

**TALAT Lectures 5103**

**Corrosion Control of Aluminium  
-Forms of Corrosion and Prevention-**

20 pages, 11 figures

Basic Level

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**Objectives:**

- To understand the corrosion principles and to select protection methods
- To be able to use aluminium optimally even in aggressive environments

**Prerequisites:**

- Metallurgy of aluminium
- Electrochemistry

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# 5103 Corrosion Control of Aluminium - Forms of Corrosion and Prevention -

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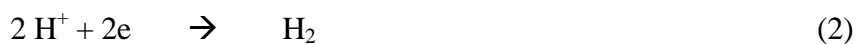
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## 5103.01 General Corrosion

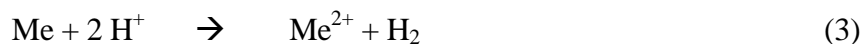
- Corrosion in acid solutions
- Corrosion in neutral solutions
- Passivation
- Corrosion of aluminium and aluminium alloys

### Corrosion in Acid Solutions

Corrosion of a metal (such as Me) occurs in acid solutions due to the simultaneous metal oxidation and proton reduction :



The overall reaction is a spontaneous reaction :

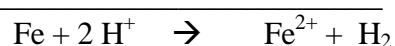


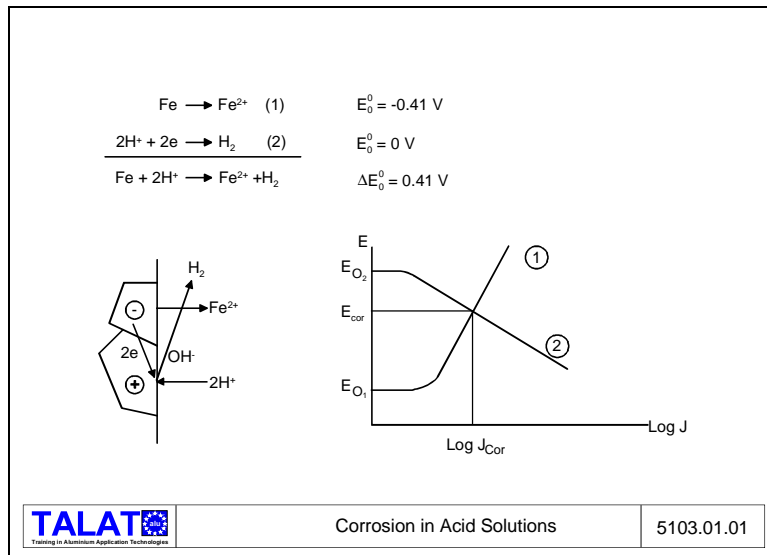
because protons are an oxidizing reagent.

Because electrons are set free by the anodic reaction and absorbed by the cathodic reaction the current flowing into the cathodic reaction must be equal (and opposite in sign) to the current flowing out of the anodic reaction.

In the case of general corrosion the area of the cathodic and anodic sites is the same and thus the current densities are equal.

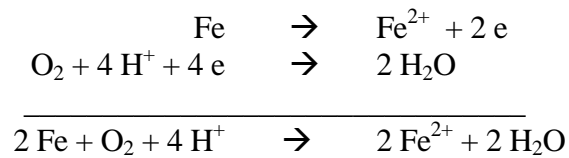
The rate determining step of metal oxidation (e.g. iron) and proton reduction is the charge transfer. The corrosion rate (corrosion current density J) and the corrosion potential can be determined as shown in **Figure 5103.01.01**.



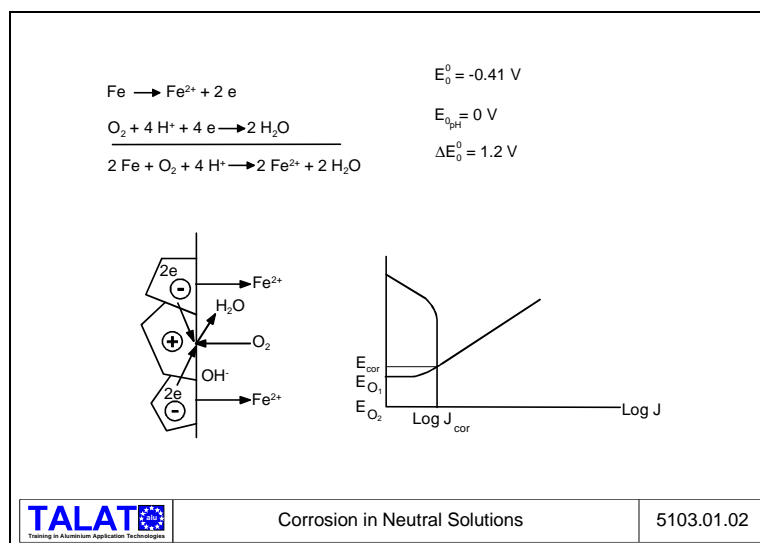


### Corrosion in Neutral Solutions

As protons, oxygen can corrode iron :



