TALAT Lecture 1252

Corrosion and Corrosion Protection

17 pages, 15 Figures

Advanced level

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Objectives:

Outline of the metallurgical principles of corrosion and corrosion protection of aluminium alloys.

Prerequisites:

Basic knowledge of physics and chemistry. Familiarity with the contents of TALAT lectures 1201 through 1205.

Date of Issue: 1999

1252 Corrosion and Corrosion Protection

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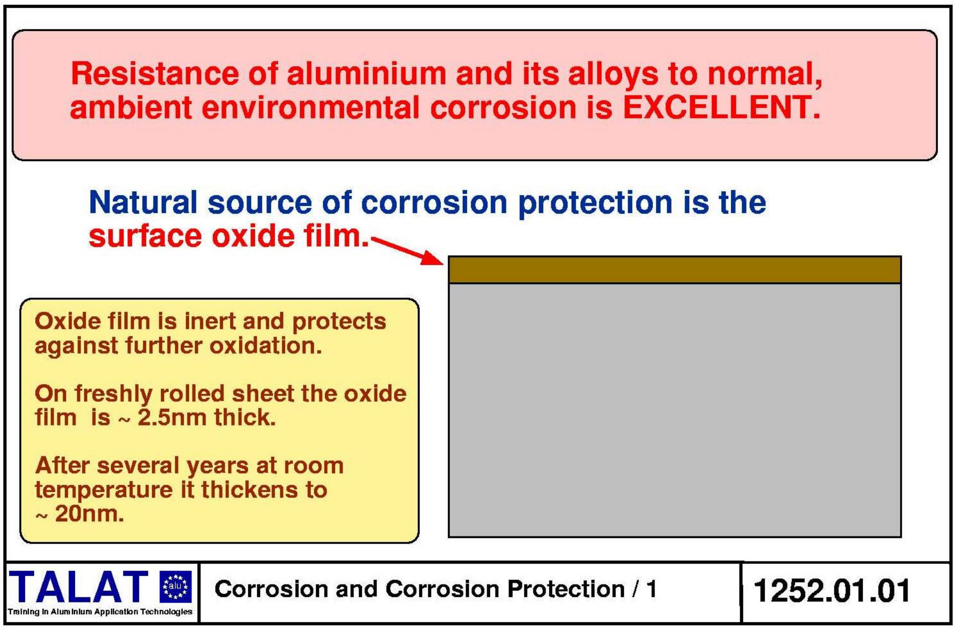
1252.01 Corrosion of Aluminium

1252.01.01 Introduction

The first point to emphasise is that the resistance of aluminium and aluminium alloys to normal, ambient environmental corrosion is excellent. Its natural corrosion resistance is one reason why aluminium alloys find such diverse applications, from beverage cans, via architectural uses to aircraft construction. The chief source of the protection to corrosion, **Figure 1252.01.01**, comes from the adherent, self-healing oxide film which is always present in an ambient air atmosphere.



Resistance of aluminium and its alloys to normal, ambient environmental corrosion is EXCELLENT.

Natural source of corrosion protection is the surface oxide film.

Oxide film is inert and protects against further oxidation.

On freshly rolled sheet the oxide film is ~ 2.5nm thick.

After several years at room temperature it thickens to ~ 20nm.

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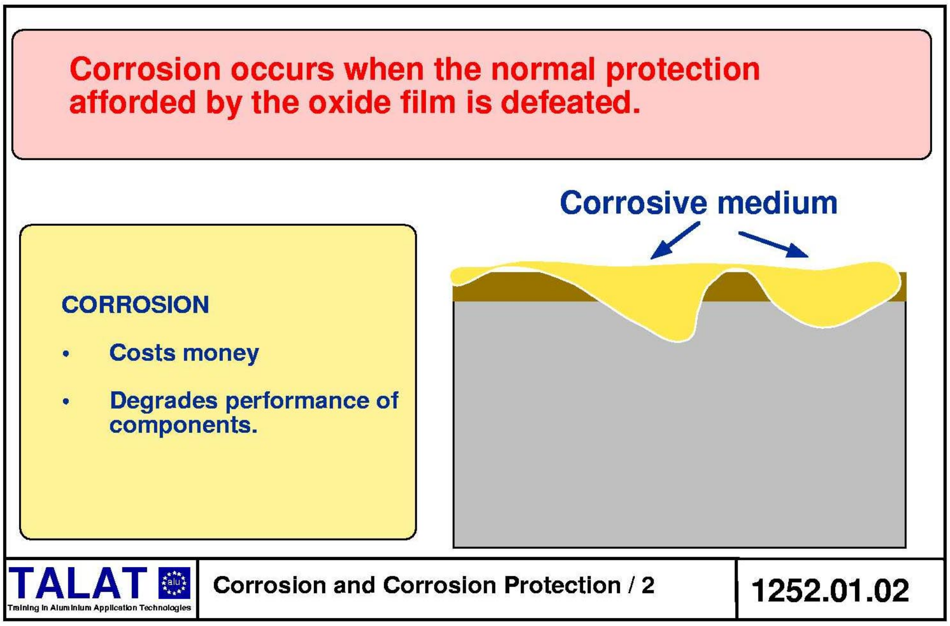
Although aluminium is reactive, the oxide film that forms on it is inert and protects it from further oxidation. The oxide film is about 2.5nm thick on fresh rolled sheet and it builds up over several years to some 10-20nm (1nm = 10^{-9} m) in thickness.

It is only when the normal protection afforded by oxide film is defeated, **Figure 1252.01.02** , that corrosion, in its various forms, will occur.

There are two important points to remember about corrosion:

1. It can cost money
2. Component may no longer be able to perform.



Corrosion occurs when the normal protection afforded by the oxide film is defeated.

CORRODION

- Costs money
- Degrades performance of components.

