ELECTRODISSOLUTION STUDIES OF THREE ALUMINUM ALLOYS IN ACID, NEUTRAL AND ALKALINE SOLUTIONS

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Although aluminum and its alloys are chemically reactive, they are resistant to corrosion in solutions of pH 4 to 9 whenever aggressive ions chloride, iodine, bromide are not present. The resistance is attributed to the presence of a protective thin oxide film. The aim of this paper is to study the electrochemical behavior of three aluminum alloys Al-Cu-Mg1.5-Si-Mn0.6; Al-Li$_2$-Cu$_2$-Zr-Mg and Al-Li$_2$-Ti-Zr-Cu$_2$ in three elaborated states.

Electrodissolution and localized corrosion characteristics of these alloys have been investigated by adequate electrochemical techniques including impedance spectroscopy in the pH range of 4 to 9 in the absence and in the presence of chloride ions.

Potentiodynamic polarization curves for three alloys in acid, neutral and alkaline solutions in the absence and in the presence of chloride ions show that the corrosion parameters of these alloys (OCP, ϵ_{corr}, R_p, i_{corr}, ϵ_{pitt}) depend especially on the concentration of halide ions and of the pH values of solutions.

Impedance spectra for all alloys were similar in shape. The appearance of two semicircles in the impedance diagram was common to all alloys electrodes. The high frequency semicircle corresponds to a capacitive loop and the low frequency semicircle corresponds to an inductive loop. The semicircle radii were dependent on the pH values of solution and of the chloride ions concentration.

The high frequency capacitive loop is related to the dielectric properties of the surface film and the low frequency inductive loop is attributed to the relaxation of adsorbed chloride ions and local metal dissolution.

INTRODUCTION

Corrosion of aluminum alloys has been the object of the study for numerous technical and scientific workers, due to the importance of these materials in contemporary technical world. High strength alloys can be obtained by addition of specific elements such as Cu, Mg, and Zn *et al.*, and by specific heat treatment procedures.

Alloying elements age hardening treatments and impurities induce the formation of intermetallic precipitates in the matrix of the alloy, which, by exposure of the material to specific corrosive environment produce a highly localized attack such as S.C.C. or pitting.

This is due to the fact that well known anions such as Cl$^-$ induce the local dissolution of the protective passive film and consequently the local destruction and failure of the material.

Extensive investigations have been carried out on the role of halide and other ions in the formation, breakdown and repassivation of passive protective films and initiation of localized corrosion of aluminum alloys.[1-7] Also studies have been reported concerning the effect of alloy content, heat and mechanical treatment electrolyte composition, on film formation and dissolution in connection with the localized attack of the material.

This paper deals with the electrochemical study of the electrodissolution, and electroformation of the anodic films on some 2024 and 2090 Al alloys in different pH media in the presence and absence of chloride ions. The aim of the work is to emphasise on the film formation and dissolution.

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RESULTS AND DISCUSSION

1. The Open Circuit Potential (OCP)

In corrosive solutions of pH between 4 and 9 aluminum and its alloys tend to be covered by a thin adherent oxide film which gives the metal and alloys a good corrosion resistance. In such solutions the film is slightly soluble, the solubility depending on the pH. As is presented in [8] by M. Pourbaix the minimum solubility occurs at a pH of 5.1. The minimum solubility depends also on the degree of aging of the hydrated aluminum oxide.

