

INFLUENCE OF THE ANODIC OXIDATION TREATMENT ON THE CORROSION BEHAVIOUR OF ALUMINIUM AND ALUMINIUM ALLOYS

Valentin DUMITRAȘCU, Lidia BENEĂ*

Research (Competences) Centre: Interfaces-Tribocorrosion and Electrochemical Systems (CC-ITES),
Engineering Faculty, Dunărea de Jos University of Galati, 47 Domnească Street, RO-800008, Galati, Romania

*Corresponding author
e-mail: Lidia.Benea@ugal.ro

ABSTRACT

This paper deals with the effect of anodic oxidation treatment on the corrosion behaviour of 6061 aluminium alloy in natural sea water. Anodic oxidation treatment leads to the formation of an amorphous oxide layer on the top surface of 6061 aluminium alloy as shown by optical microscopy results. The corrosion behaviour was investigated in natural sea water, harvested from the Black Sea, Mangalia harbour. The study was done by in situ electrochemical methods such as: open circuit potential (OCP), electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (PD) and cyclic voltammetry polarization (CV). The results show that the untreated 6061 aluminium alloy undergoes severe corrosion in natural sea water in comparison with anodized 6061 aluminium alloy. The results obtained by different electrochemical methods were in good agreement with each other and showed an improved corrosion resistance of the anodic oxide layer formed on aluminium alloy in natural sea water. The results were confirmed by optical microscopy.

KEYWORDS: anodic oxidation, aluminium, corrosion, aluminium alloy

1. Introduction

Materials with unusual combination of properties like low densities, strength, stiffness and impact resistance and which are not easily corroded are needed for aerospace, underwater and transportation applications and all of these conditions cannot be met by metals, conventional metallic alloys, ceramics and polymeric materials [1].

The nanocomposite and nanostructured materials can be fabricated by different physico-chemical methods such as chemical vapour deposition, sol-gel deposition, electrodeposition, electroless deposition. Electrodeposition and anodic oxidation are bottom-down methods to fabricate functional surfaces with nanoscale structures.

Aluminium alloys are widely employed within the spacecraft industry and they provide the required mechanical and corrosion properties, the choice of alloy series depending on application [2].

The surface modifications of aluminium alloy are generally performed by anodic oxidation, chemical oxidation, coatings, electroplating, etc. In

order to improve the mechanical and electrochemical performance of aluminium alloys for corrosion protection, anodic structured oxide layers are always preformed before their application in automobile, marine and construction industries [3].

The development and application of anodic oxidation technology is the most rapid and versatile. Anodic films, composed of amorphous alumina, are formed by application of an anodic potential to aluminium that is immersed in a suitable electrolyte. For slightly alkaline electrolytes or those close to neutrality, when the solubility of the oxide is low, compact oxides (barrier-type films) are usually generated. In contrast, in electrolytes in which the solubility of the oxide is increased, porous oxides can be formed. The porous oxides are very important for industrial applications [4].

The major topics for corrosion research in relation to aluminium alloys have included localised corrosion of aluminium alloys containing magnesium, stress corrosion cracking of alloys used in aerospace applications, galvanic corrosion of aluminium in atmospheric and automotive applications, corrosion

inhibition and most recently the filiform corrosion of aluminium sheet [5].

The structural characteristics of the anodic oxide film formed on the aluminium surface and the intensity of corrosion attack are influenced by (i) the chemical composition of the exposed alloys, (ii) the presence and distribution of micro-defects (vacancies, voids, etc.) as well as macro-defects (inclusion, second phase particles) and (iii) by electrolyte composition (pH, halide concentration, temperature). In general, pitting on the aluminium alloy surface takes place in the presence of an electrolyte within a 4.5–8.5 pH range and tends to increase with an increase in temperature, concentration of aggressive ions and stagnation of the electrolyte [6].

Different types of aluminium alloy present different corrosion behaviour in marine environment due to the distribution of the intermetallic phases. The presence of different alloying elements can promote the formation of corrosion micro-cells and initiates the local corrosion process [7].

