

금속 소재의 환경노출거동: 11주차
Degradation Behavior of Metals and Alloys
after Exposure to Elements: 11th Lecture

날짜: 2020년 11월 13일

■ 강의 내용

1. Passivation:

- (Fe, Ni, Cr, Ti, Co) 전극의 전위가 어떤 임계치를 넘어서 높아지는 경우 부식 속도가 현저하게 (보통은 $10^3 - 10^6$ 정도로 부식 속도가 감소한다.)

- 이 경우 potential이나 부식성 분위기의 특성에 따라 (aerated or deaerated, 304 SS) 금속이나 합금이 passive or active state에 있을 수 있다.

Passivity

Engineering materials that are resistant to corrosion have a naturally-occurring thin film, called a passive film on the surface.

metal oxide
metal

Very thin (usually nm in thickness) oxide film that acts as a barrier between the metal and the electrolyte.

Examples: Al alloys, Ni-based alloys, stainless steels

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

- Cr이 철, 니켈과 합금을 이루면 passivity 향상되나 oxide film 손상 시 pitting, crevice corrosion, SCC 등의 부식 발생

Passivity – when certain metals form very thin oxidized protective film on surface in corrosive solution with high anodic polarization

which metals do and which metals don't?

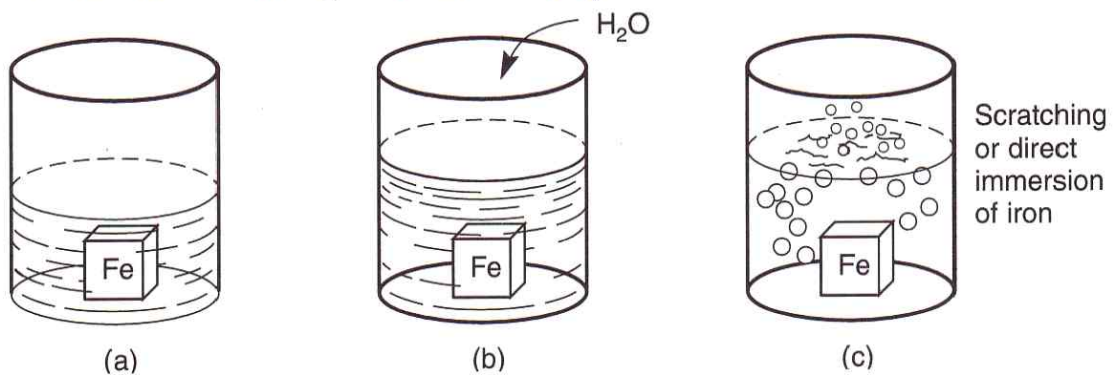
- 이제 부동태 개념을 ① 실험 결과와 ② Evans 도표로 설명 ⇒

typical example – the ‘Faraday experiment’

**Consider a lump of iron sitting in fuming nitric acid ($\text{pH} \rightarrow 0$)
iron is inert! – even if scratched**

**If subsequently diluted – remains inert until scratched – then
vigorous corrosion occurs**

- brown nitrous oxide gas bubbles clearly seen



Why?

concentrated HNO_3 : $\text{pH} \rightarrow 0$

- thin surface oxide film forms
- stable at low pH

when diluted: $\text{pH} \rightarrow 4-5$

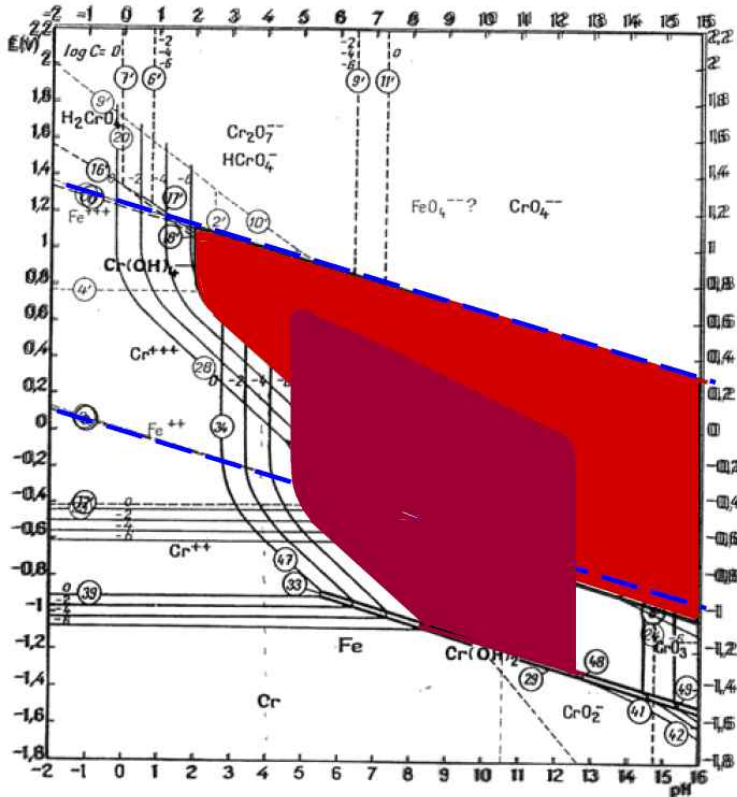
- oxide film becomes unstable at this pH
- when removed – doesn't regrow and acid corrosion of iron begins

Doesn't appear on Pourbaix diagram – as mechanism = unknown

- Principles and Prevention of Corrosion by Denny A. Jones의 p. 118 (FIGURE 4.1~4.3)를 ① p. 2 위의 실험 결과를 적용하여 설명 ② Fe- H_2O 도표 (Pourbaix 도표)와 ③ Evans 도표를 이용하여 설명.

