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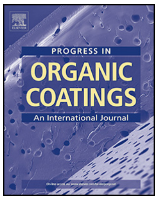

Improving the corrosion performance of hybrid sol–gel matrix by modification with phosphonic acid

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ABSTRACT

Sol–gel films were prepared using different ratios of two silica precursors, vinyltrimethoxysilane (VTMS) and tetraethylorthosilicate (TEOS), targeting the anticorrosion treatment of aluminum alloy 2024-T3. The electrochemical behavior of the alloy coated with such films, which was studied in a 0.05 mol L^{-1} NaCl solution, revealed that the VTMS/TEOS ratio drastically affects the anticorrosion performance. Electrochemical impedance spectroscopy (EIS) results provided evidences that the best anticorrosive response occurs with the films prepared from 50% (v/v) ethanol, 46% (v/v) water, 3% (v/v) VTMS and 1% (v/v) TEOS. Moreover, the effects of the addition of ethylenediamine tetra(methylene phosphonic acid) (EDTPO) to a hybrid sol–gel matrix were examined. The corrosion resistance was considerably improved when the concentration of added phosphonic acid was 3.75×10^{-5} mol L^{-1}. Scanning electron microscopy, energy dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy analyses revealed that EDTPO-containing films provide a more uniform coverage. Results evidenced the formation of Si—O—Al linkages in the VTMS/TEOS and VTMS/TEOS/EDTPO systems and that the VTMS/TEOS/EDTPO system contained P—O—Al linkages. The P—O—Al bonds, combined with the modified silica network action, may be responsible for the good anticorrosive behavior of the VTMS/TEOS/EDTPO films.

1. Introduction

Environmental restrictions have led to the accelerated development of new environmentally friendly coating technologies at both the academic and industrial levels. In this context, sol–gel coatings have been investigated as potential replacements for chromate-based surface treatments for several metals [1–5]. Different alkoxysilane derivatives have been used to protect metals from corrosion by forming a thin coating that acts as a physical barrier to delay the access of aggressive species to the substrate. The molecular structure, degree of organization and properties of the resulting sol–gel materials depend on the chemical nature of their components [6]. Thus, the choice of alkoxysilane, which is usually denoted as silane, is a critical task.

Previous studies have shown that silanes bearing vinyl groups improve the corrosion resistance of aluminum and its alloys [7–12], iron [13], galvanized steel [14], and cooper [11]. According to Bajat et al. [10], the performance of vinyltriethoxysilane (VTES) films on 99.5% Al was satisfactory, even in presence of a high concentration of chloride ions (3% NaCl). Such performance was shown to depend on both the concentration of the silane solution and the curing time. The longest curing time (30 min) and greatest VTES concentration (5% v/v) improved the corrosion protection, which was attributed to an enhancement of the silane crosslinking and to the formation of a more hydrophobic and thicker film [10].

Previous studies on the performance of silane films formed from mixtures of TEOS and silanes bearing vinyl groups are very scarce. Among the few published studies, Hu et al. [15] evaluated two precursor systems of silica (*i.e.* TEOS and TEOS/VTES) onto magnesium alloy AZ91D. Scanning electronic microscopy (SEM) images of TEOS films revealed the presence of some white particles and cracked areas produced by agglomeration of SiO_2 during the heating process (350 °C for 2 h), which reduced the corrosion protection. In contrast, TEOS/VTES coatings subjected to the same heating process showed a more compact structure and good barrier properties for the protection of the magnesium alloy.

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Another key point for the design of more environmentally friendly and efficient treatments is the use of starting solutions with relatively low alcohol concentrations. Sol–gel chemistry is well known to consist primarily of hydrolysis and condensation reactions of alkoxysilane precursors. The ratio between the water content and the hydrolysable silane content determines the condensation and growth mechanism of the sol–gel matrix [6].

On the other hand, phosphonic acids are an important class of self-assembled molecules with high ability to react with a range of metal oxide surfaces [16], which has been proposed as a new method for corrosion protection [17–19]. The formation of phosphonate layer was shown to be a spontaneous process that could be accomplished by simple immersion of the metal into the phosphonic acid solution [17]. Thus, metalo-phosphonate bonds (Me—O—P) are formed through a condensation reaction [16]. This seemingly simple process depends on the metal substrate [20], the chemical nature of the phosphonic acid [18,19], and the pH of the solution [21], thereby requiring a careful assessment.

