

Improving Pitting Corrosion Resistance of Aluminum by Anodizing Process

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Summary: Anodizing of aluminum was studied in sulphuric/citric/boric acid electrolyte system to improve pitting corrosion resistance. Maximum oxide film thickness was obtained using 5% sulphuric acid, 3% citric acid and 0.5% boric acid electrolyte composition. The corrosion resistance of aluminum sample was determined to find the effectiveness of oxide coating by potentiodynamic polarization test. The surface morphology of aluminum samples was investigated using scanning electron microscope (SEM) before and after corrosion test. It was found that the coated aluminum sample obtained by anodizing in sulphuric/citric/boric acid electrolyte system exhibited better pitting corrosion resistance with no significant difference in surface morphology.

Keywords: Anodizing; aluminum alloy; corrosion; oxide coating.

Introduction

The corrosion protection of aluminum and aluminum alloys is important due to its application in number of industries like aircraft, automotive and aerospace, for both technical and economic considerations. Aluminum alloys suffer pitting corrosion. Pitting is a highly localized type of corrosion in the presence of halide ions, of which chloride ion is more aggressive in service. Pits are initiated at weak sites in the oxide by chloride attack [1]. The chromic acid anodizing process for aluminum and aluminum alloys was initially developed by Bengough and Stuart [2]. However the use of Cr (VI) is not advised from a health and environmental point of view since it is toxic and carcinogenic, and the process is gradually limited even prohibited [3-5]. Wong and Moji developed boric/sulphuric acid anodizing as a replacement for chromic acid anodizing [6]. Kallenborn and Emmons developed a thin film sulphuric acid anodizing (TFSA) process [7]. In our previous paper, anodizing of aluminum was studied in sulphuric/oxalic/boric acid electrolyte system to obtain a corrosion resistant oxide coating [8]. In the present work, anodizing of aluminum was studied in sulphuric/citric/boric acid electrolyte system to obtain an oxide coating with improved pitting corrosion resistance.

Results and Discussion

The anodizing of aluminum was carried out at relatively higher temperature (35°C) in sulphuric/citric/boric acid electrolyte system to increase its resistance to pitting corrosion. It was

observed that anodic oxide coating having maximum film thickness was obtained in 5% wt. sulphuric acid and 3% citric acid electrolyte composition as shown in Fig. 1 (Table-1). Anodizing of aluminum was carried out at 20V using this composition to produce relatively thicker oxide coating (3029.7mg/ft² or 13.6 μm). The effect of boric acid addition in 5% wt. sulphuric acid and 3% citric acid electrolyte composition was also studied at 35°C and 20V as shown in Fig. 2 (Table-2). Maximum oxide film thickness (3244.3mg/ft² or 14.6 μm) was obtained using 5% sulphuric acid, 3% citric acid and 0.5% boric acid electrolyte composition. The sulphuric acid in the electrolyte tries to dissolve the oxide coating formed on aluminum and yields a porous oxide film. However aluminum oxide is insoluble in borate medium and these ions present in sulphuric acid tend to decrease the dissolution rate of oxide film. Some citrate ions are also migrated into the porous coating of aluminum, thus causing an increase of oxide film thickness [9].

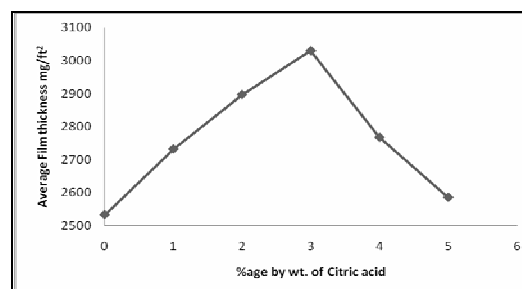


Fig. 1: Effect of citric acid concentration in 5% wt. sulphuric acid at 35°C, 20V and 25 minutes anodization time.