Open circuit potential versus time curves at various values of pH corrosive solution without Cl⁻ions are presented in Fig. 1. The results show that, firstly the OCP rapidly decreased, showing minimum potential value at approximately –600 –700 mV in all the solution. This is attributed to the solubility of naturally formed film in the atmosphere, which enters directly in contact with the aqueous solutions. After that, the OCP gradually increased to more noble potential values and finally achieved steady state potential values at approximately –300 mV for alloy 1,2 and 3 at pH=4; approximately –350 mV for alloys 1, 2 and 3 at pH=7. At this potential alloys 2 and 3 present oscillations phenomena (passivation/depassivation of the film) due to the presence of Al Li Cu Mg precipitation compounds which have a higher dissolution than others constituents.
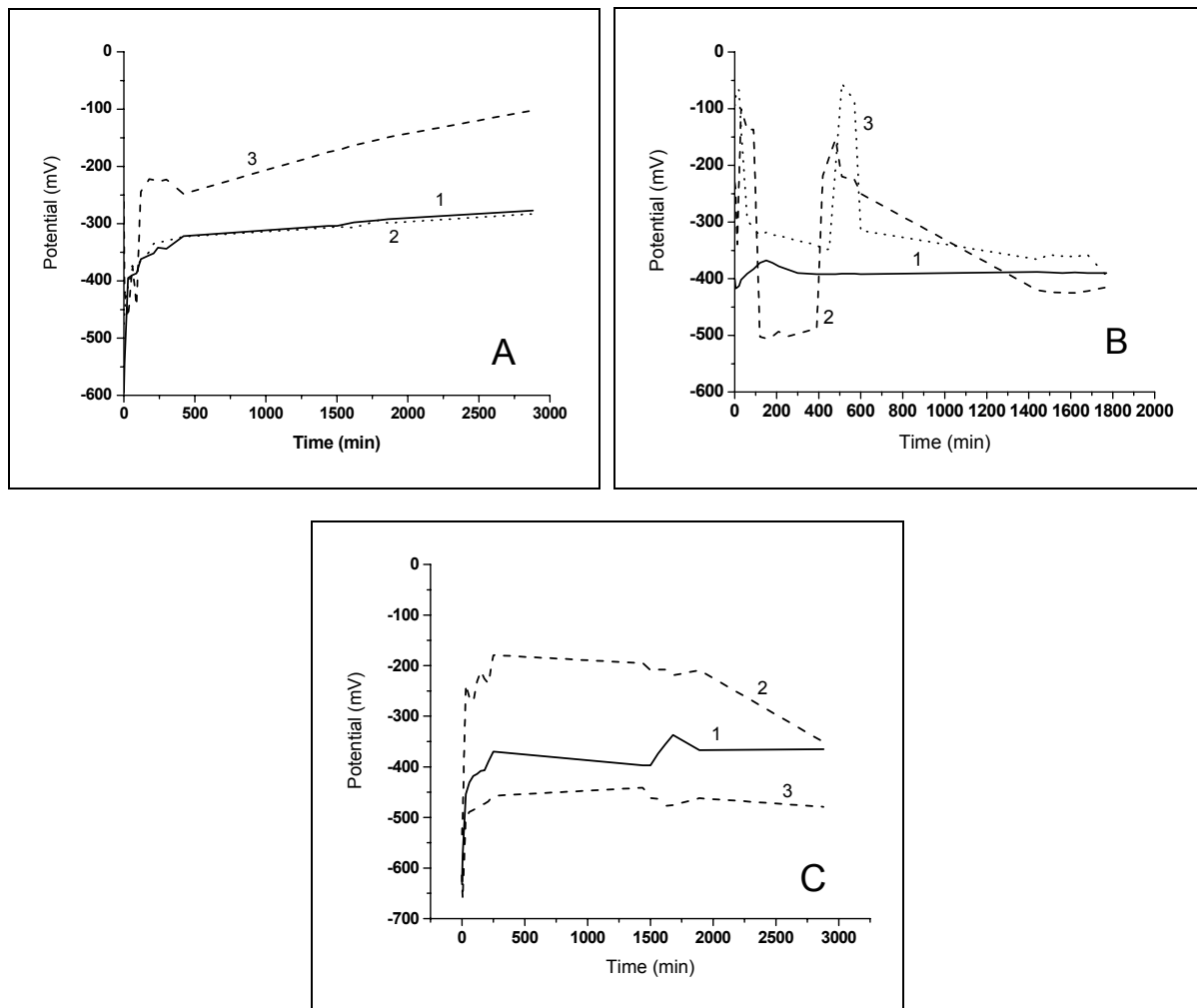

Fig. 1 – The OCP *vs.* time evolution of Al alloys in buffer solution: A)-pH=4;
B)- pH=7, C)-pH=8. 1) -alloy 1; 2)-alloy 2; 3)-alloy 3.

When the compound is dissolved the potential is decreased and when the solubility product of the oxide is achieved the potential starts to rise again; approximately –400mV for all the three alloys, at pH=8. As shown in Fig.1 (A), the higher value of the pH, the less noble the steady state potential values.

The OCP stability of the reaction film allows us to determine the formation rate of the passive film of the alloys. For example, the steady state potential of the alloys is achieved after approximately 1,000 minutes in all pH media.

In Fig.2 is presented the OCP *vs* time values for all alloys in corrosive solution at pH in the presence of chloride ions.