Film = 1-10nm thick and contains hydrogen

Another example – chromium (dashed area below)



Overlay of
Fe and Cr
Pourbaix
diagrams

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Chromic oxide – stable at lower pH than iron oxide

- corrosion resistant in acidic environments (iron is not)

This is the basis for corrosion-resistant stainless steel

Chromium – too brittle to be used on its own

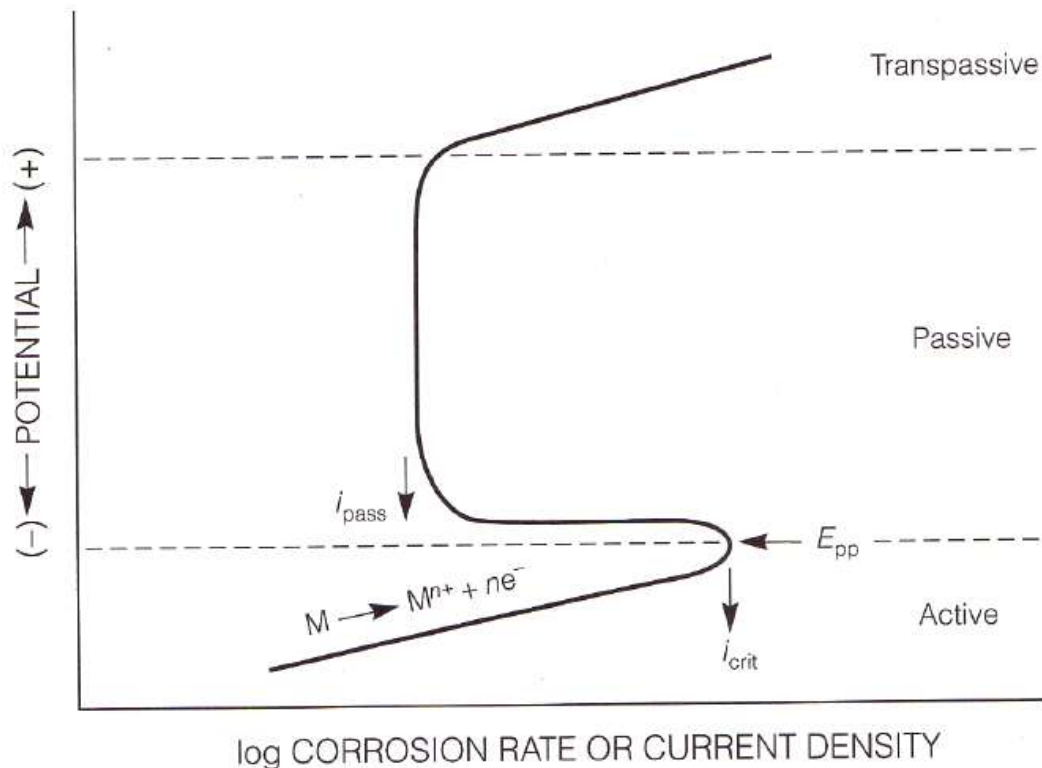
- always used as an alloying element

Fe + Cr + Ni = austenitic stainless steel – very corrosion resistant
(except in chlorine)

Other examples of passive metals – Al, Si, Ti, Ta, Nb

- . p. 4 밑의 그림 왼편의 Active-passive 영역으로 바뀌면서 부식속도는 대략 () 감소.

Active-passive corrosion behaviour



What's happening?

At low potentials:

corrosion rates are **high** and increase with potential as before...

At E_{pp} – passive film becomes stable and corrosion rates drop off then stabilize

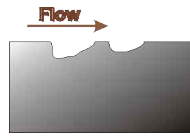
Significantly – if potential gets too high – film breaks down and anodic corrosion resumes

If temperature and acidity increase – curve shifts to the right

READING TOPICS

How does solution velocity (agitation) affect passivity behaviour and the formation of passive layers?

2. 마모 부식 (Erosion) ⇒
Physical causes



- 부식 액체의 급격한 이동으로 보호성 부식 생성물이 마모되어 제거됨.

