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# ELECTROCHEMICAL CORROSION BEHAVIOR OF 7075 ALUMINUM ALLOY AFTER AGEING TREATMENT

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## ABSTRACT

*The electrochemical corrosion behavior of 7075 aluminum alloy subjected to different artificial ageing treatments maintaining times was examined. This aluminum alloy is typically used in aerospace structural components such as the wing spars of aircrafts and maritime industry as different mechanic parts. Heat treatments applied on this kind of alloys influence considerably the material properties like corrosion resistance.*

*The specimens from the electrochemical corrosion point of view were investigated in aerated and recirculated seawater solution – source Mediterranean Sea. Using a scanning electron microscope the material surface was analyzed before and after electro-tests following the microstructure, modifications, pitting holes appearance and the effects of corrosion tracked through EDAX and VoltaMaster results analysis.*

KEYWORDS: electrochemical corrosion, aluminum alloy, artificial ageing.

## 1. Introduction

The corrosion behavior of metallic materials is determined not only by their chemical compositions but also by their microstructures [1].

Aluminum, a very reactive metal, forms a thin solid protecting film of oxide, which prevents the further corrosion of the material. However, in contact with solutions containing complex agents (i.e. halides), aluminum undergoes localized corrosion. Due to lightweight and high strength properties, the aluminum alloys find application in aerospace industries. Over the years, various protection methods have been developed to prevent the degradation processes of the aluminum and its alloys. Application of organic coating is a good way of taking advantage of the mechanical property of the metal while protecting it from corrosion. Adhesion of these organic coatings on aluminum is very poor and needs some pretreatment like chromating.

The chromate coatings are formed by immersion of clean substrate in an acid or alkaline solution containing hexavalent chromium Cr (VI), which provides corrosion protection [2]. The carcinogenic nature of chromate conversion coatings forces an alternative method and there is a high demand for a friendly environmental surface treatment. Localized corrosion (pitting, exfoliation, and intergranular attack) degrades fatigue performance of high strength of aluminum alloys [3–6].

The expense of replacing aircraft components as well as the intrinsic human variability and qualitative basis associated with corrosion grind-out techniques suggest the benefit of the next generation of damage tolerant prediction of the effect of existing corrosion on subsequent fatigue.

Introduced in 1943, alloy 7075 has been the standard workhorse 7XXX series alloy within the aerospace industry ever since. It was the first successful Al-Zn-Mg-Cu high strength alloy using the beneficial effects of the alloying addition of chromium to develop good stress-corrosion cracking resistance in sheet products. Although other 7XXX alloys have since been developed with improved specific properties, alloy 7075 remains the baseline with a good balance of properties required for aerospace applications.

This heat treatable alloy is considered high in strength. Corrosion resistance and workability is appreciated as fair, rated low on workability and welded only by the resistance process. Alloy 7075 is available in bare and alclad sheet and plate product forms in the annealed state as well as several tempers of the T6, T73 and T76 types.

Alloy 7075, a cold finished aluminum wrought product, has the highest strength of all aluminum screw machine alloys. The -T6 and -T651 tempers have a typical tensile strength of 83 ksi, which is higher than many mild steels. Due to its very high strength, alloy 7075 is used for highly stressed structural parts. Applications include aircraft fittings, gears and shafts, fuse parts, meter shafts and gears, missile parts, regulating valve parts, worm gears, keys, and various other commercial aircraft, aerospace and defense equipment. Rod and bar product forms can machine on multi-spindle and CNC machining equipment. Alloy 7075 has moderate corrosion resistance.

The overaged -T73 and -T7351 tempers offer good stress-corrosion cracking resistance as compared to the -T6 and -T651 tempers. (Caution: direct contact with dissimilar metals can cause galvanic corrosion.)

It is well known that aluminum and its alloys have excellent resistance to general corrosion except in solutions of low or high pH. The purpose of the present investigation was to study the corrosion and protection of aluminum alloy Al 7075 (UNS A97075) (1) in sea water [7].

In this study electrochemical corrosion behavior of this material in different heat treatment states, like artificial ageing or extra-ageing is analyzed and compared with cycling thermal heating at the same temperature, reduces the maintaining period from 5 to 7 cycles.

## 2. Experimental details

For these studies, a “7075” trademark aluminum alloy was used. This is an aluminum alloy with many applications, mentioned earlier in the introduction as having the composition:

Zn = 6.088%, Fe = 0.4980%, Mn = 0.31%, Si = 0.412%, Cu = 1.987%, Mg = 2.873%, Cr = 0.895%, Ti=0.21% and the rest is aluminum.

