Investigation on a Sol-gel Coating Containing Inhibitors on 2024-T3 Aluminum Alloy

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Abstract

For a long time, chromate incorporated conversion coatings have been drawn special attention in corrosion protection of aircraft-used aluminum alloys. However, ever-increasing environmental pressures require that non-chromate conversion coatings be developed because of the detrimental carcinogenic effects of the chromate compounds. In recent years, the sol-gel coatings doped with inhibitors were developed to replace chromate conversion coatings, and showed real promise. A sol-gel coating was prepared and its anti-corrosion behavior was investigated using the potentiodynamic scanning (PDS) and the electrochemical impedance spectroscopy (EIS). It is found that the sol-gel coating obtained by the hydrolysis and condensation of 3-glycidoxypropyltrimethoxysilane (GPTMS) and tetramethoxysilane (TMOS) is prone to form defects if cured at the room temperature, whereas if cured at a higher temperature (100 °C), these flaws can be avoided. Furthermore, it can be seen that addition of anti-foam agents and surfactants will reduce the faults if cured at the room temperature. Effects of the corrosion inhibitors, CeCl₃ and mercaptobenzothiazole (MBT), in the sol-gel coatings on 2024-T3 aluminum alloy were also investigated. Results show that the corrosion resistance of the sol-gel coatings containing CeCl₃ proves to be better than that of the pure and MBT added sol-gel coatings by the electrochemical methods.

Keywords: corrosion protection; sol-gel coating; electrochemical impedance spectroscopy (EIS); inhibitor; potentiodynamic scan (PDS); aluminum alloy

1 Introduction

Aluminum alloys are very important materials in modern life, and are commonly used in aerospace industry or other applications. Durability and safety require that these materials have excellent corrosion resistance. However, due to the existence of alloy elements such as Cu, Mg, Zn, Si, aluminum alloys are prone to generate localized corrosion. Chromate conversion coating is currently widely used to protect aluminum alloys used in aircraft. But chromium is among the US Environmental Protection Agency’s top toxic substance, since in its hexavalent form it is a known carcinogen and is environmentally hazardous as a waste product[1]. Advances in the chemical tailorability of mixed alkoxide sol-gel coatings have led to attempts to create a long-lived, environmentally compliant, conversion coating for aluminum alloys. Coatings can be tailored to produce a functionally gradient coating that will provide covalent bonding for strong coating adhesion and act as a barrier coating to limit the transport of water to the surface of the alloy[2].

In recent years, researchers have attempted to design and prepare chromate replacement coatings that have excellent barrier property, self-healing effect and easy coating ability. It is believed that
The dip-coating application, the coupons were transferred to oven and cured at 100 °C for 5 h. Also, coupons were dried at room temperature for comparison. The final coating thickness was on the order of 1 µm.

Morphologies of the sol-gel coatings were observed using XL30 type environmental scanning electronic microscope (ESEM) from Philips, Holland. Additionally, an AFM (CSPM 3000 Model) was operated in tapping mode, performing 20 µm×20 µm scan. Electrochemical Impedance Spectroscopy and Potentiodynamic Scan measurements were preformed using Gamry pc4/750 potentiostat coupled with the Gamry corrosion measurement system. Test system consisted of a three-electrode cell, in which, a saturated calomel electrode (SCE), a platinum foil electrode and a dip-coated coupon were used as reference, counter, and working electrodes, respectively. Working area of cell was 1 cm². EIS spectra were acquired in the frequency range from 100 kHz to 10 MHz with an ac wave of 10 mV. All measurements were carried out at room temperature in a Faraday cage. Coatings were immersed in dilute Harrison’s solution (0.35 wt% (NH₄)₂SO₄ and 0.05 wt% NaCl) solution 5 min prior to the test when performing the PDS. PDS was acquired in the region from -0.5 V vs. Eoc (open circuit potential) to +1 V vs. Eoc. For EIS measurement, the coatings were immersed in dilute Harrison’s solution (0.35 wt% (NH₄)₂SO₄ and 0.05 wt% NaCl) 30 min before the data were acquired.