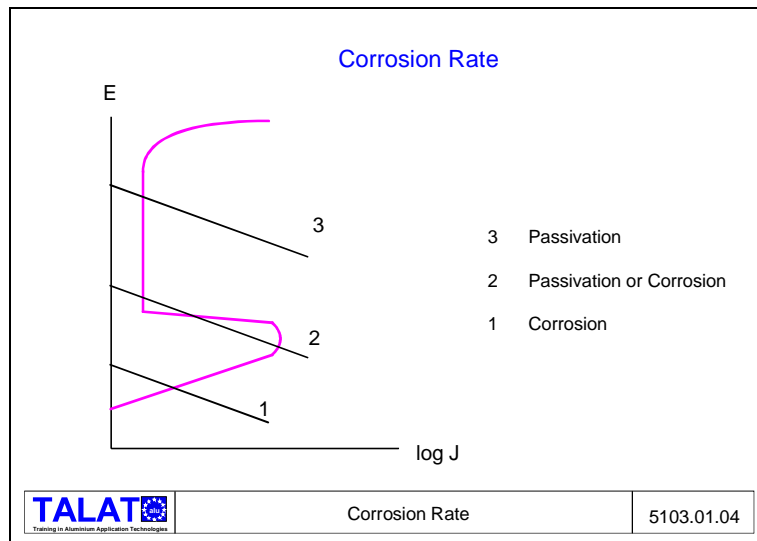
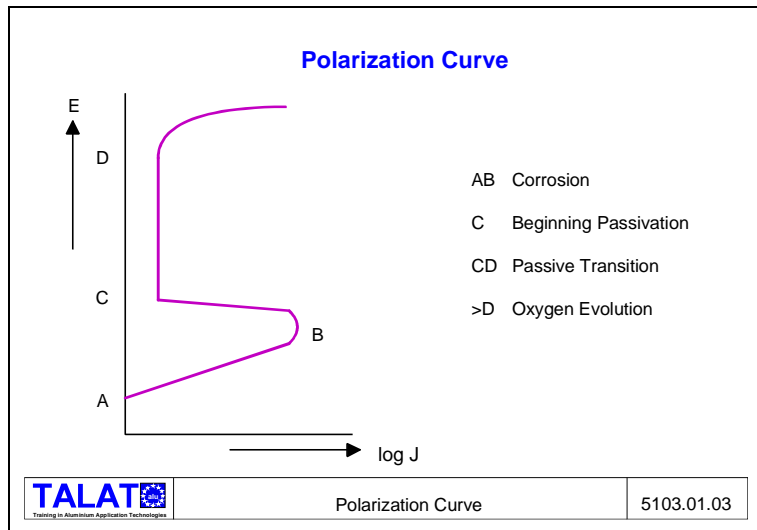
Due to the low oxygen concentration in aqueous solution in equilibrium with the atmosphere the kinetic of oxygen reduction is controlled by mass transport and thus also the corrosion rate (**Figure 5103.01.02**).



## Passivation

A metal can be passivated chemically (spontaneous formation of alumina on aluminium) or electrochemically (metal corrosion products form an insoluble salt or hydroxide at the metal surface). **Figure 5103.01.03** shows a polarization curve of a metal undergoing an active passive transition.

**Figure 5103.01.04** shows the impact of various cathodic reactions on the corrosion current and potential for a metal capable of undergoing an active passive transition.

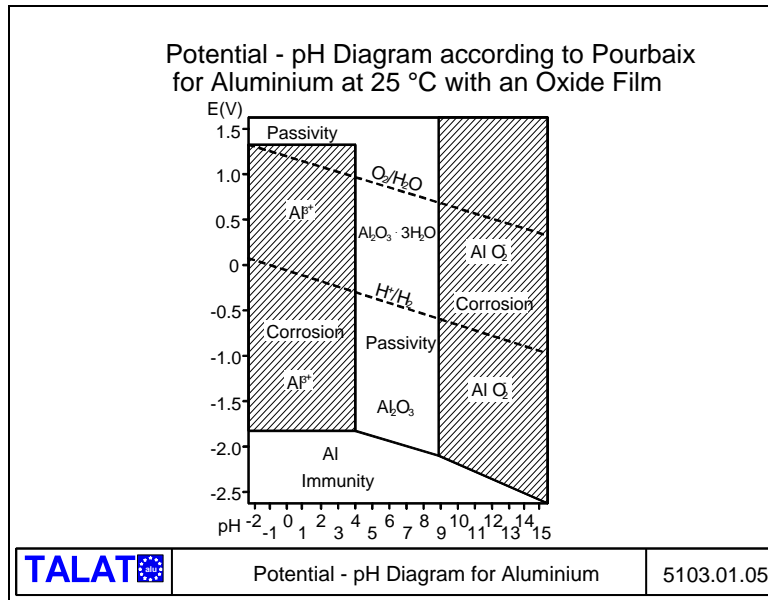


## Corrosion of Aluminium and Aluminium Alloys

Aluminium is a thermodynamically reactive metal but it owes its excellent corrosion resistance to the natural formation of a thin but very stable oxide film (**Figure 5103.01.05**).

