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Effect of Acetic Acid on Electrochemical Behavior of Sealed AA2319-T3 Al-Alloys Anodized in Phosphoric Acid Electrolytes

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Abstract

The present study investigates the effect of acetic acid on corrosion behavior and its potential of hydrothermally sealed anodized AA2319-Al-alloys. Anodizing treatment was performed in stagnant phosphoric acid electrolyte with or without addition of acetic acid. Hydrothermal sealing was carried out in boiling water for each anodized specimen. The open circuit potential of the unsealed and sealed anodized samples was examined using open circuit potential measurement for the purpose of starting in scanning polarization diagrams. The potentiostatic polarization technique measurements were performed to assess corrosion behavior and sealing quality (i.e., degree of sealing) of the unsealed and sealed anodized aluminum. It was shown that the potentiostatic anodic and cathodic polarization of anodized aluminum was sensitive to degree of seal, which was more efficient in the case of anodized aluminum formed in acetic-phosphoric acid electrolyte mainly due to their higher corrosion potential and lower corrosion current, generally passes lower anodic and cathodic currents obtained at sealing exposure time 60 min. This suggests a specific role of the species on the sealed anodized aluminum surface coating, which contributes to the increasing of the performance in terms of corrosion improvement. The present study clearly validates the beneficial role of acetic acid in phosphoric acid anodizing baths for the corrosion protection of AA2319-Al-alloys.

Keywords: *Phosphoric Acid, Acetic Acid, Aluminum Alloy 2319, Anodizing, Polarization Technique.*

1. Introduction

Aluminum-Copper (Al-Cu) alloys have a low density and high electrical and thermal conductivity [1]. AA2319 (~ 6% Cu), composed of an Al_2Cu phase and Al-rich areas, is particularly promising due to its high strength and thus it is currently used in aerospace applications [1, 2]. Unfortunately, these alloys suffer from poor corrosion resistance, due to their high Cu content, and are highly susceptible to water-initiated pitting corrosion, potentially leading to fatigue failure [2].

The widely using of Chromic acid (CrO_3) anodizing in the aeronautic industry is to improve corrosion resistance of aluminum alloys [3]. The incorporation of Cr (VI) and Cr (III) into the oxide gives higher corrosion resistance than that produced by other anodizing processes. Since the beginning of the 1990s, the uses of Cr (VI) have been restricted in industrial applications due to their high toxicity. As a consequence, numerous attempts have been made to find less toxic alternatives, but with limited success [4, 5]. During the last decade, interesting to phosphoric acid (H_3PO_4) anodizing and acetic-phosphoric acid (CH_3COOH-H_3PO_4) anodizing as alternatives to replace CrO_3 anodizing has increased [6, 7, 8]. Anodizing with phosphoric acid (H_3PO_4) has been introduced to obtain thin anodic films approximately (1-5.4 µm) that increase fatigue resistance for specific structural materials [9]. Even though the fatigue resistance of the specimens anodized in phosphoric acid is increased, the corrosion resistance is lower than that of specimens anodized in CrO_3. Nazree, et al. [10] have proposed a new anodizing procedure involving the addition of acetic acid in phosphoric acid electrolyte, called acetic-phosphoric acid (CH_3COOH-H_3PO_4) anodizing. Acetic acid is sometimes used as anodizing electrolyte for aluminum alloys due to its ability to form anodic films [11, 12]. However, the use of acetic - phosphoric acid mixtures as anodizing electrolytes is poorly reported in the literature. Ma Song-Jiang et al. [13] has been reported that mixed acid solution as anodizing electrolytes can decrease the film dissolution rate, then increase the film formation efficiency and improve the film properties. Wahab and Derman [14] have investigated the influence of the addition of acetic acid to phosphoric acid electrolyte on anodizing of pure aluminum (99%). Yaro and Al-Asadi [18] have investigated the effect of hydrothermal sealing time on the anodic polarization of anodized aluminum alloy AA5052 in different conditions. The authors showed that the addition of acetic acid reduced by ~20% the steady-state current during film growth at constant voltage. Neither of the research groups attempted to investigate corrosion behavior of the anodic films formed in the two solutions [10, 14]. The role of acetic acid in the anodizing bath still remains unclear.

