Oxide Film Destruction on Al-Mg Alloys in HCl Solutions

S. Abd El Wanees[1, 2] Mohamed I. Alahmdi[2] S M. Abd El Haleem[1] A. Abd El Aal[1] K. M. Abo Zeed[3]
1.Chemistry Department, Faculty of Science, Zagazig University, Zagazig, Egypt
2.Chemistry Department, Faculty of Science, Tabuk University, Tabuk, Saudi Arabia
3.Department, Faculty of Science, Geuzain University, Geuzain, Saudi Arabia

Abstract

Open circuit potential technique is used to follow the oxide film destruction of three of Al-Mg alloys in HCl solutions of varying concentrations. Dissolution of the passive film on pare metal surface takes place in two distinct steps indicating that the film is composed mainly of a barrier layer of Al_2O_3 adjacent to the metal surface and an outer porous modification on the top of the first one. The rates of oxide film destruction and/or dissolution (δ_1^{-} and δ_2^{-}) follow a direct logarithmic law. The extent of oxide film destruction and metal dissolution were found to increase with increasing the acid concentration and the percent of Mg content in the alloy sample.

1. Introduction

Al –Mg alloys has been used in many applications among of which is the shipbuilding and food industries. The corrosion resistance of alumniuim and its alloys is highly attributed to the presence of a compact protective surface oxide film. The formed film is relatively stable in a wide range of pH (from pH 4 to pH 9) and can be destroyed at lower pH values.

Various mechanisms have been advanced to explain the role of Cl^- ions in the breakdown of Al_2O_3 films [1-3]. According to the complex ion theory of corrosion, Foley [4] showed that anions function in a specific manner, forming chemical species in aqueous solutions and the subsequent acceleration of dissolution or repassivation of the metal depends on the stability of these species [5]. The migration of Cl^- ions through the film is essential for the breakdown of passivity as they reach the metal/film interface [3, 6]. This is attributed either to the inability of Cl^- ions to enhance oxide film growth and repair, owing to the formation of soluble salts [7], or to the chemisorption onto the anodic areas of the metal surface, ending with the formation of soluble oxide-chloride complexes [5].

Since hydrochloric acid solutions are always used for pickling and for chemical and electrochemical etching of Al, it is, therefore, of interest to investigate its behavior as function of acid concentration under natural corrosion conditions. In the present study the technique of open circuit potential measurement, is used to study the rate of oxide film destruction of three of Al-Mg alloys in different concentration of HCl solutions.

2. Experimental

2.1. Materials and methods

Sheets made out of different Al-Mg alloys, such as, Al-0.5% Mg, Al-2.5% Mg and Al-5.0% Mg alloys with the dimensions 2.5, 5 and 0.7 cm were used. Prior to each experiment, the surface of Al-Mg specimens was abraded with the finest grade emery papers to mirror finish, rinsed with acetone and finally washed with bi-distilled water.

The potential of the Al–Mg electrodes were measured in naturally aerated HCl solutions. Potential-time curves were constructed by measuring the potential of the Al- Mg electrode to the nearest mV on a Wenking potentiometer type PPT 70 relative to the saturated calomel electrode (SCE). The steady state potentials were considered as those values that did not change by more than 1 mV in 10 min. Each experiment was carried out in a freshly prepared solution and with a newly abraded electrode surface.

3. Results and discussion

The corrosion behavior of three different Al-Mg electrodes in solutions of HCl of various concentrations is followed by measuring the open-circuit potential of the working electrode as function of time until steady-state potential is reached. The curves of Figs 1-3 represent the behavior of such electrodes in HCl solutions of concentrations vary between $5x10^{-4}$ M and 0.1 M. As can be easily seen from the curves of these figures, the steady-state potential, E_{st}, is approached from noble values and becomes more active the higher the acid concentration. This behavior could be attributed to the destruction of the air formed pre-immersion Al_2O_3 film followed by the continuous dissolution of the bare metal [8-9]. The extent of oxide film destruction and metal dissolution were found to increase with increasing the acid concentration and the percent of Mg content in the alloy sample.

The more interesting features of the curves of Figs 1-3 is the fact that the *E*-time curves are composed of two distinguished segments before reaching the final steady-state potentials. The first segment of these curves occurs within the first 20 minutes of immersion of the alloy in the corrosive solution, while the second segment takes longer time depending on the HCl concentration. The slope of both segments increases with increasing the acid concentration indicating increased rate of oxide film destruction. The two reported *E*-time segments could be attributed to the consequent dissolution of two different air pre-formed Al_2O_3 films on the metal surface. These films are mainly composed of a barrier layer of Al_2O_3 adjacent to the metal surface and an outer porous modification developed on the top of the first one [8-15].

