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CORROSION BEHAVIOR OF 1050 AND 3003 ALUMINUM ALLOYS USED IN NAVAL INDUSTRY

Valentin Marian DUMITRAȘCU, Camelia STAICU, Lidia BENEA[*]
Research (Competences) Centre: Interfaces-Tribocorrosion and Electrochemical Systems (CC-ITES), Faculty of Engineering, “Dunarea de Jos” University of Galati, 47 Domneasca Street, RO-800008, Galati, Romania
e-mail: lidia.benea@ugal.ro

ABSTRACT

The most important requests for new materials used in marine aggressive corrosion environment are the corrosion resistance and the susceptibility to localized and pitting corrosion. The corrosion behavior of 1050 and 3003 aluminum alloys in natural seawater were characterized by electrochemical measurements, including open circuit potential, linear polarization, polarization resistance and cyclic voltammetry. Stability, polarization resistance, corrosion rate and pitting susceptibility were determined. 1050 aluminum alloy shows an increase of polarization resistance and improved corrosion resistance in natural seawater compared to 3003 aluminum alloy. The optical micrographs taken after corrosion assays are in good agreement with the recorded electrochemical measurements.

KEYWORDS: aluminum alloys, corrosion behavior, marine environment, electrochemical measurements

1. Introduction

Material competition in the marine industry has been traditionally intensive. Even if steel is the most common material used for ship and off-shore constructions, new materials are developed in order to decrease the weight, to increase the life time and also to decrease the maintenance costs and exhaust emissions. The increase of corrosion resistance and enhance the environmental protection are the most important requests for new materials used in marine aggressive corrosion environment. Weight reduction associated with increasing corrosion resistance have led to the development of lightweight materials such as aluminum alloys or polymeric materials.

Due to their workability and low density, aluminum and its alloys have been the first-choice material for different industries [1, 2]. Different aluminum alloys are used in marine industry, due to their mechanical properties such as: hardness, elongation, tensile strength or thermal conductivity. Generally, these properties are offered by the alloying elements or impurities entrapped into aluminum matrix.

Usually aluminum alloys of 1xxx and 3xxx series have been widely used for cooling exchange or heat exchange systems due to their high thermal conductivity and corrosion resistance in comparison with traditional material used such as stainless steel or copper alloys [3, 4].

After exposure to an oxygen-containing environment, aluminum and its alloys are immediately covered by a dense thin aluminum oxide film. Unfortunately, the native aluminum oxide film has thickness of a few nanometers and present vacancies, faults and voids [5, 6] or inclusions, second phase particles [7], that cause the susceptibility to corrosion in the presence of chloride ions and therefore restricting their applications [8]. Different forms of corrosion such as localized corrosion (pitting corrosion, intergranular corrosion) or generalized corrosion, exfoliation corrosion even stress corrosion may occur after exposure of aluminum and its alloys in corrosive environments [1].

The mechanism of the corrosion process is not established considering the specific role of alloying elements. The increased number of alloying elements in the materials led to a very complex corrosion behavior [9].

The corrosion initiation is generally believed to begin by the rupture or breakdown of the passive film upon the metallic surface, usually into defects zone or around intermetallic particles which exhibits different surface film characteristics to the aluminum matrix [10, 11].

This study intends to investigate by electrochemical methods and optical microscopy the corrosion resistance of two different aluminum alloys: 1050 aluminum alloys (Al1050) and 3003 aluminum alloy (Al3003) after immersion in natural seawater sampled from Black Sea, Navodari port.

2. Materials and methods

The samples with dimensions of 40 mm x 20 mm x 2 mm were cut from Al1050 and Al3003 sheets. The chemical compositions are presented in Table 1. The samples were mechanically wet-polished with SiC grinding paper (between #1500 and #2000), cleaned with alcohol, etched with NaOH 5M for 30 seconds, rinsed with deionized water, cleaned with alcohol into ultrasonic bath for 5 minutes, rinsed again with deionized water and finally dried with hot air at 60 °C for 60 minutes. As prepared Al1050 and Al3003 samples were isolated with epoxy resin in order to obtain 1 cm^2 active surface area.

