

Enhancing Pitting Corrosion Resistance of Aluminium by Anodizing Process

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In present study, the anodizing of aluminium was carried out in sulphuric acid/tartaric acid electrolyte system to increase pitting corrosion resistance. The corrosion resistance of the oxide coating of aluminium was determined by potentiodynamic polarization test. The surface morphology was investigated using scanning electron microscope before and after the corrosion test. It was found that anodic oxide coating obtained in sulphuric acid/tartaric acid showed higher pitting corrosion resistance.

Key Words: Anodizing, Aluminium alloy, Corrosion, Oxide coating.

INTRODUCTION

Aluminium alloys suffer pitting corrosion and corrosion protection is important due to their application in number of industries like aircraft, automotive and aerospace, for both technical and economic considerations. 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 attack¹. The chromic acid anodizing process for aluminium and aluminium alloys was initially developed by Bengough and Stuart². However the use of hexavalent chromium is not advised from a health and environmental point of view since it is toxic and carcinogenic and the process is gradually limited even prohibited³⁻⁵.

Wong and Moji developed boric acid/sulphuric acid anodizing as a replacement for chromic acid anodizing⁶. Kallenborn and Emmons developed a thin film sulphuric acid anodizing (TFSA) process⁷. Sarganov and Gorokh studied the growth of oxide cells during formation of anodic alumina films in tartaric acid electrolyte⁸. In our previous paper, anodizing of aluminium was studied in sulphuric acid/oxalic acid/boric acid electrolyte system to obtain a corrosion resistant oxide coating⁹. In present work, the anodizing of aluminium was studied in sulphuric/tartaric acid electrolyte system to obtain an oxide coating with greater pitting corrosion resistance.

EXPERIMENTAL

Analysis of aluminium alloy of 7000 series was carried out 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 aluminium balance. After degreasing using acetone, the aluminium alloy samples were rinsed in distilled water. Chemical cleaning was done to remove polishing composition, oil and general dirt from the aluminium in 10 % sulphuric acid (v/v) at 90 °C so as to leave a clean surface ready for anodizing process. Acid contents were removed by thorough rinsing with distilled water. After pretreatment, the aluminium 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 aluminium 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 tartaric acid and boric acid to produce oxide coating with enhanced pitting corrosion resistance. The effect of tartaric acid concentration in 5 % wt. sulphuric acid on anodic oxide film thickness was studied at 30 °C temperature and 20 V. The maximum film thickness was obtained using 5 % wt. sulphuric acid and 2 % tartaric 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 30 °C and 20 V and results are shown in Table-2 and Fig. 2.

Anodic oxide film evaluation

Gravimetric determination of anodic oxide coating mass and thickness: The mass of deposited oxide film was determined by stripping a sample of known area in a solution

TABLE-1
EFFECT OF TARTARIC ACID CONCENTRATION
IN 5 % SULPHURIC ACID AT 30 ± 1 °C, 20 V AND
25 min ANODIZATION TIME

Conc. of tartaric acid (Wt. %)	Film thickness (mg/ft ²)	Film thickness μm (μ)
0.0	2340.1	10.5
1.0	2632.9	11.8
2.0	2802.7	12.6
3.0	2637.5	11.8
4.0	2510.5	11.3
5.0	2372.2	10.6

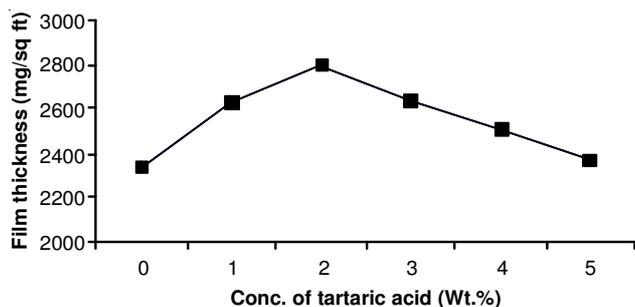


Fig. 1. Effect of tartaric acid concentration in 5 % sulphuric acid at 30 °C, 20 V and 25 min anodization time

TABLE-2
EFFECT OF BORIC ACID CONCENTRATION IN
5 % SULPHURIC ACID + 2 % TARTARIC ACID AT
 30 ± 1 °C, 20 V AND 25 min ANODIZATION TIME

Conc. of boric acid (Wt. %)	Film thickness (mg/ft ²)	Film thickness μm (μ)
0.0	2802.7	12.6
0.5	2665.7	12.0
1.0	2428.9	10.9

