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Influence of aging time on the corrosion behavior of 6061 Al alloy in alkaline solution

Olandir V. Correa[a], José A.B. de Souza[b], Mara C.L. de Oliveira[c], Renato A. Antunes[d]

Abstract

Al alloys of the 6XXX series (Al-Mg-Si) are employed as structural materials in a variety of industrial applications due to a combination of high mechanical strength and good corrosion resistance. The final mechanical properties are achieved after specific precipitation hardening heat treatments. The aging time during precipitation hardening is known to affect these properties and can also influence the corrosion resistance of the alloy. The susceptibility of Al alloys to corrosion in alkaline media is well-known. In this work the effect of aging time on the corrosion behavior of 6061 Al alloy was evaluated in NaOH and NaCl solutions. The material was aged at 200 ºC for times ranging from 1 to 36 h. The corrosion behavior of the aged alloy was studied using potentiodynamic polarization and electrochemical impedance spectroscopy. The results showed that the corrosion resistance was progressively lower for increasing aging times up to 8 h in NaCl and up to 24 h in NaOH. Longer aging times led to a decrease of the corrosion current density.

Keywords: 6061, Al alloy, precipitation hardening, aging time, corrosion

Introduction

Aluminum alloy 6061 is a wrought Al-Mg-Si alloy. It is hardened by heat treatment. Additions of Mg and Si are made to alloy the formation of secondary precipitates consisting of Al-Mg_2Si or Mg_2Si which form upon heat treatments, thus hardening the aluminum matrix by affecting the mobility of dislocations within the metallic crystals (1,2). The 6XXX aluminum alloys combine good mechanical strength and corrosion resistance (3). As a consequence, they are considered excellent structural materials for a variety of engineering applications in aerospace and automotive industries (4). Furthermore, the 6061 alloy has been used to manufacture nuclear fuel elements for research reactors (5). Spent aluminum-claddings are stored in demineralized water basins. It's been showed that pitting corrosion is a serious issue in this case, possibly leading to the release of fissile materials (6).

The heat treatment procedure to enhance the mechanical properties of 6XXX aluminum alloys consists of a first solution treatment followed by water quenching. The solution annealing step is encompassed in the temperature range between 460 ºC and 550 ºC during the necessary time to dissolve the alloying elements in the aluminum matrix. Next, the solution-annealed and quenched material is once more heated, but at lower temperature which is generally

[a] Graduado, Licenciado em Química – IPEN/CNEN-SP
[b] Mestre, Engenheiro Metalurgista – IPEN/CNEN-SP
[c] Doutora, Engenheira de Materiais - ELECTROCELL
[d] Doutor, Engenheiro de Materiais - UFABC

between 160 ºC and 200 ºC. This step is called artificial aging or age hardening (3,7). The aging time is closely related to the size and distribution of precipitates nucleated in the aluminum matrix. The corrosion behavior of the aged alloys is influenced by the chemical nature, size and distribution of the precipitates formed during the heat treatment (8). The precipitates can be more active or more cathodic than the aluminum matrix, thus leading to the onset of localized corrosion processes. It’s been reported that most precipitates are cathodic with respect to the aluminum matrix in 6XXX aluminum alloys (9,10). Optimized application of these materials as structural components should be based on favorable heat treating conditions.
In this work the corrosion behavior of 6061 Al alloy submitted to different aging times was assessed in NaOH solution. The electrochemical characterization comprised monitoring of the open circuit potential, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization measurements.

Methodology

The material used in this work was 6061 Al alloy whose chemical composition is shown in Table 1. The as-received material was a rectangular sheet with a thickness of 1 mm. This sheet was cut in rectangular dimensions of 2 cm x 2 cm.

Table 1 - Chemical composition (wt.%) of the 6061 Al alloy used in this work.

Cu	Cr	Mg	Mn	Si	Fe	Ti	Zn	Al
0.25	0.04	0.94	0.12	0.65	0.24	0.04	0.03	Bal.

The as-received samples were initially solution-treated at 550 ºC for 2 h in resistive furnace under argon atmosphere and water-quenched to guarantee an initial homogeneous condition. Next, the solution-annealed samples were aged at 200 ºC under argon atmosphere for different times: 1 h, 8 h, 24 h and 36 h. the aged specimens were stored in a freezer until the electrochemical measurements to avoid natural aging.
Prior to the electrochemical tests the samples were ground using SiC papers up to 1000 grit size. The tests were carried out in an Autolab PGSTAT 100 potentiostat/galvanostat. The cell arrangement was comprised of a conventional three-electrode cell using a saturated calomel electrode (SCE) as reference and a platinum wire as counter-electrode. All potentials mentioned in this work are referred to the SCE. The measurements were carried out with in two different electrolytes. The first one was a sodium hydroxide solution at a concentration of 0.1 M at room temperature. After the potential has reached a steady state the samples were submitted to potentiodynamic polarization tests from -250 mV with respect to the open circuit potential (OCP) up to -1.0 V at scanning rate of 1 $mV.s^{-1}$. The second electrolyte was a 3.5 wt.% NaCl solution at room temperature. In this case, the OCP was monitored until it reached steady state. Next, electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency range from 100 kHz to 10 mHz with an amplitude of the perturbation signal of $\pm$10 mV and an acquisition rate of 10 points/decade. Right after the EIS measurements, potentiodynamic polarization curves were acquired in the potential range from -250 mV versus OCP up to 0.5 V at a scanning rate of 1 $mV.s^{-1}$. The experiments were

