

Localized Corrosion

Localized corrosion defined as an intense metal dissolution at the selective sites or zones on the surface of a component whilst the rest of the surface is corroding at a much lower rate.

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Sources of Selective Sites/Zones

Sources of selective sites or zones on the component that lead to localized corrosion can be:

- ❑ Variation in corrosion environment along the surface
- ❑ Variation in alloy composition/microstructure and properties of the oxide film
- ❑ Mechanical aspects such as stress within the metal or oxide film
- ❑ Geometry of the component

Variation in Corrosion Environment

- ❑ Oxygen concentration
 - Enhances rate of cathodic reaction and leads to increase in pH at cathode
- ❑ pH
 - Increase in pH (more alkaline) tends to enhance passivity
 - Decrease in pH (more acidic) tends to prevent passivity and cause corrosion
- ❑ Chloride ion presence
 - Prevent repassivation of oxide films at anode
- ❑ Flow rate
 - Removes corrosion product
 - Changes concentrations of oxygen, chlorides and other active species
 - Removes metal by cavitation or erosion by suspended particles

Variation in the alloy microstructure

- ❑ Segregation
 - Different concentration of solutes at different parts of ingot or casting (macro segregation – hard to remove)
 - Different concentration of solutes across grains (micro segregation – may be removed or reduced by heat treatment)
- ❑ Inclusions
 - May be soluble and/or electrochemically active (e.g. sulphides in steel)
 - Cause defect in passive film
- ❑ Different phases
 - Phases will have differing electrochemical activity, hence act as local anodes or cathodes
- ❑ Grain boundaries
 - Sites of micro segregation (may be enhanced by heat treatment)

Mechanical Variations within the Metals

Static stress

- Stress corrosion cracking
- Hydrogen embrittlement
- Liquid metal embrittlement

Fluctuating stress

- Metal fatigue
- Corrosion fatigue

Types of Localized Corrosion

Large zones of the metal are dissolving
Metal is in active state of dissolution

- Galvanic Corrosion
- Dealloying
- Differential Aeration
- Flow Assisted Corrosion

Numerous micro-sites are actively dissolving
Metal is in its passive state

- Crevice Corrosion
- Pitting Corrosion
- Filiform Corrosion
- Intergranular Corrosion
- Exfoliation

Metal is dissolving with additional assistance of mechanical deformation

- Stress Corrosion Cracking
- Corrosion Fatigue
- Environmentally Induced Cracking

Galvanic Corrosion

Electromotive Force Series (EMF)

is an orderly arranged the standard electrochemical potentials of the metals.
The more negative potentials correspond to the more reactive metal.

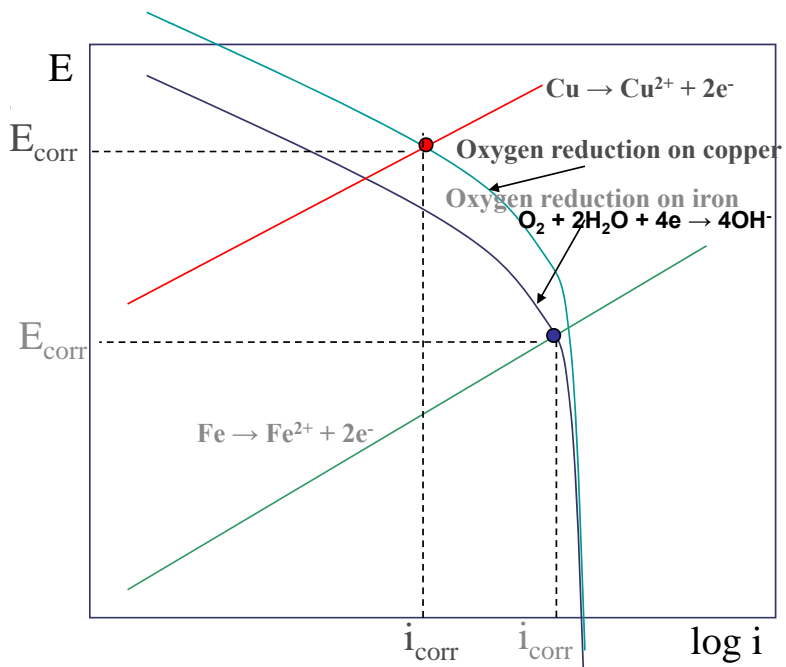
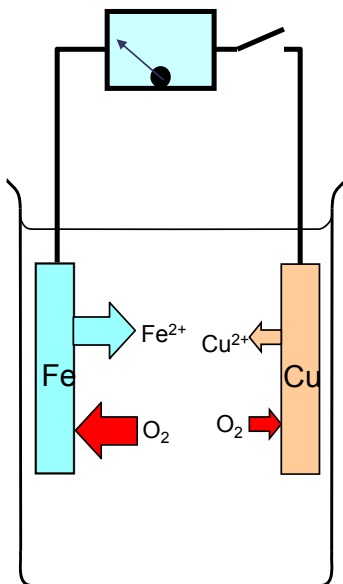
- Described by basic thermodynamics
- Does not account for passivation
- Does not apply to alloys

