

## Anodizing of Aluminum with Improved Corrosion Properties

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**Summary:** Anodizing of aluminum was studied in sulphuric/oxalic/boric acid electrolyte system. The corrosion resistance of the anodic oxide coating of aluminum was determined by potentiodynamic polarization test and scanning electron microscope (SEM) was used to investigate the surface morphology before and after corrosion test. It was found that the oxide coating obtained by this method showed better corrosion resistance with no significant difference in surface morphology.

### Introduction

The corrosion protection of aluminum and aluminum alloys is important since it is used in a number of industries like aircraft, automotive and aerospace, for both technical and economic considerations. Anodizing of aluminum comprises electrochemical conversion of the surface to aluminum oxide, with the aluminum serving as the anode in an aqueous electrolyte and the oxygen being provided by the electrolytic dissociation of water. Although the electrolyte is not consumed directly in anodic film formation, it has an important effect on film properties and usefulness [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 and even prohibited [3-5]. Thus the replacement of chromic acid anodizing process has been an important and urgent problem in industrial sectors and for environmental pollution issues. 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]. Zhang and his coworkers studied the bonding strength and corrosion resistance of aluminum alloy by anodizing treatment in a phosphoric acid modified boric acid/sulphuric acid bath [8]. In the present study, anodizing of aluminum was studied in sulphuric/oxalic/boric acid electrolyte system to obtain a relatively thick and corrosion resistant oxide coating.

### Results and Discussion

The anodizing of aluminum was carried out at a relatively higher temperature (35°C) in sulphuric/oxalic/boric acid electrolyte system to increase its corrosion resistance. It was observed that anodic oxide coating having maximum film thickness was obtained in 5 % wt. sulphuric acid and 3% oxalic 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 (3679.7 mg/ft<sup>2</sup> or 16.5 µm). The effect of boric acid addition in 5 % wt. sulphuric acid and 3 % oxalic acid electrolyte composition was studied at 35°C and 20V as shown in Fig. 2 (Table-2). Maximum oxide film thickness (4112.5 mg/ft<sup>2</sup> or 18.4 µm) was obtained using 5 % sulphuric acid, 3 % oxalic 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 oxalate ions are also migrated into the porous coating of

Table-1: Effect of oxalic acid concentration in 5% wt. sulphuric acid at 35 ± 1 °C, 15V and 25 minutes anodization time.

%age by wt. of oxalic acid	Average film thickness mg/ft <sup>2</sup>	Average film thickness µm (micron)
1.0	1624.0	7.3
2.0	1773.5	8.0
3.0	3137.5	14.1
4.0	1971.0	8.8
5.0	796.0	3.6

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Table-2: Effect of boric acid concentration in 5% wt. sulphuric acid +3 % oxalic 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 <sup>2</sup>	Average film thickness $\mu\text{m}$ (micron)
0.0	3679.7	16.5
0.5	4112.5	18.4
1.0	4056.6	18.2

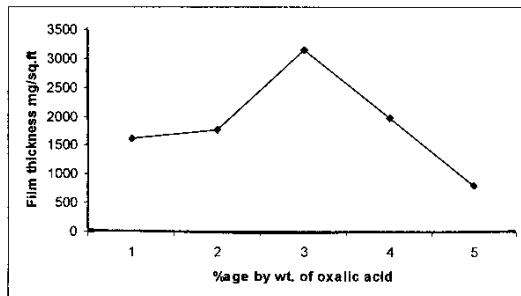


Fig. 1: Effect of oxalic acid concentration in 5 % wt. sulphuric acid at  $35^\circ\text{C}$ , 15V and 25 minutes anodization time.

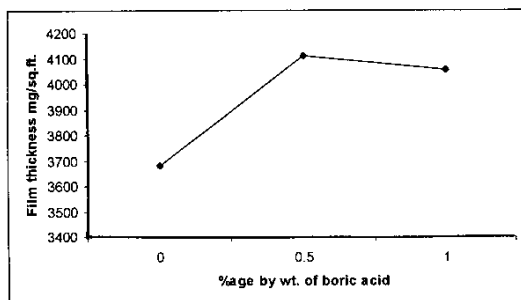


Fig. 2: Effect of boric acid concentration on film thickness in 5% sulphuric acid and 3% oxalic acid electrolyte composition.

aluminum, thus causing an increase of oxide film thickness [9].

