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Corrosion-protective coatings based on fluorocarbosilane

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ABSTRACT

This study discusses the effect of 3-(1,1,2,2,3,3,4,4-octafluoropentyloxy)propyltriethoxysilane (OFTES) based coatings on the anti-corrosive properties of 304 type stainless steel, which has not been described to date. The coatings were deposited from methanol using the anhydrous deposition method and influence of the sonication on this process has also been investigated. Anti-corrosive properties of modified and unmodified steel surfaces have been characterized by electrochemical and surface analysis methods. Since silicon is an element capable of forming bonds with both organic and inorganic substrates, these features allow to combine organofunctional silanes with metal as well as steel surfaces through metal−O−Si covalent bonds. A fluorinated alkyl chain, which is attached to the silicon atom, forms an effective barrier against an aggressive aqueous environment.

1. Introduction

The use of silanes for protection of metals against corrosion has been foreseen a long time ago, however an intensive research on this aspect has been carried out only within the past few years [1–9]. This is mostly a response to the request to seek an alternative to conventional chromating processes in metal-finishing industries. The growing chromate use restrictions has led to numerous studies focused on developing environmentally friendly solutions for metal protection [10–14]. Silane surface treatments provide not only corrosion protection but also paint adhesion to a broad range of metals [15,16]. Steel and stainless steel are widely used in different industrial applications due to their mechanical and anti-corrosive properties. However, they still tend to corrode in the presence of halide ions. The corrosion resistance behavior of sol–gel coatings or thin films deposited onto the steel substrate has been intensively studied in the past [2,6,7,9,17–22]. Hydrolysis and condensation reactions may occur in typical sol-gel solutions [23–28]. The former can lead to the formation of Si−OH groups with water present in the solvent. The subsequent two types of condensation reactions between Si−OH and Si−O−CH_2CH_3 moieties create a well-developed, cross-linked network consisting of Si−O−Si covalent bonds. Thus, the obtained gel is deposited on the modified surface and covalent bonds are formed. Alkoxysilanes can modify the hydroxylated surface under anhydrous conditions to also produce a thin monolayer coating [29,30]. Only methoxysilanes are effective in this kind of silanization [31] and Si−O−CH_3 group can react only with a hydroxyl group presented on the modified surface. Next, the trace water molecules (e.g. from moisture during drying and aging processes) can hydrolyze the remaining Si−O−CH_3 groups to form the siloxane bonds.

The use of sonication in synthesis and modification of functional materials is well-established [32,33]. It is through the chemical and physical effects of acoustically induced microbubble formation and collapse (acoustic cavitation), creating extreme localized heating and violent fluid flow effects, that ultrasound attains its great versatility and applicability in material, environmental and medicinal science. It has been reported as an efficacious tool in the synthesis of metal, polymeric and composite nanomaterials [34,35] also used in sol-gel processes [36,37]. Recent studies have exploited high intensity ultrasound in the pretreatment of metal surfaces to produce novel, functionalized materials, for example, surfaces with anticorrosive or superhydrophobic properties [37–39].

Organosilicon derivatives containing fluorine are of interest mainly because of their application in the production of modern materials. Fluoroalkylsilanes are used as surfactants, for surface modification of lenses and optical fibers, as components of many cosmetic preparations and as modifiers of fluorine and silicon rubber. Especially interesting branch of their application is production of oil-, dirt- and water-repellent surfaces [40–44]. The unique properties of perfluorinated silicon compounds, especially the lower surface energy, which results from the presence of fluoroalkyl groups [45], is the most considered property in corrosion phenomena studies. Unfortunately, due to the limited availability of starting materials as well as complicated

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synthesis of such compounds, use of fluoroalkylsilanes for protective coatings on the metals surface is limited [9].

In this study, we would like to present the anti-corrosive properties of fluorocarbosilane (3-(1,1,2,2,3,3,4,4-octafluoropentyloxy)propyltriethoxysilane) coatings deposited on the surface of 304 stainless steel, which were not described to date. Recent work of our laboratory group allowed to develop two-step synthetic protocols and synthesize a group of fluorinated derivatives of organofunctional silanes [46]. This work studies the influence of sonication on coatings deposition. The anti-corrosive properties of deposited coatings were examined using different electrochemical and surface analysis methods.

2. Experimental

2.1. Treatment of 304 stainless steel surface

All reagents were purchased from Sigma Aldrich. The 304 stainless steel discs (2.79 cm in diameter) with the following nominal composition: max 0.015 wt-% S, max 0.045 wt-% P, max 0.07 wt-% C, max 0.11 wt-% N, max 1.00 wt-% Si, max 2.00 wt-% Mn, 8.00–10.50 wt-% Ni and 17.50–19.50 wt-% Cr; were purchased from Rowitex Ltd. Company. 3-(1,1,2,2,3,3,4,4-Octafluoropentyloxy)propyltriethoxysilane (OFTES) with the following formula: $HCF_2(CF_2)_3CH_2O(CH_2)_3Si(OCH_2CH_3)_3$ was synthesized according to the procedure described in the literature [46].

