ELECTROCHEMICAL BEHAVIOR OF ANODIZED AA7075 ALUMINUM ALLOY IN 0.1M NaCl SOLUTION AS INVESTIGATED BY POTENTIOSTATIC POLARIZATION TECHNIQUE

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ABSTRACT

The electrochemical behavior of chemical conversion coatings of AA7075 Al-Alloy with both 12% (v/v) H_2SO_4 *and 10 wt.%* CrO_3*, besides its behavior at optimum conditions immersion (i.e., in* H_2O *for 7 days) were investigated in 0.1M NaCl solutions using potentiostatic polarization technique. Anodized coatings provide a protective and attractive finish on Al-Alloys in many industrial applications. Atmospheric deterioration depends strongly on anodizing practices and to form such coatings*[1]*. Electrochemical polarization measurements were found to be sensitive to the presence of surface films formed as a result of anodizing. An attempt was made to discuss the results in light of mechanism of ionic current flow through the coatings during anodic polarization.*

INTRODUCTION

During the last decades, many kind of metal coatings are used in commercial practice for the protection of metals against corrosion. Pitting corrosion is the most common corrosion form on aluminum alloys and may lead to perforation in a relatively short time under corrosive conditions. The factors usually promote pitting corrosion are: Cl^- ion content; presence a more noble metal in contact with aluminum, presence heavy-metal ions in the medium (i.e., copper ions) or other noble corrosion products, stagnant flow conditions, and low temperature[2].

Electrochemical corrosion reactions on Al-surface, involves two separate reactions taking place at different areas on surface of the metal. At anodic sites, metal dissolution (i.e., $Al \rightarrow Al^{+3} + 3e^-$) competes with anodic passivation, while at cathodic sites, the reaction of oxygen (i.e., $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$) and the evolution of hydrogen (i.e., $2H^+ + 2e^- \rightarrow H_{2(g)}$) occur. Corrosion inhibition can be achieved if the rates of these reactions, or any partial steps involved can be decreased[3].

The present paper examines the following: (1) Corrosion resistance of AA7075 Al-alloy in 0.1M NaCl solution, (2) Corrosion resistance of H_2SO_4 and CrO_3 anodized AA7075 Al-alloy in 0.1M NaCl solution, (3) corrosion resistance of an anodized AA7075 Al-alloy in NaCl solution after immersion for 7 days in the solution, and (4) corrosion resistance of inhibited AA7075 Al-alloy at optimum condition[4] in H_2O (blank solution) then examine its behavior in 0.1M NaCl solution directly and after 7 days of immersion.

EXPERIMENTAL WORK

Three cm square AA7075 Al-alloy sheets, 0.33 cm thick, were H_2SO_4 and CrO_3 acid anodized. Coating thickness in both media depends on the amount of current density and the immersion time.

Chemical analysis of the alloy in weight percent was found to be: Si, 0.04; Fe, 0.5; Mn, 0.3; Mg, 2.5; Cr, 0.23; Zn, 5.6; Ti, 0.2; the balance, Al. Sheets preparation and anodizing procedure were found as follows[5-8].

1. Chemical treatment process which includes removal of heavy oils and greases that may coated the specimens during fabrication, by degreasing them with benzene and acetone.
2. Immerse the specimens in 10% (v/v), H_2SO_4 solution at 90°C for 2 minutes followed by rinsing with distilled water. This step express the chemical cleaning to obtain clean surface ready for anodizing process.
3. Etching 5% wt. NaOH solution at 45°C for two minutes followed by rinsing with distilled water, then dried.

4. Immerse the specimens in solution composed of 35% (v/v) H_3PO_4 (sp. gr. = 1.75) and 65% (v/v) H_2SO_4 (sp. gr. = 1.841) at 90°C for about 2.5 minutes to obtain a chemical brightening surface ready for anodizing after rinsing with distilled water.
5. Anodize in 12% (v/v) H_2SO_4 acid at 16 volts supplied from stabilized power supply, for 1 hr immersion at 30°C.
6. Anodize in 10% chromic acid at 20 volts supply for 1 ht immersion at 55°C. Its important to mention here, that a lead cathode was used in H_2SO_4 anodizing and a stainless steel cathode was used in chromic acid anodizing. The specimens were rinsed thoroughly in distilled water for 5 minutes followed each anodizing process.
7. The specimens after anodizing were sealed by immersion in boiling H_2O at 99-100°C for 1 hr for those H_2SO_4 and for 20 minutes for those chromic acid anodized.

