

Corrosion Inhibition of Alloy Al-Cu-Mg by Lanthanum Chloride in 0.5 M NaCl

**Siham OUCHENANE, Siham ABDERRAHMANE
and Abdelaziz HIMOUR**

Laboratoire d'Ingénierie des Surfaces (L. I. S.), Université Badji Mokhtar,
B. P. 12, Annaba, Algeria
E-mail: abderrahmanesihem@yahoo.fr

Received: 23 November 2013 /Accepted: 12 January 2014 /Published: 26 May 2014

Abstract: This work studies the corrosion behavior of Al-Cu-Mg alloy in 0.5M NaCl with rare earth salt inhibitor, lanthanum chloride (LaCl_3). LaCl_3 concentrations used are: 100, 200, 400, 800 and 1000 ppm. The study was carried out by potentiodynamic measurements, impedance electrochemical spectroscopy, cyclic voltammetry and gravimetric method. The results obtained show that lanthanum acts as cathodic inhibitor by the reduction of the Tafel cathodic slopes. The inhibition mechanism can be explain by the hydroxide formation between the cations La(III) and ions OH^- . This hydroxide precipitates forms a passive film on the alloy surface in the chlorinated medium. The inhibiting effectiveness reaches 89.09 % for 1000 ppm of LaCl_3 .
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Keywords: Corrosion, Inhibitor, Rare earths, Aluminum alloy, NaCl.

1. Introduction

Localized corrosion is a very complex process involving many heterogeneous and homogeneous reactions. The inter metallic particles important role for the initiation and propagation of aluminum alloys is localized corrosion which is often used in aerospace industry due to excellent weight- resistance ratio. This alloy is well-known and was discussed in many works [1-3]. One from the used alloys in commercial applications is AA2024 most prone to localized corrosion attack. Two localized corrosion main types occurring on AA2024 in neutral chloride solutions, called pitting corrosion and grain boundaries corrosion. Rare earth (RE) elements provide corrosion inhibition effect to aluminum alloys; they control the cathodic reaction by precipitating metal hydroxide (La(OH)_3) at local

regions [4-8]. Another approach is the cerium conversion coating technique use to seal the porous film of anodized aluminum alloy [9]. The cerium-based inhibitors can be also introduced in the thin hybrid coatings used as pretreatment for aluminum alloys and showed positive results [10-12].

The aim of the present work is to study LaCl_3 inhibitor effect at different concentrations on the AA2024 alloy corrosion behavior in 0,5M NaCl.

2. Experimental Procedures

The composition of the AA2024 alloy was (in wt.%) 93.50 % Aluminum (Al), 4.4% Copper (Cu), 0.6% Manganese (Mn), and 1.5% Magnesium (Mg). Specimens for electrochemical studies were coated in epoxy resin, except for a section of 1 cm^2 . All

surfaces of the specimens were mechanically polished down to fine emery paper (starting from grit number 320 to 1200), and polished with diamond paste (3 μm). Then it was degreased with acetone, rinsed with distilled water and dried under airflow before being used for each electrochemical experiment. All experiments were repeated three times.

Corrosion tests were carried out in freely aerated 0.5 M NaCl solution. The studying inhibitor is Lanthanum chlorides ($\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$); it was added at concentrations of 100, 200, 400, 800 and 1000 ppm. Freshly prepared NaCl solution was used in all the experiments. All the experiments were conducted at room temperature (25 $^{\circ}\text{C}$). Separate samples were immersed for 30 min in solutions containing different concentrations of inhibitors. Electrochemical measurements were performed in a Pyrex cell (Gamry, USA) using a *Gamry Ref 600* potentiostat controlled through *Gamry framework* software. In the Pyrex cell, the area of exposure of the sample was 1 cm^2 . An Hg/HgCl electrode was employed as the reference electrode. The potential of this electrode with respect to standard hydrogen electrode was 0.224 V. All electrochemical experiments were performed after stabilization of free corrosion potential (FCP). Potentiodynamic polarization curves were plotted in a range of potentials -1000 to -300 mV/ECS using a scan rate of 1 mV/sec. Electrochemical impedance spectroscopy (EIS) measurements were performed by applying a sinusoidal potential perturbation of 10 mV at the FCP. The impedance spectra were measured with frequency sweep from 100 kHz to 10 MHz in logarithmic increment. The impedance data were analyzed using the Zview 2.00 software. The impedance data were fitted to an appropriate equivalent electrical circuit using a complex nonlinear least-squares fitting routine, using both the real and imaginary components of the data. Different parameters obtained from the best fit equivalent circuit were tabulated and analyzed.

