

Effect of the heat treatment on the behaviour of the corrosion and passivation of 3003 aluminium alloy in synthetic solution

M. Belkhaouda ¹, L. Bazzi ^{1,*}, R. Salghi ², O. Jbara ³, A. Benlhachmi ¹,
B. Hammouti ⁴, J. Douglad ³

¹ Laboratoire Matériaux & Environnement, Faculté des Sciences, BP 8106, 80000 Agadir, Morocco.

² Laboratoire d'Ingénierie des Procédés de l'Energie et de l'Environnement, Ecole National des Sciences Appliquées, BP 1136, Agadir - Morocco.

³ Laboratoire d'Analyse des solides Surfaces et Interfaces, UTAP EA 3802, Faculté des Sciences, Université de Reims, UMR 6089, Moulin de la housse, BP :1039, FR-51687 Reims Cedex 2, France;

⁴ LCAE-URAC 18, Faculté des Sciences, Université Mohammed Premier, BP 717, 60 000 Oujda, Morocco.

*Corresponding author: L. Bazzi: lahcen_bazzi@yahoo.fr, Tel: 212 548 220 057 Fax: +212 548 220 100

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Abstract

The corrosion and passivation of 3003 aluminium alloy in synthetic solution similar to industrial water at pH = 8.2 were studied by electrochemical techniques. The effect of the following factors on the dissolution and passivation of this alloy are discussed: heat treatment, pH solution, temperature of medium and chloride ions. Surface analysis was investigated by X-ray analysis (EDS) and scanning electron microscope (SEM). Heat treatment was carried out during 2h at temperatures varying between 350 and 550°C. Potentiodynamic polarization result showed that the corrosion behaviour is performed for treated sample at 450°C. The ability of pitting corrosion increases with the elevation of chloride concentration and the uniform corrosion is affected by the temperature of corrosive medium.

Keywords: Corrosion, 3003 Aluminium alloy, Pitting, Heat treatment.

1. Introduction

Aluminium and its alloys have good electrical and thermal conductivities, low density, high ductility and good corrosion resistance. They are widely used in many industrial applications, especially for automobiles, aviation, household appliances, containers, electronic devices and food industry [1-3]. The behaviour of aluminium and its alloys in aqueous environments depends on several parameters such as the surface properties of the material, the nature, the temperature, pH and the composition of the aggressive solution [4-6]. Furthermore, mechanical and heat treatment processes influence the structure and the composition of the oxide layer on the material surface, which becomes more resistant against the effect of corrosion. This treatment was the object of numerous works in the case of the aluminium and its alloys [7-12].

The corrosion resistance of aluminium alloy is the results of their ability to form a natural oxide film on the surface in different media [13-15]. However this oxide film can easily undergo corrosion reactions in chloride solutions ¹⁶⁻¹⁷. The breakdown of passive film is due to the attack of chloride ions on the flawed areas, consequently, apparition of a pitting corrosion [17-20].

The degree of dissolution depends also on the heat treatment of aluminium alloys [21,22]. The effect of microstructural heterogeneity on the pitting tendency of aluminium alloy after heat treatment has been studied [23].

Many works studied the effect of the heat treatment on the corrosion resistance of aluminium alloys [24,25]. Most works have been achieved in neutral solutions of sodium chlorides [6]. The obtained results show that the resistance to the localized corrosion of these alloys is influenced strongly by the thermal treatment type [25-27]. In our laboratories, effect of heat treatment on the corrosion behaviour of titanium, tinplate, 3003 Al and amorphous Fe-Cr-P-Si alloy was investigated in several corrosive media [28-31].

The aim of this paper is to study of the effect of heat treatment on the corrosion and passivation of 3003 aluminium alloy in synthetic industrial solution. The effects of the pH, the addition of chloride ions and the variation of temperature of the medium on the behaviour of 3003 aluminium alloy are also studied.

2. Methods and materials

The material investigated in the present study is 3003 aluminium alloy. Its chemical composition is reported in Table 1. The heat treatments are carried out in a programmable continuous pipe still under inert atmosphere of going nitrogen.

Table 1. Chemical composition of 3003 aluminium alloy (wt.%)

Alloy	Mn	Mg	Si	Fe	Cu	Zn	Ti	Cr	Sn
3003 Al	1.270	0.950	0.12	0.31	0.008	0.01	0.015	0.005	0.002

Samples treated were studied in the following conditions:

Heat-treated for 2h at temperatures varying between 350 and 550 °C.

