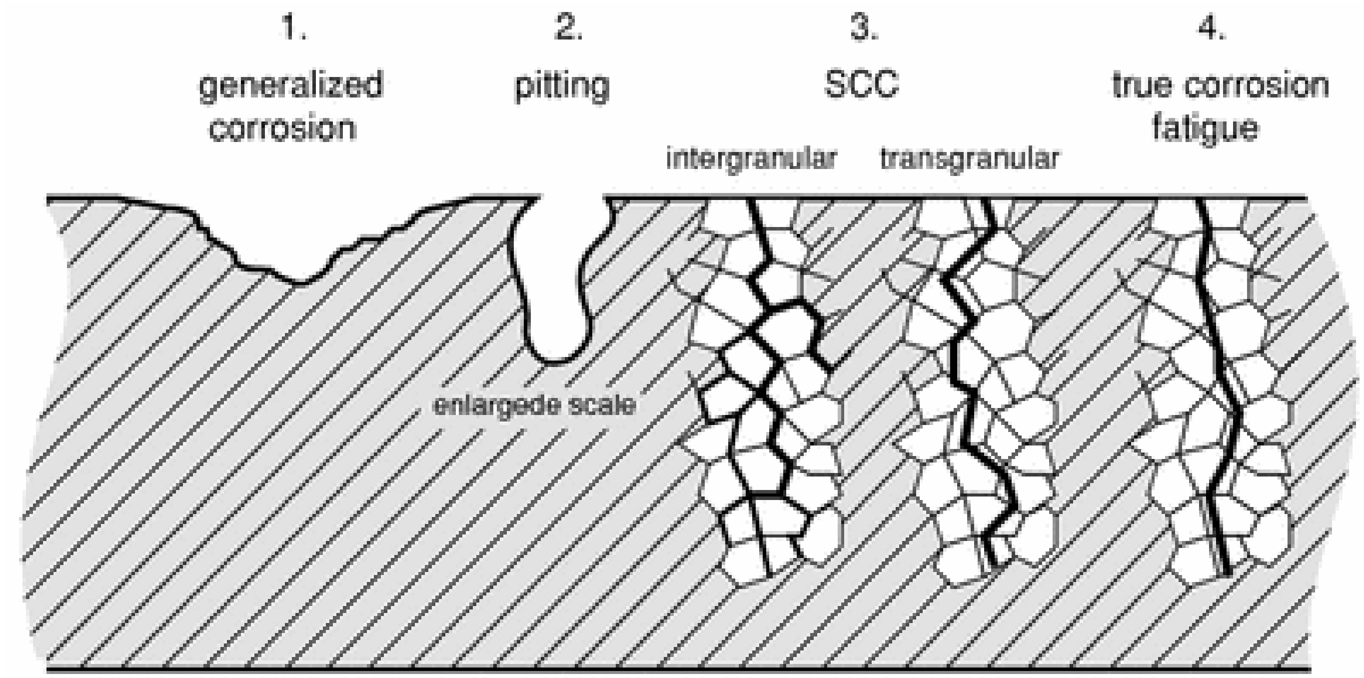


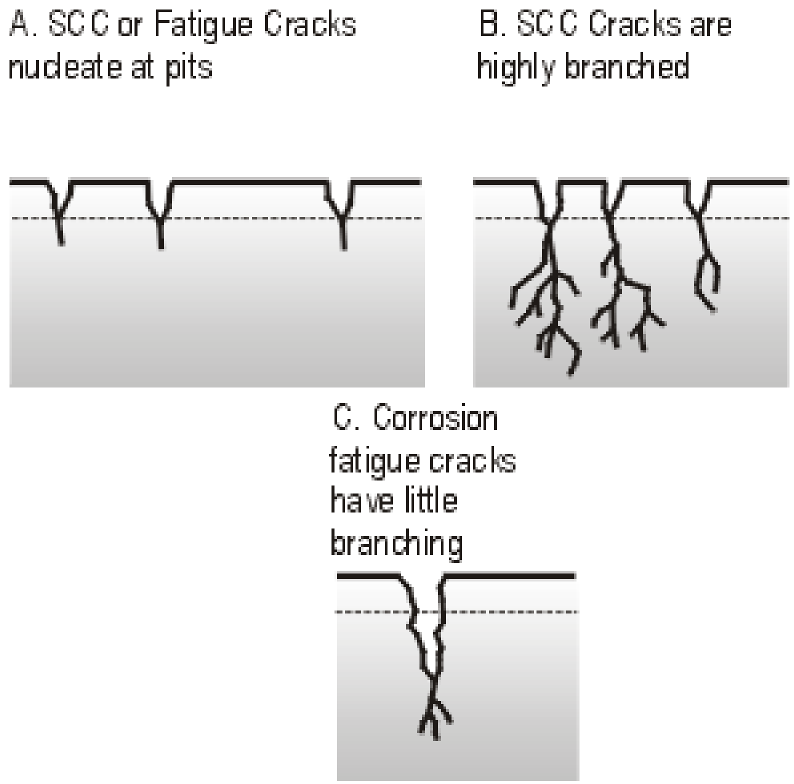
Fig. 14.33. Schematic difference between fatigue and corrosion fatigue.

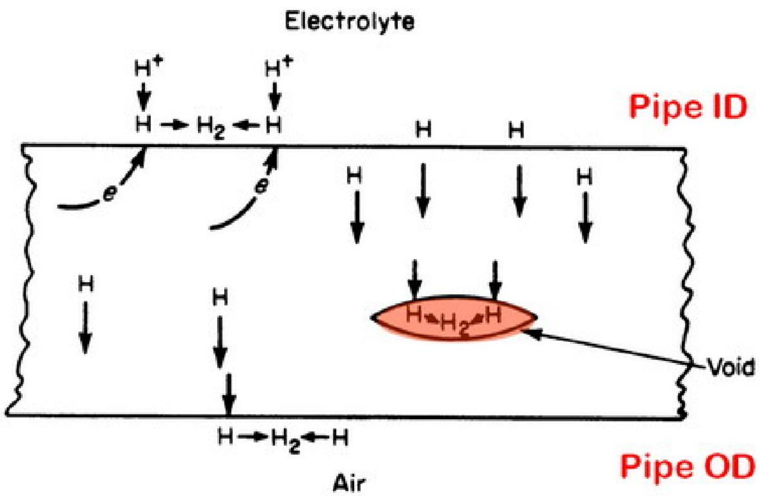
Fatigue corrosion

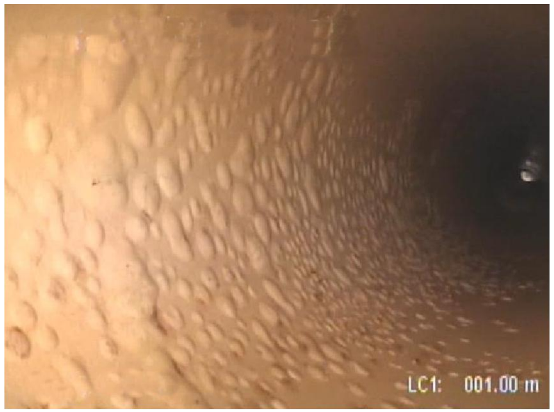


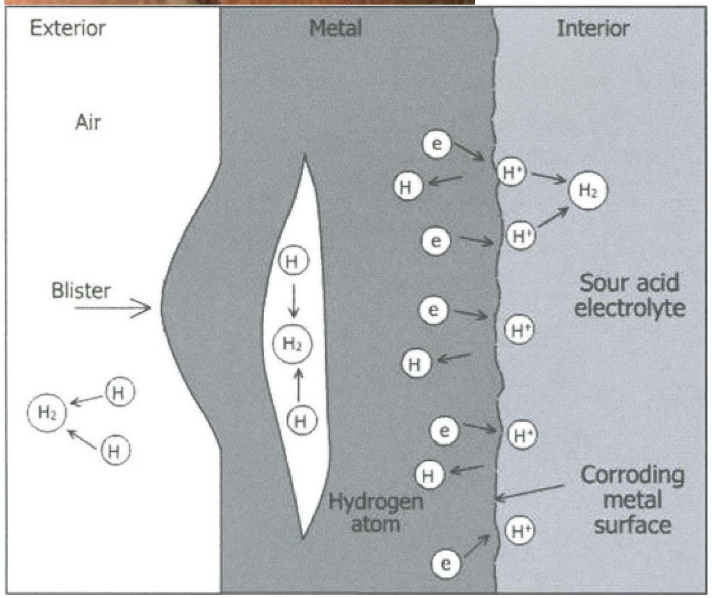
Fatigue corrosion


1.
generalized
corrosion
2.
pitting
3.
SCC
intergranular
transgranular
4.
true corrosion
fatigue
enlargede scale

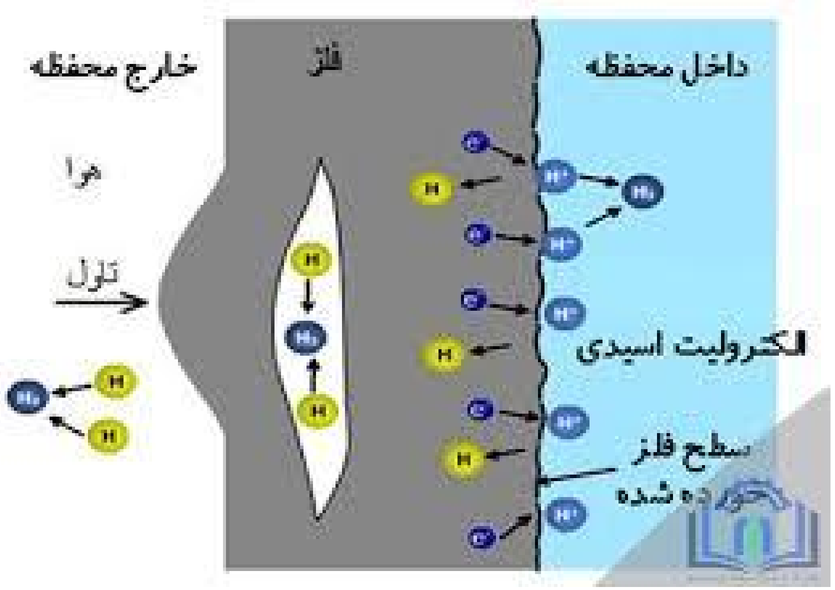

A. SCC or Fatigue Cracks nucleate at pits
B. SCC Cracks are highly branched
C. Corrosion fatigue cracks have little branching