3. Results and Discussion

3.1. Open Circuit Potential

Fig. 1 shows the variations of the open circuit potentials (E_{corr}) AA2024 alloy in 0.5 M NaCl without and with LaCl_3 at different concentrations. The open circuit potential shifts towards electronegative values when the concentration inhibitor increase. For 800 and 1000 ppm, the open potential moves towards more positive values versus time. This behavior can be attributed at slowdown rate reaction of the cathodic process, due to the inhibiting effect of LaCl_3 and/or the corrosion products deposition on the alloy surface [13].

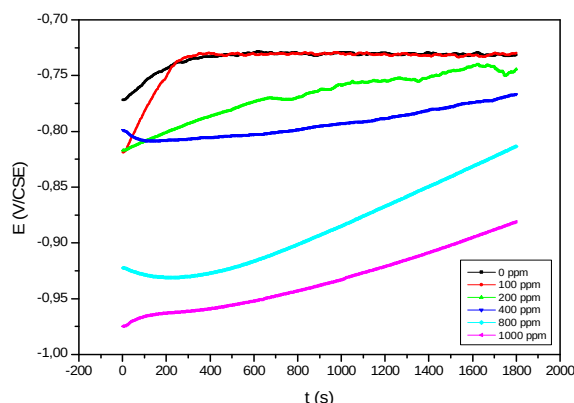


Fig. 1. AA2024 alloy Open circuit potential in 0.5 M NaCl.

3.2. Potentiodynamic Measurements

Fig. 2. Represents Tafel curves obtained with LaCl_3 at different concentrations in 0.5 M NaCl. Inhibitor additions change the cathodic branch. Only the curve without inhibitor shows current plateau. It is due to diffusion-controlled oxygen reduction. On the anodic branch the inhibitor addition has insignificant effect. The increase in inhibitor concentration from 100 to 1000 ppm, resulted in a decrease of the cathodic current density. All this observations are typical characteristics of a cathodic inhibitor [14].

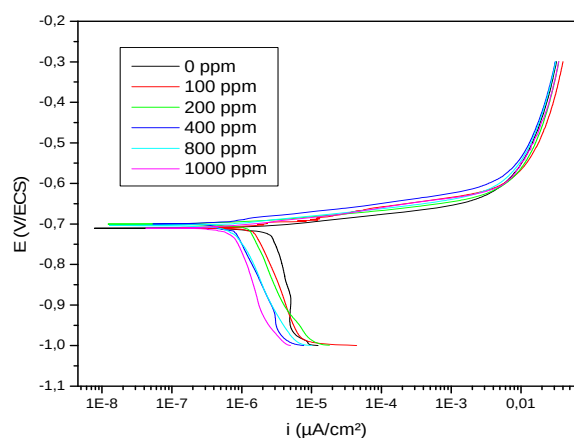


Fig. 2. AA2024 alloy polarization curves in 0.5 M NaCl.

The inhibiting efficiency (IE%) was evaluated from the current density by the following relationship:

$$IE_{i_{\text{corr}}} (\%) = \frac{i_{\text{corr}}^0 - i_{\text{corr}}}{i_{\text{corr}}^0} \times 100 \quad (1)$$

where i_{corr}^0 is the corrosion currents densities without inhibitor; i_{corr} is the corrosion currents densities with inhibitor. Or from the polarization resistance by the following relationship:

$$IE_{R_p}(\%) = \frac{R_p - R_p^0}{R_p} \times 100 \quad (2)$$

where R_p^0 is the polarization resistance without inhibitor; R_p is the polarization resistance with inhibitor.

In Table 1 we observe that the polarization resistance (R_p) increases and the current density (i) decreases with increasing inhibitor concentration. The current density decreases progressively in the presence of LaCl_3 , and reaches $0.752 \mu\text{A}/\text{cm}^2$ for 1000 ppm. These results suggest that LaCl_3 protect the alloy surface. R_p is $4.12 \text{ k}\Omega\cdot\text{cm}^2$ in absence of inhibitor and increases with inhibitor concentrations. R_p reaches $37.78 \text{ k}\Omega\cdot\text{cm}^2$ for 1000 ppm. The inhibition efficiency reaches 89.09 % at 1000 ppm of inhibitor.

