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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.

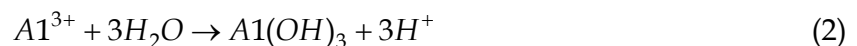
3.1 Galvanic corrosion

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:

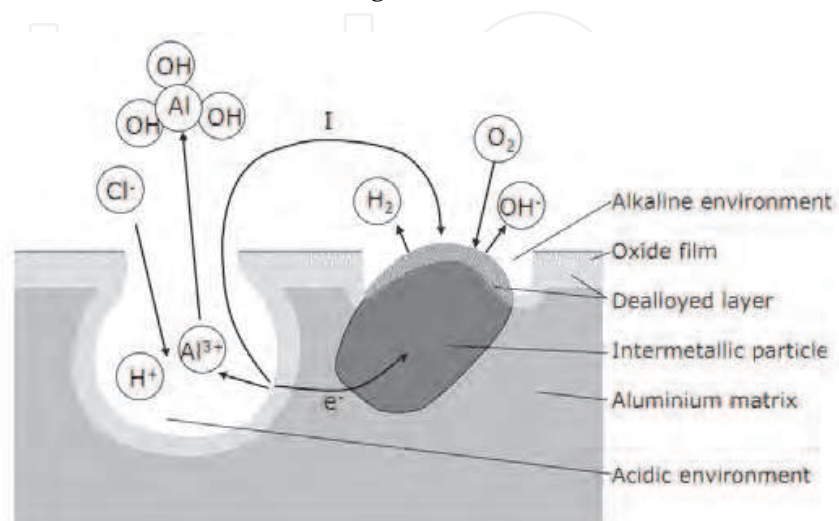


Fig. 2. Pitting corrosion mechanisms for the aluminium.



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 alkalinisation 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.

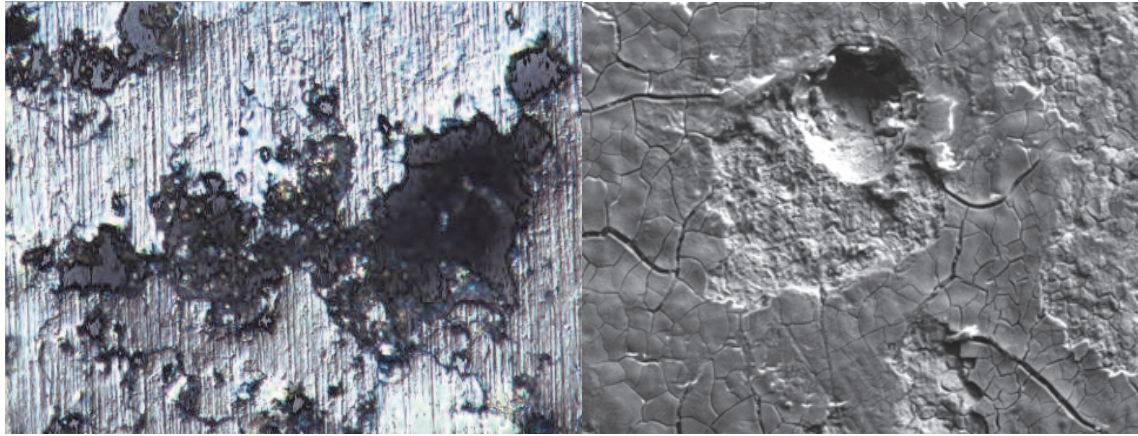


Fig. 3. SEM images showing the pitting corrosion for the aluminium

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.