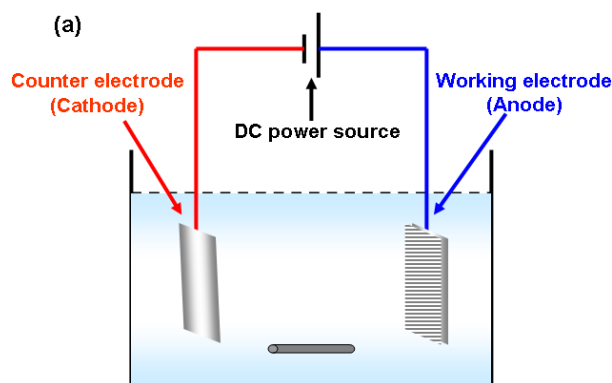
However, the corrosion behaviour of the aluminium alloys is poor in marine environmental and tends to localized corrosion, pitting corrosion, intergranular corrosion, etc. which can affect the service life of aluminium alloy components.

The anodic oxide film on the surface of 6061 Aluminium alloy was generated in sulphuric acid anodization bath. The aim of this work was to evaluate and compare the corrosion behaviour of 6061 aluminium alloy before and after the anodic oxidation process, in sea water harvested from the Black Sea, Mangalia harbour by electrochemical methods.

2. Experimental procedure

2.1. Materials

The tested material selected for study is 6061



aluminium alloy. The composition of the 6061 aluminium alloy specimens is given in Table 1.

Table 1. Composition of the 6061 aluminium specimens (% by weight)

Element	Composition (%)
Si	0.4
Fe	0.2
Cu	0.15
Mn	0.15
Mg	0.8
Cr	0.04
Zn	0.25
Ti	0.15
Al	Balance

2.2. Preparation of anodic films

Before the anodization process, the samples of 6061 aluminium alloy with rectangular shape of 20x20x2 mm were connected with a copper wire and isolated with epoxy resin to delimit the active surface. The samples were degreased with acetone, rinsed with deionized water and dried at room temperature.

The electrochemical cell set-up used in anodization process, shown in Fig. 1 (a), consists of two electrodes, the first one being the sample of 6061 Aluminium alloy used as working electrode (anode) and the other one being the counter electrode (cathode). The anodizing process was carried out in 300 mL electrolyte of 1M H₂SO₄ to which 1 gL⁻¹ of Al₂(SO₄)₃·18H₂O was added. The temperature was maintained at 25 ± 1 °C.

After the anodization process, the samples were washed with deionized water and boiled in deionized water for 5 min. at 95 °C in order for the pores to be sealed.

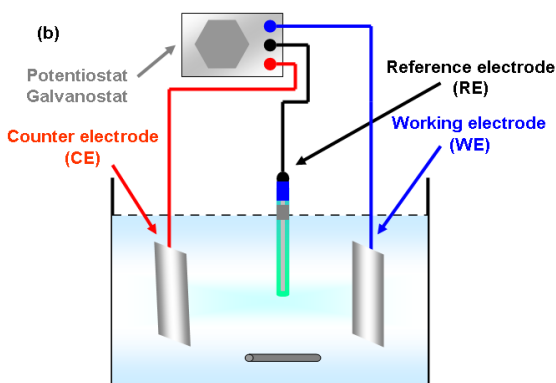


Fig. 1. (a) The anodization cell set-up and (b) the electrochemical cell set-up for corrosion tests

2.3. Characterization methods

The comparative corrosion behavior was tested in natural sea water, harvested from the Black Sea, Mangalia harbor. The characteristics of sea water are presented in Table 2.

Table 2. Characteristics of sea water

pH	Conductivity [mS]	Salinity [ppt]
7.63	21	12.4

The surface morphology of anodized 6061 aluminium alloy was compared with that of polished metal surface using the optical microscope OPTIKA XDS-3 MET.

The optical microscope images were recorded to establish the interaction of sea water environment with the surface of 6061 aluminium alloy. After the immersion of untreated and anodized 6061 aluminium alloy in natural sea water, the surface morphology was compared to the images recorded before immersion.

Electrochemical tests were carried out using a VoltaLab PGZ 100 potentiostat/galvanostat. It was used a conventional three-electrode cell shown in Fig. 1 (b) consisting of 6061 aluminium sample as working electrode (WE), an Ag/AgCl (saturated solution of KCl, $E=199$ mV vs. Standard Hydrogen Electrode) as reference electrode (RE) and Pt-Rh grid as counter electrode (CE). The surface area exposed to the electrolyte was about 1.7 cm^2 . The electrochemical methods applied were: open circuit potential, potentiodynamic polarization and cyclic voltammetry.

3. Results and discussion

3.1. Surface characterization of the coatings before and after anodic oxidation

Fig. 2. displays the comparative surfaces morphologies of untreated 6061 aluminium alloy and 6061 aluminium alloy after the anodic oxidation treatment.