repeated three times. The results presented here express the representative behavior observed for each condition.

Results and Discussion

a) Measurements in 0.1 M NaOH solution at room temperature

Potentiodynamic polarization curves obtained in 0.1 M NaOH solution at room temperature for the 6061 alloy submitted to different heat treatments are shown in Fig. 1. The corrosion potentials (E_{corr}) and corrosion current densities (i_{corr}) obtained from these curves are presented in Tab. 2.

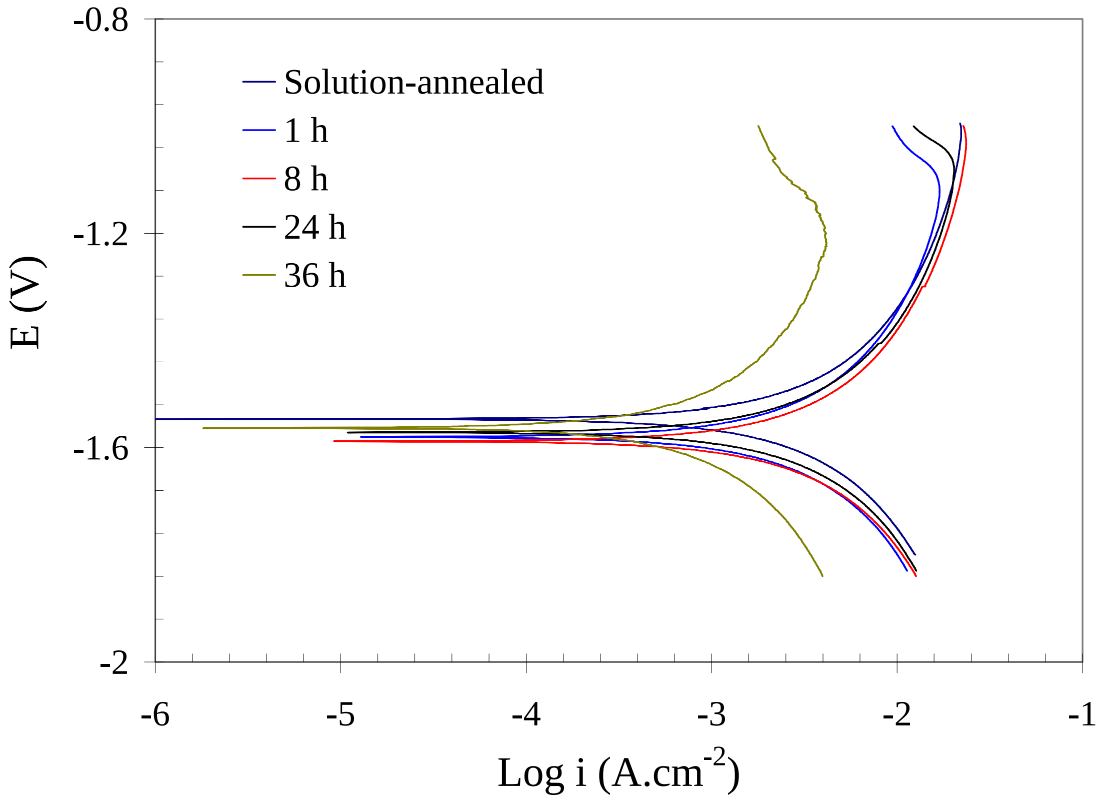

Figure 1. Potentiodynamic polarization curves obtained in 0.1 M NaOH solution at room temperature for the 6061 alloy submitted to different heat treatments

Table 2 – Electrochemical parameters determined from the potentiodynamic polarization curves shown in Figure 1.

