

**(Corrosion)**

**Introduction 1**

By the end of this tutorial, you should have an understanding of:

- relative susceptibility of different metals to corrosion
- effects of different environments on corrosion
- corrosion between dissimilar metal contact
- different methods of corrosion protection



**What is corrosion?**

**Corrosion is the destructive and unintentional degradation of a material caused by its environment.**

Unfortunately for metals almost all environments can cause corrosion to some degree, since the corroded state is the more stable state.



**Corrosion Examples**

A common example of corrosion is the rust on roofs or bridges.

Other examples include the corrosion of steel reinforcing bars causing cracking in concrete, and corrosion on metallic window-frames.



**Cost of Corrosion**

Economically, corrosion is very important - it is estimated that 5% of an industrialised nation's income is spent on direct costs of corrosion such as prevention or replacement. There are also indirect costs of corrosion: lost production, lost efficiency, contamination and overdesign.



An understanding of corrosion is important so that we can take measures to stop it occurring.

## Electrochemistry :

In this section we will examine

- chemical processes of corrosion,
- necessary components for corrosion
- electrochemical series (explained later)

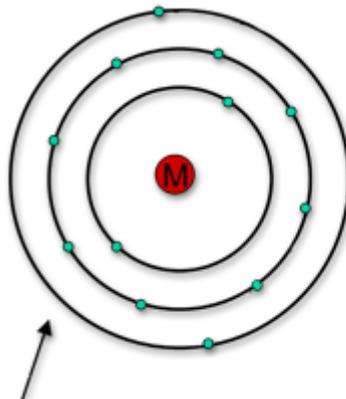
Corrosion of metals occurs through **electron transfer**, involving two processes, oxidation and reduction. In **oxidation**, the metal atoms lose electrons. The surrounding environment then gains the electrons in **reduction**.

The metal (or part of the metal object) where electrons are lost, is called the **anode**. The metal, liquid or gas which gains the electrons is called the **cathode**.

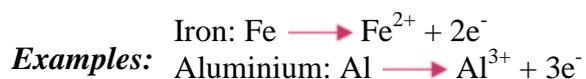
Typically in corrosion metal atoms give up electrons to become positively charged ions, in the oxidation reaction:



(for metal M with n valence electrons)



The site at which oxidation takes place is called the anode.

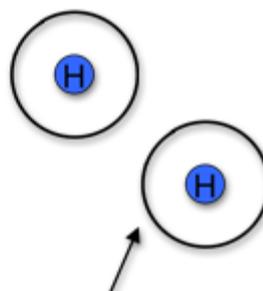


---

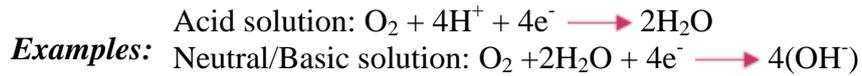
The electrons generated from the metal are transferred to another material. This is a reduction reaction:



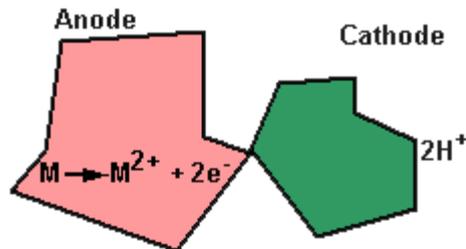
(in this reduction reaction)



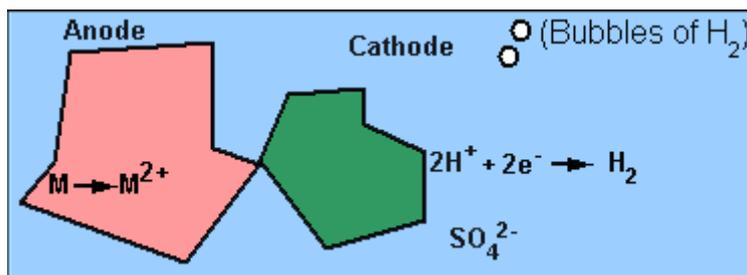
The site at which reduction takes place is called the cathode.