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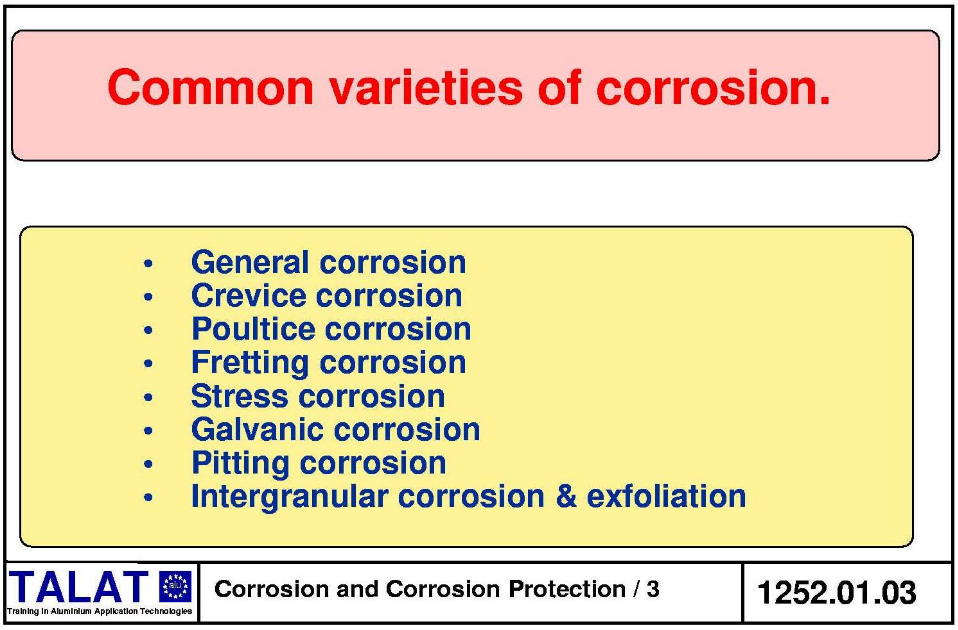
Consequently, it is important to understand the circumstances under which corrosion may occur and also how such corrosion may be prevented.

1252.01.02 Corrosion Types

There are many types of corrosion [1]. Common varieties (**Figure 1252.01.03**) which may be met in an industrial and/or component service situations are:

(a) General corrosion
(b) Crevice corrosion
(c) Poultice corrosion
(d) Fretting corrosion
(e) Stress corrosion
(f) Galvanic corrosion
(g) Pitting corrosion
(h) Intergranular corrosion and exfoliation



Common varieties of corrosion.

- General corrosion
- Crevice corrosion
- Poultice corrosion
- Fretting corrosion
- Stress corrosion
- Galvanic corrosion
- Pitting corrosion
- Intergranular corrosion & exfoliation

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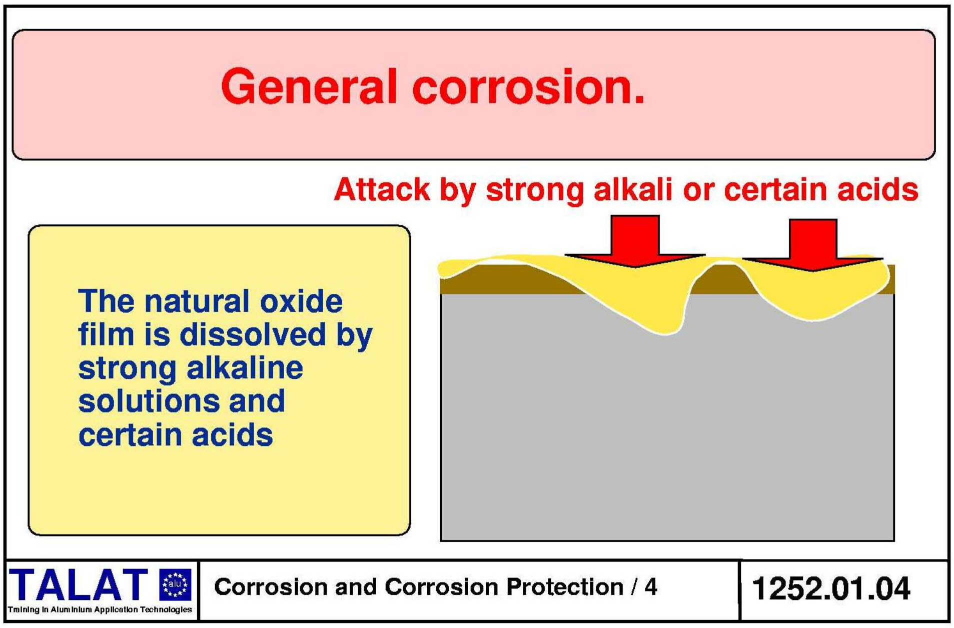
(a) General corrosion

(**Figure 1252.01.04**)



General corrosion.

Attack by strong alkali or certain acids

The natural oxide film is dissolved by strong alkaline solutions and certain acids