Uhdfrgr#	H ⁺ #W ⁵ F/#	#
DxOx ⁶ #	.47<#	↑#
SwS ⁵ #	.45#	Q red#u#
DjOj ⁵ #	.31:<<#	fdwrglf#
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K ₅ (K #	3B33#	#
#	#	#
QOQ ⁵ #	0B583#	#
IhIH ⁵ #	0B773#	#
Fu(Fu ⁶ #	031:77#	#
lqlQ ⁵ #	0B1:96#	#
DOD ⁶ #	041995#	Dfwy#u#
Pj(Pj ⁵ #	051696#	dgrglf#
QdQd#	0B1:47#	↓#
DwghEhwxq#Bq#Drxg#	#	#

Galvanic Corrosion

Two different metals (iron and copper) in neutral aerated solution (tap water) are electrically unconnected

Iron and copper corrode with oxygen reduction and free corrosion potential of copper is more positive than that of iron



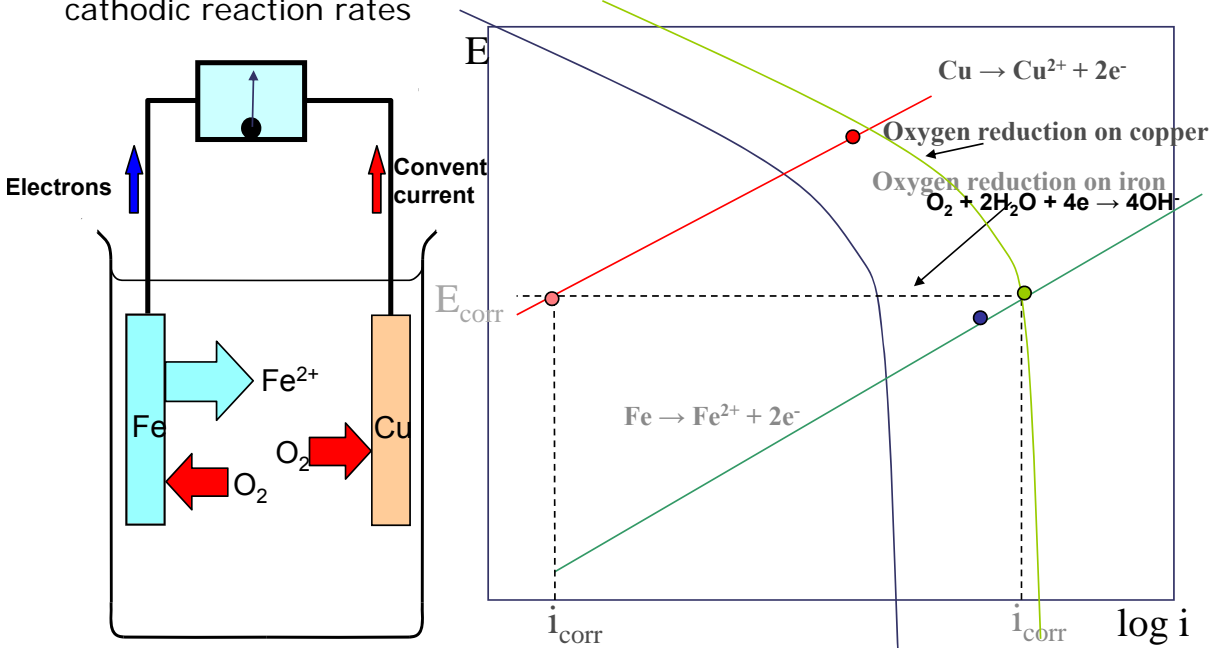
Galvanic Corrosion

Metals connected, potentials of iron and copper become the same.

Potential of copper reduces, and corrosion rate of Cu drops to near zero.

Potential of iron increases, and corrosion rate of Fe increases.

Electrons flow from iron to copper to support differences in anodic and cathodic reaction rates



Galvanic Corrosion

Galvanic Series

indicate relative activity of the metals and alloys in specified environment

- Determined by experiment/experience
- Only valid for the environment in which it was determined
- Does not give information on rate

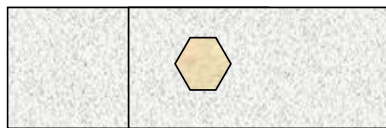
Some alloys may be present twice, once in the passive state, and once in the active state

#	Weld#	J	do	q	f	h	h	g	h	z	d	w	#
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↑#	#	S	w	l	x	p	#						
Q	r	e	d	n	#	J	r	o	g	#			
f	d	w	k	r	g	f	#	V	b	y	#		
#		4	;	;	;	r	#	w	l	q	d	w	#
#		Q	l	f	n	h	#	s	d	w	y	h	#
#		F	x	s	r	q	l	f	n	h	#	9303	#
#		F	r	s	s	h	#						
#		Q	l	f	n	h	#	d	f	w	y	h	#
#		4	;	;	;	r	#	w	l	q	d	w	#
#		V	h	h	h	#	u	r	q	#			
#		5357	#	l	q	x	#	718	#	x	#	18	#
#		F	d	p	l	x	#						
D	f	w	h	#	u	#	F	r	p	p	h	u	f
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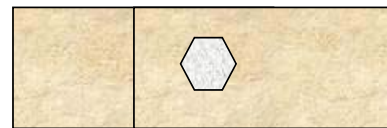
Factors in Galvanic Corrosion

- ❑ Relative areas of anode and cathode
 - Large cathode, small anode is very bad
 - Large anode, small cathode is not so bad
- ❑ Difference in potential between anode and cathode
 - Large potential difference will cause large change in potential of anode and hence large effects
- ❑ Anode and cathode polarization
 - Passive anode may not be affected much
 - Active anode may passivate
 - Cathodic oxygen reduction may be at limiting current density
 - Cathodic hydrogen evolution is strongly dependent on metal

Which is better?