In neutral aqueous solutions ( $4 < \text{pH} < 9$ ) a  $50 \text{ \AA}$  thick oxide film protects the metal (passivation). Only in a very acid solution aluminium is homogeneously corroded by forming  $\text{Al}^{3+}$  and in alkaline solution with formation of aluminates ( $\text{AlO}_2^-$ ). The resistance and stability of the oxide layer is a function of the environment and alloy composition and of the microstructure of the metal (influenced by heat treatments).

In order to maintain the excellent corrosion resistance of aluminium alloys it is necessary to take into account a certain number of precautions. Some kinds of localized corrosion can occur if the metal is used in unfavourable conditions. Some of the most important cases of corrosion will be discussed and preventive methods will be mentioned.



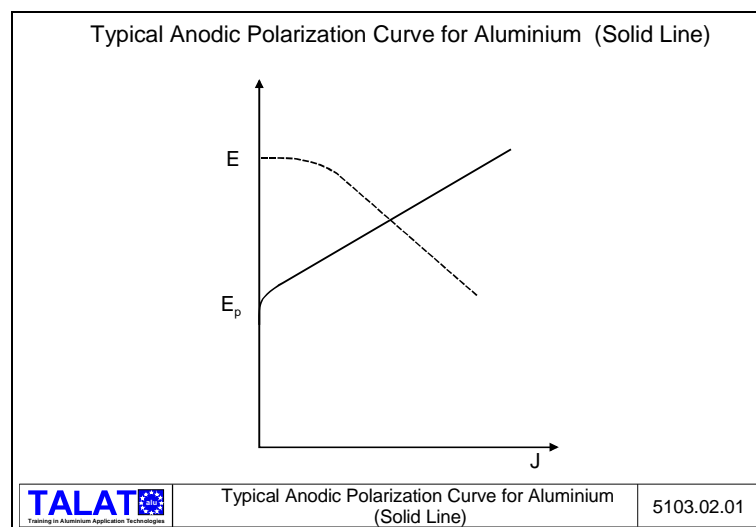
## 5103.02 Localized Corrosion

- Environmentally influenced corrosion
  - Pitting corrosion
  - Crevice corrosion
  - Filiform corrosion
  - Biological corrosion
- Metallurgically influenced corrosion
  - Galvanic corrosion
  - Intergranular corrosion
- Mechanically assisted degradation
  - Erosion
  - Fretting corrosion
  - Corrosion fatigue
- Environmentally induced cracking
  - Stress corrosion cracking
  - Hydrogen embrittlement

### Environmentally Influenced Corrosion

#### *Pitting Corrosion*

In aerated aqueous solutions and in the presence of  $\text{Cl}^-$  ions random formation of pits can be observed at defects in the protected oxide film. Pitting develops only at potentials more cathodic than the pitting potential  $E_p$  (**Figure 5103.02.01**). The intersection of the anodic curve for aluminium (solid line) with a curve for the applicable cathodic reaction (one of the representative dashed lines) determines the potential to which the aluminium is polarized, either by cathodic reaction on the aluminium itself or on another metal electrically connected to it. The potential to which the aluminium is polarized by a specific cathode reaction determines corrosion current density and corrosion rate.

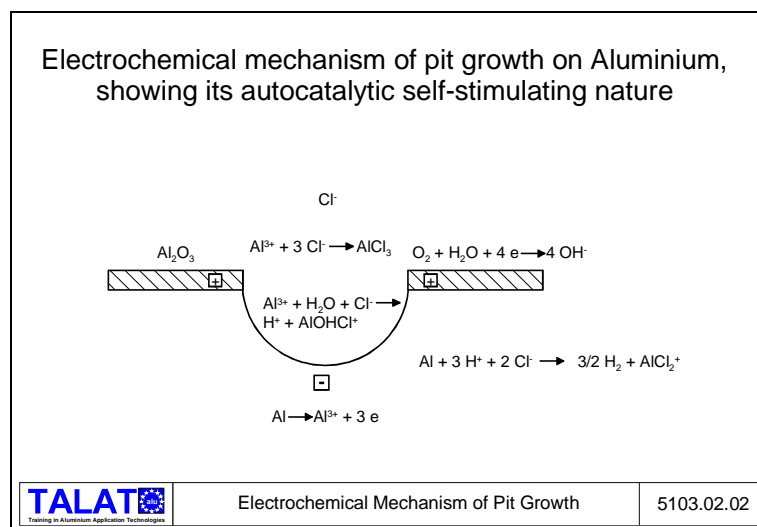


The potential above which pits will initiate ( $E_p$ ) decreases with an increase of the  $\text{Cl}^-$