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Table-1: Effect of citric acid concentration in 5% wt. sulphuric acid at $35 \pm 1^\circ\text{C}$, 20V and 25 minutes anodization time.

%age of citric acid	Average Film thickness mg/ft ²	Film thickness μm (micron)
0.0	2532.0	11.4
1.0	2732.0	12.3
2.0	2897.0	13.0
3.0	3029.7	13.6
4.0	2767.2	12.4
5.0	2585.5	11.6

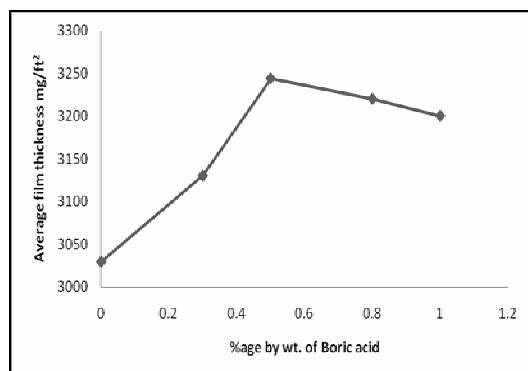


Fig. 2: Effect of boric acid concentration on film thickness in 5% sulphuric acid and 3% citric acid electrolyte composition.

Table-2: Effect of boric acid concentration in 5% wt. sulphuric acid + 3% citric acid at $35 \pm 1^\circ\text{C}$, 20V and 25 minutes anodization time.

%age by wt. of boric acid	Average film thickness mg/ft ²	Average film thickness μm (micron)
0.0	3029.7	13.6
0.3	3130.6	14.1
0.5	3244.3	14.6
0.8	3220.5	14.5
1.0	3200.6	14.4

The corrosion resistance of aluminum sample was determined to find the effectiveness of oxide coating by potentiodynamic polarization test. Corrosion test results for the anodized aluminum samples with optimum conditions and the original aluminum alloy sample in a 3.5% NaCl solution are given in Table-3. It was observed that there was a considerable decrease in the anodic current of the anodized sample compared to the uncoated aluminum alloy sample. The corrosion current density of the anodized sample was also significantly lower than that of uncoated aluminum alloy. The corrosion protection efficiency of the anodic coatings can be explained and interpreted by both the increase in corrosion potential as well as the decrease in the corrosion current density [10]. It was also found that increase in polarization resistance (R_p) reveals enhanced corrosion protection by the coated samples (Table-3). Therefore aluminum sample coated in sulphuric/citric/boric acid

electrolyte system showed a higher corrosion resistance than the uncoated aluminum alloy sample. Since the uncoated aluminum sample S-01 has very thin oxide film naturally present and when it is broken down during the corrosion process, the corrosion of bare aluminum sample was severe, showing least corrosion protection [11]. That is why it is usually recommended that aluminum metal should be protected from corrosion and abrasion effects by oxide coating using anodizing process. Aluminum alloy sample S-02 was obtained by anodizing in 5% sulphuric acid electrolyte solution (w/v) at $35 \pm 1^\circ\text{C}$ and 20V. It was observed from corrosion test results that there was increase in corrosion potential and decrease in corrosion current density. The polarization resistance was relatively higher as compared to the uncoated aluminum sample but this oxide coating did not provide good and effective corrosion protection due to the formation of some cracks in the oxide film [12]. Therefore 5% sulphuric acid electrolyte composition was later modified by introducing some additive to get good and corrosion resistant oxide coating. In our previous paper, anodizing of aluminum was studied in sulphuric/oxalic/boric acid electrolyte system to obtain a corrosion resistant oxide coating [8]. In present work, 5% sulphuric acid electrolyte composition was further modified by introducing citric acid and boric acid to produce better and corrosion resistant oxide coating. Aluminum alloy sample S-03 was obtained by anodizing in 5% sulphuric acid, 3% citric acid and 0.5% boric acid electrolyte composition at $35 \pm 1^\circ\text{C}$ temperature and 20 V. It was observed from corrosion results given in Table-3 that there was significant increase in corrosion potential and decrease in corrosion current density. The corrosion potential E_{corr} -0.796 V for bare aluminum alloy sample was increased to -0.576V and corrosion current density $5.425 \times 10^{-7} \text{ A/cm}^2$ for bare aluminum sample was decreased to $0.048 \times 10^{-7} \text{ A/cm}^2$ for the coated sample. It was also observed that the polarization resistance R_p for bare aluminum sample was increased from $1.30 \times 10^4 \Omega/\text{cm}^2$ to $8.81 \times 10^4 \Omega/\text{cm}^2$, thus providing better corrosion protection as compared to the aluminum sample S-02. It was most probably due to the formation of uniform oxide film and involvement of some citrate and borate ions in the oxide coating and giving better corrosion resistance [13, 14]. The presence of these ions in the oxide coating inhibits the penetration of chloride ions, resulting in better pitting corrosion resistance. The corrosion rate was also quite limited indicating the better corrosion protection of coated aluminum sample. The corrosion results of the coated sample obtained by

