

# Chapter 10

## CORROSION BEHAVIOUR OF ALUMINIUM IN MARINE ENVIRONMENTS

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# 10. CORROSION BEHAVIOUR OF

**T**HE MARINE ENVIRONMENT is highly aggressive towards most materials, as amply demonstrated by the dilapidated state of old ships and wrecks (whether made from wood or steel) that can be seen lying abandoned around our coasts.

There are few metals capable of withstanding this hostile environment unprotected. Bronze is one of these metals, and in museums around the Mediterranean we may admire statues recovered from the ancient wrecks which they once adorned and which have lain submerged in the sea for centuries, even millennia.

Based on our very long experience of aluminium's corrosion behaviour in marine atmospheres and in sea water <sup>[1]</sup>, we can now assert that the service life of aluminium in marine environments will be exceptionally long and can be measured in decades!!! We can truly claim that aluminium is the "metal of the sea" of the modern age.

Although this evidence is now widely accepted, the issue of the resistance of aluminium to corrosion in marine applications is important enough to merit a digression of some length and detail to review a number of basic principles and in doing so

perhaps to prevent disappointments and avoid unnecessary protection.

Even though, around the middle of the 20<sup>th</sup> century, metallurgists and corrosion specialists perfected alloys that are "intrinsically" resistant to corrosion in marine environments – the aluminium-magnesium alloys that belong to the 5000 series – cases of corrosion still occur now and then. An examination of these cases shows that very often the cause of the corrosion lies in the design of the structure and in service conditions to which aluminium is not suited.

TRICAT 50



# ALUMINIUM IN MARINE ENVIRONMENTS

## 1. CHARACTERISTICS OF MARINE ENVIRONMENTS

A distinction must be made between sea water and sea atmosphere.

### 1.1 Sea water

The sea is a liquid medium that contains the following substances in equilibrium:

- dissolved mineral salts, some 30 to 35 g per litre,
- dissolved gases, including 5 to 8 ppm (1) oxygen,
- living organisms,
- decomposing organic matter,
- mineral matter in suspension.

This mix forms a very complex medium in which the influence of each individual factor, whether chemical (composition), physical (temperature, pressure) or biological (flora and fauna), on the resistance to corrosion of metals can be neither truly isolated nor separately quantified.

The great oceans – the Atlantic, the Indian and the Pacific – which connect with one another in the

southern hemisphere have a virtually uniform total salinity, 32 to 37 g.l<sup>-1</sup>, including 30 g.l<sup>-1</sup> of sodium chloride or “salt”.

The salinity of enclosed or isolated seas can be very different from that of the great oceans, and may vary seasonally down the year. The Baltic for example has a total salinity of 8 g.l<sup>-1</sup>, the Black Sea 22 g.l<sup>-1</sup>, the Mediterranean 41 g.l<sup>-1</sup> and the Persian Gulf 57 g.l<sup>-1</sup> [2].

The hostility of sea water to metals and other materials is due to its abundance of chlorides “Cl<sup>-</sup>”.

Experience and the results of corrosion tests show that aluminium’s resistance to corrosion is the same whatever the sea or ocean. Comparative tests carried out on the same alloys submerged in the North Sea (16 to 17 g.l<sup>-1</sup> chlorides, annual temperature variation 0 to 18 °C) and the Arabian Gulf (26 to 34 g.l<sup>-1</sup> chlorides, annual temperature variation 17 to 30 °C) show that there is no significant difference between the two sites despite their difference in salinity (ratio of 1:2) [3].

The corrosion behaviour of aluminium may change when the water in a port is polluted by urban or industrial waste, provided of

course the polluting elements modify the corrosivity of sea water vis à vis aluminium (2).

### 1.2 Sea atmosphere

The aggressive nature of sea air is aggravated by moisture and sea spray consisting of very fine droplets of sea water borne on the wind. The effect of sea air depends on the direction and strength of the prevailing winds, and is greatly diminished at a distance of a few kilometres inland.

(1) ppm = parts per million or mg.l<sup>-1</sup>.

(2) The diluted sea water in river estuaries is usually more aggressive to materials, including aluminium, than water off shore. This paradox can be explained in various ways: the precipitations of calcium and magnesium carbonate which deposit a more or less protective film on the metal do not occur in diluted sea water. Biological activity is slower. Domestic or industrial wastes modify physical-chemical balances and may themselves contain corrosive agents.

LIVING QUARTER



## 2. CORROSION BEHAVIOUR OF ALUMINIUM UNDER CONTROL OF THE NATURAL FILM OF OXIDE

Aluminium owes its excellent corrosion resistance to the presence on the metal of a permanent film of natural oxide that consists of alumina ( $\text{Al}_2\text{O}_3$ ) and makes the metal "passive" to the environment.

Although it is extremely thin, between 5 and 10 nanometers (3), the oxide film forms a protective barrier between the metal and the surrounding environment as soon as the metal comes into contact with an oxidizing medium such as atmospheric oxygen or water. The film forms within about one thousandth of a second and can even form under oxygen pressures as low as 1 millibar.

The physical-chemical stability of the oxide film is therefore key to aluminium's resistance to corrosion, and depends on the characteristics of the environment, such as its pH, and on the composition of the alloy itself.

## 3. INFLUENCE OF THE PH

The rate of dissolution of the oxide film is determined by the pH of the environment (figure 123). It is very fast in acid and alkaline media and slow in media that are close to pH-neutrality (pH 5 to 9). The oxide film is therefore very stable in sea water whose pH is 8 – 8.2.

Contrary to widespread belief, the pH is not the only criterion that must be taken into account when predicting the behaviour of aluminium in an aqueous environment – the nature of the acids or bases also plays an essential part. This is very important when selecting a cleaning or pickling product for aluminium.

Thus while hydrogen acids such as hydrochloric and sulphuric are very aggressive towards aluminium (the more so in a strong solution), concentrated nitric acid has no effect on aluminium (4) and can be used in concentrations stronger than 50% to pickle aluminium and its alloys. Organic acids only have a very moderate action on aluminium.

This is equally true in alkaline environments – caustic soda and potassium attack aluminium fiercely, whereas the effect of concentrated ammonia is much less severe. The same applies to organic bases.

## 4. INFLUENCE OF ALLOYING ELEMENTS

Some alloying elements of aluminium alloys actually reinforce the protective character of the natural oxide film, while others weaken it. The former include magnesium, whose oxide (magnesia) combines with the alumina to enhance the protective properties of the natural oxide film, accounting for the remarkable corrosion performance of magnesium alloys in the 5000 series: 5754, 5083, 5383, 5086 etc.

Copper on the other hand is one of the elements that weaken the protection provided by the oxide film, which is why the use of copper aluminium alloys in the 2000 series and those belonging to the 7000 series with added copper is not advisable in marine applications unless special protection is provided.