Fig 4 represents the variation of the steady-state potential, E_{st}, with the logarithm of HCl concentration. Using the least square method, a straight line is obtained satisfying the relation [16-21]:

$$E_{st} = a_1 - \left(\frac{2.303RT}{ZF}\right) \log C_{\mathrm{HCl}} \qquad (1)$$

where a_1 is a constant which represents the steady-state potential, E_{st}, in a solution of 1 M HCl and amounts to -1058, -1078 and -1093 mV_{SCE}, for Al-0.5 % Mg, Al- 2.5 % Mg and Al-5.0 % Mg, successively. Similar behavior was also noted for Fe [18], Ni [19], Al [10, 11], steel [22, 23] and Zn-alloy [24]. Equation 1 describes a general phenomenon, irrespective of whether the anodic reaction leads to film destruction or film repair. Abd El Kader and Shams El Din [19] derived this equation theoretically, based on the specific adsorption of anions on the surface of the metal or the metal oxide.

The way by which the open-circuit potential of the aluminium electrode, *E*, approaches the final steady-state values is of interest. As could be seen from the curves of Figs 5-7, the open circuit potential, *E*, varies linearly with the logarithm of the immersion time, *t*, along the two distinguished segments of the curves of Figs 1-3, before reaching the final steady-state values. This behavior could be attributed to the stepwise dissolution of the two previously reported air formed films of Al_2O_3.

The stepwise destruction and/or dissolution of the Al_2O_3 films, under the prevailing experimental conditions, follows a direct logarithmic dissolution law and increases with increasing the HCl concentration [19]. This behavior could be understood when the physical and chemical properties of the Al_2O_3 film covering the metal surface are taken in consideration. There are two forms of aluminium oxides, namely, α- Al_2O_3 and γ- Al_2O_3. The oxide when forms on the metal is of the α- Al_2O_3 type, in which the oxide ions form a hexagonally close-packed array and the Al^{3+}ions are distributed symmetrically among the octahedral interstices [25]. The α- Al_2O_3 has still another structure, which is a defect rock salt like structure with an arrangement of Al^{3+} and O^{2-} ions in the rock salt ordering with every third Al^{3+} ion missing [25]. However, other authors [26] reported that the porous oxide exhibits a uniform array of hexagonal cells, each one containing a cylindrical pore.

Abd El Kader and Shams El Din [19] assumed that only under the influence of a strong electric field, of the order of magnitude of RT/ZF per atom layer of the oxide, can detectable ionic currents flow. With this high field strength, Ohm's law does not apply, and ion transport is governed by the familiar Guntherschulze & Betz relationship [27]:

$$i_a = K_a e^{(\beta H)} \qquad (2)$$

where K_a and β are constants, and *H* is the effective field strength[8]. Under open circuit conditions, i_a can originate from the specific adsorption of the present anions on the oxide covered metal [19]. This creates image charges of the same magnitude but of opposite sign at the oxide/metal interface, sufficient to promote ion transfer through the oxide to the film/solution interface. The field strength depends on the nature and charge of the anion, and to a lesser extent on its concentration. Assuming, however, that all the potential differences in the electrical chain, other than the one across the oxide film are constant and small, the field strength *H* of equation 2 is substituted by the term E/δ, where *E* is the measured potential relative to the reference half-cell, and δ is the thickness of the oxide film. Therefore, one can apply equation 3 to explain the straight-line relationships of the two linear segments of Figs. 5-7. This equation describes the variation of the open-circuit potential of the metal, *E*, with time, *t*, via:

$$E = \text{const.} \pm \left(\frac{2.303\delta^-}{\beta}\right) \log t \qquad (3)$$

where δ^- represents the rate of oxide film thickening or destruction per unit decade of time and β is a constant which is identified as [28]:

$$\beta = \frac{n\,F}{RT\alpha\delta`} \qquad (4)$$

where α is the transfer coefficient similar to that encountered in normal electrochemical reactions[20], ($0 < \alpha < 1$), and $\delta`$ is the width of the energy barrier surmounted by the ion during transfer.

The growth of an anodic oxide film on Al surface in aqueous solutions takes place by counter migration of Al^{3+} and O^{2-} ions through the film thickness, under a high field, with the formation of amorphous Al_2O_3 at the metal/film interface and film/electrolyte interface [30-33]. If, however, foreign ions like Cl^- ions incorporated the oxide film on Al, the properties of the film can be altered. Anions present in solutions may substitute some O^{2-} ions in the oxide film [30-33]. On the other hand, according to the complex ion theory of corrosion [34], anions function in a specific manner, forming chemical species in the solution. However, accelerated dissolution or repassivation of the metal depends on the relative stability of these species and varies with the nature of anions

[35].