Previous studies were devoted to investigate the addition of phosphonic acid onto TEOS, evidencing a remarkable improvement of the corrosion performance for the AA2024 alloy coated with films of such combined system [22,23]. However, the silica network produced by TEOS exhibited hydrophilic characteristics, which resulted in poor corrosion protection [22]. The main aim of the present study, which represents a significant extension of those previous works, is to evaluate the improvement of the anticorrosive performance of coatings with vinyltrimethoxysilane (VTMS). More specifically, in this work we study the influence of both (i) the VTMS/TEOS ratio and (ii) the concentration of ethylenediamine tetra(methylene phosphonic acid) (EDTPO) added to the VTMS/TEOS sol–gel matrix on the corrosion protection of the AA2024 alloy. For this purpose, the anticorrosion properties of the coated samples were investigated using electrochemical impedance spectroscopy (EIS) measurements after different immersion times in a 0.05 mol L^{-1} NaCl solution. The chemical structures of the films were determined by FTIR spectroscopy, whereas the morphologies and compositions of films were examined by SEM, energy dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Pretreatment

AA2024-T3 samples were prepared by grinding with silicon carbide papers up to 1200 grit, being subsequently immersed in a 0.05 mol L^{-1} acetic acid solution for 5 min. After this, the samples were washed with distilled water and dried under a hot air stream. We verified that this pretreatment decreased the Cu amount of the metallic surface resulting in the reduction of galvanic corrosion and the increment on metalosiloxane and metal–phosphonic bonds, as reported in a study previously conducted in our group [22].

2.2. Coating deposition

For the preparation of the starting solutions, TEOS (Merck, 98%), VTMS (Aldrich, 97%), ethanol (Nuclear, 99.5%) and deionized water (18.3 MΩ cm) were mixed in the proportions (v/v) described in Table 1, which also shows the abbreviations used for their identification. Starting solutions containing phosphonic acid were prepared by dissolving EDTPO in deionized water, their compositions being displayed in Table 1.

Table 1
Composition (v/v) of the different starting solutions. The labels used to identify these systems are also displayed.

Ethanol	Water	VTMS	TEOS	EDTPO concentration (mol L^{-1})	Label
50	46	4	–		4V
50	46	3	1		3V
50	46	2	2		2V
50	46	1	3		1V
50	46	3	1	3.75×10^{-5}	3VE5
50	46	3	1	3.75×10^{-4}	3VE4

Starting solutions were stirred for 1 h at room temperature and were then stored for 3 days prior to their use. Immediately after their pretreatment, AA2024-T3 samples were immersed in solution for 30 min, the withdrawal rate being of 20 cm min^{-1}, and cured in an oven at 110 °C for 1 h. The thickness of the films, which was measured by profilometry Dektack Veeco 150, was *ca.* 145 nm for 1V samples and for other films this value is between 190 and 200 nm.

2.3. Measurements

2.3.1. Electrochemical impedance spectroscopy

Electrochemical measurements were performed using an AUTOLAB PGSTAT 30/FRA 2 system. A three-electrode electrochemical cell arrangement was used and consisted of an AA2024-T3 panel with 1 cm^2 of exposed area (working electrode), a saturated calomel electrode (SCE) (reference electrode), to which all of the potentials are referred, and a Pt mesh (counter electrode). EIS measurements were performed in the potentiostatic mode at the open-circuit potential (OCP). The amplitude of the EIS perturbation signal was10 mV, and the studied frequency range was 10^5–10^{-2} Hz. Experiments were performed at 25 °C, and a 0.05 mol L^{-1} NaCl solution was employed. At least three samples were evaluated for each condition.

2.3.2. FTIR spectroscopy

Fourier-transform reflection–absorption infrared (FTIR-RA) spectra of films deposited onto AA2024 were obtained using a Nicolet 6700 FT-IR spectrometer equipped with a Smart SAGA (Specular Aperture Grazing Angle) accessory and Omnic software. Spectra were collected with an incidence angle of 80° from the normal surface at a resolution of 4 cm^{-1} (total of 512 scans), using a polished bare aluminum alloy as background.

2.3.3. Scanning electron microscopy

SEM studies were carried out using a focused-ion-beam Zeiss Neon 40 scanning electron microscope equipped with an energy-dispersive X-ray (EDX) spectroscopy system and operating at 5 kV. Samples were mounted on a double-sided adhesive carbon disk and sputter-coated with a thin layer of carbon to prevent sample charging problems.

2.3.4. X-Ray photoelectron spectroscopy

XPS analyses were performed in a SPECS system equipped with a high intensity twin anode X-ray source XR50 of Mg/Al (1253 eV/1487 eV) operating at 150 W, placed perpendicular to the analyzer axis, and using a Phoibos 150 MCD-9 XP detector. The X-ray spot size was 650 μm. Samples were fixed mechanically into a special sample holder using a double side tape. The spectra were recorded with a pass energy of 25 eV in 0.1 eV steps at a pressure below 6×10^{-9} mbar. The C 1s peak was used as an internal reference with a binding energy of 284.8 eV. The atomic percentage of each element was determined by dividing the peak area of the most intense XPS signal of each element by the corresponding sensitivity factor and expressing it as a fraction of the sum of all normalized peak areas. High resolution XPS spectra were acquired by Gaussian/Lorentzian curve fitting after S-shape background subtraction.