concentration. However, only when cathodic reactions can occur (high enough concentration of O<sub>2</sub>, low overpotential) pitting corrosion of aluminium starts.

**Figure 5103.02.02** shows that the pit growth on the aluminium surface can be stimulated by different reactions :

- within the corrosion pit and preventing repassivation :
  - enrichment of Cl<sup>-</sup> ions;
  - generation of an acid solution;
  - limited O<sub>2</sub> supply;
- in the pit mouth :
  - formation of crust;
- around the pit :
  - passivation;
  - deposition of more noble metals.



Very high purity aluminium (1099) has excellent resistance to pitting. Among commercial alloys, the aluminium-magnesium alloys (5xxx) have the lowest pitting probability and penetration rates. With low (< 0.04 %) copper content aluminium-manganese (3xxx) alloys show comparable pitting behaviour. In aluminium-magnesium-silicon (6xxx) alloys pitting is combined with intergranular corrosion. Aluminium-copper (2xxx) and aluminium-zinc-magnesium-copper (7xxx) alloys are normally clad to protect against pitting.



## *Crevice Corrosion*

A very general method to improve the corrosion resistance of metals is to avoid the presence of narrow openings or spaces between metal to metal or non-metal to metal components. Localized corrosion at these sites will start due to the formation of an oxygen differential cell. The corrosion in the crevice will be accelerated by an acidification due to hydrolysis.

The factors affecting crevice corrosion are :

### Geometrical factors:

- type of crevice (metal-metal, metal-non metal)
- crevice tightness
- crevice depth
- exterior-interior surface area ratio

### Environmental factors:

- bulk solution ( $O_2$ , pH, T,  $Cl^-$ )
- mass transport
- crevice solution (hydrolysis equilibria)
- biological factors

### Electrochemical reactions :

- metal dissolution
- $O_2$  reduction
- $H_2$  evolution

### Metallurgical factors:

- alloys composition
- passive film characteristics.

To prevent crevice corrosion some precautions must be taken :

When crevice corrosion is considered possible, the crevice should be sealed with a non hardening elastomer to prevent the entry of moisture. Some sealants become hard and crack on aging, allowing moisture to enter. The elastomeric requirement is essential for joints in equipment that work in service, such as in all types of vehicles - road transport, ships, and airplanes. There are two general types of sealant:

- (1) one-component systems such as butyls or silicones, and
- (2) two-component systems such as polysulfides and epoxies.

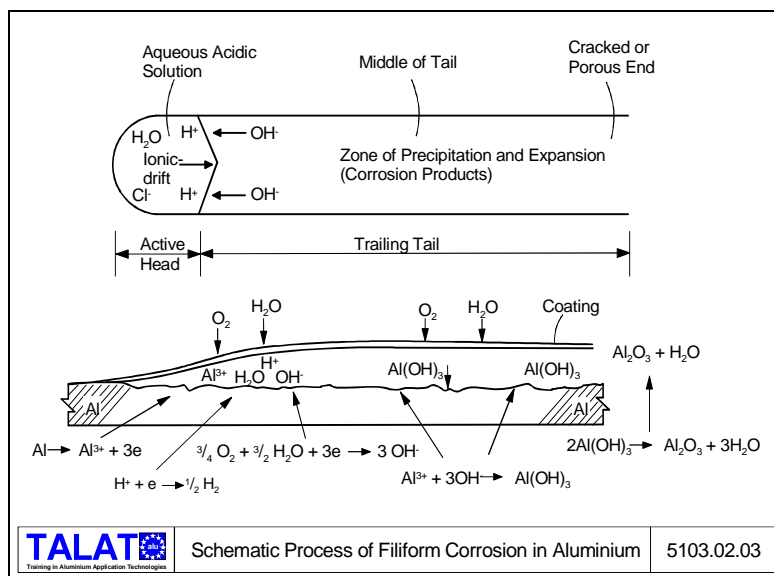
To prevent poultrice corrosion which is a special case of crevice corrosion, the contact of the bare aluminium surface with moisture-absorbing materials such as paper, cloth, wood, asbestos, and noncellular foams should be avoided.