That the dissolution of Al_2O_3 in Cl^- ions solutions is represented by two stages, was previously reported by Mazahar et al.[36] and Abd El Haleem et al. [10, 11] indicating the duplex nature of the formed Al oxide. The prevailing dissolution in both stages over oxide film thickening when Al is immersed in Cl^- ions containing solutions could be attributed to the formation of soluble chloride salt of Al [35] or to the chemisorption of Cl^- ions upon the anodic areas of the metal surface that alters the oxide film repair [10,11, 37, 38].

It has also been evident that the naturally formed film on Al surface consists of 2 layers, a layer of compact barrier-type oxide on contact with the metal and an outer porous layer [13 The barrier layer is formed by the simple combination of Al and oxygen and exhibits rectifying characteristics similar to those anodically formed barrier film [10, 13]. The maximum possible thickness of this natural barrier layer is controlled only by temperature, in the same manner that the applied voltage controls the thickness of an anodic barrier film. However, the outer portion of the naturally formed film is created from the barrier layer by reaction of the compact oxide with components of the environment, principally moisture [39]. It is different from the barrier oxide in that it passes current freely in either direction similar to the porous potion of anodically formed oxide films. The thickness of the outer portion of the natural oxide film is a function of time and the corrosivity of the environment [10, 13].

Several investigations were devoted to determine the thickness of oxide films formed on Al surface. Mathieu et al. [40] used auger electron spectroscopy, depth profiling and angle-resolved photoelectron spectroscopy for the determination of the thickness of naturally formed oxide film on Al surface. The thickness of the film evaluated by these techniques is reasonable and amounts to 1.7-1.8 nm. A.C. impedance technique was used for the determination of the thickness of the porous Al_2O_3 film [41, 42]. The measured capacitance was found to be related to thickness of the oxide film. Vrublevsky et al. [14, 39], on the other hand, determined the thickness and characteristics of the barrier layer of aluminium oxide using the re-anodizing technique. They showed that the porous alumina films consist of two layers: a thin barrier layer of anodic oxide in contact with the metal and a thick layer of porous film above it. The barrier layer thickness of porous alumina depends on the anodizing voltage, temperature and electrolyte-type [10]. The porous anodic films contain significant amounts of acid anions incorporated from the electrolyte [10, 14, 30].

In the present investigation, it is of interest to follow-up the rate of dissolution of the inner and outer layers of the naturally formed Al_2O_3 films in HCl solutions. Assuming that the destruction of the oxide film on Al surface occurs by way of the diffusion of the Al^{3+} ions out the oxide/metal interface, so that "n" in equation 5 amounts to 3 and α acquires a value of 0.5 and $\delta`$ the value of 1 nm, the constant β acquires the value of 58.5 nm/V. Therefore, from the slopes of the linear parts of the two segments of the E-log t curves of Figs 5-7, the values of the rates of destruction of the two modifications of Al_2O_3, δ_1^- and δ_2^-, in nm/unit decade of time, in different concentrations of HCl solutions, have been calculated[16-18] and shown in Table 1.

Referring to Figs 5-7 and the data of Table 1, it is quite clear that, at each HCl concentration, the rate of dissolution of the outer oxide film layer, δ_1^-, is lower than that of the inner adherent oxide layer, δ_2^-. Apparently, the outer oxide layer is more resistant to the dissolution than the inner layer [35]. The outer layer is found to be very thin in comparison with the inner layer, and consequently its rate of dissolution is low. It dissolves in HCl solutions at different concentrations within a period of the first 10 minutes, depending on the acid concentration. In addition, it is noted that, the values of δ_1^- and δ_2^- are increased as the content of Mg is increased in the alloy sample, at a comparable acid concentration. This behavior could be attributed to the fact that the increase in Mg content with Al alloy sample increase the rate of dissolution reaction due to the possible existence of imperfection of the oxide film. However, after the inflection point in the E-log t curves of Figs 5-7, the rate of dissolution of inner oxide film on Al surface, δ_2^-, is markedly increased with acid concentration or decrease in pH. This behavior could be attributed to the fact that Al is unlikely to form a stable passive film at such low pH values [43]. The dissolution of the inner oxide layer takes place apparently freely as indicated by the marked increase of the value of δ_2^-. The increased rate of dissolution is related to the possible existence of imperfection of the oxide film [35] upon which the chloride ions are adsorbed followed by the formation of soluble Al-chloride complex which diffuses into the solution [36, 44].