Polarization Apparatus and Procedure

Polarization was carried out in a cell and with electrical circuitry described in Fig. (A)

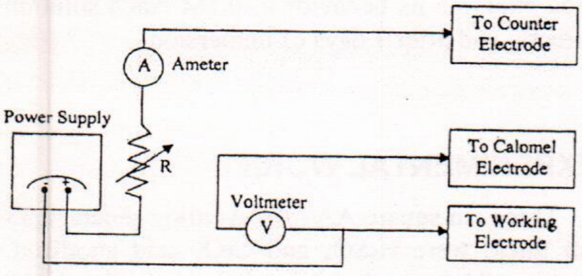

Fig. (A) Electric circuit for polarization measurements

The cell consists of a multi-neck, round bottom pyrex flask incorporating working (specimen) electrode, auxiliary (counter) electrode, Luggin-Haber probe with solution bridge to a saturated calomel reference electrode (SCE), water bath, and a thermoregulator to maintain various solution temperatures within ±1°C.

The specimen was initially exposed to the electrolyte for 1hr. Anodic polarization was then performed in about 10-20 mV increments, with current recorded after one minute at each potential.

The working electrode was a small sheet specimen (3 cm^2 exposed surface area) mounted in the holder shown in Fig. (B) with corrosion cell. Throughout assembly of the holder, normal precautions were taken to avoid touching the exposed anodized surface.

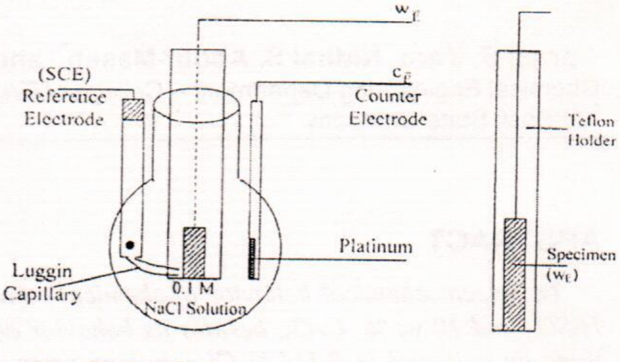

Fig. (B) Standard corrosion cell and holder for sheet specimens

RESULTS AND DISCUSSION

The variation of the open circuit potential of AA7075 Al-alloy with time (0-3 hr) of immersion in 0.1M NaCl solution has been studied. Fig. (1) shows this variation with time of immersion. The potential generally changed from an initial highly negative value to a more positive potential between -950 mV (SCE) within about one minute of contact with the solution. The potential remains at this value (i.e., -695 mV vs. SCE) ±5 mV for about 3 hr.

The analysis of the variation of open circuit potential with time of immersion was an attempt and as a prime requisite in the study of corrosion of AA7075 Al-alloy. The published data reveal a scatter of values for the OCP of aluminum ranging over several hundred milivolts even under identical experimental conditions[9]. The reasons of this variation with time are conflicting[10] depends and affected by many parameters (i.e., material purity, surface treatment, oxygen content, …etc.). It can be concluded that the open circuit potential of the AA7075 Al-alloy is a mixed potential, i.e., the factors control this mixed potential are the cathodic potential [11]:

i. cathodic reactions include:

a. Reduction of dissolved O_2; $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

b. Reduction of H+ ions; $2H^+ + 2e^- \rightarrow H_2$

ii. Anodic reactions include:

a. $Al \rightarrow Al^{+3} + 3e^-$

b. $Al + 3OH \rightarrow Al(OH)_3$

c. $Al + 3Cl \rightarrow AlCl_3 + 3e^-$

Fig. (2) shows the anodic and cathodic polarization curves relevant to H_2SO_4 anodizing process after an immersion of one week in the 0.1M NaCl aerated solution. The corrosion (E_{corr}) of unprotected and anodized Al alloy after one week immersion appears to be significantly unaffected (i.e., E_{corr} remains constant), while E_{corr} for H_2SO_4 anodized alloy appears shifted to more active potential by about 20 mV, with respect to unprotected one. The cathodic branches of the polarization curves show over a wide potential range that in the case of anodized and (anodized + 7 days) immersion, the coating surface is less catalytic to the H_2 evaluation reaction than the unprotected surface, i.e., the anodizing coating has an electronic resistivity of order: H_2SO_4 anodized > anodized + 1 week immersion > unprotected one.

