



Adhesion aspects of hydrophobic silane zeolite coatings for corrosion protection of aluminium substrate



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ABSTRACT

The adhesive properties of an anti-corrosion silane–zeolite coatings on aluminium substrates have been evaluated in this work. The coated samples were obtained by dip-coating sol–gel solution. Four different composite coatings at increasing zeolite amount (60–90 wt% of zeolite) have been investigated.

The composite coatings evidenced a high hydrophobic behaviour (contact angle between 125° and 140°) and good adhesive properties with the aluminium substrate. The best results were obtained at low concentrations of zeolite. A structural model of the composite coating able to interpret phenomenologically the performances of this new protective coating has been proposed.

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1. Introduction

One of the most widely adopted procedures, used to protect metals from corrosion phenomena, consist in coating metal surface with protective layers. In addition to an anti-corrosion action, the market requires the development of multifunctional products, able to offer good performances in several environmental conditions. Additional prerequisites were also imposed, such as gloss, good adhesion with the substrate, durability, high hydrophobicity etc.; traditional materials may fail in their performances.

Consequently, several research activities have been initiated to develop hybrid coatings, that combine in a single one, in synergistic way, different materials with complementary properties to produce a new class of materials with more effective performances [1,2] and suitable to meet the main imposed requirements [1–3].

Adhesive and hydrophobic properties of the protective film are two important prerequisites in order to obtain an effective anti-corrosion coating [3–5], however these two features are not always compatible. In a composite coating, in order to enhance its adhesive properties, it is preferable that constituents would have good chemical affinity each other and with the metal substrate.

To improve coating adhesion, the compounds used as coating materials are usually polar. The goal is to create hydrogen bonds or chemical bonds with the metal substrate. Unfortunately, however, the presence of these polar groups results in a concomitant increase in the absorption of water by the coating [6,7].

The phenomenon of water absorption reduces the protective action and coating durability. Swelling phenomena [8,9], voids or cracks in the matrix of the coating [10] could occur, when the coating is wetted by an aggressive electrolyte solution, so affecting its functionality.

Therefore, to improve corrosion protection by polymeric coatings, water sorption of the coating materials must be reduced and water diffusion to the coating–metal interface must be slowed down [11].

In this contest, the developments of hydrophobic, homogeneous, adherent coating materials become important, particularly in corrosion protection technology.

A hydrophobic coating can reduce the contact between water and metal surface slowing down the corrosion process, so it can be considered a promising technology for improving the anti-corrosion performance.

In this work the addition in a silane matrix of a particle component, such as zeolite SAPO-34 crystals, was proposed. The silane matrix operate as coupling agent and offer mainly a protective barrier action having no active electrochemical behaviour [12].

SAPO zeolites, being crystalline structures based on phosphor–silica–alumina framework show some chemical reactivity due to the formation of surface silanol groups. On the basis of this

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reactivity, various agents, as well as silanes, can react by means of a superficial interaction [13].

The addition of a zeolite filler to silane coatings is proposed to promote the electrochemical interaction between the coating and the electrolyte solution in order to enhance its active protective action [14]. The high chemical affinity of the filler with the silane matrix is able to optimize the performance of the composite films. Furthermore, the functionalization with silane molecules of the zeolite surface enhances its hydrophobicity [15,16].

In the present work, composite coatings, made of zeolite particles filler in a silane matrix, on aluminium 6061 was produced. The coatings were characterized by a bilayer structure, with an external silane–zeolite composite film, prepared by using different concentrations of zeolite micro-particles (in the range 60–90% by wt of silane amount), while the interface layer with the aluminium substrate was made without zeolite particles.

Wettability and adhesion performances were evaluated. In particular, contact angle measurements were carried out on the coating surface in order to evaluate the homogeneous deposition of the composite coating and to extrapolate the hydrophobic properties of the coating. In order to better understand the chemical interaction between the substrate and the silane–zeolite composite coating we performed several adhesion tests characterized by different interfacial stress conditions: qualitative (peel test) and quantitative (single lap shear test and pull-off).

The results showed that the hydrophobic properties of this hybrid coating are due to the synergistic action of a physical and a chemical barrier. Furthermore, the chemical interaction among metal, silane and zeolite interfaces influenced positively the adhesion performances of these coatings.