The difference in the rates of dissolution of the outer and inner layers of the barrier film is controlled by the amount of incorporated acid anions in the oxide layer [14]. The possibility of the simultaneous dissolution of the bare Al metal with the process of dissolution of the outer modification cannot be excluded, as could be detected from the longer noted periods associated with this step, especially at high acid concentrations.

The data of Figures 1-9 and Table 1 indicates that the presence of Mg in Al alloy enhances the process of the oxide film destruction and metal dissolution, which increases with increasing the Mg percentage in the alloy sample. This conclusion was discussed before by Zhou et al. [45, 46] who studied film formation by anodizing two samples of different Al-Mg alloys in ammonium pentaborate solutions to develop barrier- type anodic film. During anodizing Al and Mg are oxidized at the alloy/film interface, entering the film as Al^{3+} and Mg^{2+} ions. The greater outward migration rate of Mg^{2+} relative to Al^{3+} is related to the metal-oxygen bond energies

References

[1] W-J. Lee and Su-Il Pyun, Mater. Sci. and Eng. A, **279** (2000) 130–137.
[2] A. R. Trueman, "Corros. Sci., **47** (2005) 2240–2256.
[3] R. Ambat, E.S. Dwarakadasa, J. Appl. Electrochem.**, 24** (1994) 911.
[4] R.T. Foley, "Complex Ions and Corrosion", J. Electrochem. Soc., **122** (1975) 1493-1504.
[5] A.A. Mazhar, W. A. Badawy and M. M. Abuo-Romia, Surf. and Coat. Techn., **29** (1986) 335-345.
[6]T. R. Beck, Electrochim. Acta, **33** (1988) 1321-1327.
[7] K. F. Lorking and J. E. O. Mayne, J. Appl. Chem.**, 11** (1961)170-1980.
[8] S. Gudic´, J. Radoševic´, A. Višekruna, M. Kliškic´, Electrochim.Acta, **49**, (2004) 773-783.
[9] V P Parkhutik and V I Shershulsky, J. of Physics D: Applied Physics, **25** (1992)1258-1263.
[10] S.M.Abd El Haleem, S.Abd El Wanees, E.E. Abd El Aal, A.Farouk, Corros. Sci. 68 (2013) 1-13.
[11] S.M. Abd El Haleem, S.Abd El Wanees, E.E. Abd El Aal, A. Farouk, Corros. Sci. 68 (2013) 14-24.
[12]H. Takahashi, K. Fujimoto, and M. Nagayama, J. Electrochem. Soc., **135** (1988) 1349**-**1353.
[13]M. S. Hunter and. and P. Vowle, J. Electrochem. Soc., **103** (1956)482-485.
[14**]**I. Vrublevsky**,** V. Parkoun**,** V. SokolandJ. Schreckenbach**,** Appl. Surf. Sci.,**236**(2004) 270-277.
[15] P. G. Miney, P. E. Colavita, M. V. Schiza,R. J. Priore, F. G. Haibach and M. L. Myrick, Electrochemical and Solid–State Letters, **6** (2003) B42-B45.
[16] S.M. Abd El Haleem, E.E. Abd El Aal, S. Abd El Wanees and A. Diab, Corros. Sci., **52** (2010)3875–3882.
[17]S.M. Abd El Haleam, S. Abd El Wanees, E.E. Abd El Aal and A. Diab, Corros. Sci.**, 52** (2009) 292–302.
[18]E. E. Abd El Aal and S. M. Abd El Haleem, Corros. Eng. Sci. and Techn. **43** (2008) 219-224.
[19]M. Abd El Kader and A.M. Shams El Din, Br.Corros. J., **14** (1979) 40–45.
[20] H. A. El Shayeb, F. M. Abd El Wahab and E. A. Abd El Meguid, Br. Corros.J., **36** (2001) 215-220.
[21] Z. Szklarska-Smialowska, R.W. Staehle, J. Electrochem. Soc.,**121**(1974) 1146–1153.
[22] S.M. Abd El Haleem, E.E. Abd El Aal, S. Abd El Wanees and A. Baghat, Corros. Sci., **75** (2013)1–15.
[23] S.M. Abd El Haleem, E.E. Abd El Aal, S. Abd El Wanees and A. Baghat, Corros. Sci. **87** (2014) 320–333.
[24] S. M. Abd El Haleem and S. S Abd El Rehim, Revue Romanine de Chimie, **25** (1980) 493-499.
[25]F. Albert Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Interscience pub. J. W & Son, London (1966) p. 439.
[26] J.P. O'Sullivan and G. C. Wood, Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences Ser. A, **317**(1970) 511-543.
[27] A. Güntherschulze and H. Betz, "Die Bewegung der ionengitter von isolatoren bei extremen elektrischen feldstärken", Zeitschrift für Physik, **92** (1934) 367-374.
[28] K. J. Vetter, H. Fisher, K. Hanfe and W. Wederholt, "Pssivierende filme und deckschichten", Berlin Springer Verlag (1956) p.72.
[29] T. Hurlen, H. Lian, O. S. Ødegard and T. Valand, Electrochim. Acta, **29** (1984)579-585.
[30]I. Vrublevsky, V. Parkoun, J. Schreckenbach, Werner and A. Goedel, Appl. Surf. Sci., 252 (2006) 5100-5108.
[31]J. Oh and C.V. Thompson, Electrochim. Acta, **56** (2011) 4044–4051.
[32]T. Hurlen**,** E. Gulbrandsen, Electrochim. Acta, **39** (1994)2169-2172.
[33]H. Habazaki, K. Shimizu, p. Skeldon, G.E.Thompson and G. C. Wood, Thin Solid Films,**300** (1997) 131-137
[34] R.T. Foley, "Complex Ions and Corrosion", J. Electrochem. Soc., **122** (1975) 1493-1504.
[35]K. F. Lorking and J. E. O. Mayne, J. Appl. Chem.**,11** (1961)170-176.
[36] A.A. Mazhar, W. A. Badawy and M. M. Abuo-Romia, Surf. and Coat.Techn.,**29** (1986) 335-345.
[37] M. S. El Basiouny and A. A. Mazahar, NACE, **38** (1982) 237-240.
[38]A. Jagminas**,** I. Vrublevsky**,** J. Kuzmarskytė and V. Jasulaitienė, Acta Materialia,56 (2008) 1390-1398.
[39] I.Vrublevsky**,** V. ParkounandJ. Schreckenbach**,** Appl. Surf. Sci., **242**(2005) 333-338.
[40] H. J. Mathieu, M. Datta and D. Landolt, J. Vac. Sci. Technol. A, **3**(1985)331- 334.
[41 F. Debuyck, L.Lemaitre, M. Moors, A. P. Van Peteghem, E. Wettinck and L. Weyten, Surf. and Coat. Techn. **34**(1988) 311-318.
[42] Han-Jun, kyung-WookJank, and Choong-Soo Chi, Bull. Korean Chem. Soc., **20**(1999) 1340-1344.
[43]M. Pourbaix, "Atlas of electrochemical equilibria in aqueous solutions",Pergamon Press, Oxford (1966) p.171.
[44]T**.** R. Beck, Electrochim. Acta, **33** (1988) 1321-1327.
[45] X. Zhou, G. E. Thompson, P. Skeldon, G. C.Wood, K. Shimizu, H. Habazaki, Corrosion Science 40 (1999)1599-1613.
[46] G.E. Thompson, P. Skeldon, G.C. Wood, X. Zhou, U. Kreissig, E. Wieser, H. Habazaki, K. Shimizu. Surf.