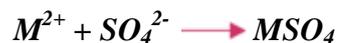
For the flow of electrons to take place, there must be a conducting connection between the cathode and the anode. Usually this occurs by physical contact. Electrons flow from the anode to the cathode.



Finally, for the flow of electricity to take place in corrosion, there must be an electrolyte, or a moist conductor, present to complete the circuit. An electrolyte contains charged ions and can conduct by migration of the ions.



*Anode:*

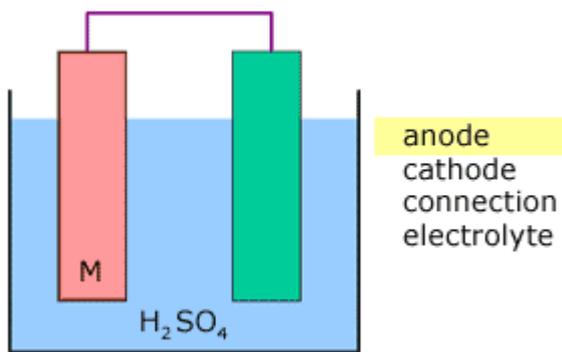


*Cathode:*



Corrosion occurs if an "electrochemical cell" is established. There are four things necessary for an electrochemical cell:

1. **Anode** - to produce electrons
2. **Cathode** - to accept electrons
3. **Connection** - to conduct electrons from anode to cathode
4. **Electrolyte** - to complete the circuit by migration of ions



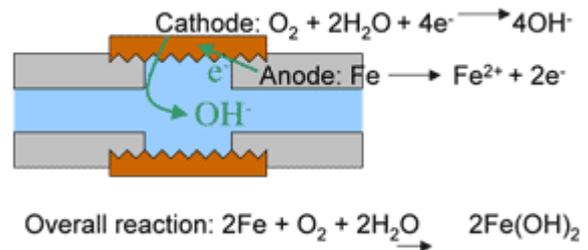
**Reactions:**



**Overall reaction:**



An example of an electrolytic cell is a copper fitting on a steel pipe carrying water. The steel pipe acts as the anode, the copper fitting is the cathode, and the water is the electrolyte.



**Standard Electrode Potentials**

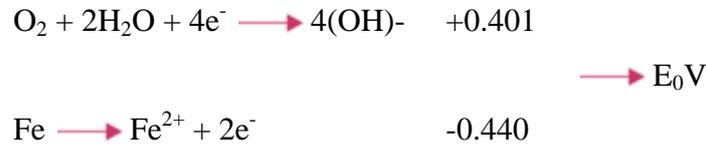
Metal Reaction	$E_0(V)$
$Au \longrightarrow Au^{3+} + 3e^-$	+1.498
$Ag \longrightarrow Ag^+ + e^-$	+0.799
$O_2 + 2H_2O + 4e^- \longrightarrow 4(OH)^-$	+0.401
$Cu \longrightarrow Cu^{2+} + 2e^-$	+0.337
$2H^+ + 2e^- \longrightarrow H_2$	0
$Pb \longrightarrow Pb^{2+} + 2e^-$	-0.126
$Sn \longrightarrow Sn^{2+} + 2e^-$	-0.136
$Ni \longrightarrow Ni^{2+} + 2e^-$	-0.250
$Fe \longrightarrow Fe^{2+} + 2e^-$	-0.440
$Zn \longrightarrow Zn^{2+} + 2e^-$	-0.744
$Al \longrightarrow Al^{3+} + 3e^-$	-1.662
$Mg \longrightarrow Mg^{2+} + 2e^-$	-2.363

In order to determine which material will corrode as the anode and which will be the cathode, the driving force for the dissociation reaction, or "half equation" is measured relative to the  $H_2$  reaction.