3.3. Electrochemical Impedance Spectroscopy

In order to have an electrochemical parameters on the interface metal/solution, electrochemical impedance measurements were carried out in 0.5 M NaCl without and with LaCl_3 concentrations after 30 minutes of immersion Fig. 3a. In the presence of inhibitor, Nyquist plots were characterized by the appearance of two resolved time constants related to the capacitive loops; at high frequency (HF) capacitive loop refers to an activation-controlled reaction, while a diffusion-limited process through a corrosion layer at low frequency (LF), showed a Warburg impedance.

The increase in the size of the capacitive loop with the addition of inhibitor shows that a barrier gradually forms on the AA2024 alloy surface. The barrier is probably related to the formation of an inhibitor film on the electrode surface. The same experimental were presented in Bode and Bode-phase format, Fig. 3b and Fig. 3c respectively; all impedance curves increases with inhibitor concentration and phase angle shift, obviously correlating with the increase of film adsorbed on alloy surface.

Nyquist plots were simulated by the equivalent circuit with the ZView software; without inhibitor (Fig. 4.a), equivalent model can be represented by $R_s(Q_1(R_1(Q_2R_2)))$, and $R_s(Q_1(R_1(W_01)))$ with inhibitor (Fig. 4b). Where R_s : solution resistance, Q_1 : film

constant phase element (CPE), R_1 : film resistance, Q_2 : double layer (CPE), R_2 : double layer resistance and W_01 : Warburg impedance. The CPE defined as [15]:

$$Z_{CPE} = [Q(j\omega)^n]^{-1}, \quad (3)$$

where Q and n are frequency independent parameters, which usually depend on temperature and $-1 \leq n \leq 1$. CPE describes an ideal capacitor for $n = 1$, an ideal inductor for $n = -1$ and an ideal resistor for $n = 0$.

The overall response of the system is obtained as a result of the superposition of the responses due to the film (R_1 - Q_1) and to the metal-solution interface (R_2 - Q_2). It is important to note that the elements (R_1 - Q_1) encompass all the information related to the surface layer and the possible defects that may be present within it. On the other hand, all the processes related to charge transfer at the electrical double layer and also diffusional transport from the metal-solution interface would be included in the (R_2 - Q_2) loop. This model can be represented as $R_s(Q_1(R_1(Q_2R_2)))$.

The results of regression calculation to reproduce experimental impedance spectrum are overlaid in experimental one in Figs. 5 and 6; the green represent the fitted value. The agreement between experimental and calculated values is satisfactory.

The inhibition efficiency was calculated from R_t by the following relationship:

$$IE_{R_t}(\%) = \frac{R_t - R_t^0}{R_t} \times 100, \quad (4)$$

where R_t^0 is the transfer resistance without inhibitor; R_t is the transfer resistance with inhibitor.

The calculated electrolyte resistance R_s is the independent of experiments, and the average value is about $7.85 \Omega\cdot\text{cm}^2$. According to Newman, the electrolyte resistance of a disk electrode can be expressed as [16]:

$$R_s = \frac{\pi r p_s}{4} \quad (5)$$

where p_s is the electrolyte conductivity, for 0.5 M NaCl ($\approx 5 \Omega\cdot\text{cm}$); r : radius of disc electrode (cm).

Table 1. Alloy AA2024 electrochemical parameters obtained from Tafel curves in 0.5M NaCl with and without inhibitor concentrations.