From Fig. 2 (a) it can be observed that the surface of untreated 6061 aluminium alloy is characterized by irregular shape with no homogenous distribution. Fig. 2 (b) shows the typical surface of 6061 aluminium alloy after the anodic oxidation in $1 \text{ M H}_2\text{SO}_4$ to which $1 \text{ g/L Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ was added for 45 min at a constant current density of 15 mA/cm^2 . Anodizing time, current density and electrolytes are important parameters in determining the film thickness of porous alumina. The specified parameters are established after many experiments regarding the current density and time of the anodizing process.

After oxide film formation, the samples were boiled in deionised water for 5 min. at 95°C to obtain a real barrier oxide layer with closed pores. From Fig. 2 (b) it can be observed that the anodized aluminium surface presents a rough surface. The anodic film generated on the 6061 aluminium alloy appears to be more regular, with relatively straight pores and continuous cell walls. This occurs because the oxidation of the major alloying element, magnesium, proceeds immediately with aluminium and does not induce oxygen generation within the barrier layer and consequent lateral porosity [8].

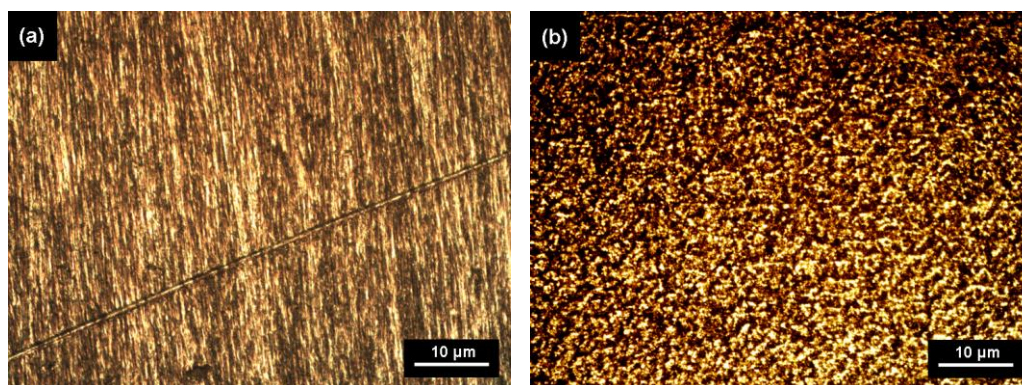


Fig. 2. Optical micrograph of 6061 aluminium alloy (a) before and (b) after the anodic treatment

3.2. Evolution of open circuit potential (OCP)

When an electrically conductive material is immersed in an electrolyte, a potential difference

called electrode potential appears at the solution material interface. The analysis of the potential versus time offers useful information about the behavior of material in contact with a wet corrosive environment. In Fig. 3. is shown the evolution of the open circuit

potential (OCP) of untreated 6061 aluminium alloy and anodized 6061 aluminium alloy.

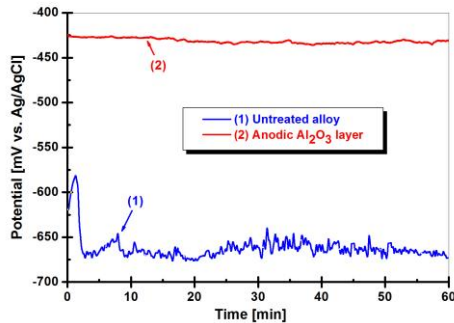


Fig. 3. Evolution of open circuit potential for: (1—) untreated and (2—) anodic oxidized 6061 aluminium alloy in sea water

From Fig. 3 it can be observed that the potential of anodic aluminium oxide layer is stable around -425 mV vs. Ag/AgCl. After the immersion of untreated 6061 aluminium alloy in sea water it can be observed that the potential initially decreased rapidly because of dissolution of air-formed aluminium oxide and after that, the potential is stabilized around 660 mV vs. Ag/AgCl. This trend was observed also by F.J. Garcia-Garcia *et al.* [9] when they studied the influence of Ni on corrosion behaviour for 1050 aluminium alloy.

The open circuit behaviour during immersion time indicates that the anodized 6061 aluminium alloy shows more noble and stable corrosion potential value compared to the untreated aluminium alloy. This behaviour of ennoblement of corrosion potential by controlled oxide film formation was also observed by L. Benea *et al.* [10] when they studied the influence of anodic oxidation on the corrosion behaviour of Ti-6Al-4V alloy in physiological fluids.