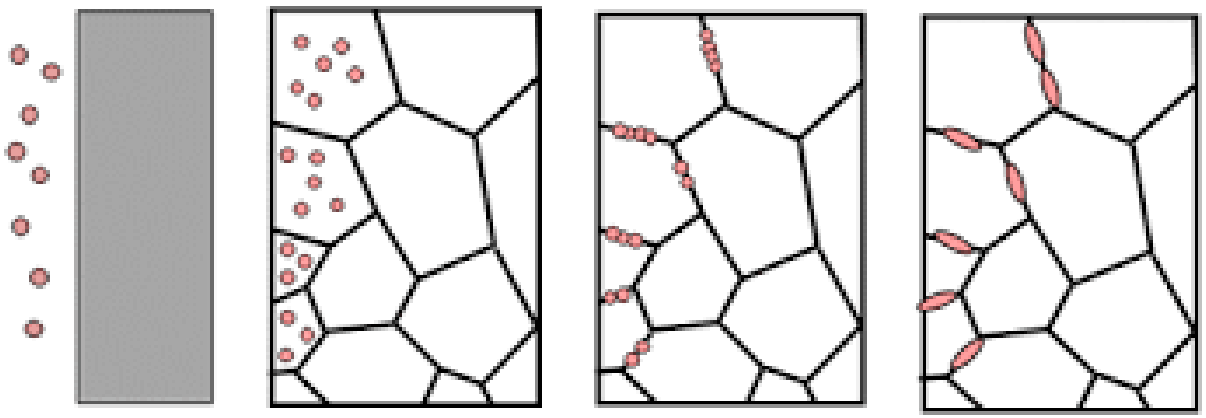




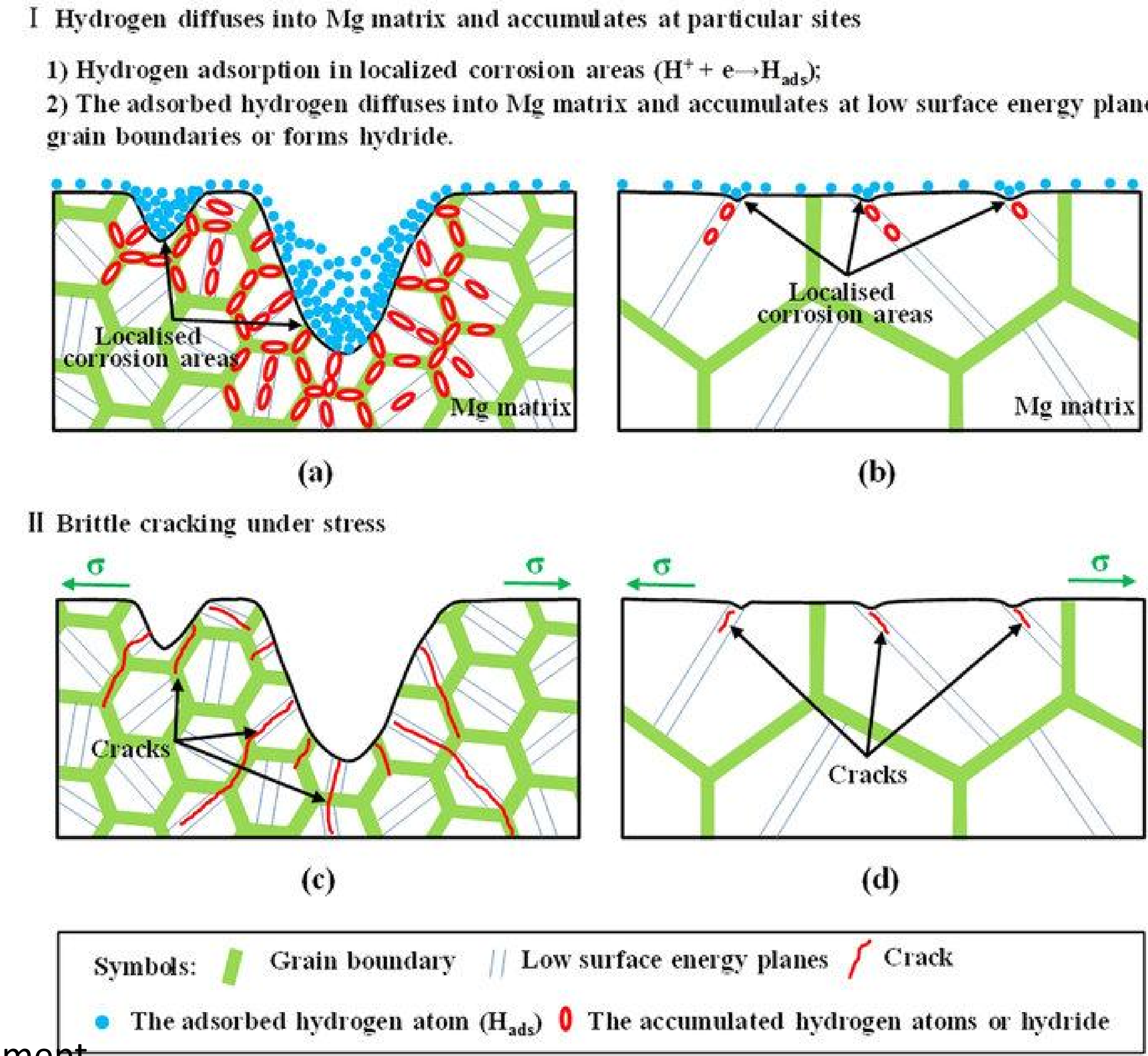
Hydrogen blistering



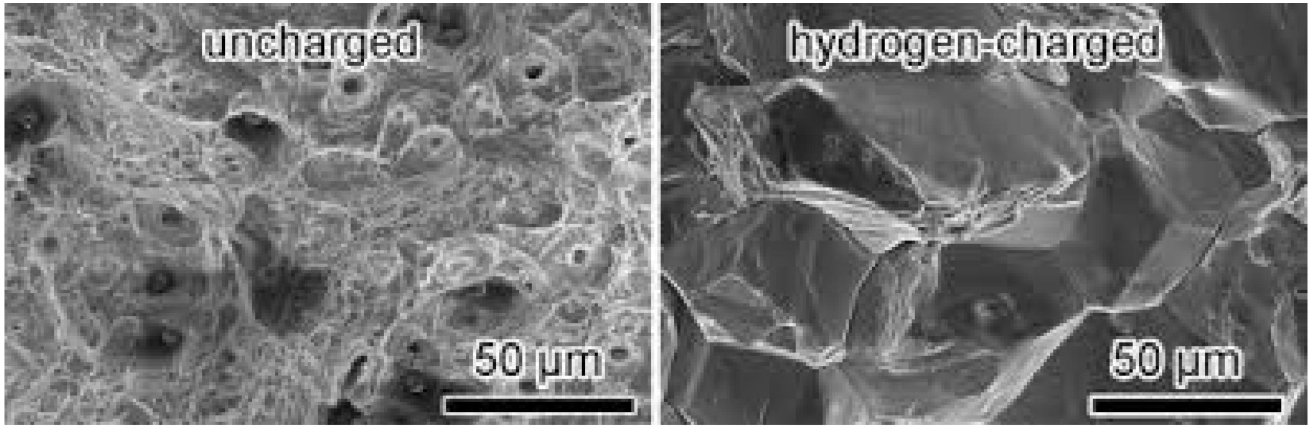
Hydrogen blistering



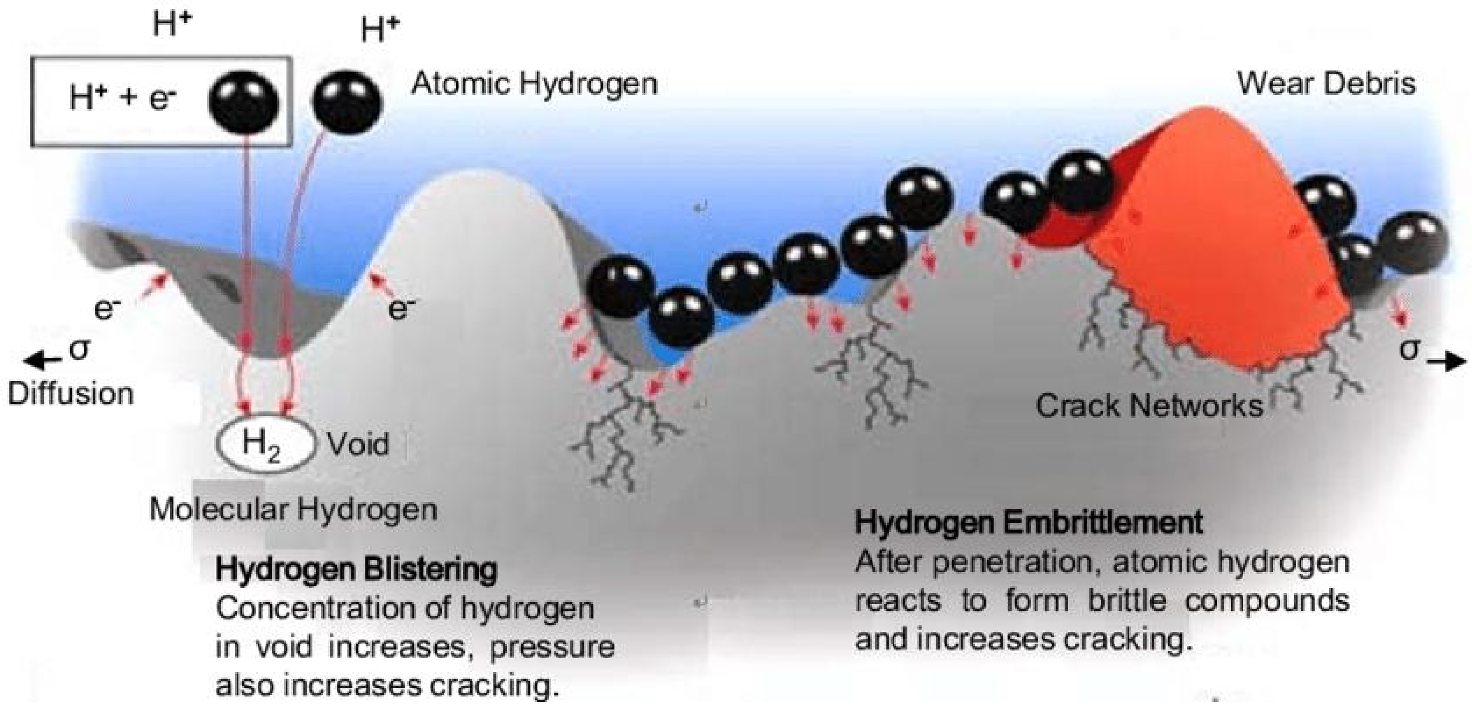
Hydrogen embrittlement



Hydrogen embrittlement

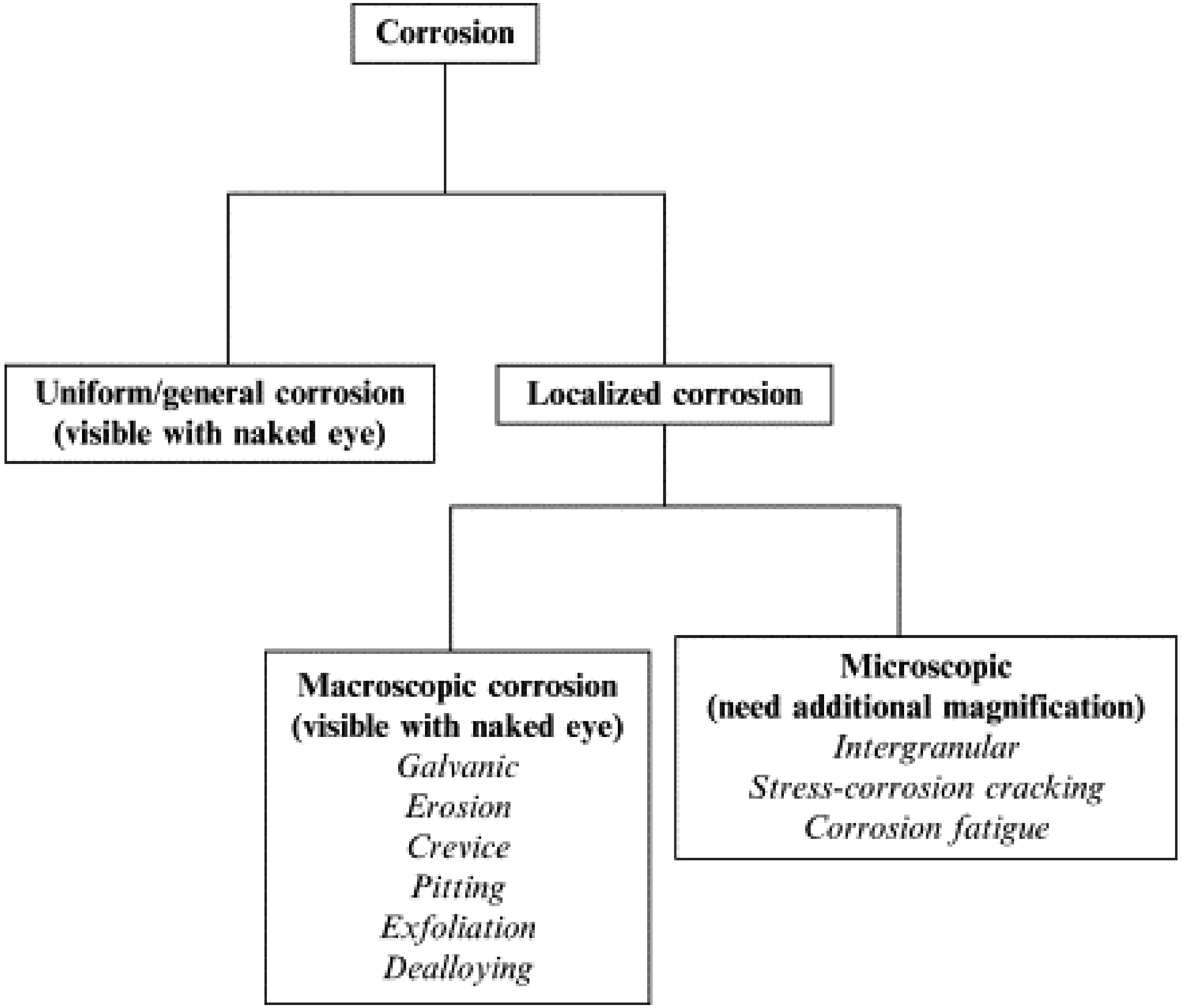


Hydrogen embrittlement

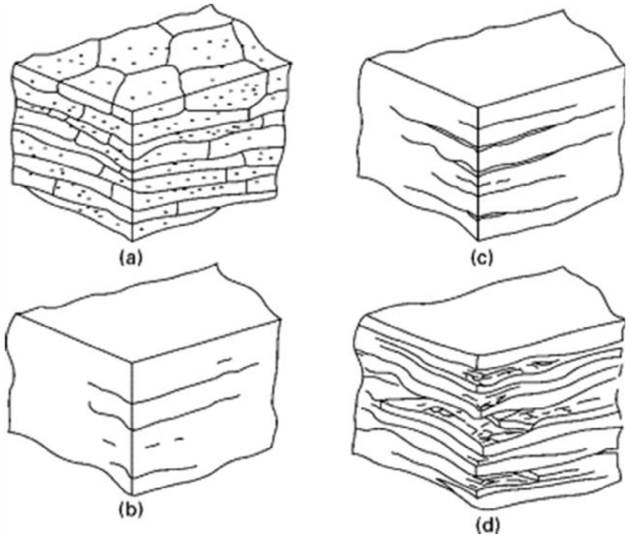

H+
H+
H+ + e-
Atomic Hydrogen
Wear Debris
e-
e-
σ
Diffusion
σ
H2
Void
Crack Networks
Molecular Hydrogen
Hydrogen Blistering
Concentration of hydrogen in void increases, pressure also increases cracking.
Hydrogen Embrittlement
After penetration, atomic hydrogen reacts to form brittle compounds and increases cracking.

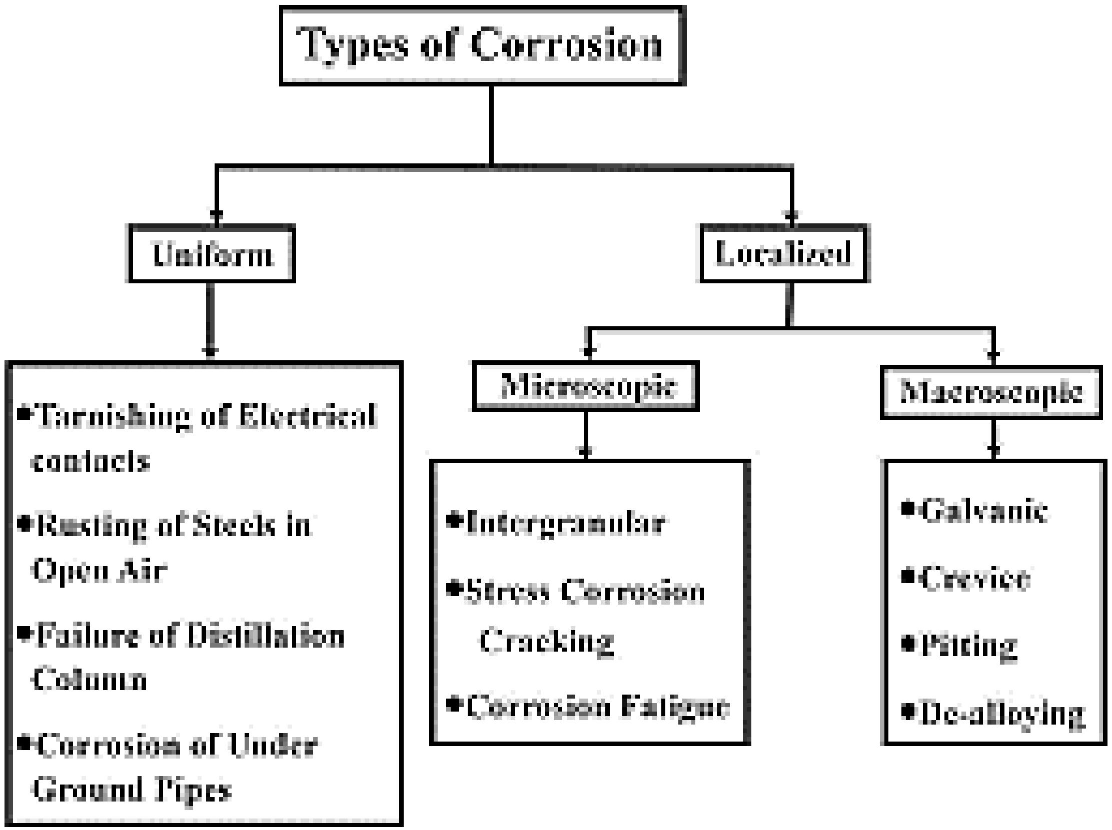


Hydrogen attack

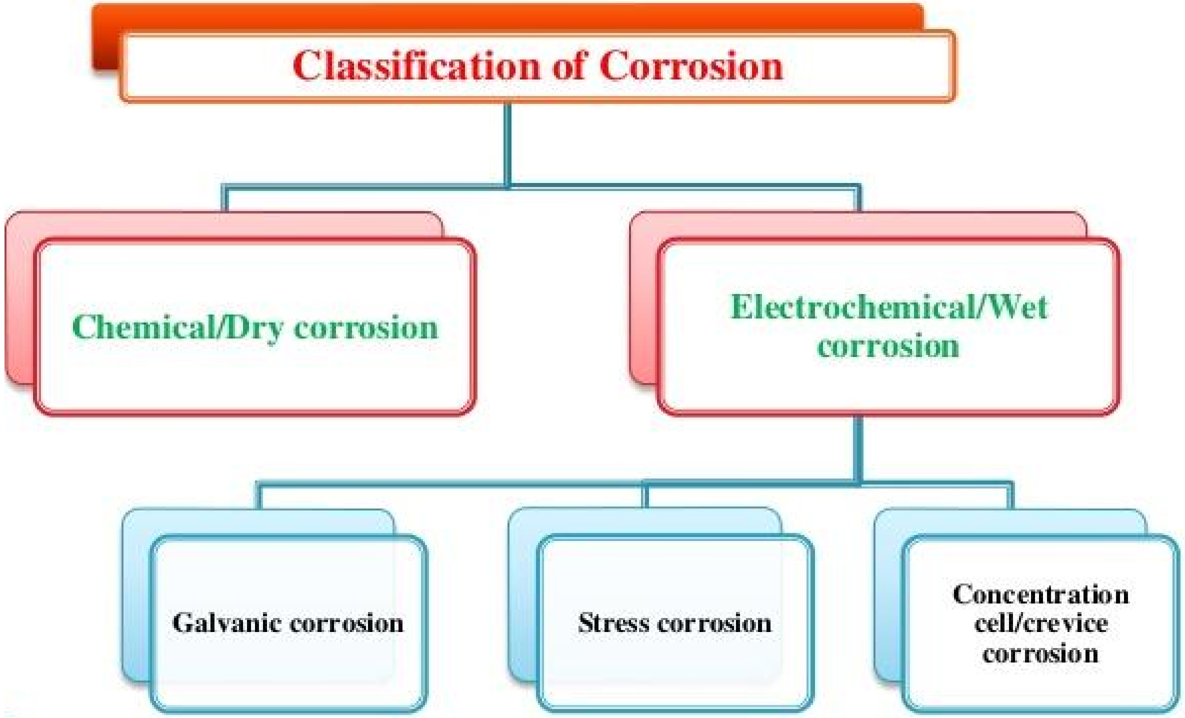

Corrosion
Uniform/general corrosion (visible with naked eye)
Localized corrosion
Macroscopic corrosion (visible with naked eye)
Galvanic
Erosion
Crevice
Pitting
Exfoliation
Dealloying
Microscopic (need additional magnification)
Intergranular
Stress-corrosion cracking
Corrosion fatigue