Inter. Anal. 27 (1999) 57.

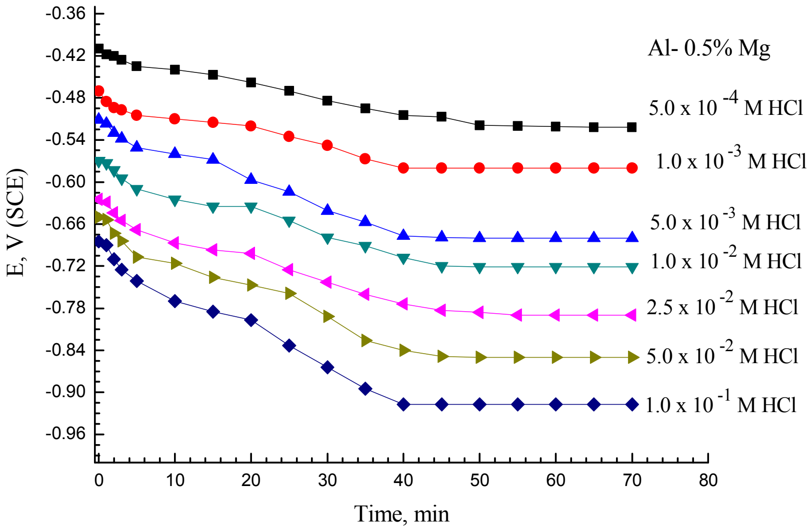

Fig 1. Variation of the potential of Al-0.5%Mg electrode, immersed in different concentration of HCl.

