

## CORROSION RESISTANT Sol-Gel COATING on 2024-T3 ALUMINUM

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**Abstract:** The inherent reactivity of the Al-Cu alloys is such that their use for structural, marine, and aerospace components and structures would not be possible without prior application of a corrosion resistance system. Historically these corrosion resistance coatings were based on the use of chemicals containing Cr (VI) compounds. Silane coatings are of increasing interest in industry due to their potential application for the replacement of current toxic hexavalent chromate based treatments. In this study, hydrophobic coating sol was prepared with methyltriethoxysilane (MTES), methanol (MeOH), and water (as 7M  $\text{NH}_4\text{OH}$ ) at a molar ratio of 1:25:4.31 respectively. The coatings were applied by a dip-technique to 2024-T3 Al alloy, and subsequently cured at room temperature and there after heat treated in an oven at 150°C. The anticorrosion properties of the coatings within 3.5 wt% NaCl solution were studied by Tafel polarization technique. The sol-gel coating exhibited good anticorrosion properties providing an adherent protection film on the Al 2024-T3 substrate. The surface properties were characterized by water contact angle measurement, scanning electron microscopy (SEM), and the composition was studied by Fourier transform infrared spectroscopy (FTIR).

**Keywords:** Sol-gel, Al-Cu alloys, Hydrophobic, Anticorrosion.

### 1. INTRODUCTION

Aluminum alloy, series 2000, are widely used in manufacturing airplane parts such as hull, wheel and wing skin and also in transportation and automotive industries like truck wheels and suspension components due to their high strength to weight ratio, good ductility, suitable fracture toughness and excellent thermal stability. One of the most common alloys that is widely used in aerospace industries is 2024 aluminum alloy [1]. A major disadvantage of aluminum alloy for these applications is that it corrodes easily, especially in aqueous environment containing  $\text{Cl}^-$  ions, even trace amounts of  $\text{Cl}^-$ , which limits the application of this alloy.

Conventionally, pre-treatment (chromate coatings) exploiting Cr (VI) compounds as corrosion inhibitors, have been widely used for the corrosion protection of Al 2024-T3 due to the strong oxidation properties of Cr (VI). Unfortunately, the superior oxidation of Cr (VI) also causes serious health problems to humans and is a known carcinogen. Consequently, the use of pre-treatments based upon Cr (VI) is gradually being restricted for health and safety reasons and also environmental concerns. In order to reduce

the application of Cr (VI) based products, numerous processes have been introduced as possible alternatives, namely, plasma-enhanced chemical vapour deposition (PECVD), plasma-assisted physical vapour deposition (PAPVD), sol-gel technology and the keronite electrolytic ceramic coating process. One of the most promising alternative pre-treatments for the corrosion protection of metals is that of sol-gel technology. Sol-gel derived coatings offer a number of advantages in that the coating can be formulated to provide high corrosion resistance and compatibility with subsequent organic top coats whilst being non-toxic and environmentally compliant. The corrosion resistance of a sol-gel derived coating is considered to be attributed to its physical barrier properties, which restrict the penetration of the electrolyte towards the metallic substrate [2-5]. The keyword of this technology is the composition of the sol and the processing parameters which controls the structure and the properties of the film [6].

A large amount of sol-gel research, including the work presented here, is based on silicon precursors because of their balance of reactivity and ease of handling, as well as their ready availability.

The anodizing technology is an effective method to improve the corrosion resistance of the aluminum and aluminum alloys, and it has been universally applied [7]. When aluminum is polarized anodically in an electrolytic solution, an oxide film will be formed on its surface and this process is called anodizing [8]. The anodic films are known to present a duplex structure: a thick porous layer separated from the metal matrix by a thin non-porous layer called the barrier layer. Due to their porous structure, the anodic film is sensitive to aggressive environments. So it is necessary for the anodic film to proceed to seal post treatment [7]. The sealing in sol prepared by sol-gel process is based on the formation of silica film in the pores of the ANOX layer to hinder the effect of the corrosive solution [9].

## 2. EXPERIMENTAL PROCEDURE

### 2. 1. Materials

The chemicals used were methyltriethoxysilane, (merck), methanol, and ammonia (NH<sub>3</sub>), sulphuric acid. Double distilled water was used for all the experiments. All the reagents were used as received.

### 2. 2. Anodizing

The composition of the 2024-T3 alloy is shown in Table. The 40mm × 20mm × 1.5mm specimens were cut from the alloy for the subsequent use. Prior to the anodizing, the surfaces of the samples were ground using SiC abrasive papers up to number 1200, and cleaned with deionized water and acetone. The samples were alkaline cleaned, chemically polished and finally de-smuted. After each step, the samples were rinsed with deionized water and air dried. Table 2 lists the chemical composition of the solutions used for surface preparation and the holding time and temperature.