Brass bolt in a steel structure

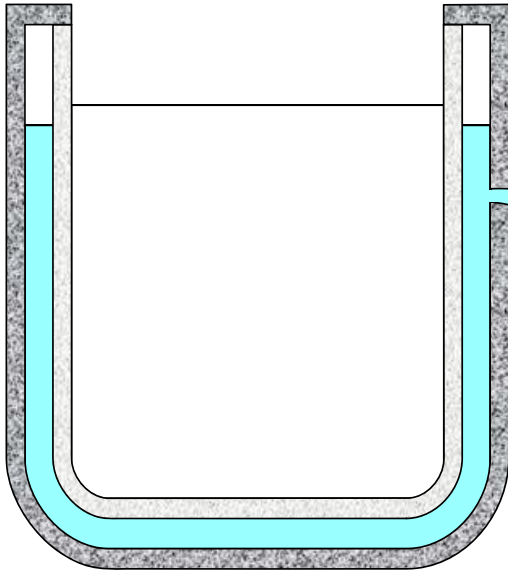


Steel bolt in a brass structure

Small brass cathode will cause small increase in corrosion of steel structure. Bolt will be protected from corrosion by coupling to steel

Small steel anode will suffer large increase in corrosion due to coupling with brass structure.

What should we paint?



A milk cooler has an inner liner of stainless steel, and an outer casing of mild steel. Cooled brine is used between the steel and stainless steel to cool the milk.

This would be a very bad idea as any pinholes in the paint would act as the anode, with the full area of the stainless steel as the cathode.

Positive Uses of Galvanic Corrosion

Sacrificial anode in cathodic protection

- In the iron-copper couple, the corrosion of the copper is reduced by connection to iron
- Similarly iron can be protected by connection to zinc, magnesium or aluminium

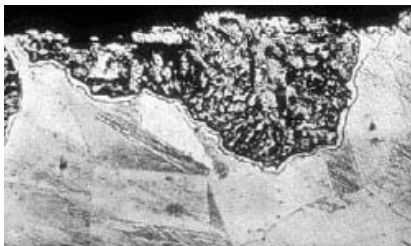
Maintenance of passivity

- Passivity can be lost if the potential becomes too negative
- Deliberate addition of noble precipitates can act as efficient local cathodes and thereby maintain passivity (e.g. Pd additions to titanium)

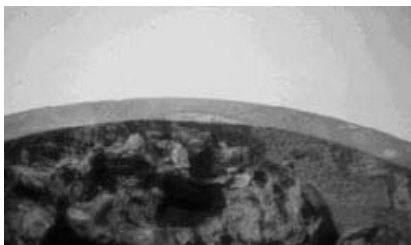
Dealloying

- ❑ Dealloying is generally known for copper alloys (e.g. brass, Cu + Zn) and gray cast iron (Fe + C).
- ❑ The alloy loses the less noble element of the alloy and retains the more noble element forming a porous "sponge" on the metal surface.
 - dezincification of brass
 - graphitization of grey cast iron
- ❑ It can also occur by redeposition of the noble component on the surface
- ❑ Causes loss of mechanical strength without obvious change in shape
- ❑ Control is by the use of more resistant alloys-inhibited brasses and malleable or nodular cast iron.

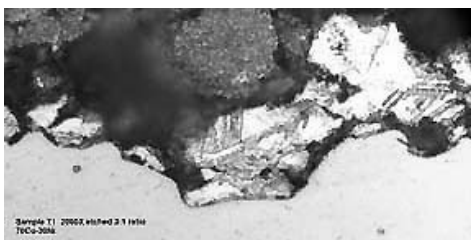
Dealloying



The brass has dezincified leaving a porous copper plug on the surface.