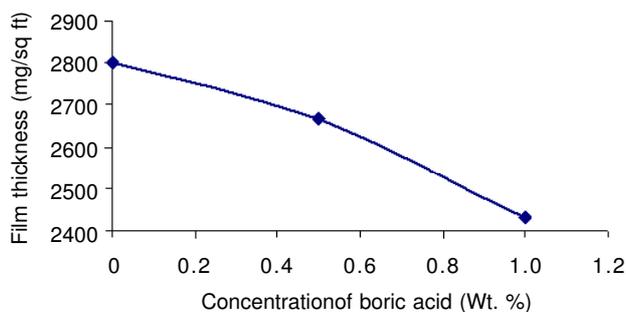


Fig. 2. Effect of boric acid concentration in 5 % sulphuric acid + 2 % tartaric acid at 30 °C, 20 V and 25 min anodization time

containing 20 g chromic acid and 35 mL (85 %, $d = 1.75$ g/cm³) phosphoric acid per dm³ (with distilled water) held at boiling point (99 °C). The oxide coating was dissolved after 20 min immersion time. The aluminium sample was weighed before and after oxide coating removal. Film thickness was determined by using formula⁹.

The results of oxide coating thickness with different compositions of tartaric acid and boric acid are shown in Tables 1 and 2, respectively.

Corrosion studies by potentiodynamic polarization test:

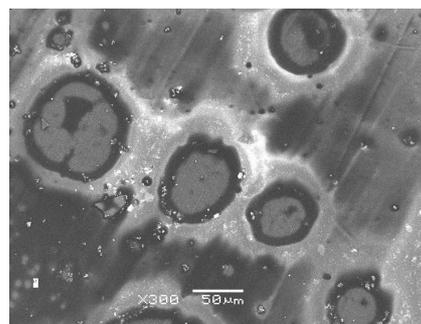
The general corrosion resistance of the samples (the oxide coatings and the aluminium alloy substrate) was studied by

potentiodynamic polarization tests at 298.5 K 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 solution¹⁰. 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.

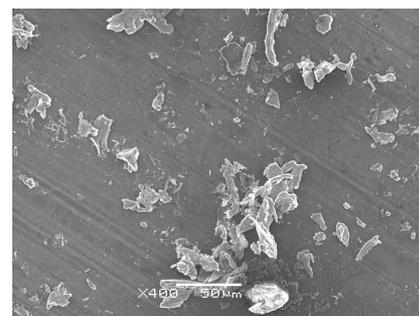
TABLE-3
RESULTS OF THE POTENTIODYNAMIC CORROSION TESTS
IN A 3.5 % NaCl SOLUTION AND 298.5 K TEMPERATURE

	Al substrate S-01	S-02	S-03
E_{corr} (V)	-0.796	-0.654	-0.591
I_{corr} ($\times 10^{-7}$ A/cm ²)	5.425	1.672	1.176
β_a (V/decade)	1.758	0.119	4.8478
β_c (V/decade)	0.316	3.058	0.8263
R_p ($\times 10^4$ Ω /cm ²)	1.300	1.482	13.03
Corrosion rate (R_M) $\times 10^{-3}$ (mm/year)	5.910	1.820	1.28

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

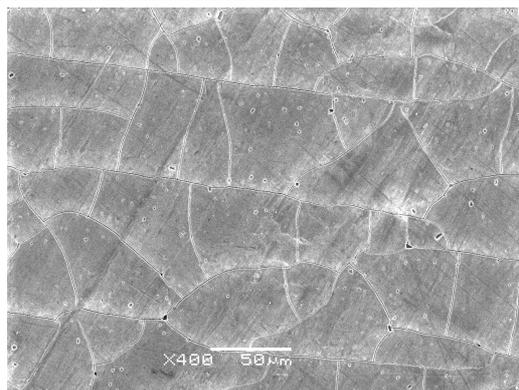


(a)

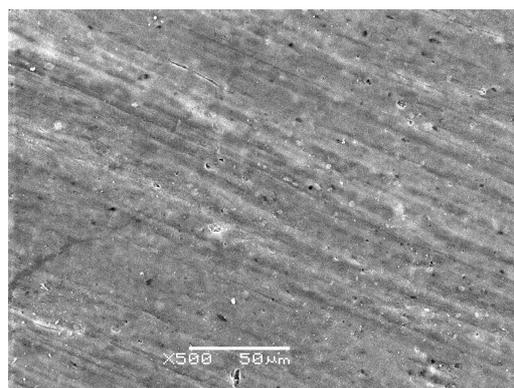


(b)

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

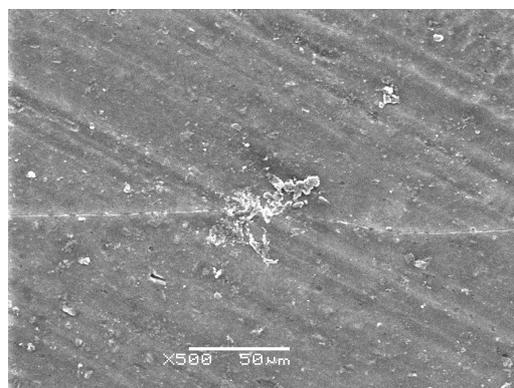


(c)