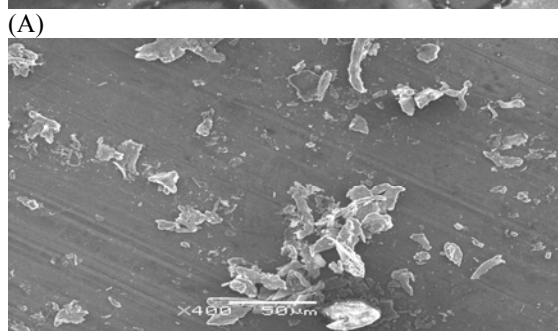
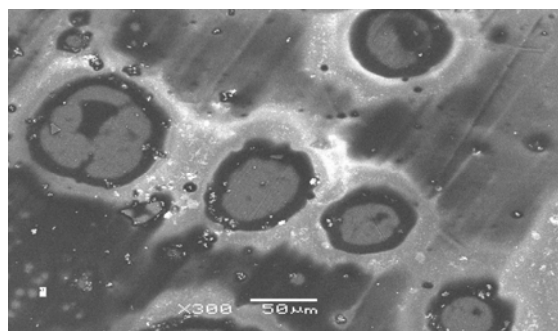
this method were also found better as compared to our previous results [8].

Table-3: The results of the potentiodynamic corrosion tests in a 3.5% NaCl solution and 298.5 K Temperature.

	Al Substrate S-01	S-02	S-03
E_{corr} (V)	-0.796	-0.654	-0.576
I_{corr} ($\times 10^{-7}$ A/cm ²)	5.425	1.672	0.048
β_a (V/decade)	1.758	0.119	0.245
β_c (V/decade)	0.316	3.058	0.021
R_p ($\times 10^4$ Ω /cm ²)	1.300	1.482	8.810
Corrosion rate(R_M) $\times 10^{-3}$ (mm/year)	5.910	1.820	0.053