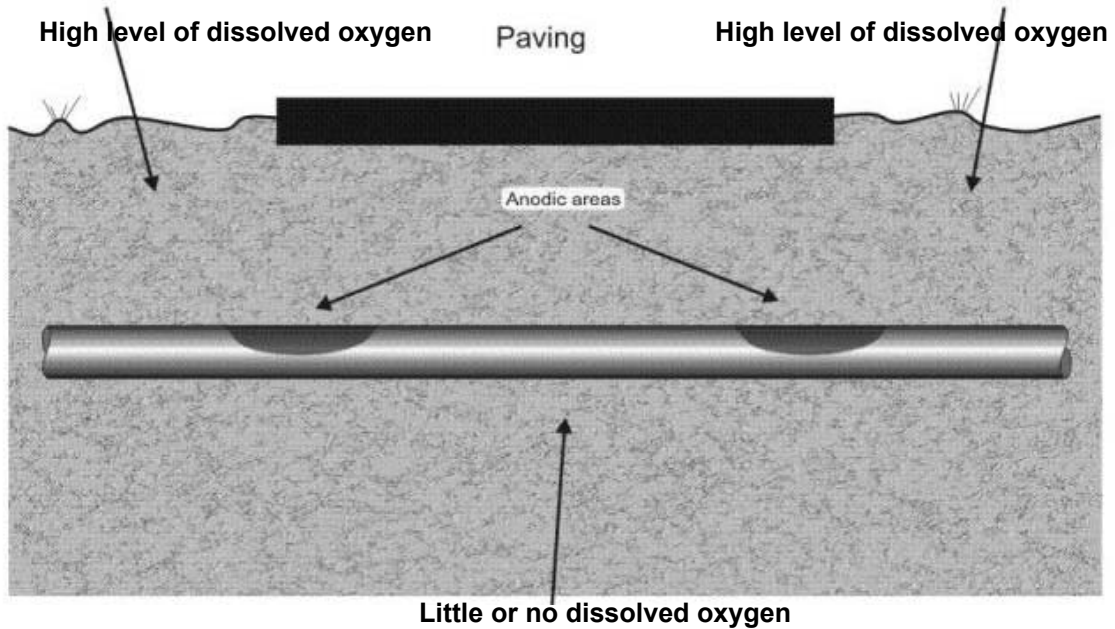
The gray cast iron water pipe has graphitized and left graphitic surface plugs which can be seen on the cut surface.



A layer of copper on the surface of a dealloyed 70% copper-30% nickel heat exchanger tube removed from a ship.

Differential Aeration

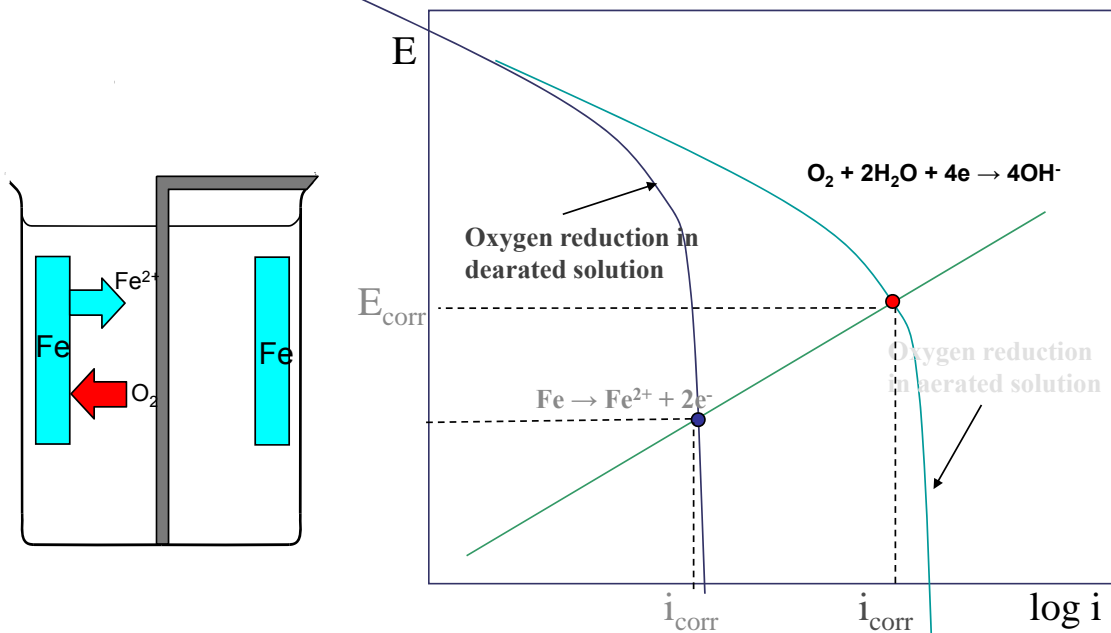
Corrosion due to differences in oxygen concentration along the surface of the metal



<http://corrosion-doctors.org/Corrosion-Factors-Cells/corrosion-cells-aeration.htm>

