

## 4. Localised corrosion

The kinetic models in chapter 3 produce a single value of current density which describes the speed of corrosion of a metal. If the metal experiences uniform corrosion then a single number is enough to describe it. However, there are many localised corrosion mechanisms in which deterioration is concentrated into small areas of a material, or where material properties deteriorate without much obvious loss of metal. It is important for chemical engineers to know how these processes occur so that bad consequences can be avoided.

Localised corrosion may be

- ♦ Hard to predict – there are many types with various causes
- ♦ Difficult to detect – occurring in small or hidden areas.
- ♦ Rapid – due to concentration into a small area

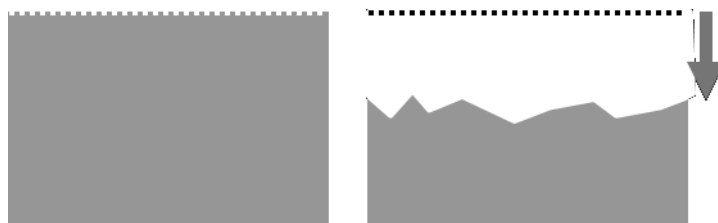
Localised corrosion is often caused when a metal that is supposed to be in a passive state actually experiences active corrosion due to factors that exacerbate corrosion in a local area.

- ♦ Corrosive micro-environments
- ♦ Mechanical effects (stress and abrasion)

### 4.1 Uniform corrosion

This may be called “generalised corrosion” or “uniform attack.”

- ♦ In this case the entire surface corrodes at a spatially-uniform rate.  
For example, the slow oxidation of weathering steel.
- ♦ Uniform corrosion is often visually detectable, and predictable with simple equations.
- ♦ The widespread nature of uniform corrosion makes it easy to detect. It is perhaps the least dangerous form of corrosion because severe deterioration is likely to become obvious before it causes a failure.
- ♦ It is often slow, because oxidation is widely spread out.



## 4.2 Bimetallic corrosion

This is also called galvanic corrosion.

If two different metals are in electrical contact then the more reactive metal will form a corrosion anode. It may corrode faster than it would in isolation, because the other metal provides an additional cathode (often a much more effective one), but the more reactive metal suffers almost all of the oxidation.

The more noble metal may be a more effective cathode if it

- (a) Has higher exchange current density, e.g. for  $(\text{H}_2|\text{H}^+)$
- (b) Supports additional cathode reactions (e.g. electroplating)
- (c) Is clean metal with little barrier to oxygen adsorption

### 4.2.1 Example: a bimetallic strip of Zn and Fe

Consider a strip of iron with zinc coated on one side, dissolving in acid.

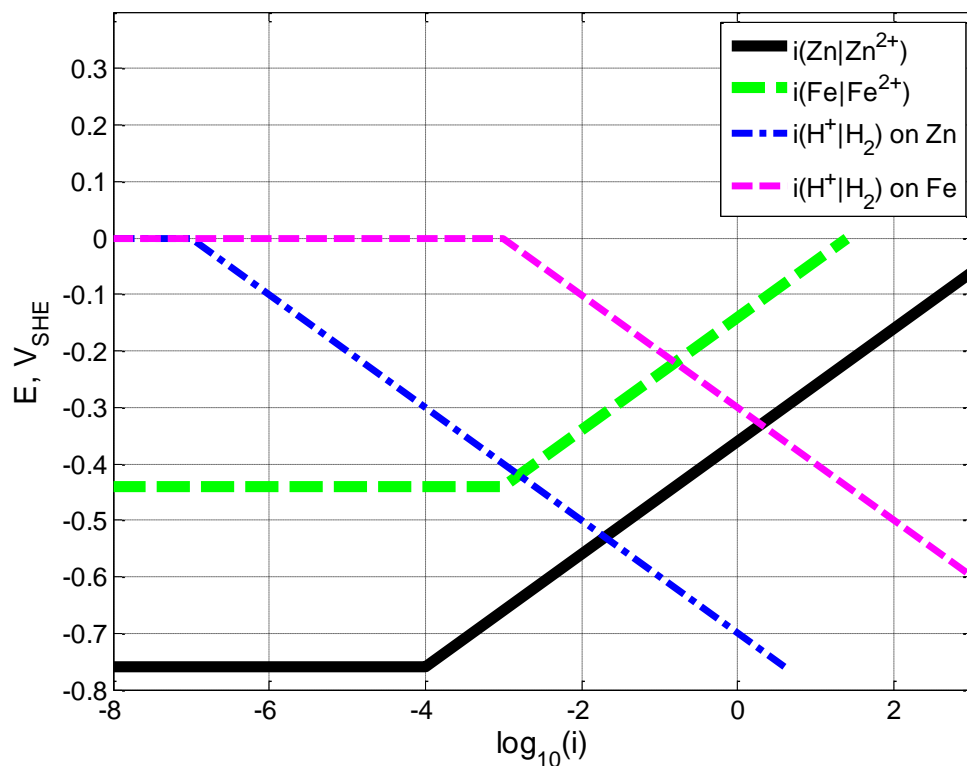
Conservation of charge means that

$$\sum |I_{\text{anodes}}| = \sum |I_{\text{cathodes}}| \quad (4.1)$$

We can simplify by considering only metal dissolution and hydrogen evolution.

$$A_{\text{Zn}} i(\text{Zn}|\text{Zn}^{2+})_{\text{a}} + A_{\text{Fe}} i(\text{Fe}|\text{Fe}^{2+})_{\text{a}} = A_{\text{Zn}} |i(\text{H}_2|\text{H}^+)_{\text{Zn,c}}| + A_{\text{Fe}} |i(\text{H}_2|\text{H}^+)_{\text{Fe,c}}| \quad (4.2)$$

One way to approximately predict the rate of corrosion is to plot an Evans diagram for the four possible processes, and estimate the surface potential by considering the dominant (fastest) pair.



Compared with pure metals, the bimetallic strip has a faster anode reaction for  $\text{Zn} \rightarrow \text{Zn}^{2+}$ , and a much slower anode reaction for  $\text{Fe} \rightarrow \text{Fe}^{2+}$ .

Bimetallic corrosion is a common problem.

- 1763: the copper sheathing of HMS Alarm, installed by the Royal Navy in a (successful) anti-biofouling test, caused most of the iron nails used to affix the copper plating to corrode completely in only 2 years.
- Today: copper tubes are often used in heat exchangers. They may cause rapid corrosion where they are attached to a steel body. This should be allowed for when specifying the steel thickness!

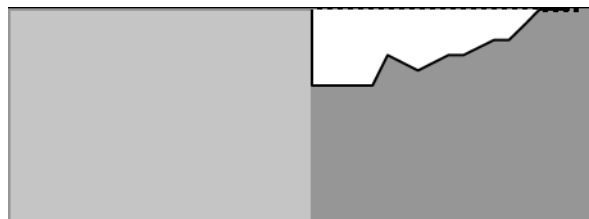
In bimetallic corrosion, the area effect causes fast corrosion when a large cathode (e.g. copper hull plating) is connected to a small anode (e.g. an iron bolt). [Refer to the equations in section 3.9.]