GANGWAY

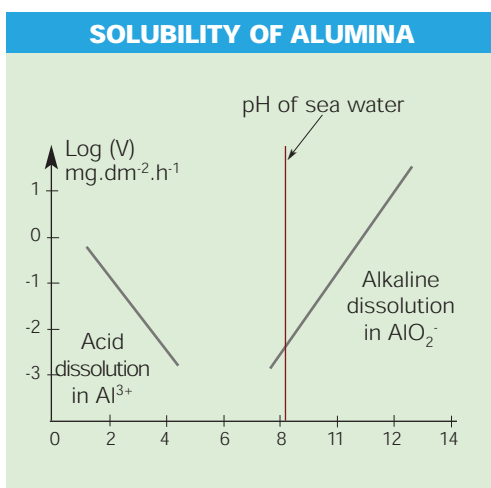


Figure 123

(3) 1 nanometer = one thousand millionth of a metre ( $10^{-9}$  m).

(4) Its oxidizing function even reinforces the oxide layer very slightly.

## 5. FORMS OF ALUMINIUM CORROSION

This section only deals with the forms of corrosion that might be found in marine environments on wrought alloys of the 1000, 3000, 5000 and 6000 series, and on the silicon casting alloys (40000) or magnesium casting alloys (50000).

These are:

- uniform corrosion,
- pitting corrosion,
- transcrystalline corrosion,
- intercrystalline corrosion,
- exfoliation corrosion,
- waterline corrosion,
- crevice corrosion,
- bimetallic corrosion.

### 5.1 Uniform corrosion

This type of corrosion is accompanied by a regular, uniform decrease in thickness over the whole surface area of the metal. The rate of dissolution can vary from a few microns per year in a non-aggressive environment to several microns per hour depending on the type of acid or base in solution in the water.

In marine environments, whether immersion in sea water or exposure to sea air, uniform corrosion is minuscule, of the order of one micron per year, and is not measurable.

We can therefore say that the service life of aluminium alloy equipment properly designed and built for use in a marine environment will not be limited by this type of corrosion.

### 5.2 Pitting corrosion

This very localised form of corrosion is common to many metals (figure 124) and is characterised by the formation of cavities in the material. The diameter and depth of the cavities vary depending on a number of parameters inherent in either the metal itself (type of alloy, manufacturing process etc.) or its environment, e.g. concentration of mineral salts.

Aluminium is sensitive to pitting corrosion in environments where the pH is close to neutral, which essentially means all natural environments such as surface water, sea water and atmospheric moisture.

Unlike in other common metals, this type of corrosion is worthy of our attention because the corrosion pits of aluminium are always covered by very large white blisters of gelatinous hydrated alumina  $\text{Al}(\text{OH})_3$ . The blister is always much larger than the underlying cavity.

Pitting corrosion occurs at sites where the natural film of oxide is imperfect due to thinning, local rupture or gaps caused by various factors associated with manufacturing conditions, additives and so forth. Experience shows that areas which are ground or scored

during sheet metal working, folding or welding operations provide ideal pockets where pits can develop during the first few weeks of immersion in sea water.

What is important for the user is to know the rate at which the pits deepen once they are initiated. Unlike other metals, e.g. zinc, whose corrosion products are soluble, alumina  $\text{Al}(\text{OH})_3$  is insoluble in water so that, once formed, it adheres to the surface of the metal inside the pit cavities. In this way, hydrated alumina considerably inhibits exchanges between the metal and sea water or atmospheric moisture.

The rate of pitting corrosion in aluminium and its alloys therefore decreases very rapidly in most media including sea water, and measurements of pit depths taken at regular intervals have shown that the rate of pitting "v" is a factor of time "t" by equations of the type  $v = Kt^{1/3}$ .

Many decades of experience with the use of unprotected aluminium in coastal construction (roofs, wall panels) and in shipbuilding corroborate the results obtained in the laboratory, from natural exposure or at corrosion testing stations over long periods of time: the depth of pits hardly changes once they have formed during the initial months of service.

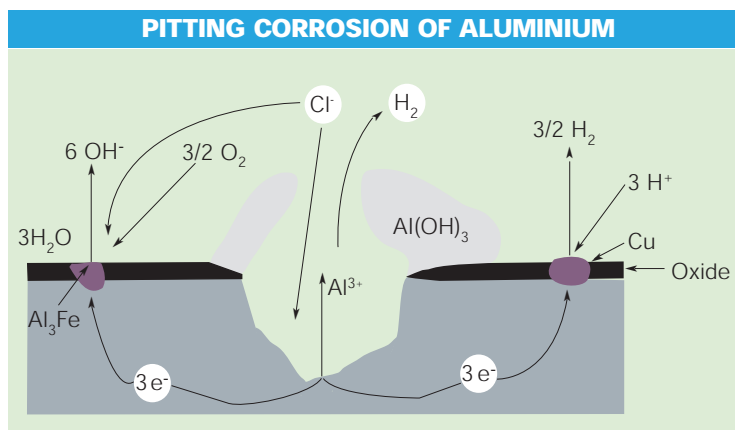


Figure 124

This slowdown in the rate of pitting corrosion explains the fact that aluminium equipment can be used for decades in certain natural environments (country air, sea air, sea water) without any protection. This applies as much to sea air (figure 125) as it does to immersion in sea water (figure 126). In both cases the pits are rarely deeper than one millimetre even after several years.

### 5.3 Transcrystalline corrosion and intercrystalline corrosion

Corrosion inside the metal, at grain level, can spread in two ways (figure 127):

- in all directions: corrosion affects all metallurgical constituents indiscriminately, it is not selective. This is transgranular or transcrystalline corrosion, so called because it spreads inside the grains,
- along preferential paths: corrosion spreads along the grain boundaries. Unlike transgranular corrosion, this type of corrosion consumes very little metal.

It is invisible to the naked eye, and micrographic examination is needed to detect it, usually with a magnification of 50. When it penetrates deep into the metal it affects its mechanical properties, especially elongation, and can even cause component failure.

Intercrystalline corrosion spreads from pits. There is no correlation between the depth to which intercrystalline corrosion penetrates and the diameter of the corrosion pits. In other words, intercrystalline corrosion can spread in depth from very small superficial pits.

Intercrystalline corrosion is caused by the difference in electrochemical potential that can exist between the actual grain and the grain boundary zone where intermetallic compounds, such as the  $\beta\text{Al}_3\text{Mg}_2$  phase for magnesium alloys, can precipitate. The dissolution potential of this intermetallic is very electronegative: -1150 mV SCE (saturated calomel electrode) compared with the grain: -750 mV.

Intercrystalline corrosion can occur when three conditions come together:

- presence of a corrosive aqueous medium,
- difference in potential of at least 100 mV between the intermetallics and the solid solution,
- continuous precipitation of intermetallics in the grain boundaries.

Given the 400 mV difference in potential between the  $\beta\text{Al}_3\text{Mg}_2$  phase and the grain, aluminium-magnesium alloys are sensitive to this form of corrosion under well defined and well known conditions, as reviewed in Section 10.2. They depend on the conditions of working and the conditions of service.