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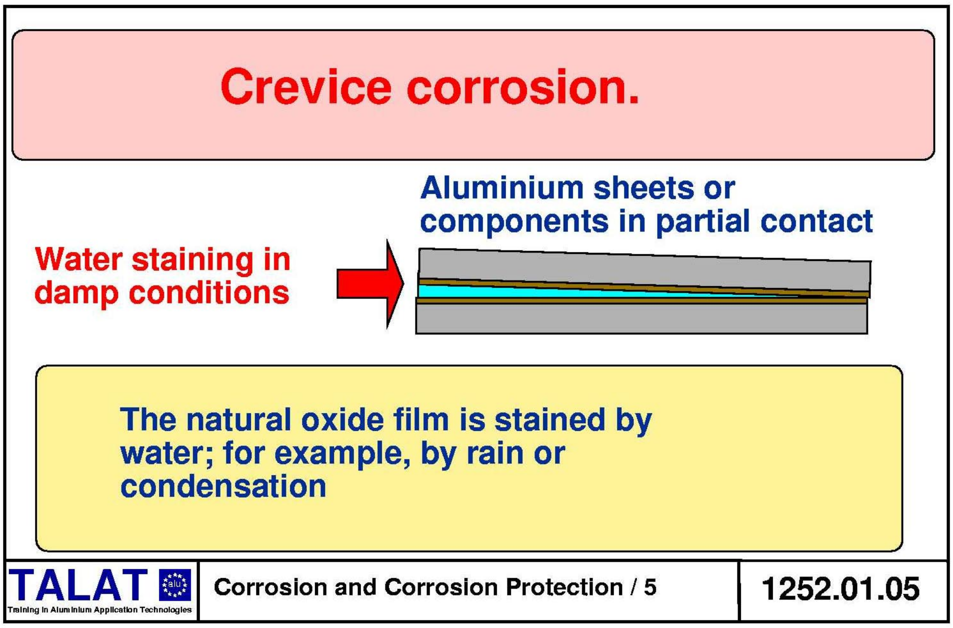
The natural oxide film on aluminium dissolves in strong alkaline and certain strong acid solutions. For example, severe attack occurs in concentrated sodium hydroxide (caustic soda) solution and in dilute nitric acid - for a comprehensive list, see reference [3].

(b) Crevice corrosion

(**Figure 1252.01.05**)



Crevice corrosion.

Aluminium sheets or components in partial contact

Water staining in damp conditions

The natural oxide film is stained by water; for example, by rain or condensation

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This is often known as water staining. There are two main conditions which will induce crevice corrosion:

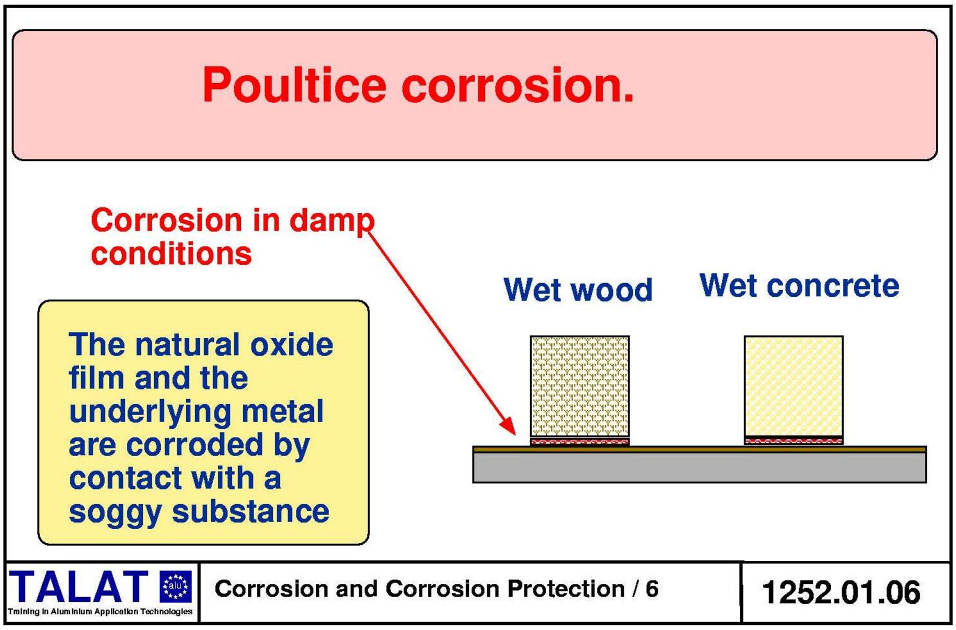
> **firstly**, metal sheet and sheet components stacked in packs form the crevices in which corrosion will occur;
> **secondly**, the active ingredient of moisture is required, from rain or condensation.

Clearly, rain damage can happen as a result of a number of circumstances- for example, in the mill, during transport, during service.

Water staining is superficial corrosion [2] and is rarely harmful to the metal itself. It can usually be removed by rubbing with a cloth or, in severe cases, with the aid of abrasion.

(c) Poultice corrosion

(**Figure 1252.01.06**)



Poultice corrosion.

Corrosion in damp conditions

The natural oxide film and the underlying metal are corroded by contact with a soggy substance

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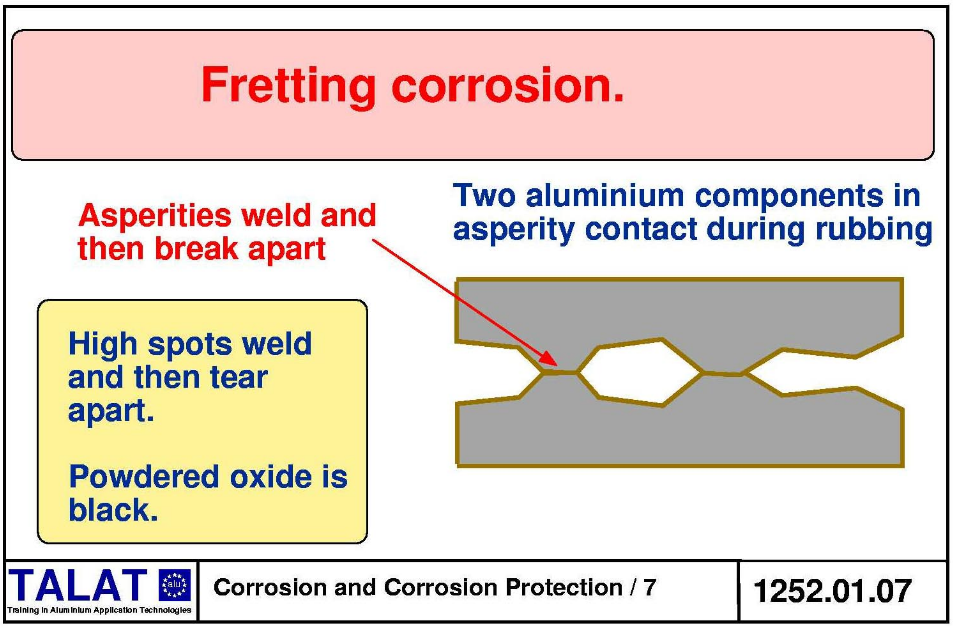
This is caused by contact with a wet soggy substance. The substance may have chemicals in it which may accelerate the attack. Usually this is a customer problem due to either bad design or maintenance.