- ◆ This can be exploited for corrosion protection:
  - When bolting metal sheets, using bolts made of a more noble metal than the metal sheet will cause the sheet to act as a sacrificial anode that protects the bolt. Hence Type 316 stainless steel bolts are often used to connect Type 304 stainless steel sheet (which is slightly more reactive).

#### 4.2.2 Protecting against bimetallic corrosion:

- Prevent electrical contact between different metals (insulating gaskets)
- If different metals must be in contact, use similar metals
- Allow for loss of metal

#### 4.2.3 Schematic diagram of bimetallic corrosion



### **4.3 Deposition corrosion**

Electronic separation of different metals may not permanently prevent them from suffering bimetallic corrosion.

- ◆ Dissolved ions of relatively noble metals such as copper may be present in aqueous solutions.
- ◆ If the solution contacts a base metal (e.g. aluminium), the copper ions may electroplate onto the base metal surface.
- ◆ The copper then causes bimetallic corrosion of the base metal.
  - Deposition corrosion is a problem in aluminium water pipes, radiators, and heat exchangers because copper-alloy pipes are often found elsewhere in the system, or upstream in the water supply.

#### 4.3.3 Protecting against deposition corrosion

- ◆ Avoid using copper and  $\text{Cu}^{2+}$  in combination with incompatible metals.

## 4.4 Crevice corrosion

This is intense local corrosion that can occur in areas of restricted liquid access. It is especially severe when chloride ions are present.

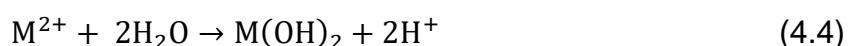
### Initial stage

- ♦ Uniform corrosion with a metal anode ( $M \rightarrow M^{2+}$ ) and an oxygen cathode

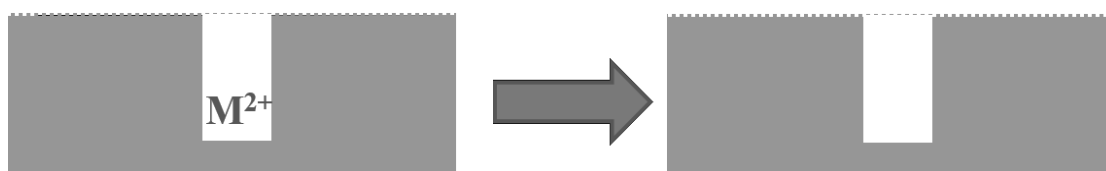


### Development

- ♦ The liquid in the crevice is stagnant, and so the oxygen within it becomes depleted due to restricted mass transport.
- ♦ The oxygen reaction now only takes place on the external metal surface, but the metal dissolution continues within the crevice.
- ♦ In the crevice, the metal ions may react in solution, releasing protons.



- ♦ Because there is no dissolved oxygen in the crevice, these protons are not used up. This means the electrolyte near the anode can become acidic (pH changes from 8 in the bulk liquid to 2 in the crevice are possible).
- ♦ Chloride ions can be drawn into the crevice to balance the positive charge of the ions produced at the anode.
- ♦ The corroding metal is exposed to low pH and high chloride ion concentration, both of which promote rapid corrosion.
- ♦ As a result of this, active **crevice corrosion is autocatalytic**: once it starts, the situation gets worse at a fast and accelerating rate.



Passive metals such as stainless steel can be particularly vulnerable to crevice corrosion. The lack of dissolved  $O_2$  means that the oxide film cannot easily regenerate, and repassivation is weakened.

### 4.4.1 Protecting against crevice corrosion

- ♦ Zinc-containing paints – both as a barrier to water and as a sacrificial anode.
- ♦ Robust design (avoid causing water, especially saltwater, to pool on vulnerable areas).

## 4.5 Pitting corrosion

A “pitted” surface is a common sight on aged metals.

The late stages of pitting corrosion are similar to crevice corrosion. But this process begins with the development of a **pit**, often only microns in size, on a metal surface.

The initial formation (called initiation or nucleation) of a pit often depends on local imperfections at the surface such as:

- Scratches
- Fluctuations in composition (e.g. after welding)
- Differential aeration under a water droplet

Once a pit forms, it may progress by crevice corrosion, eventually perforating the metal.

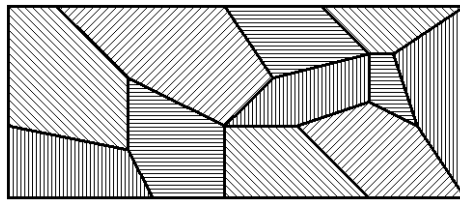
- Alternatively the pit may lose its cover due to mechanical damage, and stop growing.

Note that most metals exhibit crevice corrosion, but only some show pitting initiation behaviour.

- Many stainless steels are vulnerable to pitting corrosion in seawater. This is because the passive  $\text{Cr}_2\text{O}_3$  surface can provide a covering for a microscopic pit in which the less-passive iron alloy dissolves.
- Copper pipes can be pitted by atmospheres containing acetic acid (a common hardener in glues).
- Microscopic pits can compromise the integrity of pipes! This may produce leaks, which are a major hazard when flammable, explosive or toxic gases could be released.

## 4.6 Intergranular corrosion and weld decay

Most metals are polycrystalline materials. Many crystallites form during solidification of a molten metal, with various orientations. These crystallites grow and link up, leading to grains in the final solid.



Grain boundaries in metal are more vulnerable to corrosion than bulk metal due to:

- Voids (cracks can lead to pitting)
- Less passive phases precipitated between grains
- Bimetallic corrosion due to contact between the less passive material and the rest of the metal.

### 4.6.1 Weld decay

Both carbon steels and stainless steels are vulnerable to weld decay.

- Welding often creates regions of metal with many grain boundaries and a 'poor quality' microstructure compared to the bulk metal.
- Carbon steel and stainless steel also have (different) chemical problems. Heating metals to 600-850°C for a few minutes, which often occurs in the vicinity of welding, can produce regions with weakened alloy composition, as follows.

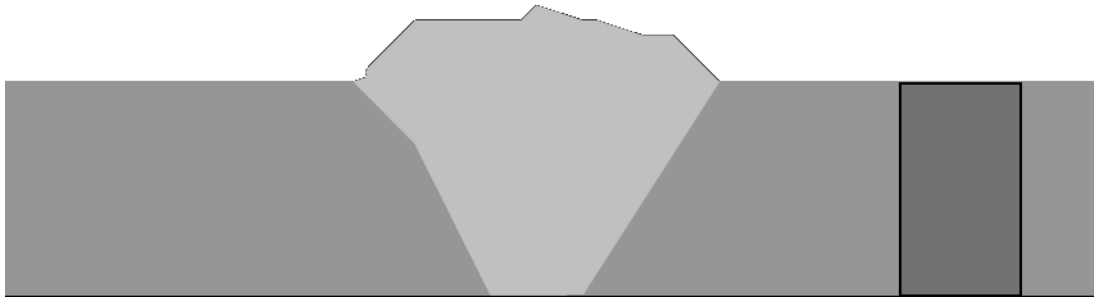
### 4.6.2 Carbon steel weld decay

- ♦ Carbon only remains dissolved in steel at concentrations above 0.03% if the metal is prepared by cooling rapidly from above 1000°C. Otherwise it tends to separate into iron carbides such as  $\text{Fe}_3\text{C}$ .
- ♦ Carbon steel may form carbides if it is heated during a welding operation. The heat-treated microstructure is vulnerable to corrosion.