## Filiform Corrosion

Filiform corrosion is another case of localized corrosion that may occur on an aluminium surface under an organic coating. It takes the form of randomly distributed thread-like filaments, and is sometimes called vermiform or worm track corrosion.

Aluminium is susceptible to filiform corrosion in a relative humidity range of 75 to 90% with temperatures between 20 to 40°C. Typical filament growth rates average about 0.1 mm/d. Filament width varies with increasing humidity from 0.3 to 3 mm. The depth of penetration in aluminium can be as deep as 15µ. Numerous coating systems used on aluminium are susceptible to filiform corrosion, including nitrocellulose epoxy, polyurethane, alkyd, phenoxy and vinyls. Condensates containing chloride, bromide, sulphate, carbonate and nitrate ions stimulate filiform corrosion.

Filiform corrosion is an oxygen concentration cell in which the anodic active area is the head of the filament and the cathode is the area surrounding it, including the tail (**Figure 5103.02.03**). At the head pH values as low as 1.5 to 2.5 have been reported.



Anodic reaction produces Al<sup>3+</sup> which react to form insoluble precipitates with the hydroxyl (OH) ions produced in the oxygen reduction reaction occurring in the tail.

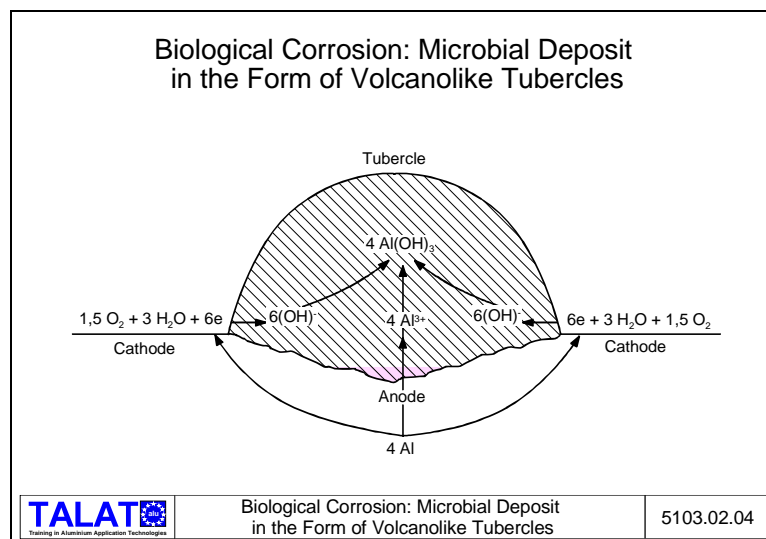
Phosphate coatings or chromium containing conversion coatings applied to the metal surface prior to organic coating are widely used to protect against filiform corrosion but they are not always completely successful.

## Biological Corrosion

Biological organisms are present in virtually all natural aqueous environments and can attack and grow on the surface of structural materials, resulting in the formation of a biological film or biofilm. The presence of a biological film does not introduce some new type of corrosion, but it influences the occurrence and/or the rate of known types of corrosion, e.g.:

- increase or decrease of the corrosion rate due to oxygen reduction;
- production of different aeration or chemical concentration cells;
- production of organic and inorganic acids as metabolic by-products;
- production of sulfides under anaerobic conditions.

For example, pitting corrosion of integral wing aluminum fuel tanks in aircraft that use kerosene-base fuels has been known to occur. The attack proceeds under microbial deposits in the water phase and at the fuel/ water interface. The organisms grow either in continuous mats or sludges, or in volcanolike tubercles with gas bubbling from the center (Figure 5103.02.04).



The organisms commonly held responsible are *Pseudomonas*, *Cladosporium* and *Desulfovibrio*. *Cladosporium resinae* produces a variety of organic acids (pH 3-4) and metabolizes certain fuel constituents. These organisms may also act with the slime forming *Pseudomonads* to produce oxygen concentration cells under the deposit.

Control of this type of attack has usually focused on a combination of reducing the water content of fuel tanks, coating and using biocides and fuel additives.


## Metallurgically Influenced Corrosion

### Galvanic Corrosion

Due to the fact that different metals must be used very often electrically coupled in an integrated structure a corrosion cell can occur resulting in acceleration of the corrosion process in less resistant metals.

**Figure 5103.02.05** gives the galvanic series of aluminium alloys and other metals in a NaCl solution. This galvanic series, however, is not necessarily valid in non saline solutions. For example aluminium is anodic to zinc in an aqueous 1 M sodium chromate ( $\text{Na}_2\text{CrO}_4$ ) solution and cathodic to iron in an aqueous 1 M sodium sulfate solution ( $\text{Na}_2\text{SO}_4$ ). Under most environmental conditions, aluminium and its alloys are the anodes in galvanic cells with most other metals, protecting them by corroding sacrificially. Contact of aluminium with more cathodic metals results in an increase of the potential of aluminium; this must be avoided in any environment in which aluminium itself is subject to pitting corrosion.