These half equations are ranked in a series, called the electromotive force (**emf**) series. A metal with a higher electrode potential is more resistant to corrosion. For example gold, which is very resistant to corrosion is the highest on the list, with a potential of +1.498V.

Corrosion will occur if the total difference between two half equations is positive.

For example, to determine if iron will corrode if in contact with water, we find the difference between the half equations:



$$E_0^{\text{cathode}} (\text{water}) - E_0^{\text{anode}} (\text{iron}) = +0.841\text{V}, \text{ therefore iron corrodes.}$$

As a counter-example, gold does not corrode in water, because the difference is:

$$0.401 - 1.420 = -1.019\text{V}$$

Position on the emf series will give an indication of how quickly a metal will corrode. For example, iron corrodes more readily than tin in water, because it has a more negative electrode potential.

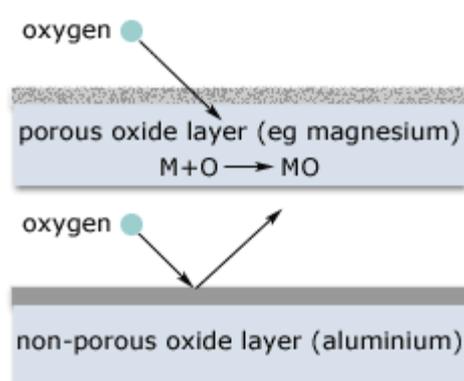
### Conditions 1

This module will examine the effect of different conditions on corrosion. We will firstly investigate oxidation or dry corrosion. We will then examine the effects of water and sea water on corrosion.

### Corrosive Atmospheres

Industrial or marine atmospheres are particularly corrosive.

Atmospheric corrosion occurs primarily due to moisture and oxygen, but is accelerated by sulphur gases from pollution and atmospheric salts. Steel corrodes 400 to 500 times faster on the coast than in a desert area.



Waste or exhaust gases such as sulphur gases form sulphurous and sulphuric acids in the presence of moisture, and thus industrial atmospheres can be 50 to 100 times more corrosive than desert areas.

Most metals are naturally coated with an oxide, but the effectiveness of the oxide layer in protecting the metal from oxidation depends on two factors:

1. the continuity of the film and how well it is bonded to the metal.
2. the conductivity of ions through the oxide film - if ions are mobile within the film oxidation of the metal can continue.

For example, aluminium is resistant to atmospheric oxidation because it forms a continuous film of oxide on the surface which has a low ion conductivity.

The ability of the oxide to protect the metal from further oxidation depends on the relative volumes of the oxide and metal, which is called the Pilling-Bedworth ratio

$$\text{P-B Ratio} = \frac{A_o \rho_m}{A_m \rho_o}$$

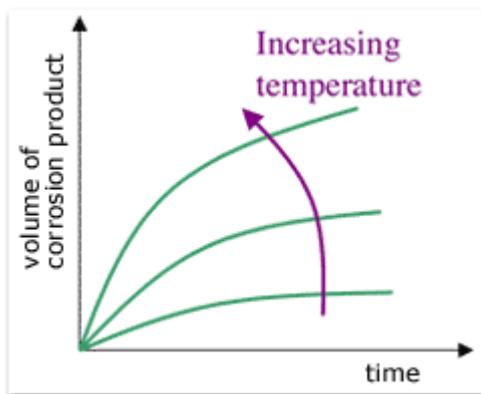
$A_o$  = molecular weight of oxide  
 $A_m$  = atomic weight of metal  
 $\rho_m$  &  $\rho_o$  are the oxide and metal densities

P-B ratio <1 These oxide films tend to be porous and unprotective. An example is magnesium.

1 < P-B ratio < 2 These oxide films tend to be protective. An example is aluminium.

P-B ratio >2 Compressive stresses in the oxide film cause the coating to crack and fall off.