### 4.6.3 Stainless steel weld decay

- ♦ Chromium has a strong affinity for carbide formation.
- ♦ Welding stainless steel therefore causes sensitisation.
- ♦ If stainless steel is heated to 600-850°C for a few minutes, then chromium carbides may form at the grain boundaries.
- ♦ Precipitation of chromium-rich carbides causes chromium depletion in the adjacent area. If the chromium composition drops below 11%, then the alloy is no longer "stainless" – it no longer forms a uniformly passive chromium oxide surface when it reacts with water or air.
- ♦ Severe local corrosion can then occur near welding work.

#### 4.6.4 Schematic diagram of corrosion in weld decay



#### 4.6.5 Protecting against weld decay:

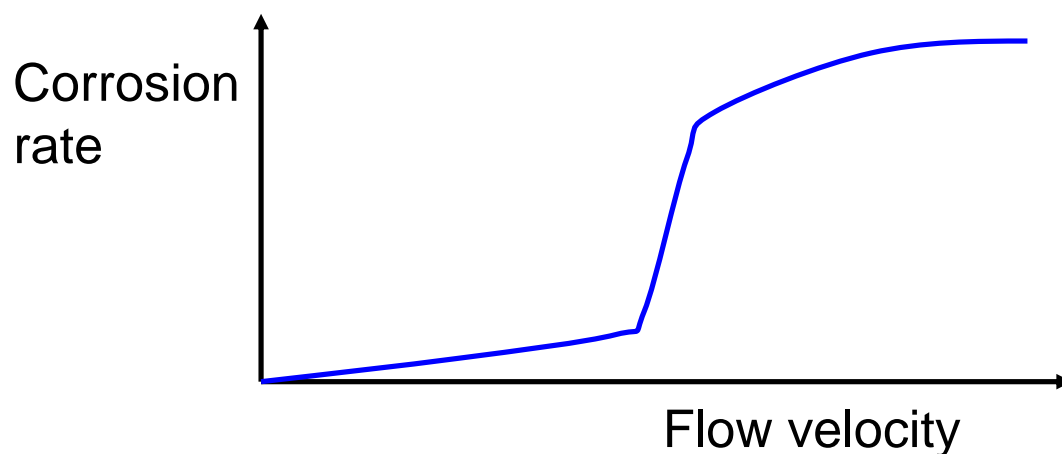
- ◆ Low-carbon steel ( $\leq 0.03\%$  C): this amount of carbon is “stable” when dissolved in iron, and carbon steels will not experience iron-carbide formation.
  - Note that carbon can be added accidentally during welding
- ◆ ‘Stabilised’ stainless steel. Titanium and niobium are even stronger carbide-formers than chromium, so alloys including Ti or Nb ensure that these carbides precipitate in preference to the chromium carbide, and the alloy is still protected by chromium.
- ◆ Post-weld heat treatments (heat to above  $1000^{\circ}\text{C}$ , maintain for some minutes, and then quench rapidly) can dissolve the precipitates that have formed.

## 4.7 Flow induced corrosion

Motion of a fluid over a metal surface may speed up corrosion due to a combination of:

- (a) Erosion due to entrained particles or fines which scour away protective layers.
- (b) Cavitation in high Reynolds number flow can also damage metal and remove passive oxide layers.
- (c) Faster flow increases mass transport of dissolved oxygen to a metal surface.

### 4.7.1 Erosion-corrosion rate when abrasion dominates the effect of fluid flow



### 4.7.2 Effect of oxygen transport

An example of flow induced corrosion, where oxygen transport is important, is considered in the second examples sheet.

### 4.7.3 Protecting against flow-induced corrosion

- Filters
- Avoid sharp bends in pipes that may create areas of fast flow or pressure drops.
- Smooth surfaces prevent bubble nucleation
- Stainless steels are usually very resistant to cavitation damage, because their passive oxide layer is mechanically strong (compared with, say, copper).



## 4.8 Stress corrosion cracking (SCC) and corrosion fatigue

Corrosion can cause unexpected brittle failure of structures and pressure vessels. There are two distinct situations.

Stress corrosion cracking is a risk for metals experiencing:

- ♦ A constant tensile stress and a corrosive environment

Example: structural stainless steel supporting rods can fail due to SCC if used in humid, chloride-rich atmospheres above indoor swimming pools.

Corrosion fatigue is a risk in cases with

- ♦ A varying tensile stress and a corrosive environment

Example: crack growth in a pressure vessel wall during cycles of pressurisation and depressurisation can lead to brittle failure.

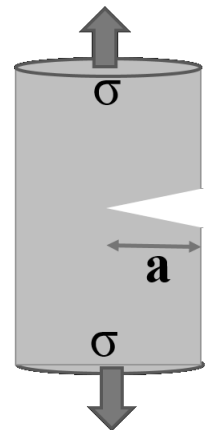
### 4.8.1 Brittle failure

In the absence of a corrosive environment, materials in simple tension are predicted to fail by fast fracture if:

$$K_{\text{applied}} = \alpha \sigma_{\text{applied}} \sqrt{\pi a} > K_{\text{IC}} \quad (4.5)$$

Where:

- $\alpha$  is a geometric factor (close to 1)
- $\sigma_{\text{applied}}$  is the applied stress
- $a$  is the crack length
- $K_{\text{IC}}$  is the fracture toughness of the material.



### 4.8.2 Reasons why stress corrosion cracking can lead to brittle failure

- ♦ Decreased fracture toughness due to oxidised surface

In a corrosive environment, cracks appear when the stress intensity factor,  $K_{\text{ppd}} = \alpha \sigma_{\text{applied}} (\pi a)^{0.5}$ , exceeds a new value,  $K_{\text{ISCC}}$ , that depends on the environment and is smaller than  $K_{\text{IC}}$ .

- ♦ Crack nucleation and growth

Corrosion produces large surface cracks, e.g. by pitting.

### 4.8.3 Corrosion fatigue is mainly caused by slow crack growth per stress cycle

- ♦ Passive surface oxides may be ruptured by varying tensile stress even if the bulk metal object does not crack.
- ♦ The exposed metal is then oxidised to a more brittle material.
- ♦ This new oxide then cracks further.

Crack growth per cycle is often described by an approximate model.

- ♦ A common model is Paris' law, which defines a constant increment of crack length per stress cycle.
- ♦ In Paris' law, the crack length is  $a$  and the crack growth is defined by some parameters  $C$  and  $n$  which depend on the situation.

$$\frac{da}{dN} = C \Delta K^n \quad (4.6)$$

Where

$$\Delta K = \alpha \Delta \sigma \sqrt{\pi a} \quad (4.7)$$

In which  $\alpha$  is a geometric factor and  $\Delta \sigma$  is the range of applied stresses.