The corrosion resistance of aluminum sample was determined to find the effectiveness of oxide coating by potentiodynamic polarization test. Potentiodynamic polarization 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

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
$E_{\text{corr}}$ (V)	-0.796	-0.654	-0.559
$I_{\text{corr}}$ ( $\times 10^{-7}$ A/cm <sup>2</sup> )	5.425	1.672	1.597
$\beta_a$ (V/decade)	1.758	0.119	3.804
$\beta_c$ (V/decade)	0.316	3.058	0.317
$R_p$ ( $\times 10^4 \Omega/\text{cm}^2$ )	1.300	1.482	4.187
Corrosion rate( $R_{\text{M}}$ ) $\times 10^{-3}$ (mm/year)	5.910	1.820	1.740

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 can also be seen from Table-3 that increase in polarization resistance  $R_p$  reveals enhanced corrosion protection by the coated samples. Therefore aluminum sample coated in sulphuric/oxalic/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 electrolytically coated with oxide coating by anodizing process to prevent it from corrosion and abrasion effects. 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 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 the oxide film formed in 5 % sulphuric acid electrolyte solution was later modified by introducing some additive to get good corrosion results. Aluminum alloy sample S-03 was obtained by anodizing in 5 % sulphuric acid and 0.5 % boric acid electrolyte composition at  $35 + 1^\circ\text{C}$  temperature and 20 V. It was observed from corrosion results given in Table-3 that there was considerable increase in corrosion potential and decrease in corrosion current density. The corrosion potential  $E_{\text{corr}}$  -0.796 V for bare aluminum alloy sample was increased to -0.559V and corrosion

current density  $5.425 \times 10^{-7} \text{ A/cm}^2$  for bare aluminum sample was decreased to  $0.597 \times 10^{-7} \text{ A/cm}^2$  for the coated sample. It was also observed that the polarization resistance  $R_p$  for bare aluminum sample was increased from  $1.3 \times 10^4 \text{ } \Omega/\text{cm}^2$  to  $4.187 \times 10^4 \text{ } \Omega/\text{cm}^2$ , thus providing good 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 oxalate and borate ions in the oxide film making it more corrosion resistant [13, 14]. The corrosion rate of coated aluminum sample was also quite less indicating the good corrosion protection of coated sample.

SEM micrographs of original aluminum alloy sample S-01 are shown, before (Fig. 3 a) and after (Fig. 3 b) 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 3 b). SEM micrograph of aluminum sample S-02 before corrosion test (Fig. 4 c) 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 4 d) 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. 5 e) corrosion test revealed few cracks in the oxide coating, but it was observed after corrosion test (Fig. 5 f) 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. 5 e and f) and no localized corrosion was observed.

It was concluded that the coated aluminum sample obtained by anodizing in sulphuric/oxalic/boric acid electrolyte system was more corrosion resistant with no significant difference in surface morphology and without environmental hazards. The increase in polarization resistance  $R_p$  in corrosion test revealed enhanced corrosion protection by the coated sample than the

uncoated aluminum alloy sample, thus proving the effectiveness of the oxide coating.

### 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  $90^\circ \text{C}$  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 ( $96\text{-}99^\circ \text{C}$  temperature) 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. The effect of oxalic acid concentration in 5 % wt. sulphuric acid on anodic oxide film thickness was studied at relatively high temperature ( $35^\circ \text{C}$ ) and 15V. The maximum film thickness was obtained using 5 % wt. sulphuric acid and 3 % oxalic acid electrolyte composition. The oxide film thickness results are shown in Table-1 and Fig. 1. The voltage was increased from 15 to 20V using this composition to increase the film thickness and the effect of boric acid addition in this electrolyte composition was also studied at  $35^\circ \text{C}$  and 20V. The 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  $\text{dm}^3$  (with distilled water) held at boiling point ( $99^\circ \text{C}$ ) [15, 16]. The oxide coating was dissolved after 20 minutes immersion time. The aluminum sample was weighed

