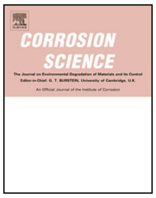
Corrosion Science xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci



Electrodeposited silica films post-treated with organosilane coupling agent as the pretreatment layers of organic coating system

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ARTICLE INFO

Article history:
Received 17 August 2015
Received in revised form 29 January 2016
Accepted 31 January 2016
Available online xxx

Keywords:
A. Mild steel
B. EIS
C. Electrodeposited films
C. Paint coatings

ABSTRACT

This work presents a new type of coating system based on the use of electrodeposited SiO_2 (E-SiO_2) film post-treated with (3-glycidoxypropyl)-trimethoxysilane (GPTMS) as the pretreatment layer. The silane-modified E-SiO_2 films take advantage of not only the highly rough and porous features provided by E-SiO_2 skeleton, but also the chemical functionalization offered by organosilane molecule. As a result, the composite pretreatment layer provides improved adhesion to the topcoat. In addition, the experimental results of electrochemical impedance spectroscopy, salt spray test, iron-dissolution measurement and the scanning vibrating electrode technique suggest that painting system constructed on GPTMS-treated E-SiO_2 films exhibits excellent corrosion performance.

1. Introduction

Corrosion is one of the major destructive processes of metals that leads to a significant environmental and economic impact [1]. Till now, coating system is still one of the most commonly used and effective measures to prevent corrosion of metal. Generally, the coating system consists of at least two layers including a pretreatment layer and an organic coating layer. The ideal pretreatment layer should not only have certain protective performance, but also provide good adhesion to both metal surface and organic top coating. Although, the conventional chromate or phosphate pretreatment layer can meet the requirements of the proposed, chromium (VI) is highly toxic and carcinogenic [2], while phosphorus can lead to water eutrophication when ignoring proper wastewater treatment [3]. Therefore, it is urgent for both academic research and industrial applications to find environmentally friendly pretreatment technique with effective corrosion prevention property.

The sol–gel process based on the use of organosilane compounds is quite promising for the preparation of assorted environmentally friendly pretreatment layer, and was considered as one of the potential alternatives of conventional chromating and/or phosphating processes [4,5]. The merit of silane films mentioned above lies in two aspects. One is that the film provides a certain extent of barrier property due to the existence of —Si—O—Si— network in the film and Metal—O—Si covalent bond on the interface [6]. The other is that the proper selection of organofunctional group in silane compound provides desired adhesion to top coat, as a result of chemical interaction between silane and polymeric coatings [4,7]. However, one of the major shortages of organosilane films is their low surface roughness [8], that is caused by both the limited film thickness (usually hundreds of nanometer [9]) and the soft and flexible bulk structure of silane film itself. The low surface roughness and non-porous structure results in a small contact area between silane film and top coat, which in turn impedes strong adhesion from the geometrical point of view.

Electrochemically assisted technique allows for generating much thicker and rougher sol–gel films [10], as a result of producing catalyst of sol–gel process (OH^-) in the solution near the electrode surface when applying negative potentials [11,12]. In addition, the separation of the gelation process from the solvent evaporation during the electrodeposition benefits for the formation of sol–gel films with greater porosity [8]. Silica-based sol–gel films prepared by electro-assisted method have been intensively investigated in the application fields of analysis [13,14], bio-sensors [15] and corrosion protection [16–18]. Recently, we have reported a novel painting system using electrodeposited silica (E-SiO_2) film as the pretreatment layer [19]. The highly rough and porous matrix structure of E-SiO_2 film ensures satisfied adhesion with top coat. As a result, the total painting system constructed provides comparable corrosion performance as conventional chromating process. However, the pure E-SiO_2 film fails to provide chemical interaction with the top coat, because of the lack of functional group on the surface.

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http://dx.doi.org/10.1016/j.corsci.2016.01.032
0010-938X/© 2016 Published by Elsevier Ltd.

Please cite this article in press as: Y.-H. Liu, et al., Electrodeposited silica films post-treated with organosilane coupling agent as the pretreatment layers of organic coating system, *Corros. Sci.* (2016), http://dx.doi.org/10.1016/j.corsci.2016.01.032

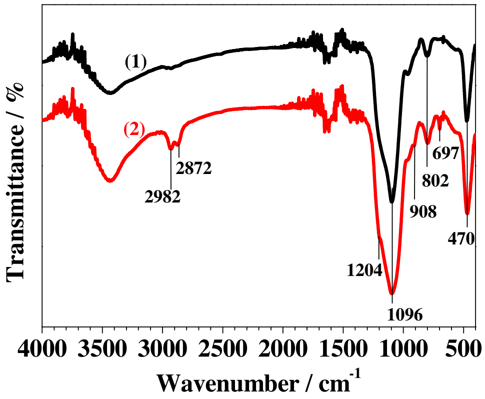

Fig. 1. FT-IR spectra of E-SiO_2 films before (1) and after (2) GPTMS-modification. E-SiO_2 films were electrodeposited on mild steel at −1.2 V vs. Ag/AgCl for 300 s.

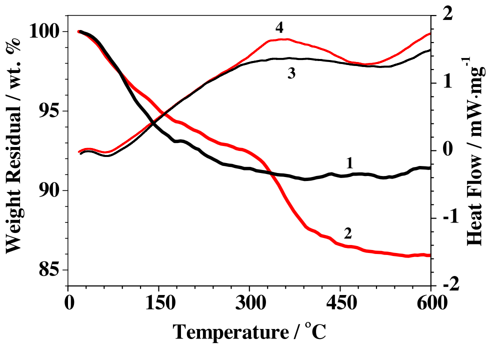

Fig. 2. TGA (1, 2) and DSC (3, 4) curves of E-SiO_2 films before (1, 3) and after (2, 4) GPTMS-modification.