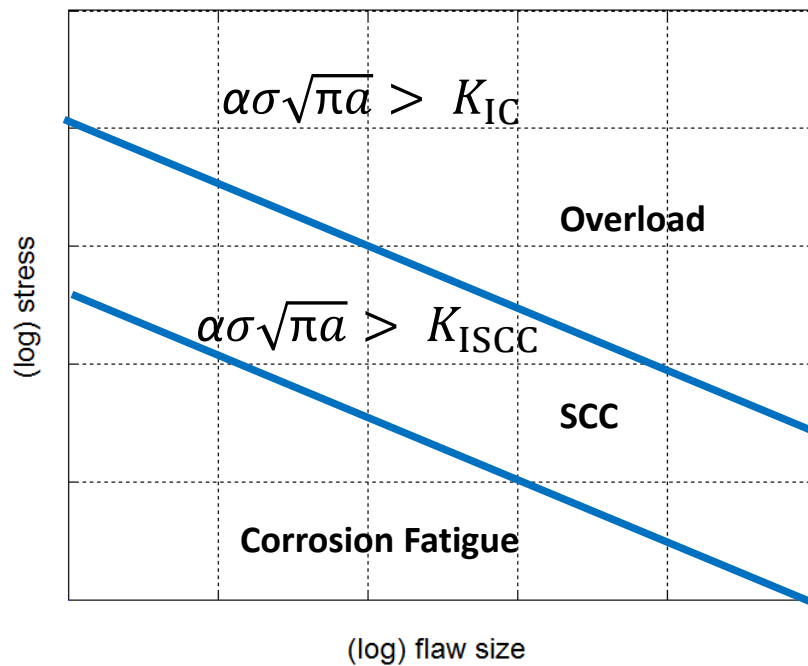


Figure. Brittle failure mechanism by flaw size.

#### 4.8.4 Protecting against SCC and corrosion fatigue

Use thicker materials to ensure lower stress.

Use alloys known to deteriorate slowly.

Inspection and replacement.

Coatings / anodic protection.

## 4.9 Hydrogen damage

Metals may be exposed to hydrogen because:

- ♦  $H_2$  is present in a process stream (in petrochemicals, for example), or
- ♦ Hydrogen is produced by a cathodic process (often as the cathode of a corrosion reaction).

Hydrogen can interact with metals in special ways. Crucially:

- Hydrogen may dissociate into protons which diffuse through metals.
- Hydrogen may react with metals to form hydrides (which may be brittle).

Hydrogen embrittlement is a term which refers to a combination of damaging processes that occur due to hydrogen.

- ♦ Hydride formation

Some steel alloys contain titanium or niobium. These components react with hydrogen to form brittle hydrides, decreasing fracture toughness.

- ♦ Decarburisation

At high temperatures, dissolved H atoms in metal react with carbon in steel, producing methane and leading to a loss of strength and ductility provided by carbide phases.

- ♦ Hydrogen blistering.

If a metal contains void defects, then the H atoms can combine back to form  $H_2$  in these voids. The pressure of  $H_2$  in a void can cause a blister (bubble-like swelling) or even rupture of the material.

### Preventing hydrogen damage

- ♦ Choice of alloy

- Austenitic stainless steels can be better because

1. They are less brittle (as FCC metals possess more slip planes)
2. They have lower H-atom diffusivity

- ♦ Avoid unintentionally producing  $H_2$ . (E.g. if a metal is cathodically protected, do not polarise it so strongly that lots of hydrogen is produced.)
- ♦ Annealing at  $150^\circ\text{C}$  in hydrogen-free environments can reverse most of the effects of hydrogen embrittlement.

## 4.10 Damage caused by expanding corrosion products

- ♦ Reinforced concrete can be cracked by the compressive strain of the corrosion products on steel rebars.
- ♦ Aluminium sheets can delaminate due to rivets being burst by hydrated oxides building up between layers.

## 5. Corrosion protection

Sections 1–4 of this course suggest there are several ways to prevent corrosion completely, or slow it to an acceptable rate. Sensible material selection is one approach, based on pH-potential diagrams or corrosion rate models.

There are also several corrosion protection methods that can be applied to decrease corrosion even if a vulnerable metal is used.

- ♦ Thermodynamic methods, also called electrochemical methods
- ♦ Corrosion inhibitors
  - Environmental modification
- ♦ Coatings

### 5.1 Sacrificial anodes

- ♦ Loss of metal by the  $M \mid M^{n+}$  oxidation reaction occurs at the anode.
- ♦ Electrical contact with another metal that is more reactive in the galvanic series (e.g. zinc) can decrease the polarisation for the corrosion of another metal (e.g. iron). The more reactive metal is called a sacrificial anode.
- ♦ An example is the bimetallic strip of iron and zinc discussed in section 4 (bimetallic corrosion).
- ♦ Sacrificial anodes are widely used to protect ship hulls, underground pipelines, offshore oil/gas platforms and some domestic hot-water tanks.
- ♦ Possible materials for use as sacrificial anodes:
  - Zinc, magnesium and aluminium alloys. These are all more active than copper or iron.
  - Titanium cannot be used (despite a highly negative standard electrode potential), because its chloride-resistant passive oxide surface makes it too inert to spontaneously dissolve.
- ♦ Do not paint over a sacrificial anode!

### 5.1.1 Sacrificial anodes in practice

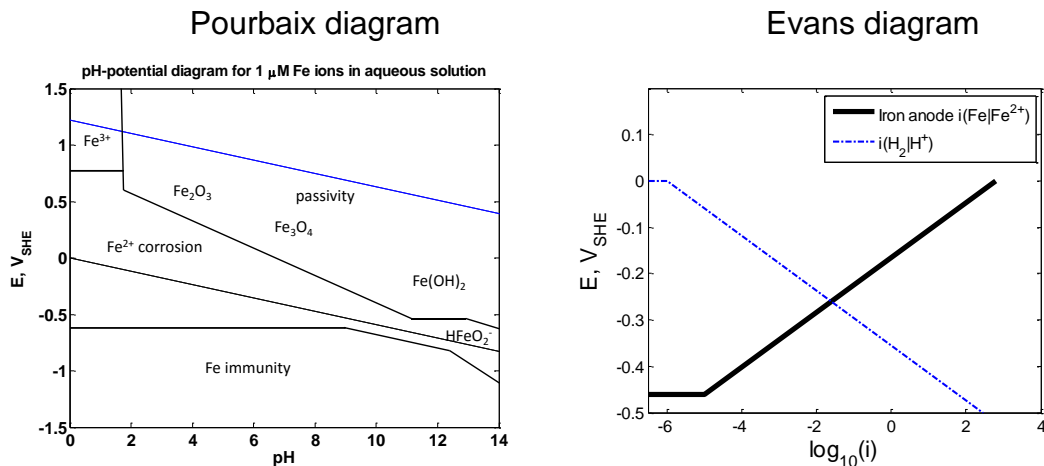
- ◆ An underground pipeline will probably be coated by a polymer lining.
  - A sacrificial anode is only needed to deal with breaks in the plastic coating of the pipeline.
- ◆ The designer must specify how many sacrificial anodes are required, their spacing, and their dimensions (volume and exposed surface area are both important).
- ◆ Design decisions will be based on the following data which is typically specified for sacrificial anode materials:
  - The maximum output of the anode material (in  $A/m^2$ ); i.e. what current a given surface area can provide.
  - The capacity of the anode material (in  $A.h/kg$ ); i.e. the charge that can be provided per unit mass.
  - The wastage rate of the anode material (in  $kg/A.yr$ ); i.e. how long the anode will last.
  - The “throwing power” of the device: due to the resistance of the material being protected, metal a long way from the sacrificial anode will be less protected than that near the anode. On oil rig platforms there are thus many small anodes (rather than a few colossal ones).
- ◆ A key factor for the design of offshore platforms is that sacrificial anodes add weight to the structure.
  - See example on problem sheet 2.
  - Note that sacrificial anodes do eventually need to be replaced.
- ◆ Recall that hydrogen embrittlement takes place at the cathode, and sacrificial anodes may make this problem worse!