The manufacturer indicates that the 7075 base alloy is suitable for producing corrosion resistant long life metal frameworks and plate casting, easy to process and polish providing an aesthetic outlook. The material meets AMS 4154 (Extruded Shapes), AMS 4323 (Forging - Open Die) and ASTM B209 Directive prescriptions.

From this commercial material by hardening heat treatments, with different maintaining temperatures and cyclic treatments with a different cycle number samples were obtained and researched from the electrochemical corrosion behavior point of view.

Corrosion behavior was realized by rapid electrochemical tests, particularly by dynamic potentiometry.

The measurements of open potential circuit and potentiodynamic polarizations were performed on a VoltaLab 21 Electrochemical System (PGP201 - Radiometer Copenhagen) equipped with the acquisition and processing data software VoltaMaster 4. A three-electrode electrochemical cell was used [8]. From the prepared samples, the working electrodes performed in cylindrical form and mounted in a Teflon support to enable the connection to rotating port-electrode of the electrochemical cell. The free area was precisely measured before embedding in the Teflon support. A saturated calomel electrode (SCE) was used as a reference and platinum as auxiliary electrode.

Each specimen was polished with SiC paper, gradually, down up to 4000 grit specification, degreased with acetone and washed in distilled water.

As corrosion medium an aerated solution of Mediterranean sea-water was used, having the composition**:** $Cl^-$ - 8.26: $HCO^-_3$ – 0.183; $CO^{2-}_3$ – 0.022; $SO^{2-}_4$ – 1.137; $Na^+$ - 4.47; $K^+$ - 0.158; $Ca^{2+}$ - 0.203; $Mg^{2+}$ - 0.557 and for this chemical composition the solution has a salinity of 15.0 g $L^{-1}$. Linear polarization measurements were performed, in aerated solution, at potentials near the $E_{corr}$, in the potential range ± 150 mV against the open circuit potential and a potential scan rate of 0.5 mV/s. The polarization resistance ($R_p$) was calculated as tangent slope at the electrode potential vs. current density curve in the $E_{corr}$ point.

The cathodic Tafel slope ($b_c$) was calculated as the potential change over one decade (one order of magnitude) decrease in the current density at potentials near the $E_{corr}$. The anodic Tafel slope ($b_a$) was determined in a similar way.

Linear polarization method is used to determine when a test electrode is at its steady state. Polarization resistance is used to estimate the general corrosion rate of the metal.

Based on these data, the corrosion current density ($J_{corr}$) - which is a measure of the corrosion rate, was calculated with the Stern-Geary equation:

$$J_{corr} = \frac{b_a b_c}{2.3 R_p \left(b_a + b_c\right)} \qquad (1)$$

The corrosion rate, expressed as penetration rate - the layer thickness of the metal removed from the alloy surface in the time unity, was evaluated with the relation:

$$v_p = 3.27 . \left(\frac{A}{z}\right) . \frac{J_{cor}}{\rho} \quad , \mu\text{m/year} \qquad (2)$$

where: A – is the atomic mass of the corrodible metal (g/mol), z – number of electrons changed in the corrosion process, ρ - density of the removed component (g/cm$^3$) and $J_{corr}$ – instantaneous current density (μA/cm$^2$). After the electrochemical treatments, a study of the modifications of the alloys surface was performed on a VEGA-TESCAN

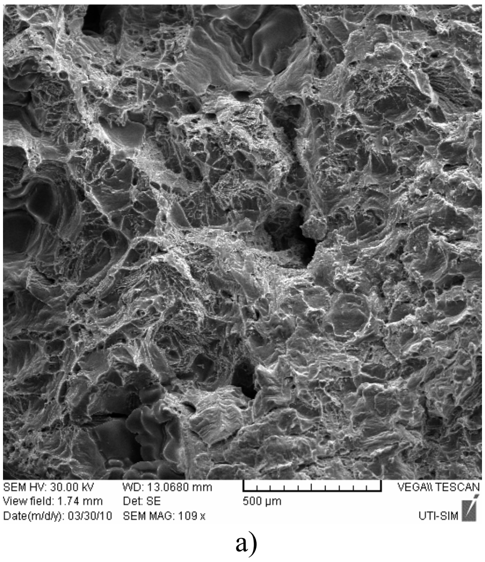
Scanning Electron Microscope equipped with QUANTAX Bruker AXS Microanalysis system.