### Conditions 2



Most engineering metals have a slow oxidation rate in the atmosphere at room temperature. Differences in oxidation rate depend on the conductivity of the oxide because the ions have to move through the oxide layer.

Oxidation occurs much more rapidly as temperature increases, as shown on the graph, because the mobility of ions within the oxide film on the surface increases with temperature.

Seawater is normally more corrosive than fresh water, because it has higher conductivity and the chloride ion in the seawater penetrates through surface films. For example, aluminium will corrode in seawater because the chloride ions break down the protective layer of oxide.

The rate of corrosion will depend on the chloride content, oxygen availability and temperature. Oxygen solubility actually increases as temperature decreases, so it is found that some cold currents of seawater are more corrosive because of the higher oxygen content.

Although most metals corrode in sea water, stainless steel, brass and some other alloys are actually corrosion resistant in seawater.

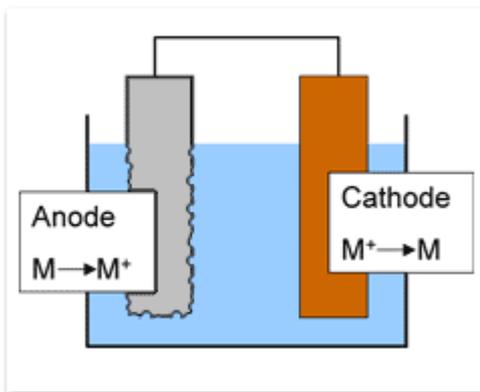
## Galvanic



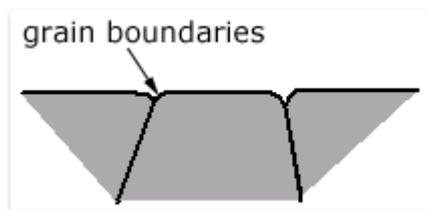
A common type of corrosion is galvanic corrosion, or corrosion between dissimilar metals.

Two different metals are immersed in an electrolyte, and acquire different electrode potentials and so when connected, a current flows. **The anodic electrode corrodes and the cathodic electrode is protected.**

Anodes and cathodes arise in many ways. As well as connection between two different metals, a plain metal surface can have anodic and cathodic areas.



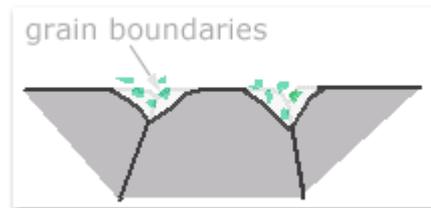
Example of galvanic corrosion



For example:

- Grain boundaries can be anodic with respect to grain interiors

regions are anodic to regions not cold worked



From the galvanic series, metals close to one another generally do not have a strong effect on each other, but the further apart two metals are, the stronger the corroding effect on the one higher in the list.

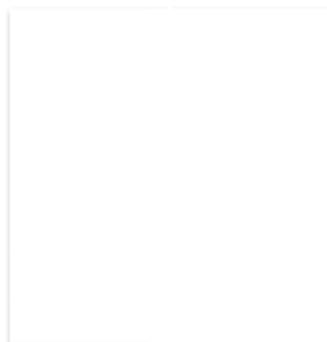
To observe the effect of the galvanic series, **click on** the metal combinations below to observe the effects of these metals in a galvanic couple.

**BRONZE**  
with  
copper  
steel  
zinc  
aluminium

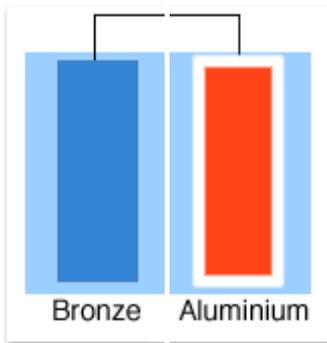
**COPPER**  
with  
steel  
zinc  
aluminium