### 5.2 Impressed current corrosion protection (ICCP)

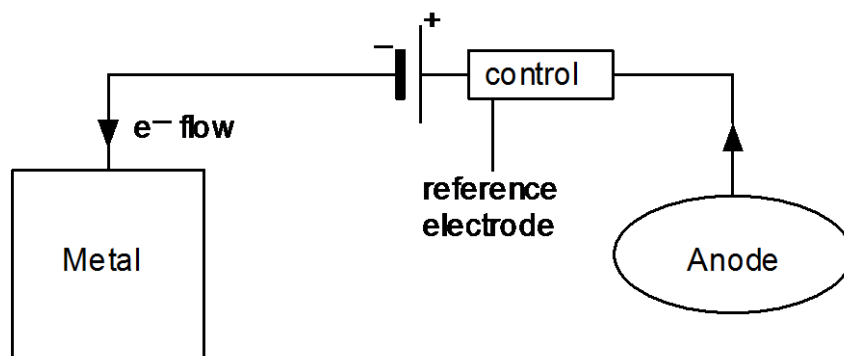
Another method for applying a cathodic potential to protect a metal is to drive an electronic current using an electrical power source. In this **impressed current** method, the electrons are drawn from a driven (not spontaneous) anode, and can exert electronically-controlled protective potentials on the specimen.

- ◆ The thermodynamics of corrosion are typically forced into an immune region of the pH-potential (Pourbaix) diagram.

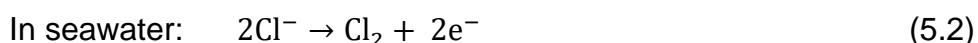
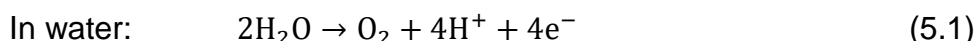
- ♦ Alternatively we can use Evans diagrams to predict the new rate of corrosion at the imposed potential.



- ♦ A **potentiostat** is used to keep the corrosion potential fixed at a potential, typically one at which the metal is just immune from corrosion,  $E_{\text{ICCP}}$
- ♦ Supplying a fixed potential electronically, rather than a mixed potential applied by attaching a sacrificial anode, allows for changes in corrosion environment over time – for example if the local dissolved oxygen concentration varies, the potential on the surface can still be held constant.
- ♦ The circuit needs to be able to supply a current equal to  $A(|i_c| - |i_a|)$  in the above diagram.



- ♦ Unlike the sacrificial anode, the driven anode in ICCP is not short-circuited to the protected metal. The electron path must go via a power source. The two electrodes are not at the same corrosion potential.
- ♦ The driven anode may be an electrocatalyst, such as a platinised titanium gauze, which may support the following anodic reactions:



In both cases the anode is in plentiful supply. It is important the anode does not run out, since this would remove corrosion protection.

- ♦ Sometimes a “consumable driven anode” such as scrap iron may be used instead of a platinised titanium.

Advantages of ICCP over sacrificial anodes:

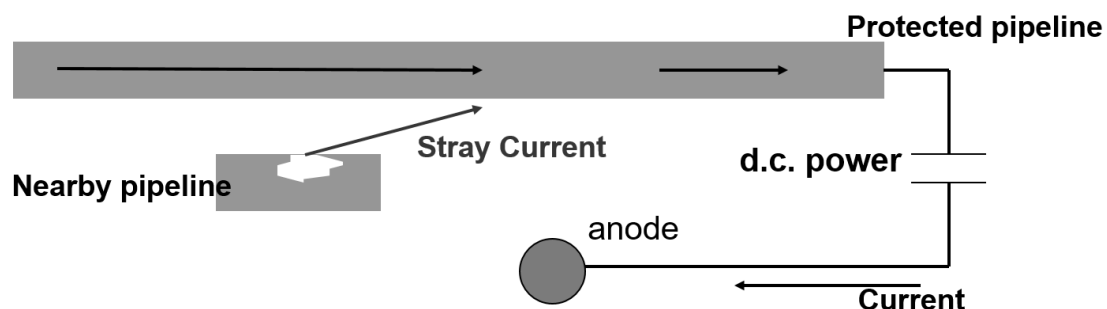
- ♦ No need to replace anode

- ◆ Precise control and monitoring of object electronically.

#### Disadvantages of ICCP

- ◆ Electronic failures: power loss; corrosion of electrical contacts; driven anode failing mechanically; and...
- ◆ Systems connected the wrong way around!
- ◆ Cost of electrical power (and the need for an on-site supply).
- ◆ Stray current corrosion can damage nearby metal objects

#### 5.2.1 Stray current corrosion



### 5.3 Anodic protection

Some metals become passive in very strong oxidising environments.

- ◆ Iron is passive in concentrated nitric acid.
- ◆ ICCP can be used to exert oxidising potentials to protect metals that form passive layers.
  - The cost of electricity is far lower.
  - The only current that must be provided is the current to drive the passive oxide formation (and maintenance).
- ◆ There is an element of risk
  - Rapid corrosion might occur if the metal de-passivates. (E.g. if the environment changes pH so there is no longer passivation.)
  - If the applied oxidising potential drifts to an insufficiently oxidising level. This possibility can be prevented by proper electronic design.
- ◆ Anodic protection does not work if the metal does not have a passive state at high oxidation potential (e.g. in many chloride solutions); however in neutral soils it can work well for iron and steel.

