Progress in Organic Coatings xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Progress in Organic Coatings

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

A sulfuric acid surface treatment of mild steel for enhancing the protective properties of an organosilane coating

Seyed Siamak Rouzmeh [a], Reza Naderi [a], Mohammad Mahdavian [b,*]

[a] School of Metallurgy and Materials Engineering, College of Engineering, University of Tehran, P.O. Box 11155-4563, Tehran, Iran
[b] Department of Surface Coatings and Corrosion, Institute for Color Science and Technology, P.O. Box 16765-654, Tehran, Iran

ARTICLE INFO

Article history:
Received 15 February 2016
Received in revised form 9 June 2016
Accepted 27 October 2016
Available online xxx

Keywords:
Mild steel
Surface treatment
EIS
XPS
AFM
SEM

ABSTRACT

This work intends to study the effect of mild steel treatment with sulfuric acid solutions on the protective properties of subsequent organosilane coating. For this purpose, acid solutions were prepared at different pHs including 1.5, 3, 4 and 5. FE-SEM, AFM, XPS and water contact angle measurements was used to investigate the surface chemistry and morphology changes on the mild steel after acid treatments. EIS was employed to evaluate the electrochemical properties of organosilane coatings on mild steel treated by the acid solutions. The results showed that the optimal surface treatment was obtained at pH 3.

1. Introduction

Steel is widely used in the oil and petroleum industries as it is cost efficient and has good mechanical properties. However, it is vulnerable to corrosive environment and it needs protection against corrosion. Organic coatings are one of the most common choices to increase life time of the steel structures [1]; however, their adhesion to the steel surface is very important. Low adhesion of organic coatings to metallic substrates restricts their use for industrial purpose [2,3].

Many metal surface pretreatments before application of organic coatings have been already introduced. Chromate conversion coating was used as the pretreatment of carbon steel due to its excellent corrosion resistance. However, due to carcinogenic characteristics of Cr(VI) in chromate conversion coatings, application of this pretreatment has been prohibited in recent two decades [3–6]. One of the green approaches is to use sol-gel organosilane based pretreatments. Organosilane compounds are environmentally friendly and can provide major properties of conversion coatings [7,8].

It has been shown that various factors such as silane concentration, pH of silane solution, immersion time and temperature, surface condition and corrosion inhibitors have a significant effect on the protective performance of silane coating [5,9–12].

To achieve silane film with desirable barrier protection, a surface treatment before coating application should be considered. Silane molecules form a film on the steel substrate by reaction between silanol group (Si-OH) of the silane and hydroxide group present on the substrate surface. At first, hydrogen bond forms between two groups, then during the subsequent condensation reaction, covalent metallo-siloxane bond (M—O—Si) forms at the interface [3,4]. Therefore, it's obvious that the presence of sufficient hydroxide groups on the metal substrate plays an important role on the adhesion of silane molecules. A few studies have been done on the surface treatment before application of silane coatings. Franquet et al. [13] compared the aluminum samples treated in alkaline solution to the ones stored in desiccator and exposed to air. They showed that by using alkaline solution for the surface treatment, hydroxyl groups formed uniformly on substrate. Wang et al. [14] demonstrated that among three different pHs (1, 9.5, 12.4) for treatment of cold rolled steel, the pH 9.5 provided the highest corrosion protection due to formation of FeOOH group on the substrate surface which are ready to react with silane molecules.

In this research we intend to study the effect of sulfuric acid treatment of mild steel on the corrosion protection properties of subsequent organosilane coating. For this purpose, different pHs for pickling solutions were considered. The barrier and elec-

* Corresponding author.
E-mail address: mahdavian-m@icrc.ac.ir (M. Mahdavian).

http://dx.doi.org/10.1016/j.porgcoat.2016.10.033
0300-9440/

trochemical properties of silane coatings on mild steel substrate were evaluated by electrochemical impedance spectroscopy. Surface analysis such as FESEM, AFM, XPS and contact angle was used to investigate the chemical and physical changes on the steel substrate. This work is novel over and critical of the previous studies on this subject as it reveals the impact of acid treatment on the silane coating quality providing much better performance than the conventional alkaline treatment reported in literature.

2. Experimental

2.1. Materials

Glycidoxypropyltrimethoxysilane (γ-GPS), tetraethylorthosilicate (TEOS) and methyltriethoxysilane (MTES) were the silane coating precursors and all of them were synthetic grade of Merck (Germany). Acetic acid (used for adjusting pH of silane coating solution) and sulfuric acid (used for adjusting pH of surface treating solution) were all synthetic grade obtained from Merck (Germany). Benzothiazole, synthetic grade, used as corrosion inhibitor for acid treating solutions was obtained from Merck (Germany). The substrates were mild steel (St-37) with $3 \times 7\,cm^2$ dimension. All the substrates were abraded with 400, 600, 800 and 1000 silicon carbide paper; then, degreased with acetone. Double distilled water was used to prepare all test solutions.

2.2. Sample preparation

Sulfuric acid was added to water to prepare acid treating solutions with different pHs (1.5, 3, 4 and 5). All the sulfuric acid solutions contained 1 mM benzothiazole to reduce severe acid attacks on the substrate. Mild steel substrate were immersed in sulfuric acid solutions with different pHs for 60 s and then rinsed with distilled water and dried.

