

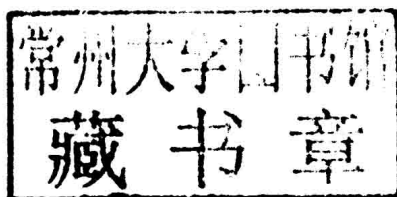


Advances in
**Corrosion
Evaluation
and Protection**

Guy Lennon

Advances in Corrosion Evaluation and Protection

Edited by **Guy Lennon**



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Advances in Corrosion Evaluation and Protection

Preface

I am honored to present to you this unique book which encompasses the most up-to-date data in the field. I was extremely pleased to get this opportunity of editing the work of experts from across the globe. I have also written papers in this field and researched the various aspects revolving around the progress of the discipline. I have tried to unify my knowledge along with that of stalwarts from every corner of the world, to produce a text which not only benefits the readers but also facilitates the growth of the field.

This book deals with latest techniques in corrosion assessment and prevention. It discusses various significant topics like the role of EIS (Electrochemical Impedance Spectroscopy) to assess the potency of E-coating, corrosion and its preventive measures; new techniques for pigments formation; and the impact of plasma deposited films on corrosive carbon steel materials. The book also provides a detailed study regarding material deterioration as a result of electrochemical tests and theoretical evaluation. Furthermore, it deals with organic-inorganic hybrid coatings, which are highly effective corrosion resistors.

Finally, I would like to thank all the contributing authors for their valuable time and contributions. This book would not have been possible without their efforts. I would also like to thank my friends and family for their constant support.

Editor

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Corrosion Protection of Al Alloys: Organic Coatings and Inhibitors

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1. Introduction

Aluminium and its alloys have excellent durability and corrosion resistance, but, like most materials, their behaviour can be influenced by the way in which they are used. Aluminium is commercially important metal and its alloys are widely used in many industries such as reaction vessels, pipes, machinery and chemical batteries because of their advantages. Aluminium is a well-known sacrificial anode if couple with more passive metal as it is most reliable and cost effective anode. Aluminium sacrificial anode has been used in major project all over the world. It is used in offshore application including structures, platforms, pipelines, jetties and power plants. Aluminium anode is also used for ship-hull and ballast-tank protection.

Aluminium is an active metal and its resistance to corrosion depends on the formation of the protective oxide film (Sastri et al. 2007). There are several methods to protect the aluminium and its alloys from corrosion such as coatings (Metallic, Inorganic, conversion and organic coatings), control of environment (operating variable i.e. pH, dissolved oxygen, temperature and etc.) and corrosion inhibitors (organic and inorganic additives).

This chapter describes the corrosion and corrosion prevention of the aluminium alloys by organic coatings and inhibitors. Industrial applications and common corrosion form of different Al alloys are carried out in this chapter. The corrosion prevention methods for different Al alloys are also mentioned in this chapter. A recent literature review of more than 30 papers is summarized at the end of this chapter.

2. Industrial applications of different Al alloys

Aluminium can be alloyed with different elements like zinc, magnesium, silicon, copper, manganese, as well as lithium. As a result, it can be used for different applications like manufacturing of aluminium foil covering, food packaging industry, food and chemical industry, vehicle panelling, mine cages, air frames, chemical plants, pressure vessels, road tankers, transportation of ammonium nitrate, irrigation pipes and window frames. Some industrial applications for aluminium alloy are listed below:

1. Aluminium alloys are highly resistant to non-heat treatments. They are good conductors of heat and electricity and that is why they are being used in different chemical industries for preparation of aluminium products.

2. Aluminium alloys get hardened during the process of reactions. That is why they are highly favourable alloys for the factor of weld ability as well as formability. Also, they are superior for the cryogenic uses even in the condition of annealed treatments.
3. Aluminium alloys is its high resistance to corrosion. They deter it from different harsh chemical treatments and help in retaining its lustre and strength. It also has high resistance to sea and ocean water. Therefore, it can be used for different air cages without any hassles.
4. Aluminium alloys can be converted into any form as they are ductile in nature. Be it sheets or wires, they can be drawn into various shapes without any inconvenience.
5. Aluminium alloy also used as sacrificial anode for the cathodic protection system (pipeline cathodic protection, oil tank, ship hull aluminium cp anode, Figure 1, boiler anodes, aluminium rod and aluminium bracelet anodes).