3 Results and Discussion

3.1 Morphological studies

The SEM and AFM were used to observe the morphologies of the different sol-gel coatings. Fig.1 shows the SEM images of the sol-gel film coated on 2024-T3 aluminum alloy diluted by different amount of distilled water or added with anti-foam agent and cured at room temperature. As reported in Ref.[13], different gel structures will be produced with different ratios of water content to hydrolysable silane. Here, the typical morphologies of the
sol-gel films with different factors of water content to hydrolysis solution are given. Fig. 1(a) shows the surface morphology of the sol-gel film with addition of one factor of diluted distilled water to hydrolysis solution. As shown in Fig. 1(a), surface imperfection represented by holes through entire coating thickness, could be observed. Moreover, it was found that sol-gel film is fragile and prone to crack. Additionally, the average thickness of the film was 12 µm- 15 µm, more than that with 1.75 factors of water content (less than 10 µm). In order to reduce the surface defects, anti-foam agent BK (product of BYK company, Germany) was added into sol-gel solution. Fig. 1(b) shows the morphology of the sol-gel film with hydrolysis solution diluted by 1.75 factor of distilled water. Although water content was increased, void defects still appear on the film due to evaporation of water during curing process. With the addition of BK, the defects were still unavoidable, but were gradually healed with the increase of BK content, as shown in Fig. 1(c) and (d). No defects up to substrate could be observed in Fig. 1(d).

Since surfactant could effectively decrease the surface tension, a fluoro-surfactant FC-M12 with concentration of 1‰ (v/v) was added into sol-gel solution, and as can be seen in Fig. 1(e) and (f), holes and defects could be avoidable. The addition of FC-M12 indicates that certain surfactant is capable of reducing interfacial tension between water phase and organosiloxane phase, and therefore reinforces the polymerization of organosiloxane. It can be conferred that the addition of proper surfactant is necessary to form integrate sol-gel film when cured at room temperature. From the above analysis, it can be concluded that anti-foam is necessary to reduce the air bubbles that are brought out when stirring and surfactant favors to reinforce the integration between water phase and organosiloxane phase, which are both beneficial to formation of integrate sol-gel film when curing at room temperature.

As described above, hybrid sol-gel film cured at ambient condition tends to produce defects, which will act as channels in corrosion process and eventually accelerate the peeling of coating film, so high temperature curing is traditionally used in the preparation of sol-gel coatings. Additionally, curing at room temperature needs much more time (8 days
Fig.1 SEM images of the sol-gel film coated on 2024-T3 aluminum alloy. (a) diluted by 1 factor of distilled water after addition of diethylentriamine; (b) diluted by 1.75 factor of distilled water; (c) diluted by 1.75 factor of distilled water and addition of 0.4 g BK; (d) diluted by 1.75 factor of distilled water and addition of 1.2 g BK; (e) diluted by 1.75 factor of distilled water and addition of 1.2 g FC-M12; (f) magnification of (e).

-10 days) than curing at high temperature (several hours). Therefore, comparison is made between pure sol-gel coating and coatings with addition of corrosion inhibitors curing at 100 ℃. Fig.2 shows the plane view and cross-section view of the sol-gel film with addition of mercaptobenzothiazole (MBT), diluted by 1.75 factors of distilled water and cured at 100 ℃ for 5 h. As shown in Fig.2(a), the surface morphology is absent of any defects; however, it can be observed that the surface of the film is waved, basically consistent with the direction of polishing trace of substrate of aluminum alloy. Moreover, the unevenness of film thickness from 5 µm to 20 µm is presented, in agreement with the AFM morphology shown in Fig.3(c). For the hybrid coatings doped with different organic corrosion inhibitors, the above wave and unevenness also could be found (not shown for others). In contrasting to organic inhibitors, when CeCl₃, as an inorganic inhibitor, was added into hydrolysis solution, although no defect was found in the ultimate film, the inhomogeneity was more serious, as shown in Fig.3(b). The occurrence of such unevenness was undesirable; as the thin place may serve as the initial point for corrosion, thus the electrolyte can quickly arrive to substrate and the inhibition effect of the inhibitors was partly counteract. Further work is required to explain the reason of the unevenness and to prepare the smooth film with inhibitors.