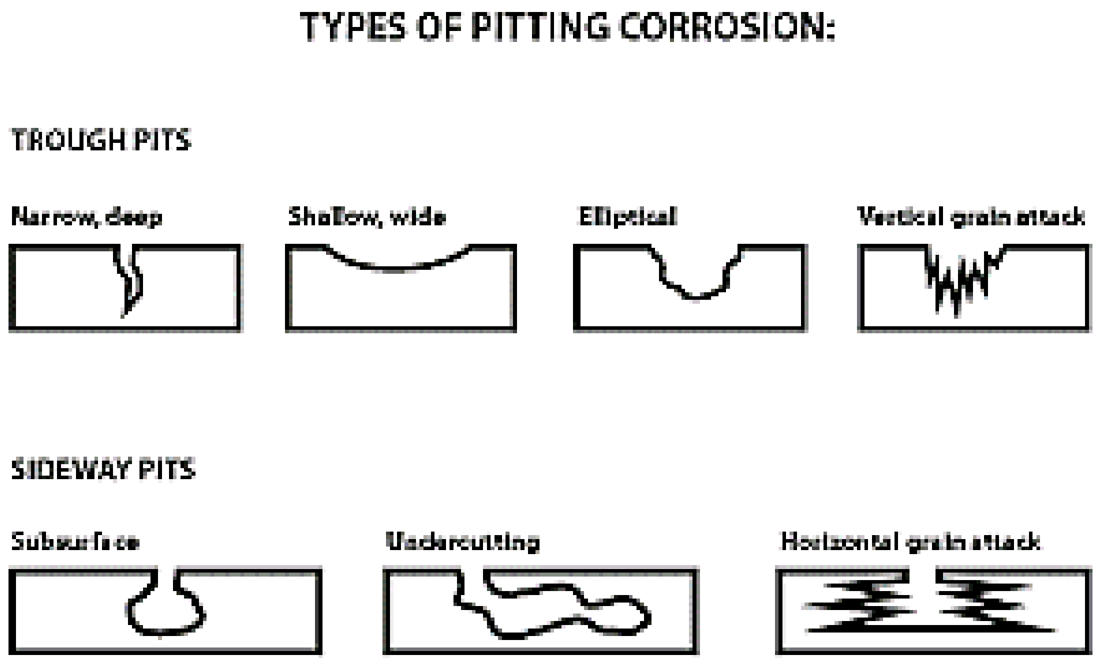
Exfoliation corrosion *(lamellar corrosion) is a severe type of intergranular corrosion that raises surface grains from metal by forming corrosion products at grain boundaries under the surface.*





Types of Corrosion
Uniform
Localized
Microscopic
Macroscopic
•Tarnishing of Electrical contacts
•Rusting of Steels in Open Air
•Failure of Distillation Column
•Corrosion of Under Ground Pipes
•Intergranular
•Stress Corrosion Cracking
•Corrosion Fatigue
•Galvanic
•Crevice
•Pitting
•De-alloying


Classification of Corrosion
Chemical/Dry corrosion
Electrochemical/Wet corrosion
Galvanic corrosion
Stress corrosion
Concentration cell/crevice corrosion


TYPES OF PITTING CORROSION:
TROUGH PITS
Narrow, deep
Shallow, wide
Elliptical
Vertical grain attack
SIDEWAY PITS
Subsurface
Undercutting
Horizontal grain attack

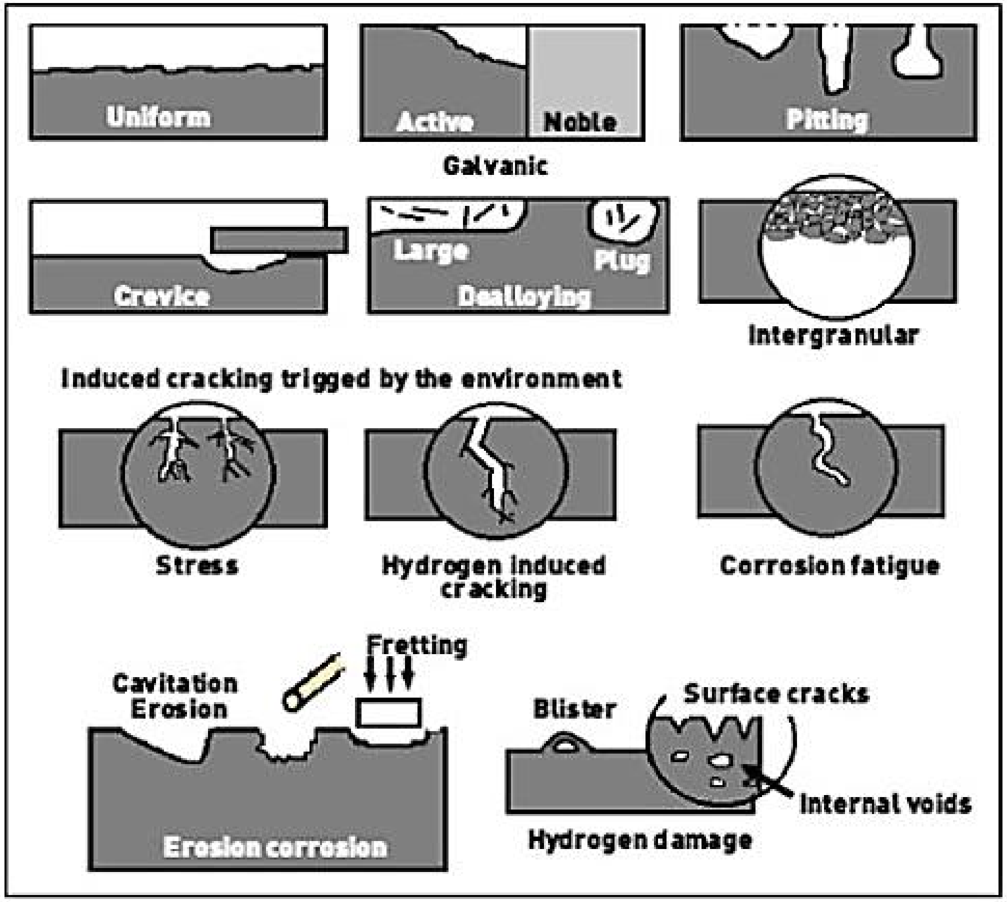
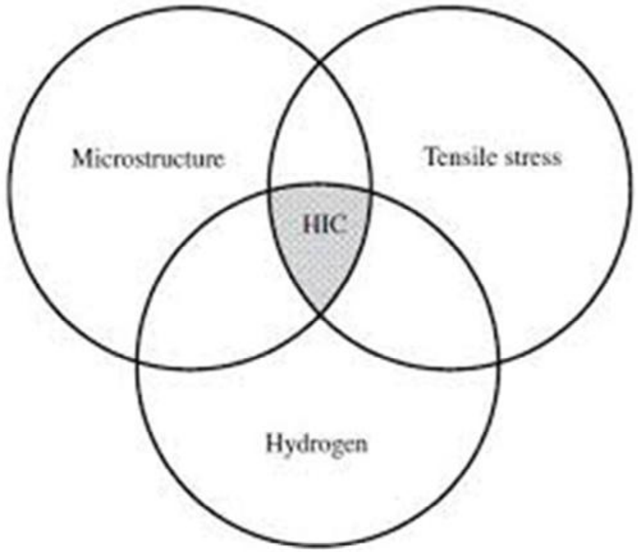
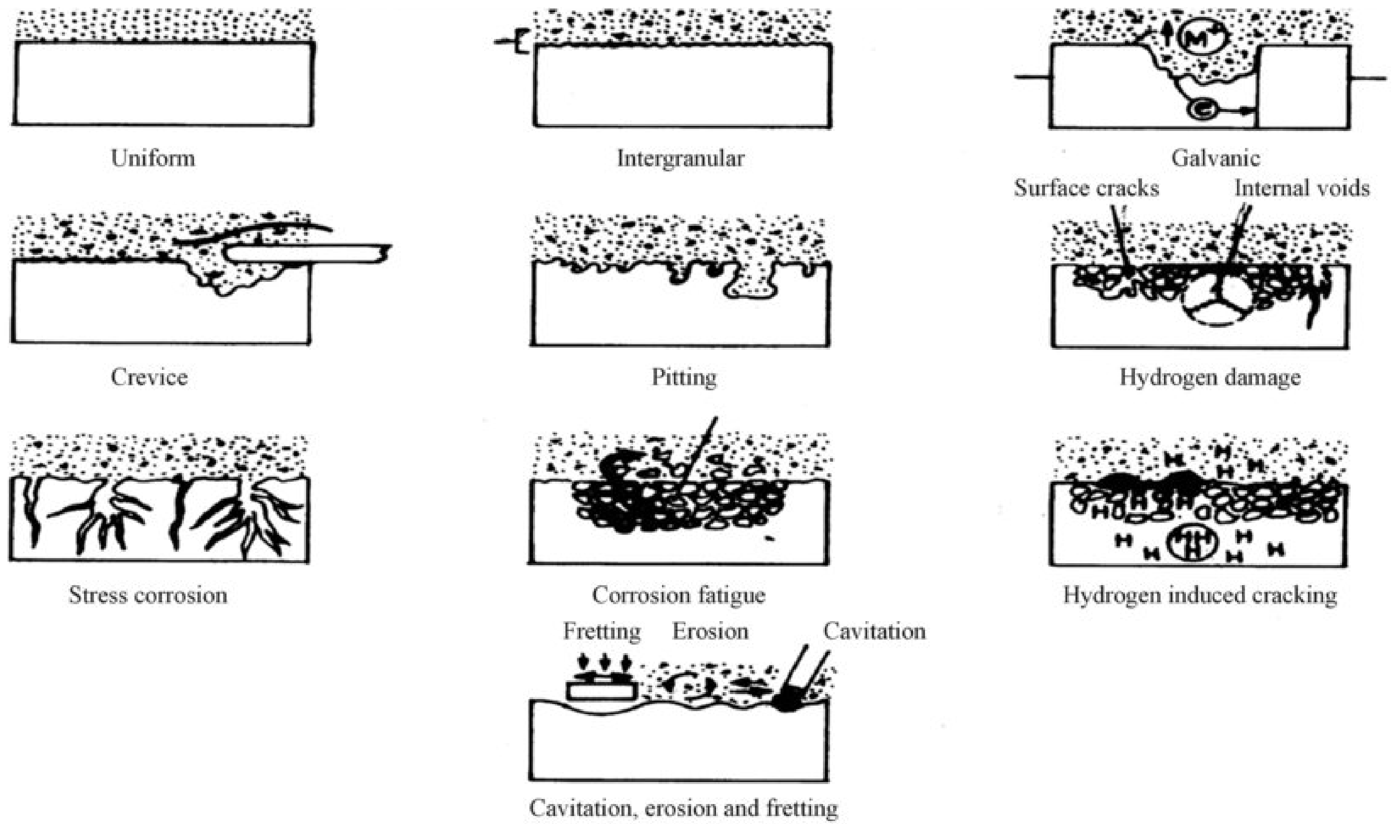


Fig. 4 - Illustration of different types of corrosion. Adapted from [51].

Hydrogen Induced Cracking *(HIC)*

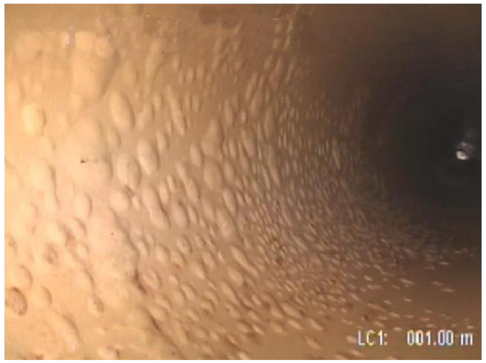
is a common form of wet H_2S **cracking** *caused by the blistering of a metal due to a high concentration of* **hydrogen**.

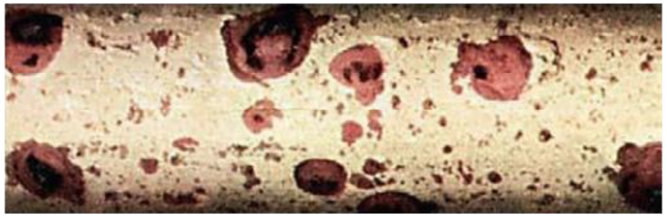



Uniform
Intergranular
Galvanic
Surface cracks
Internal voids
Crevice
Pitting
Hydrogen damage
Stress corrosion
Corrosion fatigue
Hydrogen induced cracking
Fretting
Erosion
Cavitation
Cavitation, erosion and fretting







LC1: 001.00 m




341242-2
LOWER

- خشک و تر شدن و یا گرم و سرد شدن سرعت SCC را افزایش می دهد.

اثر محصولات خوردگی

- محصولات خوردگی حجمی بیشتر از فلز داشته باشند و در ناحیه ای تشکیل شوند که امکان خروج راحت را نداشته باشند تنش زیادی را به اطراف خود وارد می کنند. به این فرایند wedging action یا اثر گوه ای گفته می شود.

- **فولاد زنگ نزن آستنیتی در حضور تنش فقط در محیط های کلر دار دچار SCC می شود و در حضور آمونیاک مشکلی ندارد. اما برنج در محیط آمونیاک دار دچار SCC می شود اما در محیط کلر دار مشکلی ندارد.**

- استفاده از پوشش پلاستیک نرم

عدم قرار گیری در هوای مرطوب

– استفاده از فیلتر برای حذف ذرات معلق

استفاده از جوشکاری به جای پیچ و مهره و پرچ و پرس کاری.

- روغنکار و استفاده از گیریس

از عایق کاری در اتصال بین فلزات غیر هم جنس استفاده شود.

خوردگی- فرسایشی شیاری گالوانیکی حبابی فیلامنتی سایشی

Chapter 5 Materials

Metals and Alloys

Nonmetallics

METALS AND ALLOYS

5-3 Cast Irons

Cast iron is a generic term that applies to high carbon-iron alloys containing silicon. The common ones are designated as gray cast iron, white cast iron, malleable cast iron, and ductile or nodular cast iron. Ordinary *gray irons* contain about 2 to 4% carbon and 1 to 3% silicon. These are the least expensive of the engineering metals. The dull or grayish fracture is due to the free graphite flakes in the microstructure (Fig. 5-1). Gray cast irons can be readily cast into intricate shapes because of their excellent fluidity and relatively low melting points. They can be alloyed for improvement of corrosion resistance and strength.

5-4 High-Silicon Cast Irons

When the silicon content of gray cast iron is increased to over 14%, it becomes extremely corrosion resistant to many environments. The notable exception is hydrofluoric acid. In fact, these high-silicon irons are the most universally resistant of the commercial (nonprecious) metals and alloys. Their inherent hardness makes them resistant to erosion corrosion. A straight high-silicon iron, such as Duriron, contains about 14.5% silicon and 0.95% carbon.

5-8 Stainless Steels

The main reason for the existence of the stainless steels is their resistance to corrosion. Chromium is the main alloying element, and the steel should contain at least 11%. Chromium is a reactive element, but it and its alloys passivate and exhibit excellent resistance to many environments. A large number of stainless steels are available. Their corrosion resistance, mechanical properties, and cost vary over a broad range. For this reason, it is important to specify the exact stainless steel desired for a given application.

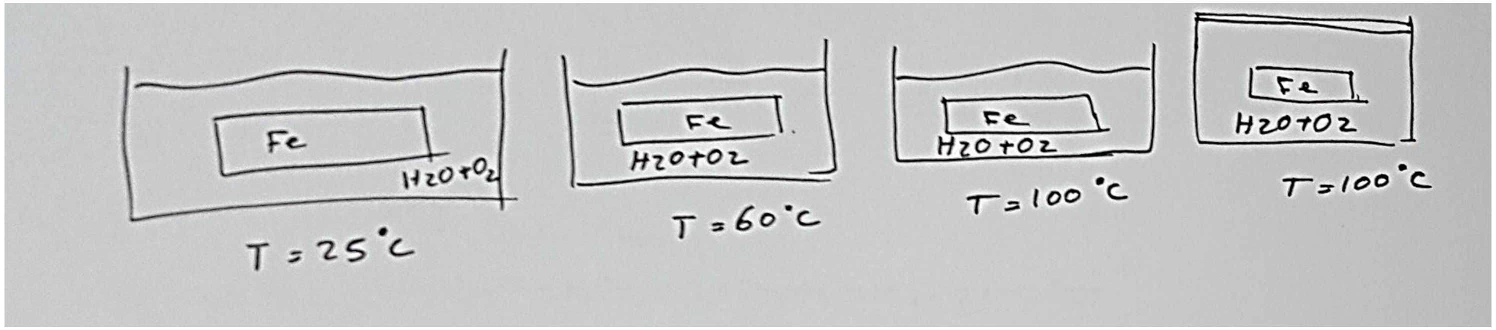
5-9 Aluminum and Its Alloys

Aluminum is a reactive metal, but it develops an aluminum oxide coating or film that protects it from corrosion in many environments. This film is quite stable in neutral and many acid solutions but is attacked by alkalies. This oxide film forms in many environments, but it can be artificially produced by passage of electric current. This process is called anodizing. The high-copper alloys are utilized mainly for structural purposes. The copper-free or low-copper alloys are used in the process industries or where better corrosion resistance is required.