Metal Corrosion Potential (V/ SCE)	
Magnesium	-1.65
Zinc	-1.02
Aluminium Alloys 7072	.088
Aluminium Alloys 5xxx	-0.77 - -0.79
Aluminium Alloys 7075-T3	-0.76
Aluminium Alloys 1XXX, 3xxx, 6xxx	-0.72 - -0.75
Cadmium	-0.74
Aluminium Alloys 2024-T6	-0.73
Low-Carbon Steel, Cast and Wrought Iron	-0.50
Lead	-0.47
Tin	-0.41
Lead-Tin Solder (60-40)	-0.37
Brass (60-40)	-0.20
Copper	-0.12
Inconel	-0.04
Stainless Steel (19-8, passive)	-0.01
Bronze (95-5)	+0.00
Nickel	+0.01
Monel	+0.02

 Galvanic Series of Metals in NaCl Solutions 5103.02.05

To prevent the galvanic corrosion some precautions must be taken:

- Low potential difference (< 50 mV)
- High ratio area anode-cathode; e.g. stainless steel bolts in bare aluminium structures
- Low conductivity of the corrosion medium
- Slow kinetic of cathodic reduction, e.g. by inhibitors in closed loop circuits

Of course, without aqueous environment and without oxydants ( $\text{O}_2$ ) no galvanic corrosion can start.

The galvanic corrosion can occur after deposition of heavy metals on aluminium. Reduction of only a small amount of these ions can lead to severe localized corrosion. The influence of Cu, Pb, Hg, Ni and Sn is very important in acidic solutions. A  $\text{Cu}^{2+}$

concentration of 0.02-0.05 ppm in neutral or acidic solutions is generally considered to be the threshold value for initiation of Al pitting. This value is a function of the pH value and the concentration of  $\text{Cl}^-$ ,  $\text{HCO}_3^-$  and  $\text{Ca}^{2+}$ .

### *Intergranular Corrosion*

Galvanic corrosion can occur on the macroscopic but also on microscopic level.

Intergranular corrosion is a form of localized surface attack in which a narrow path is corroded preferentially along the grain boundaries of a metal. The driving force is a difference in corrosion potential that develops between a thin grain boundary zone and the bulk of the immediately adjacent grains.

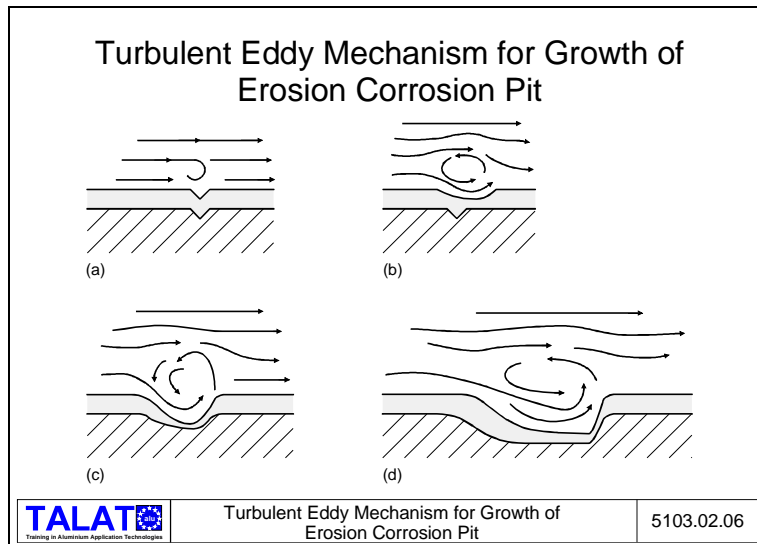
In the 2xxx series alloys the anodic path is a narrow band on either side of the boundary that is depleted in copper; in the 5xxx series alloys  $\text{MgAl}_3$  is anodic to aluminium and is preferentially dissolved when the constituent forms a continuous path along grain boundaries; copper free 7xxx series alloys are Zn and Mg - bearing constituents on the grain boundary and generally considered to be the anodic. In the copper bearing 7xxx series alloys, it appears to be the copper depleted bands along the grain boundaries, which cause intergranular corrosion. The 6xxx series alloys generally resist this type of corrosion, if the Si-content is kept at values near the stoichiometric  $\text{Mg}_2\text{Si}$  composition or below.