The present study aimed for a better understanding of the effect of acetic acid on the corrosion behavior and its potential of hydrothermally sealed anodized AA2319-Al-alloys.

2. Experimental Work

2.1. Materials and Conditions

The substance used was a 2319 T3 aluminum alloys. The average chemical composition of the alloy is given in Table (1). The dimensions of samples are 125 × 8 × 1.6 mm plates machined from an AA2319 T3 rolled plate. Aluminum samples before anodizing and corrosion tests were abraded in sequence on 220, 320, 400 and 600 grades of emery paper under running tap water on a Metasern hand grinder tray washed with tap water followed by distilled water, dried with a clean tissue, degreased by immersing them in acetone & benzene, then dried with paper tissue and kept in a dissector over a silica gel bed. The treatment of anodizing was performed in a 40 g L^{-1} (0.41 M) phosphoric acid (H_3PO_4) solution in the presence or absence of 80 g L^{-1} (1.33 M) acetic acid (CH_3COOH). Experiments of anodizing were carried out at a constant cell voltage of 15 V for 30 min. The operating temperature was maintained within 35 ± 1 °C by a thermometer. Sealing was carried out in (DI) water at a temperature of 100 °C.

Table 1,
Chemical Composition of 2319 T3 Aluminum Alloy (% wt).

Si	Fe	Cu	Mn	Mg	Zn	Ti	Al
0.20	0.30	6.3	0.30	0.02	0.10	0.15	92.63 min

2.2. Polarization Measurements

The polarization measurements were carried out in a corrosion cell (three-electrode electrochemical cell) which is contain the auxiliary electrode, reference electrode and working electrode. It contained a platinum foil type (Tacussel Pt-F05/30) as auxiliary electrode (area of ~ 30 cm^2), a saturated calomel reference electrode (SCE) type (Tacussel type C4) bridged by a laggin-Haber probe. The reference electrode, which was bridged by a luggin Haber capillary was set at about the optimum value of 1 mm to minimize the experimental error. The AA2319 T3 samples as working electrode (exposed area of 10 cm^2 and other side and thickness of the samples were coated with the epoxy to prevent exposure to the solution), held by aluminum jigs in order to hold the samples, it was coated with rubber tube to hold it stable in the cell and prevent the short circuit contact. Open circuit potential (OCP) measurments were carried out and measured from off-circuit potential-immersion time measurments [17]. The corrosion cell parts were joined to each other, and then connected to potentiostat, ammeter and voltmeter as described in Figure 1 and polarization was carried out in electrochemical cell with electrical circuit shown in Figure 2. The auxiliary electrode was a platinum electrode of (2.7×11 cm), held by plastic plate set directly opposite to the working electrode. The potentiostat device using in this article is modern computerize type Wenking M Lab device of Bank Electronic, Germany. The scan rate is 10 mV/min.

Reference electrode calibration was carried out by 30 % KCl solution for activation. The polarization figures were plotted under potentiostatic conditions at the actual corrosion potential. The electrochemical cell was maintained at 25 °C and open to surrounding. The open circuit potential (OCP) of the unsealed and sealed anodized aluminum samples were measured after 1.5 h of immersion at room temperature in a 0.5 M Na_2SO_4 solution and 3.5 M NaCl solution respectively. Sodium sulfate was chosen toward aluminum and aluminum alloys due to its property (low corrosiveness). The polarization behavior of sealed and unsealed anodized samples was investigated in 3.5 M NaCl solution, at different sealing times. Anodizing treatment was performed in stagnant phosphoric acid electrolyte with acetic - phosphoric acid or without (H_3PO_4) addition of acetic acid. Hydrothermal sealing was carried out in boiling deionized (DI) water for each anodized sample. The corrosion behavior of the hydrothermally sealed and unsealed anodic films was carried out using potentiostatic polarization technique. The sensitivity of potentiostatic polarization makes it a successful technique for assessing the sealing quality and corrosion parameters of the anodic films from polarization curves [7, 15 and 16]. Stagnate solutions of chloride containing solutions at 25ºC have been investigated using polarization technique was carried out to characterize the properties of the unsealed and sealed anodic films. The electrochemical parameters obtained from a fitting procedure of the polarization diagrams allowed the corrosion behavior difference of the two samples to be shown and discussed. The corrosion potential results were correlated with the open circuit potential (OCP).