As shown in Fig. 2, the strong-lowering of the OCP values for all alloys toward negative values is due to the fact that the chloride ions interact with the passive film which starts to dissolve slowly.
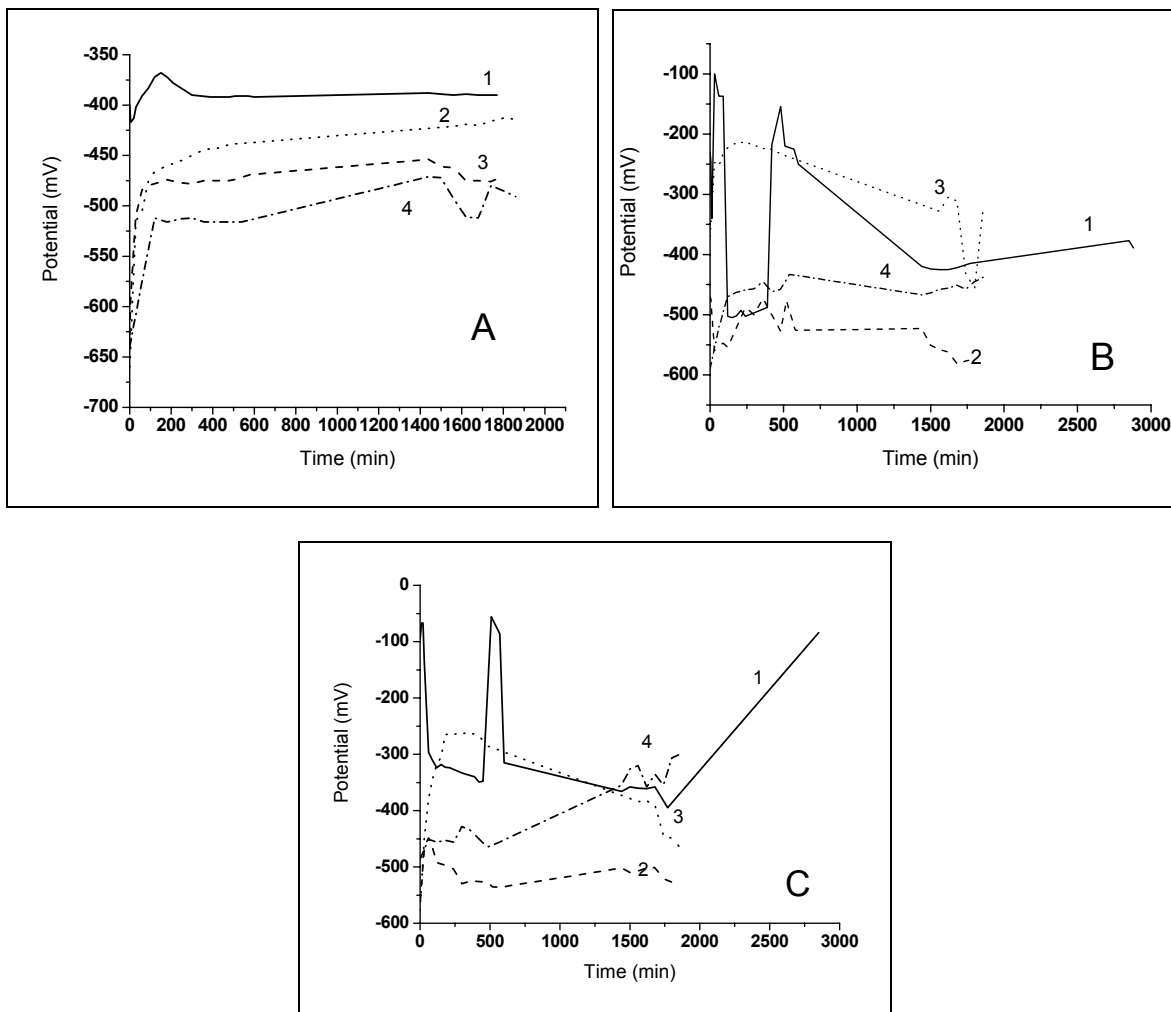

Fig. 2 – The OCP *vs*. time evolution of Al alloys in buffer solution without and with Cl⁻.
1)-without Cl⁻; 2-0.6 M NaCl; 3-0.01M NaCl; 4-0.001M NaCl. A)-alloy 1; B)-alloy 2; C)-alloy 3.

