



Comparative Study of Corrosion Protection of Sol–Gel Coatings with Different Organic Functionality on Al-2024 substrate



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ABSTRACT

In this paper we have studied the effect of addition of amino silane and sulfur silane by 2 wt% into a reference coating solution by using two basic silane coupling agents methyl-tri-ethoxy silane (MTEO) and glycidoxy-propyl-tri-ethoxy silane (GPTS) in 1:1 molar ratio by sol–gel technique. The change in hydrophobicity due to the addition of amino group and thiol group was investigated by contact angle study and sol–gel kinetics was studied by Fourier transform infrared spectroscopy. The thermal resistance and surface morphology was analyzed by thermo gravimetric method and scanning electron microscope. The anti corrosion property of all three coatings were evaluated by potentiodynamic polarization study, AC impedance and salt spray method. X-ray photoelectron spectroscopic method was used to monitor the bonding mechanism of coating matrix with the metal surface. All type of investigations revealed that, addition of thiol group containing silane coating to the reference coating solution has caused remarkable improvement in hydrophobicity and corrosion resistance properties where as amine group rendered the surface less hydrophobic and showed no sign of improvement in corrosion protection. The most probable reason behind this improved performance is due to the additional hydrophobicity imparted by much less polar thiol group. But amino silane provided comparatively poor performance due to the presence of polar amine group.

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1. Introduction

Aluminum 2024 alloy is vastly used in transportation industry due to its high strength and low density. But high susceptibility toward localized corrosion requires necessary pretreatment to improve corrosion resistance [1]. Recently the corrosion experts have adopted various efficient technologies to prevent the corrosion resistance of aluminum. Traditionally, chromate conversion coating offers good corrosion protection. However, due to the presence of carcinogenic Cr (VI) salts, the usage of environment friendly alternative methods have drawn tremendous attention of researchers in last few years worldwide [2]. Magnesium powder is being employed in organic coating (also termed as sacrificial anode) as sacrificial anode pigment to protect aerospace grade aluminum alloy from corrosive environment [3]. Battocchi et al. [3,4] investigated electrochemical behavior of Mg rich primer on different aluminum alloys by using electrochemical impedance,

open circuit potential and potentiodynamic polarization study. It was found that, Mg rich primers provided excellent sacrificial protection to aluminum substrate. Another widely accepted method to resist aluminum corrosion is usage of polyvinyl butyral resins formed by the well-known reaction between polyvinyl alcohols and aldehydes. They have combined properties of outstanding binding efficiency, adhesion to large number of surfaces and toughness along with flexibility [5]. Vanadate conversion coating (VCC) is a new type of inorganic conversion coating, which inhibits the aluminum corrosion by soluble vanadate. In neutral solution the vanadate increases the pitting potential and thereby reducing the oxygen reduction reaction rate AA2024-T3 [6]. Another revolutionary, environment friendly and widely accepted new base coating system for protecting aluminum based alloy is Alodine EC² Electro ceramic coating formed through electro-deposition of titanium oxide. Along with toughness and flexibility this coating provides long-term chemical resistance over aluminum and aluminized surface [7]. Organic–inorganic hybrid thin coating materials have also been proven to have excellent corrosion protection performance on Al-2024 alloy. This organic–inorganic hybrid material is commonly prepared by sol–gel method. Sol–gel method has received

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considerable attention for research because of following reasons; (a) one can fine tune the sol formulation to achieve corrosion resistance; abrasion and scratch resistance and thermal resistance and (b) it is possible to control the gel formation to obtain nano-particle of desired shapes. Since large scale coating solutions can be made easily by using sol–gel method, therefore large numbers of formulation have been found in available literatures with different sol–gel precursors. Generally, the precursors having hydrolyzable alkoxide groups participate in the controlled hydrolysis and condensation reactions to form stable sols for the thin coating applications. On the other hand, sols got over hydrolyzed to form gels and powder nano-materials. The sol formulation is entirely dependent upon the hydrolysis and the condensation reactions [8–15]. These reactions are catalyzed either by an acid or a base [16–21]. The organic components impart considerable hydrophobicity, flexibility, and functional compatibility with organic systems; the inorganic components provide an increase of scratch resistance, adhesion and durability to the metal substrate due to the formation of covalent metal–O–metal bonds [22–24]. Most of the silanes possess a hydrolysable reactive center, which reacts with a wide range of metal oxide/hydroxide to promote adhesion and a non-hydrolyzable organic substitution that alters surface chemistry. Depending upon the polarity of the organic substitution a metal surface becomes hydrophobic or hydrophilic.

In this present work the reference coating solution has been prepared from glycidoxy-propyl-triethoxy silane (GPTS) and methyl-tri-ethoxy silane (MTEO) in 1:1 molar ratio. The other two coating solutions have been prepared by adding 3-phenyl-aminopropyl-triethoxysilane (PAPTS) and mercapto-propyl-tri-methoxysilane (MPTMS) by 2 wt% separately to the reference coating solution to evaluate the effect of nitrogen and sulfur groups. Electrochemical analysis, such as potentiodynamic polarization, EIS and salt spray tests were carried out to monitor the effect of nitrogen and sulfur group based formulations on corrosion behavior of coating system under corrosive electrolytic medium. The hydrophobicity and surface morphology of the coated samples were studied by contact angle measurement and scanning electron microscope.