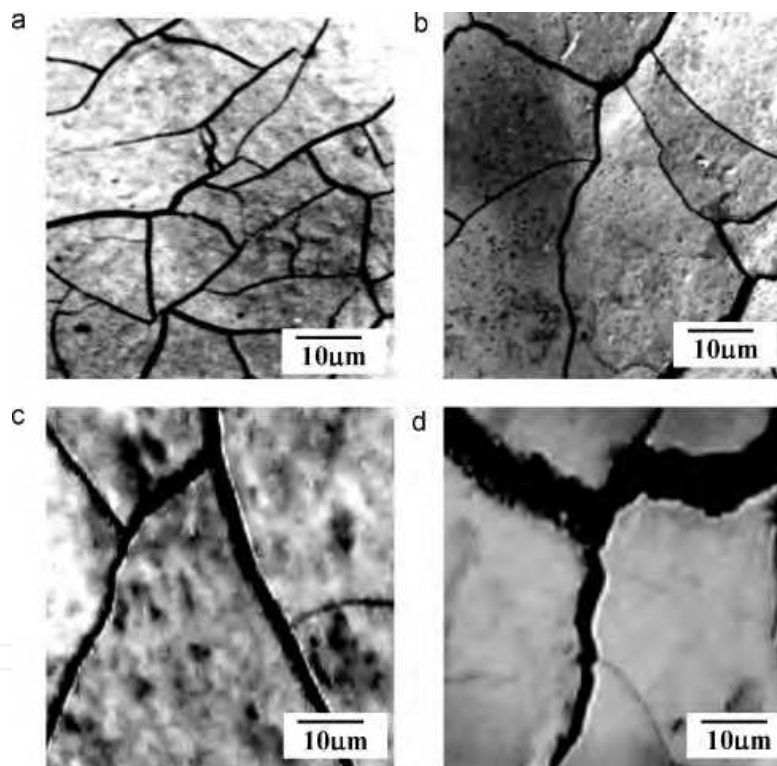


Fig. 4. Optical micrographs of the surfaces of 7075-T6 aluminium alloy specimens exposed to a deaerated 0.5 M NaCl solution at -685 mVSCE: (a) as-received specimen and (b), (c) and (d) specimens with grain sizes of 40, 130 and 290 μm , respectively (El-Amoush, 2011)

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.

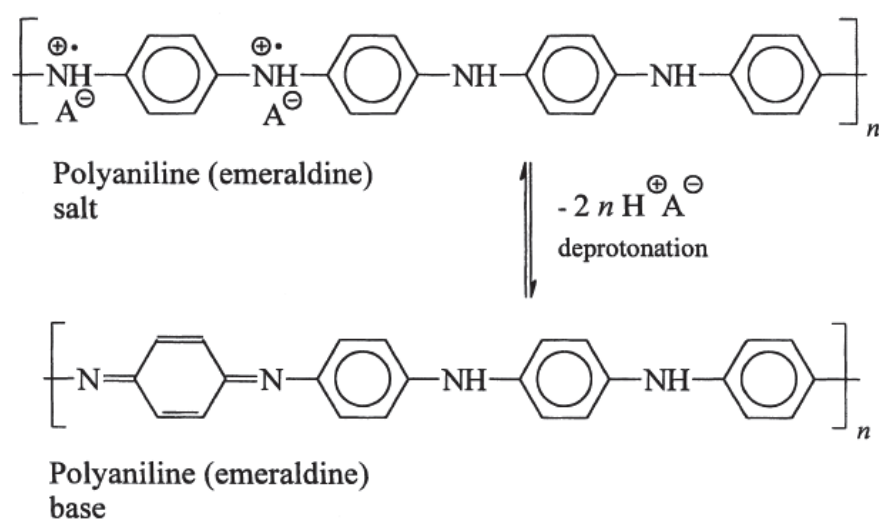


Fig. 5. Polyaniline (emeraldine) salt is deprotonated in the alkaline medium to polyaniline (emeraldine) base. (A $^-$ is an arbitrary anion, e.g., chloride.)

Medium	Coating	$-E_0$ (V)	i_{corr} (μ A/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-glycidoxypropyltrimethoxysilane (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

complex and results in the generation of green, uniform and strongly adherent polyaniline coatings. The potentiodynamic polarization and EIS studies reveal that the polyaniline acts as a protective layer on Al against corrosion in 3.5% NaCl solution.