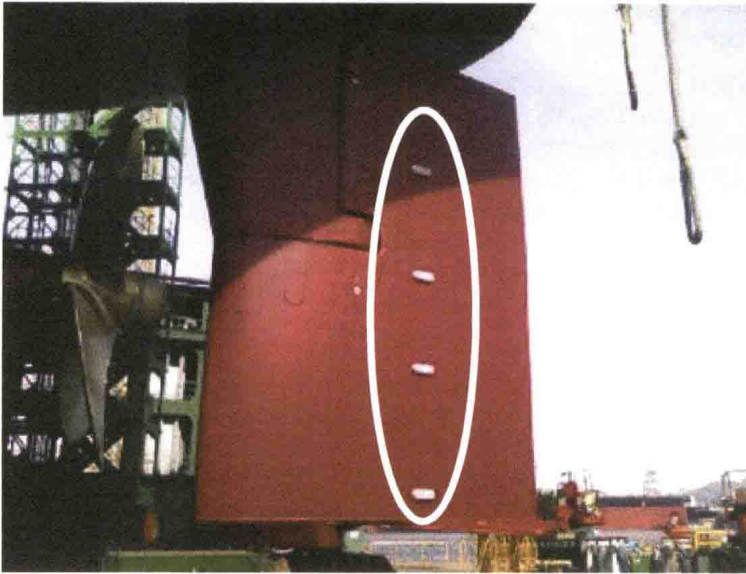


Fig. 1. Sacrificial aluminium anode attached to the hull of a ship.

3. Most common corrosion mechanism for Al alloys

Many different corrosion mechanisms exist for Al alloys. The most common types are generally well understood. For each, the process is complex, incorporates many factors, and varies according to metal and specific operating conditions. Yet all still remain difficult to control, and represent a very serious threat to most industries. Once established, most corrosion problems will produce future years of operating difficulty and expense at varying levels of severity.

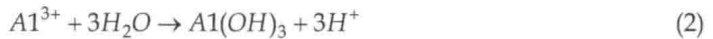
3.1 Galvanic corrosion

Galvanic corrosion occurs, when a metallic contact is made between a nobler and a less noble one (Wallen 1986; Dexter 1999; Bardal et al. 1993). A necessary condition is that there is also an electrolytic condition between the metals, so that a closed circuit is established.

The area ratio between cathode and anode is very important. For instance, if the nobler cathodic metal has a large surface area and the less noble metal has a relatively small area, a large cathodic reaction must be balanced by a correspondingly large anodic reaction concentrated in a small area resulting in a higher anodic reaction rate (Wallen 1986). This leads to a higher metal dissolution rate or corrosion rate. Therefore, the ratio of cathodic to anodic area should be kept as low as possible. Galvanic corrosion is one of the major practical corrosion problems of aluminium and aluminium alloys (Dexter 1999) since aluminium is thermodynamically more active than most of the other common structural materials and the passive oxide which protects aluminium may easily be broken down locally when the potential is raised due to contact with a nobler material. This is particularly the case when aluminium and its alloys are exposed in waters containing chlorides or other aggressive species such as SO_4 (Bardal et al. 1993). The series of standard reduction potentials of various metals can be used to explain the risk of galvanic corrosion; however these potentials express thermodynamic properties, which do not take into account the kinetic aspects (Valen et al. 1989). Also, if the potential difference between two metals in a galvanic couple is too large, the more noble metal does not take part in corrosion process with its own ions. Thus, under this condition, the reduction potential of the more noble metal does not play any role. Therefore establishing a galvanic series for specific conditions becomes crucial.