5-10 Magnesium and Its Alloys

Magnesium exhibits good resistance to ordinary inland atmospheres due to the formation of a protective oxide film. This protection tends to break down (pits) in air contaminated with salt, and protective measures are required. These include coatings and "chrome" pickling, which also provides a good base for the coating. Corrosion resistance generally decreases with impurities and alloying. Alloys are quite susceptible to stress corrosion and must be protected. Presence of dissolved oxygen in water has no significant effect on corrosion. The metal is susceptible to erosion corrosion. Magnesium is much more resistant than aluminum to alkalies. It is attacked by most acids except chromic and hydrofluoric. The corrosion product in HF acts as a protective film.

Chapter 6 Corrosion Prevention


Fe
H2O+O2
T = 25°C
Fe
H2O+O2
T = 60°C
Fe
H2O+O2
T = 100°C
Fe
H2O+O2
T = 100°C

- If more oxidizing agent (passivator) is added, the corrosion rate shows a sudden decreases.
- This is the passive state of the metal.

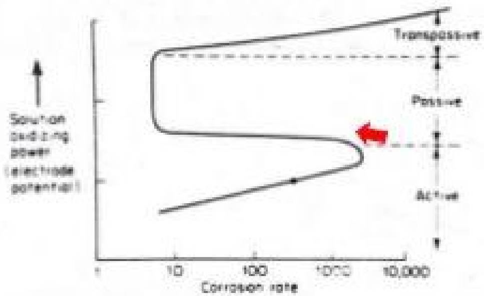
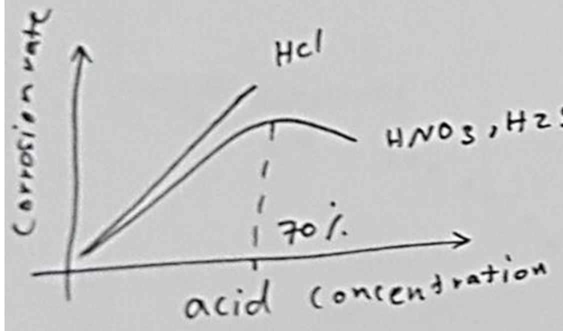


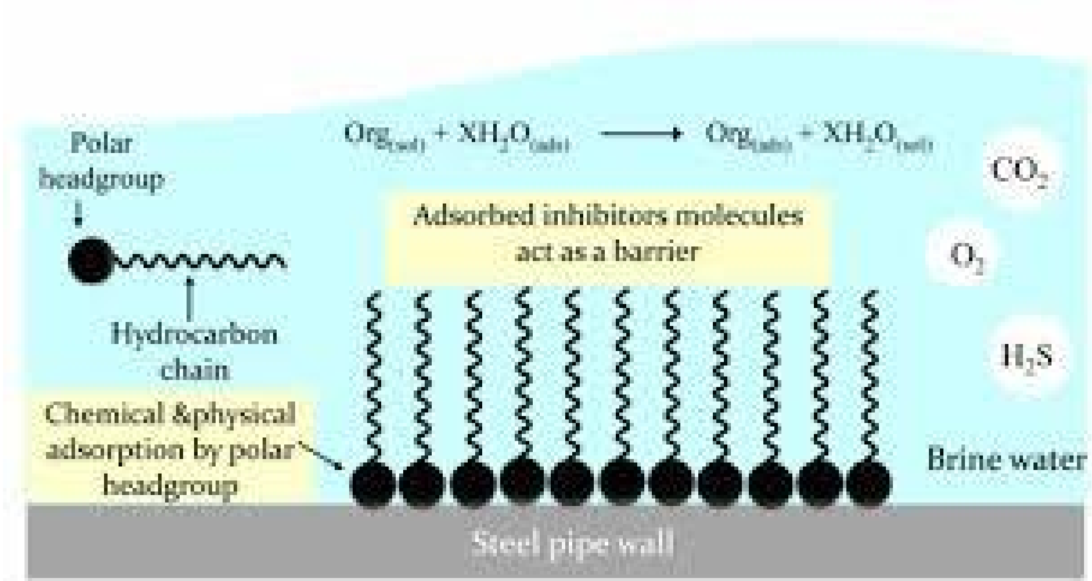
Figure: corrosion characteristics of an active-passive metal as a function of oxidizing power



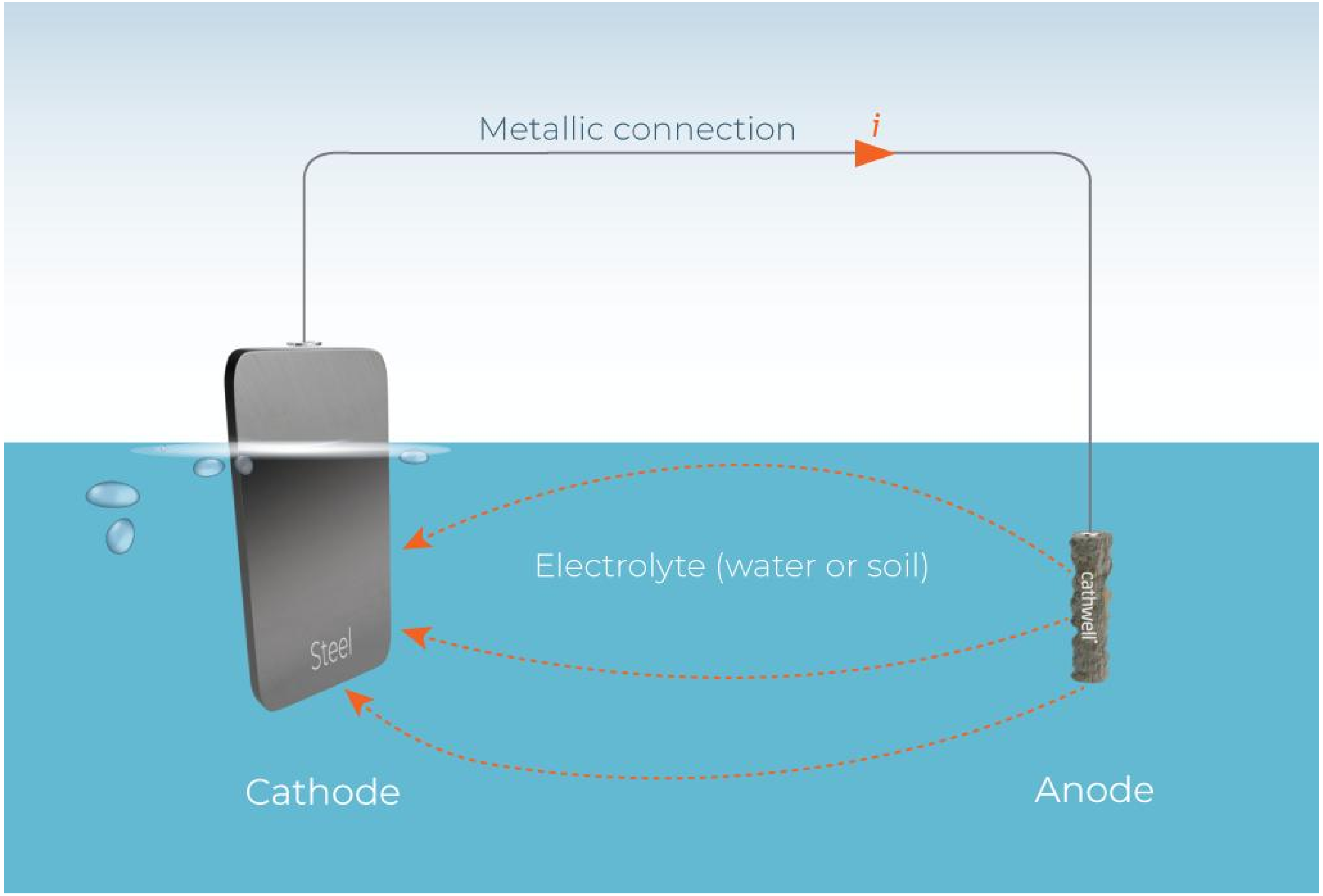
$2H^{+}, SO_4^{-2}$: in Low concentration

$H_2SO_4 \rightarrow O + H_2O + SO_2$

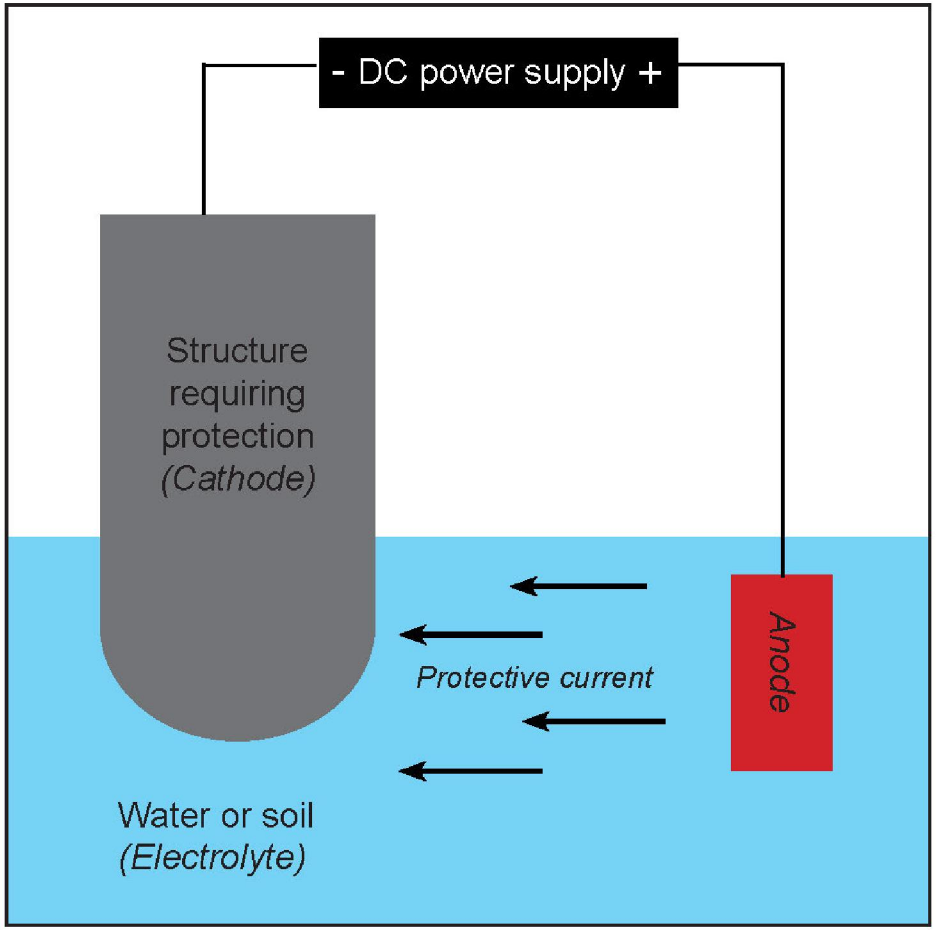
$Fe + O \rightarrow FeO$

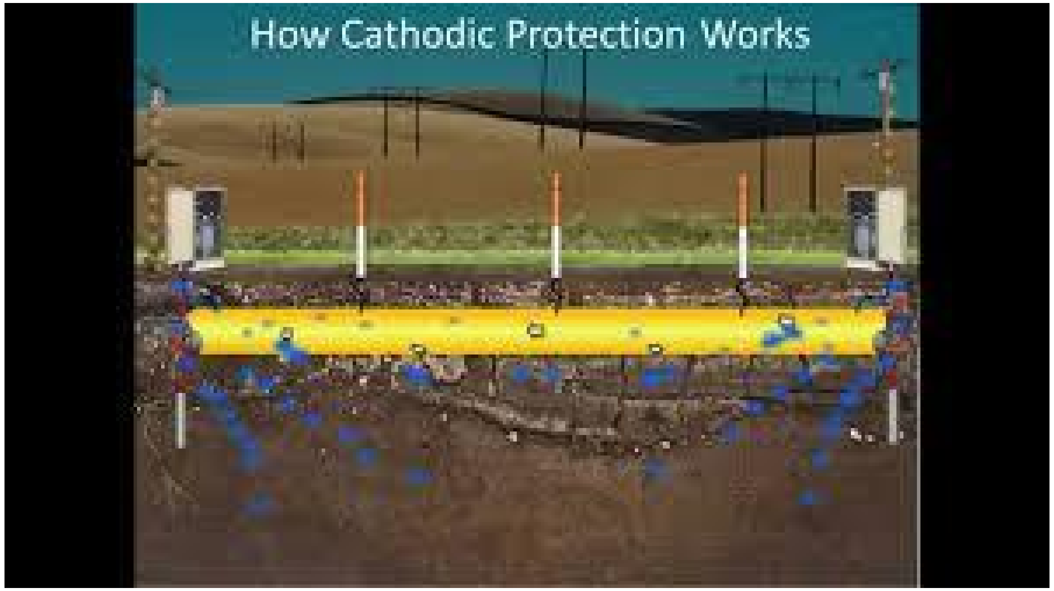


Polar headgroup
$Org_{(sol)} + XH_2O_{(ads)} \longrightarrow Org_{(ads)} + XH_2O_{(sol)}$
CO_2
Adsorbed inhibitors molecules act as a barrier
O_2
Hydrocarbon chain
H_2S
Chemical &physical adsorption by polar headgroup
Brine water
Steel pipe wall

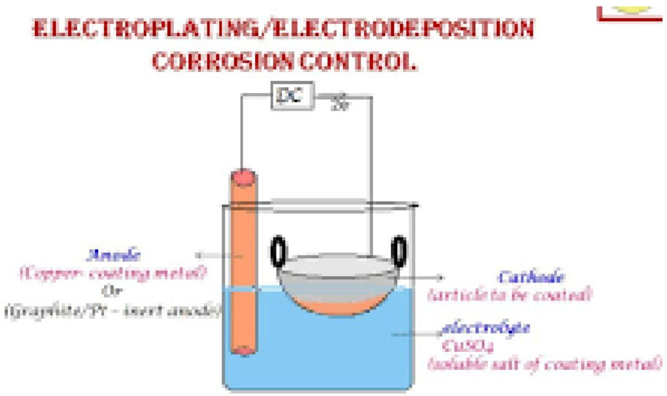


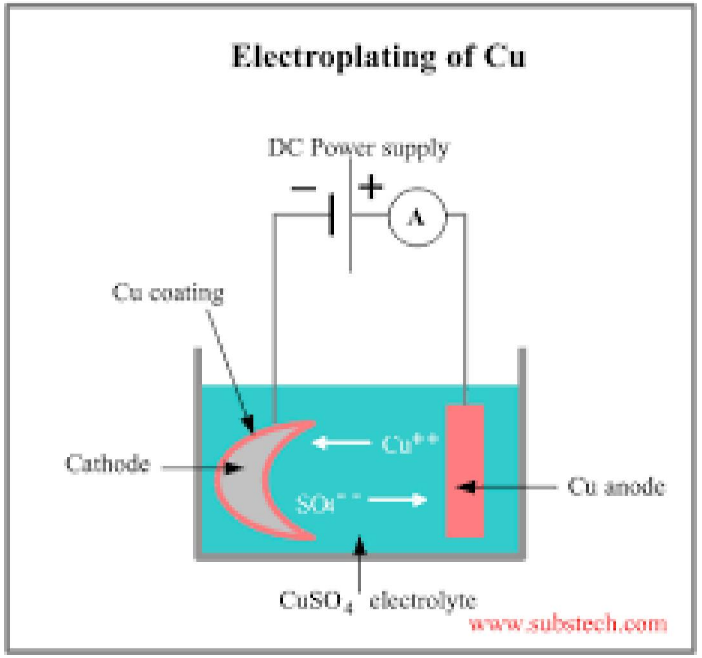
Metallic connection
i
Electrolyte (water or soil)
Steel
cathwell
Cathode
Anode