It is normal to quantify the intensity of intercrystalline corrosion by the number of grain layers that are

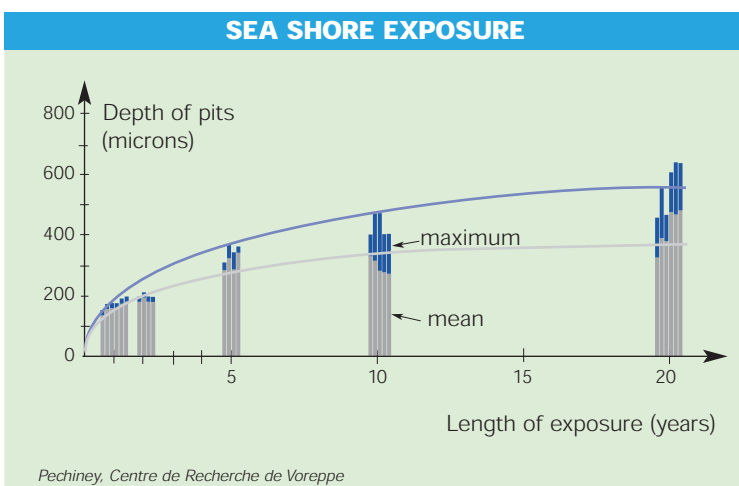


Figure 125

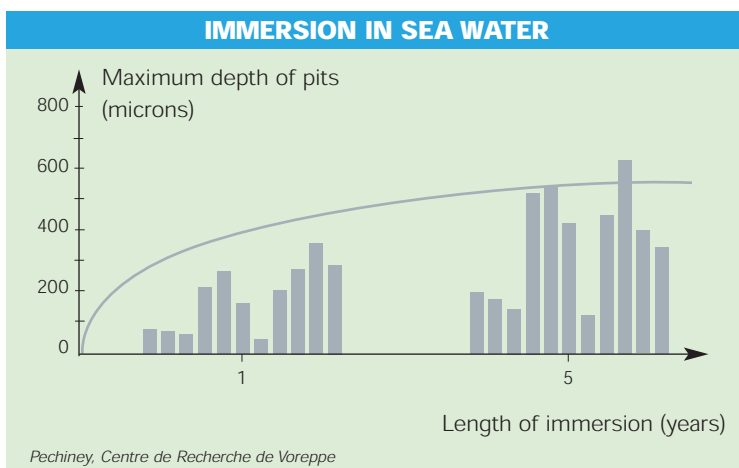


Figure 126

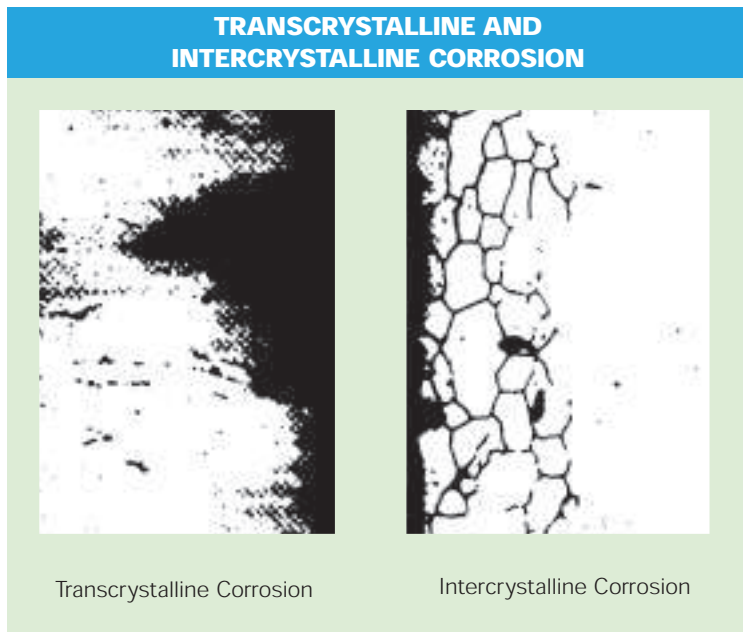


Figure 127

affected by it, and it is accepted that intercrystalline corrosion is superficial and harmless when it does not spread beyond 3 or 4 layers, as is observed in the alloys of the 6000 series.

Selective tests that can be used to detect the sensitivity of aluminium alloys to intercrystalline corrosion are given in Section 11.

### 5.4 | Exfoliation corrosion

Exfoliation corrosion is a form of corrosion that spreads along planes parallel to the direction of rolling (or extrusion). Between these planes are very thin sheets of sound metal. The build-up of corrosion products causes the corroded zone to swell, peeling away leaves of metal like the layers of an onion, hence the name "exfoliation corrosion".

The sensitivity of aluminium alloys to this very characteristic form of corrosion (figure 136, p. 162) depends on the production conditions (the rolling or extrusion process, rates of work hardening

and the elongated texture of grains). In the aluminium-magnesium alloys (5083, 5383, 5086 etc.), the H116 temper, examined with the ASSET test (5), is immune to this type of corrosion.

### 5.5 | Waterline corrosion

This form of corrosion affects semi-submerged metal structures, especially steel, in which the submerged zone close to the air/water boundary can suffer preferential corrosion that is sometimes severe (6).

In aluminium, this corrosion is due to the difference in the concentration of chlorides caused by evaporation in the thinnest part of the film of water wetting the metal (figure 128). The result is a difference in dissolution potential which can be significant between the bottom and top of the meniscus which is anodic and therefore corroded <sup>[4]</sup>.

Aluminium and its alloys are largely immune from this form of corrosion in sea water, so the

waterline of barges and boats with unpainted hulls is not particularly corroded by this medium. The same applies to foundation piles and the floats of landing-stages etc. in marinas.

In flowing water this effect is very weak as the meniscus is continually being renewed.

In stagnant water, the area either side of the air/water boundary line must be painted to avoid the risks of waterline corrosion.

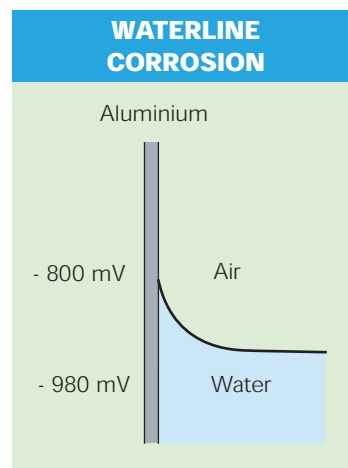


Figure 128

(5) Cf. Section 11.

(6) In steel, this form of corrosion, known as "corrosion by differential aeration", is due to the difference in the concentration of oxygen between the layer of water that is in direct contact with air – which is therefore richer in oxygen – and the layer beneath. Corrosion occurs below the waterline.

## 5.6 | Crevice corrosion

Crevice corrosion, also known as deposit attack, occurs in tiny recesses beneath deposits where water penetrates but is not refreshed (figure 129).

The spread of crevice corrosion in aluminium is usually minimal, due no doubt to the precipitation of alumina – a product of corrosion – which quickly seals off access to the crevices. When a bolted or riveted joint that has been immersed for a very long time in sea water is dismantled, a continuous deposit of alumina is very often found between the two sheets. When joining components however it is essential to avoid leaving recesses that might provide a foothold for corrosion in the long term. Intermittent welds on structures that are permanently or even only occasionally immersed should therefore be avoided.

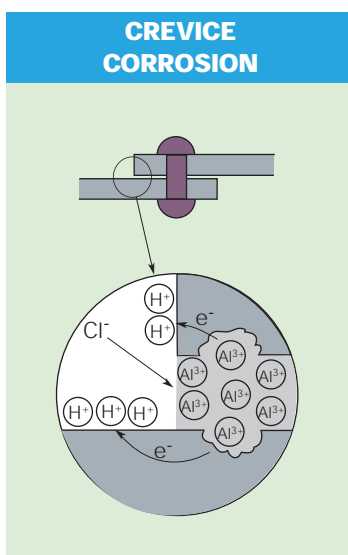


Figure 129

## 6. | BIMETALLIC CORROSION

For a long time, the often exaggerated fear of bimetallic corrosion impeded growth in the use of aluminium, both in naval construction and in coastal equipment.

