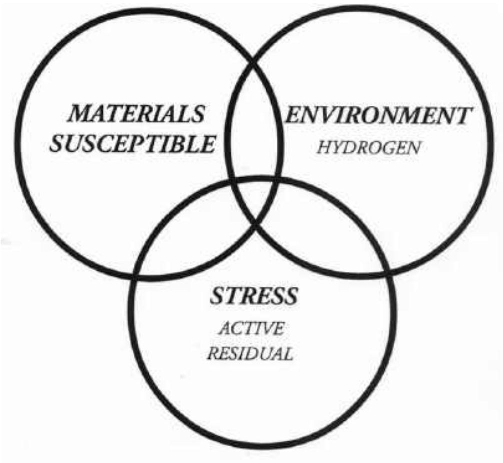
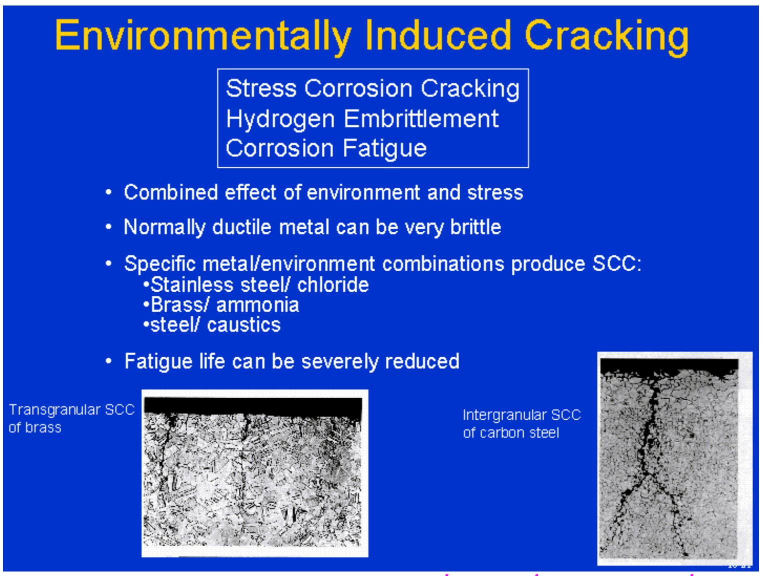
금속 소재의 환경노출거동: 13주차
Degradation Behavior of Metals and Alloys after Exposure to Elements: 13th Lecture

날짜: 2020년 11월 27일

■ 강의 내용

1. 응력 부식 균열 (환경 기인 균열: Stress Corrosion Cracking, Environmentally Induced Cracking) ⇒





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

-. Stress Corrosion Cracking (SCC): static tensile stress에 놓인 재료와 부식 분위기의 짝이 있다.

STRESS CORROSION

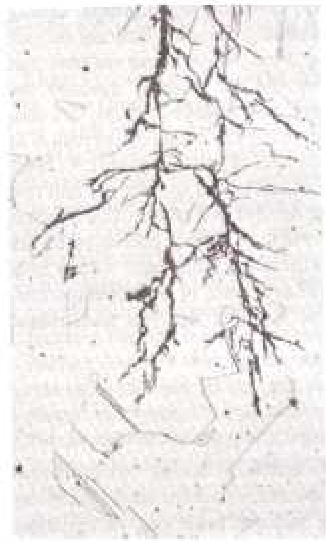
Combination of corrosive medium and mechanical stress (usually tensile)

Main characteristic – no corrosion!

Instead – very localised crack growth – where crack front has been weakened by corrosion
- very difficult to see

top surface = top side
= very little to see

but inside…



very dangerous form of corrosion – very little on surface as a clue
+ causes failure at loads well below the design threshold

The two classic stress corrosion cases:

1) season cracking of brass
2) caustic embrittlement of steel

A particularly severe case of season cracking on an Australian .303, even the jacket of the projectile has cracked.

1) in cartridge brass usually

brass – when used in hot conditions (e.g. tropics) during heavy rainfall – cracks very quickly

why?

ammonia – in the environment due to breakdown of organic matter

ammonia + rain + heat = stress corrosion

caused major problems during WW 2 with ordinance, vessels etc.