It can be concluded that all cathodic branches of the polarization curves (except unprotected one) in Fig. (2) didn't show a diffusion depending trend which is mainly related to the oxygen reaction (i.e., the hydrogen evaluation controlled by activation is more pronounced).

The anodic portion of the polarization curves shown in Fig. (2), were also very important to compare the pitting potentials of the aluminum alloy in all cases, (i.e., unprotected, anodized, and anodizing + immersion). For unprotected sample, at potentials more positive than the corrosion potential, E_{corr} = -698 mV (SCE), the current density rises sharply indicating the beginning of pitting and clearly showing that E_{pit} is very close to E_{corr}. For the other two cases, (i.e., H_2SO_4 anodized, and anodized + immersion Al-alloy) the pitting potential does not change, but shifts the E_{corr} of anodized sample to more active direction (i.e., about 20 mV (SCE)).

The anodizing process reveals a very clear picture, concerning the anodic portions of polarization curves which is suppressing the thickness of these curves at anodic sites on the surface compared with the unprotected one (i.e., 600 mV (SCE)) for example the anodic current was reduced about 93% for both anodized and (anodized + immersed) compared with unprotected sample.

Fig. (3) shows the CrO_3 anodizing case which is generally identical with what was shown in Fig. (2). In this figure:

1. E_{corr} for unprotected and (anodized + immersed) samples remain the same.
2. E_{corr} for CrO_3 anodized alloy shifted to more noble direction compared with unprotected one due to sharp anodic kinetic changes because of anodizing and film formation and growth.
3. Diffusion depending trend relating to O_2 reaction in cathodic branches of polarization curves is more pronounced in unprotected sample compared with other branches which are clearly activation control due to H_2 evaluation.
4. There is no indication that there is a very large difference between E_{corr} and E_{pit}, but they are very close.
5. Suppressing the kinetic of anodic polarization curves at anodic sites on the surface are more pronounced in CrO_3 anodizing than H_2SO_4 anodizing (i.e., at 600 mV (SCE)), the anodic current was reduced about 98% for both anodized and (anodized + immersed) samples compared with unprotected one.

Fig. (4) shows the situation when AA7075 Al-alloy was immersed in H_2O (not 0.1M NaCl) under the effect of optimum conditions[4] (i.e., about 10.2 days and Co^{+2}/1000 ppm Ni^{+2} ratio of 0.745, then its electrochemical behavior was examined directly and after immersion for 7 days in 0.1M NaCl solution compared with unprotected sample.

Fig. (4) reveals a complex picture, where the protected alloy at optimum conditions in H_2O and its immersion in 0.1M NaCl solution does not show a significant change in the pitting potential, but moves the corrosion potential toward more cathodic potentials, compared with unprotected Al-alloy.

It can be concluded that: (1) the AA7075 Al-alloy exposed to H_2O at optimum conditions containing $NiCl_2$ and $CoCl_2$ have shown that [Ni/Co] oxides/hydroxide film formed on the surface is responsible for the suppression of O_2 reduction and hydrogen evolution. (2) The protected Al-alloy at optimum conditions after immersion in 0.1M NaCl for 7 days shows an increase in both anodic and cathodic currents at certain potential within the range studied compared with that at optimum conditions without exposing to NaCl, this can be attributed[12,13]; either (i) to NaCl solution penetration at microcracks occurs at coating surface, and (ii) the film formed by the additives is porous lead to this behavior.