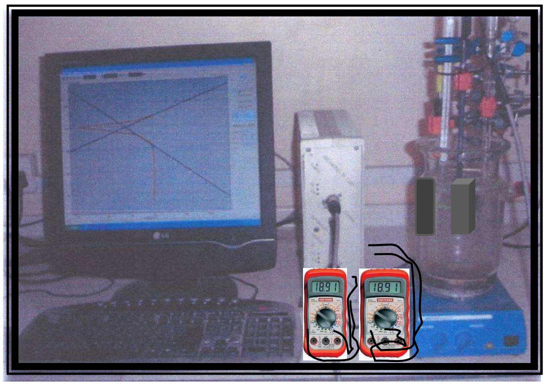

Fig. 1. Wenking M Lab device.

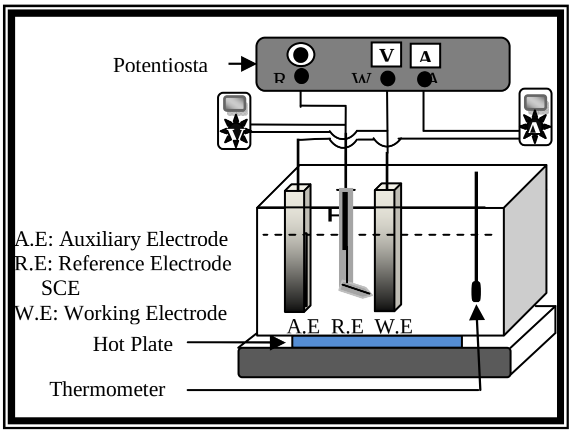

Fig. 2. Schematic diagram of corrosion cell used in polarization.

3. Results and Discussion

The corrosion potential diagrams obtained after different sealing times (5, 15, 30, 45 and 60 min.) for the hydrothermally sealed anodized samples formed in phosphoric acid have the different shape as those obtained for the samples formed in acetic-phosphoric acid. Figure 3 compares the corrosion potential (E_{corr}) values for both systems. It appears that for the anodic films formed in acetic-phosphoric acid, the variation is linear, whereas for the films in phosphoric acid it is not, and the E_{corr} values always remain lower than those obtained with acetic-phosphoric acid. For the shortest sealing time, E_{corr} was < - 850 mV, which reveal the low level of the anodic film sealing. Sealing times of > 30 min. are necessary to obtain acceptable sealing of the anodic film. These results show that the lower part of the porous structure of the anodic film formed in phosphoric acid was not perfectly sealed after 30 min. of reaction, corroborating the trends deduced from electrochemical potential results. The corrosion potential results stress that film sealing differs, depending on the initial anodic film. A better sealing efficiency (higher E_{corr}) was obtained for the anodic films formed in the presence of acetic acid. Then, to investigate the influence of sealing quality on the corrosion behavior of unsealed and sealed anodized AA2319 samples, the open circuit potential of the unsealed and sealed anodic films formed in phosphoric acid and acetic-phosphoric acid was investigated by plotting the open circuit potential diagrams versus exposure time (from 0 to 1.5 h) in 0.5 M Na_2SO_4 and 3.5 M NaCl solutions respectively is presented in Figures 4, 5 & 7.