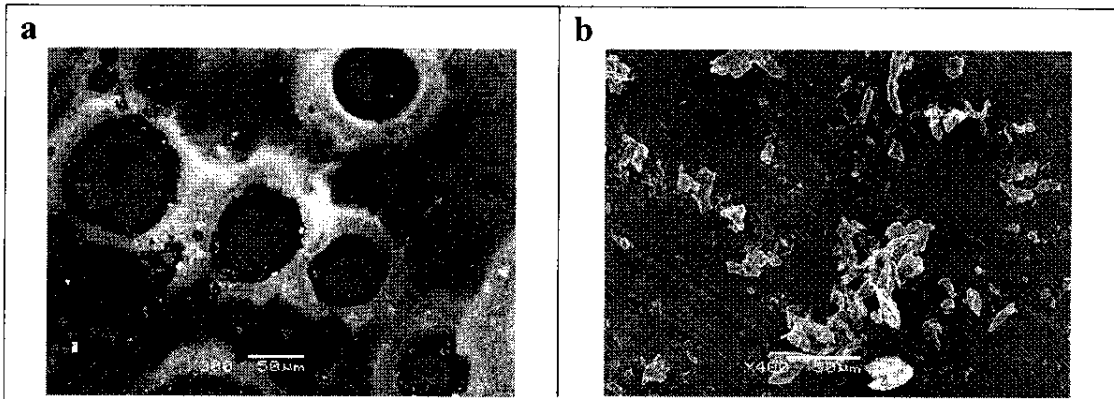


Fig. 3: SEM micrographs of the Al alloy substrate sample S-01 (a) before and (b) after corrosion test.

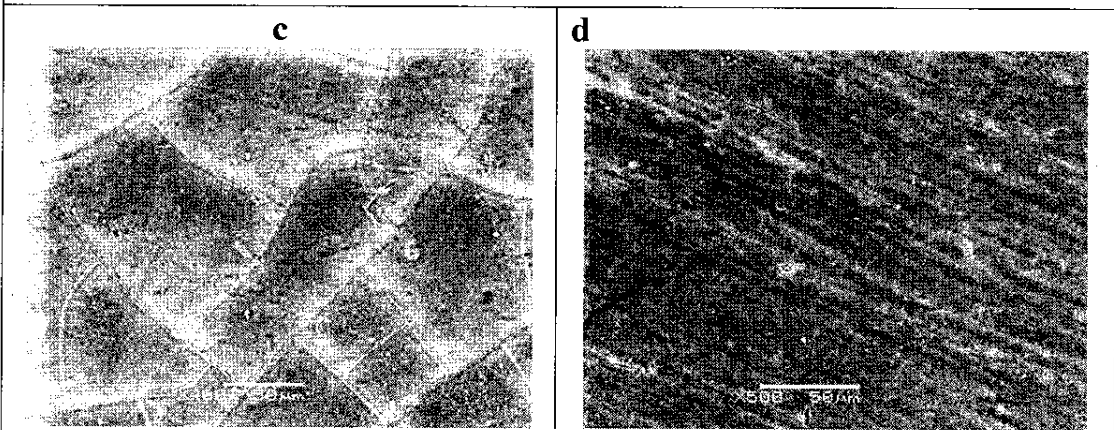


Fig. 4: SEM micrographs of the anodized Al alloy sample S-02 (c) before and (d) after corrosion test.

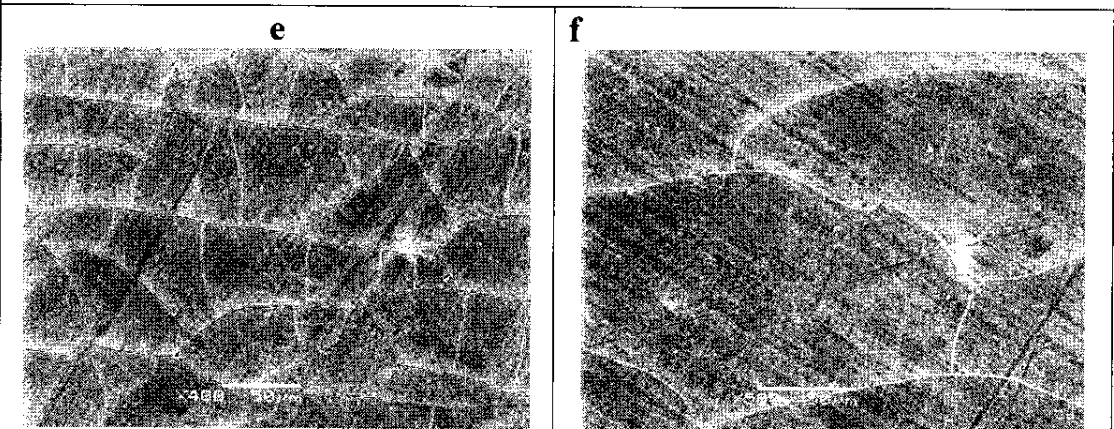


Fig. 5: SEM micrographs of the anodized Al alloy sample S-03 (e) before and (f) after corrosion test.

before and after oxide coating removal. Film thickness was determined by using formula.

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

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

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

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 oxalic acid and boric acid are shown in Tables-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. The polarization resistance and corrosion rates of the tested samples were determined for comparison [10]. 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 give information about the sample's surface morphology. 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 stick 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 Figs. 3-5.

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