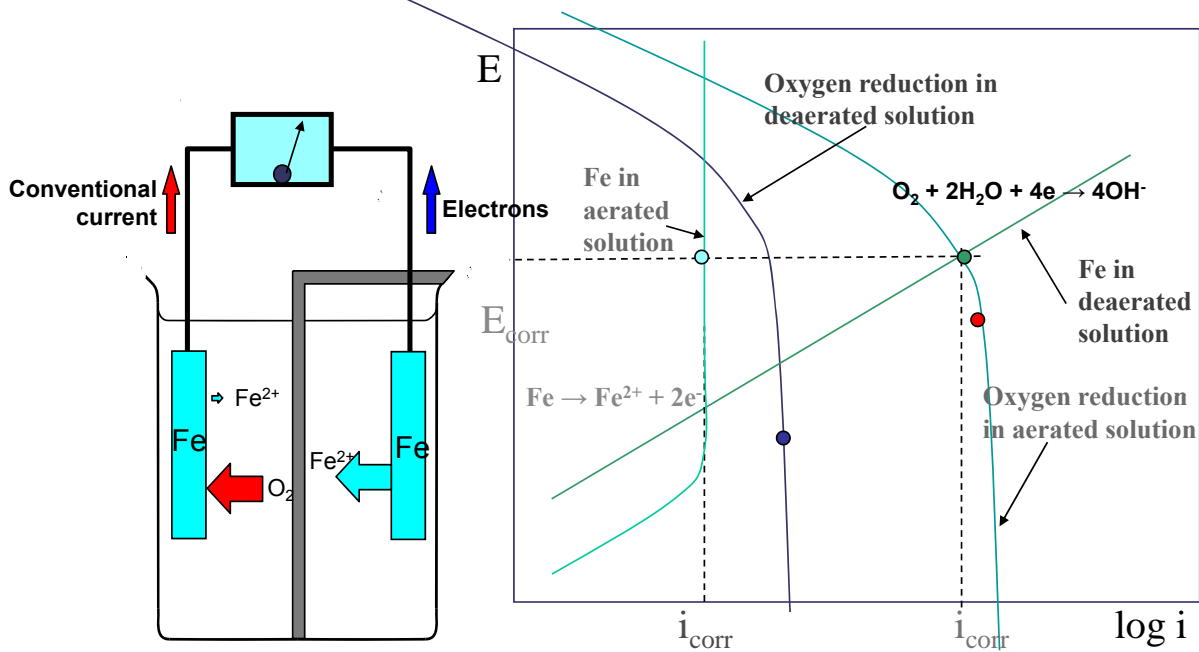
Differential Aeration

Iron dissolution is limited by oxygen transport. Iron in deaerated section corrodes very slowly. Iron in aerated section corrodes relatively fast.

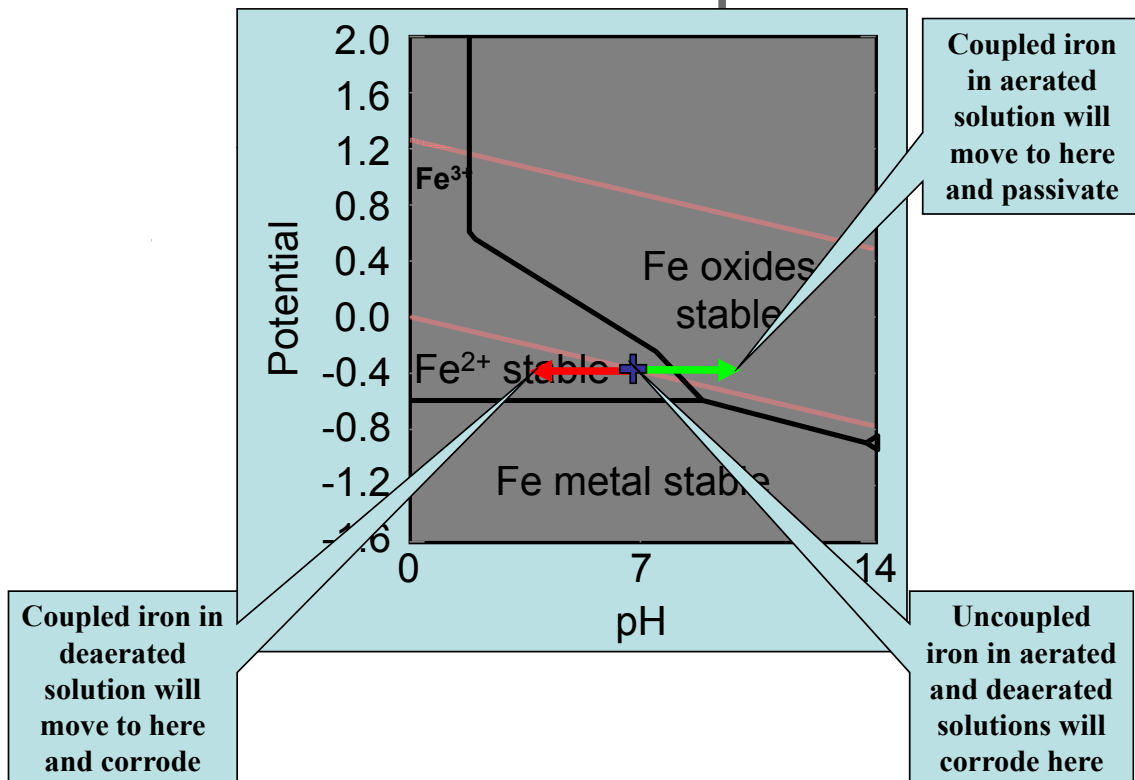


Differential Aeration

- ❑ Deaerated section. Hydrolysis of Fe^{2+} causes pH to fall and corrosion continues in acidic solution ($\text{Fe}^{2+} + \text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})^+ + \text{H}^+$)
- ❑ Aerated section. Cathodic reaction dominates and OH^- produced causes pH to rise. Iron passivates in alkaline solution



Differential Aeration E-pH



Flow Effects

❑ Flow can

- increase transport of oxygen to the metal surface (may help to passivate)
- increase the rate of dissolution of corrosion product films
- mechanically remove oxides

❑ Terminology is poorly-defined, and often contradictory

Crevice Corrosion

Crevice corrosion is usually associated with a stagnant solution in a narrow gap or crevice formed under gaskets, washers, fastener heads, surface deposits and coatings.