**STEEL**  
with  
zinc  
aluminium

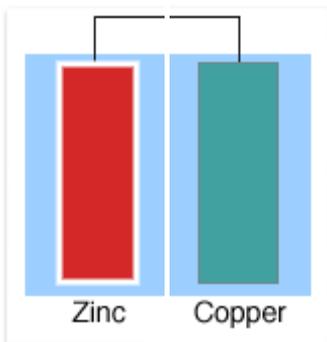
**ZINC**  
with  
aluminium



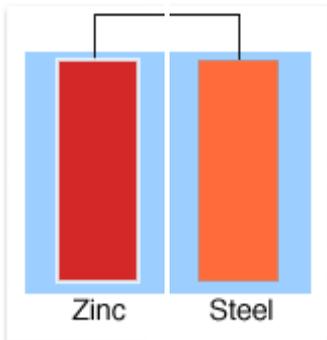
Corroded end (anodic)	Magnesium
	Zinc
	Aluminium 2017
	Steel or iron
	Cast iron
	Lead-tin solders
	Lead
	Tin
	Brass
	Copper
Protected end (cathodic)	Bronzes
	Silver
	Gold



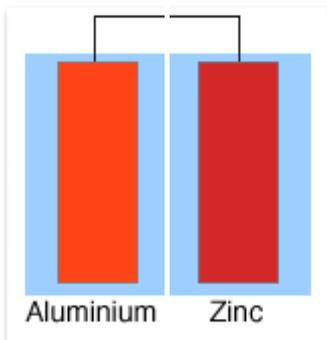
<b>Corroded end (anodic)</b>	<ul style="list-style-type: none"> <li>Magnesium</li> <li>Zinc</li> <li>Aluminium 2017</li> <li>Steel or iron</li> <li>Cast iron</li> <li>Lead-tin solders</li> <li>Lead</li> <li>Tin</li> <li>Brass</li> <li>Copper</li> <li>Bronzes</li> <li>Silver</li> <li>Gold</li> </ul>
<b>Protected end (cathodic)</b>	



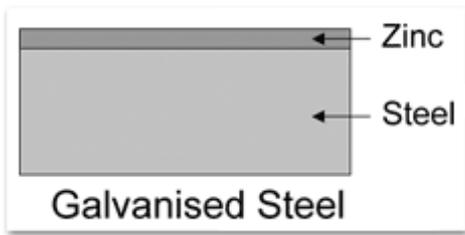
<b>Corroded end (anodic)</b>	<ul style="list-style-type: none"> <li>Magnesium</li> <li>Zinc</li> <li>Aluminium 2017</li> <li>Steel or iron</li> <li>Cast iron</li> <li>Lead-tin solders</li> <li>Lead</li> <li>Tin</li> <li>Brass</li> <li>Copper</li> <li>Bronzes</li> <li>Silver</li> <li>Gold</li> </ul>
<b>Protected end (cathodic)</b>	



<b>Corroded end (anodic)</b>	<ul style="list-style-type: none"> <li>Magnesium</li> <li>Zinc</li> <li>Aluminium 2017</li> <li>Steel or iron</li> <li>Cast iron</li> <li>Lead-tin solders</li> <li>Lead</li> <li>Tin</li> <li>Brass</li> <li>Copper</li> <li>Bronzes</li> <li>Silver</li> <li>Gold</li> </ul>
<b>Protected end (cathodic)</b>	



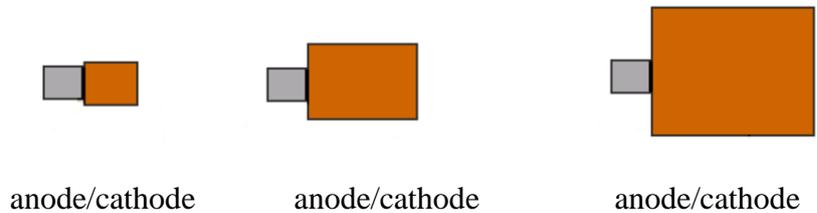
<b>Corroded end (anodic)</b>	<ul style="list-style-type: none"> <li>Magnesium</li> <li>Zinc</li> <li>Aluminium 2017</li> <li>Steel or iron</li> <li>Cast iron</li> <li>Lead-tin solders</li> <li>Lead</li> <li>Tin</li> <li>Brass</li> <li>Copper</li> <li>Bronzes</li> <li>Silver</li> <li>Gold</li> </ul>
<b>Protected end (cathodic)</b>	