Kenneth et. al. (2003) have electrodeposited the polyaniline films at pure aluminium from a tosylic acid solution. They found that these polymer films exhibited similar characteristics as pure polyaniline electrosynthesized at an inert platinum electrode, when removed from their respective substrates. A galvanic interaction between the polymer and the aluminium was observed giving rise to oxidation of the aluminium substrate and reduction of the polymer. Although the aluminium substrate was oxidized there was little evidence of any corrosion protection by the polyaniline coatings. The coated electrode was tested by polarizing the electrode, they found that attack at the aluminium substrate occurred underneath the polymer, and this indicate that chloride anions diffuse across the polymer to react at the underlying substrate.

Martins et al. (2010) have synthesised the polyaniline films on aluminium alloy 6061-T6 in sulphuric acid by electrodeposition using cyclic voltammetry and potentiostatic polarization. They tested the coated electrode using electrochemical techniques to assess the anticorrosive properties of the coatings. From anodic polarization curves, they found out that the corrosion resistance of the coated alloy was not higher than the bare alloy. The values of the corrosion and pitting potentials remain unchanged and the system undergoing pitting corrosion. Due to the conductive character of the polymer, the tests were not conclusive.

Kamaraj et al. (2009) have electropolymerised aniline on AA 7075 T6 alloy from oxalic acid bath by galvanostatic polarization. FTIR spectroscopy studies revealed the presence of both benzenoid and quinoid structures confirming the presence of partially oxidized polyaniline (Emeraldine salt) which is known for its conducting nature. They evaluate these coatings in 1% NaCl by electrochemical impedance spectroscopy and potentiodynamic polarization. They found that there is poor corrosion resistant behaviour due to galvanic action of polyaniline. However, cerium post-treatment for the polyaniline coatings on AA 7075 T6 alloys exhibited very high corrosion protection performance. This is due to decreased rate of oxygen reduction reaction by forming cerium oxide coating on the pinholes in corrosive media containing chloride anions.

4.2 Corrosion inhibitors

Corrosion inhibitors are organic or inorganic chemical substances which, when added at low concentrations, are capable of preventing or controlling corrosion in 80–90% in most cases (Gonza et. al. 2008). According to ISO 8044, corrosion inhibitor is defined as chemical substance that can reduce the corrosion rate with the present of in small concentration without changing the concentration of corroding agent in a corrosion system. Corrosion inhibitor reduces the rate of corrosion with increase the polarization behaviour of anode and cathode. Apart from that, lower the movement of ion to absorb to metal surface and finally increase the electrical resistance on metal surface (Roberge, 2000).

The shortage of inorganic corrosion inhibitors has increased the demands and interest in organic compounds. Many organic compounds have been reported as effective corrosion

inhibitors in the literature, but not a great many are ever used in practical systems. Any practical inhibitor must possess properties beyond its ability to control corrosion including cost, toxicity, and compatibility with the expected environment. Available references to corrosion phenomena in the technical literature appeared by the end of the 18 century. The first patent in corrosion inhibition was given to Baldwin, British Patent 2327. Robinson and Sutherland in 1900, US Patent 640491, were using starch as corrosion inhibitor (Hackerman 1990). Since 1950s, the scientific tone on studying corrosion inhibition mechanism was increased and the conversion of the field from art to science has started with the recognition of adsorption phenomena (Hackerman 1990). Good inhibition in any system requires an understanding of the chemistry of the system with the inhibitor plus the knowledge of the parameters involved. Corrosion inhibition is reversible, and a minimum concentration of the inhibiting compound must be present to maintain the inhibiting surface film. Good circulation and the absence of any stagnant areas are necessary to maintain inhibitor concentration. Specially designed mixtures are required when two or more alloys are presented in a system (Jones 1996).

