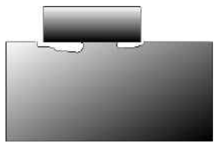
금속 소재의 환경노출거동: 12주차

Degradation Behavior of Metals and Alloys

after Exposure to Elements: 12th Lecture

날짜: 2020년 11월 20일

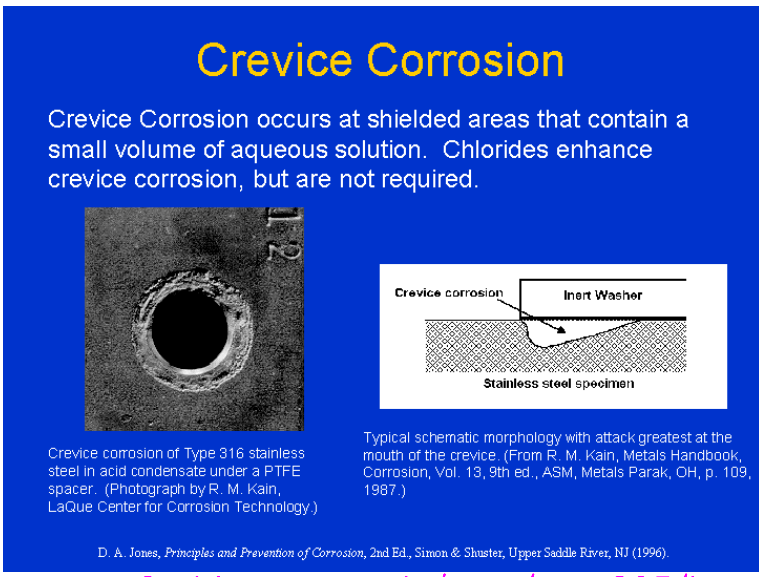
■ 강의 내용

1. 틈 부식 (Crevice Corrosion) ⇒ 

-. Source of crevice: mud, sand, insoluble solid

-. Crevice corrosion of stainless steel in aerated hot salt solution

-. 이종 금속 간 전기적 접촉 수반 시 galvanic corrosion effect도 부가되어 부식이 가속화 됨



(출처:www.ecr6.ohio-state.edu/mse/mse205/lectures)

CREVICE CORROSION

Intensive local corrosion in crevices or other shielded areas on a metal structure.

Symptomatic of stagnant areas (no fluid flow)

Essentially – concentration cell condition

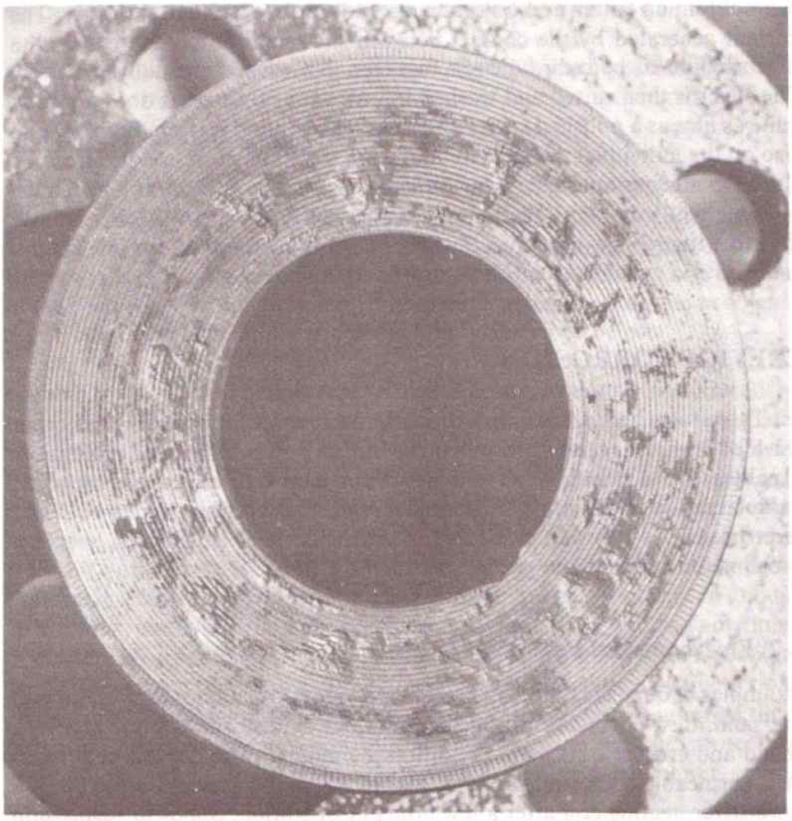
- very common on metal surfaces containing deposits of sand, dirt etc.
deposit – acts as shield and creates stagnant conditions underneath

Also common when metal + non-metal in contact
e.g. rubber, wood, glass etc.