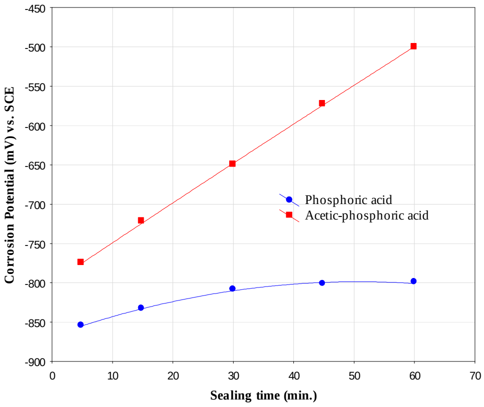

Fig. 3. Corrosion potential values vs. sealing time for the sealed anodized aluminum AA2319 in phosphoric acid and acetic-phosphoric acid solutions in 3.5 M NaCl solution at 25 ºC.

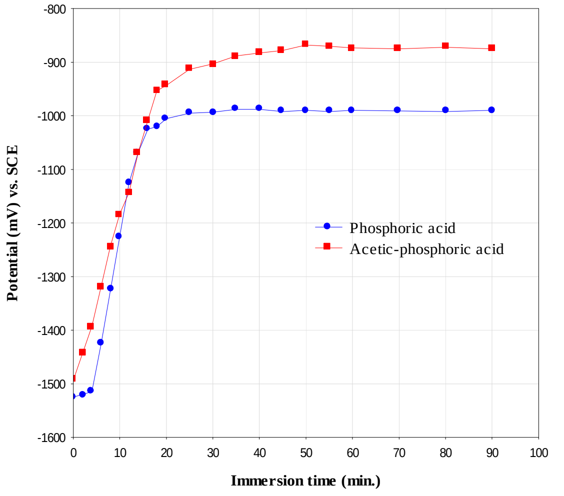

Fig. 4. Open circuit potential of unsealed anodized aluminum AA2319 in phosphoric acid and acetic-phosphoric acid solutions in 0.5 M Na_2SO_4 solution at 25 ºC as a function of immersion time.

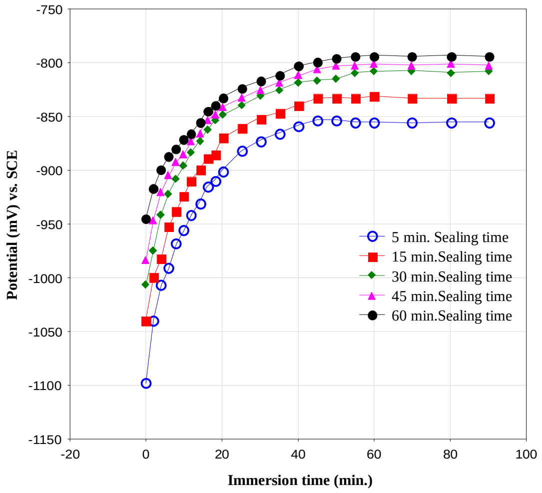

Fig. 5. Open circuit potential of sealed anodized aluminum AA2319 in phosphoric acid solution after different sealing times in 3.5 M NaCl solution at 25 ºC as a function of immersion time.

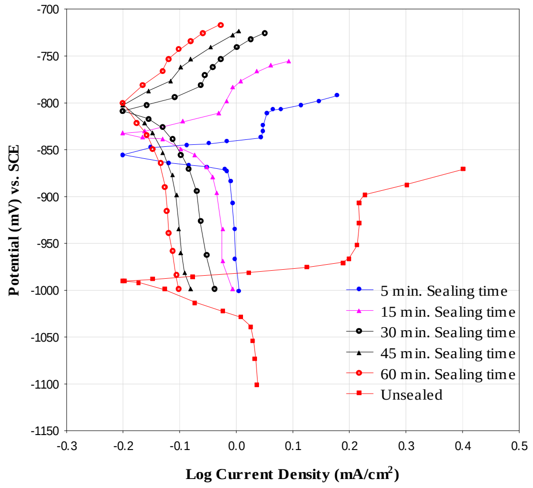

Fig. 6. Potentiostatic polarization curves of unsealed and sealed anodized aluminum AA2319 in phosphoric acid solution after different sealing times in 3.5 M NaCl solution at 25 ºC.