(d) Fretting corrosion (also called traffic marking)

(**Figure 1252.01.07**)



Fretting corrosion.

Asperities weld and then break apart

Two aluminium components in asperity contact during rubbing

High spots weld and then tear apart.

Powdered oxide is black.

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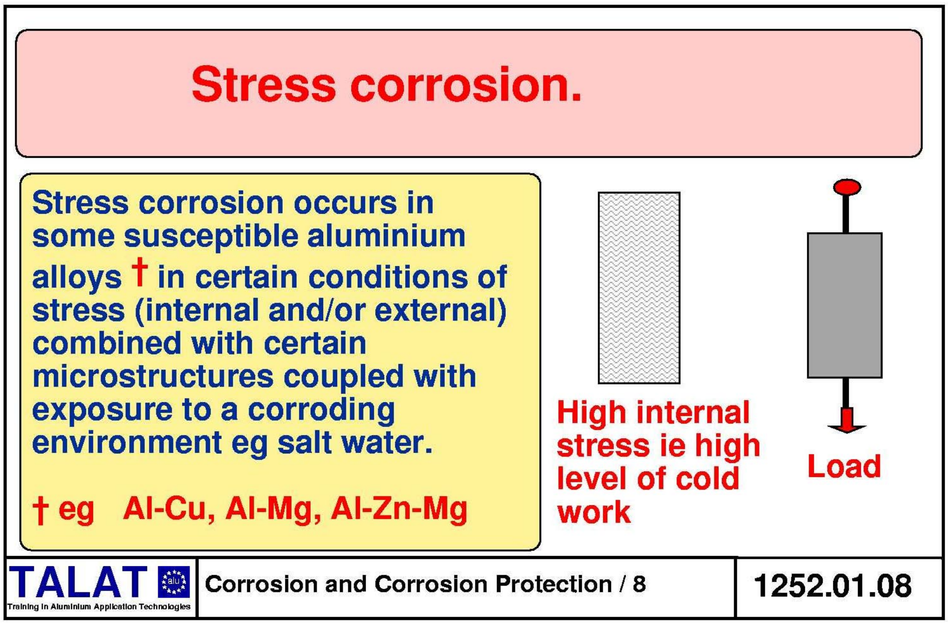
Fretting corrosion manifests itself as black spots on the metal surface underneath which can be deep pits.

Fretting corrosion is caused by the rubbing together of two aluminium components. High spots weld together and are then torn apart. The aluminium oxide is a fine powdered form which appears black.

(e) Stress corrosion

(**Figure 1252.01.08**)



Stress corrosion.

Stress corrosion occurs in some susceptible aluminium alloys † in certain conditions of stress (internal and/or external) combined with certain microstructures coupled with exposure to a corroding environment eg salt water.

† eg Al-Cu, Al-Mg, Al-Zn-Mg

High internal stress ie high level of cold work

Load

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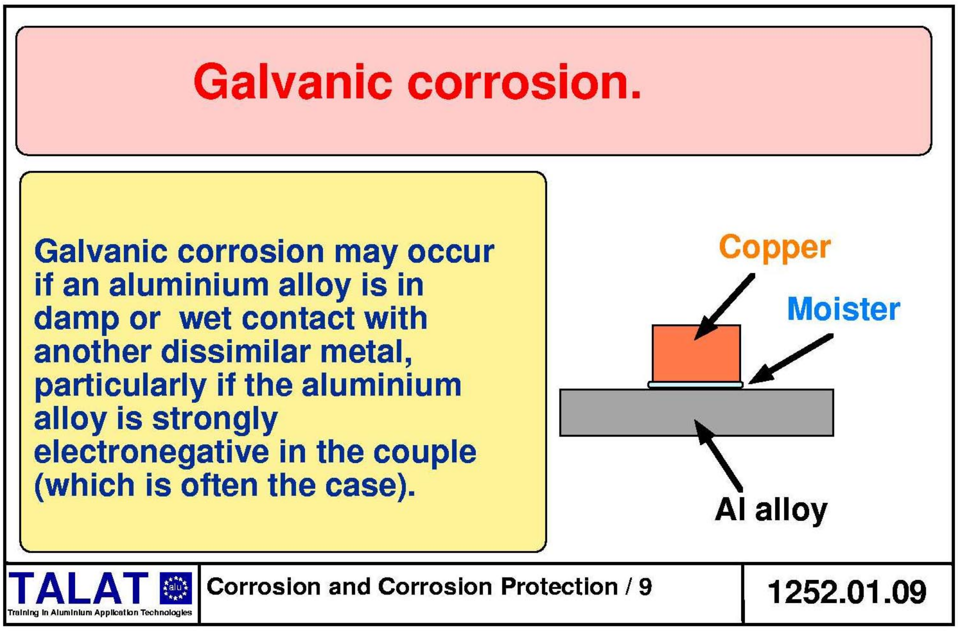
There are three conditions which are essential to cause stress corrosion cracking:

- stress
- a susceptible alloy structure
- a suitable environment

The absence of any of these will stop stress corrosion cracking.

(f) Galvanic Corrosion

(**Figure 1252.01.09**)



Galvanic corrosion.

Galvanic corrosion may occur if an aluminium alloy is in damp or wet contact with another dissimilar metal, particularly if the aluminium alloy is strongly electronegative in the couple (which is often the case).