## 5.4 Inhibitors

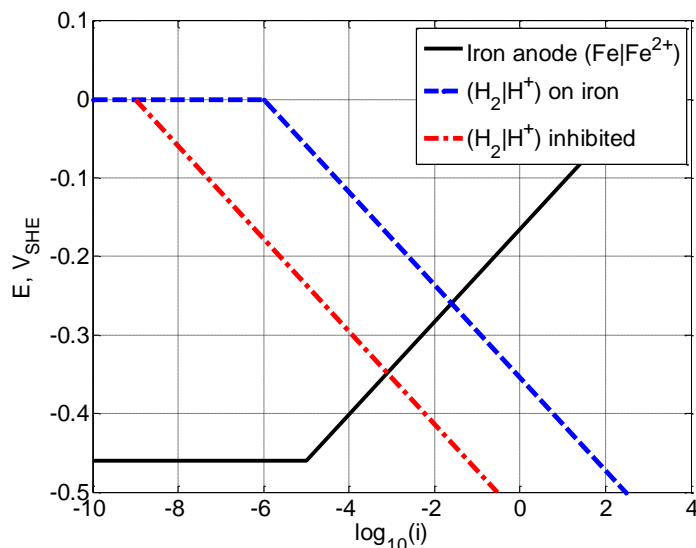
Corrosion inhibitors are chemicals that are added to a liquid environment to slow down corrosion.

- ♦ Some inhibitors are toxic (e.g. arsenic ions).
- ♦ Inhibitors are often added to closed loops such as central heating systems. They are also commonly added to crude oils streams.
- ♦ Recall that electrochemical corrosion involves both an oxidising agent (cathode) and the metal undergoing oxidation (the anode). Inhibitors can be successful by slowing down either of these mechanisms.

### 5.4.1 Cathode inhibitors

These inhibitors slow down the rate of the oxidising agent reaction at a cathode. The choice of inhibitor depends on which oxidising agent needs to be blocked.

- ♦ Some heavy metal ions like arsenic ( $\text{As}^{3+}$ ) are electrocatalyst poisons for the proton reaction ( $\text{H}_2 \mid \text{H}^+$ ). They are adsorbed onto vulnerable metals such as steel, and decrease  $i_0(\text{H}_2 \mid \text{H}^+)$ , slowing down corrosion.



- ♦ The dissolved oxygen reaction (e.g.  $2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- \rightarrow 4\text{OH}^-$ ) can be slowed down by a diffusion barrier which decreases  $i_{\text{lim}}$  for the oxygen reaction. In neutral or mildly alkali solutions, zinc or magnesium ions can form insoluble hydroxides deposits. Calcium ions do the same thing – by forming limescale!
- ♦ Adsorption-type inhibitors: these are normally organic compounds (e.g. organic amines) that adsorb on the metal surface and reduce the rate of the cathode reactions by blocking mass transport.



#### 5.4.2 Anode inhibitors

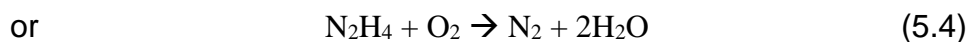
These chemicals slow down the anodic half-reaction of corrosion. They typically work by making the metal surface become passive.

- ♦ Water can be deliberately added to anhydrous streams of crude oil. The presence of water is needed for metals like stainless steel or titanium to form a passive oxide surface. The protective oxide then prevents the metal reacting with chemicals in the crude oil.
- ♦ Chromate solutions can deposit passive layers onto the surface of metals, protecting them even if the underlying metal is unable to passivate.

#### 5.4.3 Oxygen scavengers

These chemicals deplete the concentration of corrosive reagents in solution.

- ♦ For example, addition of sodium sulphite or hydrazine removes dissolved oxygen through the reactions



## 5.5 Coatings

Corrosion could be prevented entirely by eliminating contact between a vulnerable material and the corrosive environment.

- ◆ Barrier lifetime needs to be known, usually from measurements

Corrosion underneath coatings may be important

- ◆ Aggravated rusting refers to corrosion under a coating – somewhat similar to crevice corrosion
- ◆ Expanding corrosion products can exert high pressure and crack coatings and bolts.

### Paint

Paints are suspensions of pigments, adhesives, etc. in a liquid that evaporates away.

- ◆ Paint coatings tend to be slightly porous: they provide a partial mass transport barrier. This may decrease corrosion but not stop it completely.
- ◆ Hence inhibitors may be added to paint; any water reaching the metal surface becomes saturated with these inhibitors.
- ◆ Some paints also have metals in suspension that provide some sacrificial protection.
- ◆ Paint coatings are cheap and work well in mild corrosive conditions (e.g. metals exposed to atmospheric corrosion). Their effectiveness depends on proper surface preparation and application.

### Plastic, rubber, glass and ceramics

These coatings may provide an impermeable mass transport barrier.

- ◆ Common polymer coatings are
  - Polyurethane: resistant to seawater
  - PTFE (Teflon): resistant to virtually all chemicals, but prone to microporosity and detaching
- ◆ Glass-lined vessels are commonly used in the chemical industries to protect carbon steel vessels from corrosive contents.

### Metallic coatings

Zinc is commonly applied to steel components and has two benefits.

- The zinc coating typically corrodes (by active dissolution) more slowly than the bare steel would in the same environment.
- If the coating is scratched or compromised, the resulting bimetallic corrosion protects the underlying steel.
- ◆ Chromium, nickel, and tin coating are also commonly applied to metals.
  - They are generally passive, but offer no cathodic protection to steel.

## 5.6 Other corrosion control methods

### Robust design

- ◆ Thicker walls allow for wastage
- ◆ Minimise erosion corrosion by filtering entrained solids and fines.

### Environmental modification

- ◆ Drainage to remove standing water and stop electrochemical corrosion.
- ◆ Temperatures can be lowered (slowing chemical corrosion reactions).
- ◆ pH can be modified by additive (water hardening) – pH modification is similar to **corrosion inhibition**.
- ◆ Dissolved oxygen can be depleted.
  - By boiling, nitrogen bubbling,
  - ... or chemical scavengers
- ◆ Dehumidifiers and dessicants
  - E.g. surprisingly slow corrosion within salt mines!

### Regular inspection and maintenance

- ◆ Visual inspection
- ◆ Ultrasonic thickness checks and flaw detection
- ◆ X-ray measurement (thickness, flaws)
- ◆ Electrical monitoring (as part of an ICCP system)

## 6. High temperature oxidation of metals

There are many high temperature environments experienced by, for example, turbine blades, combustion manifolds, filament lamps, and heat exchangers, where the electrochemical corrosion considered in the main part of this course is not relevant. In “dry corrosion” it is hot gases such as  $O_2$ ,  $H_2S$ , and  $SO_2$  which cause the metals to deteriorate by oxidation.

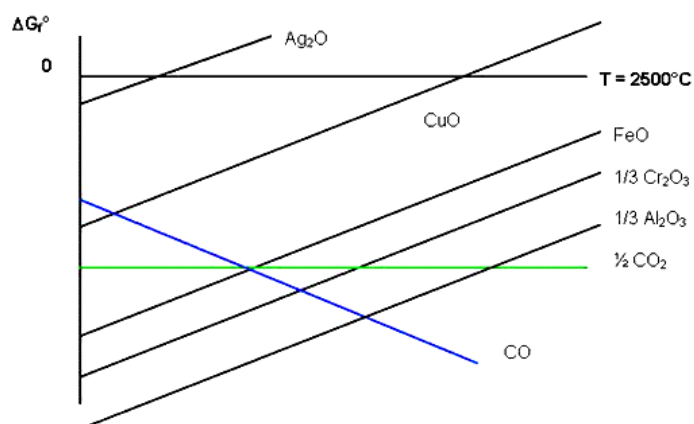
In high temperature applications there might also be deterioration of materials by **creep**, and loss of the metal (or the oxide) by evaporation (!) or melting.

