금속 소재의 환경노출거동: 10주차

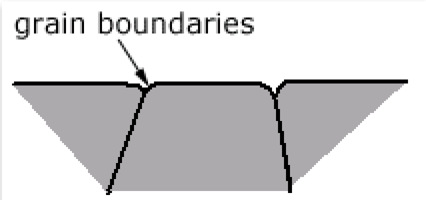
Degradation Behavior of Metals and Alloys after Exposure to Elements: 10th Lecture

날짜: 2020년 11월 6일

■ 강의 내용

1. Intergranular Corrosion

Intergranular corrosion is a localised corrosion that occurs preferentially along grain boundaries inside a metal.

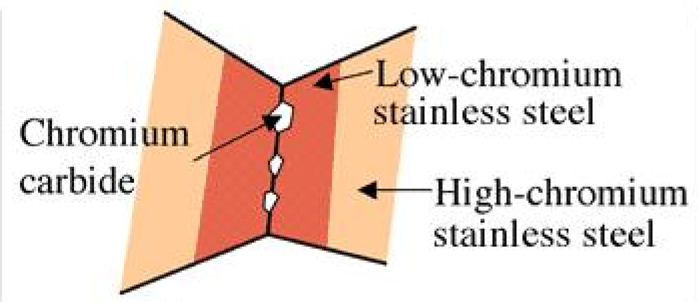


(1) Grain Boundary Attack

Grain boundary regions are generally subjected to a higher degree of corrosion, because of the relatively higher free energy state, chemical segregation and impurity concentration. However, in most cases grain boundary corrosion does not impose a serious problem to the performance of a structural component.

(2) Sensitisation of Austenitic Stainless Steels

Austenitic stainless steels tend to form carbide precipitates ($Cr_{23}C_6$) along grain boundaries at 400-850°C, causing a local depletion of Cr. The sensitised regions are anodic to the grains and are attacked preferentially. A common cause of sensitisation is

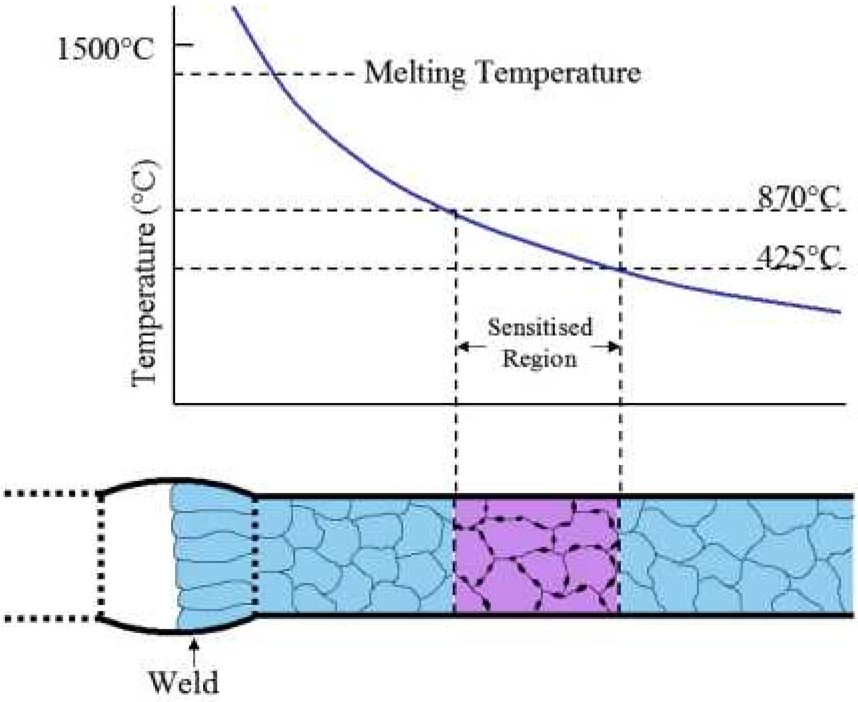


welding, known as weld decay.