Lid of the stainless steel autoclave

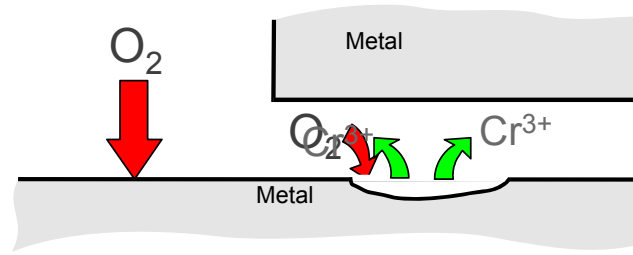
Crevice corrosion under washers and fasteners heads

Pitting under insulation



Crevice Corrosion

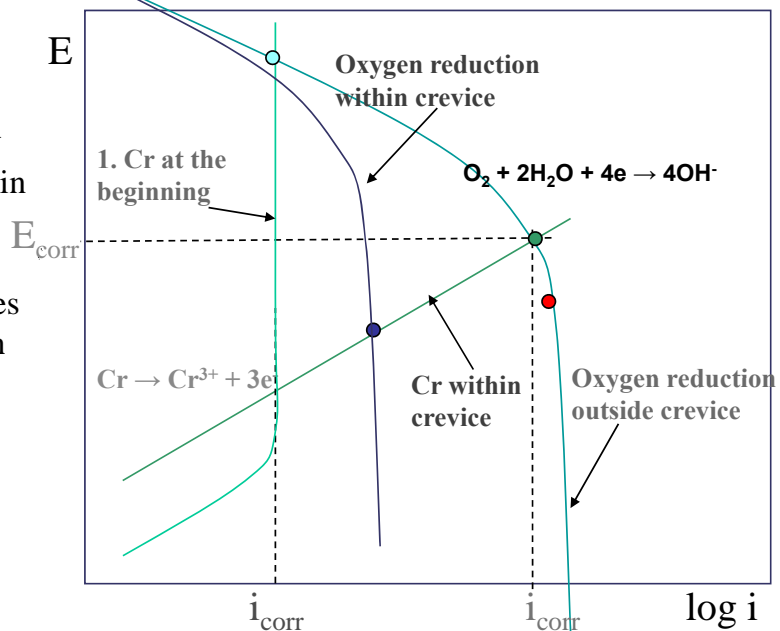
Mechanism is similar to differential aeration (driven by changes in local chemistry of electrolyte), except that metal is initially passive.



1. Oxygen is consumed in crevice by slow passive corrosion
2. Passive corrosion continues, and pH falls by Cr^{3+} hydrolysis $2\text{Cr}^{3+} + 6\text{H}_2\text{O} \rightarrow \text{Cr}_2\text{O}_3 + 6\text{H}^+$
3. Passive film breaks down in acid and rapid active corrosion starts
4. The active corrosion causes even stronger acidification and stabilises the crevice corrosion

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Crevices on Active Alloys

- ❑ 'True' crevice corrosion requires the alloy to be passive
- ❑ If an alloy is suffering from active corrosion (e.g. carbon steel in seawater), then crevice corrosion will not normally occur
- ❑ Cathodic protection of steel will normally protect crevices by the increase of the pH and passivation (exception is organic coatings, where O₂ can diffuse through the coating)

Crevices on Active Alloys

Corrosion can occur in crevices due to retention of water or poor penetration of protective treatments (e.g. folded seams in car bodies)

The flange at the top of the wing panel is open on the inside to mud from the road and can rot through within a couple of years unless the joint is sealed properly

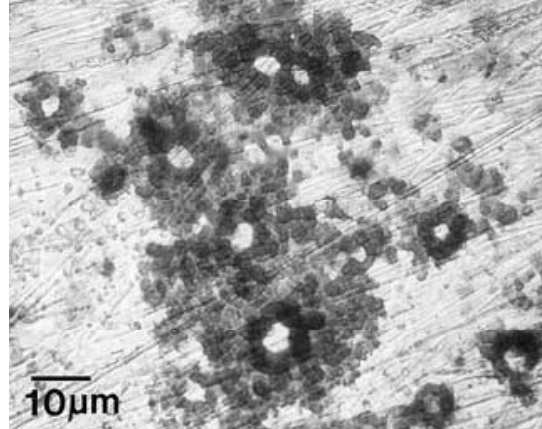


Pitting Corrosion

Pitting corrosion, leads to the development of small holes in the metal. It has similar mechanism to crevice corrosion (driven by local chemistry of electrolyte), but occurs on a free surface.