Heat treatment	E_{corr} (V)	i_{corr} ($mA.cm^{-2}$)
Solution-annealed	-1.55	1.32
Aged for 1h	-1.58	1.28
Aged for 8 h	-1.59	1.39
Aged for 24 h	-1.57	1.46

Aged for 36 h	-1.56	0.57

The curves shown in Fig. 1 reveal that the 6061 alloy has an active electrochemical behavior in the NaOH solution independently of the heat treatment. The current densities are high and no passive region is formed during immersion in NaOH. The corrosion potential was little affected by the aging condition which did not allow to identifying a clear trend with the aging time. In the regard, the values of i_{corr} present an apparently complex variation. However, it is possible to infer some interesting hypothesis: it is known that the formation of precipitates depends on the aging condition of the Al 6061 alloy. The main phases formed during aging are β'' (Mg_2Si) and Q' ($Al_4Mg_8Si_7Cu_2$) (11). The precipitates mostly behave cathodically with respect to the aluminum matrix. The presence of copper in the alloy can lead to galvanic effects, thus accelerating the corrosion rate (12). For short aging times, the precipitates are formed as fine particles and close inter-spacing. This leads to an increase of the corrosion current density due to the increase of the cathodic area in the alloy, therefore enhancing the dissolution of the anodic sites around these particles. This effect should manifest up to the peak aged condition. Longer aging times can lead the alloy to an overaged condition, yielding the coarsening of precipitates. This would decrease both the number and are of cathodic sites. Consequently, the corrosion current density decreases as well (8). The variation of icorr shown in Tab. 2 seems to follow this trend. However, this effect has been most often observed in neutral aqueous solutions. In this respect, in order to confirm these indications, we performed additional electrochemical tests in a less aggressive electrolyte, consisting of a 3.5 wt.% NaCl solution at room temperature as shown below.

b) Measurements in 3.5 wt.% NaCl solution at room temperature

Nyquist plots of the Al 6061 alloy submitted to different heat treatments are shown in Fig. 2.

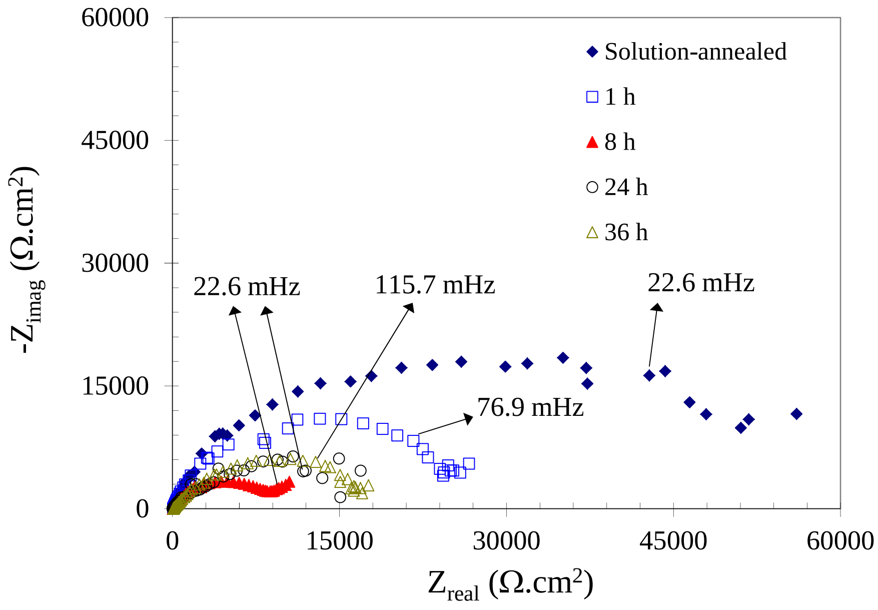

Figure 2. Nyquist of the Al 6061 alloy submitted to different heat treatments.

It is known that the low frequency impedance of an electrode can be related to its corrosion resistance. The diameter of the capacitive loop should correspond to the charge transfer resistance (R_{ct}) and can be used to compare the corrosion resistance of different samples (13). The Nyquist plots shown in Fig. 2 indicate that the solution-annealed alloy present the highest diameter of the capacitive loop. The diameter of the capacitive loop gradually decreases with the aging time at 200 ºC up to 8 h for which it reached the lowest impedance value. Then, it increases again for the longer aging times. This behavior seems to follow the trend reported by El-Menshawy et al. (8), where the corrosion rate would increase for short aging times, followed by a decrease for long aging times due to the coarsening of cathodic precipitates.
The electrochemical characterization was completed by performing potentiodynamic polarization tests right after the EIS measurements. The polarization curves of the Al 6061 alloy submitted to different heat treatments are shown in Fig. 3. The electrochemical parameters obtained from these curves are presented in Tab. 3.