- Cooling in bidistilled water to room temperature.
- Alkaline etching for 10 s (in 10% NaOH at 60°C).
- Desmutted for 1min in concentrated nitric acid at 20°C.
- Degreasing by acetone followed by rinsing by bidistilled water.

The potentiokinetic current-voltage characteristics are recorded with a potentiostat PGP 201, controlled by a computer, at a scan rate of 1 mV s^{-1} . The potential started from $-1500 \text{ mV SCE}^{-1}$. Before recording each curve, the working electrode is maintained with its free potential of corrosion for 30 min. For all electrochemical tests a cell with three electrodes thermostats with double wall (Tacussel Standard CEC/TH) was used. Saturated calomel electrode (SCE) and platinum electrode are used as reference and auxiliary electrodes, respectively. The working electrode is a disc of 0.78 cm^2 surface made of 3003 Aluminium alloy. Prior to each electrochemical experiment, the electrode surface was abraded successively with emery paper of different grain sizes and then rinsed with acetone and bi-distilled water.

The experiments were carried out in synthetic industrial solution (0.001 M NaCl, 0.003 M NaHCO_3 , 0.008 M Na_2SO_4). The solution test is also de-aerated with pure nitrogen. Gas pebbling is maintained prior and through the experiments. All experiments have been performed at a desired temperature to within 1°C and a pH of the medium.

3. Electrochemical results

3.1. Effect of the temperature

Electrochemical polarization curves for untreated 3003 aluminium alloy in synthetic solution at different temperatures are plotted in Fig. 1. As can be seen from this figure, cathodic polarization curves give rise to parallel Tafel lines indicating that the water evolution reaction is activation controlled. The cathodic reaction is mainly controlled by water reduction [32-34]. This process is not affected while the temperature increases from 20 to 60°C .

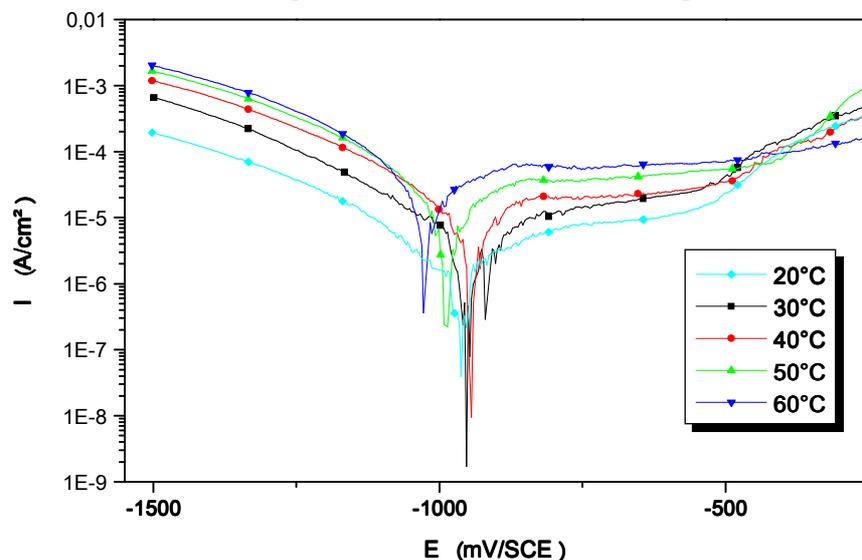


Fig. 1. Polarization curves for untreated 3003 Al in synthetic solution at different temperatures (pH=8.2)

The examination of anodic curves shows that 3003 aluminium alloy presents a passivation phenomenon with a breakdown of passivity in the synthetic medium. In fact, the anode current density increases with the electrode potential to reach a current plateau called passivation plateau. The passive current density remains almost constant and then increases abruptly when the pitting potential E_{pit} is exceeded. This potential denotes the film breakdown and pitting corrosion.

Table 2 reports the electrochemical parameters such as the corrosion potential (E_{corr}), the corrosion current density (I_{corr}) determined by extrapolation of cathodic Tafel lines to the corrosion potential (E_{corr}), the passivation current density (I_{pass}), the cathodic Tafel slope (β_c) and the pitting potential (E_{pit}).

Table 2. Electrochemical parameters for untreated 3003 Al alloy in synthetic solution at different temperatures

T/°C	$I_{corr}/\mu\text{A cm}^{-2}$	$E_{corr}/\text{mV SCE}^{-1}$	$I_{pass}/\mu\text{A cm}^{-2}$	$E_{pit}/\text{mV SCE}^{-1}$	$\beta_c/\text{mV dec}^{-1}$
20	4.6	-979	8.2	-518	-274
30	8.4	-954	13.6	-545	-267
40	17.9	-942	20.4	-481	-270
50	35.9	-992	37.1	-407	-269
60	60.7	-1029	56.7	-325	-265

The results show clearly that both passivation and corrosion currents increase with increasing the medium temperature. This variation of current density values is mainly due to the sensitive effect of temperature leading to a uniform corrosion process. The other electrochemical parameters are not affected by the temperature increase.