C (ppm)	β_a (mV/dec)	β_c (mV/dec)	E_{corr} (mV/ECS)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	R_p ($\text{k}\Omega\cdot\text{cm}^2$)	C.R. (mpy)	IE_{R_p} (%)
Blank	36.7	543.1	-710	4.17	4.12	1.791	/
100	31.1	530.9	-710	1.88	12.13	0.807	66.03
200	27.2	521.1	-700	1.26	20.87	0.540	80.25
400	26.9	490.8	-700	0.99	22.03	0.441	81.29
800	25.8	482.8	-703	0.93	28.84	0.399	85.71
1000	26.6	457.3	-711	0.75	37.78	0.303	89.09

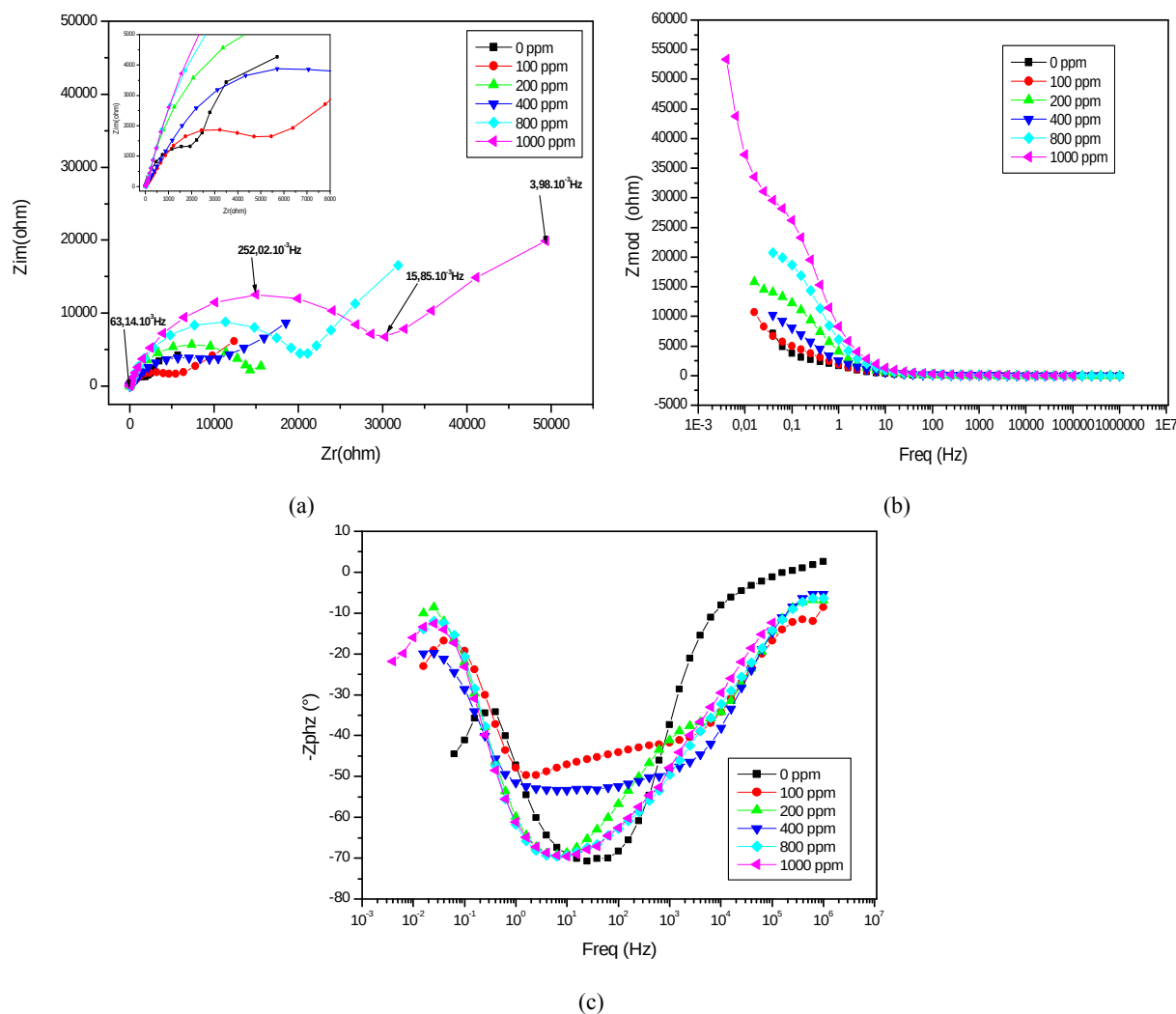


Fig. 3. AA2024 alloy electrochemical impedance plots in 0.5M NaCl with and without inhibitor: (a) Nyquist, (b) Bode, and (c) phase angle plots.