2) riveted boilers in steam driven locomotives

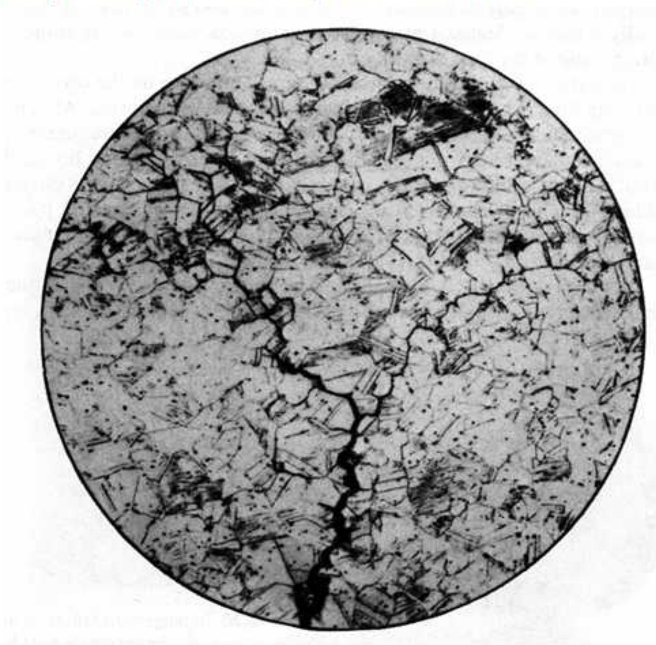
- rivet holes would fail very quickly
  - due to NaOH (caustic soda) deposits around holes
  - rendered the material brittle
    - causes brittle fracture at the holes

Stress corrosion is very environment-dependent

e.g.	stainless steel:	chloride = bad
		ammonia = good
	brass:	chloride = good
		ammonia = bad

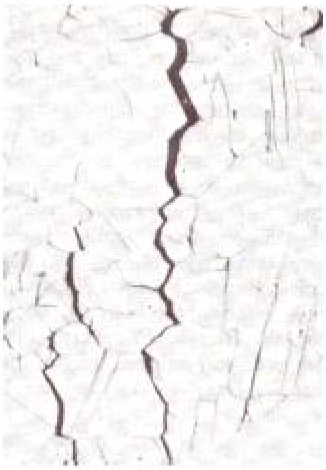
Important variables = T, composition, stress level, microstructure…

- Sustained Tensile Stress (internal or external)
- Corrosive Environment
- Susceptible Metal
- = SCC
- E.g., 7075-T6 in moist air (salt air worse)
- S-T direction most susceptible



SCC in Brass Alloy

Crack morphology



generally – resembles brittle fracture
- either intergranular or transgranular

e.g. brass (intergranular)

crack paths – usually perpendicular to load axis

in multiaxis loads,
cracks are more random

Environmental factors

Biggest environmental factor = oxidizers
e.g. chlorides etc.

dissolved oxygen – very bad for austenitic stainless steel

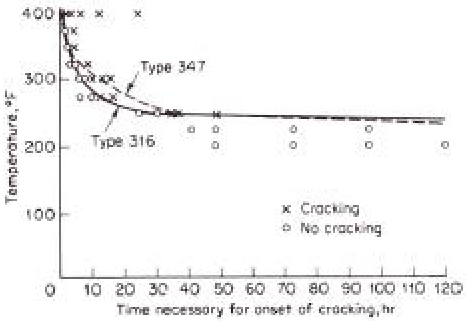
usually – in unstressed conditions

– material won't corrode

Material	Environment	Material	Environment
Aluminum alloys	$NaCl-H_2O_2$ solutions NaCl solutions Seawater Air, water vapor	Ordinary steels	NaOH solutions $NaOH-Na_2SiO_3$ solutions Calcium, ammonium, and sodium nitrate solutions Mixed acids ($H_2SO_4-HNO_3$) HCN solutions Acidic H_2S solutions Seawater Molten Na-Pb alloys
Copper alloys	Ammonia vapors and solutions Amines Water, water vapor		
Gold alloys	$FeCl_3$ solutions Acetic acid–salt solutions		
Inconel	Caustic soda solutions	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
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	Titanium alloys	Red fuming nitric acid, seawater, N_2O_4, methanol-HCl

hot environments – far more corrosive

e.g. 347 and 316 stainless steel:



Metallurgical considerations

many metallurgical factors affect stress corrosion cracking:

composition	precipitate composition and dispersion
grain orientation	dislocation phenomena
stability of phases	

generally, though – not as critical as other factors listed previous

in high strength aluminium alloys
- rolling direction is very important

i.e. more susceptible in the transverse direction than longitudinal
- due to preferred precipitate orientation