Fig. 2 represents Arrhenius plots for I_{corr} et I_{pass} of untreated 3003 aluminium alloy in the synthetic medium. Table 3 gathers the values of apparent activation energy E_a , related to different current densities and calculated by the following relation:

$$I = A \exp(-E_a / RT) \tag{1}$$

where A is a constant, I corresponds to the corrosion current density I_{corr} or the passivation current density I_{pass} , T is the absolute temperature and R = 8.314 J mol⁻¹ the gas constant.

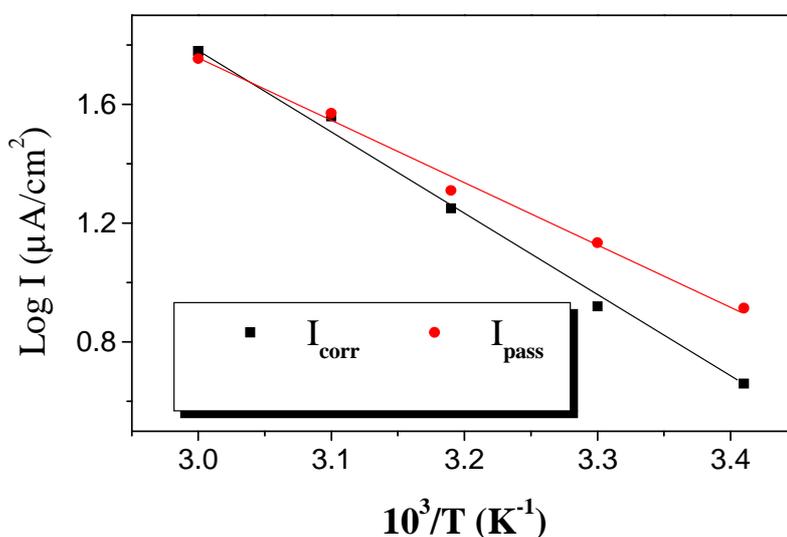


Fig. 2. Arrhenius plots for I_{corr} and I_{pass} of 3003 aluminium alloy in the synthetic medium

Table 3. Values of activation energies for I_{corr} and I_{pass} of 3003 aluminium alloy in the synthetic medium

Current density	Activation energy $E_a/\text{kJ mol}^{-1}$
I_{corr}	23.367
I_{pass}	17.144

3.2. Effect of pH solution

The influence of pH (around the value 8.2) on the polarization curves of untreated 3003 aluminium alloy in synthetic industrial solution is shown in Figure 3. The corresponding electrochemical parameters are listed in Table 4.

Table 4. Electrochemical parameters for 3003 aluminium alloy in synthetic solution at various pH

pH	$I_{corr}/\mu\text{A cm}^{-2}$	$E_{corr}/\text{mV SCE}^{-1}$	$I_{pass}/\mu\text{A cm}^{-2}$	$E_{pit}/\text{mV SCE}^{-1}$	$\beta_c/\text{mV dec}^{-1}$
7.2	2.7	-930	2	-510	-284
8.2	4.6	-979	8.2	-518	-274
9.2	14.5	-1031	29.2	-502	-302

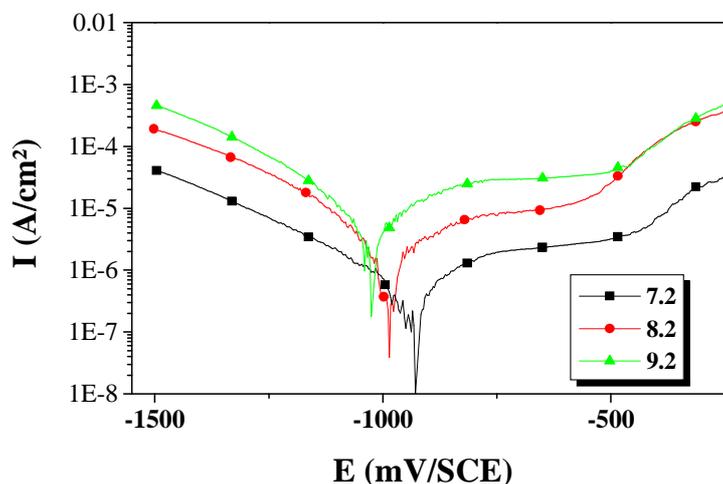


Fig. 3. Polarization curves for 3003 aluminium alloy in synthetic solution at various pH (T=20°C)

We note that the polarization curves keep the same characteristics. The corrosion current density increases when the value of pH increases. This result shows that the aluminium alloy tends to undergo a more pronounced dissolution when the pH of the solution becomes more alkali. However, the pitting behaviour of aluminium alloy is not affected by the pH change.