## 3. Experimental results

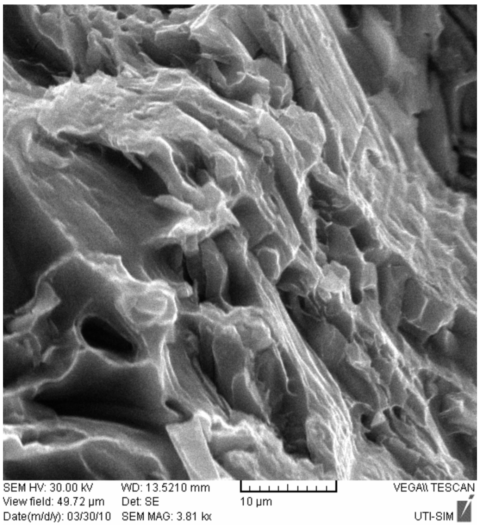
Investigations of material 7075 in equilibrium state, using an AES equipment reveal compounds like MgZn and $Al_{4.2}Cu_{3.2}Zn_{0.7}$, but other energies equivalent to compounds like $Mg_2Si$, $Al_3Mg_2$, $AlCr_2$, AlCu, $Al_2Fe$, $Al_5Fe_2$, $Al_6Cu_2Fe$, $Al_2CuMg$, $Al_6CuMg_4$, $Al_{23}CuFe_4$ [9-11] were observed on energy spectrum but with difficulties of being separated from all the spectrum energies. Scanning electron microscopies of the material, helping to determine the alloy compounds by their crystallization system, are presented, in fracture, in Figure 1 at 100 a) and 5000 b) orders of magnitude.

Surfaces examination of the specimens showed that microstructure is compact with different compounds formed on the surface of the specimen and with appearance of the pits. Other studies have found that pits were the initiators of cracks as well [12–17]. Multiple pit sites could be found on coupons in all the highest stress levels (i.e., DS = 700 MPa and DSsc = 350 MPa), and in most cases cracks would be initiated from several sites where pits could be found on the surface of the specimen. It is believed that these pits formed at the site of inclusions (such as particles of $Al_{23}CuFe_4$, and $Al_2CuMg$.) These inclusions are typical in heterogeneous alloys such as 7075-T651 [14, 16].

Anodic slip dissolution appears to be in the dominant mechanism for many cases of crack propagation in high stress regions, while pitting was the cause of crack propagation in specimens subjected to lower cyclic stress levels [18].



a)



b)

***Fig. 1.*** *Magnification of fracture surfaces by SEM microscopies of aluminum based alloy equilibrium state a) 100 and b) 5000 x order of magnitude*