3.2 Pitting

Pitting is a highly localized type of corrosion in the presence of aggressive chloride ions. Pits are initiated at weak sites in the oxide by chloride attack. Pits propagate according to the reactions



while hydrogen evolution and oxygen reduction are the important reduction processes at the intermetallic cathodes, as sketched in figure 1:

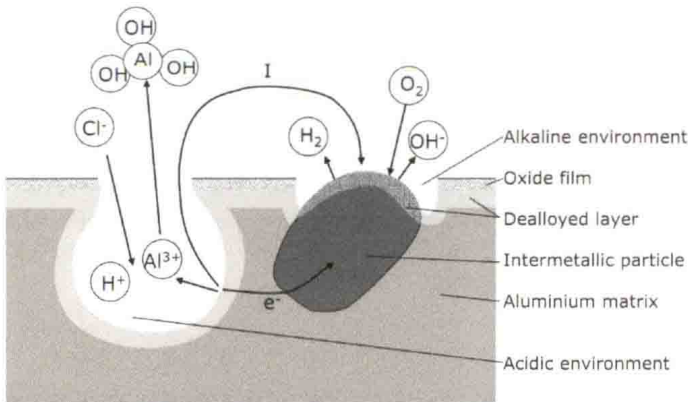


Fig. 2. Pitting corrosion mechanisms for the aluminium.



As a pit propagates the environment inside the pit (anode) changes.

According to reaction 2 the pH will decrease. To balance the positive charge produced by reaction 1 and 2, chloride ions will migrate into the pit. The resulting HCl formation inside the pit causes accelerated pit propagation. The reduction reaction will cause local alkalisation around cathodic particles. As previously mentioned aluminium oxide is not stable in such environment, and aluminium around the particles will dissolve (alkaline pits). The active aluminium component of the particles will also dissolve selectively, thereby enriching the particle surface with Fe and increasing its cathodic activity. Etching of the aluminium matrix around the particles may detach the particles from the surface, which may repassivate the alkaline pits. This may also reduce the driving force for the acidic pits causing repassivation of some in the long run. Figure 3 show pitting on an Al alloy.



Fig. 3. SEM images showing the pitting corrosion for the aluminium

3.3 Intergranular corrosion

Intergranular corrosion (IGC) is the selective dissolution of the grain boundary zone, while the bulk grain is not attacked. IGC is also caused by microgalvanic cell action at the grain boundaries. The susceptibility to IGC is known to depend on the alloy composition and thermomechanical processing. Grain boundaries are sites for precipitation and segregation, which makes them physically and chemically different from the matrix. Precipitation of e.g. noble particles at grain boundaries depletes the adjacent zone of these elements, and the depleted zone becomes electrochemically active. The opposite case is also possible; precipitation of active particles at grain boundaries would make the adjacent zone noble. These two cases are illustrated in figure 3. Figure 4 shows examples of intergranular corrosion on 7075-T6 aluminium alloy.

3.4 Exfoliation corrosion

Exfoliation is yet another special form of intergranular corrosion that proceeds laterally from the sites of initiation along planes parallel to the surface, generally at grain boundaries,

forming corrosion products that force metal away from the body of the material, giving rise to a layered appearance. Exfoliation is sometimes described as lamellar, layer, or stratified corrosion. In this type of corrosion, attack proceeds along selective subsurface paths parallel to the surface. It is possible to visually recognize this type of corrosion if the grain boundary attack is severe otherwise microstructure examination under a microscope is needed. In Al alloy, exfoliation corrosion occurred when the metal exposed to tropical marine environment. Also note the paint failures caused by corrosion of aluminium at the coating/aluminium interface. Exfoliation corrosion can be prevented by coatings, selecting a more exfoliation resistant aluminium alloy and using heat treatment to control precipitate distribution.