- DC power supply +
Structure requiring protection (Cathode)
Protective current
Anode
Water or soil (Electrolyte)

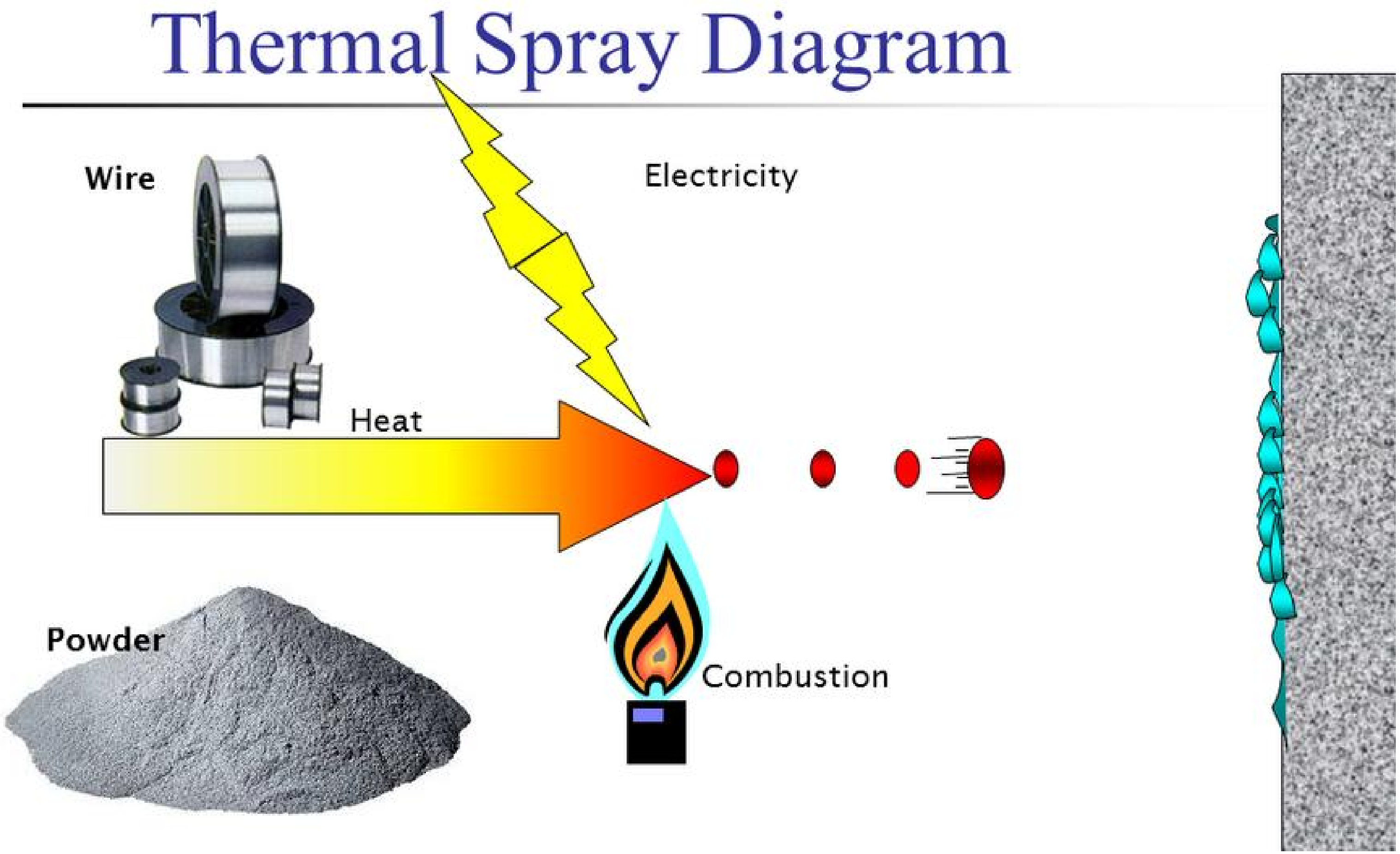

How Cathodic Protection Works

electrodeposition process

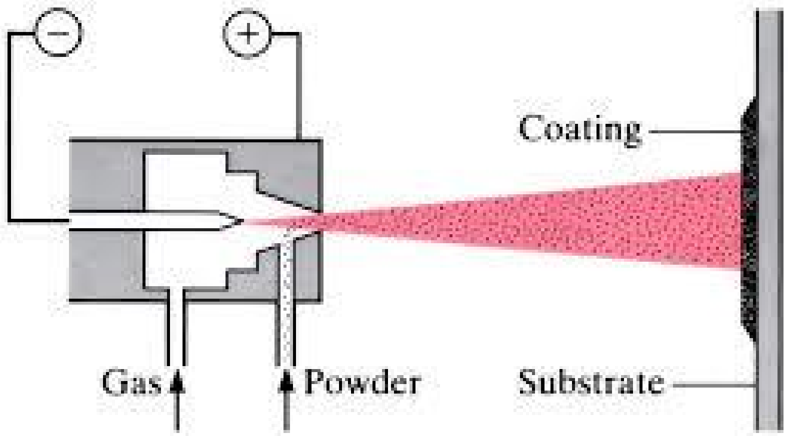




flame spraying process

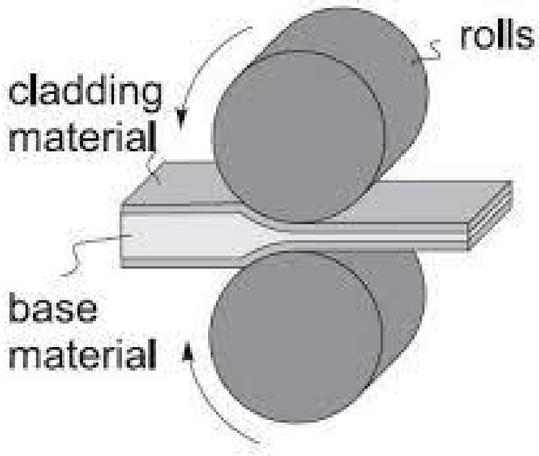


Plasma spraying process

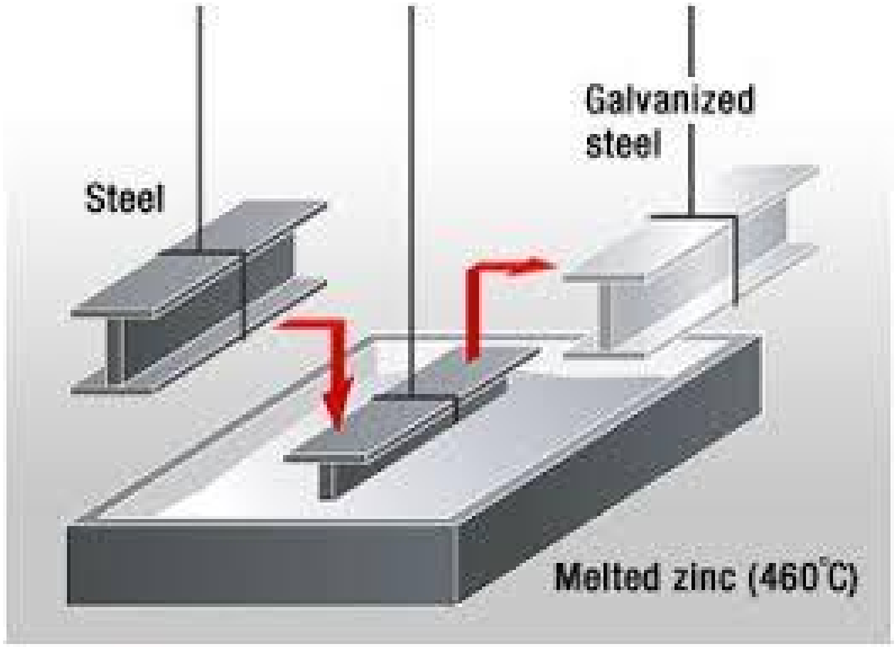


Plasma

cladding process



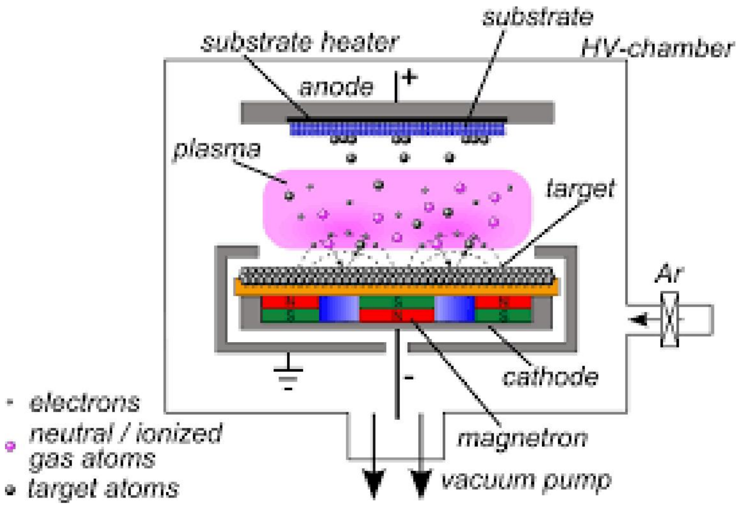
hot dipping process



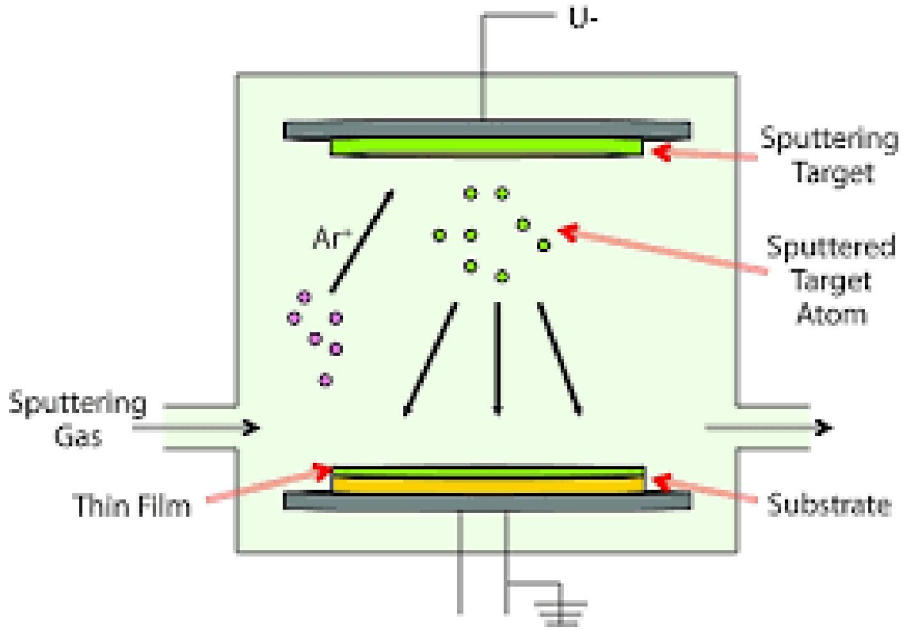
Vapor deposition

- PVD process
- CVD process

PVD process

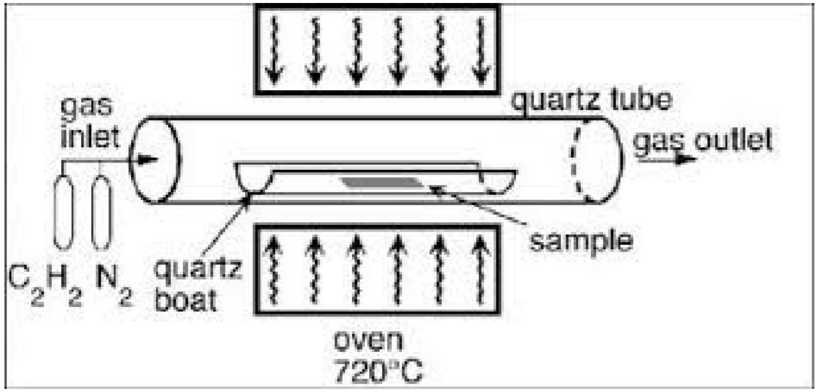


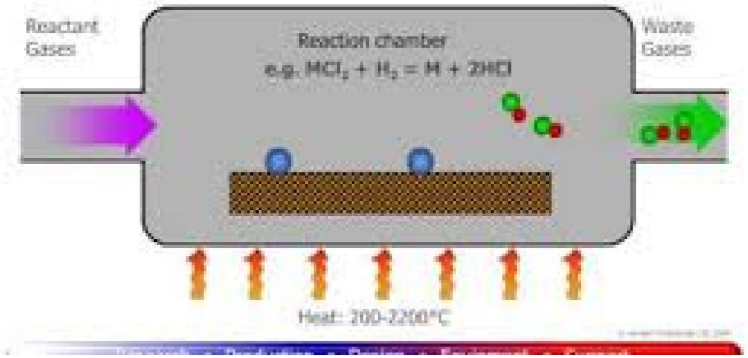
substrate heater
substrate
HV-chamber
anode
+
plasma
target
Ar
cathode
-
magnetron
vacuum pump
electrons
neutral / ionized gas atoms
target atoms

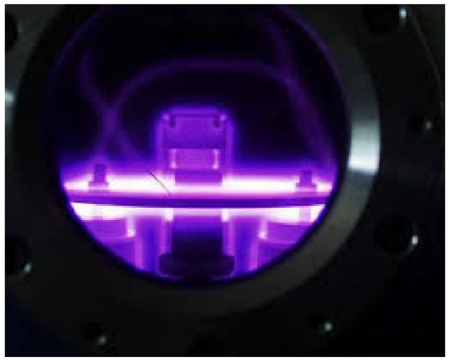


U-
Sputtering Target
Ar+
Sputtered Target Atom
Sputtering Gas
Thin Film
Substrate

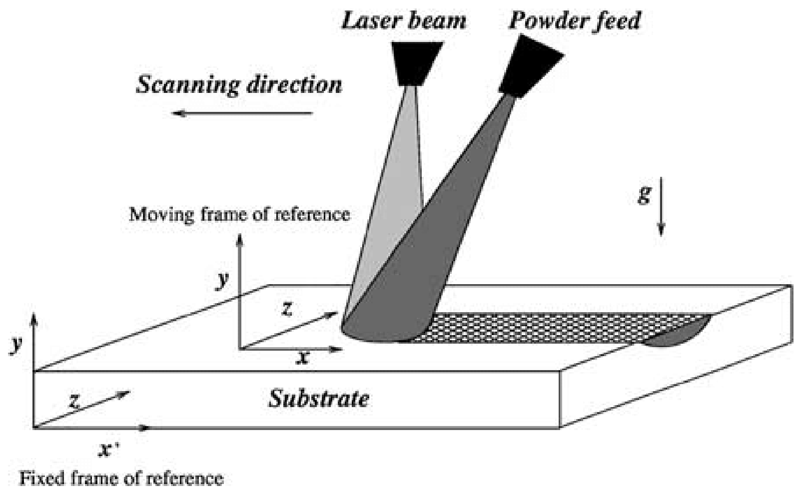
CVD process


gas inlet
quartz tube
gas outlet
sample
C_2H_2
N_2
quartz boat
oven
720°C

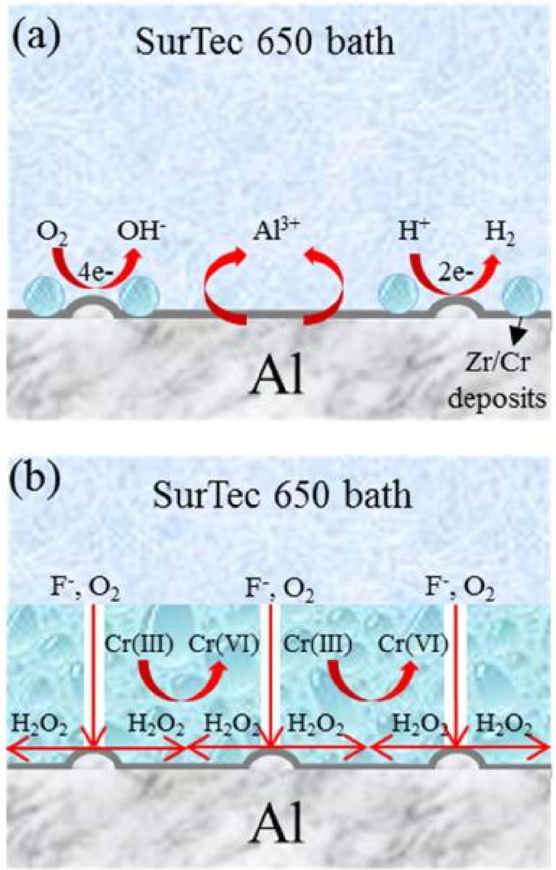

Reactant Gases
Reaction chamber
e.g. $MCl_2 + H_2 = M + 2HCl$
Waste Gases
Heat: 200-2200°C