3.3. Effect of chloride ions

The effect of the addition of different concentrations (0.05-1M) of chloride ions concentration on the polarization curve of 3003 aluminium alloy in synthetic industrial medium is shown in Figure 4. The electrochemical parameters are reported in Table 5.

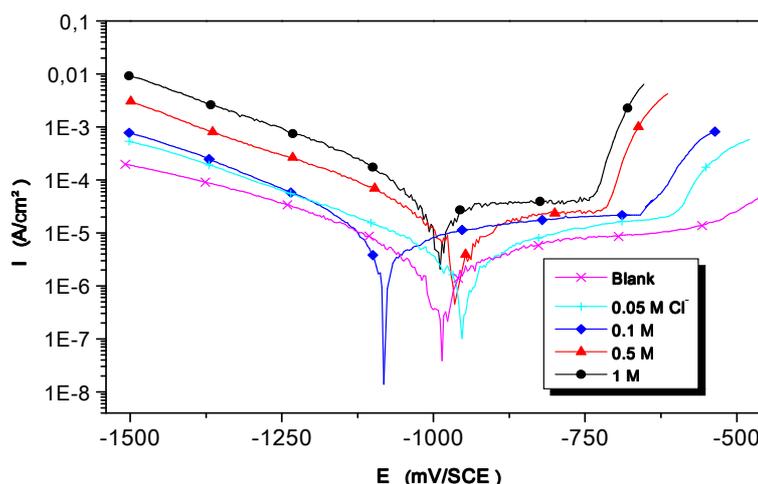


Fig. 4. Polarization curves for 3003 Al in synthetic solution at various concentration of Cl⁻ (T=20°C, pH = 8.2)

The results indicate that the presence of Cl⁻ at various concentrations has a significant effect on the nature (uniform or/and pitting) of 3003 aluminium alloy corrosion. The addition of Cl⁻ ions causes an increase of both corrosion and passivation current densities but affects slightly the corrosion potential E_{corr} . On the other hand, E_{pit} shifts towards more negative potentials. According to these results, it's revealed that the aggressiveness of the chloride ions can be attributed to their easy adsorbability on the surface of the passive film and their penetration through the pores leading to the rupture of the layer which forms on the material surface.

Table 5. Electrochemical parameters for 3003 Al alloy in synthetic solution at various concentration of Cl⁻

[Cl ⁻]/M	$I_{corr}/\mu\text{A cm}^{-2}$	$E_{corr}/\text{mV SCE}^{-1}$	$I_{pass}/\mu\text{A cm}^{-2}$	$E_{pit}/\text{mV SCE}^{-1}$	$\beta_c / \text{mV dec}^{-1}$
Blank	4.6	-979	8.2	-518	-274
0.05	5.8	-946	10.1	-605	-254
0.1	17.5	-1080	18.9	-662	-251
0.5	24.7	-961	24.9	-719	-268
1	99.1	-993	40.1	-744	-259

Figure 5 represents the evolution of the pitting potential E_{pit} as a function of the chloride ions concentration. This figure shows that E_{pit} is linearly dependent on Log [Cl⁻] according to the equation:

$$E_{pit} = a + b \text{Log} [\text{Cl}^-] \tag{2}$$

where a and b are a constants.

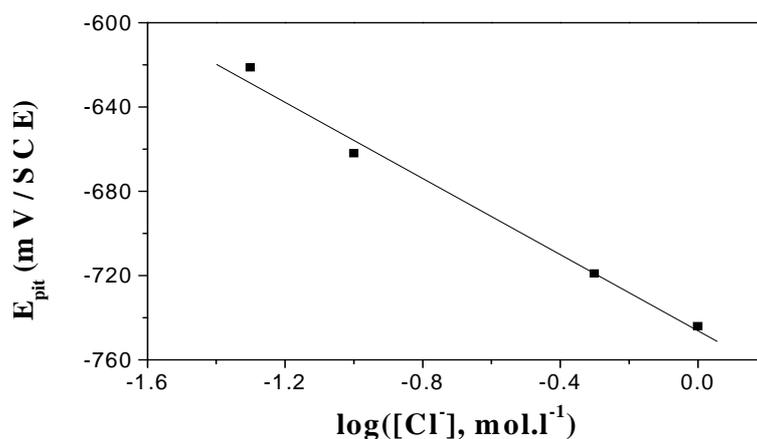


Fig.5. Dependence of E_{pit} on log [Cl⁻] for 3003 aluminium alloy in synthetic solution at 20°C.