3.3. Potentiodynamic polarization

The diagrams $I = f(E)$ (intensity-potential curves) shown in Fig. 4 were recorded in a range of potentials starting from -1.2 V to +0.2 V vs. Ag/AgCl at a scan rate of 5 mV/s. Corrosion current density is an important parameter to evaluate the kinetics of the corrosion reactions [11].

The polarization curves were performed to assess the polarization domains for the untreated and anodized 6061 aluminium alloy after immersion in the natural sea water. If the passive state covers a higher potential domain and the passivation current value is smaller, then the metal or alloy shows a high corrosion resistance.

From Fig. 4 it can be observed that for both of the studied surfaces, the cathodic domain is not

present. For anodized 6061 aluminium alloy, the passive current density is very low, being close to zero, indicating a good corrosion resistance for the entire studied domain. For untreated 6061 aluminium alloy, the passive domain is ranged between -1.2 V vs. Ag/AgCl and -0.4 V vs. Ag/AgCl and after that the transpassive domain is observed, where the current density increases since this is a transpassive dissolution. In this domain, the passive film is dissolved and loses its protective properties and even disappears at high potential values.

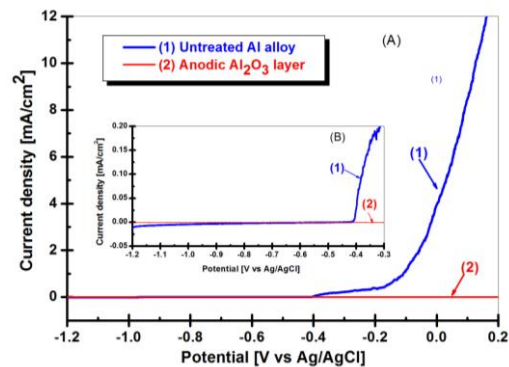


Fig. 4. Potentiodynamic diagrams for: (1—) untreated and (2—) anodic oxidation 6061 aluminium alloy. Layer (A) gives the entire potential domain scanned while layer (B) provides the zoom of recorded diagrams in the passive domain.

From the polarization diagrams by applying the Stern Geary formula (Equation 1) there were calculated the polarization resistances and corrosion current densities. For simple corrosion systems, the corrosion reactions are strictly controlled by charge transfer and the corrosion current density (i_{corr}) can be correlated with the polarization resistance (R_p) by Equation (1).

$$i_{cor} = \frac{B}{R_p} \quad (1)$$

Where: the corrosion rate (i_{corr}) is expressed as corrosion current density in A / cm² and B is a constant related to the system material environment given by the relation:

$$B = \frac{b_a | b_c |}{2,303(b_a + b_c)} \quad (2)$$

Where: b_a and b_c are the Tafel slopes for anodic and cathodic reactions.

The increase of polarization resistance means the decrease of corrosion current density, therefore the decrease of corrosion rate.

From the polarization diagrams, the values of corrosion current densities and polarization resistance for both surfaces are presented in Table 3.

Table 3. The values of corrosion current densities and polarization resistance

Nr crt	Type of surface	Polarization resistance [$kohm \cdot cm^2$]	Corrosion current density [$\mu A / cm^2$]
1	Untreated Al alloy	17.2	0.5
2	Anodized Al alloy	3160	0.0016

The polarization resistance increases from 17.2 $kohm \cdot cm^2$ for untreated 6061 aluminium alloy to 3.16 $Mohm \cdot cm^2$ for anodized aluminium alloy. The corrosion current density decreases from 0.5 $\mu A/cm^2$ for untreated 6061 aluminium alloy to 0.0016 $\mu A/cm^2$ for anodized aluminium alloy.

3.4. Cyclic voltammetry

The cyclic voltammograms (Fig. 5) of untreated and anodized 6061 aluminium alloy were recorded in the potential range of -1.2 V vs. Ag/AgCl to +0.2 V vs. Ag/AgCl at a scan rate of 5 mV/s and then reversed with the same scan rate till the starting potential to form one complete cycle.

The highlighted areas with localized corrosion susceptibility can be seen very well due to the specific hysteresis aspect, in the presence of chloride ions, which presents the anodic transpassivation part of the untreated 6061 aluminium alloy curves [6]. The specific hysteresis aspect indicates that untreated 6061 aluminium alloy is susceptible to pitting and crevice corrosion in marine environment. In comparison with untreated aluminium alloy, anodized aluminium does not reveal pitting corrosion susceptibility behaviour, since the specific hysteresis aspect is completely missing [12].