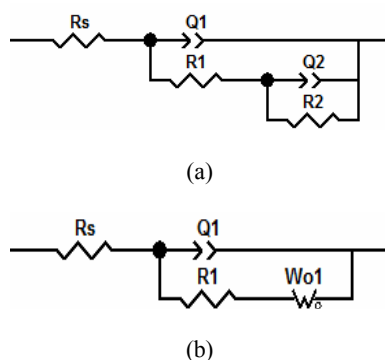


Fig. 4. Equivalent circuit model used to model the experimental impedance data, (a) in the absence of inhibitor, (b) in the presence of inhibitor.

The calculated R_s value for an ideal cell configuration, namely the reference electrode set at

the infinite distance is 1 Ohm.cm² in a good agreement with experimental data.

In Table 2, it can be noted that Q_1 is 137.61 $\mu\text{F}/\text{cm}^2$. It decreases progressively and reaches 32.63 $\mu\text{F}/\text{cm}^2$ for LaCl₃ 1000 ppm. These results suggest that LaCl₃ film is formed on alloy surface. R_t is 4.41 kOhm.cm² without LaCl₃, increases with inhibitor addition and reaches 29.98 kOhm.cm² for LaCl₃ 1000 ppm. EIS measurements showed that R_s and n_1 increase with the inhibitor concentration indicating a surface behavior enhancement. Q_1 decreases and R_1 increase with LaCl₃ addition. n_2 value without inhibitor showed nearly capacitive behavior. After LaCl₃ addition, Warburg impedance increase this may be associated with precipitates formed by lanthanum oxides/hydroxides on the cathodic regions. W higher is 130.560 kOhm.cm² and the maximum inhibition efficiency is 85.29 % for 1000 ppm.

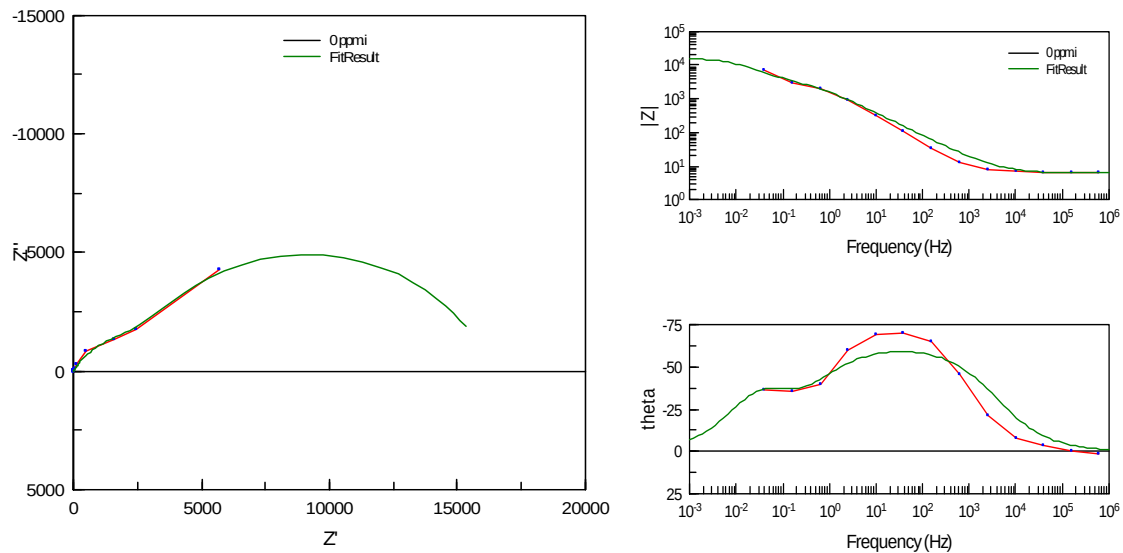


Fig. 5. Regression calculation to reproduce experimental impedance spectrum without inhibitor.