3.4. Effect of heat treatment

Fig. 6 shows the polarization curves of treated and untreated samples of 3003 aluminium alloy. The corresponding electrochemical parameters listed in Table 6.

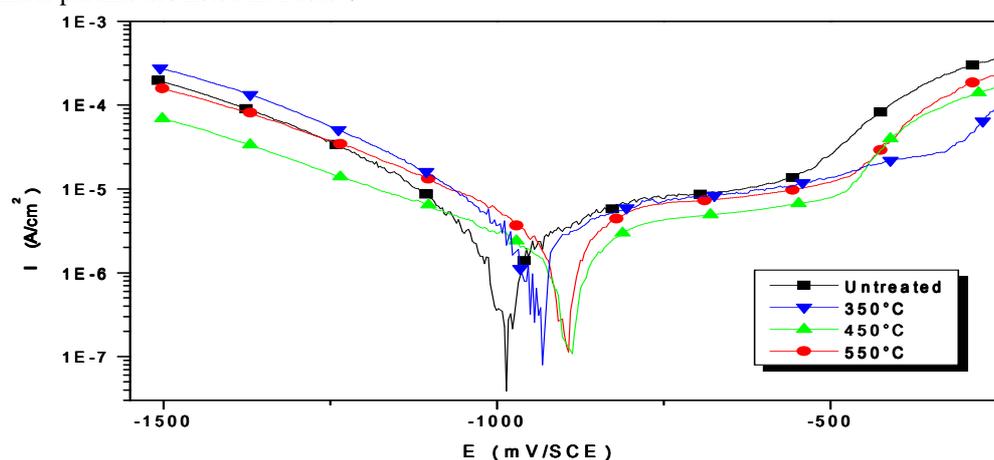


Fig. 6. Polarization curves for untreated and treated 3003 aluminium alloy in synthetic solution.

Table 6. Electrochemical parameters for untreated and treated 3003 aluminium alloy in synthetic solution.

T/°C	$I_{corr}/\mu\text{A cm}^{-2}$	$E_{corr}/\text{mV SCE}^{-1}$	$I_{pass}/\mu\text{A cm}^{-2}$	$E_{pit}/\text{mV SCE}^{-1}$	$\beta_c / \text{mV dec}^{-1}$
untreated	4.6	-979	8.2	-518	-274
350	2.8	-936	7.2	-330	-228
450	1.7	-885	4.2	-481	-383
550	3.2	-895	6.6	-476	-329

We note that all shapes of these curves are not affected by the heat treatment. However, the values of both I_{corr} and I_{pass} lower than untreated sample. The weak value of current density of corrosion I_{corr} is obtained at 450 °C. Moreover, the sample heat treated at 450 °C presents the lowest critical passivation current density I_{pass} equal to 4.2 $\mu\text{A cm}^{-2}$. The big displacement of the potential of pitting E_{pit} toward the positive values is observed for treated sample at 350°C.

3.4. SEM observations and EDS analysis results

3.4.1. Characterisation of aluminium alloy

The untreated and treated samples at different temperatures were characterized using SEM and EDS techniques. The topography of the surface and the chemical composition of the samples studied are then obtained using SEM micrographs and x-ray spectra (Fig