Pipe flange – in contact with a rubber gasket

localized crevice corrosion occurs

- considerable problem with stainless steel



Interesting fact:

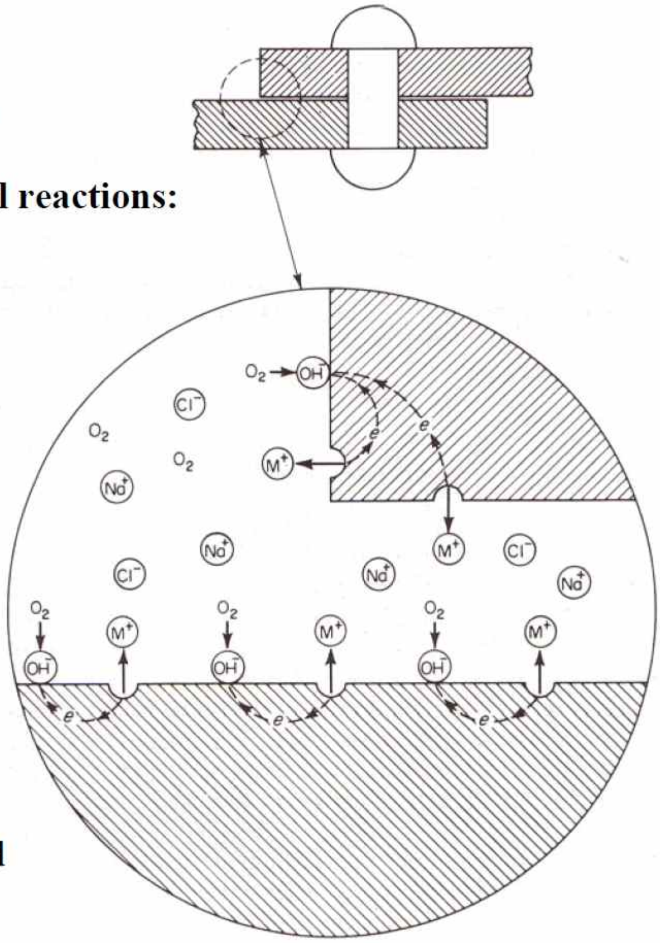
To cut a sheet of 18-8 stainless steel…

Stretch a rubber band over it and immerse in sea water!

Mechanism

Best explained through an example of riveted plates:

Metal = M



environment = sea water

Standard electrochemical reactions:

Oxidation:
M → M+ + e-
Reduction:
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Initially
– reactions are uniform over all surfaces *including* interior of the crevice

After 6-12 months –
O_2 in crevice is used up (depleted) due to reduced convection (turbulence)

Not a problem on its own…

However – no more O_2 reduction possible
∴ leads to surplus of M^+ ions which is then balanced by migration of Cl^- ions into the crevice (and limited OH^-)
giving $M^+ + Cl^- + H_2O \rightarrow MOH\downarrow + H^+ + Cl^-$

Presence of H^+ and Cl^-
- accelerates metal dissolution in crevice

More M^+ ions causes more Cl^- migration

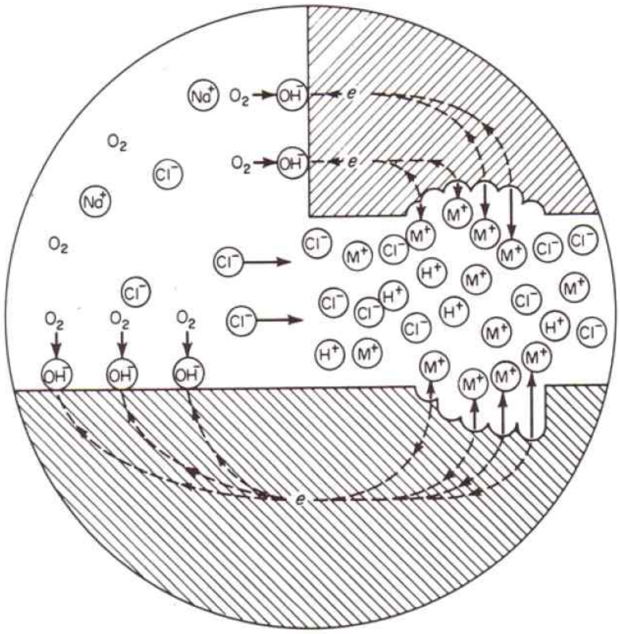
∴ process accelerates (autocatalytic)

∴ very rapid

Causes rate of O_2 reduction on other surfaces to increase

renders them cathodic

∴ no corrosion occurs other than in crevice



NOTE:
Particularly severe with passive metals
- passive coatings often broken down by chlorine

e.g. stainless steel aluminium etc.