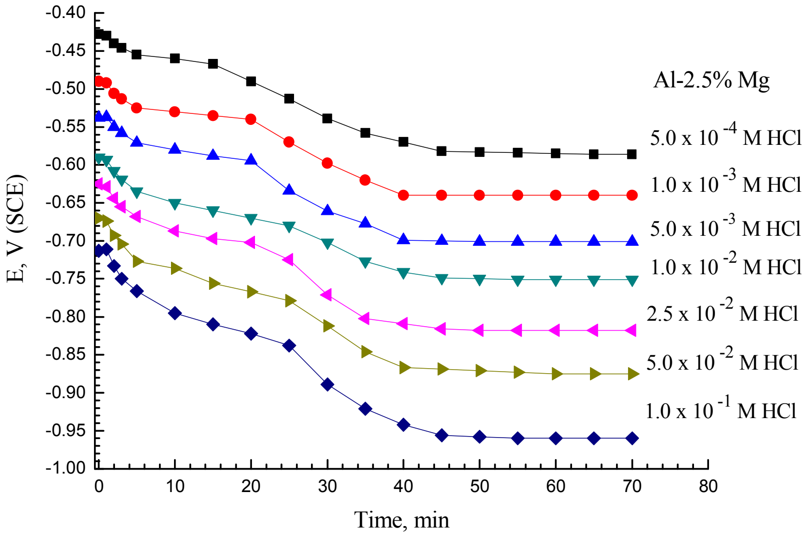

Fig 2. Variation of the potential of Al-2.5%Mg electrode, immersed in different concentration of HCl.

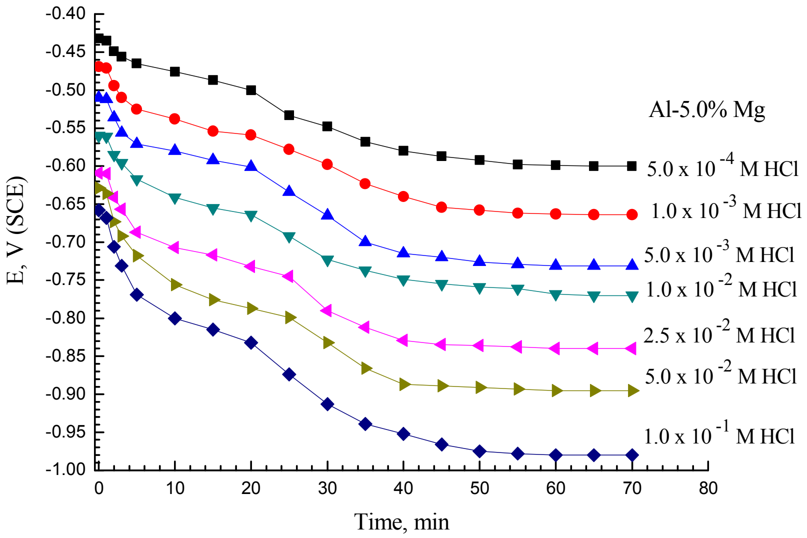

Fig 3. Variation of the potential of Al-5.0% Mg electrode, immersed in different concentration of HCl.

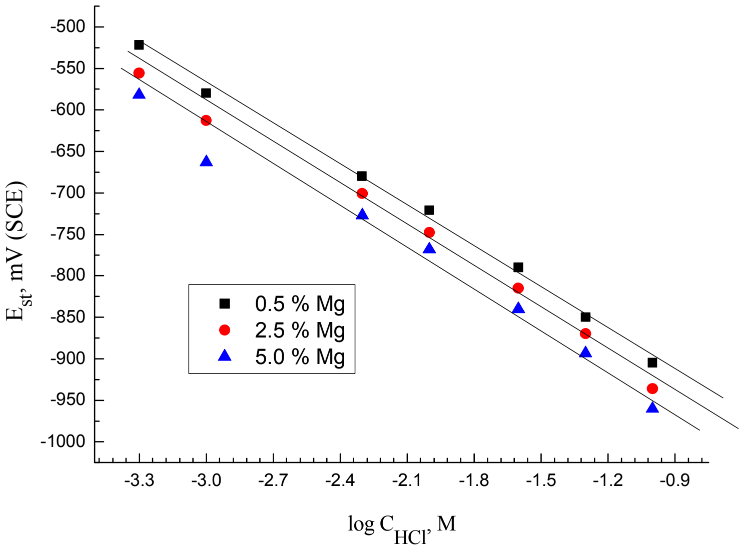

Fig 4. Variation of the steady state potential, E_{st}, with the logarithm of concentration of HCl.