Organic compounds, mainly containing oxygen, nitrogen and sulphur atoms and having multiple bonds, are recognized as effective inhibitors of the corrosion of many metals and alloys. In different media, for a given metal, the efficiency of the inhibitor depends on the stability of the formed complex and the inhibitor molecule should have centres, which are capable of forming bonds with the metal surface via an electron transfer. Generally, a strong co-ordination bond causes higher inhibition efficiency, the inhibition increases in the sequence $O < N < S < P$ (Musa et al. 2009).

Acid solutions are used for pickling, chemical and electrochemical etching of Al foil and lithographic panels which substitute metallic zinc. Since the metal dissolution in such solutions is rather large, it is necessary to inhibit it by the addition of inhibitors, which should provide a good quality pickled metal surface. For cleaning and descaling; acid solution is also widely used in industry (Yao et al. 2007). Acid cleaning baths are employed to remove undesirable scale from the surface of the metals. Once the scale is removed, the acid is then free for further attack on the metal surface. The use of inhibitor is one of the most practical methods for protection against corrosion, especially in acidic media (Touir et al. 2008).

Umoren et al (2008) have studied the inhibition of aluminium corrosion in hydrochloric acid solution by exudate gum from *Raphia hookeri*. In this research, the corrosion inhibition of aluminium in HCl solution in the presence of exudate gum from *Raphia hookeri* at temperature range of 30 to 60°C was studied using weight loss and thermometric techniques. The exudate gum acts as an inhibitor in the acid environment. Results of this research are the inhibition efficiency increases with increase in inhibitor concentration. However, the inhibition efficiency decreases with an increase in temperature. Elewady et al. (2008) have studied the effect of anions on the corrosion inhibition of aluminium in HCl using ethyl trimethyl ammonium bromide as cationic inhibitor. The corrosion inhibition of aluminium in hydrochloric acid solution in the presence of ethyl trimethyl ammonium bromide (ETMAB) at temperature range of 30-50°C was studied using the weight loss and polarization techniques. The effect of addition of anions (I⁻, SCN⁻, Br⁻) is also reported. The

inhibition efficiency (%IE) increased with increase in concentration of ETMAB. The addition of the anions increased the inhibition efficiency to a considerable extent. The inhibitive action of ETMAB was discussed on the bases of its adsorption on the metal surface, which follow Freundlich adsorption isotherm. The synergistic effect of ETMAB and anions was discussed. Galvanostatic polarization curves indicated that the inhibitor behaves as mixed-type inhibitor. Pinto et al. (2011) have characterized the inhibitory effect of 4-(N,N-dimethylamino) benzaldehyde thiosemicarbazone (DMABT) on the corrosion behaviour of 6061 Al-15 vol. pct. SiC(p) composite and its base alloy at different temperatures in acid mixture medium containing varying concentrations of hydrochloric acid and sulphuric acid using Tafel extrapolation technique and ac impedance spectroscopy (EIS). They have found that inhibition efficiencies increase with the increase in inhibitor concentration, but decrease with the increase in temperature and with the increase in concentration of the acid media. They have determined the thermodynamic parameters for dissolution process and they found that the adsorption of DMABT on both the composite and base alloy was physisorption obeying Freundlich adsorption isotherm. Figure 6 shows the SEM images of the composite in uninhibited and inhibited solutions.