For an active-passive metal to be resistant to crevice corrosion

it must have
- **a narrow active-passive transition**
- **a small critical current density**
- **an extended passive region**

e.g. titanium

PREVENTION

1 use butt welded joints – not rivets of bolts
- must weld from both sides!

2 in existing lap joints – close crevices!

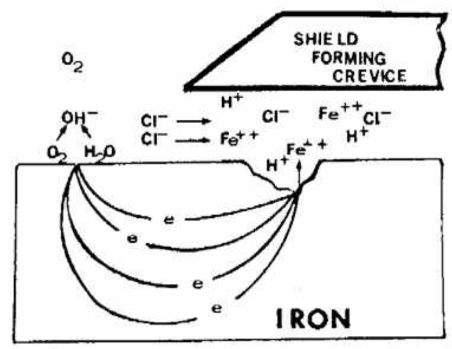
3 design to avoid sharp corners and stagnant pools

4 keep structures clean and inspect frequently

5 where possible – remove precipitates and solids from solution
i.e. filters!

6 remove wet packing materials during long shutdowns

7 if metal/non-metal contact must occur – ensure non-metal is as non-porous as possible e.g. TEFLON

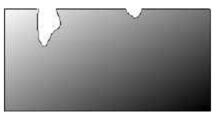


Crevice corrosion on the face of a flange caused by absorbent gasket, also known as gasket corrosion

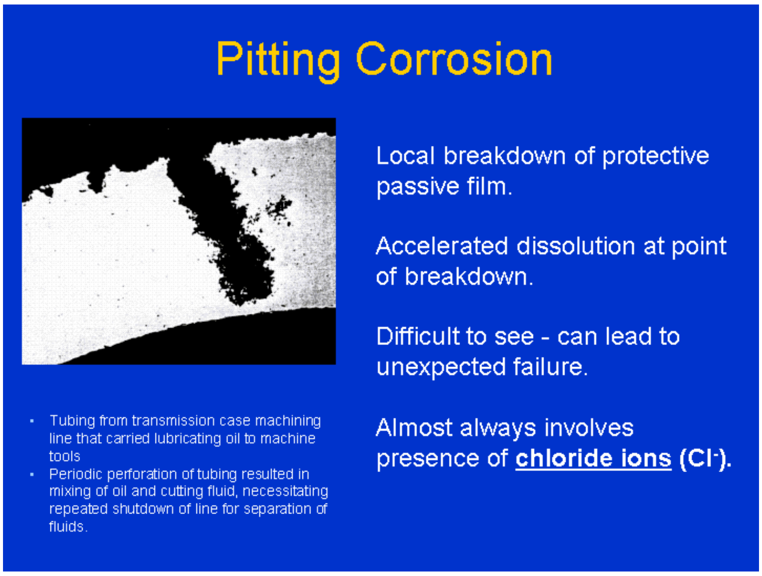
Crevice corrosion is auto-catalytic

Crevice corrosion of a bolt

2. Pitting Corrosion ⇒



-. Passive film이 국부적 손상 시 발생하고 crevice corrosion과 유사: stagnant solution and auto-catalytic (self-serving) nature of pitting → p. 18 of the Denny A. Jones book



초기 단계에서 전체적으로 반응이

$M \rightarrow M^{+} + e^{-}$ (산화 반응)

$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-}$ (환원 반응)

진행 됨. 그러다가 반응의 후기 단계에 들어가면 crevice에서 용존 산소가 우선적으로 고갈되어 이곳의 부식이 집중적으로 일어나고 M^{+}의 농도가 과잉이 되어 전하의 중성을 유지하고자 Cl^{-}가 어떤 전기적 인력에 의해서 crevice로 들어오게 된다.

그 결과로 다음의 가수 분해가 발생하여 M^{+} 이온이 소모되는 자발적 반응이 일어나므로 H^{+}와 Cl^{-} ion의 농도가 급속히 증가하여 용액의 부식성이 증가하게 된다. 그 결과 금속이나 합금의 용해가 촉진됨.