In order to evaluate the effect of anodizing pretreatment on improvement of the corrosion resistance of sol-gel coating, anodizing process was performed as below. Anodization was carried out at 25 °C and 1A/dm<sup>2</sup> for 60 min in 170 g/L

H<sub>2</sub>SO<sub>4</sub> aqueous solution. After the anodization, the samples were taken out immediately, washed thoroughly and coated according to the process is described in section3.

### 2. 3. Sol-Gel Coating

The 20mm × 10mm × 1.5mm specimens were cut from the alloy for the subsequent use. The surfaces of the samples were ground using SiC abrasive papers up to number 600. Samples were cleaned and degreased ultrasonically with acetone, ethanol and distillate water for 10 minutes.

The coating solution was prepared under basic condition from the MTES, CH<sub>3</sub>OH, and H<sub>2</sub>O (as 7M NH<sub>4</sub>OH) in the molar ratio of 1:25:4.31 respectively. First, methanol and base catalyst (NH<sub>4</sub>OH) was stirred for 30 min and then MTES was added droplet by droplet while stirring. The final coating solution was stirred for approximately 20 minutes. After substrate cleaning and sol preparation, the film deposition on the aluminum substrates was achieved by a simple dip-coating process. The substrates were dipped in the sol at a constant rate of 6 mm/min, immersed in the sol for approximately 45 min,

**Table 1.** The Chemical composition of the 2024-T3 Al alloy.

| Alloy   | Al    | Cu   | Mg   | Mn   | Fe   | Zn   | Si  | Other |
|---------|-------|------|------|------|------|------|-----|-------|
| 2024-T3 | 92.79 | 4.62 | 1.55 | 0.57 | 0.18 | 0.15 | 0.1 | 0.04  |

**Table 2.** The composition of solutions used for surface preparation and holding time and temperature.

| Surface preparation | Chemical composition of solution                                                                    | Temperature °C | Time min |
|---------------------|-----------------------------------------------------------------------------------------------------|----------------|----------|
| Alkaline cleaning   | 12 g NaOH+ 100 mL H <sub>2</sub> O                                                                  | 60             | 3        |
| Chemical polishing  | 54 mL H <sub>3</sub> PO <sub>4</sub> (85%) + 2 mL HNO <sub>3</sub> (66.4%) + 13 mL H <sub>2</sub> O | 90             | 4        |
| Deoxidizing         | 35 mL HNO <sub>3</sub> (66.4%)+ 65 mL H <sub>2</sub> O                                              | 26             | 2        |

withdrawn at the same constant rate, and then air-dried for approximately 45 min. This process was conducted once only. Following deposition, the substrates were dried at 45 °C for 1 h and then at 150 °C for 3 h in an oven to ensure densification of the gel network.

## 2. 4. Characterization

The microstructure of the films were observed by using scanning electron microscopy (s-360, Cambridge). The surface chemical composition of the films were studied using Fourier transform infrared spectroscopy (Shimadzu, Japan), which gave information about the various chemical bonds. The wettability of the films were evaluated by measuring the contact angle of a water droplet placed on the film surface using the DINO camera (AM4815T Dino-Lite Edge) at ambient temperature. Electrochemical measurements were carried out in a conventional three-electrode setting. The Electrochemical glass cell consisted of an auxiliary electrode of platinum, reference electrode of Ag/AgCl and corrosion sample.

Tafel plots were obtained using Autolab software in the range of  $\pm 250$  mV polarization with respect to open circuit potential (OCP). The electrochemical parameters  $I_{corr}$ ,  $E_{corr}$  and corrosion rates were calculated by Tafel extrapolation.