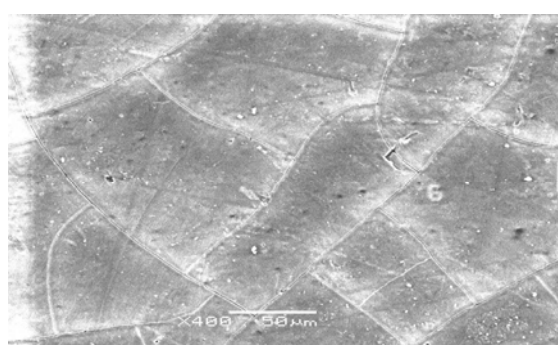
SEM micrographs of original aluminum alloy sample S-01 are shown, before (Fig. 3a) and after (Fig. 3b) corrosion test. Pitting corrosion was observed before corrosion test (Fig. 3a) due to the destruction of thin oxide film naturally present on the surface of aluminum. It was clear from SEM micrograph that the surface of the uncoated aluminum alloy sample suffered severe corrosion and a uniform corrosion was observed due to the extensive dissolution of aluminum after corrosion test (Fig. 3b). SEM micrograph of aluminum sample S-02 before corrosion test (Fig. 4c) revealed some cracks in the oxide film and were considered most likely caused by the internal stress generated by the growth of the oxide at the substrate /oxide interface [12]. It was observed after corrosion test (Fig. 4d) that the corrosion resistance of the coated sample was not good, even though the coating was thicker. The oxide coating did not prove effective against corrosion as compared to the original alloy sample and a uniform corrosion was observed. SEM micrograph of aluminum sample S-03 before (Fig. 5e) corrosion test revealed no cracks in the oxide coating. It was observed after corrosion test (Fig. 5f) that the corrosion resistance of the coated sample was better as compared to the sample S-02. The surface morphology of this coated sample before and after corrosion test revealed no significant difference (Fig. 5e and 5f) and no localized pitting corrosion was observed.

It was concluded that the coated aluminum sample obtained by anodizing in sulphuric/citric/boric acid electrolyte system exhibited better pitting corrosion resistance with no significant difference in surface morphology and are environmentally safe as compared to the use of toxic Cr (VI). The increase in polarization resistance (R_p) in corrosion test revealed superior corrosion protection by the coated sample than the uncoated aluminum alloy sample, thus proving the effectiveness of the oxide coating.

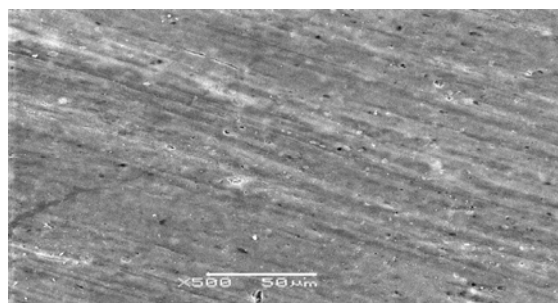


(A)

(B)



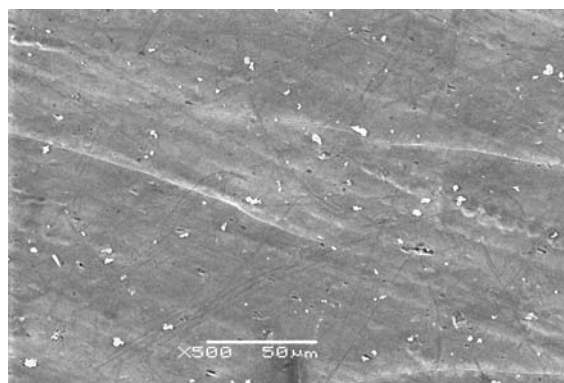
(C)



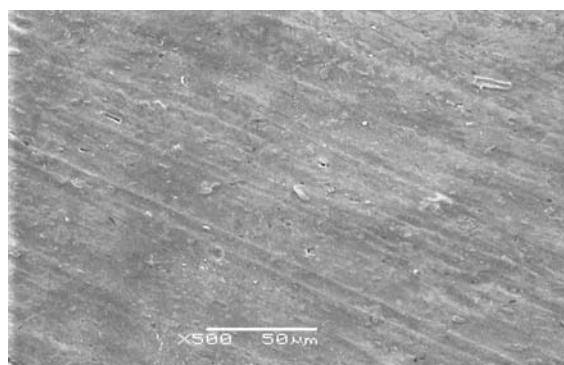
(D)

Fig. 3: SEM micrographs of the Al alloy substrate sample S-01 (a) before and (b) after corrosion test.

Fig. 4: SEM micrographs of the anodized Al alloy sample S-02 (c) before and (d) after corrosion test.



(E)



(F)

Fig. 5: SEM micrographs of the anodized Al alloy sample S-03 (e) before and (f) after corrosion test.