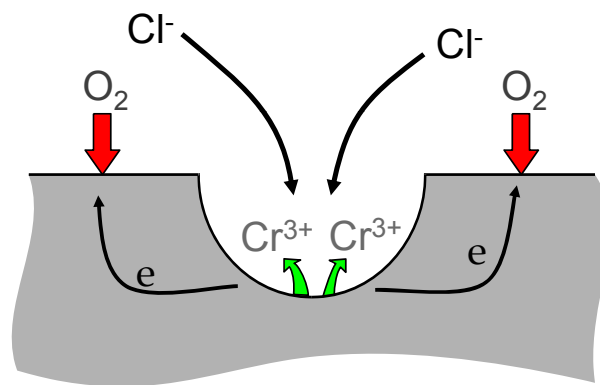


An example of general deep pitting corrosion on external side of pipeline with some pits joining to form larger pits and interconnected pitting.



Pitting corrosion on 316S stainless steel that was caused by a biofilm, whose presence modified local electrochemistry on the surface of the steel. *Image, courtesy of Z. Lewandowski and W. Dickinson, MSU-CBE*

Pitting



The presence of chloride is important, as it allows a low pH (HCl is a strong acid, and does not associate) and the metal chlorides are very soluble

pit

Characteristics of Pitting Corrosion

The alloy is passive

- Pitting requires a passive external surface that can provide a high potential to cause the current to flow into the pit; if the external surface is active, this driving force is not available

Characteristics of Pitting Corrosion

Passivity broken down locally, usually by chloride

- The cause of the initiation of pitting corrosion is still not entirely clear, but it involves a very small pit nucleus that grows over periods of the order of seconds

Characteristics of Pitting Corrosion

- ❑ Pits become more stable as they become larger
 - For very small pits the acidity will be neutralised by diffusion into the bulk solution very easily

Characteristics of Pitting Corrosion

- ❑ Small pits are often stabilised by a film of oxide or metal that partially covers the entrance
 - This allows pits that would not otherwise be stable to continue growing (these are known as metastable pits)

Characteristics of Pitting Corrosion

- ❑ Pitting becomes more likely as the potential becomes more positive
 - This provides a greater driving force for the corrosion process, and helps to stabilise the metastable pits

Management of Pitting

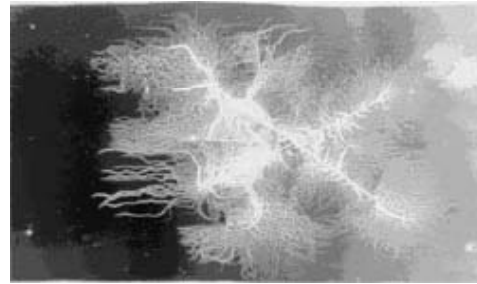
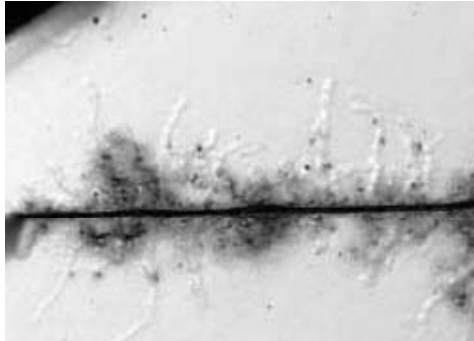
- ❑ Stainless steels
 - Pitting breakdown potential (that potential above which the anodic current starts to increase) indicates susceptibility to pitting
 - Critical pitting temperature (temperature at which pitting is observed in aggressive conditions) is a good indicator of behaviour in service
 - Pitting Resistance Equivalent (formula based on composition e.g. $Cr + 3Mo + 30N$) gives ranking of alloys

Improve pitting resistance by

- Using higher % Cr
- Using high % Mo
- Adding N (but limited)

Filliform Corrosion

Filliform corrosion usually occurs under painted or plated surfaces when moisture and oxygen permeates the coating. The mechanism is similar (driven by changes in local chemistry along the surface) to pitting and crevice corrosion.



(Courtesy of www.cp.umist.ac.uk)

Filliform corrosion manifests as "worm-like" filiform tunnels formed under a coating. Usually such corrosion does not result in structural failure.

<http://corrosion.ksc.nasa.gov/dealloying.htm>

Filliform Corrosion

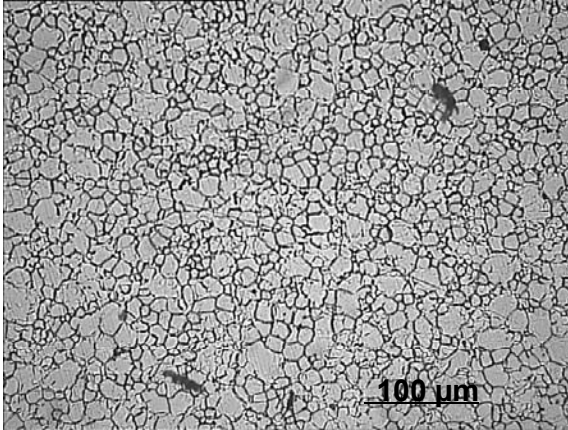
Filliform corrosion is minimized

- by careful surface preparation prior to coating
- by the use of coating that is resistant to this form of corrosion, for example avoid using lacquers and quickly drying paints.
- by careful inspection of coatings to insure that holidays, or holes, in the coating are minimized.