## **Mechanically Assisted Degradation**

### *Erosion*

In noncorrosive environments, such as high purity water, the stronger aluminum alloys have the greatest resistance to erosion-corrosion because resistance is controlled almost entirely by the mechanical components of the system. In a corrosive environment, such as seawater, the corrosion component becomes the controlling factor; thus, resistance may be greater for the more corrosion-resistant alloys even though they are lower in strength. Corrosion inhibitors and cathodic protection have been used to minimize erosion-corrosion, impingement, and cavitation on aluminum alloys.

**Figure 5103.02.06** illustrates the mechanism for growth of erosion corrosion pits.



### *Fretting Corrosion*

Fretting corrosion is a combined wear and corrosion process in which material is removed from the contacting surface when motion between the surfaces is restricted to very small amplitude oscillation.

Factors affecting fretting are:

- contact load
- amplitude
- frequency
- number of cycles
- relative humidity
- temperature

### *Corrosion Fatigue*

Fatigue strengths of aluminum alloys are lower in such corrosive environments as seawater and other salt solutions than in air, especially when evaluated by low-stress long-duration tests. Such corrosive environments cause smaller reductions in fatigue strength in the more corrosion-resistant alloys, such as the 5xxx and 6xxx series, than in less resistant alloys, such as the 2xxx and 7xxx series.

Like SCC of aluminum alloys, corrosion fatigue requires the presence of water. In contrast to SCC, however, corrosion fatigue is not appreciably affected by test direction with respect to the rolling, forging or extrusion direction, because the fracture that results from this type of attack is predominantly transgranular.

## Environmentally Induced Cracking

### *Stress Corrosion Cracking (SCC)*

SCC is a complex mechanism involving metallurgical, mechanical and environmental parameters. SCC in aluminium alloys is characteristically intergranular. According to the electrochemical theory, this requires a condition along the grain boundaries that makes them anodic to the rest of the microstructure so that corrosion propagates selectively along them.

This theory is confirmed by the fact that cathodic protection retards or eliminates SCC.

Parameters :

- magnitude and duration of tensile strength acting at the surface;
- residual stresses during quenching;
- grain structure and stress direction (resistance in short transverse direction controls applications of products);
- environment :  $\text{Cl}^-$  and a decrease of the pH-value accelerate the attack.

The SCC of high-strength aluminium alloys such as 2024, 7075 and 7079 is often caused by sustained residual or assembly tension stresses acting in the short transverse direction. The stresses developed by service loads are usually intermittent and are designed to operate in a favorable direction (longitudinal or long transverse) relative to the grain structure.

The following guidelines should be considered by the designer to minimize SCC :

- select alloys and tempers that are resistant to SCC;
- use stress-relieved parts;
- perform forming and straightening on freshly quenched material, W-temper, to ensure less severe effects;
- machine exterior surfaces before heat treating, because quenching causes more desirable compressive surface stresses;
- machine internal surfaces after heat treating to partially remove internal stresses;
- avoid fitup stresses by careful attention to tolerance. Poorly fitted parts and misaligned parts should not be forced into place.
- Where built-in surface tensile stresses cannot be avoided, techniques such as shot peening and surface rolling, or thermal stress relief from second stage ageing, can be utilized to reduce the undesired stresses.
- postweld heat treat weldments.

### *Hydrogen Embrittlement*

Hydrogen embrittlement is a form of environmentally assisted failure that results most often from the combined action of hydrogen and residual or applied tensile stress.

Only recently it has been found that hydrogen embrittles aluminium. For many years, all environmental cracking of aluminium and its alloys was represented as SCC. Hydrogen damage in aluminium alloys may take the form of intergranular or transgranular cracking or blistering. Hydrogen diffuses into the aluminium lattice and collects at internal defects (e.g. during annealing of solution treating in air furnaces prior to age hardening).

Dry hydrogen gas is not detrimental to aluminium alloys; however, with the addition of water vapor, subcritical crack growth increases dramatically.

The threshold stress intensity of cracking of aluminium also decreases significantly in the presence of humid hydrogen gas at ambient temperature.

Hydrogen embrittlement of the 7000 series has been more intensively studied.

### **5103.03 Corrosion Prevention**

- Alloy and temper selection
- Design of equipment
- Organic coating
- Inhibitors
- Anorganic surface treatments
- Cathodic protection

A number of corrosion preventives measures, special to specific types of aluminium corrosion, have already been mentioned. This section deals with the main methods of preventing corrosion of aluminium equipment :

- alloy and temper selection
- design of equipment
- organic coating (and sealants)
- inhibitors
- cathodic protection
- surface treatment
- modification of the environment



## **Alloy and Temper Selection**

The choice of an aluminium alloy for a given use is often based on strength, formability, ease of welding, or product availability. However, corrosion resistance must be included when making the choice.