Today, after many years of experience with the use of aluminium in marine environments, we can properly assess and quantify the risks of bimetallic corrosion of aluminium in mixed assemblies between aluminium and other common metals of the type found in shipbuilding (or other applications).

Such an assessment is a necessary exercise, as it is neither possible nor even desirable for commercial and technical reasons to construct ships and equipment that are made entirely of aluminium. On pleasure craft for example, transmission shafts, screws, valves and pipes are almost never made from aluminium.

It is therefore the task of the designer and operator to ensure that contact between aluminium and other metals in marine environments cannot cause bimetallic corrosion. This is a straightforward matter provided they follow a number of elementary rules based on fundamental principles, in particular the concepts of the galvanic cell and the potential scale, and of course on experience.

## 6.1 | The galvanic cell

When two dissimilar metals or alloys such as copper and zinc are placed in direct contact (or are electrically connected) in a wet and electrically conductive environment, e.g. a sulphuric acid solution, one of the two metals, in this case zinc, will dissolve while the other, copper, retains its integrity and appearance.

This is a battery (7) (or galvanic cell) consisting of two electrodes, each of which is a metal (figure 130):

■ the one that is consumed – called the *anode* – undergoes an oxidation reaction:

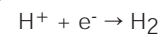


or



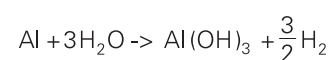
when it is aluminium,

■ the other – the *cathode* – undergoes a reduction reaction, usually to the  $H^+$  ions present in the water (8):



The amount of hydrogen that is given off bears no direct relationship to the mass of metal that is dissolved at the anode. Under standard conditions – 25 °C at a pressure of 1013 mbar – it is 33.6 litres for 27 grams of aluminium.

The reactions at the anode and the cathode occur simultaneously and are balanced in electrical charges "e<sup>-</sup>". The complete reaction for the bimetallic corrosion of aluminium is as follows:



(7) So called because the first current generator invented by Alessandro Volta in 1800 was a "pile" of zinc and copper discs insulated from one another by felt and immersed in a diluted solution of sulphuric acid.

(8) The  $H^+$  ions are produced either by the dissociation of the water itself or by an acid dissolved in the water.



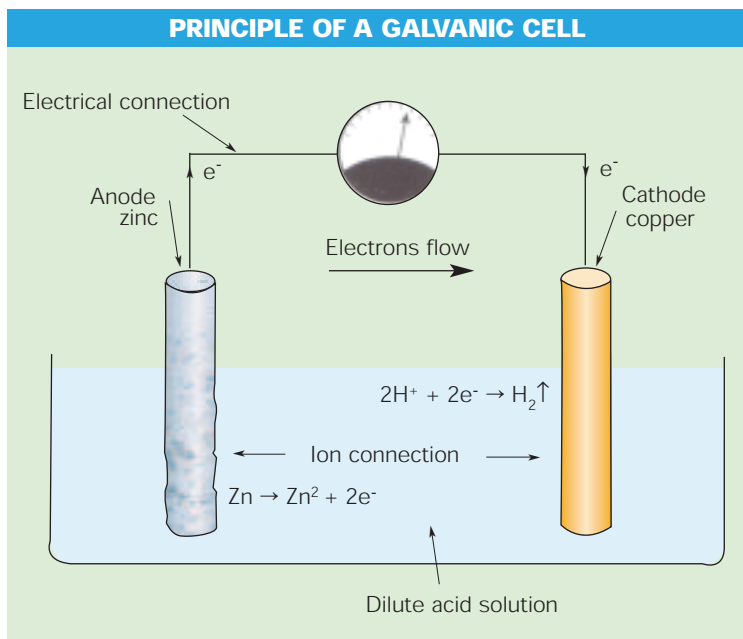


Figure 130

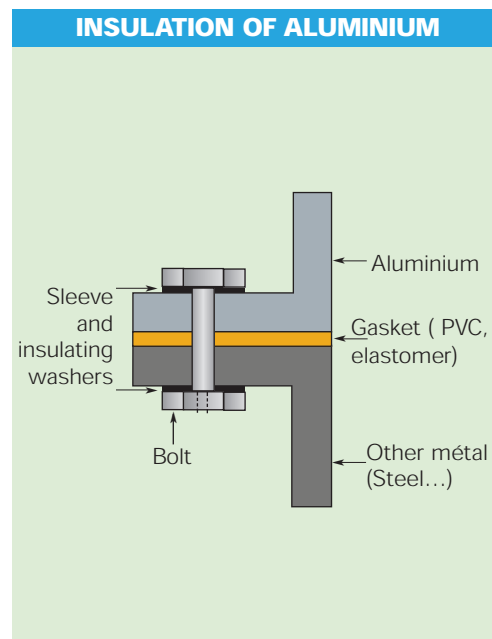


Figure 131

Hydrogen is given off (at the cathode) and aluminium (the anode) dissolves, forming alumina  $Al(OH)_3$ .

## 6.2 Conditions of bimetallic corrosion

These simplified equations show that for bimetallic corrosion to take place, 3 conditions must come together simultaneously:

- presence of an electrolyte,
- electrical continuity,
- dissimilar metals.

■ Presence of an electrolyte: the contact area between the metals must be wetted by fresh water or sea water. The more conductive the medium, the stronger the bimetallic corrosion, and it is therefore much more intense in sea water whose resistance is of the order of 10 to 25  $W.cm^{-1}$  than in fresh water (or rainwater) whose resistance attains several thousand  $W.cm^{-1}$ , depending on the source of the water.

■ Electrical continuity between the two metals, either through direct contact or made by means of a fastener such as clamp screws.

One simple way of avoiding bimetallic corrosion therefore is to insulate the two metals from one another as carefully as possible, and this is easily done with a high ohmic resistance, i.e. an insulating material (figure 131) such as neoprene (9).

As with any battery (or galvanic cell), anything that retards or inhibits the electrochemical reactions on the electrodes reduces its output – this is referred to as “polarisation.” Applied to the case of bimetallic corrosion, the accumulation of corrosion products in the contact zone between the two metals slows down the process.

When hybrid joints made from plates of steel and aluminium alloy that are bolted together without any insulation are taken apart after

years of immersion in sea water, a very dense alumina “poultice” is therefore found in the contact area. The extent of the corrosion will be limited because the alumina has significantly slowed the exchange of ions (10).

■ Dissimilar metals. This raises the concept of potential which we shall now discuss.

(9) Once a much-used technique in shipbuilding, it has been superseded by cathodic protection for immersed structures (cf. Chapter 11).

(10) It goes without saying that this initial corrosion cannot be expected to provide reliable long term protection.

### 6.3 | Concept of potential

This is a thermodynamic phenomenon that measures a metal's tendency to oxidize. The more electronegative the potential, the more the metal tends to oxidize.

Potential is measured in millivolts (mV) against a reference electrode and in a defined medium. Corrosion specialists usually use the saturated calomel electrode (SCE) as the reference.