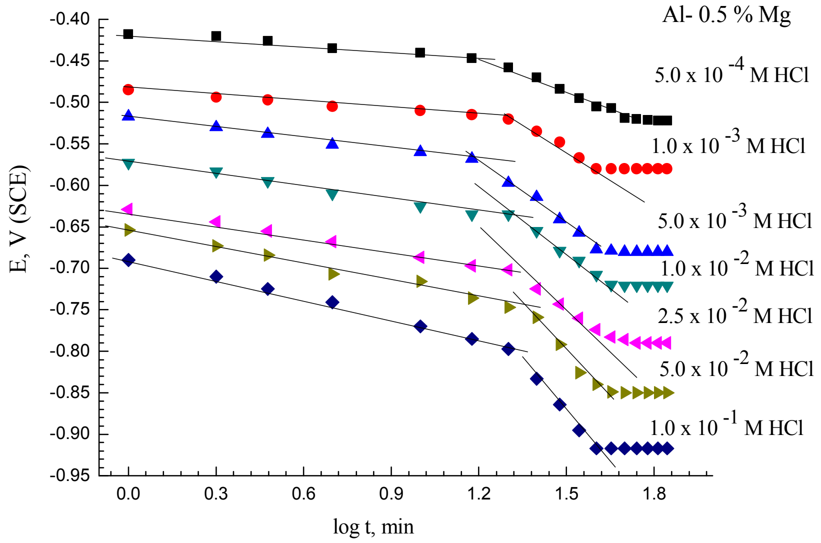

Fig 5. Variation of the open circuit potential, *E*, with the logarithm of immersion time for Al- 0.5% Mg alloy in different concentrations of HCl.

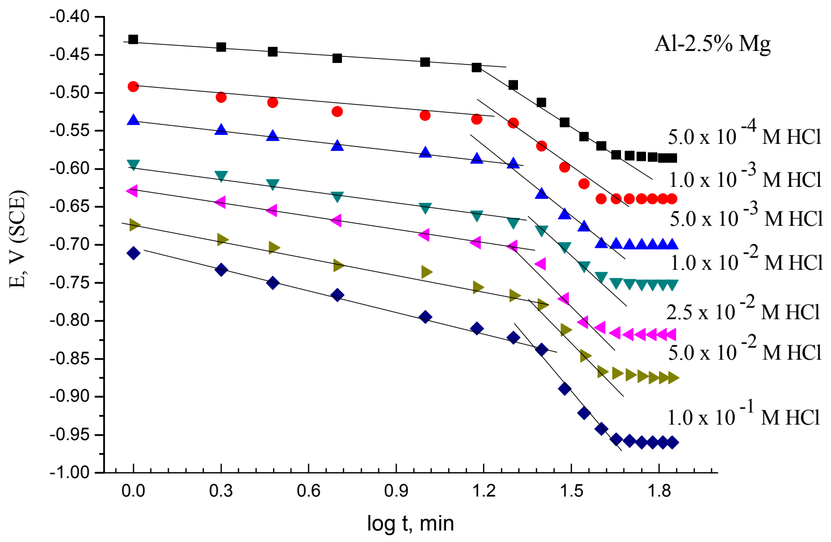

Fig 6. Variation of the open circuit potential, *E*, with the logarithm of immersion time for Al-2.5 % Mg alloy in different concentrations of HCl.

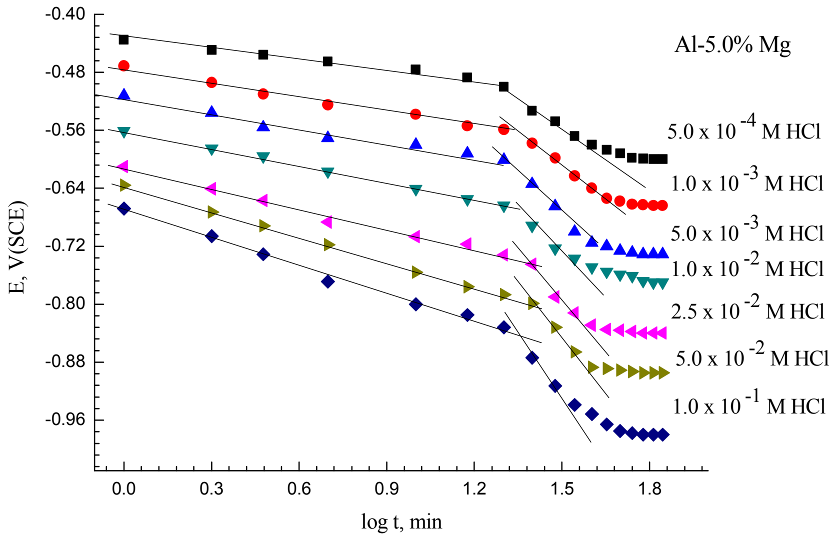

Fig 7. Variation of the open circuit potential, *E*, with the logarithm of immersion time for Al- 5.0 % Mg alloy in different concentrations of HCl.