2. Potentiodynamic polarization curves

We studied the potentiodynamic anodic polarization curves of alloys 1, 2, 3 in buffered electrolyte solution of pH=7 in the absence and in the presence of 3.5% NaCl. The experiments were carried out in stagnant condition potential sweep of 150 mV/min, in the range –1 to 1.5V.

The electrochemical parameters of the anodic polarization curves of the alloys in aggressive solution are presented in Table 1.

The main electrochemical and corrosion parameters of aluminum alloys in buffer solution without and with NaCl solution at 25°C and natural aeration conditions

Alloy	Solution	ε_{corr}, mV/esc	I_{corr}, mA	b_a mV/dec	b_c mV/dec	R_p kΩ cm^{-2}	v_{corr} mm/y	E_{pit} mV
Alloy 1	Buffer pH=7	-482	0.0147	0.12	0.12	1.75	1.002	
	Buffer pH=7 +NaCl	-482	0.0141	0.12	0.12	1.85	0.953	-400
Alloy 2	Buffer pH=7	-548	0.0097	0.12	0.12	2.8	4.4	
	Buffer pH=7 +NaCl	-546	0.0085	0.12	0.12	3.05	4.1	-320
Alloy 3	Buffer pH=7	-655	0.0016	59.1	0.51	13.1	1.15	
	Buffer pH=7 +NaCl	-599	0.0043	0.12	0.12	5.9	0.37	-320

All the anodic curves exhibit an apparent active region and a potential-quasi-independent intermediate plateau, indicating the existence of an oxide layer on the electrode surface. In the presence of 3.5% NaCl solution an abrupt current rise at –0.4 V for alloy 1, and –0.32 V for alloy 2 and 3 is correlated with a breakdown of passivity *i.e,*. pitting potential E_{pit}. Many pits developed on the specimen anodically polarized in aggressive solutions with 3.5% NaCl.

The activation of the dissolution process of the anodic film in the presence of the Cl$^-$ ions is due to the fact that Cl$^-$ ions generate the formation of complexes with water, hydroxyl ions $Al(OH)^{++}$, $Al(OH)^+$, AlO^+ with higher dissolution rate.

3. EIS measurements

EIS measurements were made at the OCP after exposure to the test solutions at 0, 1440 and 1880 minutes. Data in the complex plane (Nyquist plot) are presented in Fig. 3. Fig. 3 shows that at least two time constants can be observed in all cases. The first time constant corresponds to the capacitive loop at higher frequencies and the second to the inductive loop at lower frequencies. In some cases a third time constant was also observed. There is no general agreement about the origin of the different time constants, but impedance spectra in the complex plane for alloys are generally admitted. The capacitive loop at high frequencies is attributed to the oxide layer; the inductive loop at medium frequencies is due to the relaxation of the species in the oxide layer, on the surface area modulation of the pitted active state of the alloys. The low frequency capacitive loop may be attributed to the uniform dissolution of the oxide film before the onset of pitting corrosion through the formation of chloride containing aluminum soluble complexes.
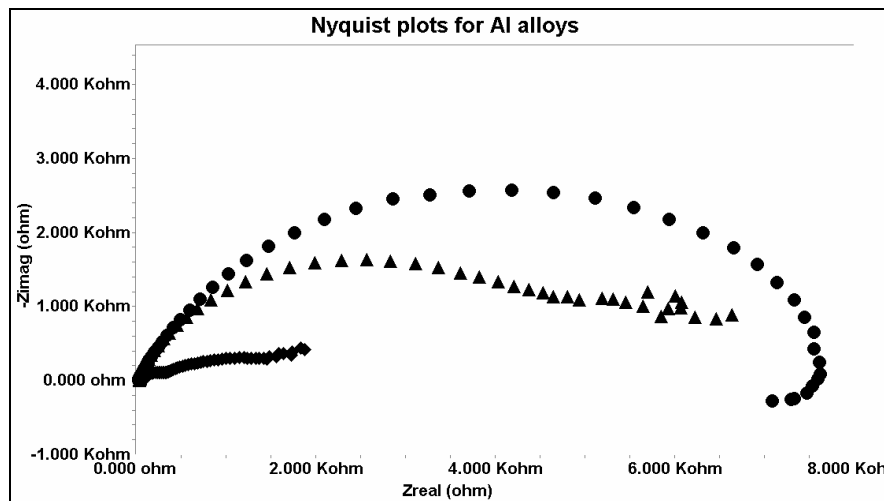

Fig. 3 – The EIS of Al alloy 1($\blacklozenge$), 2($\blacktriangle$) and 3($\bullet$) at pH=7, in solution with NaCl 0.6M.