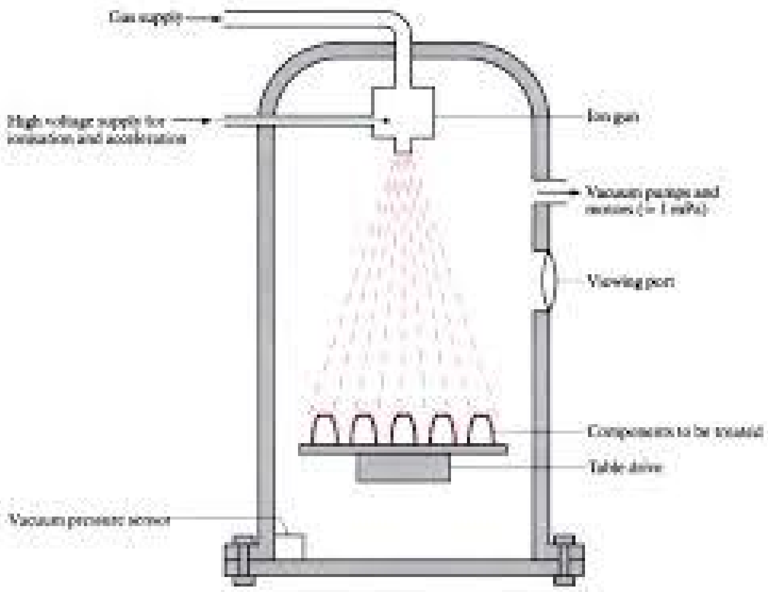
surface alloying process

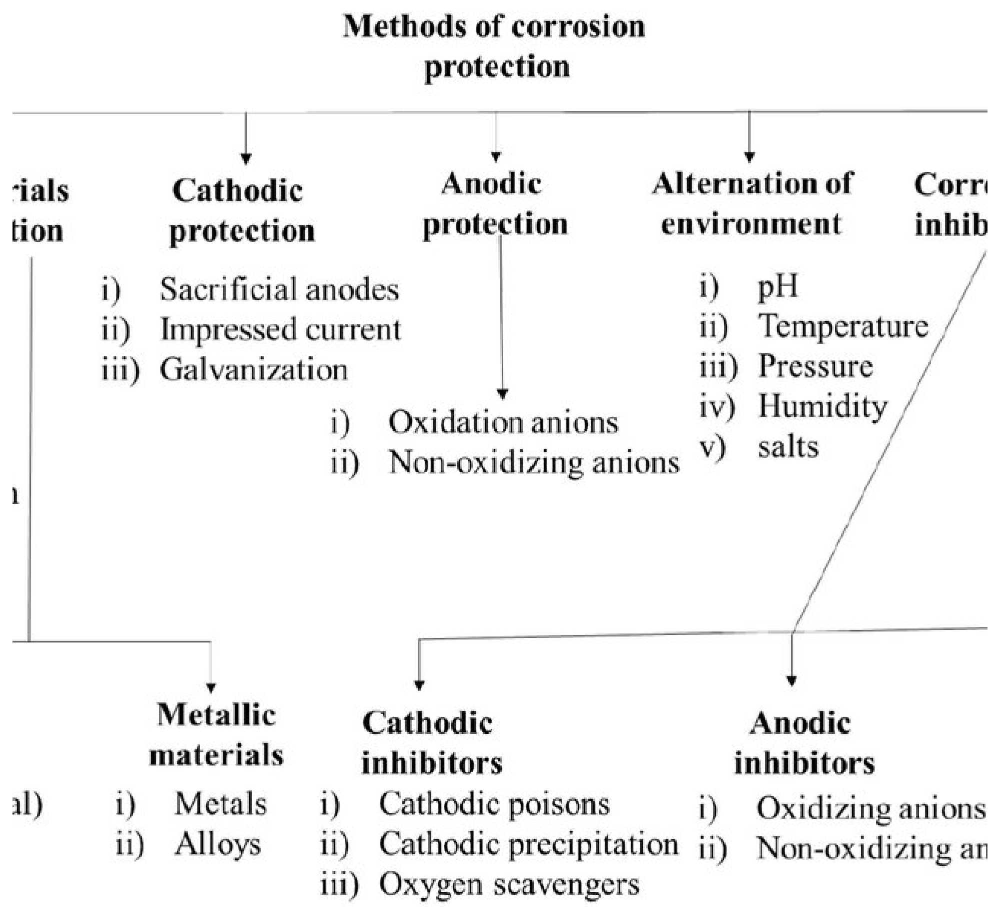


chemical conversion coating



ion implantation coating

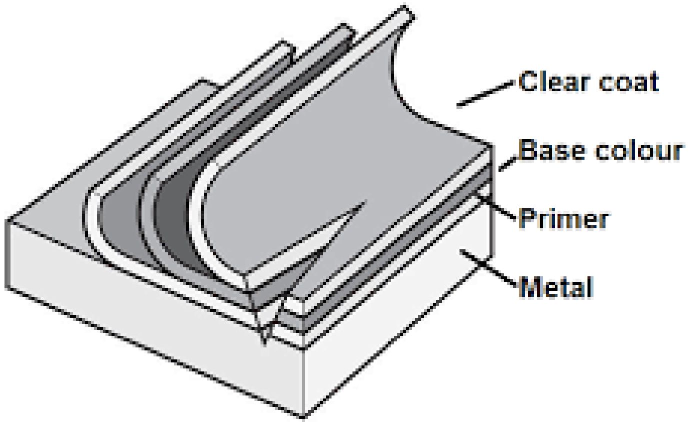



Methods of corrosion protection
rials
tion
Cathodic protection
i) Sacrificial anodes
ii) Impressed current
iii) Galvanization
Anodic protection
i) Oxidation anions
ii) Non-oxidizing anions
Alternation of environment
i) pH
ii) Temperature
iii) Pressure
iv) Humidity
v) salts
Corr
inhib
al)
Metallic materials
i) Metals
ii) Alloys
Cathodic inhibitors
i) Cathodic poisons
ii) Cathodic precipitation
iii) Oxygen scavengers
Anodic inhibitors
i) Oxidizing anions
ii) Non-oxidizing an

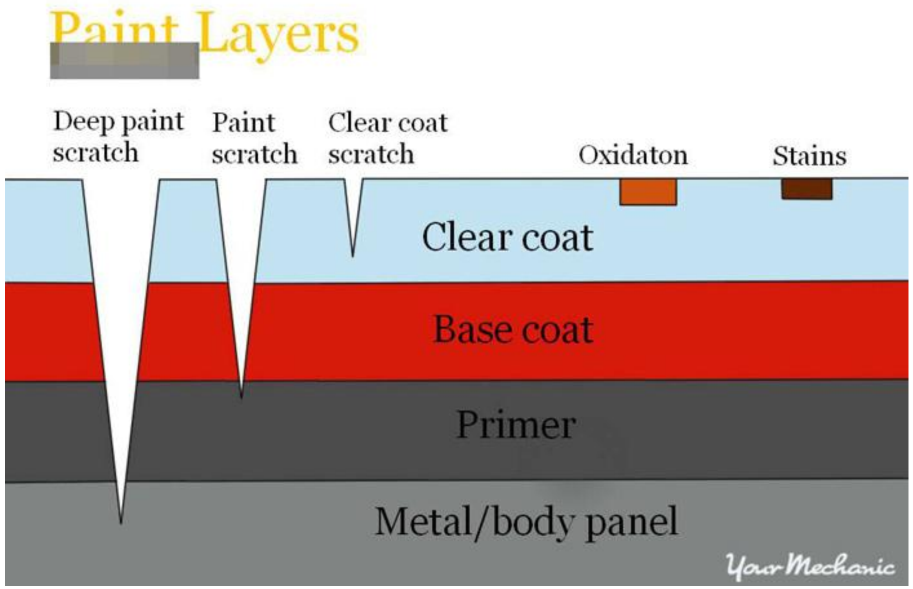
پوشش های آلی

انواع لاک ها، رنگ ها، لعاب ها، لاستیک های قیری و پلاستیک ها (از نوع وینیل یا پلی اتیلن یا تترافلوئوراتیلن یا اصطلاحا تفلون) پوشش های آلی هستند که می توانند ارتباط فلز را با محیط تا اندازه ای قطع کنند و در نتیجه موجب حفاظت فلزات گردند. عامل مهم در توسعه پوشش های آلی، صنعت نفت است که اجزای اصلی تشکیل دهنده رزین های شیمیایی را تولید می کند.

لایه های رنگ



Clear coat
Base colour
Primer
Metal



Paint Layers
Deep paint scratch
Paint scratch
Clear coat scratch
Oxidaton
Stains
Clear coat
Base coat
Primer
Metal/body panel
YourMechanic

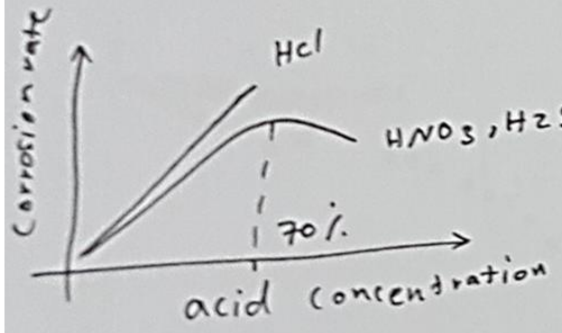
CHAPTER

SEVEN

MINERAL ACIDS

Most of the severe corrosion problems encountered involve the mineral acids or their derivatives. In this chapter we shall describe the production, use, and effects of sulfuric, nitric, hydrochloric, hydrofluoric, and phosphoric acids. The widespread use of these acids places them in an important position with regard to costs and destruction by corrosion. In some cases corrosion increases with concentration of the acid and in others it decreases. For these reasons it is important to have a good picture of corrosion by various acids. Sulfuric, nitric, and hydrochloric acids are the three most important inorganic acids. (Sulfuric and sulfamic acids exhibit about the same corrosive behavior.)

H_3NSO_3



$2H^{+}$, SO_4^{-2} : in Low concentration

$H_2SO_4 \rightarrow O + H_2O + SO_2$

$Fe + O \rightarrow FeO$

SULFURIC ACID

7-1 Steel

Ordinary carbon steel is widely used for sulfuric acid in concentrations over 70%.

7-2 Cast Iron

Ordinary gray cast iron generally shows the same picture as steel in sulfuric acid.

7-3 Chemical Lead

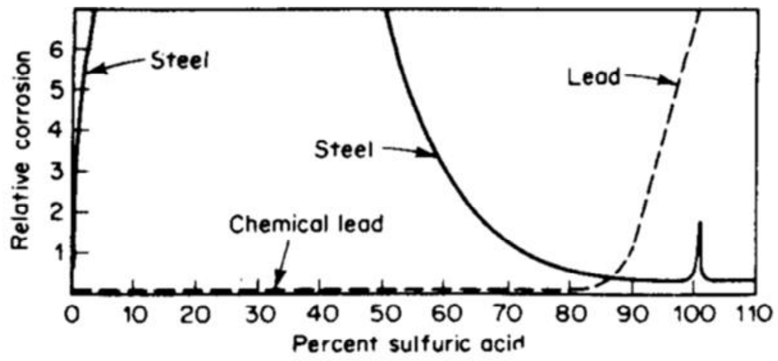


Figure 7-3 Corrosion of steel and chemical lead at atmospheric temperatures.

7-4 High-Silicon Cast Iron

A cast iron containing approximately 14.5% silicon possesses the best all-round corrosion resistance, over the range 0 to 100% sulfuric acid, of all

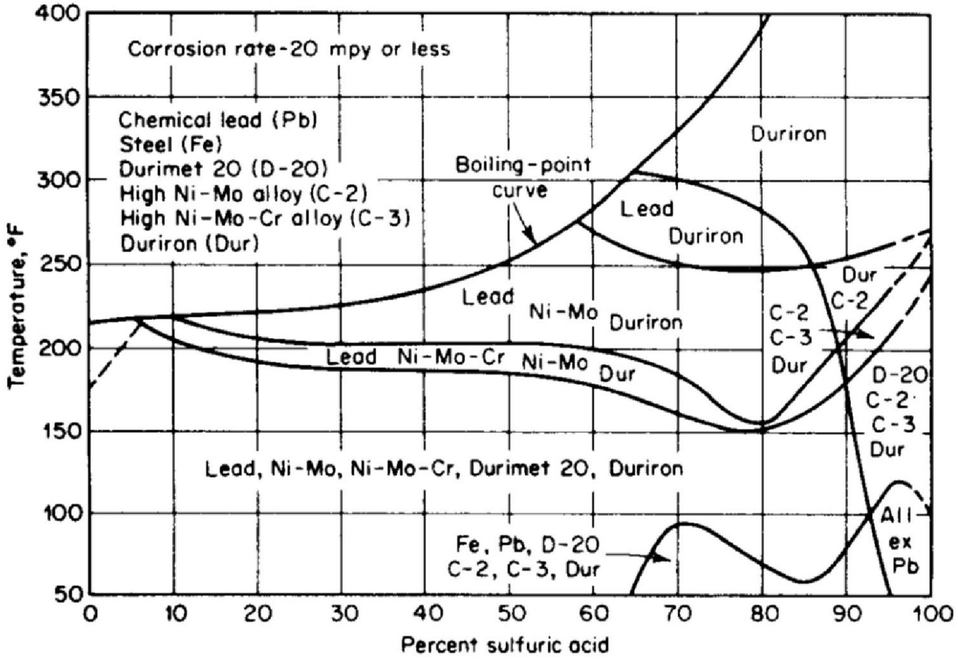


Figure 7-9 Combined chart for corrosion of six alloys by sulfuric acid.

NITRIC ACID

7-16 Stainless Steels

The stainless steels are the most widely used of the metals and alloys on a tonnage basis.

Table 7-3 Influence of chromium on resistance of low-carbon steel to boiling 65% nitric acid

% Cr	Average corrosion rate, mpy
4.5	155,000
8.0	1700
12.0	120
18.0	30
25.0	8

HYDROCHLORIC ACID

Hydrochloric acid is the most difficult of the common acids to handle from the standpoints of corrosion and materials of construction. Extreme care is required in the selection of materials to handle the acid by itself, even in relatively dilute concentrations, or in process solutions containing appreciable amounts of hydrochloric acid. This acid is very corrosive to most of the common metals and alloys.

Chlorimet 2, Chlorimet 3, Hastelloy B, Hastelloy C, Durichlor, tantalum, zirconium, and molybdenum

CHAPTER

EIGHT

OTHER ENVIRONMENTS

8-1 Organic Acids

Acetic acid is the most important organic acid from the standpoint of quantity produced. Many other organic acids show similar corrosion behavior and, in the absence of data, one must assume that they all behave alike. Types 316 and 304 stainless steels, copper and bronzes, 1100 and 3003 aluminum, Durimet 20, Duriron, and Hastelloy C are widely utilized for handling acetic acid. Type 316 is preferred for the more severe conditions involving glacial (98% +) acid or elevated temperatures. Aluminum, copper, and type 304 are good for room-temperature glacial acid and for more dilute acid. Copper was the early work horse for acetic acid but has lost much ground to the stainless steels, partly because of the reduced cost differential between these materials. Durimet 20 is used for pumps and Duriron for pumps, lines, and columns. Hastelloy C and Chlorimet 3 cannot be justified except for the most severe conditions.