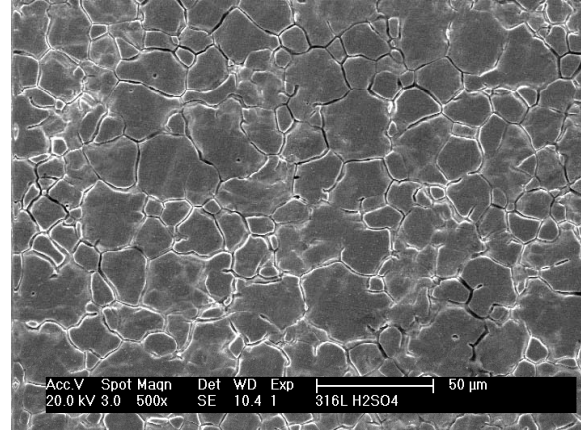
Intergranular Corrosion

Intergranular corrosion is localized attack at the grain boundaries, or at the area adjacent to grain boundaries. It propagates along the grain boundary, while the bulk of the grains remain unaffected.

Optical microscope x50



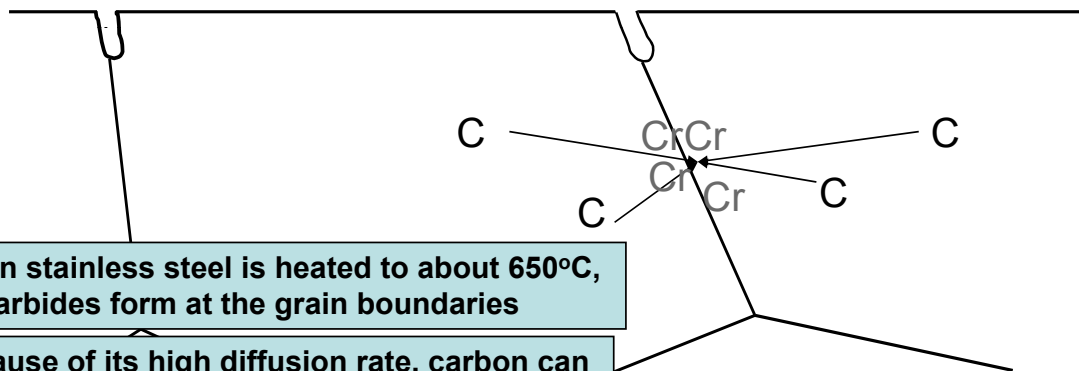
SEM



Sensitized 316type stainless steel exposed to hot sulphuric acid

Intergranular Corrosion

Intergranular corrosion is usually associated with segregation or phases precipitation on the grain boundaries. Such precipitation can produce zones of reduced corrosion resistance in the grain boundary vicinity.



When stainless steel is heated to about 650°C, Cr carbides form at the grain boundaries

Because of its high diffusion rate, carbon can diffuse a long way to form the precipitate

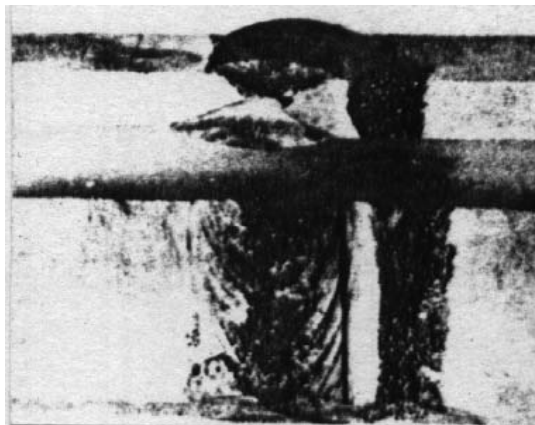
Chromium can only diffuse a short distance, and this reduces the matrix concentration of chromium at the grain boundary

If the grain boundary Cr concentration falls low enough (below about 9%), then it will no longer remain passive, and grain boundary corrodes

Intergranular Corrosion

- ❑ When grain boundary chromium carbide precipitation has occurred, the stainless steel is said to be *sensitised*.
- ❑ Sensitisation frequently occurs in the heat-affected zone during welding, and the resultant corrosion is called *weld decay*.

Weld Decay of Stainless Steel



Knife-line attack near the weld

Solving Weld Decay

- Weld decay is caused by Cr depletion due to precipitation of Cr carbides.
- How can we 'solve' a weld decay problem?

Solving Weld Decay

- Use a low carbon grade of stainless steel less than 0.02% C
- Use a stabilised grade of steel (321 and 347), which includes a strong carbide-forming element (Nb or Ti) to lock up the carbon
- For existing components that have been sensitised, heat treat to re-dissolve the carbides over 1000°C (but this is very difficult in practice)

Exfoliation Corrosion

Exfoliation is a form of intergranular corrosion, where surface of the metal is expanded by the force of large amount of corrosion products accumulated at the grain boundaries. This form of corrosion is common on aluminium, and it may occur on carbon steel.



Exfoliation of aluminium alloy.



Exfoliation of carbon steel

<http://corrosion.ksc.nasa.gov/dealloying.htm>