The equivalent circuit used to fit the experimental data consists of a constant plan element (CPE) Q in parallel with series resistors R_a and R_b and an inductance L in parallel with R_b. The CPE type impedance was extensively used in the literature for this type of study.[9-12]

We add that in the complex impedance plot, the value of R_a represents the interaction point of the low frequency semicircle on the real axis for $\omega \to 0$. The value of this interaction is used to obtain a c. polarization $R_p = \lim |Z_{real}|$.

$\omega \to 0$

R_p, in general for practical electrodes, as ours, is a complicated function determined by the rate of charge transfer, mass transport and chemical reaction. R_p values for the three alloys at different time exposures are presented in Table 2.

Table 2

The results for aluminum alloys in buffer solution studied by EIS

Nr. Crt.	Alloy	Time (minute)	pH	R_{pN} (kΩ)
1	Alloy 1	1680	7	3.8
2	Alloy 2	1680	7	6.8
3	Alloy 3	1680	7	2

As is presented in Fig. 3 a capacitive semicircle and an inductive loop are evident in the complex plan plot of alloy 1 and two clearly distinct capacitive semicircles at high frequency and an inductive loop at low frequency for alloys 2 and 3.

CONCLUSIONS

Electrodissolution and eventually pitting behavior of 2024 and 2090 aluminum alloys have been investigated by OCP potentiodynamic polarization and impedance spectroscopy. The pitting potential increases in the order: alloy 1, alloy 2, and alloy 3.

Impedance measurements showed a single capacitive loop in the Nyquist complex plan plot for alloy 1, which is attributed to the influence of the $AlCu_2$ precipitate on the dissolution of the protective film as well as two capacitive loops at high frequencies. The second capacitive loop is attributed to the presence of a Li containing precipitate.

EXPERIMENTAL

The experimental studies were carried out on electrodes obtained from 2024 and 2090 aluminum alloy rod. The composition of the three alloys is presented in Table 3.

Table 3

Chemical composition of casting aluminum alloys (% weight)

	Al %	Cu %	Mg %	Mn %	Si %	Ti %	Li %	Fe %	Zr %
Alloy1	Base	4.1	1.5	0.46	0.22	0.074	-		
Alloy2	Base	2.8	0.28	-	0.14		2.5	0.15	0.14
Alloy3	Base	2	-	-	-	1.2	2	-	-

Alloy 1 (2024) was obtained in extruded form at 420°C. Forming processes induce preferred crystallographic texturing (high elongated grains). The precipitation compounds nucleated in matrix solution (Al+Cu+Zn) are plate shaped directionally oriented. By EDAX identification the following phases were identified: $CuAl_2$, Mn_xAl_y, Al_2Cu Mg *et al*.

Alloy 2 (2090 Al Cu Li Zr) was obtained by extrusion at 420°C. Precipitated phases were produced by forming processes identified by EDAX on $CuAl_2$, AlLi, Al Li Cu Mg in matrix solution (Al Cu Si).

Alloy 3 (2090 Al Cu Li Ti) is a cast alloy. The precipitate phases include the same phases formed in alloy 2, and also $TiAl_3$. Mg_2SiTi.

The working specimens were polished by abrasive paper, degreased ultrasonically in alcoholic solution and finally in acetone and distilled water and dried in warm air.

The experiments were performed using buffered solution containing Na_2HPO_4 and citric acid added until the desired pH was obtained. The pH of the solution was 4; 7; 8.

Electrochemical measurements were carried out in a common three electrode glass cell. The counter electrode was a platinum foil and the reference electrode was a $Hg/HgCl_2$ saturated electrode. The measurement system includes a Gamry computerized equipment. Before each measurement the electrode was kept in test solution for no less than one hour, during which a steady open circuit potential (OCP) was obtained. The potentiodynamic polarization curves were obtained at a scanning rate of 150mV/min in the potential range –0.5V to 1.5V. The electrochemical impedance spectroscopy (EIS) was obtained in the frequency range from 0.01 to 100.000 Hz with a signal amplitude of 10 mV alterning current. All measurements were performed at room temperature (25°C) in normal aerated condition.

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