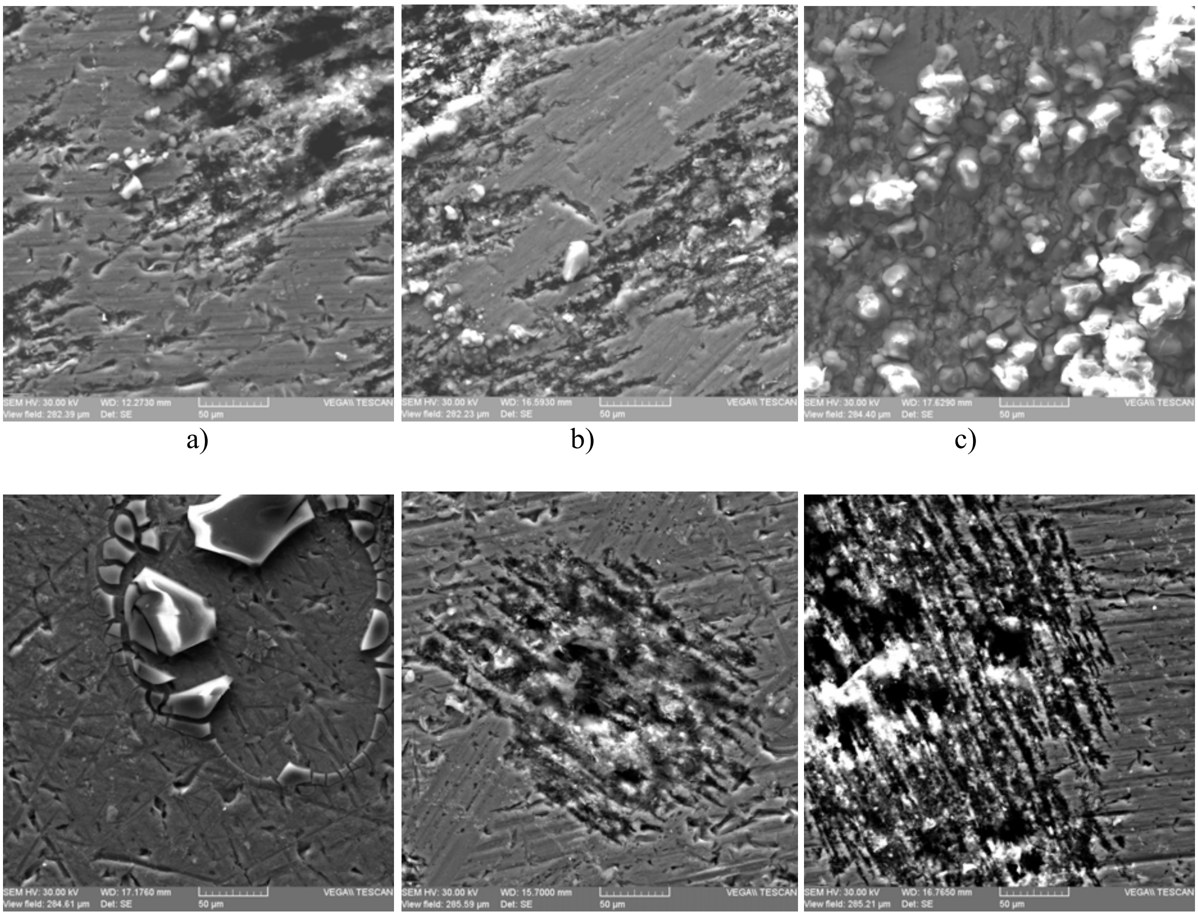
The electrochemical corrosion tests were carried out on samples heat treated by going to 120°C temperature and maintaining them at different time periods like 8, 10 or 14 hours.

In the first two cases the alloy is reaching a classical artificial ageing time that in 14 hours maintaining case the material, under precipitates increasing and connecting, reach an extra-ageing.

Having the intension of studying the effects of cyclic treatments applied on this aluminum type of alloys three different numbers of cycles like 3, 5 or 7 with temperature increasing at 120 °C as well and maintaining for them 20 minutes, in order to analyze and compare the material behavior, for all six cases, at electrochemical corrosion.

In Figure 2 are presented SEM microscopies, at 1000-x order of magnitude, for all treatments applied. The images were realized with a secondary detector using a 10 mm working distance and a 7 scanning rate.

All microstructure surfaces look affected by electrochemical corrosion test; the material under cyclic treatments seems to be cleaner. The worst behavior, as it was expected from scientific literature [19], was the extra-agenized material with 14 hours maintaining that presents a pitting affected surface, similar with the other samples, but also many chemical new compounds on the area different from the base material.



a) b) c)

d) e) f)

***Fig. 2.*** *Surface of 7075 alloy after different treatments applied like artificial aging for a) 8 hours b) 10 hours c) 14 hours or cyclic treatment of d) 3 cycles e) 5 cycles and f) 7 cycles*

Realizing the chemical compositions, with the EDAX equipment, after electrochemical corrosion test on a 285 μm (1000x amplifying power) after 10 areas average for each sample, the normal wt. % percentage of the elements are presented in Table 1.

In Table 1 are analyzed the elements of the 7075 material and the sea water corrosion solution as well looking for modifications on percentages to conclude which state is better from this point of view. At a first look, the aluminum behaves better in all cyclic treated samples having bigger percentage of this chemical element with a very big difference compared to the sample over maintained.

The presence of oxygen and the oxides appearance produce a passivation process of the material increasing the corrosion resistance but an increase percentage value represents the formation of many types of oxides.