(3) Common heat treatments of austenitic stainless steels:

(i) stress relieving at 350-450 °C to avoid sensitisation

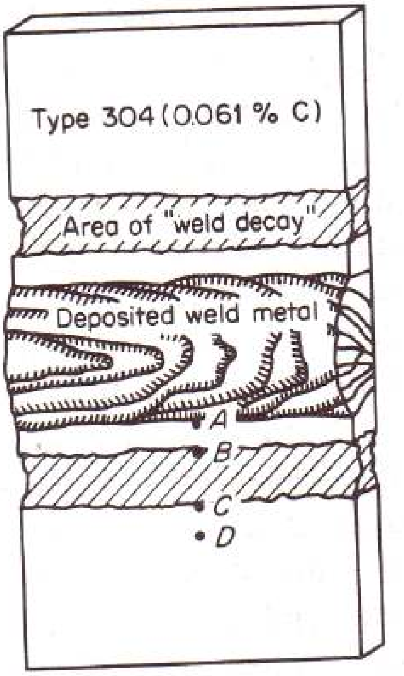
(ii) solution annealing at 1000-1100 °C followed by quenching to eliminate the effect of sensitisation; more problems with cast austenitic stainless steels



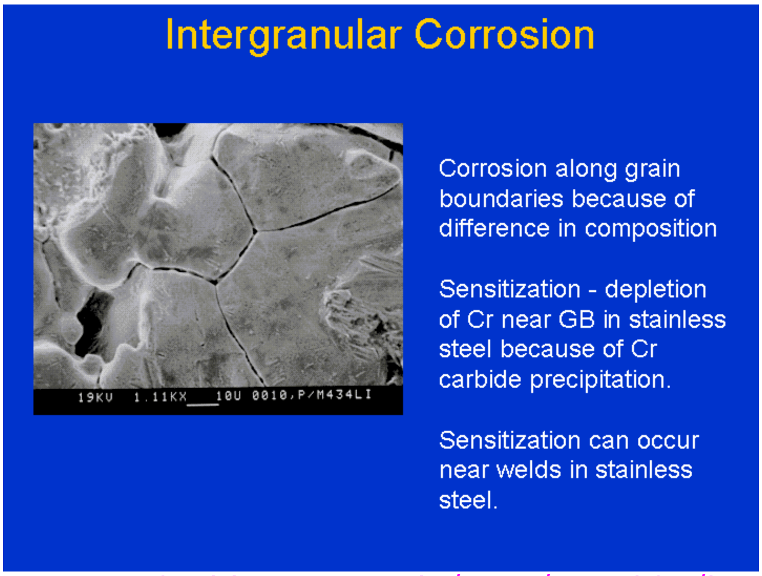
Unfortunately the heating required is just that which occurs in parts of a metal during welding. Areas to each side of the weld are heated to within this temperature range. Chromium carbides form within these bands at each side of the weld. The effect is known as sensitisation.

When the area around a weld becomes sensitised, it is very susceptible to intergranular corrosion, and this is often termed weld decay.

Intergranular corrosion occurs when the grain boundaries in a metal form an anode and the interior of the grain acts as a cathode. In serious cases this can lead to the grains falling apart. This type of corrosion is a particular problem in stainless steels, however it can also occur in other metals.In stainless steels the problem occurs after the metal is heated to between 425°C and 870°C. During the heating, the chromium in the stainless steel reacts with carbon in the steel and forms particles of chromium carbide at the grain boundaries. The regions near the grain boundaries become depleted in chromium. This means that the regions around the grain boundaries are no longer protected by the chromium passivation, and therefore corrode intergranularly.