***Table 1.** Chemical composition of Al1050 and Al3003*

	Si [%]	Fe [%]	Cu [%]	Mn [%]	Ti [%]	Cr [%]	Zn [%]	Others [%]	Al [%]
Al1050	0.5	0.5	0.05	0.1	0.05	0.01	0.1	0.01	Balance
Al3003	0.6	0.7	0.2	1	-	-	0.1	0.015	Balance

The electrochemical corrosion assays were performed in aerated natural seawater with chemical parameters presented in Table 2, using a Potentiostat/Galvanostat VoltaLab – PGZ301 controlled with VoltaMaster 4 software. For corrosion experiments it was used a standard electrochemical cell with Pt-Rh grid as counter electrode, Saturated Calomel Electrode–SCE (saturated KCl solution, E= +241 mV vs. Normal Hydrogen Electrode-NHE) as reference electrode and the prepared samples (Al1050 and Al3003) as working electrode.

***Table 2.** Chemical parameters of natural seawater harvested from Black Sea*

	pH	**Conductivity [mS]**	**Salinity [‰]**
Natural Seawater	7.98	22	13.1

The open circuit potential (OCP) was measured for 60 minute after 90 minutes of immersion into electrolyte. The evolution of polarization resistance and corrosion rate were investigated using linear polarization method around free potential value with a very small overvoltage of ± 40 mV in order to keep the steady state of analyzed surface [12].

The cyclic voltammetry was initiated from negative direction (-1.5 V vs. SCE) to positive direction (+0.5 V vs. SCE) with the sweep rate of 5 mV/s. The scan direction was reversed after the anodic current reached +0.5 mV vs. SCE.

In order to see the influence of chloride ions on surface morphology of the studied samples, optical images were taken before and after corrosion assays using the optical microscope OPTIKA XDS3 MET connected to a computer and controlled with Vision Pro Plus 5.0 software.

3. Results and discussions

3.1. Open circuit potential

The open circuit potential represents the potential difference between the working electrode with respect to the saturated calomel electrode (SCE) and was continuously monitored during 60 min after 90 minutes immersion of aluminum samples into the electrolyte (aerated natural seawater at room temperature).

The variation of OCP for the analyzed samples are illustrated in Fig. 1. For both diagrams, it can be seen that the aluminum alloys try to reach a steady state value of potential, with some fluctuations due to the fact that chloride ions destroy the passive aluminum oxide film and prevents the equilibrium of metallic aluminum alloy – electrolyte interface.

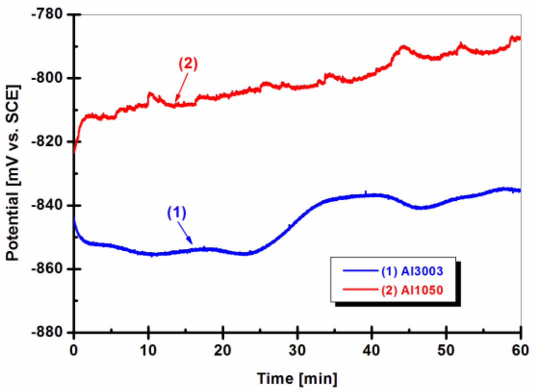

***Fig. 1.** Variation of the open circuit potential after 90 minutes immersion into natural seawater: (1) Al3003 and (2) Al1050*

From the diagrams presented in Fig. 1. it can be observed that the potential values of Al1050 changed continuously into anodic direction from -825 mV vs. SCE to -790 mV vs. SCE. That shift can be attributed to the formation of a compact adherent aluminum oxide layer on the Al1050 surface. S. Lameche-Djeghaba and his co-workers [13] observed this behavior for pure aluminum immersed in 3% NaCl electrolyte.

For Al3003, the potential values shift slowly to the cathodic direction from -845 mV vs. SCE to -855 mV vs. SCE, but after 25 minutes of monitoring, the potential values are shifted to the anodic direction, around -835 mV vs. SCE. This behavior can be related with the preferential dissolution of copper presented into Al3003 composition.

3.2. Evolution of polarization resistance (R_p) during immersion time

The linear polarization method was used to determine the polarization resistance of analyzed samples around the free potential with a very small overvoltage of ± 40 mV. In Fig. 2. are illustrated the diagrams for both aluminum alloys recorded after 3 hours of immersion.

The corrosion reactions for simple corrosion systems are strictly controlled by the charge transfer resistance and the corrosion current density (i_{corr}) is related to polarization resistance by the Stern Geary [14] equation (1)

$$i_{corr} = \frac{B}{R_p} \qquad (1)$$

where B is a specific constant of material-environment given by equation (2):

$$B = \frac{b_a |b_c|}{2.303(b_a + b_c)} \qquad (2)$$

where b_a and b_c are the Tafel slopes for anodic and respectively cathodic reaction.