The result is a classification or 'potential scale' of metals and alloys; table 67 shows a part of this scale for the common metals in natural sea water in motion.

The rankings on this scale can be used to predict which of the two metals in contact with each other in an aqueous medium, or more specifically in sea water, will be attacked:

- if both metals have electronegative potential, it will be the more electronegative,
- if one metal is electropositive it will be the electronegative.

In this combination for example:

Zinc  $E_d = - 1130$  mV

Iron  $E_d = - 610$  mV

it is the zinc that corrodes (11).

Experience shows that bimetallic corrosion only occurs when the two metals in contact have a difference in potential of at least 100 mV.

The aluminium alloys used in marine applications have dissolution potentials that are very close to one another (table 66).

(11) This accounts for the effectiveness of coating steel with zinc, and hence the use of galvanised steel in many applications where it must be protected from corrosion.

DISSOLUTION POTENTIAL OF ALUMINIUM ALLOYS (NACL SOLUTION, H2O2, ASTM G 69)	
Alloy	Potential mV SCE
1050A	- 750
3003	- 740
5052	- 760
5056	- 780
5083	- 780
5086	- 760
5154	- 770
5182	- 780
5454	- 770
5456	- 780
6005A	- 710
6060	- 710
6061	- 710
6063	- 740
42000 (A-S7G03)	- 820
51300 (A-G5)	- 870

Table 66

DISSOLUTION POTENTIALS MEASURED IN NATURAL SEA WATER IN MOTION AT 25°C	
Alloy	Dissolution Potential (mV SCE) (*)
Graphite	+ 90
Stainless steel	- 100
Titanium-	- 150
Inconel	- 170
Cupronickel 70-30	- 250
Cupro-nickel 90-10	- 280
Bronze	- 360
Brass	- 360
Copper	- 360
Lead	- 510
Mild steel	- 610
Cast iron	- 610
Cadmium	- 700
Aluminium	- 750
Zinc	- 1 130
Magnésium	- 1 600

(\*) mV SCE = millivolts, saturated calomel electrode.

Table 67

In a marine environment therefore there is no risk of bimetallic corrosion between these alloys. This is also true of casting alloys, and is the reason why stiffeners in 6000 alloys are frequently used welded to plate in 5000.

#### 6.4 Practical aspects of bimetallic corrosion of aluminium in marine environments

Bimetallic corrosion is a very localised phenomenon and very often confined to the contact zone. In theory, the current density that determines the rate of dissolution of the anodic metal is a function of the relationship:

$$\frac{\text{cathodic surface}}{\text{anodic surface}}$$

Experience shows that this area relationship is of no great relevance, as bimetallic corrosion occurs primarily in or near the contact zone, and so the anode area must be judged to be more or less equal to the cathode area.

Expressed in practical terms, a small component such as a screw or probe made from copper or copper alloy and attached to a large aluminium alloy structure without any insulation – and permanently submerged – will cause severe bimetallic corrosion at the point of attachment.

Aluminium's position on the scale of potential (table 67) means that in virtually every instance in which it is joined to another common metal (12), it will be the anode of the resulting battery and so likely to suffer bimetallic corrosion if the conditions are right.

To fully appreciate the risks of the bimetallic corrosion of aluminium in a mixed joint, we must distinguish between:

- a submerged structure (quick works)
- an emerged structure (dead works) – the type of metal must also be considered in this case.

**Note:** Anodising affords no protection from bimetallic corrosion.

#### 6.5 Submerged mixed contacts

As we have already shown, when contacts are submerged, bimetallic corrosion of aluminium is unavoidable when in contact with most common metals (13). The intensity of this corrosion will depend on the type of metal, on the composition of the environment and on the length of time if the contact area is submerged occasionally rather than continuously.

The aluminium structure must be protected, and there are a number of ways of achieving this:

- Insulation, by inserting plastic seals between the two metals. Taking pipework as an example, a gasket of sufficient thickness is fitted between the aluminium flanges of the pipe and the flange of a stainless steel or brass valve.
- Painting: the surface of the cathode, i.e. of the other metal, must first be masked. Painting the aluminium only is far less effective.
- Cathodic protection is the most practical solution (14) and the one used most often to neutralise the galvanic couples between a ship's aluminium hull and the propulsion system (shaft and screw) and other items attached to the hull (intake strainers, various accessories).

**Note.** A steel tool such as a spanner left behind in the bilge of a vessel can cause bimetallic corrosion if water is allowed to stagnate in the same area as the item made of steel (or any other metal).

#### 6.6 Emerged mixed contacts in open air

Many decades of experience with aluminium applications in marine environments, both on board ships and in on-shore coastal installations, show that contacts with mild steel, whether bare or coated (galvanised, cadmium plated), and stainless steel cause no significant bimetallic corrosion of aluminium and its alloys (15) in the 1000, 3000, 5000 and 6000 series (16).

(12) Except cadmium, zinc and magnesium. There will be no bimetallic corrosion of aluminium in contact with fasteners made from galvanised or cadmium-plated steel. Instead, as long as there is zinc or cadmium on the steel, these metals will dissolve to protect it.

(13) This will also apply to mixed contacts in the bilges of a ship if water stagnates there.

(14) Cf. Chapter 11.

(15) For a number of reasons: a layer of corrosion products (rust, alumina) forms on the contact faces, inhibiting electrochemical reactions as we have seen.

(16) In some cases copper alloys in the 2000 and 7000 series are sensitised to corrosion on contact with steel.

As a result, such contacts are now hardly ever protected on ships (17) or in coastal installations except obviously in cases where rust discoloration must be prevented on aluminium structures (in the case of contact with steel). Today, steel/aluminium transition joints (18) are used to make welded connections between a hull and aluminium alloys.

(16) In some cases copper alloys in the 2000 and 7000 series are sensitised to corrosion on contact with steel.

(17) For safety reasons (cf. Chapter 9), all metal masses on board a ship or on a structure intended to house electrical installations must be equipotentially bonded. Even if contacts are insulated for reasons of corrosion or convenience, an electrical connection by means of a cable or braided wire must still be provided at one point.

(18) Cf. Chapter 9.

## 6.7 Influence of the type of metal in contact with aluminium

The risk of bimetallic corrosion may be greater when aluminium is in contact with certain metals and alloys.

### Copper and its alloys

While contact between aluminium alloys and copper and its alloys (brass, bronze) causes no appreciable bimetallic corrosion, when emerged structures are in a wet marine environment it is advisable where possible to provide insulation between the two metals to avoid local deterioration in the appearance of the aluminium.

Verdigris however (the corrosion product of copper and its alloys) is aggressive towards aluminium and its alloys and is reduced to tiny particles of copper when in contact with them. These particles in turn cause local pitting corrosion in the aluminium, and it is therefore preferable to protect structures that are beneath an accessory that is made of copper, bronze or brass. The optimum solution is to paint them to prevent verdigris forming in the first place.