Also – ferrite-rich regions in stainless steels – help to block cracks

Mechanism

not well understood

where do cracks initiate?
maybe – in corroded pits or other stress raisers on the surface
i.e. initiate in areas of already high stress concentration
the growing crack front = very sharp

corrosive environment – effectively reduces the toughness near the crack tip – causing it to grow under the applied stress

e.g. in ductile alloys – extensive plastic deformation exists at crack tip
if a plastic-brittle transition occurs – toughness lost – crack grows

also – local phase changes could occur…

Another possible nucleation mechanism:
- cracking of a surface coating through tensile load causes localized stress concentrations

corrosive environment would then prevent coating from healing at the crack front
- anodic dissolution then occurs

PREVENTION

1. **Lower the stress levels through engineering design**
2. **Eliminate the critical environmental species**
3. **Change the alloy!**
4. **Apply cathodic protection –but this might cause embrittlement**
5. **Add inhibitors e.g. phosphates**
6. **Coatings can be used – but risky**
7. **Shot peening**

Shot peening **(shot blasting) – creates residual compressive stress in metal surface**
+ creates a stress field that must be overcome before stress cracks can occur

A clean example of annealing marks on the neck of this 7.62mm ball case. It is easily seen where the heat has been applied to the neck thus relieving the stresses built in during manufacture.

HYDROGEN DAMAGE

General term for mechanical damage of metal caused by presence of, or interaction with, hydrogen

4 types
- hydrogen blistering
- hydrogen embrittlement
- decarburization
- hydrogen attack

2. Hydrogen-induced cracking: 재료의 표면에 생성된 수소 원자가 재료의 격자 내부로 확산되어 발생 함.

HYDROGEN BLISTERING

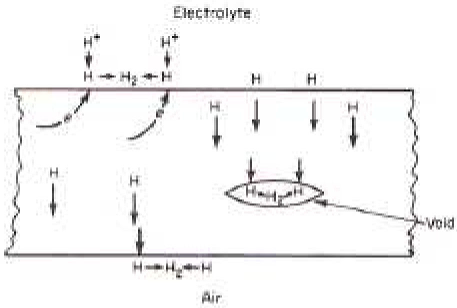
Penetration of hydrogen into a metal

causes local deformation

often in tanks and pressure vessels

common where fluid = acidic

Inner surface
- hydrogen formed due to breakdown of cathodic protection



some diffuses into metal rather than form H_2 molecules

usually – passes straight through

BUT/ can coalesce in an existing void and form H_2 molecules
therefore – cannot diffuse further
∴ pressure builds up in the void – and a blister forms

very common in the oil industry

PREVENTION

1. **Add inhibitors such as polysulphides**
2. **Use 'killed' steel (void free)**
3. **Remove hydrogen-generating 'poisons' from the fluid, e.g. S, As, CN, P compounds in oil**
   interesting – pure acids are not a problem!

3. Hydrogen Damage: Hydrogen attack (수소가 철 속의 탄화물과 반응하여 탄화수소 형성 (CH_4), hydrogen crack, hydride formation (brittleness)

HYDROGEN EMBRITTLEMENT

Mechanism – not clear

Again, H atoms diffuse into the metal and maybe form metal hydrates which are brittle regions

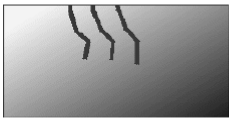
very common in martensitic steels

Another possibility:
hydrogen sits in the metal lattice as a dislocation hindrance
∴ renders the material brittle

Biggest problem – *electroplated metals*
here – there is a large amount of inherent hydrogen in the lattice
must bake above 150°C to remove it

PREVENTION

1. **Minimize hydrogen generating processes**
2. **Better electroplating processes**
3. **Baking the material**
4. **Low-hydrogen welding where possible**

4. Corrosion Fatigue ⇒ 

dynamic and repeated stress에 놓인 재료의 피로 파괴에 대한 저항력이 부식 분위기에 노출 되었을 때 감소 함.

Corrosion Fatigue

The presence of a corrodant, or the action of corrosion, tends to reduce the fatigue life, or decreases the fatigue limit, of a metal.

Little is known about corrosion fatigue beyond the knowledge of stress corrosion cracking.

Corrosion fatigue is characterised by transgranular cracks that do not show much branching. The final cracking is largely a mechanical process.

- Factors Affecting Corrosion Fatigue
  Fatigue life in the case of pure mechanical loading is determined by the number of cycles; the effect of cycling frequency is negligible. In the case of corrosion fatigue, however, stress-cycle frequency has a strong influence on the fatigue life of a metal. Corrosion fatigue is most pronounced at low stress frequencies. Low frequencies allow a better contact of corrodant to the metal at crack tips.

- Prevention
  In addition to those applied to stress corrosion cracking, vibration should clearly be avoided to prevent corrosion fatigue, by, for instance, proper designs.