It can be observed from Fig. 2. that the Al3003 have the lowest value of polarization resistance, which fluctuate around 37 kohm.cm^2, but with an upward trend. For Al1050, the value of polarization resistance fluctuates around 43 kohm.cm^2 with the same upward trend caused by the growth of oxide layer. The increasing of aluminum oxide layer thickness lead to the increasing of polarization resistance and lowering of corrosion current density.

The evolution of corrosion rate in time, corresponding to the polarization resistance from Fig. 2. is calculated as thickness loss and it is illustrated in Fig. 3.

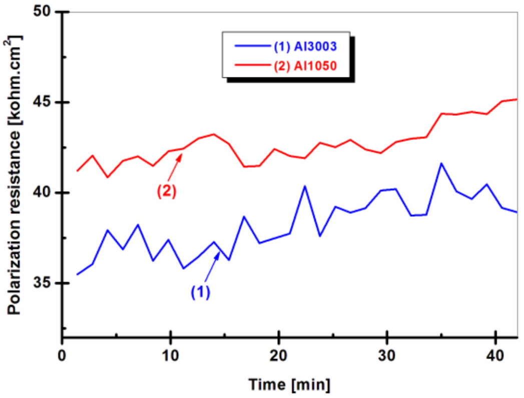

Fig. 2. *The evolution of polarization resistance of (1) Al3003 and (2) Al1050 during immersion in natural seawater*

The increased polarization resistance of Al1050 compared to the polarization resistance of Al3003 means the lowering of the corrosion current density and therefore the decreasing of corrosion rate (the loss of thickness).

These results suggest that the increased purity of Al1050 in comparison with Al3003 lead to an increased polarization resistance due to the increased homogeneity of aluminum oxide layer formed on their surface resulting an improved corrosion resistance.

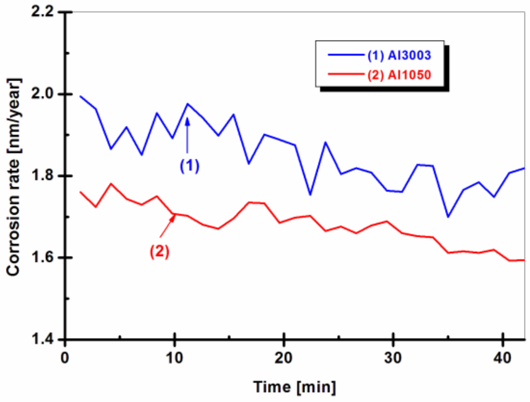

Fig. 3. *The evolution of corrosion current density (corrosion rate) of (1) Al3003 and (2) Al1050 during immersion in natural seawater*

3.3. Cyclic voltammetry

The cyclic voltammetry was initiated from negative direction (-1.5 V vs. SCE) to positive direction (+0.5 V vs. SCE) with the sweep rate of 5 mV/s. The scan direction was reversed after the anodic current reached + 0.5 mV vs. SCE to form a complete cycle and the recorded diagrams for both aluminum alloys are presented in Fig. 4.

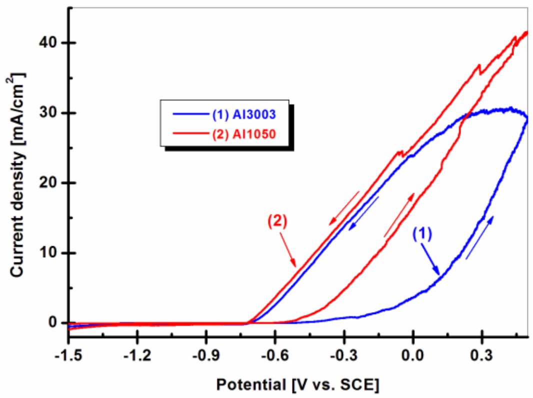

Fig. 4. *The cyclic voltammograms of (1) Al3003 and (2) Al1050 performed at 5mV/sec sweep rate during immersion in natural seawater*

Highlighting the localized corrosion susceptibility in the presence of chloride ions from natural seawater for both aluminum alloys can be seen very well due to the specific hysteresis formed in the anodic transpasivation part of the diagrams. For both materials, in the transpassive region the current density rises up until the potential is reversed and this indicates the breakdown of the passive aluminum oxide layer and a delay in the repassivation of an existing pit when the potential is scanned towards negative direction [15].

Analyzing the area of the hysteresis loop it could be observed that a larger area is present on Al3003 surface, which makes it more difficult to repasivate the pit [15, 16].