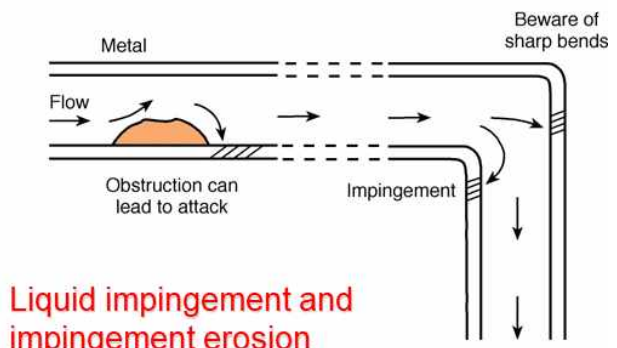
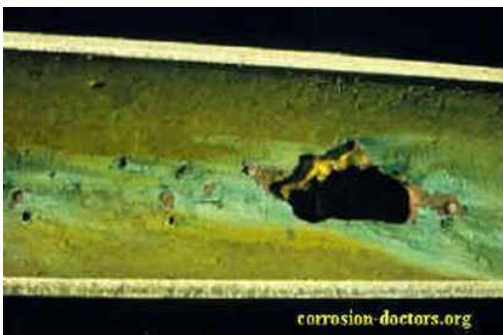
EROSION CORROSION

Erosion corrosion is a result of the combined effect of chemical attack and mechanical abrasion.

The Attack:

The damage appears as groves, waves or holes, following the direction of the flow.

- Typical conditions:
 - submarine propellers
 - interior of slurry pumps
 - exterior parts of high speed boats and ships
 - high flow rate pipelines
- Special locations:
 - elbows and junctions, extra angular acceleration
 - sudden reduction of pipe diameter, high velocity
 - sudden increase of pipe diameter, turbulence
 - valves, high velocity + turbulence
- Alloys:
 - Most alloys are susceptible to erosion corrosion, particularly those that have low hardness and rely on protective surface films for corrosion resistance, such as Al, Pb and Cu alloys, and stainless steels.

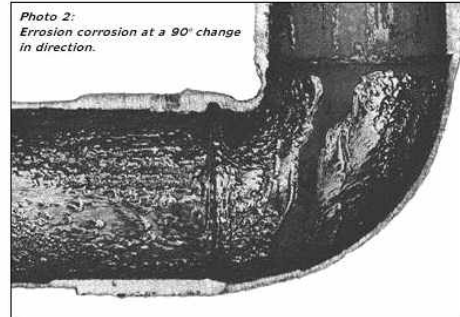


Liquid impingement and impingement erosion

Solid erosion corrosion of impellers in slurry media



Erosion corrosion at pipeline elbow



Factors Affecting Erosion Corrosion

- Medium

Many mediums can cause erosion corrosion. These include gases, aqueous solutions, organic systems, and liquid metals. Solid particles in suspension in fluid are most destructive by destroying surface films.

- Velocity

Increasing velocity generally increases erosion corrosion rate. There usually exists a critical velocity beyond which the rate of corrosion is suddenly increased.

- laminar flow moving at a velocity removes metal ions from metal surface and break local equilibrium balance, encouraging further dissolution of metal

- low flow velocity helps avoid stagnant conditions, replenish oxygen and bring inhibitors to metal surface, leading to a decrease in corrosion rate

- corrosion tests under static or slow motion conditions often do not represent the real situation.

- Turbulence

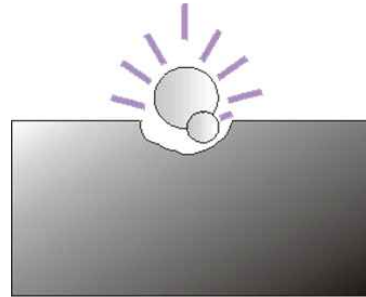
Turbulence provides a greater agitation of the fluid and greater mechanical impact to the surface of the metal. Instantaneous high pressure pulses associated with the formation and explosion of microbubbles cause most damage to metal surfaces.

- Impingement

Impingement create a local environment of very high velocity, very strong turbulence, and very high pressure pulses and thus is very destructive in causing erosion corrosion.

3. 케비테이션 손상 (Cavitation Damage)

- 금속 표면에 고속의 유체가 흐르고 유체내의 압력 변화가 있는 경우 발생하여 내식성 산화물의 피막과 금속 소재를 손상 부식을 가속화



Cavitation damages



● 마모 부식 (Erosion Corrosion)의 정리 (Summary)

- Design
 - Erosion corrosion is closely related to the structure of a system and the flow pattern of the liquid; thus, many erosion corrosion situations may be avoided or minimised by proper design.
 - Increasing tube diameter to reduce flow velocity and ensure laminar flow
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 - Using streamline bends and expanded junction section to minimise impingement effect
 - Lining with second metal at high risk locations (galvanic corrosion !!!)
 - Easy to replace
 - Protruding pipe ends at inlet and out let, delivering turbulence away from the vessel wall into the middle of liquid.
 - Very smooth surface to minimise the chance of vapour nucleation as against cavitation
- Environment
 - Settling and filtering to remove solids in suspension are helpful. Inhibitors may also be added to the liquid. Decreasing temperature always reduces the rate of corrosion.
- Surfacing
 - Some surface coatings are effective to prevent other forms of corrosion, but may not have satisfactory mechanical properties to stand against erosion corrosion, particularly when a heavily suspended slurry solution is involved. Hard facings, welded overlays and replaceable inserts are widely used.

proper design is the most effective way of preventing erosion corrosion