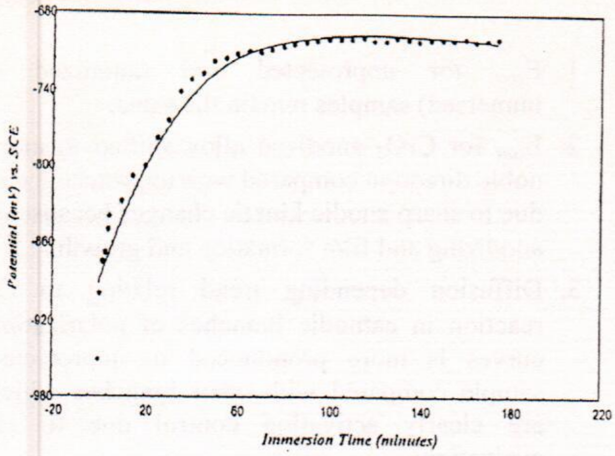

Fig. (1) Open circuit potential of unprotected AA7075 Al-alloy as a function of immersion time

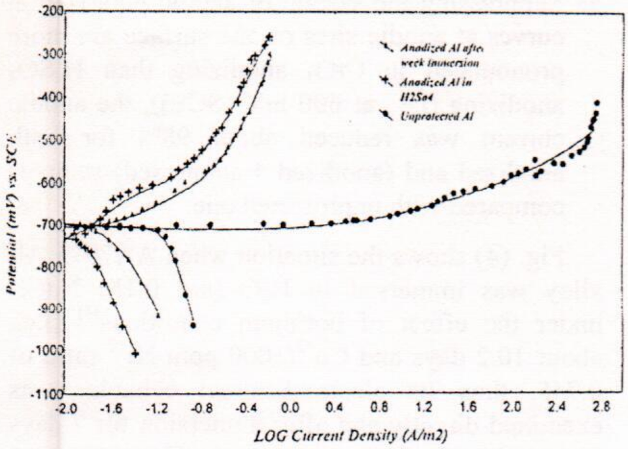

Fig. (2) Effect of immersion time on the potentiostatic polarization curves of H_2SO_4 anodized and unprotected AA7075 Al-alloy at 30°C in 0.1M NaCl solution

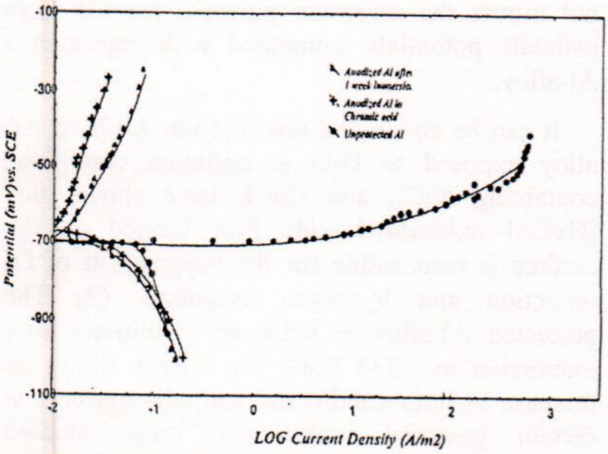

Fig. (3) Effect of immersion time on the potentiostatic polarization curves of chromic acid anodized and unprotected AA7075 Al-alloy at 30°C in 0.1M NaCl solution

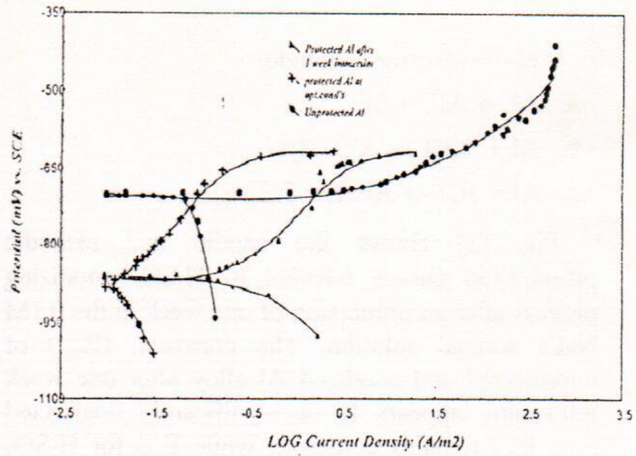

Fig. (4) Effect of immersion time on the potentiostatic polarization curves of protected AA7075 at optimum condition and unprotected one at 30°C in 0.1 NaCl solution

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