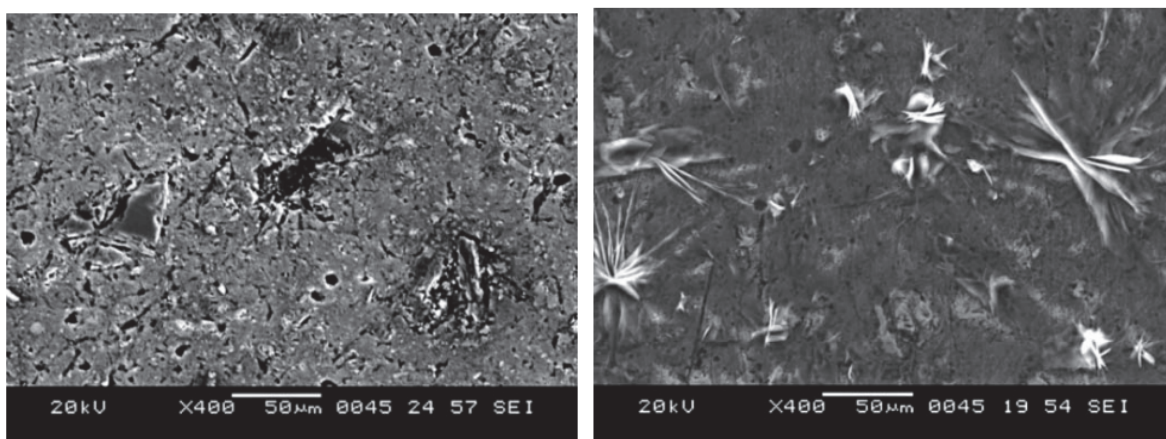


Fig. 6. SEM image of the surface of composite after immersion for 2h in 0.5 M H_2SO_4 at 30°C in (A) absence and (B) presence of 400 ppm of DMABT. (Pinto et al. 2011)

Helal and Badawy (2011) have investigated the corrosion inhibition of Mg-Al-Zn alloy in stagnant naturally aerated chloride free neutral solutions using amino acids as environmentally safe corrosion inhibitors. They have calculated the corrosion rate in the absence and presence of the corrosion inhibitor using the polarization technique and electrochemical impedance spectroscopy. They have found that Phenyl alanine has corrosion inhibition efficiency up to 93% at a concentration of 2×10^{-3} mol dm^{-3} . The free energy of the adsorption process revealed a physical adsorption of the inhibitor molecules on the alloy surface. Harvey et al. (2011) have studied a range of structurally-related compounds for their capacity to inhibit corrosion on aluminium alloys AA2024-T3 and AA7075-T6 in 0.1 M NaCl solution. Their selected compounds are shown in Figure 7. They found that the thiol group, positions para- and ortho- to a carboxylate, and substitution of N for C in certain positions strongly inhibited corrosion. The hydroxyl group is slightly inhibitive, while the carboxylate group provided little or no corrosion inhibition on its own.

In several cases, different activities are found on the different alloys, with some compounds (particularly thiol-containing compounds) being more effective on AA2024 than on AA7075. Halambek et al. (2010) have reported *Lavandula angustifolia* L. as corrosion inhibitor of Al-3 Mg alloy in 3% NaCl solution using weight loss, polarization measurements and SEM. The oil dissolved in ethanol and used as 30% (v/v) solution, is found to retard the corrosion rate of Al-3 Mg alloy even at high temperatures. The inhibiting effect of lavender oil components on Al-3 Mg surface is attributed to the Langmuir's adsorption isotherm. It was found that the *L. angustifolia* L. oil provides a good protection to Al-3 Mg alloy against pitting corrosion in sodium chloride solution, see Figure 7. Noor (2009) has studied the inhibitive action of some quaternary N-heterocyclic compounds namely 1-methyl-4[4(-X)-styryl]pyridinium iodides (X: -H, -Cl and -OH) on the corrosion of Al-Cu alloy in 0.5 M HCl solutions using potentiodynamic polarization, electrochemical impedance spectroscopy and weight loss measurements. She found that the studied compounds are cathodic inhibitors without changing the mechanism of hydrogen evolution reaction. The adsorption of all inhibitors on Al-Cu alloy obeys Langmuir adsorption isotherm. Her data revealed that the studied compounds have good pickling inhibitor's quality as they perform well even at relatively high temperature.