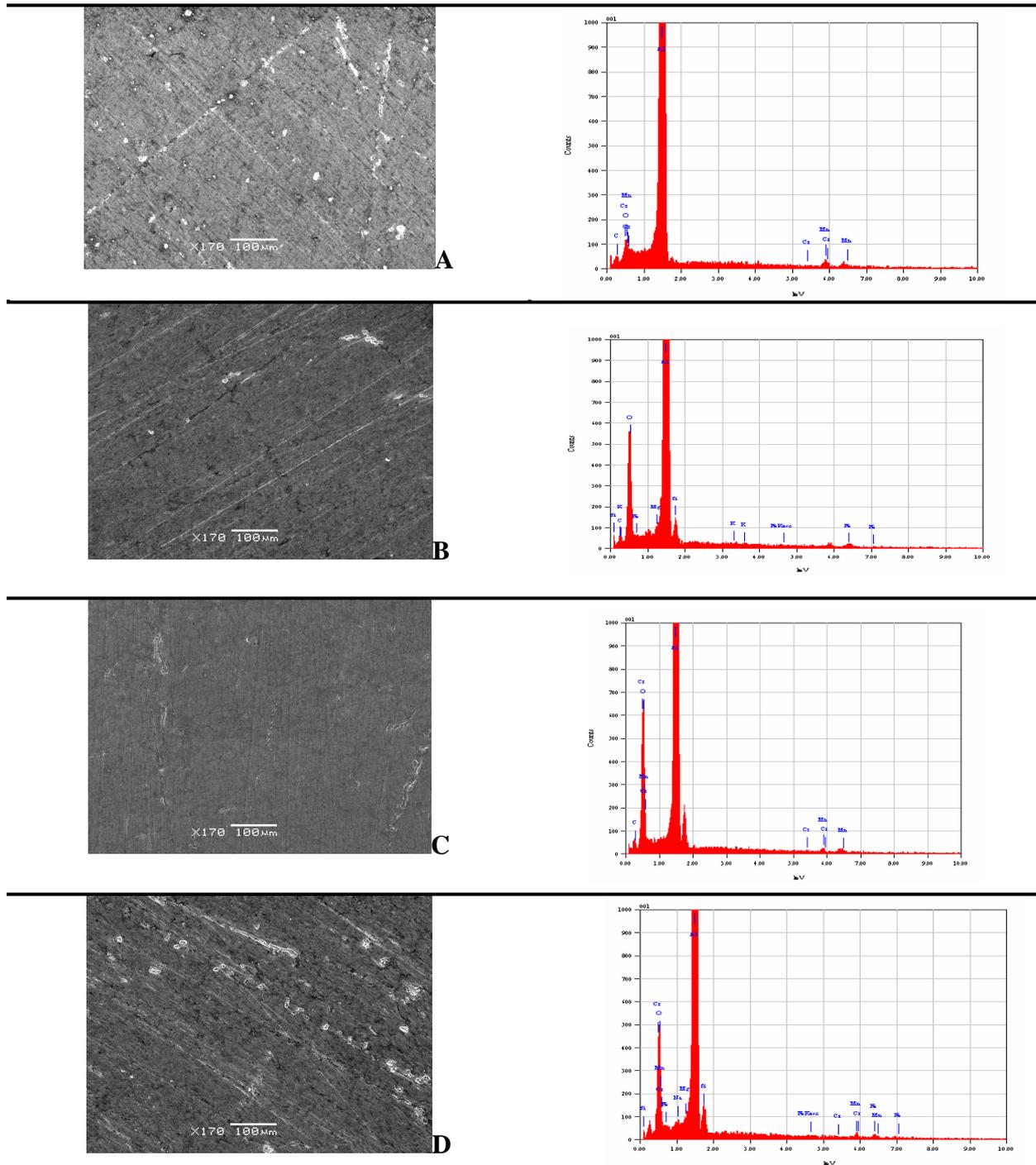


Fig. 7. SEM micrographs showing the surface appearance of aluminium alloy and EDS analysis in the following conditions: untreated (A), treated at 350°C (B), at 450°C (C) and 550°C (D).

One may note that x-ray lines associated to the elements present in majority in the alloy such as aluminium and oxygen are clearly visible, while those associated to other elements as manganese, iron, silicon, chrome, present at weak content, emerge scarcely from the background. The examination of SEM micrographs shows that the surface topography is not affected by the heat treatment.

After a heat treatment of alloy performed at different temperatures namely 350, 450 and 500°C the recorded x-ray spectra show an increase of the oxygen x-ray line intensity resulting certainly from an increase of the oxygen content in the sample. This growth of oxygen concentration may be attributed to the formation of a compact layer of aluminium oxide that improves the resistance of the alloy in the corrosive medium.

After polarisation test, the SEM observations on untreated aluminium alloy show the attack of sample surface (Fig. 8). The chemical elements identified by EDS analysis (fig.8) are aluminium and oxygen. The carbon element is certainly associated to the contamination layer. We note a reduction of the oxygen peak of the polarized sample. This result shows the destruction of the aluminium oxide layer and the total attack of the polarized surface.