Table 8-1 Corrosion by organic acids

Acid	Concentration	Temperature, °F	Aluminum*	Copper & bronze†	Type 304	Type 316	Durimet 20	Duriron
Acetic	50%	75	●	●	○	●	●	●
Acetic	50%	212	×	○	□	●	●	●
Acetic	Glacial	75	●	●	●	●	●	●
Acetic	Glacial	212	○	×	×	○	○	●
Citric	50%	75	○	□	○	○	●	●
Citric	50%	212	□	□	×	○	○	●
Formic	80%	75	○	○	○	●	●	●
Formic	80%	212	×	○	×	○	○	●
Lactic	50%	75	○	○	○	●	●	○
Lactic	50%	212	×	○	×	○	○	○
Maleic	50%	75	○	□	○	○	●	●
Maleic	50%	212	×	—	○	○	○	○
Naphthenic	100%	75	○	○	●	●	●	—
Naphthenic	100%	212	○	×	●	●	●	—
Tartaric	50%	75	○	□	●	●	●	●
Tartaric	50%	212	×	—	●	●	●	●
Fatty	100%	212	●	□	○	●	●	●

Legend: ● Less than 2 mpy, ○ less than 20 mpy, □ from 20 to 50 mpy, × over 50 mpy.

*More than 1% water for napthenic and fatty acids.

†Aeration greatly increases corrosion rate.

Source: Corrosion Data Survey, NACE.

8-2 Alkalies

The common alkalies such as caustic soda (NaOH) and caustic potash (KOH) are not particularly corrosive and can be handled in steel in most applications where contamination is not a problem. However, one must guard against stress corrosion in certain concentrations and temperatures, as described in Chap. 3. Rubber-base and other coatings and linings are applied to steel equipment to prevent iron contamination.

Nickel and nickel alloys are extensively used for combating corrosion by caustic. Nickel is suitable under practically all conditions of concentration and temperature. In fact, the corrosion resistance to caustic is almost directly proportional to the nickel content of an alloy. As little as 2% nickel in cast iron is beneficial. Monel (70% Ni), the austenitic stainless steels (8 to 20% Ni), and other nickel-bearing alloys are in many applications involving high temperatures or control of contamination.

8-3 Atmospheric Corrosion

Corrosion by various atmospheres accounts for more failures on a cost and tonnage basis than any other single environment, with an estimated cost of $2 billion in the United States. Atmospheres can be classified as industrial, marine, and rural. Corrosion is primarily due to moisture and oxygen but is accentuated by contaminants such as sulfur compounds and sodium chloride. Corrosion of steel on the seacoast is 400 to 500 times greater than in a desert area. Steel specimens 80 ft from the seashore corroded 12 times faster than those 800 ft away. Sodium chloride is the chief contaminant. This salt causes a large amount of corrosion of automobiles when it is used for deicing roads. Industrial atmospheres can be 50 to 100 times more corrosive than desert areas.

Industrial atmospheres are more corrosive than rural atmospheres, primarily because of sulfur gases generated by the burning of fuels. SO_2 in the presence of moisture forms sulfurous and sulfuric acids, which are both very corrosive. Table 8-3 illustrates the wide variation of corrosion in different parts of the world.

Small amounts of copper (tenths of one percent) increase resistance of steel to atmospheric corrosion because it forms a tighter, more protective rust film. Small amounts of nickel and chromium produce similar effects. Nickel and copper are helpful in industrial atmospheres because they form insoluble sulfates that do not wash away and thus afford some protection. For almost complete rust resistance in ferrous alloys, we must go to the stainless steels. Improving the corrosion resistance of steel with small alloy additions (low-alloy steels) is now commonly used in weight-saving applications and to increase durability of paint coatings.

8-4 Seawater

Seawater contains about 3.4% salt and is slightly alkaline, pH 8. It is a good electrolyte and can cause galvanic corrosion and crevice corrosion. Corrosion is affected by oxygen content, velocity, temperature, and biological organisms. Additional information is presented in Chap. 3.

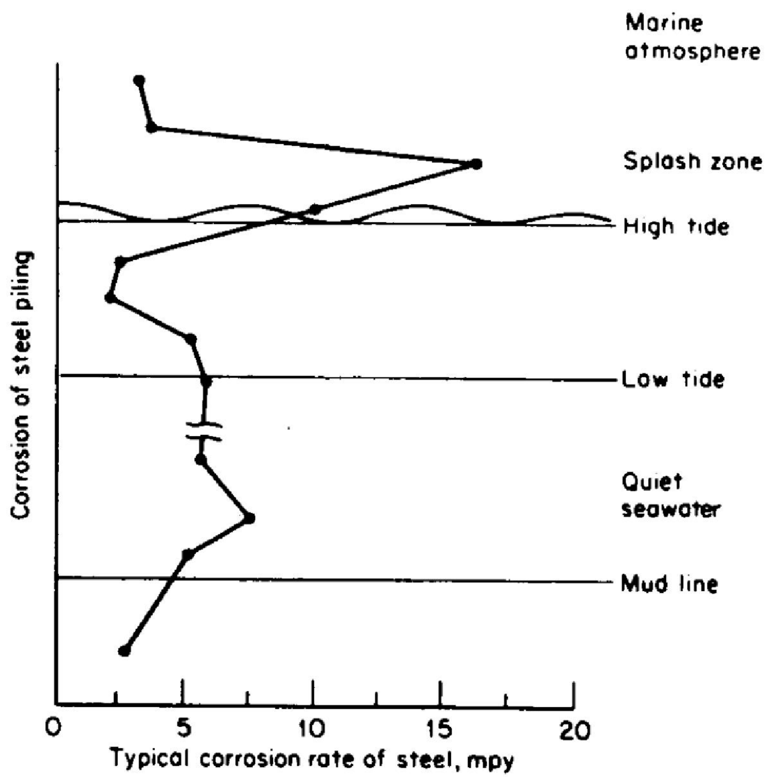


Figure 8-1 Corrosion of ordinary steel in the sea.

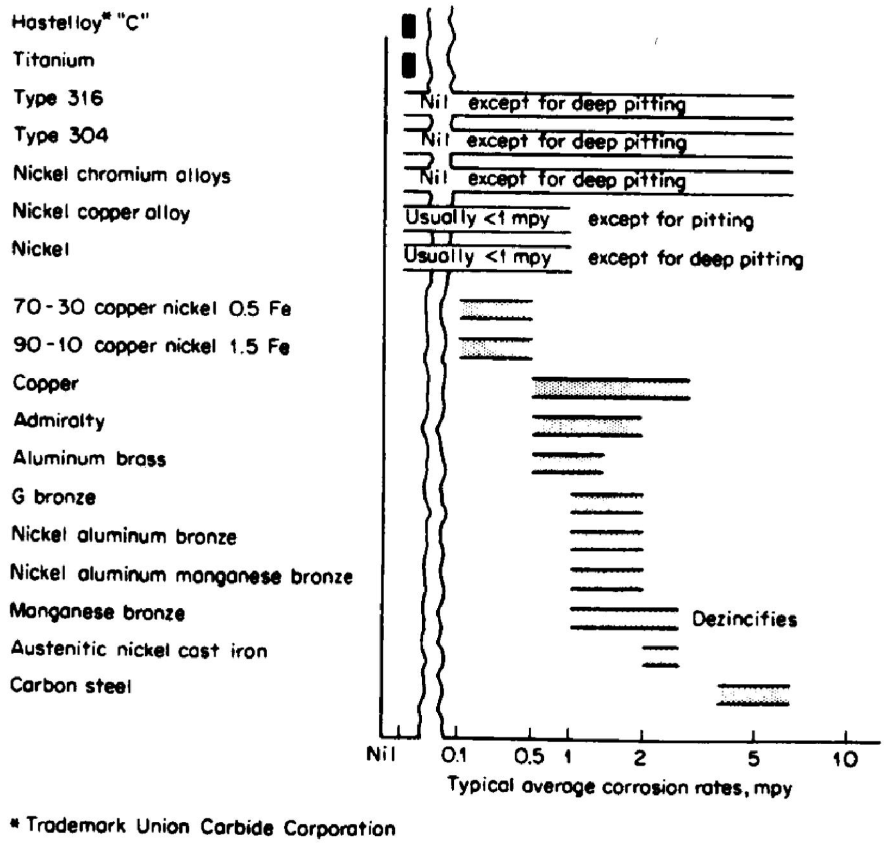


Figure 8-2 Corrosion of metals and alloys by quiet seawater—less than 2 ft/sec.

8-5 Fresh Water

Corrosivity in fresh water varies depending on oxygen content, hardness, chloride content, sulfur content, and many other factors. For example, a steel hot-water tank in a home may last 20 years in one area but only a year or two in other areas. Chloride contents may vary from a few parts per million (ppm) to several hundred within one county. Sulfur compounds in some localities in Ohio, for example, cause rapid corrosion of steel. For this reason, it is difficult to make general recommendations—it is a local problem.

Fresh water can be hard or soft, depending on minerals dissolved. In hard water, carbonates often deposit on the metal surface and protect it, but pitting may occur if the coating is not complete. Soft waters are usually more corrosive because protective deposits do not form.

Low-alloy steels do not offer any advantage over ordinary steel in water applications (as compared with atmospheric corrosion). For example, most boiler tubes and boiler-water systems are made from low-carbon steel. As is the case in atmospheric corrosion, complete corrosion resistance would require the more expensive stainless steels. Wrought iron offers no particular advantage over ordinary steel.

Cast iron, steel, and galvanized steel are the most widely used materials for handling fresh water. Copper, brass, aluminum, some stainless steels, Monel, and cupronickel are also used where temperature, contamination, or longer life are factors. Table 8-8* lists design and materials for heat exchangers using water as the coolant.

8-6 High-Purity Water

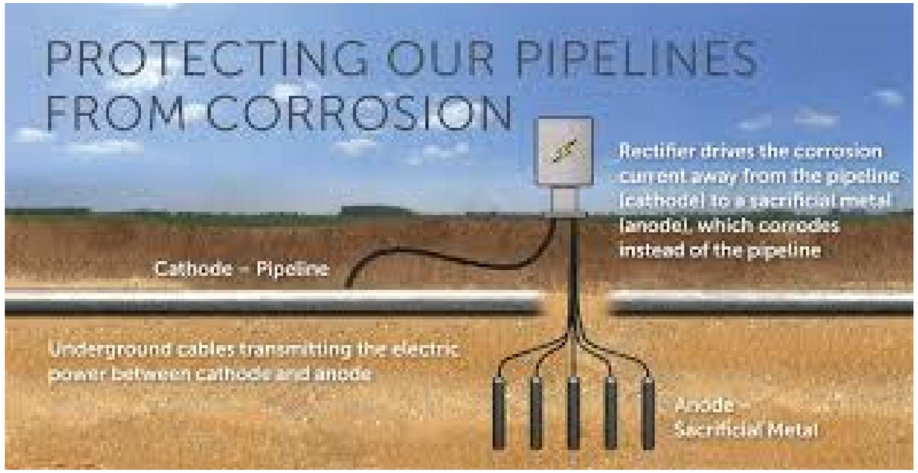
When water is used as a heat-transfer medium and very little corrosion can be tolerated, high-purity water is required. Atomic power plants and more conventional high-pressure power units are examples. Corrosion decreases with increasing purity of the water because of less solids and gases and increasing electrical resistance. Ordinary distilled water exhibits resistance around 200,000 ohm-cm. Resistance is a measure of water purity. In some atomic applications 1 to 2 megohm water is utilized. At high temperatures (600 to 700°F) about 10 ppm O_2 and H_2 are formed because of radiolytic decomposition of the water. Overpressure with hydrogen reduces the O_2 formed. Intergranular attack and cracking of solution-quenched stainless steels and alloys have been observed in high-purity water containing oxygen.

8-7 Soils

Corrosivity of soils varies over a wide range because of the variety of compositions. Tests in one location are generally applicable only to that location. Tests of several years' duration are needed to obtain reliable data. Factors affecting corrosiveness of soils are moisture, alkalinity, acidity, permeability of water and air (compactness or texture), oxygen, salts, stray currents, and biological organisms (discussed below).

. Most of these factors affect electrical resistance, which is a good measure of corrosivity. High-resistance dry soils are generally not very corrosive. Pitting is a major problem because of crevice corrosion and contact with "foreign" objects in the backfill such as stones, cinders, wood, and metal. The National Bureau of Standards has studied corrosion by soils for many years.*

Ordinary carbon steel and cast iron with and without organic coatings and cathodic protection are most common for underground structures. Other materials are generally not economical.


PROTECTING OUR PIPELINES
FROM CORROSION
Rectifier drives the corrosion current away from the pipeline (cathode) to a sacrificial metal (anode), which corrodes instead of the pipeline
Cathode – Pipeline
Underground cables transmitting the electric power between cathode and anode
Anode – Sacrificial Metal

8-8 Aerospace

In itself, the hard vacuum of space does not cause corrosion. The severe corrosion problems are due to liquids such as oxidizers and fuels and also the high temperatures encountered in blast nozzles and during reentry. Refractory metals such as tungsten are used for nozzles because of their strength at very high temperatures.

Al, Mg, Ti, and Fe and their alloys are the primary metallic materials involved for aircraft. Stress corrosion, pitting, intergranular attack, crevice corrosion, and two-metal corrosion cause difficulties. Al and Mg alloys are anodic to most other metals. Protective systems include anodizing, cladding, and conversion coatings.

8-9 Petroleum Industry

The petroleum industry contains a wide variety of corrosive environments. Some of these have been described elsewhere in the book, whereas many are unique to this industry. Thus it is convenient to group all these environments together. Corrosion problems occur in the petroleum industry in at least three general areas: (1) production, (2) transportation and storage, and (3) refinery operations.

Sweet oil wells It appears that corrosion in high-pressure flowing wells that produce pipeline oil has become almost commonplace in many areas. Three methods are used to combat this corrosion—coated tubing, inhibitors, and alloys. Coated tubing has found most favor, and until recently, baked-on phenolics have been used for almost all coating installations. Air-dried and baked epoxy resins are now being used in increasing amounts. Coatings have been discussed in Chap. 6.

Sour oil wells These wells handle oil with higher sulfur contents than sweet wells and represent a more corrosive environment. In high-H_2S wells there may be severe attack on the casing in the upper part of the well where the space is filled with gas. Water vapor condenses in this area and picks up H_2S and CO_2.

8-10 Biological Corrosion

Biological corrosion is not a type of corrosion; it is the deterioration of a metal by corrosion processes that occur directly or indirectly as a result of the activity of living organisms. These organisms include micro forms such as bacteria and macro types such as algae and barnacles. Microscopic and macroscopic organisms have been observed to live and reproduce in mediums with pH values between 0 and 11, a temperatures between 30 and 180°F, and under pressures up to 15,000 lb/in.^{2}. Thus biological activity may influence corrosion in a variety of environments including soil, natural water and seawater, natural petroleum products, and oil emulsion-cutting fluids.

Living organisms are sutained by chemical reactions. That is, organisms ingest a reactant or food and eliminate waste products. These processes can affect corrosion behavior in the following ways:

1. By directly influencing anodic and cathodic reactions
2. By influencing protective surface films
3. By creating corrosive conditions
4. By producing deposits

These effects may occur singly or in combination, depending on the environment and the organism involved.

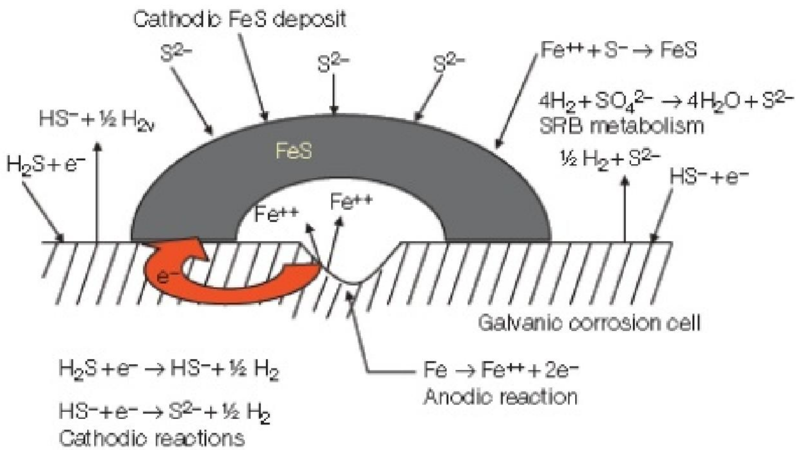
Microorganisms Usually, microorganisms are classified according to their ability to grow in the presence or absence of oxygen. Organisms that require oxygen in their metabolic processes are termed *aerobic*; they grow only in nutrient mediums containing dissolved oxygen. Other organisms, called *anaerobic*, grow most favorably in environments containing little or no oxygen.