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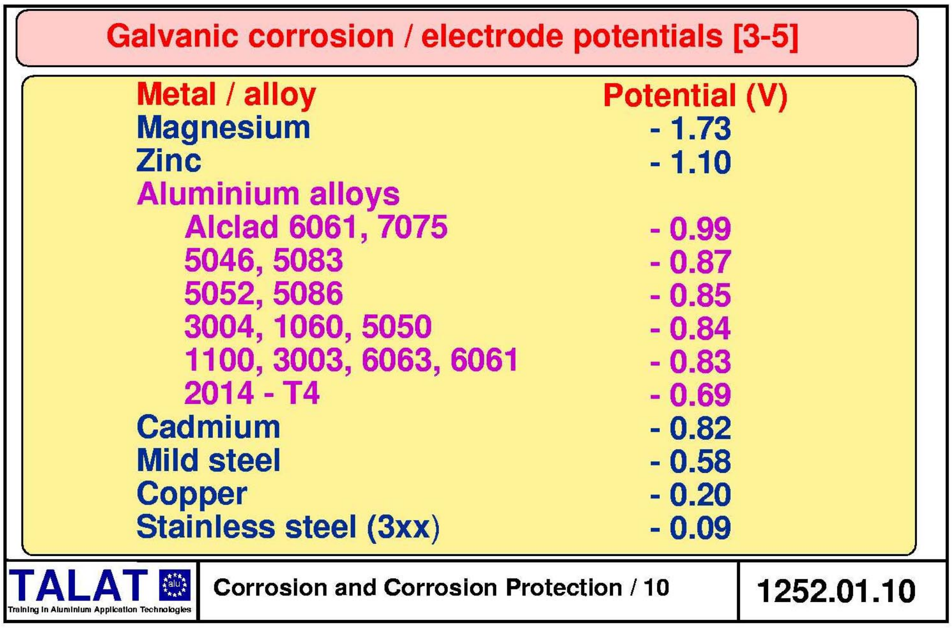
If an aluminium alloy is in contact with another metal in the presence of moisture then electrolytic corrosion may occur.

For example, aluminium in wet contact with copper leads to rapid corrosion.

Aluminium and its alloys are electronegative to many other engineering metallic alloys, as may be seen from the electrode potential series, **Figure 1252.01.10** [3-5] - see also **section 1252.02.01**, below. This rates their thermodynamic reactivities according to the electrode voltage measured with respect to the 0.1 calomel electrode ($Hg\text{-}HgCl_2$, 0.1 M KCl) for a selection of metals and alloys immersed in an aqueous solution of 1 M NaCl and 0.1 M H_2O_2.



Galvanic corrosion / electrode potentials [3-5]

Metal / alloy	Potential (V)
Magnesium	- 1.73
Zinc	- 1.10
Aluminium alloys	
Alclad 6061, 7075	- 0.99
5046, 5083	- 0.87
5052, 5086	- 0.85
3004, 1060, 5050	- 0.84
1100, 3003, 6063, 6061	- 0.83
2014 - T4	- 0.69
Cadmium	- 0.82
Mild steel	- 0.58
Copper	- 0.20
Stainless steel (3xx)	- 0.09

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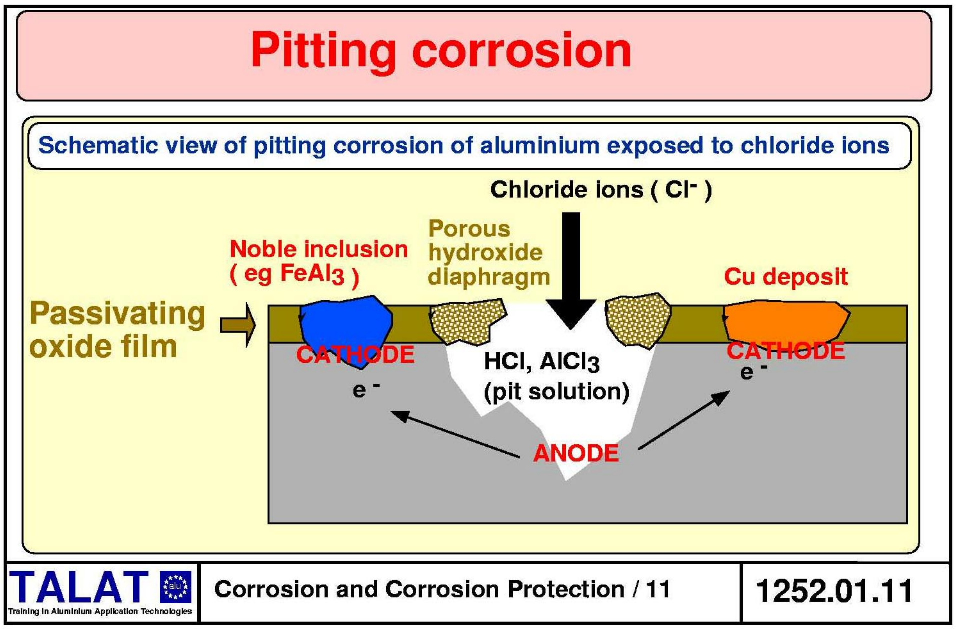
The difference in electrode potential, although important, is not the only criterion that determines the severity of corrosion. Equally important may be the electrical resistance and polarisation of the galvanic circuit ie the type of electrolytic liquid and the type of oxide film that is formed. For example [4], galvanic corrosion between aluminium and stainless steel normally gives less corrosion than might be expected from the large difference in electrode potential, whereas corrosion between aluminium and copper is very severe in spite of the smaller difference in electrode potential. This is because of the tenacious passive film on the stainless steel , which adds considerable resistance to the galvanic circuit for the aluminium / stainless steel couple.