### Lead

Lead is often used as ballast for pleasure craft. The combination of aluminium and lead reacts very strongly in sea water, and it is therefore essential to prevent water entering the keel if this is ballasted with lead shot or pig lead. The following procedure is usually used to prevent the risk of bimetallic corrosion which can be very severe (19):

- Carefully degrease the inside of the keel space that is accessible from the bottom of the boat,
- Apply a layer of resin 15 to 20 mm thick in the bottom of the keel,

- Once the resin has set, place the shot (or pig lead) in position, carefully avoiding contact with the aluminium edge of the keel,

- Now pack the spaces around the lead with resin up to a level 20 to 25 mm above the ballast,

- Finally, access to the keel should be sealed off by suitable means to prevent any ingress of moisture into the keel.

Lead ballast should never be laid on the bare hull, e.g. on the floor of a hold, but should be sealed in a watertight covering to prevent the bimetallic corrosion of the aluminium and the entrainment of lead salts generated by that corrosion in the presence of moisture. Lead salts will cause pitting corrosion in those areas of the hull where they are entrained by moisture.

If the lead ballast is fastened to the hull directly, it must be carefully insulated from it, as indicated in figure 132.

Lead-based paints should never be used to protect steel components on board an aluminium vessel because lead oxides, like copper oxides, cause severe corrosion to the aluminium in the presence of moisture.

### Mercury

Aluminium in contact with mercury suffers very severe corrosion which takes the form of flaky white 'blooms' that spread widely where the quantity of mercury is significant or finely divided. The effect of mercury is all the more insidious as it tends to occur at low points where fine droplets of mercury accumulate.

(19) All the careful precautions taken to insulate the lead from the walls of the keel will be wasted if the keel weldments are porous! Gradual penetration of sea water through cracks due to poor welding will cause irreparable corrosion to the keel in the medium term.

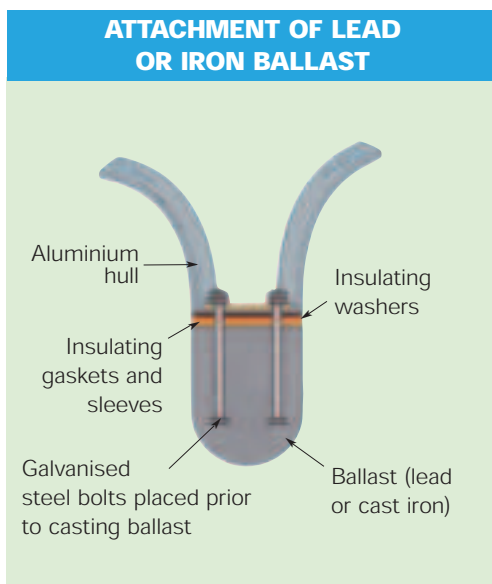


Figure 132

It is therefore most inadvisable to carry mercury instruments such as barometers or thermometers on board a ship when spillage or breakage might cause severe corrosion of the hull.

## Graphite

Although graphite is not a metal (but a metalloid), contact with it in a wet environment causes bimetallic corrosion that is more or less intense depending on the porosity of the graphite. It is therefore inadvisable to use graphite based lubricants on aluminium boats.

There is as yet insufficient experience with the use of carbon fibre equipment on board aluminium ships to be able to draw conclusions about contact between aluminium and carbon fibre composites.

Laboratory tests with immersion in synthetic sea water show that aluminium suffers a mild and very superficial attack when in contact with carbon fibre parts.

**Note:** When in port, craft should be moored/anchored using ropes made from hemp or synthetic fibres as this creates an 'open circuit' between the aluminium craft and the metal anchor or bollards on the quayside.

## 7. ALUMINIUM TARNISHING AND BLACKENING

Aluminium in a humid atmosphere or in contact with sea water or fresh water tarnishes to a degree that depends on the medium. This phenomenon, known as blackening, is not a type of corrosion but merely an alteration of the visual properties of the film of natural oxide. It does not produce any subsequent sensitivity to corrosion.

In a marine environment, blackening can be prevented on certain items by anodising or polishing them. Anodising is by far the more lasting method, and is used on boat masts.

## 8. ROLE AND PREVENTION OF MARINE FOULING

Unlike salts of copper (or mercury), aluminium salts are not toxic to living organisms and they can therefore easily attach themselves to aluminium surfaces where they will grow unchecked unless dislodged.

Such marine encrustations include barnacles, corals, algae, sponges etc., but cause no appreciable corrosion to the underlying metal apart from a very superficial attack to a depth of a few hundredths of a millimetre. Shells leave a virtually indelible impression on the metal.

As with other metals, antifouling paints can be used on aluminium to prevent the growth of marine encrustations (20).

However there is one very important restriction: antifouling paints based on salts of copper, mercury or lead cause severe corrosion (21) and should be avoided. This bimetallic corrosion is due to the reduction of copper, mercury and lead salts in contact with the aluminium surface and can do irreparable damage to the hull of a vessel.

(20) Cf. Chapter 11.

(21) The use of antifouling paints based on minerals salts is actually banned.

WELDMENT ON A GANGWAY



## EFFECT OF DESIGN ARRANGEMENTS

BAD	GOOD	BAD	GOOD

Figure 133

## 9. EFFECTS OF WELDING AND DESIGN ARRANGEMENTS

Design layouts can significantly influence the corrosion performance of aluminium alloy structures in service.

### 9.1 Effect of welding

Experience shows that the corrosion behaviour of welded structures made from alloys belonging to the 1000, 3000, 5000 and 6000 series is similar to that of non-welded surfaces. In other words, weld seams and heat affected zones will not be the site of preferential corrosion provided welding is done according with the relevant codes of practice and with the right filler alloys (22).

The same applies to adhesive bonding which does not affect the corrosion behaviour of components joined by this process.

### 9.2 Effect of design arrangements

Despite the excellent resistance to corrosion of the alloys used in shipbuilding (and in marine applications), instances of corrosion are occasionally seen in service.

An examination of these cases shows that it is most often the design layout that causes these problems. Figure 133 illustrates classic cases of design layouts that are detrimental to good corrosion performance.

Experience shows that areas where water stagnates or where dust (or soot) can accumulate can suffer very severe corrosion in the form of deep pits and even perforations.

It is therefore essential to assist the drainage of water and condensation on divisions and partitions subject to temperature variations, and to provide as much ventilation as possible for spaces that are more or less accessible (ballast tanks, holds etc.).

These areas, as well as watertight buoyancy chambers, must be regularly inspected and may require more frequent maintenance than the rest of the structure.

Finally, anything that encourages the permanent presence of moisture, such as certain types of lining, must be carefully avoided. For example, expanded foam (or insulation blankets made from rock-wool or similar materials) placed against an aluminium division for thermal insulation must be positioned so that it cannot trap condensation or attract moisture.

Floor coverings should also be adhesive bonded to prevent the ingress of moisture between the covering and the aluminium "floor".

**Note:** Stray electrical currents can be a determining factor leading to corrosion of the hull surface in contact with sea water. As is stated in Chapter 10 (23), the hull (and any other metal structure on the boat) must never act as a return conductor for the current, whether this is d.c. or a.c.

(22) Cf. Chapter 6.

(23) Chapter 9.

## 10. SENSITIVITY TO CORROSION OF ALUMINIUM ALLOYS IN MARINE APPLICATIONS

Many decades of experience with marine applications of aluminium have shown that its resistance to corrosion is remarkable.

Nevertheless:

- some series of alloys are not suited to this type of application,
- production processes must be designed to avoid accidentally sensitising 5000 series alloys to structural corrosion (intercrystalline corrosion, exfoliation corrosion or stress corrosion).