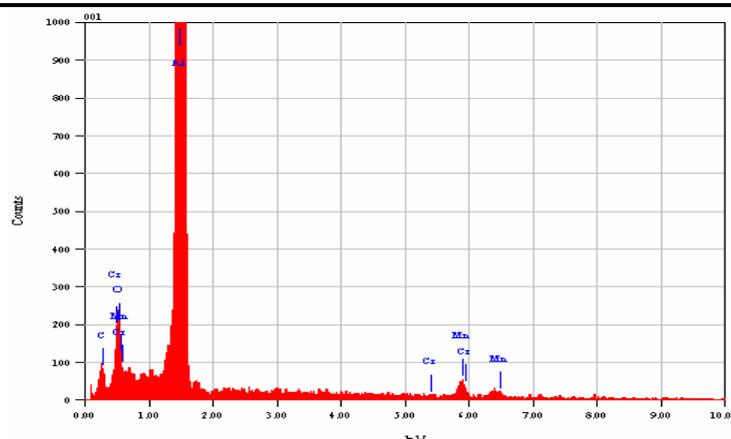
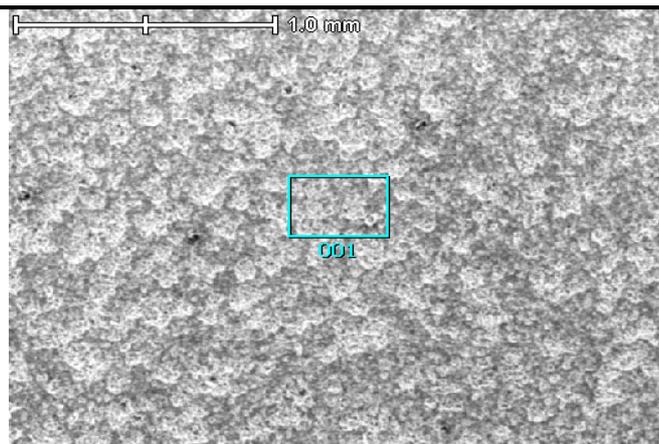


Fig. 8. SEM micrograph and EDS analysis for 3003 Al after sweeping from -1500 to -250 mV/SCE in synthetic industrial water, the rectangle shown in the image indicates the zone where the x-ray analysis is performed

3.4.2. Tests of long time

During the survey dedicated to the effect of the heat treatment the electrochemical technique is solicited as efficient and fast means for the tests accelerated of the corrosion and the passivation of aluminium alloy. To establish an interrelationship between the electrochemical results and the real phenomena of observed corrosion, we achieved tests of immersion in synthetic water for one week.

After every attack, the surface state of sample has been examined by SEM followed by the EDS analysis. In order to see the effect of the attack, a similar examination was performed on the sample before its immersion.

Figure 9 presents a SEM image obtained on the untreated alloy after its immersion in the synthetic industrial water during one week. The EDS analysis shows the presence of mainly aluminium and oxygen with an increase of the intensity of this latter.

After immersion of one week in synthetic industrial medium, a radical change of the surface state is observed (Fig. 10) for untreated and treated sample at 450°C. The increasing of oxygen peak indicates that the passive layer of the treated sample resists better than that untreated sample.

Shreir, Jarman and Burstein in their book of Corrosion [35] stated that the heat-treatable Al-Mg-Si alloys are predominantly structural materials, all of which have a high resistance to corrosion. The low Mg + Si content facilitates the production of complex extrusions with a good surface finish making Al0.7Mg0.5Si a natural choice for glazing sections and other architectural features. Higher mechanical properties are obtainable with the Al1.0Mg0.6Si0.25Cu and Al1.0Si0.8Mg0.7Mn compositions, which are therefore more suitable for load bearing structures. The corrosion resistance of the Al-Mg-Si alloys is slightly inferior to that of the Al-Mg alloys, but where maximum obtainable strength is required then a fully heat-treated Al-Mg-Si alloy would generally be preferable to an Al-Mg alloy with comparable properties obtained by cold working.

Our choice of the time of heat treatment around 2 hours agrees that cited in this book [35]. The Authors pointed out that the heat-treatable alloys containing Mn, Mg, Si, Cu... notably the Al-Cu-Mg and the Al-Mg-Si types-can be heated at 480-535°C for a period between 20min and some hours to obtain solution of the alloying elements, and then rapidly quenched. This solution treatment gives increased strength, and may also give slightly increased corrosion resistance. Further strengthening of certain alloys is achieved by an additional lower temperature heat-treatment for longer periods (1-20 h or more, according to the alloy) which promotes precipitation of the alloying elements within the metal crystal structure. With some alloys this ageing treatment takes place at room temperature. The ageing or precipitation treatment slightly reduces the corrosion resistance of most alloys.