Experimental

Aluminum alloy of 7000 series was analyzed by Emission spectrometer Metal Lab.GNR. The composition of this alloy (wt. %) was 3.544 % Zn, 1.360 % Mg, 0.643 % Cu, 0.195 % Fe, 0.150% Cr, 0.111 % Si, 0.014 % Mn and aluminum balance. The aluminum alloy samples were degreased using acetone and were rinsed in distilled water. Chemical cleaning was done to remove polishing composition, oil and general dirt from the aluminum in 10% sulphuric acid (v/v) at 90°C so as to leave a clean surface ready for anodizing process. It was rinsed thoroughly to remove acid contents with distilled water. After pretreatment, the aluminum alloy strip was anodized at constant voltage in different electrolyte solutions and at constant temperature for particular duration of time. The sealing of the anodized aluminum was carried out in near-boiling distilled water (96-99°C) usually known as hydrothermal sealing (HTS). The effect of hot water is to reduce or eliminate the ability of the coating to absorb dyes and the blocking of the pores increases

the corrosion resistance of the coating. In our present work, 5% sulphuric acid electrolyte composition was further modified by introducing citric acid and boric acid to produce oxide coating with better pitting corrosion resistance. The effect of citric acid concentration in 5% wt. sulphuric acid on anodic oxide film thickness was studied at relatively high temperature (35°C) and 20V. The maximum film thickness was obtained using 5% wt. sulphuric acid and 3% citric acid electrolyte composition. The oxide film thickness results are shown in Table-1 and Fig. 1. The effect of boric acid addition in this electrolyte composition was also studied at 35°C and 20V and results are shown in Table-2 and Fig. 2.

Anodic Oxide Film Evaluation

a) Gravimetric Determination of Anodic Oxide Coating Mass and Thickness

Film weight/mass was determined by stripping a sample of known area in a solution containing 20 g chromic acid and 35 ml (85%, $d = 1.75 \text{ g per cm}^3$) phosphoric acid per dm^3 (with distilled water) held at boiling point (99°C) [15, 16]. The oxide coating was completely dissolved after 20 minutes immersion time. The aluminum sample was weighed before and after oxide coating removal. Film thickness was determined by using formula.

Film thickness (mg/ft^2)=

$$\frac{\text{Loss in weight (mass of oxide coating in mg)}}{\text{Area (ft}^2\text{)}}$$

From the weight loss, the coating thickness (in micron) was calculated from the formula.

$$T = \frac{1000}{a d} W$$

where

T=coating thickness in micron.

W=mass of coating in milligrams.

a=surface area of the coating in square millimeters.

d=density of the coating.

The results of oxide coating thickness with different compositions of citric acid and boric acid are shown in Table-1 and 2 respectively.

b) Corrosion Studies by Potentiodynamic Polarization Test

The general corrosion resistance of the samples (the oxide coatings and the aluminum alloy substrate) was studied by potentiodynamic polarization tests at 298.5 K temperature using

Autolab PGSTAT-30 Potentiostat with GPES software. The potentiodynamic polarization measurements were carried out in a conventional three-electrode cell using a saturated calomel electrode (SCE) as a reference electrode and a platinum rod as a counter electrode. When the electrochemical system was stable, the measurements were carried out in a 3.5% NaCl solution [10]. The polarization resistance and corrosion rates of the tested samples were determined for comparison. A summary of the results of the potentiodynamic polarization tests is given in Table-3.

c) Scanning Electron Microscope Micrographs

The scanning electron microscope (SEM) micrographs provide information about the surface morphology of different samples. The SEM micrographs of aluminum samples were taken by Jeol JSM-6480LV scanning electron microscope and were used to observe and analyze the original and coated samples, both before and after the corrosion tests. The samples were stuck to aluminum stub using silver paste which was placed in the sample holder to load in the machine [10, 11]. The SEM micrographs of original aluminum alloy and coated aluminum samples are given in Fig. 3 to 5.

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