We shall consider oxidation by  $O_2$ . The same models may be used for high temperature oxidation under other gases.

### 6.1 Thermodynamics of high temperature oxidation

The chemical thermodynamics of high-temperature oxidation are based on calculating Gibbs energy change.

- The thermodynamics are very simple under hot air environments because the reaction of Metal + Oxygen  $\rightarrow$  Metal Oxide is thermodynamically favourable for virtually all metals. The few exceptions include gold; silver at  $T > 100^\circ\text{C}$ ; mercury at  $T > 500^\circ\text{C}$ , and cadmium at  $T > 900^\circ\text{C}$ .
- An Ellingham diagram plots Gibbs energy of oxidation, normalised per mole of oxygen. This shows: (a) that most metals will be spontaneously oxidised by atmospheric oxygen at any temperature, and (b) what temperature the metal can be reduced by reduction by CO.



- Knowing that most metals will form an oxide on their surface, the main question in high temperature oxidation is the speed of corrosion.

## 6.2 Model of high temperature oxidation rate

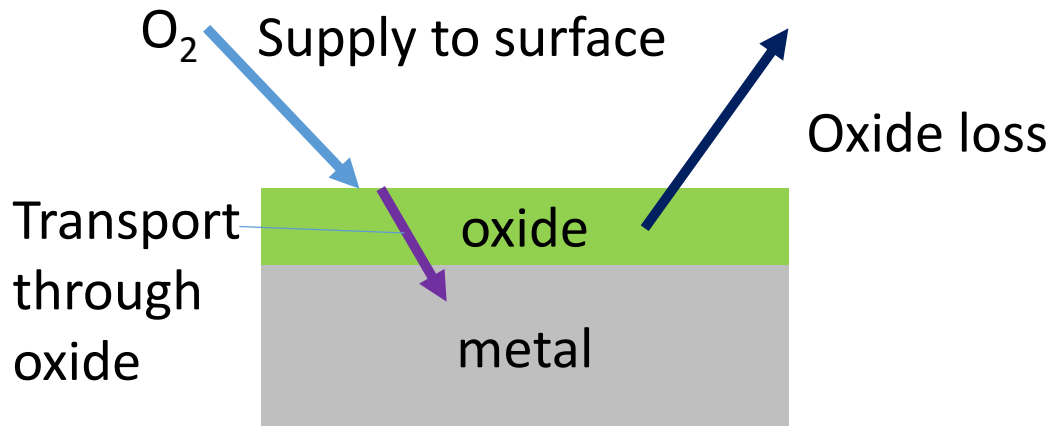


Figure. Three possible limiting steps in high temperature oxidation.

There are four types of behaviour that a metal might undergo during high temperature oxidation. They are categorised by the change of mass of the metal specimen over time.

- ◆ Linear mass loss
- ◆ Linear oxide growth
- ◆ Parabolic oxide growth
- ◆ Logarithmic oxide growth

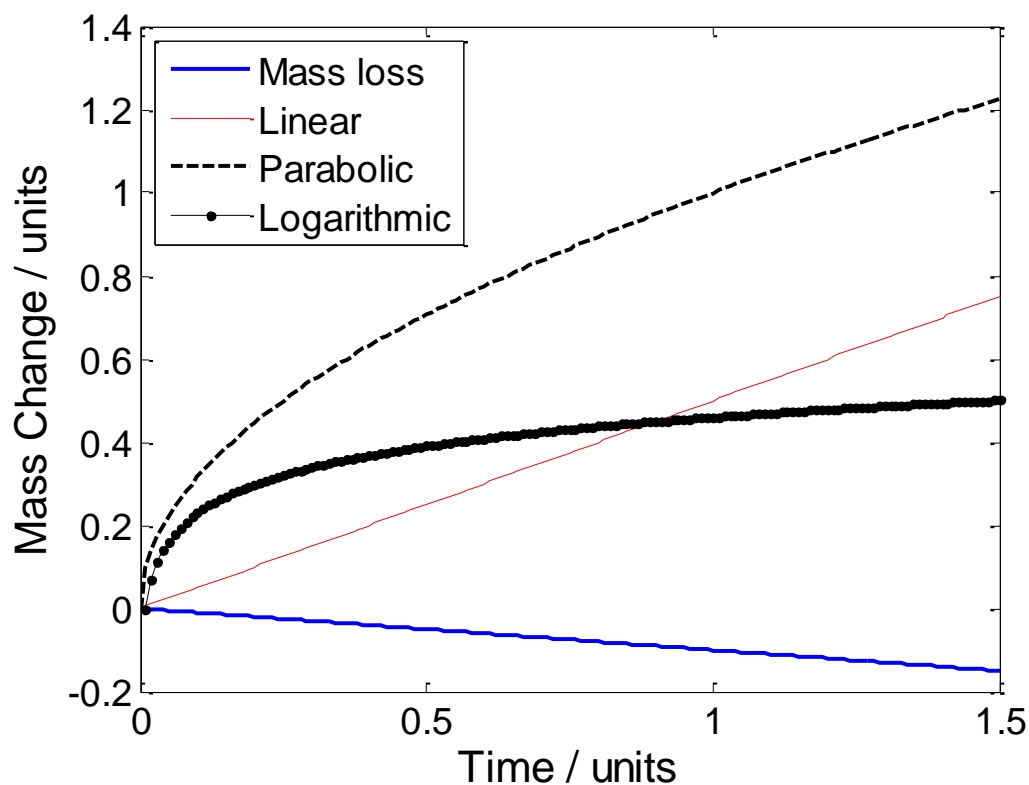


Figure. Mass change measurements of metal samples experiencing high temperature corrosion.

### 6.3 Linear Mass loss

This happens if the oxidised metal has a high enough vapour pressure to boil.

- ♦ The oxide evaporates immediately and provides no protection from further corrosion. So mass loss is continuous.
  - It is typically a constant rate process.
- ♦ Tungsten filament lamps suffer from this corrosion mechanism due to trace oxygen in the bulb, because  $\text{WO}_3$  boils at  $1700^\circ\text{C}$ .
- ♦ Other examples:  $\text{Cr}_2\text{O}_3$  vaporises at  $>1200^\circ\text{C}$ .