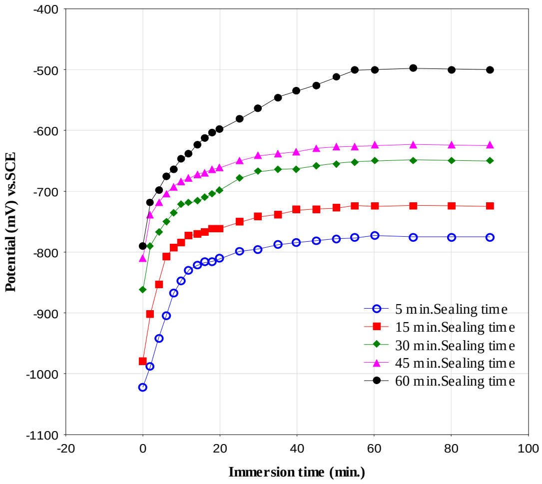

Fig. 7. Open circuit potential of sealed anodized aluminum AA2319 in acetic-phosphoric acid solution after different sealing times in 3.5 M NaCl solution at 25 ºC as a function of immersion time.

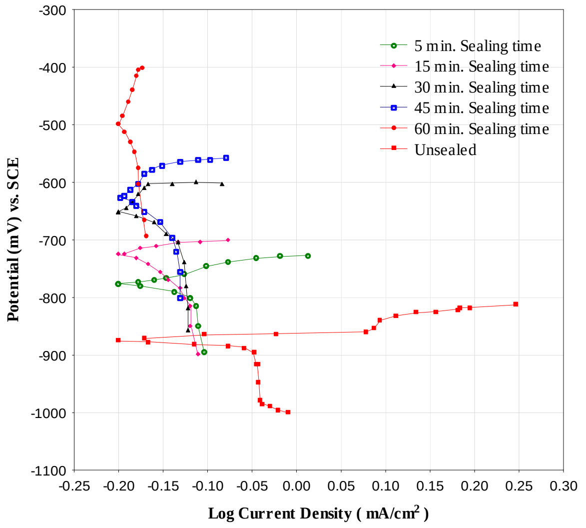

Fig. 8. Potentiostatic polarization curves of unsealed and sealed anodized aluminum AA2319 in acetic-phosphoric acid solution after different sealing times in 3.5 M NaCl solution at 25 ºC.

3.1. Potentiostatic Polarization Measurements

The potentiostatic polarization behavior of unsealed and hydrothermally sealed aluminum AA2319 anodized in phosphoric acid and acetic-phosphoric acid in 3.5 M NaCl solution at 25 ºC is presented in Figure 6 and Figure 8 respectively.

Figures 6 and 8 show the effect of acetic acid on corrosion behavior of sealed AA2319 anodized in phosphoric acid electrolyte and acetic-phosphoric acid electrolyte after different sealing times in 3.5 M NaCl solution at 25 ºC, on the relationship between current density and potential of aluminum alloy AA2319. In these figures it can be seen that:

1. The obtained corrosion potential (E_{corr}) values for sealed anodized aluminum alloy 2319 are quite sensitive to the sealing of the anodized aluminum after different sealing exposure times shift to more positive (more noble) direction compared with unsealed samples due to sharp anodic and cathodic kinetic change accompanied reduction of corrosion current densities (I_{corr}) because the initial principle purpose of sealing is to further improve the corrosion resistance of anodized aluminum. This is also in close agreement with the research done by Yaro and Al-Asadi [18].
2. The cathodic reactions behavior of the polarization curves shows over a wide potential range that in the case of sealed anodized samples, in phosphoric acid the sealed anodized surface is more diffusion (mass transfer) to the predominant oxygen reduction reaction (as the principle rate limiting reaction) than the unsealed surface and in acetic-phosphoric acid the sealed anodized surface is more activation to the predominant hydrogen evolution reaction than the unsealed surface, i.e., the sealed anodized surface has an electronic resistivity of order [19]:
   H3PO4 sealed anodized > Unsealed one
   CH3COOH-H3PO4 sealed anodized > Unsealed one
   CH3COOH-H3PO4 sealed anodized > H3PO4 sealed anodized
3. At anodic and cathodic sites on the sealed anodized surface, suppressing the kinetic of anodic and cathodic polarization curves is more pronounced aluminum alloy 2319 anodized in acetic-phosphoric acids electrolyte and the anodic and cathodic current densities for sealed anodized samples reduced high value particularly at sealing exposure time 60 min than unsealed anodized samples.