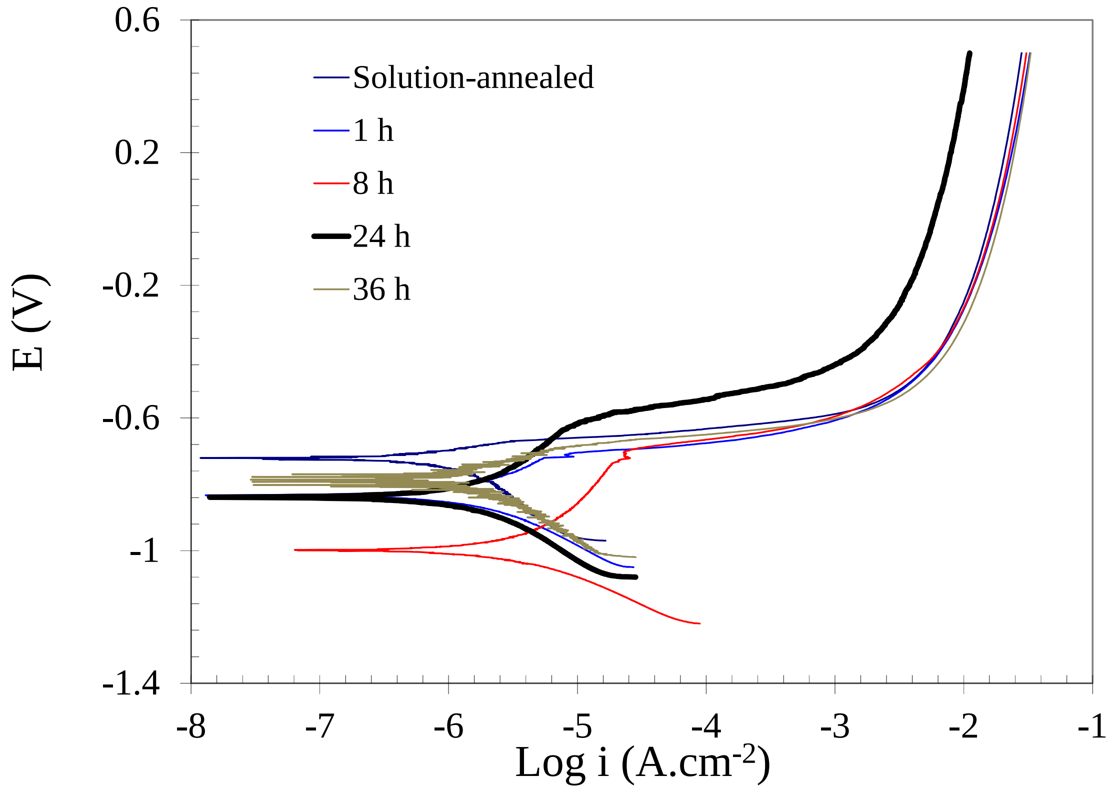

Figure 3. Potentiodynamic polarization curves obtained in 3.5 wt.% NaCl solution at room temperature for the Al 6061 alloy submitted to different heat treatments.

Qualitatively it is seen that the polarization curves are characteristic of passive metals. There is a breakdown potential (E_b) denoted by the sharp increase of the current density at a specific potential. The values of E_b were determined from the curves shown in Fig. 3 and are displayed in Tab. 3. The passive region is incipient for the solution-annealed alloy and then it increases with the aging time up to 8 h. Longer aging times decreased the passive region. This effect has been attributed to the increase of cathodic sites for underaged samples (formation of fine precipitates), followed by the decrease of these sites for overaged samples due to the coarsening of precipitates (8). This trend can be quantitatively observed in the last column of

Tab. 3. Furthermore, the corrosion current densities determined from the polarization curves point to an increase of the corrosion rate with the aging time up to 8 h, followed by a slower corrosion process upon reaching longer aging times. The lowest i_{corr} was observed for the solution-annealed alloy whereas the material aged for 8 h presented the highest i_{corr} which decreased when the aging time was extended. These results corroborate those obtained from the EIS measurements and also confirm the indications from the tests performed in NaOH solution.

Table 3 – Electrochemical parameters determined from the potentiodynamic polarization curves shown in Figure 3.

Heat treatment	E_{corr} (mV)	i_{corr} ($\mu A.cm^{-2}$)	E_b (mV)	Passive range (mV)
Solution-annealed	-721	0.48	-667	54
Aged for 1h	-834	1.18	-702	132
Aged for 8 h	-997	2.44	-685	312
Aged for 24 h	-840	1.08	-583	257
Aged for 36 h	-786	0.89	-670	116

Conclusions

The electrochemical behavior of the Al 6061 alloy is affected by the aging condition. The corrosion resistance decreased with the aging time up to 8 h, followed by an increase for longer aging times in NaCl. In NaOH the reduction of corrosion resistance was observed for samples aged up to 24 h whereas for samples aged for 36 h the corrosion resistance increased again. The material was active in NaOH and presented a well-developed passive region in NaCl.

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