***Table 1.*** *Chemical compositions of the investigated material in different states*

| **Chemical element [wt %]/ Alloy state** | **Al** | **Fe** | **O** | **Zn** | **Si** | **Mg** | **Cu** | **Na** | **Cr** | **Mn** | **Ti** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Aged 8 hours | 62.122 | 1.068 | 16.369 | 4.321 | 3.267 | 1.79 | 1.71 | 0.547 | 0.89 | 0.503 | 0.35 |
| Aged 10 hours | 69.468 | 1.097 | 17.980 | 4.831 | 3.064 | 1.85 | 0.70 | 1.01 | 0.15 | 0.515 | 0.28 |
| Aged 14 hours | 48.95 | 0.665 | 42.089 | 0.191 | 1.26 | 1.29 | 1.04 | 1.55 | 0.19 | 0.26 | 0.91 |
| Cycled 4 times | 71.09 | 1.489 | 19.012 | 5.373 | 1.67 | 1.24 | 0.54 | 0.12 | 0.62 | 0.66 | 0.75 |
| Cycled 6 times | 78.022 | 0.203 | 12.942 | 4.842 | 1.31 | 2.09 | 0.58 | 0.11 | 0.56 | 0.68 | 0.735 |
| Cycled 7 times | 73.67 | 0.228 | 14.654 | 5.431 | 1.45 | 1.68 | 0.62 | 0.35 | 0.52 | 0.55 | 0.59 |

Losing percentages of materials like aluminum or copper automatically increases the other amounts like iron, silicon or manganese [8]. The element with a weak behavior, obvious in the sample aged for 14 hours, is zinc that in extra-ageing case, probably based on what compounds are formed decreases substantially from 6,088 to 0,191 percentages. The potassium percentage indicates the salts compounds formed on the surface and affects the corrosion resistance playing a pitting starting point roll, small amounts of this element being found in every corroded hole. The corrosion potential in quasi equilibrium conditions (obtained at lower potential scan rate), $E_{0,}$ is more negative for the agenized samples than for the cyclically treated samples. Accordingly, the instantaneous current density and corrosion rate are lower in the case of the second treatments applied on the alloy.

However, the differences regarding the corrosion behavior of the samples in sea water solution are relevant by comparing those two applied treatments and by selfless comparison between them.

More over, the values of the corrosion rates are very high in some cases, indicating a reduce corrosion resistance of this alloy excepting the 3 cycles applied sample.