(g) Pitting Corrosion

(**Figure 1252.01.11**)



Pitting corrosion

Schematic view of pitting corrosion of aluminium exposed to chloride ions

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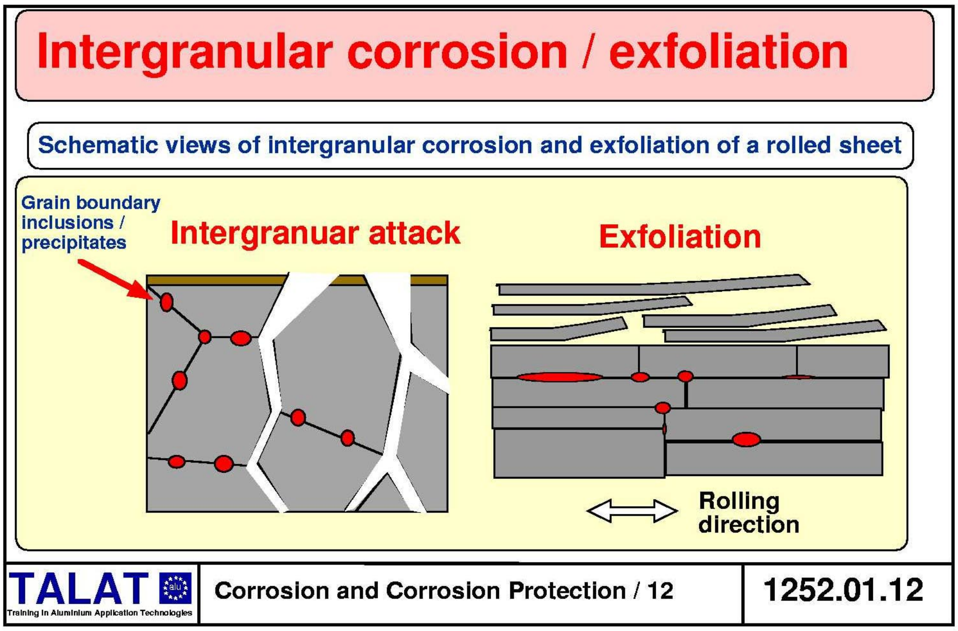
Pitting is localised galvanic corrosion and is caused by the occurrence in the base alloy of inclusions, or regions of different composition, with an electrochemical potential different from that of the matrix.

The pitting current leads to the formation of a semi-permeable hydroxide cap sealing the pit, permitting the acidic chloride solution within to concentrate. The corrosion potential is reinforced by oxygen depletion inside the pit and galvanic couples between the aluminium anode and inclusions and displaced deposits (eg Cu) which act as cathodes. The surrounding natural oxide film is cathodically protected (alkali passivation).

(h) Intergranular corrosion and exfoliation

(**Figure 1252.01.12**).



Intergranular corrosion / exfoliation

Schematic views of intergranular corrosion and exfoliation of a rolled sheet

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Normally an aluminium solid solution is reasonably resistant to general corrosion, protected as it is by its oxide film.

Heterogeneities in composition often provide the microstructural basis for localised corrosion. Large precipitate particles and dispersed impurity particles can give rise to pitting corrosion.

If the particles decorate grain boundaries, then localised attack is manifested as intergranular corrosion, with penetration by many grain diameters.

With rolled plate. the grains are elongated along the rolling direction. Severe intergranular corrosion can lead to ‘ exfoliation’ of material from the surface of the sheet.

1252.02 Electrochemistry and Aluminium

1252.02.01 Introduction

As it was emphasised above, aluminium has a strong affinity for oxygen. Its oxide has a high heat of formation. As a consequence, it was a late metal to be exploited (see TALAT **lecture 1201**) and it has a strong tendency to react electrochemically. The common ore, bauxite, is an oxide, Al_20_3, but the compounds of aluminium also contain the element in a chemically oxidised state (the Al^{3+} ion) and are correspondingly stable compared with the metal.

The relative tendencies for metals to form their ions, under chemically standard conditions, is presented in the ***Electromotive Series***, see **Figure 1252.01.10**. This rates their thermodynamic reactivities according to the electrode voltage measured with respect to the 0.1 calomel electrode ($Hg-HgCl_2$, 0.1 M KCl) for a selection of metals and alloys immersed in an aqueous solution of 1 M NaCl and 0.1 M H_2O_2. The value for pure aluminium is -0.85, whereas aluminium alloys cover a range from ~ - 0.69 to ~ -0.99 [3-5].

We note from TALAT **lecture 1201** and **Figure 1201.02.04** that aluminium atoms have three valence electrons; hence,

$$Al \rightarrow Al^{3+} + 3e^-$$

where e^- represents a negatively charged electron.

The electromotive series may also be viewed as "***standard electrode potentials***", given with reference to the reactivity of hydrogen, i.e.

$$H_2 \rightarrow 2H^+ + 2e^-$$

Metals which tend to form cations (m^{n+}) more strongly than does hydrogen are called "base", in contrast with the more stable metals, e.g. gold, copper and silver, which are "noble". Base metals, including aluminium, tend to displace hydrogen from water spontaneously, i.e.

$$2Al + 3H_20 \rightarrow Al_20_3 + 3H_2$$

Aluminium is more base than iron or zinc; it is less base, i.e. more stable, than magnesium. It will be appreciated that when aluminium is alloyed and phases are produced with different elemental compositions these may be more or less active than pure aluminium; the alloy will then be electrochemically inhomogeneous. Furthermore, for different chemical environments, the relative positions of metals in the electromotive series may change. Thus aluminium is more active in strong alkali than in acid.

1252.02.02 Kinetic Reactivity

In reality the thermodynamic reactivity of a metal is often not manifest. This is either because the reactions in themselves are sluggish or because the consequences of reaction impedes its progress. For aluminium, principal products of reaction are insoluble oxide and hydroxide. These form on the aluminium surface and constitute an effective barrier against the continuing consumption of metal. Such products will be stable under predictable chemical and electrochemical conditions.