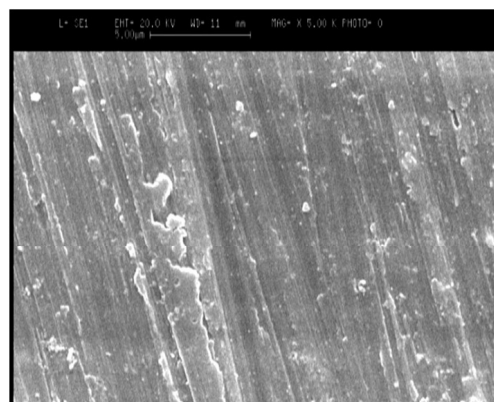
## 3. RESULTS AND DISCUSSIONS

### 3. 1. Surface Morphological Studies

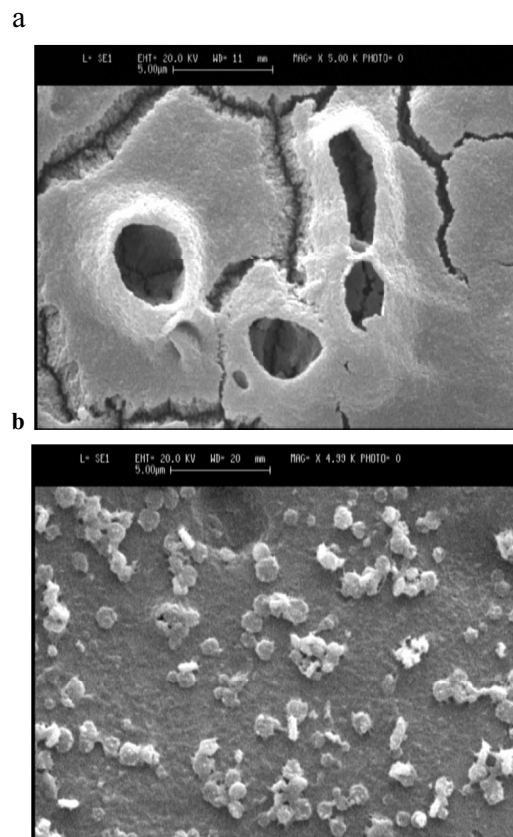
The coatings were characterized using scanning electron microscopy. Fig. 1 shows the surface morphology of the silica films prepared on aluminum surface. The sol-gel coating was rough in surface, silica particles are seen as white aggregations and clusters.

Fig. 2(a) shows an anodized sample containing porosity and microcracks. Fig. 2(b) shows the anodized specimen coated with a sol-gel film, it can be seen that porosities are sealed with the coating solution.

Thickness of anodized and sol-gel films formed on the aluminium substrates were 14.5



**Fig. 1.** The surface morphology of the silica film on aluminum.



**Fig. 2.** The surface morphology of the coatings on the aluminum substrates (a) anodized aluminum. (b) anodized aluminum with silica films.

$\mu\text{m}$  and  $44.5 \mu\text{m}$  respectively.

### 3. 2. Fourier Transform Infrared Spectroscopy

The wetting behaviour of hydrophobic surfaces is governed mainly by chemical composition of the surface. The chemical composition of the film deposited on aluminum substrate was investigated by the FT-IR spectroscopy.

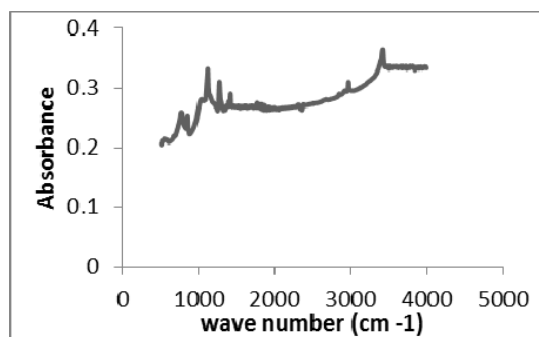
Ranges of possible absorption peaks for bonds formed in the sol gel coating have been listed in table 3[10-11].

**Table 3.** Possible absorption peaks for bonds formed in the sol gel coating.

| IR( $\text{cm}^{-1}$ )                       | Vibrational Assignment |
|----------------------------------------------|------------------------|
| 1000-1130                                    | Si-O-Si                |
| 1245-1275, 750-865                           | Si-CH <sub>3</sub>     |
| Stretching : 1300-1500<br>Bending: 2840-3000 | C-H                    |

**Table 4.** Absorption peaks for bonds formed in the sol gel coating.

| IR( $\text{cm}^{-1}$ ) | Vibrational Assignment |
|------------------------|------------------------|
| 1119                   | Si-O-Si                |
| 856, 1273              | Si-CH <sub>3</sub>     |
| 3425                   | O-H                    |
| 1420, 2971             | C-H                    |



**Fig. 3.** FT-IR spectra of the silica films.

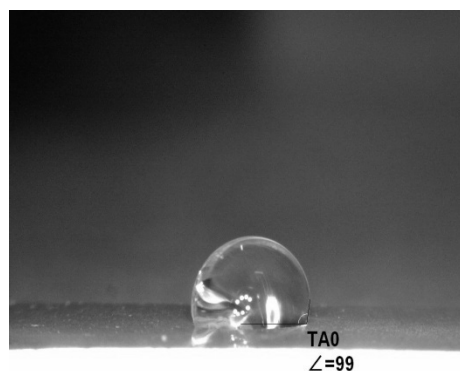
The FT-IR spectra of the silica films prepared are shown in Fig. 3. Several characteristic absorption peaks were observed in the range  $450\text{--}4000\text{cm}^{-1}$ . These peaks have been listed in Table 4 which are in accordance with peak ranges in Table 3.