First, the surface of 304 stainless steel discs was degreased with acetone and rinsed with distilled water in an ultrasonic bath (10 min). Then, all samples were placed in a hot 10% KOH solution (85 °C, 15 min) in order to activate the surface i.e. to form hydroxyl groups. Next, the discs were rinsed with distilled water and dried at 80 °C (30 min).

In the following step, two solutions containing OFTES and methanol at a 5:95 vol ratio were prepared and stirred for 30 min at 25 °C. Then, stainless steel discs were immersed in these solutions to produce sililated layer on their surfaces. Deposition was carried out in two ways. The sample labeled F1 was put into a beaker containing the solution and everything was placed in an ultrasonic bath for 15 min. The coating on the sample F2 was deposited by immersing the steel in the solution for 5 min. At the end, all the samples were cured at 80 °C for 1 h.

2.2. Analysis of surface morphology and water contact angle measurements

Scanning electron microscope (SEM Hitachi, SU3500) was used to characterize morphology of the samples surface. The analysis was carried out in low vacuum mode (70 Pa), and accelerating voltage (15 kV). FT-IR spectra were recorded on a Bruker Tensor 27 Fourier transform spectrometer equipped with a SPECAC Golden Gate diamond ATR unit. In all cases 16 scans at the resolution of 2 cm^{-1} were collected for a spectrum.

In order to determine the thickness of the deposited OFTES coatings, the steel substrates were scratched by a sharp edge of a aluminum sheet. Due to the fact that the hardness of aluminum is lower than steel, it can be assumed that only OFTES layer has been affected. Afterwards, images of the resulting features were made using an atomic force microscope (AFM, Keysight 5500). In case the read was correct, three cross-section profiles were made through the scratch. The thickness of the OFTES-based coatings were determined on the basis of the height histogram.

Static water contact angle (WCA) measurements of all samples were made using a Krüss GmbH instrument (model DSA 100 Expert), equipped with a fully automated dosing system. The measuring method was based on the analysis of the drop shape. Three different, randomly selected surface regions were selected. The average values of the obtained results were determined.

2.3. Electrochemical measurements

Electrochemical measurements were performed in a three-electrode Plexiglas® cell system. Saturated calomel electrode (SCE) and a platinum disc served as reference and counter electrodes, respectively. The 304 stainless steel samples with and without the deposited OFTES layers were used as working electrodes.

At the beginning the potential at open circuit conditions (OCP) was measured for 120 min. Afterwards, electrochemical impedance spectroscopy (EIS) study was carried out at a frequency range from 100 kHz to 10 mHz. The amplitude of the applied signal was ± 10 mV versus open circuit potential (OCP). Finally, cyclic potentiodynamic polarization (CPP) tests were performed. The working electrode was polarized cathodically (−100 mV vs. ocp) and then anodically until current values of 100 μA were reached. The scan rate was equal to 1 mV/s.

All the electrochemical tests were performed in 3.5% NaCl (Sigma Aldrich) solution at ambient conditions using an electrochemical workstation potentiostat/galvanostat VMP3 (Biologic, France) with an impedance module.

3. Results and discussion

3.1. Analysis of surface morphology and water contact angle measurements

Fig. 1(a–c) shows SEM image of the surface of bare stainless steel after surface cleaning in acetone and KOH water solution and also surfaces of samples F1 and F2. Acetone was used to degrease the steel surface and the alkaline etching helped to improve the cleanness and wettability of metallic substrates and to obtain water break-free surfaces, besides producing a hydroxyl rich surface to interact with silanol groups providing siloxane type covalent bonds [37]. The SEM image of the steel surface after treatment in an alkaline environment (Fig. 1(a)) shows that the surface has been etched as a result of this activation, grains are visible and the steel surfaces are spotted. The surface of the steel is characterized by relatively small corrosion pits and a cracked surface layer typical for austenitic steel [47]. Activation of the surface to create more hydroxyl groups caused a partial destruction of steel surface. Additionally, the signals corresponding to iron, chromium and nickel atoms were visible on the EDS spectra (Fig. 2) of the steel after the cleaning procedure, while the signal from carbon was very weak, confirming an almost complete removal of organic contaminants from the steel surface. The EDS spectra showed that bright and dark areas have identical composition.

The silanization of steel surface was carried out in methanol in an anhydrous system. Only the solvent contained small amounts of water. Anhydrous deposition of silane on the steel surface takes place effectively only for derivatives with methoxy groups [31], after dissolution of OFTES in methanol a trimethoxy-substituted OFTES derivative is created as a result of the alkoxy groups exchange reaction. Then, in contact with the hydroxylated steel surface, the $Si{-}O{-}CH_3$ groups react with hydroxyl to create metal−O−Si covalent bonds. Next, the trace water molecules (e.g. from solvent or moisture during drying and aging processes) can hydrolyze the remaining $Si{-}O{-}CH_3$ groups to form the siloxane bonds. The alkoxysilane can also partially hydrolyze with water present in methanol and then condense according to the sol-gel mechanism. This process was carried out in two ways, i.e. by immersion of the steel disc in a solution containing the OFTES and methanol, as well as by immersion of the steel disc in a solution and placing it in an ultrasonic bath. In addition, the aliphatic chain bonded to the silicon