Equal weight of three different organosilanes (γ-GPS, TEOS and MTES) was dissolved in water to prepare 10% (w/w) aqueous silane solution. The pH of silane solution was adjusted to 3 by drop-by-drop addition of acetic acid; then, the mixture was magnetically stirred for 24 h at a rate of 1000 rpm to perform hydrolysis reaction. The mild steel samples treated for 60 s by the sulfuric acid solutions at different pHs were immersed in the silane solution for 120 s, then rinsed with distilled water and dried at room temperature. Finally, the samples were kept at 150 °C for 30 min to perform condensation reaction.

An area of $1 \times 1\,cm^2$ of each mild steel sample was considered for electrochemical corrosion measurements, while the rest areas of the mild steel samples (including edges and back) were covered by a hot-melt mixture of beeswax and colophony.

2.3. Methods

Electrochemical impedance spectroscopy (EIS) was used to investigate the electrochemical behavior of coated samples by organosilanes. The EIS measurement was carried out in 0.1 M NaCl solution after 2, 4 and 6 h of immersion. The EIS measurements were employed in the frequency range of 10 mHz–10 kHz with amplitude of 10 mV peak-to-peak using AC signals at open circuit potential. An Ivium Compactstat (Netherlands) was employed to gather impedance spectra. A commercial saturated calomel electrode (SCE) and a graphite electrode were used as the reference electrode and counter electrode, respectively. All the measurements were conducted on triplicate samples and the average values of the extracted electrochemical parameters were reported.

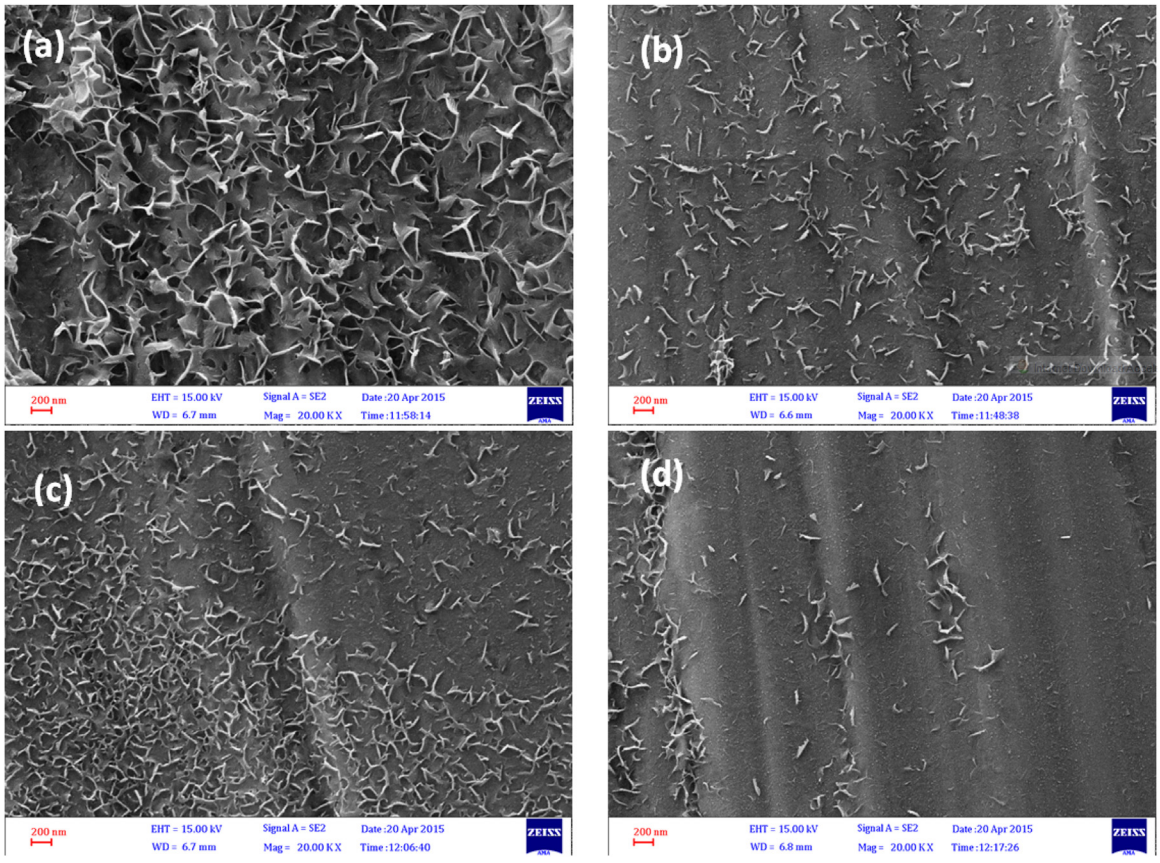

Fig 1. FESEM images from mild steel surface treated in different acidic condition: (a) pH 1.5, (b) pH 3, (c) pH 4, and (d) pH 5.

Please cite this article in press as: S.S. Rouzmeh, et al., A sulfuric acid surface treatment of mild steel for enhancing the protective properties of an organosilane coating, Prog. Org. Coat. (2016), http://dx.doi.org/10.1016/j.porgcoat.2016.10.033