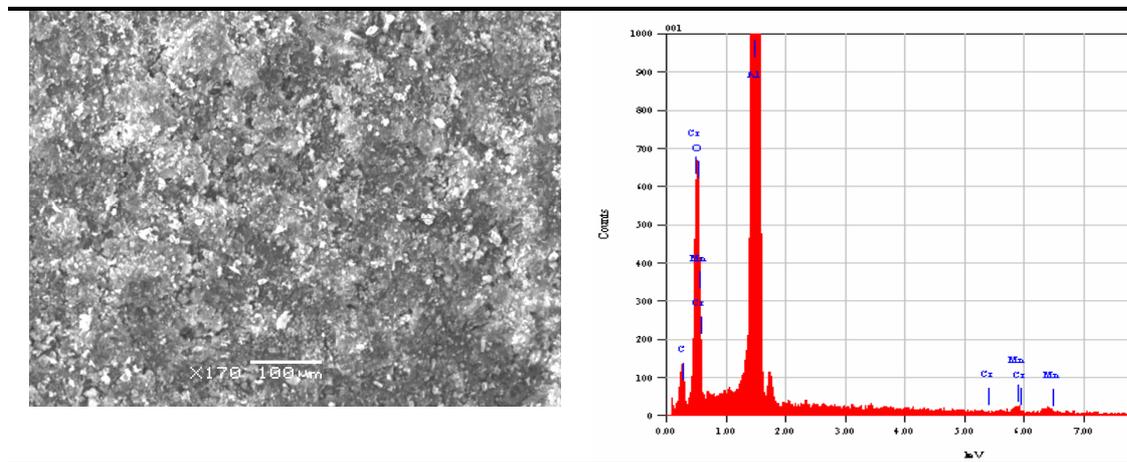


Fig. 9. SEM micrograph and EDS analysis for untreated aluminium alloy after immersion in synthetic industrial water for one week.

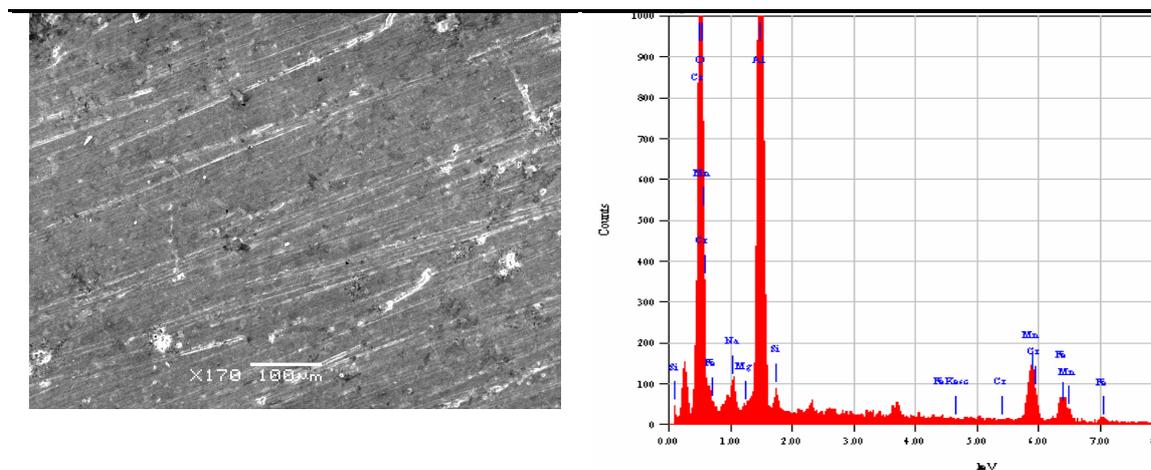


Fig. 10. SEM micrograph and EDS results for treated aluminium alloy at 450°C after immersion in synthetic industrial water for one week

4. Conclusion

In this work, we have studied the effect of the heat treatment on the behaviour of the corrosion and passivation of 3003 aluminium alloy in synthetic solution. The effect of the variation of pH, the temperature of the medium and the concentration of Cl⁻ has been also studied.

From the obtained result, we can have the following conclusions:

1. In synthetic solution, the polarization curve presents a passivation phenomenon with a breakdown of passivity.
2. The heat treatment has an effect on the corrosion of 3003 aluminium alloy. The best corrosion resistance is obtained at temperature 450 and 350°C during 2 hours.
3. After heat treatment, the performance of 3003 aluminium alloy has attributed to the formation of a compact layer of aluminium oxide on the alloy surfaces.
4. The sensibility of pitting corrosion increases with the elevation of Cl⁻ concentration.
5. The uniform dissolution of 3003 aluminium alloy is affected by temperature and pH of the medium.

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