### 3. 3. Water Contact Angle Measurements

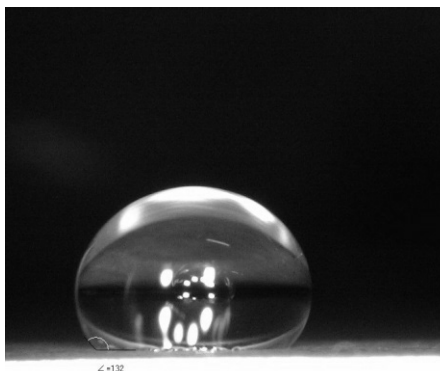
The wetting behaviour of hydrophobic surfaces is also governed by geometric microstructure. To evaluate the hydrophobic properties of the silica films, the contact angle of the water droplet on the films prepared have been measured and are seen in Fig. 4 (a).

The sol-gel coated aluminum surfaces showed the static water contact angle of  $99^\circ$ . This hydrophobic behaviour is due to methyl groups which enhanced the water repellency of the

a



b



**Fig. 4.** Contact angle of water drop on aluminum surfaces. (a) coated Al. (b) coated anodize Al.

surface. Fig. 4 (b) shows water contact angle on sol-gel coated anodized aluminum which is as high as  $132^\circ$ . Anodization of aluminum alloy forms nano-pored structure film which provides a coarse microcosmic structure of hydrophobic surface and hence enhanced hydrophobicity [12].

### 3. 4. Electrochemical Behaviour

The sol-gel coating exhibited anticorrosion properties providing an adherent protection film on the Al 2024-T3 substrate. The 'barrier properties' of the sol-gel films evaluated through potentiodynamic polarization techniques in 3.5wt% NaCl solution is shown in Fig. 5. Table 5 presents a summary of the data obtained from Fig. 5.

According to the data obtained from corrosion tests it can be seen that corrosion resistance of sol-gel coated aluminum was enhanced in comparison with the bare aluminum and sol-gel coated anodized specimens showed excellent anticorrosion resistance. The corrosion resistance of a sol-gel derived coating is considered to be attributed to its physical barrier properties, which restricts the penetration of the electrolyte towards the metallic substrate. As a result, the anticorrosion performance of aluminum and its alloys maybe improved because of a decrease in contact angle between corrosive mediums and metal surface.

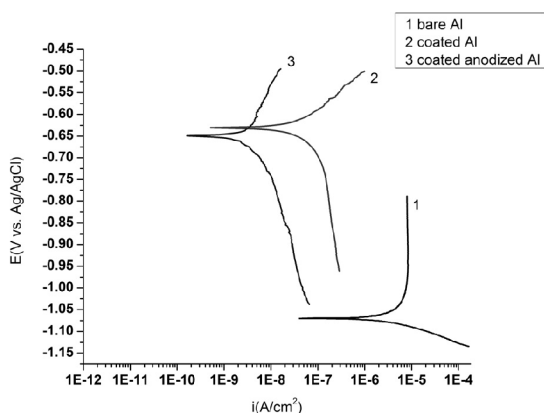


Fig. 5. Tafel plot for bare and coated aluminum. (1) bare Al. (2) coated Al. (3) coated anodize Al.

Table 5. Results of tafel tests.

| Specimen       | $I_{corr.}(\mu A/cm^2)$ | $E_{corr.}(V \text{ vs. } Ag / Ag Cl)$ | Corrosion rate (mm/year) |
|----------------|-------------------------|----------------------------------------|--------------------------|
| Bare al        | 6.62                    | -1.07                                  | $7.036 \times 10^{-2}$   |
| Coated Al      | 0.13                    | -0.631                                 | $1.342 \times 10^{-3}$   |
| Coated Anodize | 0.0062                  | -0.651                                 | $6.534 \times 10^{-5}$   |

### 4. CONCLUSION

Sol-gel coating on aluminum and anodized aluminum has been successfully developed for to be used as a surface treatment for an Al 2024-T3 alloy. Electrochemical test was conducted on bare, coated and coated anodized samples. According to data obtained from corrosion tests, it can be seen that corrosion resistance of sol-gel coated 2024-T3 aluminum alloy was enhanced and application of sol-gel coating on anodized specimens brought an excellent anticorrosion behaviour.

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