3.5 Stress-Corrosion Cracking (SCC)

Stress-corrosion cracking in aluminium alloys is characteristically intergranular. According to the electrochemical theory, this requires a condition along grain boundaries that makes them anodic to the rest of the microstructure so that corrosion propagates selectively along them. Intergranular (intercrystalline) corrosion is selective attack of grain boundaries or closely adjacent regions without appreciable attack of the grains themselves

Aluminium alloys that contain appreciable amounts of soluble alloying elements, primarily copper, magnesium, silicon, and zinc, are susceptible to stress-corrosion cracking (SCC). An extensive failure analysis shows how many service failures occurred in the industry and what kind of alloys and stresses led to initiation and propagation of stress corrosion cracks which caused these service failures. Alloys 7079-T6, 7075 -T6 and 2024 - T3 contributed to more than 90% of the service failures of all high-strength aluminium alloys. Aluminium and its alloys can fail by cracking along grain boundaries when simultaneously exposed to specific environments and stresses of sufficient magnitude. Well-known specific environments include water vapour, aqueous solutions, organic liquids and liquid metals. Stresses sufficient for crack initiation and crack growth can be far below the stresses required for gross yielding, especially in those alloy/environment combinations that are of practical importance, e.g., high strength aluminium alloys in air. This phenomenon of environment-induced intergranular cracking is often called stress-corrosion cracking. With most service failures specific causes for initiation or propagation of stress corrosion cracks have been observed. The various causes usually belong to one of the following three classes: metallurgical, environmental and mechanical. This follows quite naturally from the old observation that for stress corrosion cracking to occur, three conditions have to be fulfilled: the alloy must be "susceptible" to SCC, the environment must be "damaging" and the stress (intensity) must be "sufficient".

The electrochemical theory of stress corrosion, developed about 1940, describes certain conditions required for SCC of aluminium alloys. Further research showed inadequacies in this theory, and the complex interactions among factors that lead to SCC of aluminium alloys are not yet fully understood. However, there is a general agreement that for aluminium the electrochemical factor predominates and the electrochemical theory continues to be the basis for developing aluminium alloys and tempers resistant to SCC.

4. Corrosion protection of Al alloy

There are several methods commonly used to combat corrosion. These include passive film formation, chromating, cathodic protection, organic coatings and inhibitors (Jones 1996). This chapter is only concerned about the prevention of corrosion using organic coatings and inhibitors

4.1 Organic coatings

Organic coating provides protection either by the formation of a barrier action from the layer or from active corrosion inhibition provides by pigments in the coating. Surface condition of metal converted to more stable state by coating with organic compounds. These coatings delay the generation of electromotive force, causing the corrosion of the substrate (Schweitzer, 2001). Cathodic deposition of organic coatings has gained worldwide acceptance as a coating process for automotive, appliance and general industrial coatings which has been adopted in technology to provide the first prime coat to a variety of products.

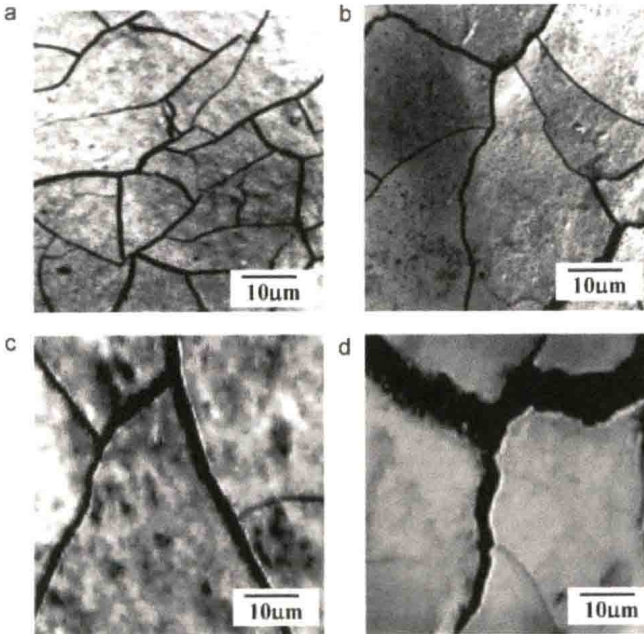


Fig. 4. Optical micrographs of the surfaces of 7075-T6 aluminium alloy specimens exposed to a deaerated 0.5 M NaCl solution at -685 mV SCE: (a) as-received specimen and (b), (c) and (d) specimens with grain sizes of 40, 130 and 290 μm , respectively (El-Amoush, 2011)