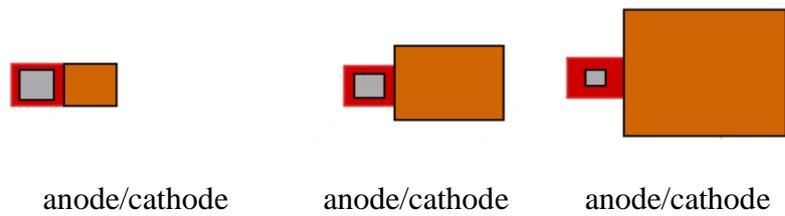
Galvanic corrosion may cause unwanted accelerated corrosion, but it can be used to an advantage, for example in galvanised iron sheet. In galvanising, iron or steel is coated with a layer of zinc. Zinc then acts as the sacrificial anode, and the steel doesn't corrode even when exposed. Even if the coating is broken, zinc will corrode in preference to steel.

The ratio of the area of the anode to the area of the cathode determines the rate of galvanic corrosion. For a given cathode area, a smaller anode will corrode more rapidly than a larger one. A situation where this is very important is in roof cladding. If fasteners are used which are anodic to the roof cladding they will corrode away very rapidly.

**Click on** each galvanic couple to observe the corrosion after equal exposure time.



Observation the corrosion after equal exposure time.



**Protection :**

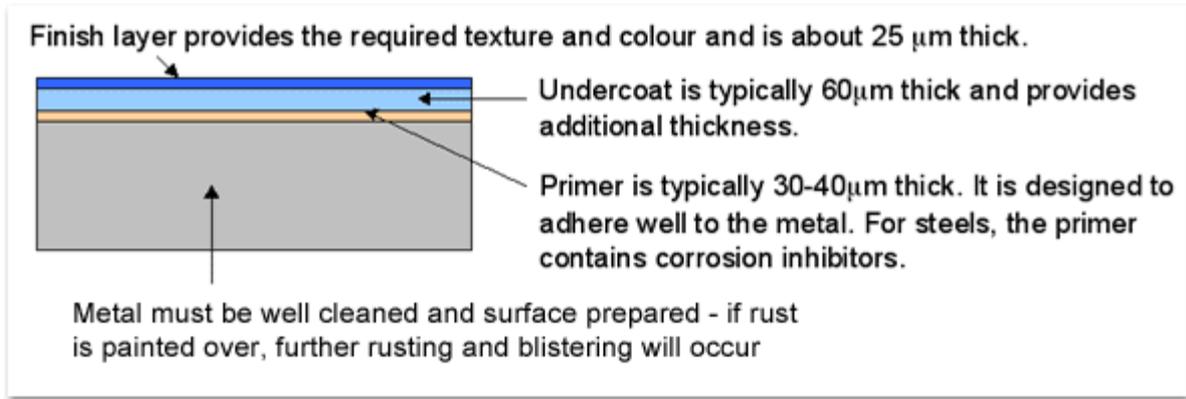
One way of avoiding corrosion is to use the most corrosion-resistant material, but if it is too expensive or impractical, there are a number of methods which can be used to protect metals from corrosion. These can be classified generally into four groups:

- Protective coatings
- Alloying
- Electrochemical methods
- Design

In this module these methods will each be examined in turn.

**1. Protective Coatings: (a) Paint:**

Paints can give good long term protection in atmospheric environments and water, but are not recommended for use in soils.