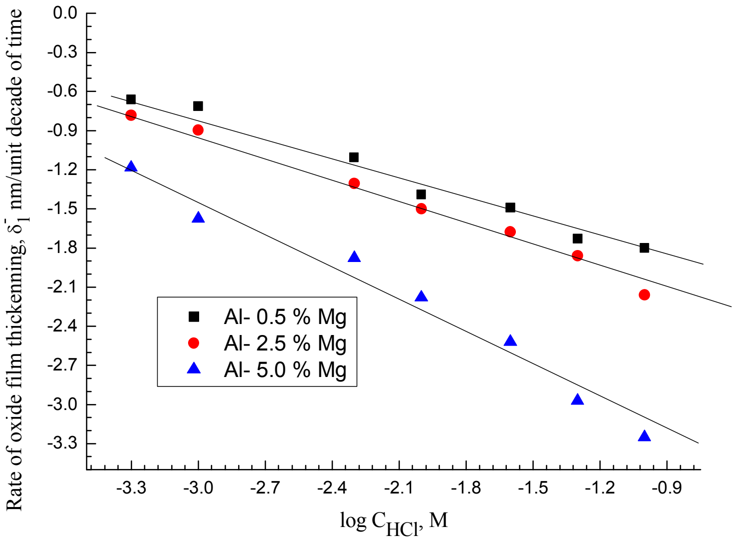

Fig. 8. Variation of the rate of oxide film destruction or healing of the inner oxide layer with the logarithm of HCl concentrations for different Al- Mg alloy.

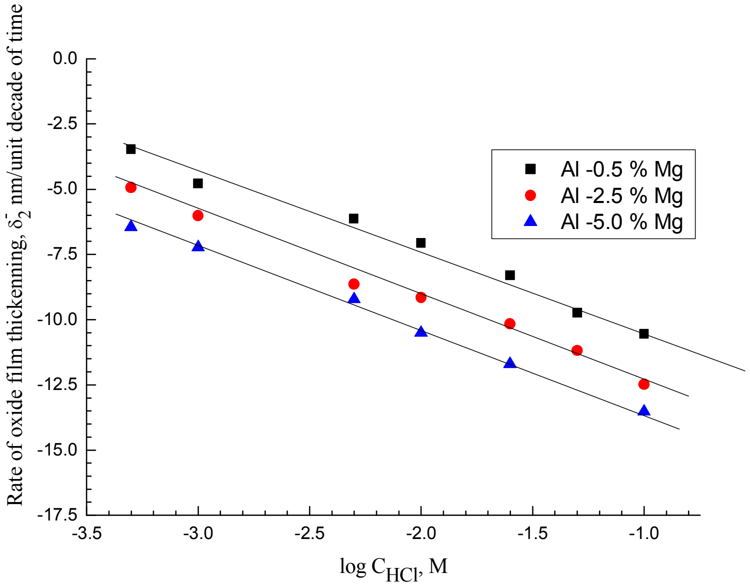

Fig. 9. Variation of the rate of oxide film thickening or healing of the outer oxide layer, with the logarithm of HCl concentrations for different Al- Mg alloys.

Table 1: Variation of the rate of the rate of oxide film destruction of the inner (δ_2^-) and outer oxide films (δ_1^-) of Al-Mg alloys with HCl concentration, at 25◦C.

Concentration of HCl, M	Al- 0.5% Mg		Al-2.5% Mg		Al-5.0 Mg	
	δ_2^-	δ_1^-	δ_2^-	δ_1^-	δ_2^-	δ_1^-
5.0x10^{-4}M HCl	3.454	0.061	6.931	0.785	6.452	1.184
1.0x10^{-3}M HCl	4.775	0.713	6.010	0.897	7.223	1.575
5.0x10^{-3}M HCl	6.120	1.105	8.637	1.305	9.221	1.877
1.0x10^{-2}M HCl	7.069	1.389	9.145	1.499	10.523	2.181
2.5x10^{-2}M HCl	8.300	1.491	10.160	1.677	11.710	2.522
5.0x10^{-2}M HCl	8.741	1.727	11.180	1.859	12.522	2.973
1.0x10^{-1}M HCl	10.54	1.822	12.479	2.159	13.521	3.254