Finally, service conditions must also be controlled to ensure that certain limits of temperature and time are not exceeded. The H116 temper has the advantage of undergoing mandatory inspection for sensitivity to exfoliation corrosion.

### 10.1 Choice of alloys for marine applications

While the 5000 and 6000 series alloys will be preferred for their resistance to corrosion, their weldability and their level of mechanical characteristics, other wrought alloys belonging to the 1000 and 3000 series are suitable for use in non-structural applications for decoration, interior fittings etc.

The use of 2000 and 7000 series alloys on the other hand must be the exception in view of their poor resistance to corrosion, and they require special protection when used in a marine environment.

The 2000 and 7000 series copper alloys cannot be welded with the classical arc processes. The 7000 series alloys without copper, e.g.

7020 or 7108, are easy to weld however, and present a high level of mechanical characteristics after welding, an attractive attribute that could be an advantage for sheet metal working in general and ship-building in particular.

Even so, the heat affected zone is highly sensitive to exfoliation corrosion in all environments, so much so that the development of these alloys has had to be abandoned except in very specific applications out normal fields.

In the absence of any significant progress in the control of sensitivity to exfoliation corrosion, it is not possible with our present level of knowledge (24) of the metallurgy of these alloys to use them in naval construction without special protection [5].

The casting alloys commonly used in marine applications are the 42100 (A-S7G03), the 42200 (A-S7G06) and the 51100 (A-G3).

## 10.2 Sensitivity of 5000 series alloys to intercrystalline corrosion

It has been well known since the early 1950s that aluminium-magnesium alloys can have a tendency to intercrystalline corrosion, the more so the higher the level of magnesium, which is why industrial alloys do not normally contain more than 5.5 % magnesium.

This sensitivity is due to the changes in the distribution of the magnesium in the metal in the solid state. The solubility of magnesium in aluminium is very high at high temperatures – 15 % at 450 °C – but is no more than 1 % at ambient.

When the temperature falls below 450 °C, the magnesium precipitates in the form of intermetallics  $Al_3Mg_2$  (or  $Al_6Mg_5$ ), commonly referred to as "β phase." But when certain conditions occur these precipitates can collect on the grain boundaries, and the metal is then "sensitised." A micrograph examination soon reveals whether the alloy is sensitised or not (figure 134).

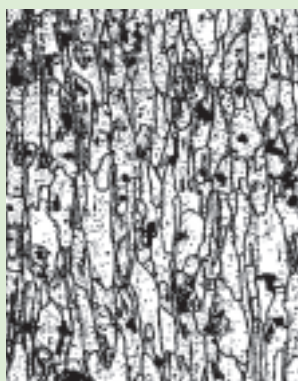
The precipitation of the β phase on the grain boundaries has a tendency to be continuous, and will be the more rapid and more dense:

- the higher the level of magnesium,
- the higher the service temperature, and
- the greater the degree of strain hardening.

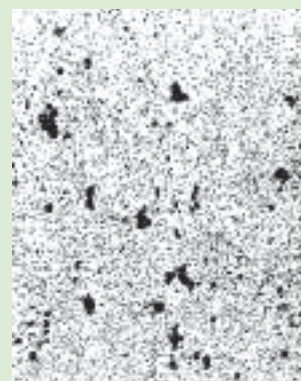
As figure 135 shows, the temperature range between 125 and 225 °C is one of high sensitisation, and sensitisation can start at even lower temperatures for the alloys with the most magnesium, over 5%.

As we have already seen, these intermetallics are anodic relative to the mass of the grain, their potential is -1150 mV SCE, a difference of some 400 mV from the solid solution, which is considerable. There is therefore a risk of intercrystalline corrosion if their precipitation is continuous on the grain boundaries and if the environment is corrosive.

### MICROGRAPHIC APPEARANCE OF SENSITISED ALLOY 5083



5083 Sensitised State



5083 Non-sensitised State

Figure 134



Temperature is not the only parameter that governs the precipitation of the  $\beta$  phase, as is often and mistakenly forgotten (25). Time, i.e. the period spent at temperature, is also a factor when evaluating the intensity of sensitisation. This should be obvious, as the rate at which the magnesium atoms migrate towards the grain boundaries obeys the laws of diffusion in the solid state (the aluminium matrix in this case). It is dependent on temperature according to the classic equation:

$$\tau = t \exp - (Q/RT)$$

where:

$\tau$  = the distance covered

$t$  = time

$T$  = absolute temperature

$Q$  is a constant that depends on the element.

Too often, the limit at which 5000 alloys with more than 3.5 % magnesium can be used has been set at 65°C (26). It is in fact the product of "Time x Temperature" that must be taken into consideration. On a 5086 for example, it will take 2 years at 65°C or several months at 100°C to cause continuous precipitation on the grain boundaries. The effect of time is cumulative.

The sensitisation of these alloys – which is always avoidable – can be due to manufacturing conditions or service conditions when they are held at temperature for long periods.

Much research has been done on all of these parameters since the 1950s (17). Sensitisation can be inhibited by thermal treatments which cause discontinuous "pearl necklace" precipitation of the  $\beta$  phase on the grain boundaries (18). For many years now, the production processes for alloys 5083, 5086 and *Sealium*® – including the H116 temper – have been specially adapted for shipbuilding (19) to avoid the supply of semi-finished

products that are susceptible to corrosion. These alloys are systematically controlled by the selective tests described below.

We should remember however that the H116 temper will not prevent precipitation of the  $\beta$  phase on the grain boundaries when the service conditions can cause it. This temper is used very widely in shipbuilding.

(25) *It is not because a metal is sensitised by precipitation at the grain boundaries that makes corrosion inevitable, it depends on the environment. Experience has confirmed this at temperatures well above 65°C, including in heat exchangers operating in sea water. There are road tankers carrying heavy fuel oil, loaded at 65°C, that have been in service for 20 years or more, with 8 to 10 hours of rotation a day, i.e. at least 50,000 hours of total time at 65-70°C. But obviously sensitisation must be avoided.*

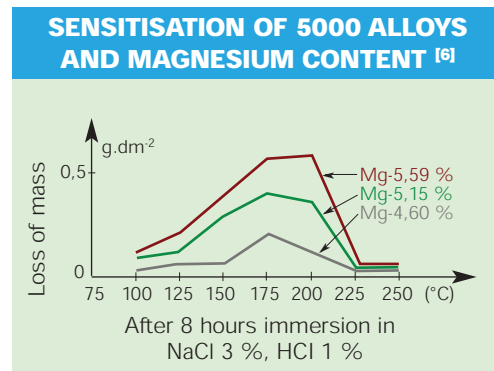


Figure 135

(26) *In the document "AD-Merkblatt W 6/1" of May 1982, published by the Vereinigung der technischen Überwachungsvereine e.V., D 4300 Essen 1, entitled "Aluminium and aluminium alloys malleable materials", the limit is set at 80°C for alloy AlMg4.5Mn, equivalent to the 5083, with tolerances of 150°C for periods not exceeding 8 hours, provided the service pressure is reduced by half and 24 hours if the service pressure is reduced to atmospheric.*

MARINA PONTOON AND FLOATS MADE OF 5754



## 11. CORROSION TESTS

European standard EN 13195-1 (27) states that alloys 5083, 5383 and 5086 supplied in the H116 temper "in the form of sheet, strip and plate must be tested to assess their resistance to intergranular corrosion and exfoliation corrosion."