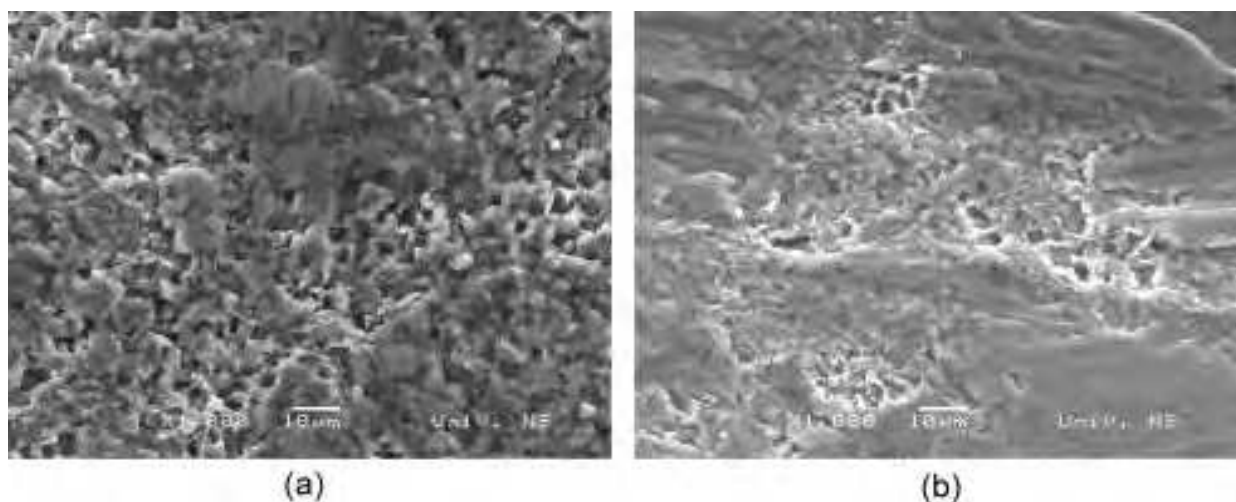


Fig. 7. SEM micrographs of the surface of Al-3 Mg alloy samples after electrochemical tests (polarization measurements) in 3% NaCl solution: (a) without lavender oil; (b) containing 20 ppm lavender oil.

Mishra and Balasubramaniam (2007) have investigated the effect of LaCl_3 and CeCl_3 inhibitor additions in 3.5% NaCl solution on the corrosion behaviour of aluminium alloy AA2014. Their results showed that polarization resistance increased significantly and the corrosion rate decreased by an order of magnitude with the addition of 1000 ppm of LaCl_3 and CeCl_3 , with maximum decrease noticed for CeCl_3 . Their SEM monographs confirmed formation of precipitates of oxide/hydroxide of lanthanum and cerium on cathodic intermetallic sites, which reduced the overall corrosion rate, see Figure 8.