Among the large number of electroconducting polymers, polypyrrole and polyaniline are the most promising conducting polymers for corrosion protection. Nevertheless, the lower price of aniline monomer comparing to pyrrole makes polyaniline more challengeable (Popovic and Grgur et. al. 2004). Polyaniline (PANI) exists in a variety of forms that differ in chemical and physical properties. The most common green protonated emeraldine has conductivity on a semiconductor level of the order of 100 S cm^{-1} , many orders of magnitude

higher than that of common polymers ($<10^{-9}$ S cm^{-1}) but lower than that of typical metals ($>10^4$ S cm^{-1}). Protonated PANI, (e.g., PANI hydrochloride) converts to a nonconducting blue emeraldine base when treated with ammonium hydroxide (Fig. 5). The changes in physicochemical properties of PANI occurring in the response to various external stimuli are used in various applications e.g., in organic electrodes, sensors, and actuators. Other uses are based on the combination of electrical properties typical of semiconductors with materials parameters characteristic of polymers, like the development of “plastic” microelectronics, electrochromic devices, tailor-made composite systems, and “smart” fabrics. The establishment of the physical properties of PANI reflecting the conditions of preparation is thus of fundamental importance (Stejskal & Gilbert 2002). Recently many attempts have been carried out to protect the aluminium and its alloy by organic base coating. Ogurtsov et al. (2004) have reported the protection ability of pure undoped PANI (emeraldine base) and PANI doped with p-toluene-sulfonic (TSA), camphorsulfonic (CSA) and dodecylbenzenesulfonic (DBSA) acids coatings for Al 3003 alloy. As it can be seen from their results, Table 1, that the highest protecting ability factor was obtained for undoped PANI being equal to 12 and 4.4 in neutral and acidic media, respectively.

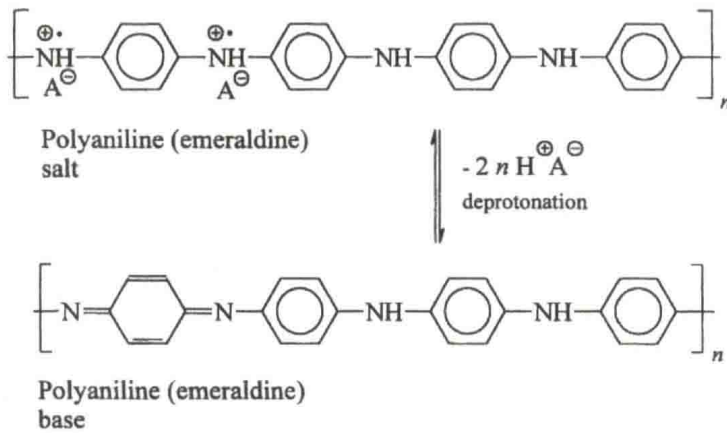


Fig. 5. Polyaniline (emeraldine) salt is deprotonated in the alkaline medium to polyaniline (emeraldine) base. (A⁻ is an arbitrary anion, e.g., chloride.)