1252.02.03 The Electrochemical Circuit

If the reaction $Al \rightarrow Al^{3+} + 3e^{-}$ is allowed to commence, aluminium ions escape from the metal, which retains the electrons and so becomes negatively charged. For the reaction to continue this charge must find a "sink" and the Al^{3+} ions also must leave the vicinity of the metal. Because we are dealing with an electrochemical process , the aluminium is called an "***electrode***"; as it is oxidised, this electrode is an "***anode***", i.e.

$Al \rightarrow Al^{3+} + 3e^{-}$ is an "***anodic process***".

The sink for the electron charge release is an equivalent electrochemical reduction, or "***cathodic***" electrode process, e.g.

$$2H^{+} + 2e^{-} \rightarrow H_2$$

or $$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-}.$$

In practice much cathodic reaction may become established on parts of a single piece of aluminium or alloy which also supports anodic reaction elsewhere. This is ***local cell*** action. Sometimes a base metal like aluminium may be in electrical contact with a less base metal, in an electrochemically active liquid environment ("***electrolyte***"). Then the base metal, aluminium, will corrode and the less base metal will support a cathodic reaction. This constitutes a ***galvanic cell***.

The necessary components of a cell are, (1) an anode, (2) a cathode, (3) electrical conduction (electronic and ionic).

1252.02.04 Aluminium as a Cathode

An important example of aluminium as a cathode is in the electrolytic extraction of the metal, **Figure 1252.02.01**. Alumina (bauxite) is melted with cryolite (Na_3AlF_6) to form a molten electrolyte. This is electrolysed with carbon anodes at which oxygen is evolved:

In cryolite, the reaction is

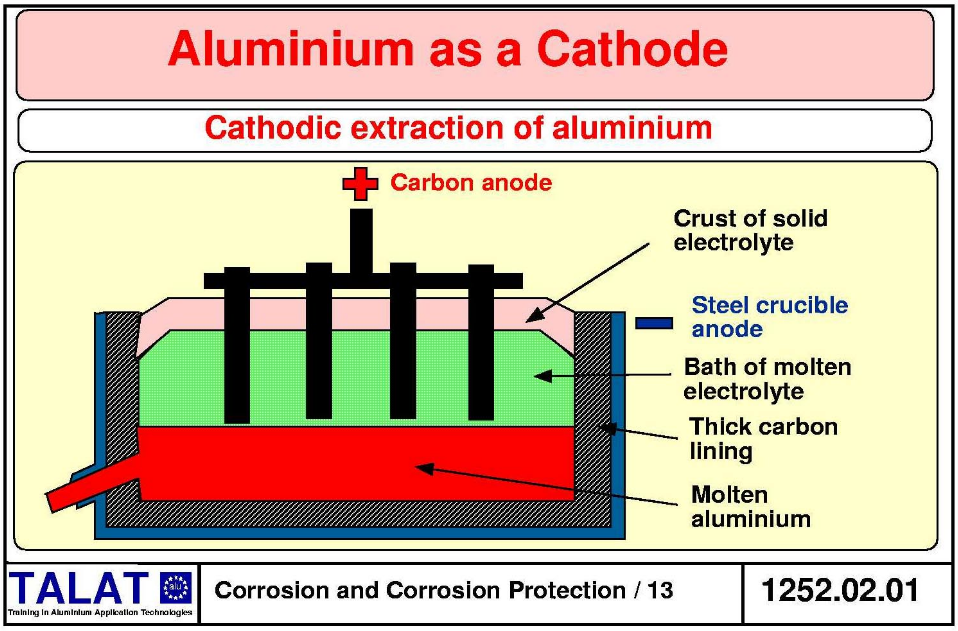
$$Al_2O_3 \rightarrow 2Al^{3+} + 3O^{2-}$$

The corresponding cathodic process is

$$Al^{3+} + 3e^{-} \rightarrow Al$$

The anodic process is

$$2O^{2-} \rightarrow O_2 + 4e^{-}$$



Aluminium as a Cathode

Cathodic extraction of aluminium

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1252.02.05 Aluminium as an Anode

The anodic behaviour of aluminium is dominated by the presence of a solid, oxide product on its surface. This oxide limits the corrosion and often determines its kind.

When a freshly formed aluminium surface is exposed to the atmosphere it is immediately covered with a thin film of oxide which reforms when local damage occurs. The initial film is amorphous with a variable degree of hydration. Repair involves local cell action, the oxidised surface supporting cathodic processes whilst at the anodic site of damage fresh oxide or hydroxide is produced.

Special treatments to increase the thickness and protective characteristics of the surface oxide film may be carried out - see **Anodising** and **Chemical Conversion Coatings** below.

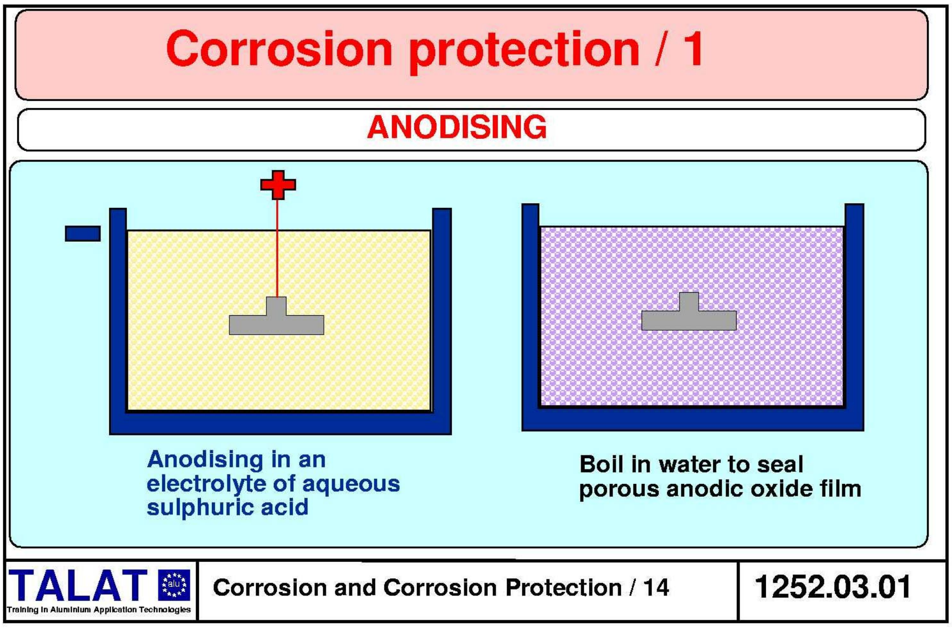
1252.02.06 Summary of Electrolytic Corrosion

