Corrosion behaviour and chemical stability of transparent hybrid sol-gel coatings deposited on aluminium in acidic and alkaline solutions

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ABSTRACT

The aim of this study was to prepare transparent hybrid sol-gel coatings to serve as a barrier for corrosion protection of aluminium. The coatings were synthesised using silicon precursors tetraethyl orthosilicate (TEOS) and organically modified silicon precursor 3-methacryloxypropyltrimethoxysilane (MAPTMS) which were then mixed with different amounts of zirconium(IV) propoxide (ZTP) chelated using methacrylic acid (MAA). The synthesis process was followed using *in-situ* Fourier transform infrared spectroscopy and liquid-state ^{1}H, ^{13}C and ^{29}Si nuclear magnetic resonance spectroscopy.

The coating properties, such as transparency, topography, chemical composition, morphology and wettability were evaluated. Corrosion properties were analysed using electrochemical methods in ~0.1 N NaCl in a pH range between 3 and 10. The chemical stability was evaluated in strongly alkaline solution.

Homogeneous composition of the coatings was achieved through condensation reactions between Si- and Zr-based precursors. Obtained coatings were highly transparent, increased the contact water angle for polar and non-polar liquids compared to bare substrate, and improved the cleaning properties. The electrochemical measurements confirmed remarkable barrier protection in NaCl solutions of various pHs, especially for coatings with high Zr/Si ratios. In harsh media such as 0.1 N NaOH, the coating with low Zr/Si ratio was more stable. The results were interpreted in terms of different degrees of polycondensation of Si species as a function of Zr content in the coating. The importance of chemical speciation of the sol during synthesis were emphasised as this affects the subsequent coating properties.

1. Introduction

Aluminium (> 99.0%) is often used in many applications such as transportation, building, household appliances i.e. electronic devices and even in aluminium batteries [1]. Generally, aluminium has excellent resistance to corrosion, which derives from the natural formation of a thin oxide layer on its surface upon exposure to air or moisture [1]. However, the protective efficiency is highly reduced in polluted acidic environments (i.e. acid rain), in marine (the presence of chloride ions) saline acid environments, or in alkaline media, such as cementitious materials and alkaline detergents [2–5]. Alumina is stable in aqueous solutions in the pH range of 4.0–8.5. The corrosion attack in inorganic acids or bases is usually uniform and regular [1,4]. One of the most aggressive media is sodium hydroxide (NaOH), where aluminate ions $Al(OH)_4^-$ are formed [4].

To improve corrosion resistance of aluminium under such aggressive service conditions, various coating systems have been employed. For many decades, chromate conversion coatings have been used for protection of aluminium, because they have high inhibition efficiency in a wide range of pH [6–8]. Cr^{6+} ions and their compounds are toxic, carcinogenic and environmentally hazardous [6]; therefore, stricter restrictions according to REACH directives have been accepted since September 2017 [9]. Volatile organic compounds (VOCs) should also be reduced from waste effluents according to Restriction of Hazardous Substances (RoHS) directives, i.e. VOC Solvents Directive 1999/13/EC [10]. Therefore, the need exists for the development of low-VOC, non-toxic and environmentally friendly surface treatments capable of providing corrosion protection and chemical stability in a wide range of pHs.

The sol-gel technique has been widely used for the preparation of hybrid organic–inorganic coatings synthesised from organically modified silanes (ormosils), that are more corrosion resistant than substrate metals in different media, and possess good thermal and electrical properties [11–15]. Ormosil coatings are chemically inert in neutral media, but silane bonds (−Si−O−Si−) are susceptible to degradation in alkaline solution [2,3,16,17]. They react with unreacted silanol

(−Si−OH) groups within the structure, thus destabilising the coating surface [18]. As chemical stability of the coating at various pHs is often required due to local pH variation during the corrosion process, it is necessary to develop coatings with improved resistance to different pH conditions [19,20].

The chemical resistance of ormosil coatings can be improved by the addition of more reactive, non-silane alkoxide precursors, such as those based on zirconium, to prepare organically modified ceramics (ormocers) [17,18,21–25]. Zirconium stimulates the kinetics of hydrolysis and condensation reactions and, consequently, the formation of Si−O−Zr hetero-metal bonds, thus reducing free silanol groups [26–28]. Such coatings have high transparency, refractive index and thermophysical properties, which are important characteristics often required for many applications [26–29].

Recently, different ormocer coatings containing zirconium have been synthesised. Research has been focused on sol-gels synthesised from 3-methacryloxypropyltrimethoxysilane (MAPTMS), with or without addition of tetraethylorthosilicate (TEOS), and doped with zirconia prepared from hydrolysed zirconium(IV) propoxide (ZTP) [18,30–39] chelated with different reagents [32,40]. In previous studies by some authors, the coatings were synthesised from TEOS, MAPTMS, ZTP and methacrylic acid (MAA) and denoted as TMZ [34–38]. The properties of TMZ coatings were characterised as a function of Zr content in near neutral saline (0.5 M NaCl, pH 5.9) [34] or Harrison's solution (3.5 g/L $(NH_4)_2SO_4$ + 0.5 g/L NaCl, pH 5.2) [37]. The presence of ZrO_2 or aluminium–zirconium propoxide seems to have a pore-blocking effect in the coating [14,41], increasing the alkaline resistance [18], fracture toughness and surface activity of the coating [28]. The presence of zirconia in the coating also promotes multifunctional properties, such as higher transparency and better chemical resistance, which are the result of an increased degree of condensation in the siloxane network [42–44]. But the influence of ageing process on these properties has not yet been studied.