This test is either the ASSET test (ASTM G66-99) which determines susceptibility to exfoliation corrosion, or any other method agreed between supplier and buyer.

Section 9 of draft standard ASTM B924 04 relates to the 5059, 5083, 5086, 5383 and 5456 alloys in the H116 and H321 tempers. Susceptibility to exfoliation corro-

sion is measured with the ASSET test (ASTM G66-99) and susceptibility to intercrystalline corrosion with the ASTM G67 test (NAMLT).

### 11.1 Exfoliation corrosion testing

This is the ASSET test (28) which is conducted according to ISO 11881 (29) and ASTM G66 (30) on samples whose dimensions (length and width) are at least 40 x 100 mm. The conditions of this test are summarised below:

After surface preparation by degreasing, alkaline pickling and nitric neutralising, the specimens are immersed for 24 hours at 65 °C in the specific reagent of the 5000 series (31):

$\text{NH}_4\text{Cl}$  - 1 M : 53 g.l<sup>-1</sup>  
 $\text{NH}_4\text{NO}_3$  - 0,25 M : 20 g.l<sup>-1</sup>  
 $(\text{NH}_4)_2\text{C}_4\text{H}_4\text{O}_6$  - 0,01 M : 1,84 g.l<sup>-1</sup>  
 $\text{H}_2\text{O}_2$  - at 30 % : 10 ml. l<sup>-1</sup>

Susceptibility to exfoliation corrosion is assessed against typical images (figure 136) and result in a grading as shown in table 68.

#### EVALUATION OF RESULTS OF THE ASSET TEST

Evaluation	Grading
No significant attack	N
Pitting corrosion	P
Generalised corrosion	G
Exfoliation corrosion	EA, EB, EC, ED

Table 68

(27) European standard EN 13195-1, December 2002, "Aluminium and aluminium alloys – Wrought and cast products for marine applications (shipbuilding, marine and offshore).

(28) ASSET = Ammonium Salt Solution Exfoliation Test

(29) ISO 11881, June 2002, Corrosion of metals and alloys – Exfoliation corrosion testing of aluminium alloys.

(30) Standard test method for visual assessment of exfoliation corrosion susceptibility of 5XXX series aluminum alloys (ASSET test).

(31)

$\text{NH}_4\text{Cl}$  = ammonium chloride,

$\text{NH}_4\text{NO}_3$  = ammonium nitrate,

$(\text{NH}_4)_2\text{C}_4\text{H}_4\text{O}_6$  = ammonium tartrate,

$\text{H}_2\text{O}_2$  = oxygenated water.

#### CLASSIFICATION OF EXFOLIATION CORROSION WITH THE ASSET TEST



From figure 6 of NF ISO 11881 Standard, June 2002

Figure 136

## 11.2 Test for intercrystalline corrosion of the 5000 alloys

Two tests can be used to determine the susceptibility of 5000 aluminium alloys to intercrystalline corrosion:

■ The NAMLT tests (32) according to ASTM G67 (33).

The samples are immersed in a 70 to 72 % solution of nitric acid  $\text{HNO}_3$  at 30 °C for 24 hours, and weighed before and after the test.

According to standard B928-04 (34):

- the batch is passed when the mass loss is  $< 15 \text{ mg.cm}^{-2}$ ,
- the batch is rejected when the mass loss is  $> 25 \text{ mg.cm}^{-2}$ ,
- for mass losses between 15 and  $25 \text{ mg.cm}^{-2}$ , the form of corrosion must be determined by micrograph examination after phosphoric attack. The batch is rejected if the corrosion proves to be intercrystalline.

■ The INTERACID test according to the protocol published in the *Journal of the European Communities* on 13/09/1974, Nos. C104/84 to 89.

Here the reagent consists of a solution made from 30 g.l<sup>-1</sup> of NaCl and 5 g.l<sup>-1</sup> of 37 % HCl (d = 1.19). The samples are immersed in the reagent for 24 hours at 23 °C. After determining the mass loss (weighed before and after the test), the samples are examined under a microscope with a magnification of x200.

These tests can be conducted on samples heated to 100 °C for 7 days (35).

## 11.3 Test for intercrystalline corrosion of the 6000 alloys

These alloys are not susceptible to exfoliation corrosion. Any susceptibility to intercrystalline corrosion can be determined by the test according to ASTM G110 (36) in the reagent with 57 g.l<sup>-1</sup> de NaCl et 0,3 % de  $\text{H}_2\text{O}_2$ .

(32) NAMLT = Nitric Acid Mass Loss Test.

(33) ASTM G67: Standard test method for determining the susceptibility to intergranular corrosion of 5XXX series aluminum alloys by mass loss after exposure to nitric acid.

(34) B 928 - 04: Standard Specification for High Magnesium Aluminum Alloy Sheet and Plate for Marine Service, February 2004.

(35) According to the formula  $\tau = t \exp -(Q/RT)$ , 7 days at 100 °C is equivalent to 6 months at 60 °C.

(36) ASTM G110: Standard practice for evaluating the intergranular corrosion resistance of heat treatable aluminum alloys by immersion in sodium chloride + hydrogen peroxide solution.

## Bibliography

- [1] *Corrosion de l'aluminium*, C. VARGEL, 502 pages, Dunod, 1999.
- [2] "Chemical aspects of physical oceanography"; J. LYMAN, R. B. ABEL, *Journal Chemical Education*, Vol. 35, 1958, pp. 113-115.
- [3] "Effect of the temperature and salt content of sea water on the corrosion behavior of aluminium"; W. HUPPATZ, H. MEISSNER, *Werkstoffe und Korrosion*, Vol. 38, 1987, pp. 709-710.
- [4] "Corrosion de l'aluminium sous couche mince électrolytique, corrosion à la ligne d'eau et corrosion au stockage"; C. FIAUD, G. AZERAD, E. GROSGOGÉAT, *Journées "Durabilité de l'aluminium et de ses alliages dans les industries électriques"*, Cefracor Paris, December 1986, pp. 33-37.
- [5] "Experience from the construction and operation of the Stena HSS"; H. NORDHAMMAR, STENA REDERI, *The Third International Forum on Aluminium Ships*, Haugesund, Norway, May 1998.
- [6] "Influence de la teneur en magnésium sur la résistance à la corrosion sous tension des alliages Al-Mg"; A. GUILHAUDIS, *Pechiney SREPC Report*, September 1959.
- [7] "Development of Wrought Aluminium-Magnesium Alloy"; E. H. DIX, W. A. ANDERSON, M. B. SHUMAKER, *Technical Paper*, No. 14, Alcoa, 1958.
- [8] "Traitements thermiques de stabilisation des alliages aluminium-magnésium à 5% contre les effets de chauffage à basse température"; A. GUILHAUDIS, *Revue de l'Aluminium*, 1955, Nos. 223 and 224.
- [9] "Aluminium-Magnesium alloys 5086 and 5456 H116"; C. L. BROOKS, *Naval Engineers Journal*, August 1970, pp. 29-32.

## NO ALUMINIUM CORROSION





CHEVY TOY