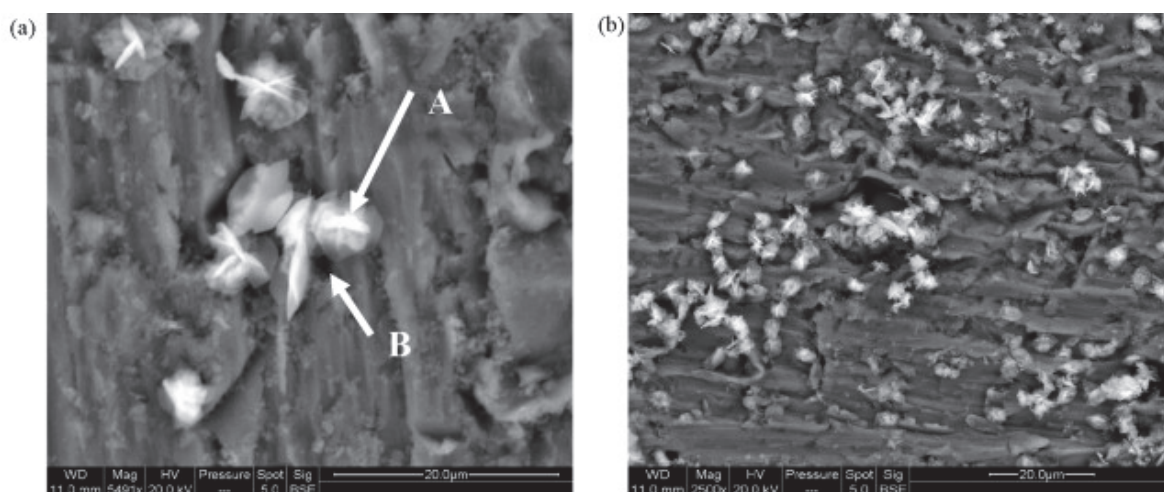


Fig. 8. SEM micrograph of surface after immersion for 4 h in 3.5% NaCl solution (a) with 500 ppm LaCl₃, (b) with 1000 ppm LaCl₃.

control	Chromate (Cr(VI))	100 ± 0	100 ± 0
1A	4,5-diamino-2,6-dimercaptopyrimidine	87 ± 0	80 ± 0
1B	4,5-diaminopyrimidine	47 ± 3	84 ± 2
1C	Na-(diethyl(dithiocarbamate))	97 ± 1	96 ± 4
1D	2-mercaptopyrimidine	89 ± 4	50 ± 2
1E	Pyrimidine	-153 ± 1	-220 ± 16
1G	Na-benzoate	-80 ± 14	-62 ± 9
1H	Thiophenol	93 ± 5	87 ± 4
1I	Pyridine	-139 ± 18	-150 ± 16
1J	Na-(4-phenylbenzoate)	-72 ± 6	-143 ± 1
1K	Na-4-hydroxybenzoate	-34 ± 5	-56 ± 28
1L	Na-4-mercaptobenzoate	97 ± 2	76 ± 1
1M	Na-(6-mercaptonicotinate)	94 ± 0	86 ± 0
1N	Na-nicotinate	-107 ± 11	-91 ± 26
1O	Na-isonicotinate	-12 ± 1	-45 ± 17
1P	Na-picolinate	58 ± 0	14 ± 2
1Q	Na-3-mercaptobenzoate	16 ± 8	-22 ± 2
1R	Na-salicylate	-175 ± 32	-89 ± 13
1S	Na-2-mercaptobenzoate	88 ± 0	80 ± 0
1T	Na-2-mercaptonicotinate	83 ± 2	70 ± 4
1U	Na-(2,3-mercaptosuccinate)	82 ± 1	48 ± 2
1V	Na-mercaptoacetate	96 ± 1	83 ± 0
1W	Na-mercaptopropionate	100 ± 0	31 ± 9
1X	Na-acetate	-12 ± 8	15 ± 8

Table 2. Compounds in Fig. 8 tested for corrosion inhibition of AA2024 and AA7075 in 0.1 M NaCl at 21 °C for 4 weeks. The prefix Na- denotes the mono-sodium salt. Positive inhibitor efficiencies indicate corrosion was retarded while negative values indicate it was accelerated. All compounds were tested at 1 mM, except 1A (0.5 mM) and 2D (0.1 mM) due to their low solubility. (Harvey et al. 2011)