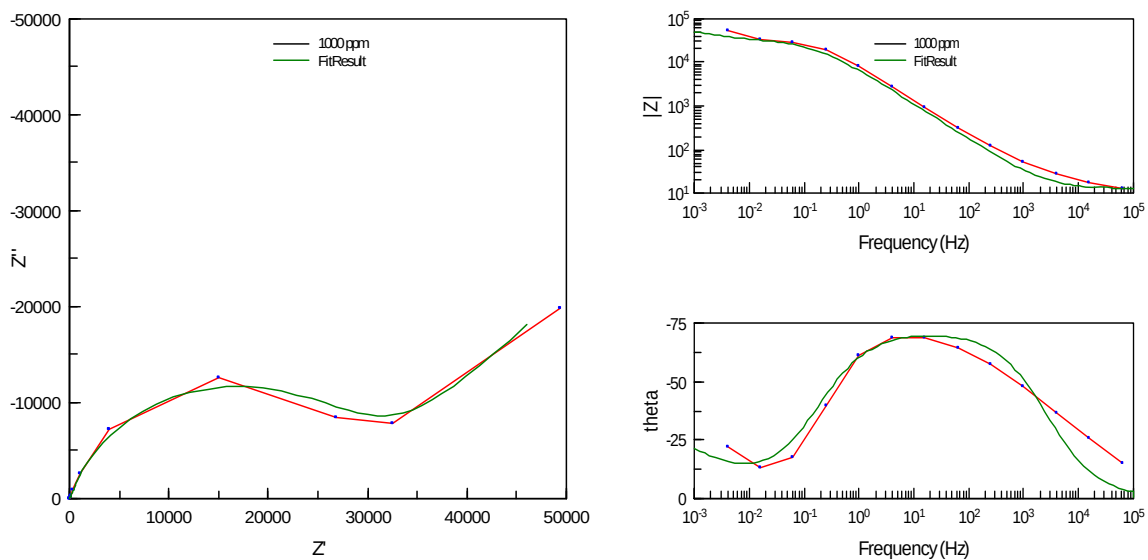


Fig. 6. Regression calculation to reproduce experimental impedance spectrum with inhibitor.

Table 2. Electrochemical parameters obtained from Nyquist curves and equivalent circuits in 0,5M NaCl with and without inhibitor.

[LaCl ₃] (ppm)	R _s (Ω.cm ²)	Q ₁ (μF/cm ²)	n ₁	R ₁ (KΩ.cm ²)	W (KΩ.m ²)	Q ₂ (μF/cm ²)	n ₂	R ₂ (KΩ.cm ²)	IE _{Rt} (%)
Blank	6.14	137.61	0.70	4.41	/	510.01	0.81	11,987	/
100	6.67	177.90	0.55	7.80	7.880	/	/	/	43.46
200	6.85	125.36	0.70	9.65	10.326	/	/	/	54.30
400	6.41	115.12	0.75	9.71	17.980	/	/	/	54.58
800	7.14	32.75	0.82	19.76	47.980	/	/	/	77.68
1000	12.29	32.63	0.84	29.98	130.560	/	/	/	85.29

4. Conclusion

In this work, AA2024 alloy corrosion in 0.5 M NaCl was investigated by electrochemical methods:

- Free potential moves towards negative values as a function of immersion time, in the solution with or without inhibitor. This behavior is attributed to superficial layer reorganization with anodic process acceleration.

-Polarization curves indicate the corrosion inhibition after LaCl_3 addition. For 1000 ppm of this latter, the maximum polarization resistance is $37.78 \text{ k}\Omega\cdot\text{cm}^2$ the corrosion potential values and the current density are respectively -711.0 mV/ECS and $0.752 \mu\text{A}/\text{cm}^2$. The corresponding inhibitive efficiency is 89.09 %.

-At the same concentration, EIS measurements confirm ions La^{3+} inhibitor effect and the inhibitive efficiency is 85.29 %, the film constant phase element (CPE) decreases progressively to $32.63 \mu\text{F}/\text{cm}^2$; R_t increases to $29.98 \text{ k}\Omega\cdot\text{cm}^2$; Warburg impedance W increases to $130.560 \text{ k}\Omega\cdot\text{cm}^2$, which may be associated with precipitates formed by lanthanum oxides/hydroxides on the cathodic regions. These results suggest that LaCl_3 film is formed on alloy surface.

The chloride ions strongly influence both rate of the corrosion processes and the hydroxide deposits formation.

According to these results, these non-ecotoxic ions La^{3+} inhibitor can be an alternative to the chromates use.

Acknowledgments

The authors thank Mrs. Nora ZENNADI for helping them to translate this work.

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