4. Conclusions

The sealing quality (i.e., degree of sealing) and the corrosion protection of AA2319 T3 anodized in phosphoric acid in absence and presence of acetic acid were investigated by potentiostatic polarization technique. The following conclusions might be withdrown from this investigation:

1. Electrochemical polarization measurements are sensitive to the presence of anodized aluminum surface films.
2. Anodizing of AA2319 T3 in presence of acetic acid led to the formation of anodic films with higher corrosion potential (i.e., improvement of the corrosion resistance of anodized aluminum surface) and lower corrosion current density than those obtained in phosphoric acid.
3. The sealing quality was better for the anodized samples formed in acetic-phosphoric acid than in phosphoric acid in agreement with the higher corrosion potential with reduction of anodic and cathodic currents of the anodized samples formed in acetic-phosphoric acid.
4. The sealed anodized samples formed in acetic-phosphoric acid are significantly more potential to corrosion than the sealed anodized samples formed in phosphoric acid.
5. The corrosion current densities for unsealed samples are found to be higher than

hydrothermally sealed anodized samples for both systems and the corrosion potential for hydrothermally sealed anodized samples are shifted more positive than unsealed samples for both systems

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تأثير حامض الخليك على السلوك الكهروكيمياوي لأنودة وختم مسامات سبيكة المنيوم ٢٣١٩ في محاليل حامض الفوسفوريك الأليكتروليتية

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الخلاصة

في هذا البحث تم دراسة التأثير لحامض الخليك على سلوك وجهد التآكل لسبيكة الألمنيوم AA2319 المأنودة المختومة المسامية بأستخدام الماء المغلي. تم إجراء عملية الأنودة في المحلول الأليكتروليتي الساكن لحامض الفوسفوريك بوجود أو بدون إضافة حامض الخليك. تم إنجاز عملية الختم (غلق المسامات) بطريقة الماء المغلي لكل نموذج مأنود. تم إجراء فحص جهد الدائرة المفتوحة للنماذج المأنودة المختومة وغير المختومة المسامية بأستخدام قياس جهد الدائرة المفتوحة لغرض البدأ في مسح مخططات الأستقطاب. تم إستخدام تقنية الأستقطاب للجهد الساكن لتعيين سلوك التآكل وجودة الختم (أي درجة الختم) للألمنيوم المأنودة غير المختوم والمختوم المسامية. من النتائج تبين أن عملية الأستقطاب الأنودي والكاثودي الساكن للألمنيوم المأنود كانت حساسة وتتأثر بدرجة الختم و كانت أكثر كفاءة في حالة الألمنيوم المأنود المتكون في المحلول الأليكتروليتي لحامض الفوسفوريك-الخليك بشكل رئيس نتيجة لجهدهم التآكلي الأعلى قيمة والأقل تيار التآكل ، بعامة يسمح بمرور أقل تيارات أنودية وكاثودية حصلت عند زمن تعرض ختم ٦٠ دقيقة. هذا يقترح للدور المحدد للدقائق على أكساء سطح الألمنيوم المأنود المختوم مساميته الذي يساهم في تحسين الأداء من وجهة نظر التآكل. أثبتت الدراسة الحالية بشكل واضح الوظيفة المفيدة لحامض الخليك في أحواض الأنودة لحامض الفوسفوريك لحماية التآكل لسبيكة الألمنيوم AA2319.