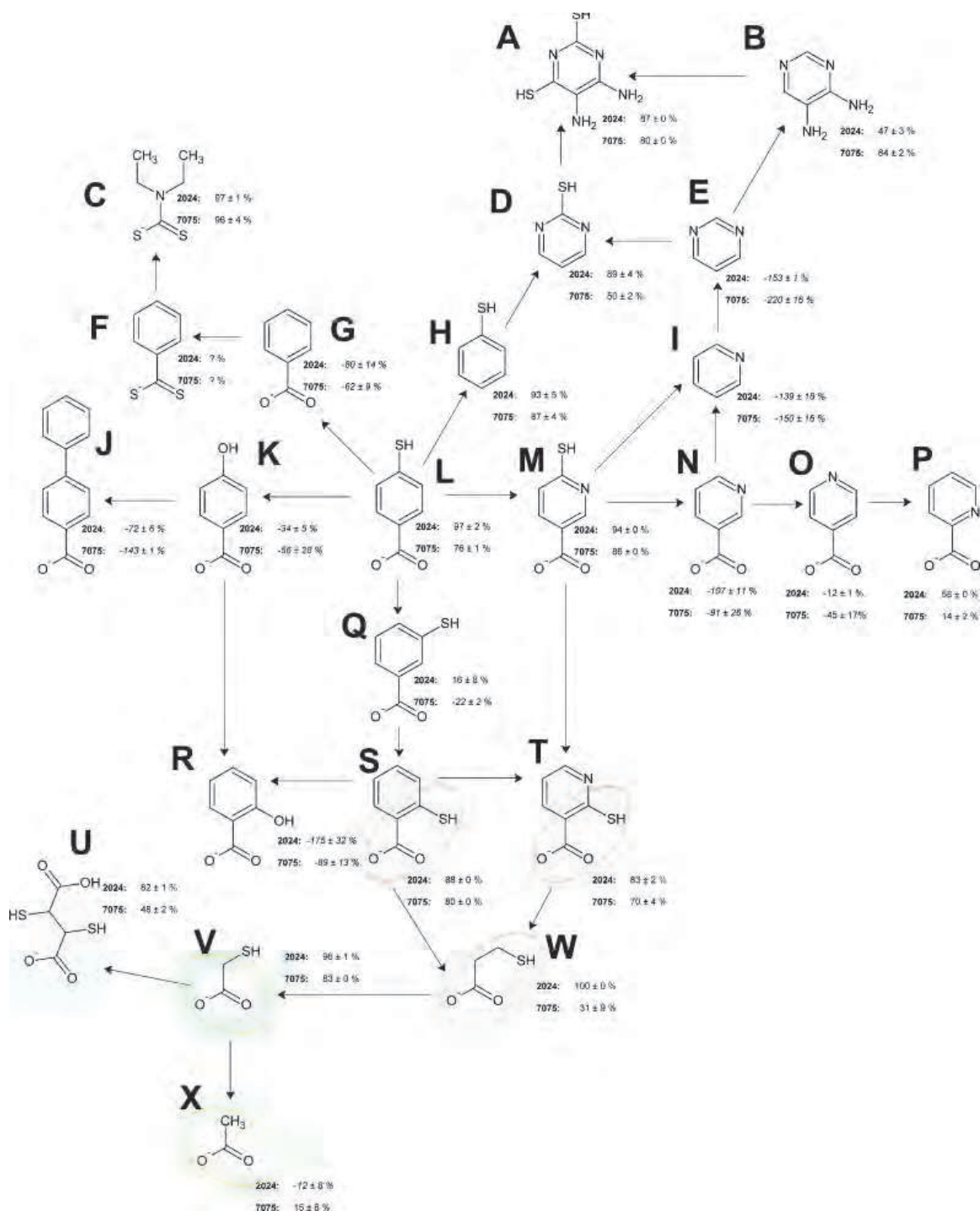


Fig. 9. Illustration of the structures of inhibitors listed in Table 2, showing structural relationships. (Note: similar sub-structures are highlighted with coloured circles.) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this paper, (Harvey et al. 2011))

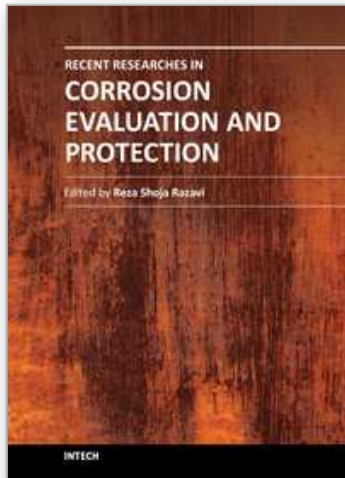
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