In this study, the synthesis process of hybrid sol-gel TMZ coatings was studied further using *in situ* attenuated total reflectance Fourier infrared spectroscopy (ATR-FTIR) and liquid state ^1H, ^{13}C and ^{29}Si nuclear magnetic resonance spectroscopy (NMR). These techniques brought a new insight into the effect of Zr content on the condensation of the hybrid silicon-based network of fresh and two-day-aged sols. The physical properties, such as transparency, surface roughness, coating composition and wettability were studied as a function of the amount of zirconium precursor added to the sol/coating. Another goal was to inspect the corrosion resistance of developed coatings in corrosive solutions of different pHs. These conditions were chosen as relevant for applications of these materials when used as final coatings, or as a pretreatment for further applications; for example, self-healing coatings after the addition of corrosion inhibitors.

2. Experimental

2.1. Substrate material

Aluminium > 99.0% 1.0 mm thick flat discs with diameter 14 mm, distributed by GoodFellow, England, were used as substrate. They were water-ground with 2400 and 4000 grit SiC emery papers to obtain a smooth surface with no visible tracks of grinding. First, the surface was rinsed with deionised water and gently wiped with a soft cloth. Then the samples were placed into a beaker filled with absolute ethanol for final cleaning using an ultrasonic cleaner for 10 min to remove all the grinding residues. Finally, the surface was dried with a stream of compressed nitrogen.

2.2. Materials for sol-gel

The sol-gel precursors were tetraethyl orthosilicate (TEOS: Si$(OC_2H_5)_4$, 99.9%, Aldrich), 3-methacryloxypropyltrimethoxysilane

(MAPTMS: $H_2C=C(CH_3)CO_2(CH_2)_3Si(OCH_3)_3$, ≥98%, Sigma), zirconium(IV) propoxide solution, (ZTP: $Zr(OPr)_4$, 70 wt%, in 1-propanol, Aldrich) and methacrylic acid (MAA: $H_2C=C(CH_3)COOH$, 99.0% Aldrich). Methacrylic acid was triple-distilled under reduced pressure to remove the polymerization inhibitor (MEHQ). The hydrolysis was initiated by addition of distilled water containing hydrochloric acid (HCl: > 37%, AppliChem).

2.3. Sample preparation

Hybrid sol-gels were synthesised by mixing two separately prepared solutions from silicon and zirconium precursors. The preparation procedure has been described in detail previously [35,37,38]. All coatings contained the reagents in molar ratios: TEOS/MAPTMS/ZTP/MAA = 0.18:1:X:Y, where X was 0.06, 0.48 and 0.96. The molar ratio of X:Y (ZTP/MAA) was always 1:2. The sols and coatings are denoted as TMZ-1 (Zr/Si = 0.05), TMZ-2 (Zr/Si = 0.41) and TMZ-3 (Zr/Si = 0.81), respectively. All syntheses were performed in a mini reactor at atmospheric pressure open to the air. The temperature of the reactor jacket was kept constant at 25 ± 0.1 °C. The sols TMZ-1 and TMZ-2 were aged for two days. TMZ-3 was prepared and characterised only as fresh sol (1 h after ZTP chelated with MAA was added to hydrolysed sol), because of the fast gelation process [36].

The sol-gel coatings were applied to the aluminium substrate using a spin-coater (Laurell − WS-650-23NPP/LITE/IND). A typical process involved depositing a small pool of fluid onto the centre and then spinning the substrate. The rotation speed was set to 4000 rpm for 30 s. The coated samples were kept in ambient conditions for 10 min and then cured on a preheated hot plate at 100 °C for 1 h in the presence of daylight.

2.4. Sol characterisation

2.4.1. In situ FTIR spectroscopy

Synthesis reactions were optimised by recording ATR-FTIR spectra *in situ* at intervals of 1 min in the range of 600–2800 cm^{-1}. The spectra were measured with a ReactIR™ 45 spectrometer with a resolution of 4 cm^{-1}, averaging 128 scans. An EasyMax 102 controller was used to control conditions during the reaction. The instruments were controlled by iControl EasyMax 4.2 and iC IR 4.2 software. Intensity of spectra are shown as log(absorbance) in absorbance units (A.U.).

2.4.2. NMR spectroscopy

Liquid-state ^1H, ^{13}C and ^{29}Si NMR spectroscopy was performed to evaluate the hydrolysis, condensation and ageing process as a function of amount of zirconium added to the sol. The measurements were performed at room temperature in samples diluted in deuterated chloroform (CDCl$_3$) using a Varian Inova 300 MHz spectrometer. Values of the chemical shifts were referenced externally to tetramethylsilane (TMS). Spectra were recorded at different steps of preparation, *i.e.* for hydrolysed sol, fresh sol and sol aged for two days. The accumulation was carried out at frequencies of 303, 76 and 60 MHz, with a pulse duration of 8 ms and a spectral width of 16.6 ppm for 20 scans, 326.3 ppm for 200–300 scans and 827.7 ppm for 3000–10000 scans to perform ^1H, ^{13}C and ^{29}Si measurements, respectively.

The reproducibility of the measurements was provided by repeating the NMR spectra at least in triplicate. Representative spectra were plotted. The ^1H and ^{13}C NMR spectra are shown only for sol TMZ-2, and are representative for the other two sols.

The evolution of various sols (hydrolysed, fresh or aged) and the distribution of various species were obtained by evaluated peak positions of the raw data in the ^{29}Si NMR spectra. The degree of polycondensation (τ) given as a percentage was calculated from the relative proportions of each T_n species in the ^{29}Si NMR spectra, according to the equation: $\tau = (T_1 + 2T_2 + 3T_3)/3 \times 100$ [45].