$M^{+}Cl^{-} + H_2O = MOH\downarrow + H^{+}Cl^{-}$ (가수 분해 반응)

PITTING CORROSION

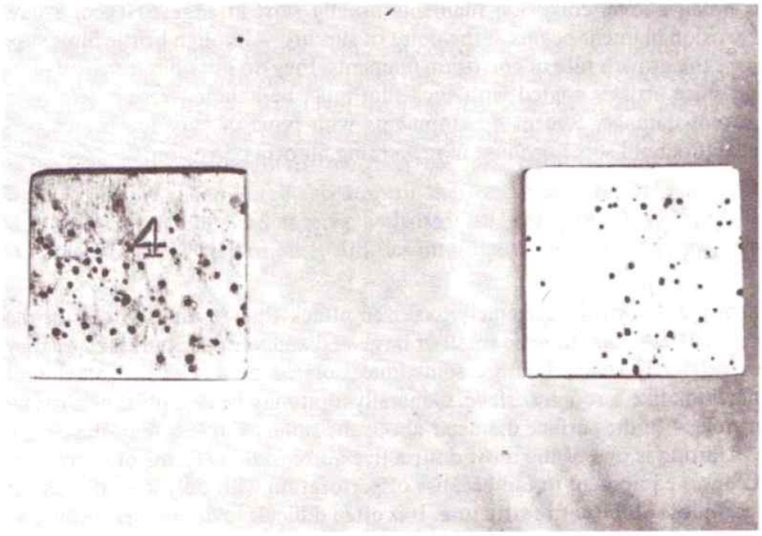
Pitting = extremely localised corrosion
- makes 'holes' in metal

can be isolated or clumped together
often called 'perforation' corrosion

very destructive and insidious – very little material removed
∴ not often detected

Pits – often covered in corrosion product
∴ difficult to see as well

Example –



stainless steel in acid chloride

Pits grow in direction of gravity i.e. downward from horizontal surfaces

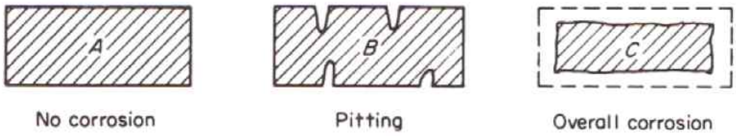
Often – take a long time to initiate

once initiated – grow very fast

Also – pits can undermine/undercut a surface layer

Pitting – often viewed as intermediate between uniform attack and no corrosion

i.e.



Mechanism

Pitting – autocatalytic process – an anodic reaction

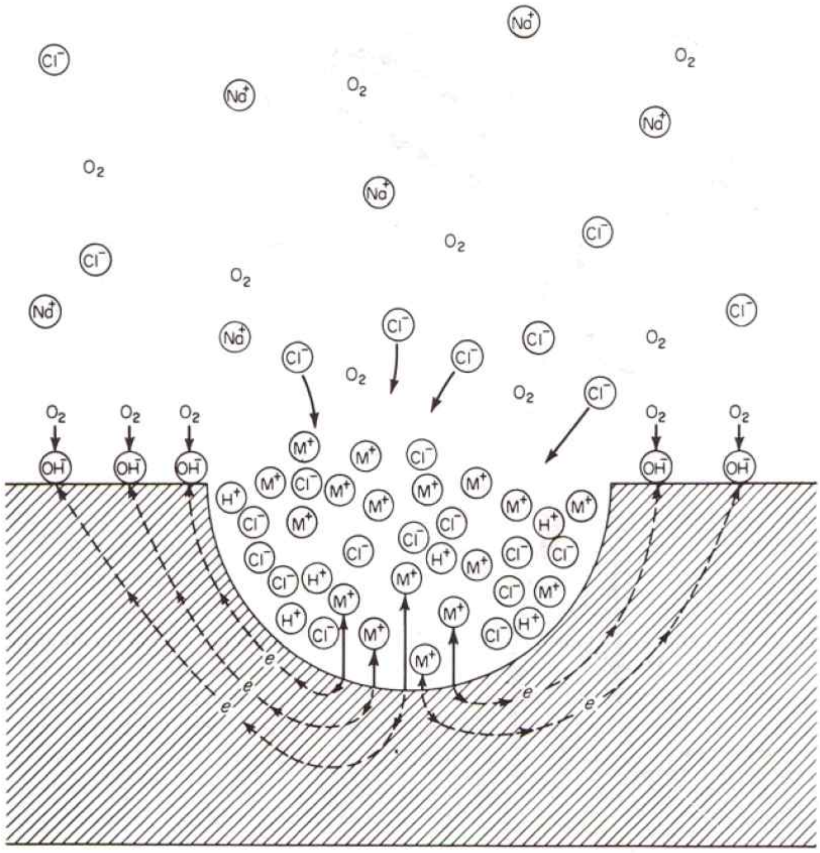
Example:

Metal M in aerated NaCl solution (brine)

Rapid dissolution of M in pit + reduction of O_2 on metal surface

∴ excess M^+ ions in pit – causes Cl^- to migrate in

(as with crevice corrosion)



No O_2 reduction in pit (insoluble)

Pits – cathodically protect rest of metal surface
∴ similar mechanism to crevice corrosion

How do the pits form?
generally – unclear

Believed to be caused by inhomogeneities on the metal surface that periodically cause above average metal dissolution
- hence Cl^- migrates and a pit commences

inhomogeneities =	**composition gradients in alloys**
	dirt or fingerprint
	localised stagnation

Composition aspects

Most pitting failures – due to Cl^- species
e.g. sea water

more aggressive – $CuCl_2$ and $FeCl_3$
they will corrode even inert metals

Stainless steels:

Many stainless steels on the market – many are very susceptible to pitting

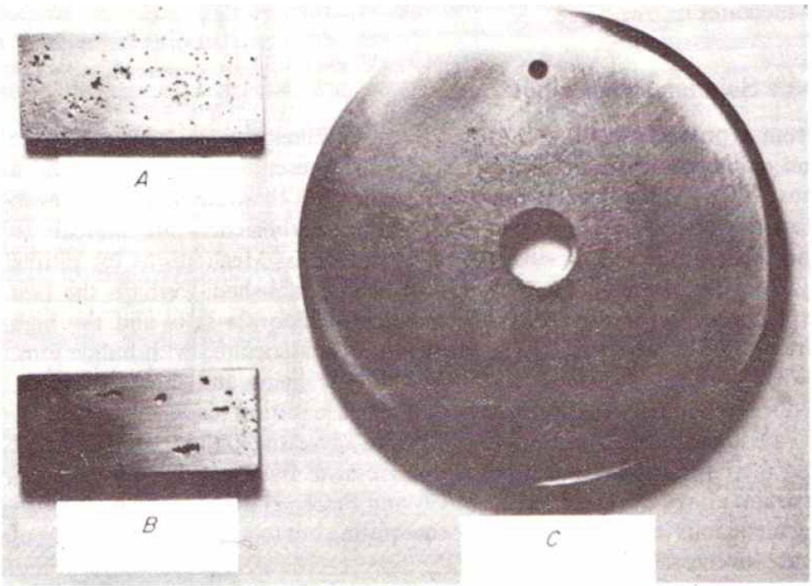
e.g. additives play an important role (Cr, Ni, Mo, Si, etc..) – therefore – compositionally quite complex
complex composition gradients – common on metal surface
hence – susceptible

A = low flow
B = no flow
C = high flow

A = extensive pitting

B = large, brutal pits

C = barely anything



Other aspects

Cold working, surface finish roughness etc. - increase susceptibility

Ordinary steel, however – more resistant to pitting

Velocity

Pitting – usually associated with stagnant conditions
e.g. liquid trapped in an inactive pipe system

e.g. stainless steel seawater pump
- when used – runs well
- when idle – corrodes!

PREVENTION

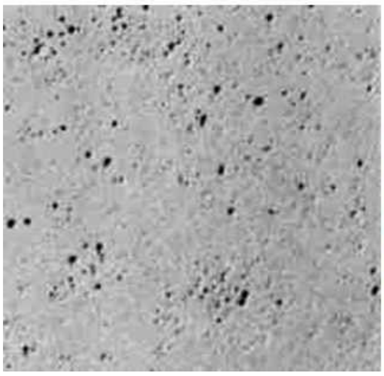
Generally – same as for crevice corrosion prevention

Specifically – 2% molybdenum addition will protect stainless steels

PITTING

Pitting is a highly localised form of corrosion. It is characterised by pits or holes of various sizes:

- small diameters and depth-to-diameter ratio of >>1
- often in clusters
- fail because of perforation with small weight loss
- most destructive
- very difficult to detect
- difficult to evaluate by laboratory tests
- develop and grow in the direction of gravity
- undercut surface as they grow



Corrosion pits