Medium	Coating	$-E_0$ (V)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	γ	S'/S
3.5% NaCl water solution	Control without PANI	0.99	3.6	–	2
	Undoped PANI	0.75	0.3	12	2.5
	PANI-TSA	0.76	0.72	5.0	12.4
	PANI-CSA	0.85	4.55	0.79	1
	PANI-DBSA	0.68	4.2	0.86	1.6
0.1 N HCl water solution	Control without PANI	0.7	3.2	–	2
	Undoped PANI	0.62	0.72	4.4	6.4
	PANI-TSA	0.72	2.3	1.4	21.7
	PANI-CSA	0.58	4.86	0.66	1
	PANI-DBSA	0.68	3.5	0.91	2

Table 1. Results of the electrochemical monitoring of coats doped and undoped PANI on Al 3003 in 3.5% NaCl and 0.1 N HCl solutions

Bajat et al (2008) have studied the electrochemical and transport properties and adhesion of epoxy coatings electrodeposited on aluminium pretreated by vinyltriethoxysilane (VTES) during exposure to 3% NaCl. The electrochemical results showed that the pretreatment based on VTES film deposited from 5% solution provides enhanced barrier properties and excellent corrosion protection. Niknahad et al. (2010) have studied the influence of various blends of hexafluorozirconic-acid (Zr), polyacrylic-acid (PAA) and polyacrylamide (PAM) pretreatment on the performance of an epoxy coated aluminium substrate. They have employed the salt spray, humidity chambers and EIS to characterize corrosion performance of coated substrates with different initial surface pretreatments. They have found that among the Zr-based formulations, PAA/Zr and PAA/PAM/Zr showed the best adhesion strength, while the later revealed a good corrosion performance as well. Pirhady et al. (2009) have developed silica-based organic-inorganic hybrid nanocomposite films by sol-gel method for corrosion protection of AA2024 alloy. The sol-gel films were synthesized from 3-glycidioxypropyltrimethoxysilane (GPTMS) and tetraethylorthosilicate (TEOS) precursors. They have utilized the potentiodynamic scanning and salt spray tests to study the corrosion protection properties of the films. Their results indicate that the hybrid films provided exceptional barrier and corrosion protection in comparison with untreated aluminium alloy substrate. Kraljic et al. (2003) have electrochemically synthesised the Polyaniline (PANI) from 0.5M aniline solution in 1.5M H₂SO₄ and 0.5M aniline in 3.0M H₃PO₄ by cycling the stainless steel at potential between 400 and 1000 mV for stainless steel. They tested the coated sample in sulphuric acid and phosphoric acid solution and that PANI layer form in H₃PO₄ acid has better protection than PANI layer form in H₂SO₄. This was due to better protection of steel with PANIPO₄ layer which have a higher quality of the oxide film and a smaller area of the PANI-free electrode surface. Ozyilmaz et al. (2004) have coated the thin layer of PANI on the stainless steel in oxalic acid solution containing aniline using potentiodynamic cycle between -0.7 and 1.65V. They have observed that the passivations of the substrate and monomer oxidation prior to film growth for both potential ranges were necessary for the polymerization process. They have investigated the corrosion performance of coated stainless steel using electrochemical impedance spectroscopy in hydrochloric acid. Nyquist curves were revealed that coated stainless steel had different corrosion behaviors according to the potential range used for the polymerization. They have observed that the permeability of PANI film was affected by synthesis condition. Bereket et al. (2005) have successfully synthesized the polyaniline (PANI), poly(2-iodoaniline) (PIANi), and poly(aniline-co-2-iodoaniline) (co-PIANi) using cyclic voltammetry in acetonitrile solution containing tetrabutylammonium perchlorate (TBAP) and perchloric acid (HClO₄) on 304-stainless steel electrodes. Their results showed that the polymer and copolymer were different from that of PANi. PIANi and co-PIANi behaved in a similar manner with regard to the corrosion protection of 304- SS in 0.5 M HCl. They found that this is related with the prevention of cathodic reaction taking place at film-solution interface. PANI coatings were able to provide an effective anodic protection addition to barrier properties for the cathodic reaction. Based on research by Shabani-Nooshabadi et al. (2009), homogeneous and adherent polyaniline coatings can be electrosynthesized on aluminium (Al) alloy 3004 from an aqueous solution containing aniline and oxalic acid using galvanostatic conditions 0.5, 1.5, 5 and 15mAcm⁻² for 1800 second. They found that the electrochemical polymerization of aniline on Al takes place after the passivation of its surface via the formation of Al oxalate