

In-situ characterisation of organosilane film formation on aluminium alloys by electrochemical quartz crystal microbalance and in-situ ellipsometry

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Abstract

Organosilane pre-treatments have been studied intensively during the last years in order to replace hexavalent chromium conversion treatments. The aim of this study is to follow in-situ the formation of this organosilane layer in solution. Two in-situ techniques, spectroscopic ellipsometry and electrochemical quartz crystal microbalance, were used to investigate the mechanism and the kinetics of this protective film formation. In-situ measurements highlight that the organosilane film observed after the drying process is not formed into the solution, but during the emersion and drying step.

Hence, it has been possible to characterise the presence of a very thin organosilane layer in the order of a few monolayers using the in-situ techniques. This layer is responsible for the adhesion and growth of the overall organosilane layer observed ex-situ after drying.

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1. Introduction

Organosilane molecules have been used for a long time as adhesion promoters between metal surfaces and organic resins. More recently, interest grew concerning the use of these molecules for corrosion protection [1–3]. In this context, corrosion protection of organosilane has been compared with chromium conversion treatment, which contains toxic and cancerogenic hexavalent chromium [4].

Corrosion resistance by thin organosilane layers is generally attributed to the capability to form a denser and crosslinked film, increasing the barrier properties as protection against aggressive species. It has been shown that organosilane film formed with bis-1,2-(triethoxysilyl)-

ethane (BTSE) presented a significant increase in barrier properties [5]. In addition, BTSE is very stable with regard to temperature and, thus, a curing step can be performed at temperature around 200 °C. This permits a higher cross-linking of the film and induces an increase of the barrier properties of the organosilane film [5].

Generally, organosilane layers are formed by dipping the substrate into the organosilane solution; subsequently, the specimen is emersed and dried in air. The experimental parameters for the deposition of BTSE organosilanes have been widely studied [6], as well as the resulting thickness [6–10], structure [8], chemical composition [11] and corrosion protection [1,12]. The film drying process after emersion (e.g., left to air, air blow drying, spin-coating, etc.) has a large influence on the thickness of the layer [6,7]. It was shown that an air blow-drying with compressed air could improve the reproducibility and the homogeneity of the organosilane layers [7]. C. Zhang has shown that, for a 1

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vol.% of γ -APS and a 1 vol.% BTSE, there is no influence of the dipping time (between 5 s and 30 min) on the thickness and coverage of the organosilane layer [6]. It is believed that organofunctional silanes bond to the aluminium surface via the formation of oxane bonds (Al–O–Si) induced by the condensation reaction of silanol groups with hydroxyl groups on the aluminium surface [13]. These bonds were observed by secondary ion mass spectroscopy [14]. However, less is known about the mechanism and the kinetics of organosilane films formation in the solution. As there is a lack of investigation performed in-situ during the film formation, this work is devoted to the study of the organosilane film formation by electrochemical quartz crystal microbalance (EQCM) and in-situ ellipsometry techniques. It is completed by ex-situ X-ray photoelectron spectroscopy (XPS) to observe the initial film formation.

2. Experimental details

2.1. Materials

Two type of aluminium substrates have been used in this study. For spectroscopic ellipsometry measurement, electro-polished aluminium 1050 from Hydro Bonn (max. 0.4% Fe, 0.25% Si, 0.05% Cu, 0.05% Mn, 0.05% Mg, 0.07% Zn, 0.05% Ti) was used. For EQCM, 5 MHz AT-cut quartz plates coated with a 100 nm thick gold electrode (MAXTEK PM 500) were used. The aluminium alloys were deposited by physical vapour deposition using a 5182 aluminium alloy target (max. 5% Mg, 0.35% Fe, 0.25% Zn, 0.2% Si, 0.2% Mn, 0.15% Cu, 0.1% Cr, 0.1% Ti). The sputtering was performed during 40 min under 0.4 Pa argon pressure. The deposits were 2 μ m thick.

Each substrate has been cleaned with an alkaline cleaner (AC1055TM (pH 10) from Brent Europe) at 65 °C during 8 min and rinsed with de-ionised water. The samples were immersed in the solution 1 h after this treatment in order to have a stable and reproducible aluminium oxide layer.

2.2. Solution preparation

A 20 vol.% BTSE hydrolysed solution was prepared by mixing 20 vol.% of pure BTSE and 20 vol.% of water, and completed with methanol. The pH was adjusted to 4.5 by adding a small amount of concentrated acetic acid. Then, the solution was stirred during 24 h to achieve a complete hydrolysis of the organosilane [15]. Afterwards, less concentrated solutions (2, 4, 6, 8 and 10 vol.%) were obtained by dilution of this 20 vol.% BTSE solution with methanol.

2.3. Density and viscosity measurements

The density ρ and the absolute viscosity η of the medium as function of the BTSE bath concentration have been

measured. The density was measured using a Digital Density Meter PAAR-DMA40 and the absolute viscosity of the solutions was determined with an Ubbelohde Viscometer. The capillary tube was a 0c Schott-Geräte for measuring kinematic viscosity between 0.5 and 3 mm²/s. All measurements were performed at 25 °C.

2.4. Refractive index

The refractive index of the different solutions was measured using an Abbe refractometer at a wavelength of 590 nm.

2.5. Electrochemical quartz crystal microbalance

The EQCM experiment was performed using a modified commercial set-up, Maxtek PM 500 and a frequency counter Phillips PM6685. The sensitivity of the EQCM was $37 \cdot 10^{-6}$ Hz g⁻¹. The vessel used for EQCM measurements is described earlier in reference [16]. Initially, this cell was filled with pure methanol, and the starting of the organosilane layer formation was performed by injecting a given amount of a 20 vol.% BTSE solution to reach the final desired BTSE bath concentration. Some experiments were performed with a titanium stirrer at 1000 rpm. All measurements were performed at room temperature.

2.6. Spectroscopic ellipsometry

Spectroscopic ellipsometry (SE) was performed using a J.A. Woollam VASE[®] working in the UV–visible–NIR (300–1700 nm) spectral range with a wavelength resolution of 10 nm.

For in-situ measurement, a special PMMA cell has been developed with two perpendicular optical windows in quartz for the entrance and the exit of the light beam. The angle of incidence is fixed to 70° and the wavelength range is reduced between 300 and 1100 nm due to the absorption of the solution. More details concerning the cell design were published elsewhere [17].

Dynamic scans have been performed to follow the influence of BTSE solution on the aluminium surface. These were performed at a wavelength of 590 nm and at a scan rate of 12 scans/min. Ellipsometric parameters (Δ , Ψ) were first measured for the aluminium surface in contact with air during 10 min and then the BTSE solution with the desired concentration was introduced into the cell. Ellipsometry measurement continued during more than 10 min. Fits were performed on (Δ , Ψ) ellipsometric couples using the WVASE32 version 3.33 software.

2.7. X-ray photoelectron spectroscopy

XPS measurements were carried out in a PHI model 1600 Omni Focus Lens III with an MgK α X-ray source (1253.6 eV) at 15 kV and 350 W. The analysed surface had a

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