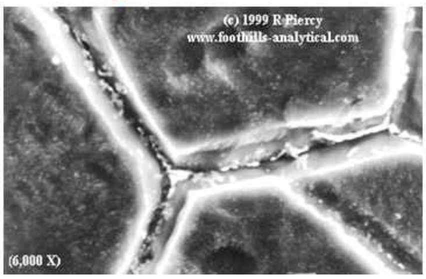


(4) Examples



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

Acceperated grain boundary corrosion due to Cr depletion caused by formation of Cr carbides



Heat affected zones provide a condition for SS sensitisation

Fusion cutting is another case

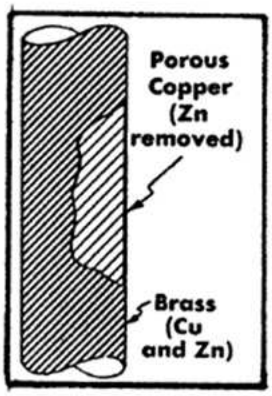
(5) Prevention

The problem of weld decay may be avoided by using:

- L grades: 304L, 317L, 316L: <0.03%C , standard 18-8 steels: 0.06-0.15%C
- Stabilisers: strong carbide forming elements: Nb, Ta (type 347), Ti (type 321)
- Electric arc welding instead of flame welding: more rapid heating cycle, narrower heat affected zone, lower tendency to form carbides in HAZ
- Laser cutting instead of oxy-flame cutting

• Other Alloys Susceptible to Sensitisation
Some high strength Al alloys are also susceptible to sensitisation. For example, the strengthening precipitates $CuAl_2$ in Al-Cu alloys cause local depletion of Cu, reducing their corrosion resistance.

2. Selective Leaching



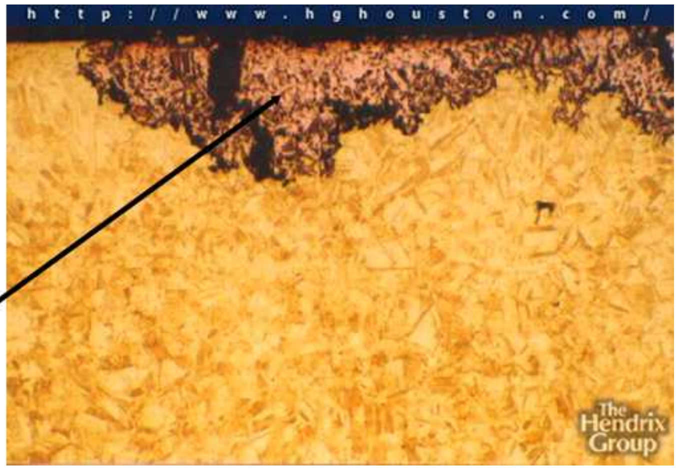
Selective leaching, also known as dealloying and parting, is the selective preferential removal of one elemental spices in an alloy system.

dezincification of yellow brass
dealuminificationof aluminium bronze
graphitisation of grey iron
dechrominification

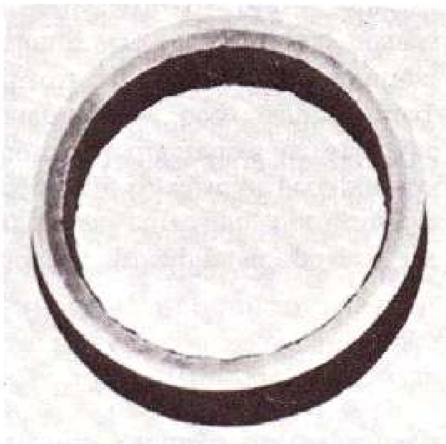
(1) Dezincification

Zinc dissolves in pure water by a hydrolytic reaction.
Better resistance to dezincification:
red brass: 85-15%Zn
alloying: "inhibitors", such as Sn, As and P

Al bronze and Si bronze are attacked by selective leaching
Al, Si and Zn are anodic to Cu



Dezincified yellow brass
showing red Cu colour



2 types: uniform and localised

Uniform – good example
= brass pipe in potable water

inner region – zinc leached out

50% leached after several years

Localized example:

brass heat exchanger pipe

inside – boiler water
outside – fuel combustion gases → **zinc 'plugs' removed**

After dezincification – remaining copper = porous and weak
thus increasing susceptibility of the Cu and brass
fracture – usually through structural weakness

Uniform corrosion – common in high Zn content brasses and in acid environments

Plug-type corrosion – common in low Zn content brasses and in alkaline/neutral environments

Also – stagnant conditions promote dezincification

Mechanism **3-step process…**

1 brass dissolves
2 Zn remains in solution
3 Cu plates back onto brass

Because Zn dissolves (slowly) in pure H_2O – no oxygen required!