2. Experimental methods and materials

2.1. Sample preparation

N-propyl-trimethoxy-silane (supplied by Aldrich, purum >97%) was used in this work as filming agent. Hydrolysis was performed in the presence of distilled water and ethanol (ethanol/water/silane 90/5/5% v/v). The pH was adjusted to 4 with the addition of acetic acid to control the self condensation tendency. The solution was then magnetically stirred, at 25 °C, for 24 h.

High silica zeolite SAPO-34 powder, synthesized in laboratory as described in [17] (mean crystals size about 3 μm) was added to the silane solution. Different amounts of zeolite (60–90 wt% of silane amount) were added into the silane/ethanol mixture. The new solution was dispersed at first in an ultrasonic bath for 15 min and then magnetically stirred for 15 min before the dip coating procedure.

Strips of commercial aluminium 6061, with size 20 mm × 40 mm × 2 mm, were cut from bars. The sample surface was mechanically polished with emery paper up to grade 500, then degreased in a diluted alkaline solution (0.1 N NaOH) for 60 s, washed in distilled water and finally with acetone. Although the linking of the silane molecules onto the metal surface is fast, due to the rapid formation of hydrogen bonds between SiOH and metal hydroxyls groups at the metal surface [18], short immersion time could induce inhomogeneity on the coating coverage [19]. Therefore, a by-layer procedure was used [20] to develop the composite coating. After the first immersion in the silane solution for 1 min the sample was cured at 80 °C for 30 min. On curing, at 80 °C for 30 min, the cross-linking reaction occurs forming aluminium–siloxane bonds (Me–O–Si) at the interface, increasing adherence of the silanes to the metallic substrates. Then, a second immersion was performed in the silane/zeolite solution for 1 min and followed by the final curing procedure for 2 h at 80 °C. The thickness of the samples ranged between 10 and 30 μm. A summary of the samples tested in this work is reported in Table 1.

Table 1
Sample summary.

Sample code	Zeolite/silane (wt%)	Coating thickness (μm)
ZEO60	60	7
ZEO70	70	8
ZEO80	80	10
ZEO90	90	15

Coating morphology and surface coverage grade were evaluated by optical and scanning electron microscope (JEOL 5600LV operated at 20 kV) and by focused ion beam scanning electron microscopy (FEI Helios NanoLab 600 Dualbeam).

2.2. Contact angle measurements

Contact angle measurements were performed by depositing 1 μl of distilled water on the coated surfaces at room temperature (20 °C). The drop was observed by a micro CCD camera and a suitable PC images analysis script written in Matlab 2012.

2.3. Adhesion test

Qualitative and quantitative adhesion tests were performed on the zeolite modified silane coating. The purpose was to have more specific information about the interfacial interaction between the aluminium substrate and the bilayer composite coating. To have a statistical significant distribution of data an average of 5 replicates for each batch were performed.

2.3.1. Peel test

Tape peel tests (according to ASTM D3359) were carried out to assess the coating adhesion to the substrate. A square grid was realized with 20 mm long cuts at a distance of 2 mm each others. A tape was placed over the grid and rubbed with the eraser end of a pencil to ensure good contact.

The tape was removed and then the samples were evaluated using a polarized light microscope. The removed grid area was rated according the ASTM specifications, from 0B (low adhesion) to 5B (high adhesion) to evaluate qualitatively the detachment of the coating from the substrate.

2.3.2. Pull-off test

The tensile adhesion strength of the composite coatings on Al6061 substrate was measured by a Lloyd Universal Testing Machine, mod. LR10, equipped with a 500 N load cell. A clamping set-up was designed to avoid the misalignment during the uniaxial tensile test. A zinc rod (5 mm diameter) was glued onto the coating surface using a cyanoacrylate adhesive and cured at room temperature for 24 h. The rod was pulled at a cross-head speed of 1 mm/min until coating failure. Occasionally small cavities were seen on the adhesive surface after pull-off, these cavities could have altered the stress distribution and effective area of contact [21] and consequently were excluded. The pull-off adhesion strength was calculated using:

$$\sigma_{PO} = \frac{4F_{max}}{\pi d^2} \quad (1)$$

where σ_{PO} is the pull-off adhesion strength, F_{max} is the force at rupture, and d is the rod diameter.

2.3.3. Single lap shear test

To determine the adhesive shear strength of the coatings a tensile single-lap-joint test was performed (according to ASTM D1002) using the same UTM reported in Section 2.3.2. The shear stress is evaluated by the formula: $\tau = P/A$, where P is the tensile load and A is the joint overlap area. The cross-head speed was 1 mm/min.

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