Electrolytic corrosion involves the basic cell requirements: anode, cathode, electronic and ionic conduction. The crucial factor is often the spatial distribution of the electrodes. On metals which are protected by surface films a critical situation is possible when small, fixed anodes are driven by large neighbouring cathodes. Quite minor heterogeneities may be sufficient to localise the anodes. The heterogeneities may be due to composition of the metal, local stress (static or cyclic) etc; they may be due to variations in the electrolyte (e.g. oxygen concentration) or to localised aggressive impurities.

1252.03 Corrosion Protection

1252.03.01 Anodising

(Figure 1252.03.01)



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ANODISING

Anodising in an electrolyte of aqueous sulphuric acid

Boil in water to seal porous anodic oxide film

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In a number of electrolytes, e.g. dilute sulphuric, chromic, oxalic and phosphoric acids, the reaction products on aluminium anodes are sparingly soluble and strongly adherent.

In anodising, the anodic oxide film consists of two layers,

an inner, dense and thin “barrier”, layer
and **an outer porous film** often with a cellular structure.

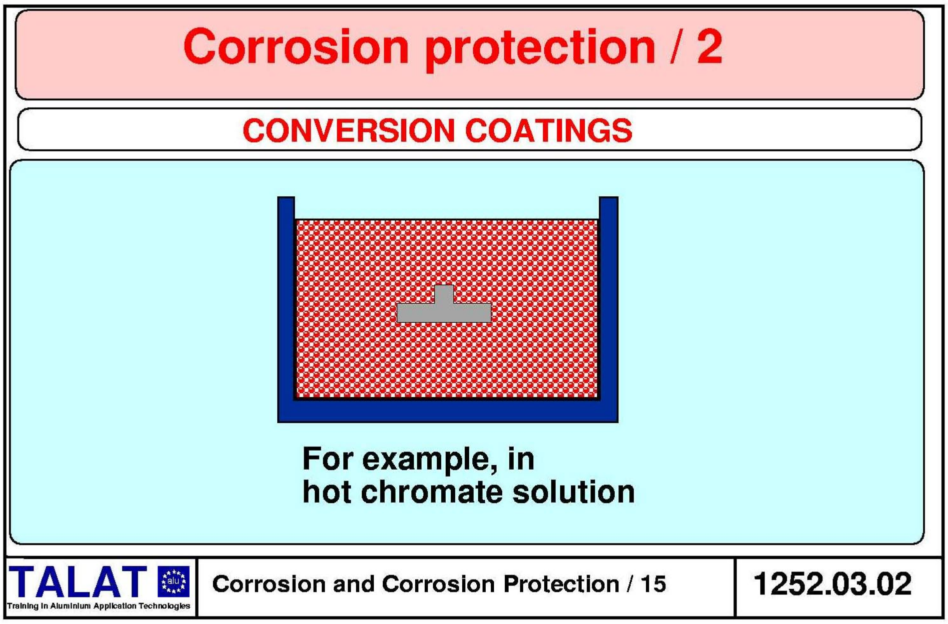
The outer layer is formed by the electrolyte from the inner layer, the dimension of which is determined by the applied anodic voltage. As formed, the outer layer is both hydrous and hydroxylated and largely amorphous. On immersing in boiling deionised water for some 30 minutes it crystallises to the stable mineral boehmite, $Al_2O_3.H_2O$. This is termed “**sealing**”. In practice, various anodising procedures are used to produce specific surface properties. For example, anodising in dilute, cold, acid produces hard, durable surfaces. More concentrated acid gives thicker, more uniform films appropriate for dyeing, before sealing.

1252.03.02 Chemical Conversion Coatings

Oxidation of the aluminium surface can easily be achieved by the use of chemical oxidants without an externally impressed current. Such processes are, however, electrochemical in nature, involving local cell actions. They are known as Chemical Conversion Coatings, **Figure 1252.03.02**. With chromic acid, for example:

Anodic reaction $Al \rightarrow Al^{3+} + 3e^{-} \rightarrow Al_2O_3$ and $AlO.OH$

Cathodic reaction $2CrO_4^{2-} + 10\,H^{+} + 6\,e^{-} \rightarrow Cr_2O_3 + 5\,H_2O$



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CONVERSION COATINGS

For example, in
hot chromate solution

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In this case fluorides are added to the chromic acid to remove the initial Al_2O_3 and allow the local cell action to proceed. With phosphoric acid this anodic product is an aluminium phosphate.

To a large extent conversion coatings are now competitors of anodising, as they provide cost-effective substrates for modern organic finishes.

1252.03.03 Other methods of Protection

Attack by alkalis, even in the form of soap, can be severe. Inhibitors, such as sodium silicate, chromates and dichromates are used [6] as conversion coatings to protect aluminium alloys used in the structure of, for example, washing machines.

Sheet products may be clad, for example with pure aluminium, which reduces susceptibility to corrosion.

1252.04 References

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