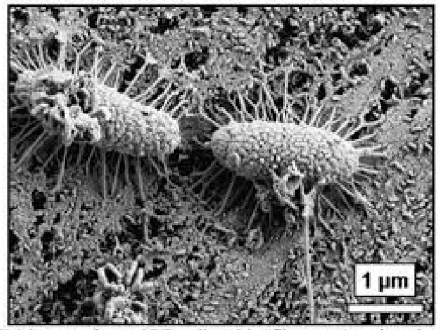
Although the acceleration of corrosion by microbiological organisms is quite widespread, there has been relatively little detailed research concerned with the identification of these species and the precise mechanism involved. Below, some of the more important and more completely studied microorganisms are discussed, together with other, lesser known types.

Anaerobic bacteria Probably the most important anaerobic bacteria that influence the corrosion behavior of buried steel structures are the sulfate-reducing types (*D. desulfuricans*). These reduce sulfate to sulfide according to the following schematic equation:

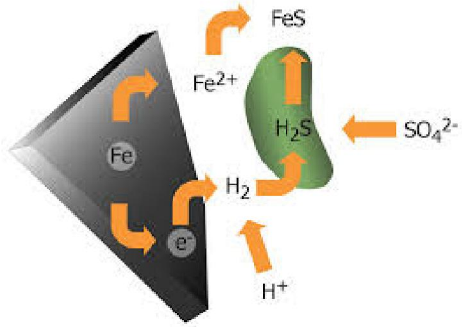
$$SO_4^{2-} + 4H_2 \rightarrow S^{2-} + 4H_2O \qquad (8.1)$$

The source of hydrogen shown in the above equation can be that evolved during the corrosion reaction or that derived from cellulose, sugars, or other organic products present in the soil.





SEM image of two SRB cells with "filaments" anchored on



Aerobic bacteria Aerobic sulfur-oxidizing bacteria, such as thiobaccillus thiooxidans, are capable of oxidizing elemental sulfur or sulfur-bearing compounds to sulfuric acid according to the following equation:

$$2S + 3O_2 + 2H_2O \rightarrow 2H_2SO_4 \tag{8.2}$$

These organisms thrive best in environments at low pH and can produce localized sulfuric acid concentrations up to 5% by weight. Thus, sulfur-oxidizing bacteria are capable of creating extremely corrosive conditions. These organisms require sulfur in either elemental or combined form for their existence and are therefore found frequently in sulfur fields, in oil fields, and in and about sewage disposal piping that contains sulfur-bearing organic waste products. In the case of sewage lines, sulfuric-oxidizing bacteria cause rapid acid attack of cement piping.

Sulfate-reducing and sulfur-oxidizing bacteria can operate in a cyclic fashion when soil conditions change. That is, sulfate-reducing bacteria grow rapidly during rainy seasons when the soil is wet and air is excluded, and sulfur-oxidizing bacteria grow rapidly during dry seasons when air permeates the soil. In certain areas, this cyclic effect causes extensive corrosion damage of buried steel pipelines. Also, it is evident that the presence of micro-organisms can accentuate conditions of differential aeration in soils.

Other microorganisms There are various other microorganisms that directly or indirectly influence the corrosion behavior of metals and but have not been studied in great detail. For example, several types of bacteria utilize hydrocarbons and can damage asphaltic pipe coatings. Iron bacteria are a group of microorganisms that assimilate ferrous iron from solution and precipitate it as ferrous or ferric hydroxide in sheets surrounding their cell walls. The growth of iron bacteria frequently results in tubercles on steel surfaces and tends to produce crevice attack. Certain bacteria are capable of oxidizing ammonia to nitric acid. Dilute nitric acid corrodes iron and most other metals. However, in most soils the amount of available ammonia is not high enough to cause an appreciable accumulation of nitric acid. However, these kinds of bacteria may be important where extensive use of synthetic ammonia fertilizers has been employed on cultivated fields above buried pipelines. Finally, most bacteria also produce carbon dioxide, which can contribute to the formation of carbonic acid and increase corrosivity.

MACROORGANISMS

Fungus and mold Actually, fungus and mold are the same inasmuch as both terms refer to a group of plants characterized by their lack of chlorophyll. These species assimilate organic matter and produce considerable quantities of organic acids including oxalic, lactic, acetic, and citric acids. Fungi are capable of growing on a variety of substrates and are a particularly troublesome problem, especially in tropical areas. The most familiar type of attack of this kind is the mildewing of leather and other fabrics. In addition, fungi can attack rubber and bare and coated metal surfaces. In many instances the presence of fungi does not cause severe mechanical damage but affects the appearance of the product, which is undesirable. In addition to producing organic acids, fungi can also initiate crevice attack of metal surfaces.

Mold growth on coated and uncoated metal surfaces can be prevented or reduced by periodic cleaning. Also, reducing the relative humidity during storage and the employment of toxic organic agents (e.g., gentian violet) have also been found effective in reducing mold growth on metal surfaces. Mold growth on rubber is particularly troublesome in underground cables, since localized perforation of the rubber coating results in electrical leakage. The substitution of synthetic instead of natural rubber has been found to be an effective method for preventing this kind of failure.

8-11 Human Body†

For more than a hundred years, foreign materials have been routinely implanted in the mouth for dental treatment. These include silver amalgams, gold, cements, porcelain, and more recently, stainless steels and plastics. As the art and science of medicine has progressed, the applications of implants have increased rapidly. Today, screws, plates, and rods are used to repair severe fractures; cosmetic surgery utilizes liquid and solid polymers; pulse rate, blood pressure, and bladder function in diseased patients are controlled by internal electric devices; reliable contraception has been achieved by the implantation of objects in the uterus; and defective heart valves have been replaced by artificial ball-check valves. Experiments with animals and limited clinical tests with humans indicate that functioning artificial hearts (and other organs) are possible.

خوردگی گالوانیک- شیاری و فرسایشی

$$ne + M^{+ne} \longrightarrow M$$

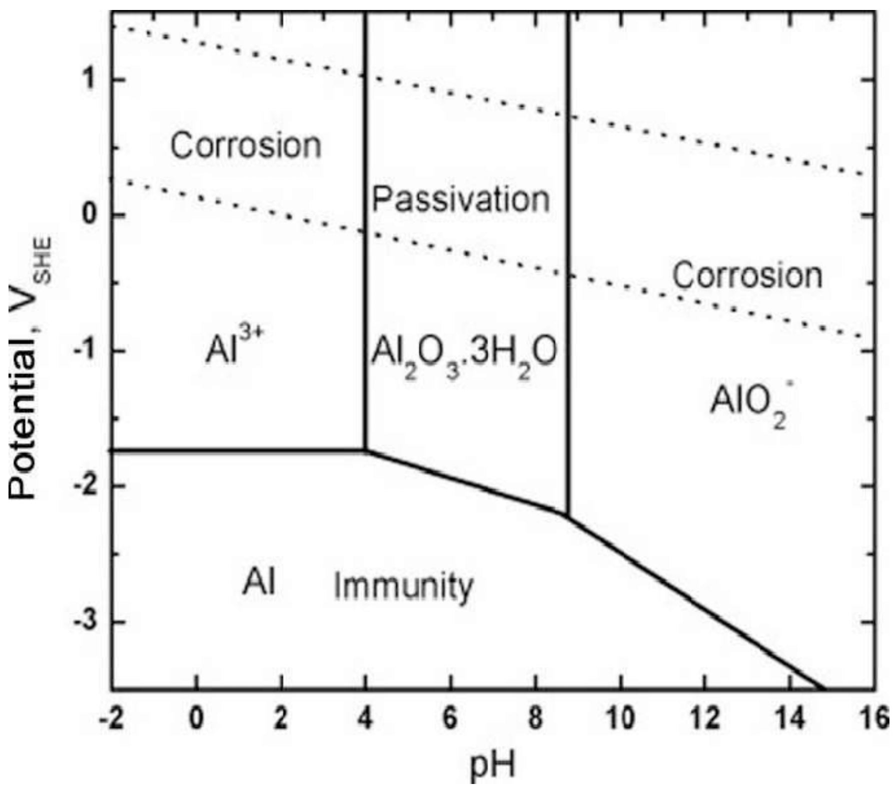
$$\Delta G = \Delta G^\circ + RT \ln \frac{a_p}{a_r}$$

$$-\frac{\Delta G}{nF} = -\frac{\Delta G^\circ}{nF} - \frac{RT}{nF} \ln \frac{a_p}{a_r}$$

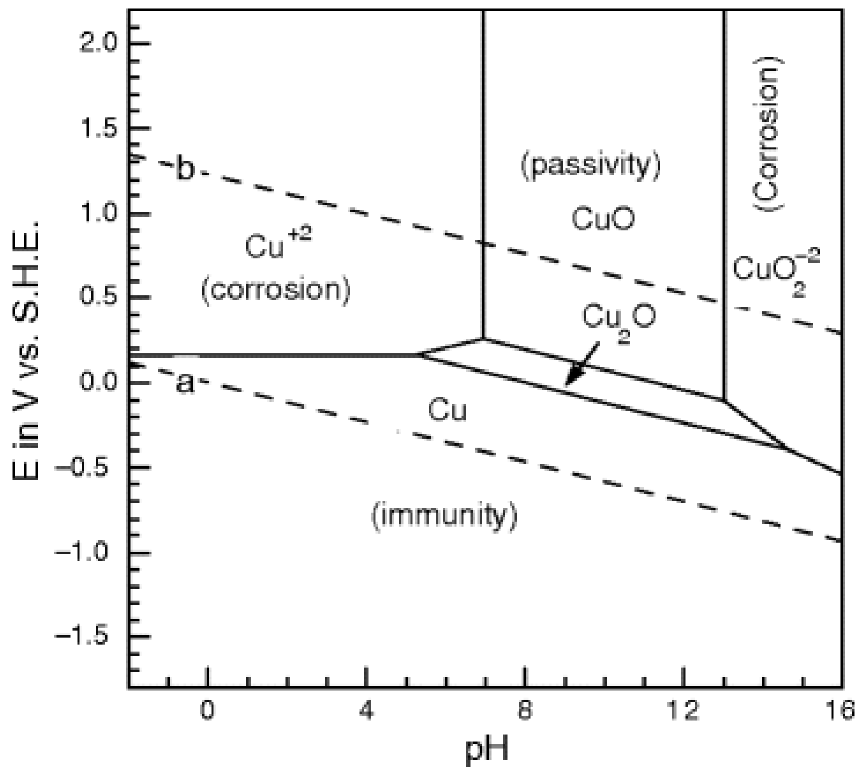
$$E = E^\circ - 2.3\frac{RT}{nF} \log \frac{a_p \rightarrow 1}{a_r}$$

$$E = E^\circ + 2.3\,\frac{RT}{nF} \log a_r$$

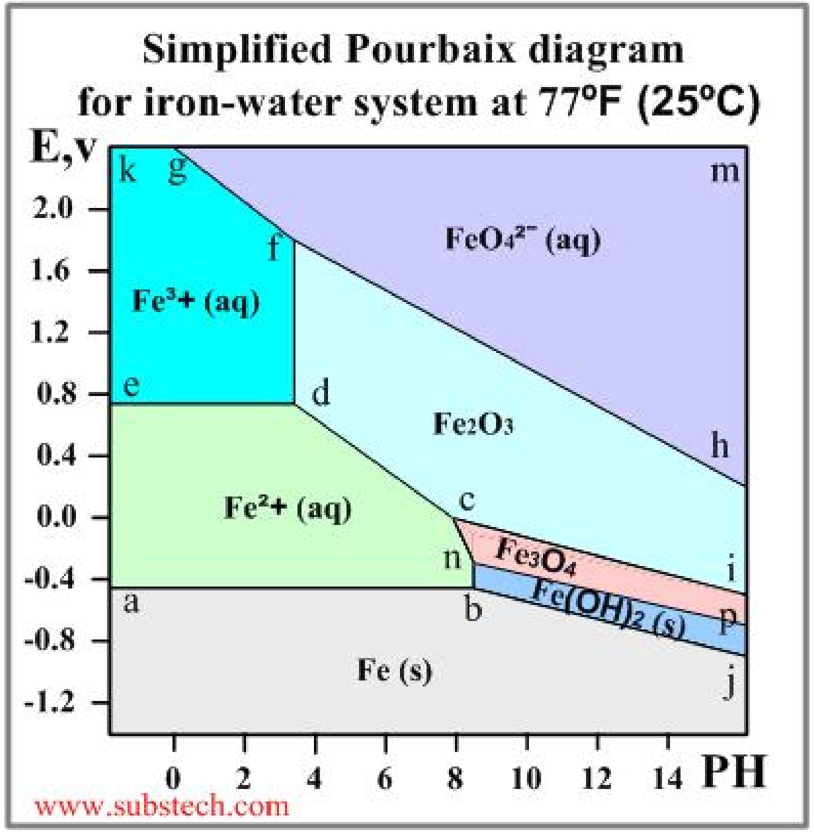
$$E = E^\circ + \frac{0.0591}{n} \log [M^{n+}]$$



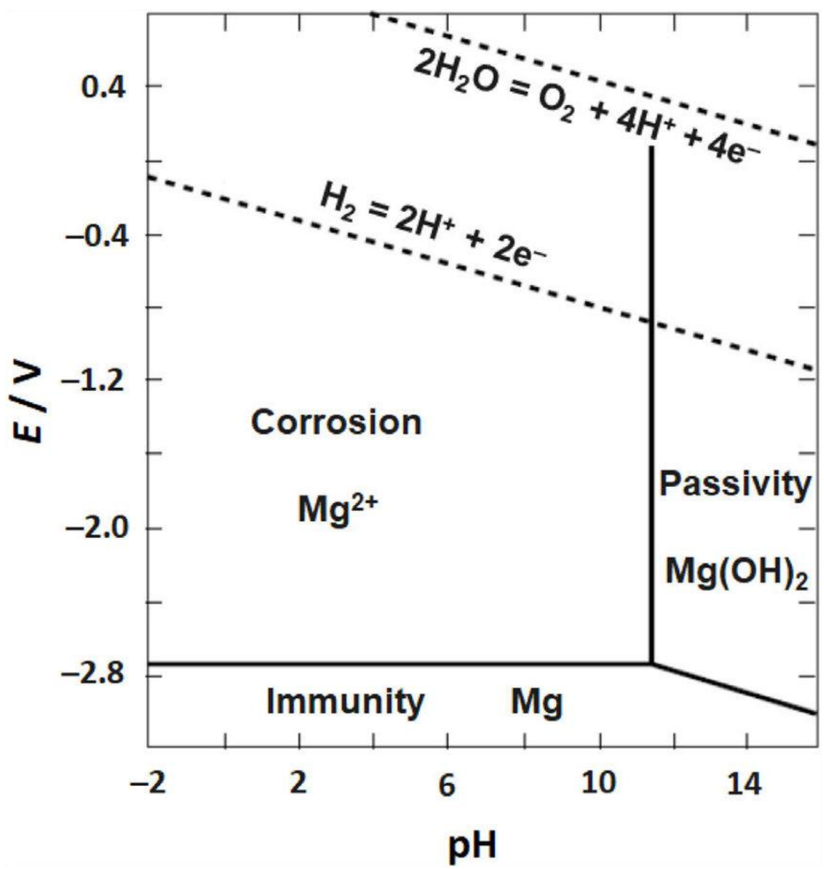
Corrosion
Passivation
Corrosion
Al3+
Al2O3.3H2O
AlO2-
Al
Immunity
Potential, VSHE
pH
1
0
-1
-2
-3
-2
0
2
4
6
8
10
12
14
16



2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
−1.5
E in V vs. S.H.E.
0
4
8
12
16
pH
b
a
Cu^{+2}
(corrosion)
(passivity)
CuO
Cu_2O
(Corrosion)
CuO_2^{-2}
Cu
(immunity)



Simplified Pourbaix diagram
for iron-water system at 77ºF (25ºC)
E,v
k
g
m
f
FeO_4^{2-} (aq)
Fe^{3+} (aq)
e
d
Fe_2O_3
h
c
Fe^{2+} (aq)
n
Fe_3O_4
i
a
b
$Fe(OH)_2$ (s)
p
Fe (s)
j
2.0
1.6
1.2
0.8
0.4
0.0
-0.4
-0.8
-1.2
0
2
4
6
8
10
12
14
PH
www.substech.com



0.4
−0.4
−1.2
−2.0
−2.8
E / V
2H2O = O2 + 4H+ + 4e−
H2 = 2H+ + 2e−
Corrosion
Mg2+
Passivity
Mg(OH)2
Immunity
Mg
−2
2
6
10
14
pH