A promising painting system, however, requires the pretreatment layer which has both the geometrical advantage (highly porous property) and desired chemical functionalization. To achieve this purpose, in the present work, we attempt for the first time to combine the surface roughing and chemical functionalization by post-silanization of E-SiO_2 films. The silane-modified E-SiO_2 films take advantage of not only the highly rough and porous features provided by E-SiO_2 skeleton, but also the chemical functionization offered by organosilane molecule. Painting system fabricated on silane-modified E-SiO_2 films exhibits a further enhanced adhesion property via both the geometric and chemical mechanism. In addition, organosilane modification provides additional short-term protective nature to inorganic SiO_2 films. Consequently, the new painting system exhibits an excellent corrosion performance.

2. Experimental

2.1. Materials and chemicals

Cold-rolled mild steel plates (MS, 1 mm thick, kindly supplied by Pentatomic Science & Technology, Hangzhou, China, wt.%: C 0.01, Si 0.35, P 0.018, Cr 0.04, Mo 0.03, Ni 0.017, Cu 0.02, Al 0.06; Fe balance) were cut into 4 cm × 2.5 cm sheet. Prior to electrodeposition, the substrates were degreased using home-made alkaline solution, rinsed with de-ionized (DI) water and ethanol, and then dried with warm air. Tetraethoxysilane (TEOS, 99.9%, Aladdin) and (3-glycidoxypropyl)-trimethoxysilane (GPTMS, 97%, Aladdin) were used without further purification.

2.2. Sliane post-treatment of electrodeposited silica films

E-SiO_2 films were prepared on MS substrates from a TEOS sol–gel precursor at −1.2 V vs. Ag/AgCl for 300 s in a three-electrode cell on a CHI 630d potentiostat (CH Instruments, Shanghai, China), using a Pt plate (4 cm × 2.5 cm) as the counter electrode and a commercial Ag/AgCl electrode (in saturated KCl solution) as the reference. The precursor contains 5 mL TEOS, 50 mL ethanol and 50 mL of a 0.2 mol/L $NaNO_3$ aqueous solution (pH 3.0, adjusted by hydrochloric acid). This mixture was stirred at 25 °C for 3 h for pre-hydrolysis prior to deposition [19]. After electrodeposition, the samples were consecutively rinsed with DI water and ethanol. The E-SiO_2 films were then obtained after dried at 40 °C in an air oven for 3 h and kept in a desiccator prior to painting. The solution used for silane modification contains 3.0 vol.% GPTMS dissolved into a 75/25 (v/v) ethanol/water mixed solvent (pH 3.5 adjusted by HCl). The obtained solution was pre-hydrolyzed at 35 °C for 48 h to form a sol–gel precursor. The E-SiO_2 films were immersed into the sol–gel precursor for 120 s at 25 °C. After then, the film samples were taken out and cured at 120 °C for 1 h in an oven. Finally, the film samples were rinsed with ethanol and dried in an oven at 120 °C for 1 h.

2.3. Coating formation

Epoxy resin and polyamide resin (5/4 mass ratio) were mixed into 7/3 (v/v) xylene and *n*-butyl alcohol solvent. The mixture was coated on the mild steel substrates by a brush with a dry thickness of 100 ± 10 μm, as measured by induced eddy current technique on coating thickness gauges (Qnix 8500, Germany). The coated panels were pre-cured at room temperature for 1.5 h, and then cured at 40 °C for a week prior to testing. For the purpose of comparison, four different coating systems were prepared and were denoted as following: epoxy coating on the bare MS substrate (MS/Epoxy), on GPTMS-treated MS substrate (MS/GPTMS/Epoxy), on E-SiO_2 film-covered MS substrate (MS/E-SiO_2/Epoxy), and on GPTMS post-treated E-SiO_2 films (MS/E-SiO_2/GPTMS/Epoxy).

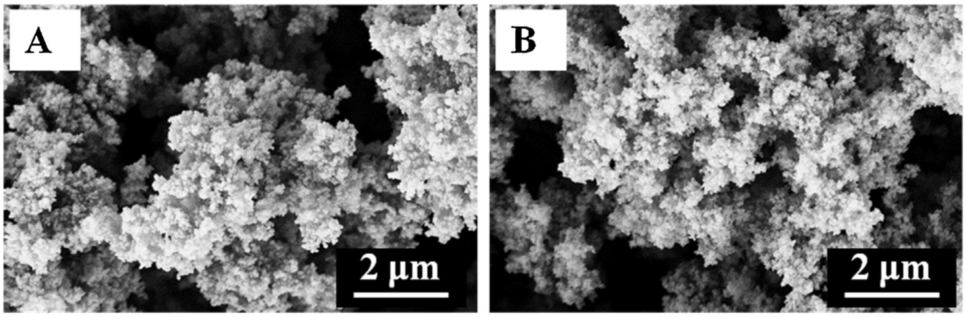

Fig. 3. SEM images of E-SiO_2 films before (A) and after (B) GPTMS-modification. E-SiO_2 films were electrodeposited on mild steel at −1.2 V vs. Ag/AgCl for 300 s.

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