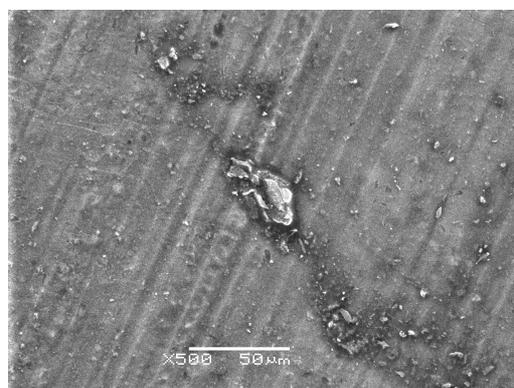


(d)

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

RESULTS AND DISCUSSION

The anodizing of aluminium was carried out in sulphuric/tartaric acid electrolyte system at 30 °C 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 2 % tartaric acid electrolyte composition as shown in Fig. 1 (Table-1). Anodizing of aluminium was carried out at 20 V using this composition to produce relatively thicker oxide coating (2802.7 mg/ft² or 12.6 μm). The effect of boric acid addition in 5 % wt. sulphuric acid and 2 % tartaric acid electrolyte composition was also studied at 30 °C and 20 V as shown in Fig. 2 (Table-2). It was observed that the oxide film thickness was decreased by the addition of boric acid. The sulphuric acid in the electrolyte tries to dissolve the oxide coating formed on aluminium and yields a porous oxide film. However aluminium oxide is insoluble in tartarate medium and these ions present in sulphuric acid tend to decrease the dissolution rate of oxide film. Some tartarate ions are also migrated into the porous oxide coating of aluminium, thus causing an increase of oxide film thickness¹².

The corrosion resistance of aluminium sample was determined to find the effectiveness of oxide coating by potentiodynamic polarization test. Corrosion test results for the anodized aluminium samples with optimum conditions and the original aluminium alloy sample in a 3.5 % NaCl solution are given in Table-3. A considerable decrease in the anodic current of the anodized sample compared to the uncoated aluminium alloy sample was observed. The corrosion current density of the anodized sample was also significantly lower than that of uncoated aluminium 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. It was found that the increase in polarization resistance (R_p) reveals enhanced corrosion protection by the coated samples (Table-3). Therefore aluminium sample coated in sulphuric acid/tartaric acid electrolyte system showed a higher pitting corrosion resistance than the uncoated aluminium alloy sample. The corrosion of bare aluminium sample was severe, since the uncoated aluminium sample S-01 has thin oxide film naturally present and when it is broken down during the corrosion process, least corrosion protection was observed. That is reason, it is usually recommended that aluminium metal should be protected from corrosion and abrasion effects by oxide coating using anodizing process. Aluminium alloy sample S-02 was obtained by anodizing in 5 % sulphuric acid electrolyte solution (w/v) at 30 ± 1 °C and 20 V. 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 aluminium sample but this oxide coating did not provide good and effective corrosion protection due to the formation of some cracks in the oxide film¹³. Therefore 5 % sulphuric acid electrolyte composition was later modified by introducing some additive to get better and corrosion resistant oxide coating. In our previous paper, anodizing of aluminium was studied in sulphuric acid/oxalic acid/boric acid electrolyte system to obtain a corrosion resistant oxide coating⁹. In present work, 5 % sulphuric acid electrolyte

composition was further modified by introducing tartaric acid to produce better oxide coating with enhanced pitting corrosion resistance. Aluminium alloy sample S-03 was obtained by anodizing in 5 % sulphuric acid and 2.0 % tartaric acid electrolyte composition at 30 ± 1 °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 aluminium alloy sample was increased to -0.591 V and corrosion current density 5.425×10^{-7} A/cm² for bare aluminium sample was decreased to 1.176×10^{-7} A/cm² for the coated sample. It was also observed that the polarization resistance R_p for bare aluminium sample was increased from 1.30×10^4 to 13.03×10^4 Ω/cm², thus providing better corrosion protection as compared to the aluminium sample S-02. It was most probably due to the formation of uniform oxide film and the involvement of some tartarate ions in the porous oxide coating and giving enhanced pitting corrosion resistance^{14,15}. The presence of these ions in the oxide coating inhibits the penetration of chloride ions, resulting in better pitting corrosion efficiency. The corrosion rate was also quite limited indicating the enhanced corrosion protection of coated aluminium sample. The corrosion results of the coated sample obtained by this method were also found better and improved as compared to previous results⁹.

SEM micrographs of original aluminium 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 aluminium. It was clear from SEM micrograph that the surface of the uncoated aluminium alloy sample suffered severe corrosion and a uniform corrosion was observed due to the extensive dissolution of aluminium after corrosion test (Fig. 3b). SEM micrograph of aluminium 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. 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 aluminium sample S-03 before corrosion test (Fig. 5e) 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 f) and no localized pitting corrosion was observed.

Conclusion

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

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