2. Experimental

2.1. Preparation of sol–gel solution

The reference coating solution (Coating I) was synthesized by drop wise addition of GPTS and MTEO (purchased from Sigma Aldrich and were used without further modification) in 1:1 molar ratio into ethanol. The (v/v) ratio of ethanol to silane is maintained 45:10 where silica content was kept about 10 wt% in total coating solution. Complete hydrolysis was ensured via acid catalyzed reaction by adding half milliliter of acetic acid. Distilled water was added drop wise under vigorously stirring condition at room temperature for 3 h to secure thorough hydrolysis and condensation of the silica network. Then the coating solution was left for aging more than 24 h at room temperature. The final coating solution was obtained where volume ratio of ethanol to silane to water was 45:10:45. The second coating solution (Coating II) was prepared by adding 2 ml of PAPTS (obtained from Dow Corning and used without any modification) into the reference coating solution (Coating solution I) followed by addition of 5 drops of acetyl acetone (acac) as chelating agent. Addition of a chelating agent or a stabilizer molecule is necessary to prevent unnecessary gelation due to high reactivity of secondary amino group toward hydrolysis [25,26]. After the addition of PAPTS and acac, distilled water was slowly added to the solution for carrying out the hydrolysis step in presence of 1 ml acetic acid as catalyst. The final solution was stirred vigorously for

2 h at room temperature. The final volume of the coating solution was 100 ml and the volume ratio of ethanol to silane to distilled water was almost 45:10:45. The third coating solution (Coating III) was synthesized following the same procedure as that of coating II. MPTMS (purchased from Sigma Aldrich and was used without any modification) was used instead of PAPTS. The stability of all three coating solutions were checked for 30 days and it was found that all coatings were in sol state and there was no gelation observed in the coating matrices for 30 days.

2.2. Sample preparation, coating application and heat treatment

Aluminum sheets of dimension 10 cm × 10 cm were cut for the investigation. These samples were cleaned with 8% (w/v) aqueous sodium silicate alkali solution and dried prior to coating application. The cleanliness of the surface was checked by water breaking test ensuring that there was no oil/grease left over. Coating solutions were applied on the surface with Apex Spin NXG-P1 spin coater with different speeds for 2 min to obtain smooth and uniform film. The coated samples were subjected to curing in a hot air oven at a temperature of hundred and fifty degree (150 °C) for 5 min to impart extra stability and hardness into cured film by extensive crosslinking in the silica network [27]. The controlled coating technique was giving rise to a final dry film thickness of 1–3 μm measured with Positest DFT-Combo Model Ferrous & non-ferrous, Defelsko, USA.

2.3. Coating characterization

Spectra of sol–gel coatings were recorded from Fourier Transform Infrared Spectrophotometer (Nicolet 5700, Thermo Electron Corporation) in the range of 400–4000 cm⁻¹.

X-ray photoelectron spectroscopy (XPS) study of coated and uncoated surface was carried out Kratos analytical photoelectron spectrometer model Axis 165 with monochromated Al K α X-ray source operated at 100 W. Deconvolution spectra of C 1s, O 1s, N 1s, Si 2p, S 2p and Al 2p were obtained with analyzer pass energy of 80 eV. Based on the value of 285.0 eV for C–C component in C 1s value, the binding energies of each deconvolution spectra are corrected.

Scanning electron microscope (SEM) using Hitachi S-3400 Model investigated the surface morphology of the coated samples. Before analysis gold was sputtered to suppress the charging.

The thermal stability of the coatings was studied by thermogravimetric analysis (TG) and differential scanning calorimetry (DSC). Approximately 5 mg of 7 days cured film was taken for the experiment. The heating rate was maintained at 10 °C/min and the temperature range was 30–500 °C in a nitrogen atmosphere.

The contact angle measurement was done by advanced sessile drop method. A contact angle system OCAH230 (Dataphysics Instrument, Germany) was used to determine the static contact angle with distilled water as testing liquid.

The corrosion analysis of bare and coated samples was performed with Potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) technique. The data were obtained using an Autolab instrument constituting frequency analyzer, potentiostat and Nova software (1.10.1.9). All the electrochemical tests were performed in 3.5 wt% NaCl solution. Each sample was sealed with waterproof tape to prevent premature corrosion along the edges of the panels [28]. A typical three electrode system was employed in this test set up where the sol–gel coated samples as working electrode (1 cm² exposed area), saturated calomel electrode was used as reference electrode and platinum electrode as counter electrode. All the EIS experiments were carried out in the frequency range of 0.1–10⁵ Hz and 0.5 mV of applied voltage. For the potentiodynamic scans an initial free

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