3.2 Electrochemical characterization

(1) Potentiodynamic screening

Fig.4 shows the polarization curves of bare 2024-T3 aluminum alloy, pure coating, CeCl₃ doped coating and MBT doped coating. Polarization curve for bare 2024-T3 aluminum alloy shows the lowest corrosive potential (−0.38 V) without any signs of passivity in the potential range. In the case of coated substrates, the corrosive potential (−0.26 V) is nobler. The potential breakdown, 𝐸ᵥ, defined as the potential at which passivity breaks and current den-
sity increases in a monotonic way with potential, reaches $-0.17$ V and $-0.2$ V for doped coating and pure coating, respectively. In addition, for coating doped with CeCl₃, it can be seen that anodic current density is smaller than the other two coatings. The above results evidence that doped coatings improve the corrosion resistance of 2024-T3 aluminum alloy, and coating doped CeCl₃ is the best in terms of coating resistance.

![Fig.4 Polarization curve of the sol-gel film coated on 2024-T3 aluminum alloy.](image)

(2) Electrochemical impedance spectra

The impedance spectra can be used to illustrate the corrosion process in the immersion tests. Fig.5 presents the evolution of the impedance spectra of the sol-gel coatings, i.e., pure coating, coatings doped with CeCl₃ and MBT, respectively, after different times of immersion in the Harrison solution. In the beginning of immersion, the three coatings distinguished in impedance values at low frequency. Pure sol-gel coating shows the highest impedance value, which is approximately $1 \times 10^6 \Omega \cdot \text{cm}^2$. In the case of coating doped with $1 \times 10^{-3}$ mol/L CeCl₃, the value is about $5 \times 10^5 \Omega \cdot \text{cm}^2$; while the value is $1 \times 10^5 \Omega \cdot \text{cm}^2$ for coating doped with $1 \times 10^{-3}$ mol/L MBT. The difference of the above impedance values can be ascribed to the unevenness of the coatings, corresponding to those shown in Fig.3. With the increase of time, the impedance value of pure coating decreases sharply. As shown in Fig.5(a), after 48 h of immersion, the value is approximately $1 \times 10^4 \Omega \cdot \text{cm}^2$, and at this time the substrate begins to expose to Harrison solution and localized corrosion can be observed. After that, the impedance value continues to decrease with time. Coating doped with MBT shows lower impedance values than those of pure coating and coating doped with CeCl₃ in the beginning of immersion because of the unevenness, however, due to the inhibition effect of MBT, the impedance value is still higher than that of pure coating in the last stage of immersion, which is shown in Fig.5(c). Compared with pure coating, CeCl₃ doped coating presents the excellent corrosion resistance, which is expressed by the slowest decrease of impedance value, as shown in Fig.5(b). After immersing for 96 h, the impedance value is approximately $1 \times 10^3 \Omega \cdot \text{cm}^2$, 1 order of magnitude more than that of pure coating and 5 times more than that of coating doped with MBT, indicating that cerium ion has formed into cerium oxide/hydroxide on the surface of aluminum alloy, which has inhibition effect, thus slow the corrosion progress.

![Fig.5 Electrochemical impedance spectra.](image)
4 Conclusions

The morphologies of the sol-gel coatings by hydrolysis and condensation of GPTMS and TMOS were investigated by SEM and AFM. The results show that sol-gel film is fragile and prone to crack with addition of one factor of diluted distilled water to hydrolysis solution. Moreover, the sol-gel film is thicker than that with 1.75 factor of water content. When curing at room temperature, the sol-gel film tends to produce defects. Addition of proper anti-foam agent and surfactant could be beneficial to the formation of integrate sol-gel film when curing at room temperature. Curing at high temperature (100 °C) is able to form continuous and integrate sol-gel film. Doped inhibitors could make the film inhomogeneous.

EIS results show that the addition of CeCl₃ and MBT (mercaptobenzothiazole) into hydrolysis solution could reinforce the anticorrosion protection of the sol-gel film in the corrosion process. CeCl₃ doped coating presents better corrosion resistance than that of pure coating and MBT doped coating.

References


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