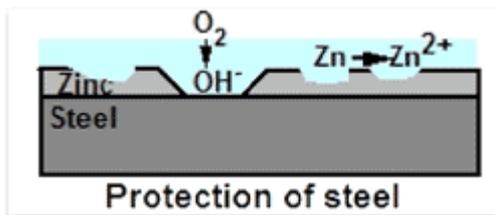


Pitch, tar, bitumen are used to coat steel structures underground, and plastics can also be used to coat metal, especially sheet metal.

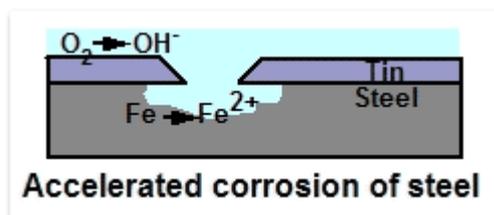
**(b)Metal:**

**Anodic coatings:** Coating acts as a sacrificial anode. Galvanising is an example of anodic coatings, where a layer of zinc is coated on steel/iron to give sacrificial protection. The zinc corrodes in preference to the steel/iron, even when the zinc is scratched.

**Cathodic coatings:** Coating acts as a cathode, preventing corrosion because the metal is more corrosion resistant. This coating is effective until the surface is broken and the substrate then becomes the anode and corrodes. For example tin coated on steel cans.



*Anodic corrosion when surface is broken*



*Cathodic corrosion when surface is broken*

**2. Alloying:**



***Changed electrode potential***

Through alloying, the electrode potential can be altered so that the metal becomes more cathodic. For example, stainless steel is more cathodic than iron or steel.

### *Protective surface film*

Alloys can produce a protective surface film, eg stainless steels or aluminium alloys

---

### 3. Electrochemical Methods:

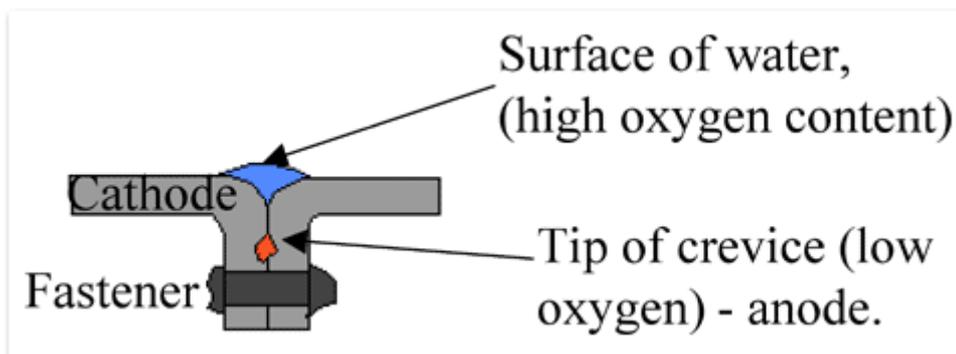
#### *Cathodic Protection:*

**Sacrificial anode.** An anode is attached to the metal that is to be protected, and corrodes instead of the metal. The sacrificial anode is typically zinc or magnesium and is periodically replaced. There is a sacrificial anode in water heaters, which corrodes in preference to the storage tank corroding.

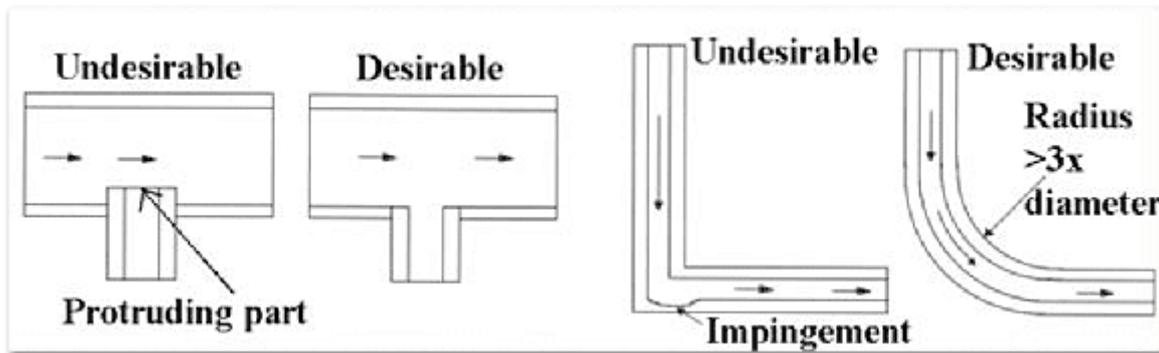
### 4. Design:

#### *Avoid Crevices*

Crevices under bolts and rivet heads, and shielded areas (such as lap joints and under dirt or sand deposits) often suffer corrosion. This is due to small amounts of stagnant moisture which accumulate there.



### *Avoid protruding sections and sharp bends*



### **Case study 1**

This module will examine a number of case studies where corrosion effects need to be taken into account.

Automobile exhaust systems undergo corrosion very rapidly and generally have a limited lifetime. It is not surprising, because exhaust systems are usually made from mild steel, which is not corrosion resistant. The interior of the system is not painted and therefore corrodes because of damp exhaust gases.



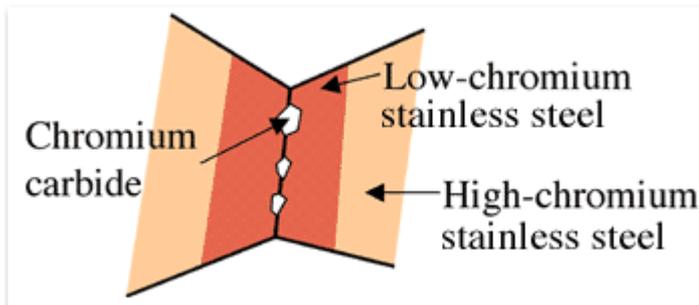
Exhaust systems could have an extended life by the use of galvanised steel, but because the steel is welded in exhaust systems, the galvanised coating burns off at the welds and the steel is exposed to the gases.

The best solution to combat corrosion in exhaust systems is the use of stainless steel, which contains chromium. Stainless steel gives a coating of  $\text{Cr}_2\text{O}_3$  on the surface of the steel to act as a corrosion barrier.

---

Turbine blades are generally made of nickel. At  $950^\circ\text{C}$ , nickel loses 0.1 mm of metal from its surface by oxidation in 600 hours, which is approximately 10% of this thickness. This oxidation is curbed by dissolving chromium in solid solution in the nickel matrix. This chromium forms  $\text{Cr}_2\text{O}_3$  on the surface, which increases the time for metal loss by ten times. However, to improve the oxidation resistance further, an oxidation resistant alloy or a ceramic coating is applied.

## Case study 2



Corrosive liquid is piped along welded stainless steel pipes. Near the welds, corrosion occurs and corrosive liquid leaks from the pipes. The reason for the corrosion is that stainless steel generally contains a small amount of carbon (~0.08% C). The heat of welding causes the carbon to form a compound with the chromium which was there to protect the steel. This depletes the

stainless steel of chromium around the welds and the low-chromium areas are then susceptible to corrosion.

---

A number of solutions to the chromium carbide problem might be possible:

- **Improve welding process.** Ensure the heating and cooling rates are very fast so that the chromium carbides do not have time to form.
- **Heat treat pipe after welding.** Heat the pipes to a moderate temperature to redissolve the chromium carbide compounds then cool the pipes rapidly. However a large pipe system may be impossible to heat treat because of its size and cost.
- **Use a stainless steel with less carbon content.** Carbides do not form in low carbon stainless steel, which has a carbon content of less than 0.03% C. This steel is more expensive, but allows us to prevent the corrosion process while using conventional joining techniques.