From Fig. 5 it can be observed that upon the onset of the transpassive region, the current still raises up until the potential is reversed in the case of untreated 6061 aluminium alloy immersed in

seawater, indicating a susceptibility to pitting corrosion. On the other hand, for anodized 6061 aluminium alloy, the potential remains constant on the entire studied range of potential.

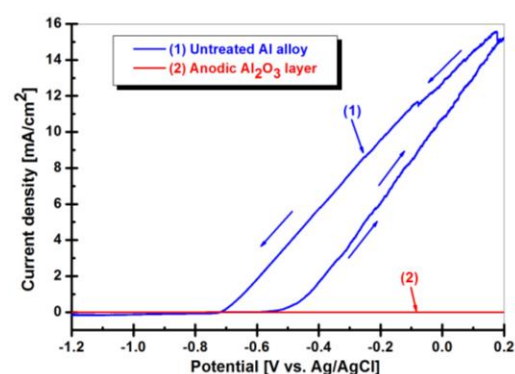


Fig. 5. Cyclic voltammetry for: (1—) untreated and (2—) anodic oxidation 6061 aluminium alloy untreated and anodized 6061 aluminium alloy

3.5. Surface morphology after corrosion tests

The optical microscopy images of freshly polished surface of 6061 aluminium alloy are given in Fig. 2 (a), which shows a polished surface with a few scratches because of polishing and anodized surface of 6061 aluminium alloy in Fig. 2 (b).

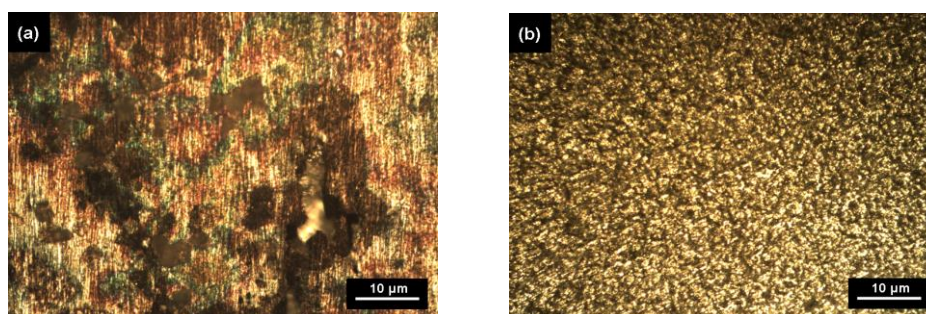


Fig. 6. Optical microscopy after corrosion in sea water for: (a) untreated 6061 aluminium alloy; (b) anodized 6061 aluminium alloy

After the corrosion tests, the surface morphologies of untreated and anodized 6061 aluminium alloy was recorded and are given in Fig. 6 (a). and Fig. 6 (b).

The image of corroded sample presented in Fig. 6 (a) shows the degradation of untreated 6061 aluminium alloy with more and less uniform attack in natural sea water. From Fig. 6 (b) it can be observed that the anodic oxide layer formed after anodic treatment does not undergo any corrosion attack.

4. Conclusion

In this work, the corrosion resistance of untreated and anodized 6061 aluminium alloy was studied by electrochemical methods. The electrochemical methods and surface morphology characterization showed that the anodic oxidation treatment enhanced the corrosion resistance due to the formation of a continuous adherent alumina layer on the aluminium alloy surface.

Electrochemical methods for corrosion resistance evaluation are ideal tools for obtaining detailed information about the characteristics of the anodized aluminium alloy compared to the untreated alloy. They can quantify the changes of the barrier layer with immersion time.

The polarization resistance increases from 17.2 $kohm \cdot cm^2$ for untreated 6061 aluminium alloy to 3.16 $Mohm \cdot cm^2$ for anodized aluminium alloy.

The corrosion rate decreases from 0.5 $\mu A/cm^2$ for untreated 6061 aluminium alloy to 0.0016 $\mu A/cm^2$ for anodized aluminium alloy.

From the cyclic voltammograms of both studied surfaces it can be observed that the untreated 6061 aluminium alloy presents the specific hysteresis which indicates the susceptibility to pitting and crevice corrosion in comparison with anodized aluminium alloy.

The better corrosion resistance of anodized oxide layer formed on aluminium alloy results is confirmed by the optical microscopy images obtained after corrosion tests.

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