Analyzing the voltammograms presented in Fig. 4. it can be seen that the Al3003 presents a larger area of hysteresis loop in comparison with Al1050, confirming the previous behaviors in measuring the polarization resistance or corrosion current density.

3.4. Optical microscopy

The optical micrograph of analyzed Al1050 and Al3003 were taken before and after the corrosion assays. From Fig. 5 (a and b) it can be observed different aspects of aluminum alloy surfaces after the pretreatment process. Al1050 shows a uniform polished surface while Al3003 presents some inclusion or impurities, as it can be observed in Fig. 5 (a) and (b).

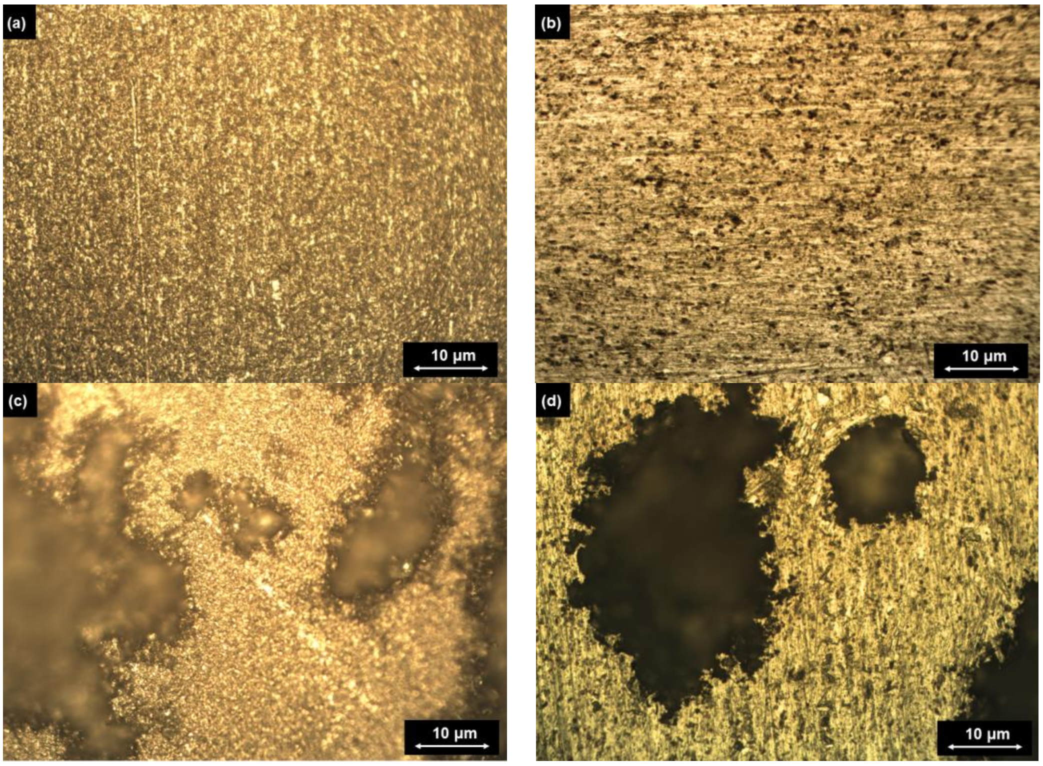

Fig. 5*. Optical micrographs of Al1050 and Al3003: (a) Al1050 polished before corrosion tests; (b) Al3003 polished before corrosion tests; (c) Al1050 after corrosion tests; (d) Al3003 after corrosion tests*

Conclusions

The aim of this paper was to study the corrosion behavior of Al1050 and Al3003 immersed in natural seawater. From the presented results, the following conclusions can be drawn:

- due to the decreased number of alloying elements, the open circuit potential value of Al1050 is nobler in comparison with the open circuit potential value of Al3003 which means a homogenous native aluminum oxide film for Al1050 and a low interaction with the electrolyte;

- equally, the homogeneity of aluminum oxide offers an increased polarization resistance for Al1050 in comparison with Al3003;

- the increased polarization resistance led to a decreased corrosion current density and thus to a lower corrosion rate for Al1050 in comparison with Al3003;

- the cyclic voltammograms reveal the susceptibility to pitting corrosion for both analyzed aluminum alloys, with a higher hysteresis area for Al3003;

- the electrochemical results illustrate the susceptibility of aluminum alloys to localized and pitting corrosion in presence of chloride ions, confirmed by optical micrographs performed after corrosion.

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