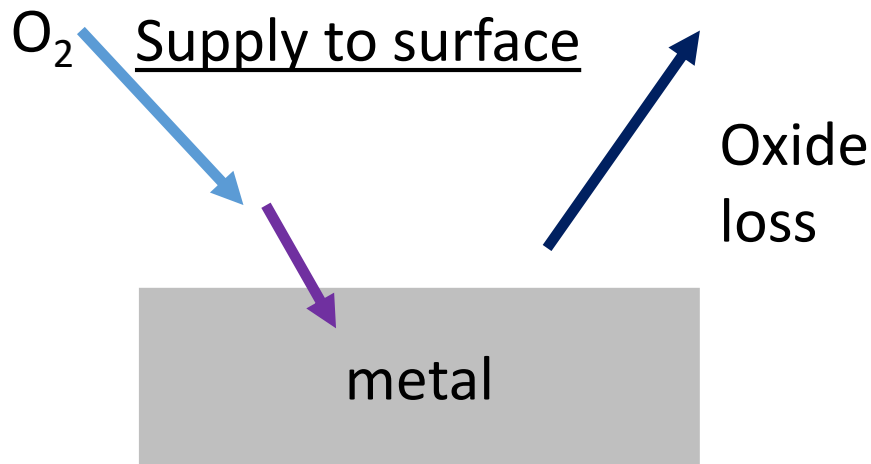


Figure. Linear mass loss.

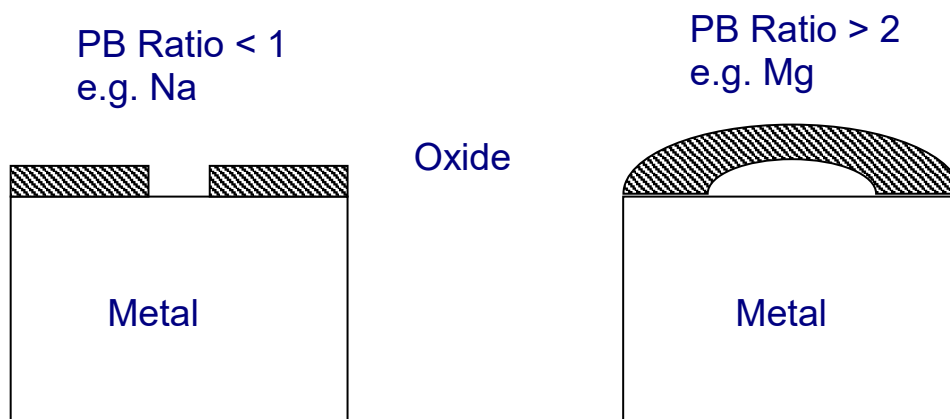
### 6.4 Linear oxide growth

Occurs with non-protective oxides that detach from the metal.

Example:  $\text{Mg} > 450^\circ\text{C}$ ,  $\text{Ta}$  at  $>500^\circ\text{C}$ .

A key parameter for determining whether an oxide is non-protective is the “Pilling-Bedworth ratio” – this is the relative volume occupied by the oxide compared to the pure metal.

- ♦ If the Pilling-Bedworth ratio is less than one, then the oxide layer will not cover the metal surface completely.
- ♦ Alternatively, if the Pilling-Bedworth ratio is large (say  $>2$ ), then the oxide layer will contain cracks due to volume strain.



## 6.5 Parabolic oxide growth

This is a common category for high temperature oxidation.

An oxide film completely covers the metal, and slows down the rate of reaction by limiting the supply of oxygen to the metal by diffusion through the oxide film. The oxide film has mass  $m$  and a thickness proportional to  $m$ , so:

$$\frac{dm}{dt} = \frac{\text{constant}}{m} \quad (6.1)$$

Implying  $(\Delta m)^2 = kt$  (6.2)

For some constant  $k$  after time  $t$ .

- Examples: Fe > 200°C, Ni > 500°C, Cu > 500°C.

**Mechanism:**

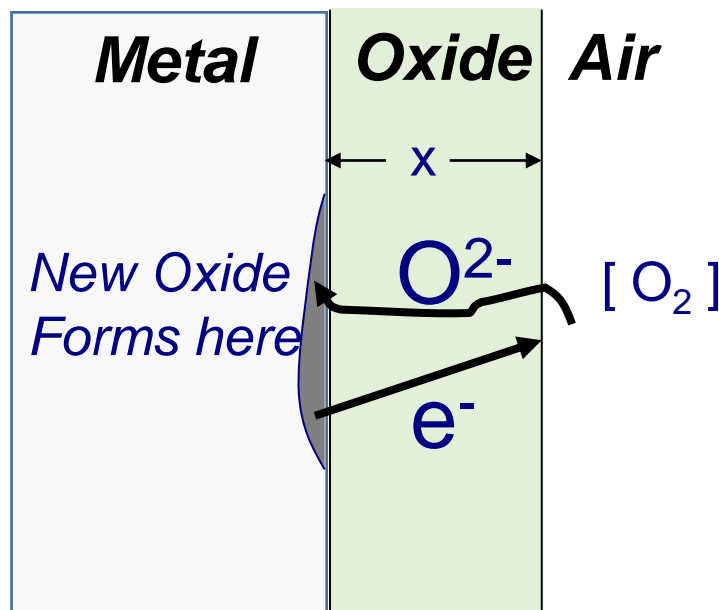


Figure. Diffusion limited growth of oxide film, limited by oxygen ion diffusion.

The rate of oxide growth due to oxygen diffusion through a surface oxide layer of thickness  $x$  with diffusion coefficient  $D$  is given by

$$\frac{dx}{dt} = \alpha D \frac{c(O_2)}{x} \quad (6.3)$$

Hence the oxide growth is “parabolic” because  $(\Delta x)^2 = k t$

### Slowing down parabolic oxide growth

- Decrease partial pressure of oxygen
- Lower temperature decreases the diffusion coefficient  $D$ .
- Alloy composition can hugely alter the diffusion coefficient  $D$ , by:
  - Preventing vacancies in a solid oxide lattice decreases  $D$ .
  - High chromium alloys form a  $\text{Cr}_2\text{O}_3$  oxide surface with a much low value of  $D$  than many other metals used at high temperature (such as nickel alloys).

## 6.6 Logarithmic oxide growth

This tends to describe oxide growth under air at lower temperatures.

- If ion mobility is too low for ions to cross the oxide film, then electron transport may be needed in order for the film to grow.
- Electron transport across an insulating oxide can be modelled as an exponential decay in current with oxide thickness.

So for oxide thickness  $x$ :

$$\frac{dx}{dt} = \alpha e^{-x} \quad (6.4)$$

Hence for some constant  $C$

$$x = C \ln(\alpha t) \quad (6.5)$$

- A thin oxide provides excellent protection from further corrosion.
- Examples: Fe<200°C, Ni<300°C. (E.g. coins under dry air.)

## Glossary of symbols for electrochemistry

Symbol	Description	Units	Section
$i$	Current density	A m <sup>-2</sup>	3.2
$i_0$	Exchange current density	A m <sup>-2</sup>	3.4
$z$	Electrons per reaction	-	2.6
$A$	Area	m <sup>2</sup>	-
$E$	Potential	V <sub>SHE</sub>	3.3
$E^\circ$	Standard electrode potential	V <sub>SHE</sub>	2.7
$E_0$	Equilibrium potential	V <sub>SHE</sub>	2.10
$F$	Faraday constant	C mol <sup>-1</sup>	-
$I$	Current	A	3.2
$R$	Universal gas constant	J mol <sup>-1</sup> K <sup>-1</sup>	-
$T$	Temperature	K	-
$\beta$	Tafel slope	V	3.5
$\eta$	Polarisation	V	3.3