In general, aluminium-magnesium alloys (5xxx) have the best corrosion resistance, followed by commercial-purity alloys (1xxx), aluminium-manganese alloys (3xxx), and aluminium-magnesium-silicon alloys (6xxx) in that order, with only small differences within families. These alloy families are normally used without protection although they are sometimes painted (sidings for buildings) or anodized (window frames) for aesthetic reasons. The aluminium-copper-magnesium alloys (2xxx) and the medium- and high-strength aluminium-zinc-magnesium-copper alloys (7xxx) are usually given a protective measure such as cladding or painting.

The importance of temper was mentioned previously. The H116 temper for 5083, 5086 and 5456 gives better resistance to intergranular and exfoliation corrosion. In 7xxx alloys, the T7x temper provides improved resistance to SCC, for example, the T73 and T76 tempers of 7075 alloy. These tempers are a compromise, because strength is somewhat lower than that of the T6 temper. The lower strength of these tempers in 7075 has been offset by the development of stress-corrosion resistant tempers in 7049, 7050 and 7010 alloys.

## **Design of Equipment**

The design of equipment can have an important influence on the corrosion behaviour, even in environments in which aluminium is normally resistant.

Some guidelines can help the designer to minimize corrosion of aluminium in service :

- avoid contacts with dissimilar metals, but if they must be used, apply suitable protection;
- avoid crevices, but if they must be present, and if thin sections are involved, prevent ingress of moisture by application of sealants;
- join by continuous welding, rather than by skip welding or riveting;
- provide for complete draining and easy cleaning;
- avoid contact of bare aluminium surfaces with water-absorptive materials, but if they must be used together, apply suitable protection;
- avoid sharp bends in piping systems;
- avoid heat transfer hot spots;
- avoid direct impingement by fluid streams;
- avoid excessive mechanical stress concentrations;
- when locating equipment, choose the least corrosive environment possible;
- eliminate sharp edges in equipment that is to be painted.

## **Organic Coating**

Organic coating systems are frequently applied to aluminium for strictly decorative purposes. But organic coatings may also be applied to aluminium for corrosion protection in special situations. In both cases, adequate surface preparation (see **Lectures 5201** and **5202**) and careful coating selection (see **Lecture 5204**) are important to long coating life.

Most organic coatings provide corrosion protection by forming a physical barrier between the aluminium surface and the environment. Some contain inhibitors such as chromate primers. Aluminium insulation jacketing and refrigerator liners are coated on the back with a vapor barrier to prevent pitting and crevice corrosion when condensation collects between foamed insulation and the aluminium. Clear organic coatings are used where the natural aluminium surface is desired and must be prevented. Temporary organic coatings are sometimes used to protect aluminium surfaces from corrosion during storage and transit. Heavy organic coatings, such as mastics and coal tars, are sometimes used to protect aluminium surfaces that are embedded in soils and concrete.

The performance of organic coating systems can be maximized by following the specific recommendations of suppliers regarding surface preparation, pretreatment, selection of compatible conversion coat, primer and topcoat, application and curing. If continuing maximum corrosion protection is required, the organic coating systems must be maintained periodically.

## **Inhibitors**

Inhibitors such as chromates that reduce the anodic corrosion reaction are termed anodic inhibitors, whereas those (e.g. polyphosphates) reducing cathodic corrosion reaction are termed cathodic inhibitors. If anodic inhibitors are used in an insufficient amount, they tend to increase pitting. Cathodic inhibitors are safer in this respect. Mixed anodic and cathodic inhibitor systems are also used.

Phosphates, silicates, nitrates, fluorides, benzoates, soluble oils and certain other chemicals alone or in combination have been recommended for use with aluminium in some services.

In mildly alkaline solutions the corrosion of aluminium can be inhibited by additions of sodium silicate. Silicates with a high ratio of silicate to soda are widely used in alkaline cleaning solutions, carbonates and phosphates. In mixed-metal, water-handling systems, such as an automobile cooling system, inhibitors mixtures have been developed to prevent corrosion of all metals in the system, including aluminium.

## **Anorganic Surface Treatments (see Lectures 5201, 5202 and 5205)**

A number of chemical and electrochemical surface treatments can be used in order to improve the corrosion resistance and/or the adhesion of organic coatings.

### **Cathodic Protection**

The corrosion of a metal can be prevented by pushing down its potential (-1 to -1.2 Cu/CuSO<sub>4</sub>) into its immunity region. The current necessary to obtain this potential decrease may be supplied by a sacrificial anode such as zinc or magnesium, by some aluminium alloys (seawater only) or by an impressed current source (electrolysis cell using an inert anode such as graphite or titanium). The magnitude of the current depends upon the overpotential and resistance characteristics of the system to be protected.

## **5103.04 References/Literature**

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