PREVENTION

1 remove oxygen from the environment (sometimes)
2 cathodic protection
3 best way – use a low Zn alloy e.g. red brass (15%Zn)
4 other alloy combinations help
e.g. Brass + 1%Sn = Admiralty brass – increased resistance
also – As, Sb, P help
in severe environments – use cupronickel (Cu+10-30%Ni)

(2) Graphitization

Graphitization is the selective removal of iron from the surface of grey cast iron due to a galvanic reaction between the graphite and iron. It is the most costly damage large-diameter underground water mains.

- Graphite is cathodic to iron, forming excellent galvanic cells
- Moist soil under the ground and aqueous solution it carries inside provide the environment for selective leaching
- Earth movement may cause failure as a result of reduced strength
- Use of nodular or malleable iron is effective in avoiding

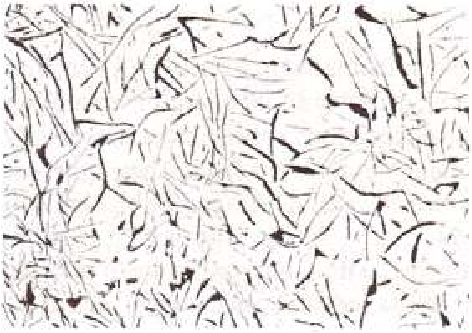
Graphitization

i.e. 'dezincification' for steels

particularly – grey cast iron

Here – Fe matrix leached out – leaving graphite on the surface

- very soft layer



Graphite – cathodic to iron ∴ remains

- usually cohabits with a rust layer

Other cast irons – not affected

It is a major cause of underground pipeline failures
e.g. rupture by earth moving equipment – common – but shouldn't happen

Why?

pipes – grey cast iron – become very weak if graphitized

3. 희생 양극

-. 두 가지 경우를 고려하여 금속의 방식법에 대한 기초개념을 학습 → 어느 코팅이 Fe를 보호하는가? Sn or Zn? Why? ⇒ 전자의 공급이 방식의 기본임.

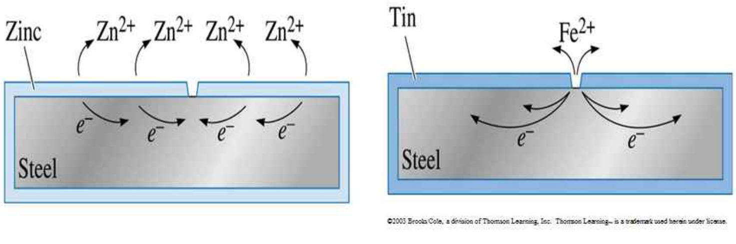


Figure 22.12 Zinc-plated steel and tin-plated steel are protected differently. Zinc protects steel even when the coating is scratched, since zinc is anodic to steel. Tin does not protect steel when the coating is disrupted, since steel is anodic with respect to tin.

-. 선체를 부식으로부터 보호하는 희생양극 (sacrificial anode): Zn (−0.763 V vs SHE), Mg (−2.36 V vs. SHE), Al (−1.66 V vs. SHE) → 해수 분위기에서도 OK ? → Galvanic Series

-. 해수 분위기에서는 대부분 표준 전극 전위와 일치하나 몇 몇 금속의 전위 순서가 달라짐 → anode, cathode가 뒤바뀜 → 예를 들어 Ti