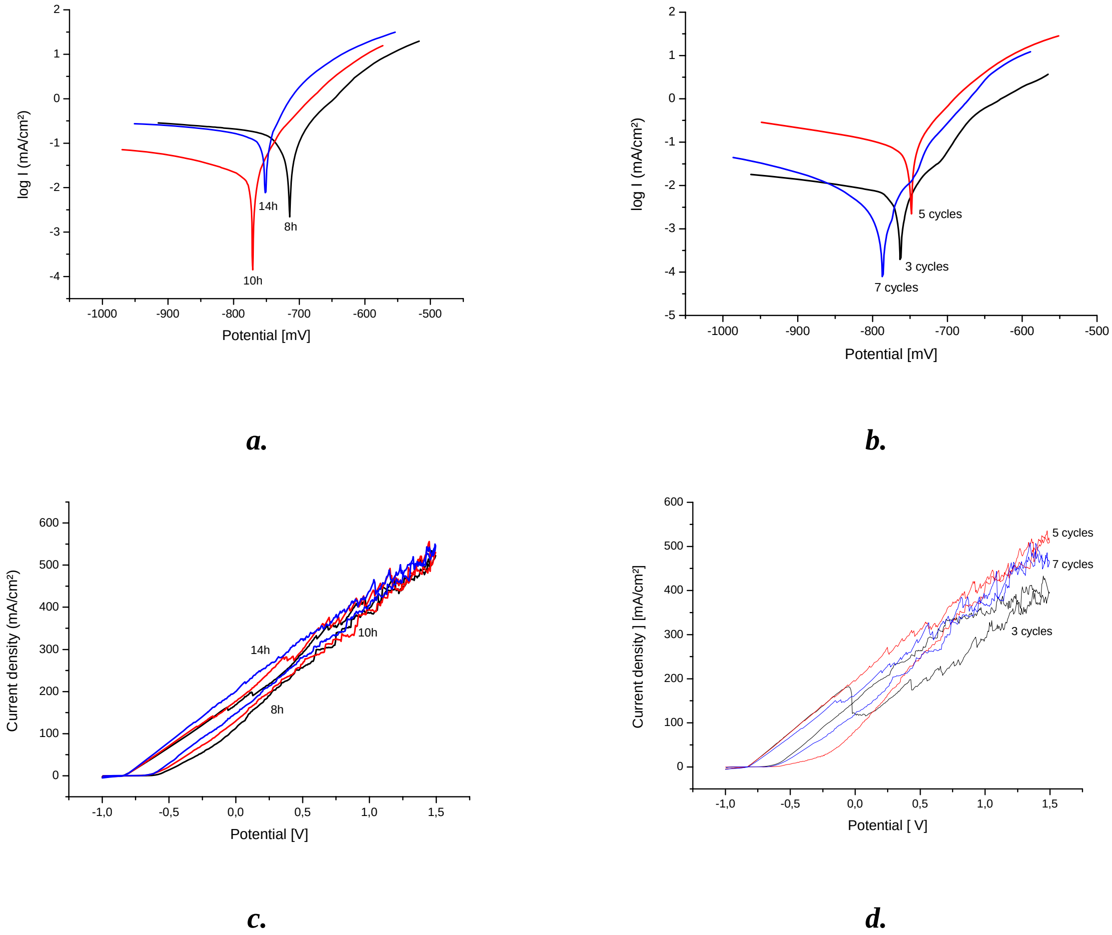


***Fig. 3.*** *Linear potentiodynamic polarization curve a) 8, 10 and 14 hours aged samples, b) 3, 5 and 7 cycles and single cyclic polarization curve c) 8, 10 and 14 hours aged samples and d) 3, 5 and 7 cycles.*

Linear potentio-dynamic polarization curves and single cyclic polarization curves are presented in Figure 3 expressing a higher corrosion character in aged samples, facts observed in Table 2 as well in all characteristics especially the informative corrosion rate per year (Vcor) with approximate values.

All the cyclic diagrams, Figure 3c) and d), represent the pitting character of the corrosion with smaller values in cyclically treated sample case. The cyclic voltammograms of all six samples show a very close similarity (Fig. 3 (c and d)); excepting the 5 cycles heat-treated sample the other curves practically overlap.

The recorded curves revealed the passive region over a large domain of potential, from a negative value to the breakdown potential situated at 557 and 523 mV (SCE) respectively.

At over-potentials higher than the breakdown potential, the corrosion currents increase appreciably and vary linearly with electrode over-potential, indicating a direct dependence between corrosion current and over-potential.

***Table 2.*** *Corrosion parameters evaluated from linear and cyclic polarization curves*

| **Sample** | **Linear polarization** | | | | | |
|---|---|---|---|---|---|---|
| | **$E_0$** | **$b_a$** | **$b_c$** | **$R_p$** | **$J_{cor}$** | **$v_{cor}$** |
| u.m. | [mV] | | | [kΩ.cm$^2$] | [μA/cm$^2$] | |
| 8 hours | 713.5 | 91.3 | 2638.5 | 180.65 | 0.2432 | **≈ 2904** |
| 10 hours | 770.2 | 72.9 | 2834.3 | 773.22 | 0.0634 | **≈ 741.6** |
| 14 hours | 751.7 | 50.8 | 1068.8 | 108.6 | 0.1814 | **≈ 2121** |
| 3 cycles | 762.6 | 60.1 | 710 | 2.92 | 0.0095 | **≈ 111.22** |
| 5 cycles | 749.4 | 54.2 | 363.3 | 208.5 | 0.0842 | **≈ 917.42** |
| 7 cycles | 785.8 | 66.7 | 703.4 | 7.94 | 0.0250 | **≈ 293.34** |

The anodic and cathodic branches of the polarization curve in this domain practically overlap, except for the potential range between $E_{BD}$ and $E_{RP}$, where a small hysteresis loop appears. The voltammogram shapes indicate rather a pitting corrosion in spite a general corrosion. Scanning Electron Microscope (SEM) studies presented in Figure 2 confirm this assertion.

The most representative parameter, the corrosion rate per year, reveals a very good resistance of sample cycled for these times, around 111.22 μm, but all the others are quite big, 741-2990 μm, for a material used in practical applications in contact with other metallic materials working in an electrolytic solution like a marine medium.

## 4. Conclusions

– A material with many practical applications and superior mechanical properties was analyzed from the electrochemical corrosion point of view in a sea water solution.

– Trying to improve this important property, six different heat treatments based on ageing and cyclic treatment were applied studying the obtaining costs, properties modification and corrosion behavior.

– Appreciating the amount of material loss in electrochemical corrosion process for ageing treated samples can be considered dangerous for any applications in a seawater environment.

– The cyclic treated samples present, in all cases, a better behavior at electrochemical corrosion having the advantages of a lower cost production as well.

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