Effect of surface preparation procedure on corrosion protection of electrodeposited silane films

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Abstract

Ceramic coatings have been the object of the most diverse studies due to its enhance mechanical and corrosion protection characteristics. In such matter it is possible to draw attention to sol-gel coatings, whose simplicity and mild operation conditions allow excellent controllability over porosity and film thickness. Most of the published papers in such field, so far, are focused on the comparison of different coating processes, improvement of process parameters, sol-gel precursors' concentration, pH, among others. However, each author uses a different surface preparation procedure for the sol-gel film deposition. On the top of it, the literature lacks explanation regarding the effect of the preparation procedure on the corrosion protection behaviour. In order to fill such gap, this paper presents the linear polarization resistance (LPR) and electrochemical impedance spectroscopy (EIS) analysis throughout time for four different surface preparation procedures, comprising two emery paper degrees (600 and 1200) and two chemical treatments (with and without alkaline ultrasonic bath). The results point out that higher emery paper degrees induce films with higher polarization resistance and that the alkaline bath presents no statistical significance on the results.

Keywords: Surface preparation, electrodeposition, silane, coatings, sol-gel.

Introduction

The electrodeposition of silane based films on metal substrate in order to prevent corrosion was first described by Schachan *et al.* (1). The process is performed in a three-electrode cell containing a solution of pre-hydrolized silane precursors on acid pH. The application of an appropriate cathodic potential or current on the working electrode induces electrochemical reactions such as the reduction of water and H^+ ions, locally increasing the pH. As described by Iler (2), pH above 5 are necessary in order to obtain higher rates of condensation reactions, and consequently, the formation of a silica based network on the metallic substrate surface, as shown in Figure 1. When compared to other sol-gel coating deposition techniques, the electrodeposition presents important advantages such as: uniform film deposition, highly

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controllable deposition variables (potential, current and deposition time) and the ability to coat complex geometries.

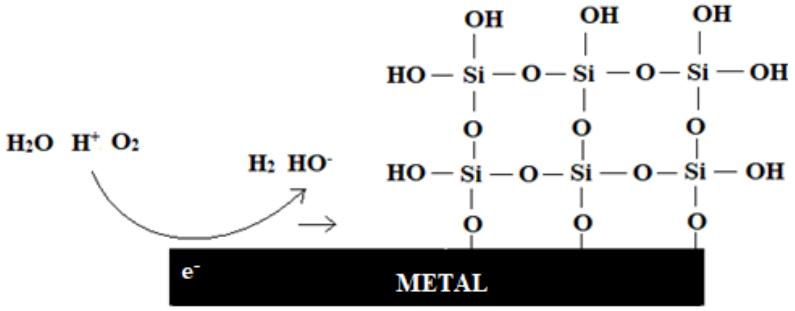

Figure 1 – Silane electrodeposition scheme. Adapted from (3)

Since Schachan's work (1), several papers have been published studying the effects of silane precursor (4,5), electrodeposition potential (3,4-6) and deposition time (3,4,6,7). Nevertheless, the literature is still quite vague on how the surface preparation affects the film structure and corrosion protection. Each of the mentioned articles uses different grinding levels and cleaning processes. Giordano *et al.* (3) simply polished the stainless steel coupons' surfaces and mentioned no cleaning process. Sherffer *et al.* (5) sanded the samples until 2000 grade, followed by alumina paste polishing and ethanol sonication. Wu *et al.* (7) abraded the samples with emery papers up to 400 grade and degreased the mild steel coupons with homemade alkaline solution in ultrasonic bath for 10 minutes. Cao *et al.* (8) performed a very similar surface preparation to (5), however, at the end of the process the first set of authors immersed the uncoated samples in ultrasonic bath of acetone for 30 minutes, in order to promote further degreasing. Therefore, from above discussion, various successful types of surface preparation methods have been employed but no author has mentioned how the surface preparation can influence the corrosion protection of the silane coating. Therefore, the present work aims to study four different surface preparation methods and study how they influence the corrosion behaviour of carbon steel coupons coated with silica films by electrodeposition.

Methodology

In order to analyse the effect of surface roughness and chemistry on the silane film formation and corrosion protection of steel coupons, four types of surface treatments were selected, as shown in Table 1. Two sets of emery paper have been selected in order to achieve different roughness patterns, while the alkaline cleaning in ultrasonic bath is used to promote surface cleaning and formation oxides that help the anchoring of silanols to the surface (9). Therefore, by comparing the results of P01-P02 or P03-P04, the effect of emery paper and roughness pattern is possible to be understood. On the other hand, by comparing the results of P01-P03 or P02-P04, the effects of the alkaline ultrasonic bath on the corrosion protection is possible to be observed.

Table 1 – Surface preparation procedures

Procedure	Emery paper	Alkaline cleaning
P01	600	No
P02	1200	No
P03	600	Yes
P04	1200	Yes

Each electrodeposition solution consisted of 33,33 mL of an aqueous solution of $NaNO_3$ (0,2 mol/L), 66,67 mL of ethanol and 3,00 mL of Tetraethoxysilane (TEOS) (98% purity, purchased from *Sigma Aldrich*), which was used without further purification. The solution pH was adjusted to 3,0 with a solution of HNO 1,0 mol/L, and stirred for 3 h prior the deposition. Meanwhile, carbon steel coupons were abraded with emery paper whose degree varied from 400 to 1200, depending on the experiment procedure (Table 1). Afterwards, the coupons were rinsed with ethanol and immersed for 5 min in an ultrasonic bath of etanol, in order to promote degrease. Depending on the experiment procedure, the coupons could also be submitted another 5 min in ultrasonic bath in a solution of NaOH 2,5%. As a final step, the coupons were blow dried in hot air and the area limited to 1 cm^2 with electric tape.
Silica films were electrodeposited during 300 s applying -1,2 V vs. Ag/AgCl on a potentiostat PGSTAT302N in a three-electrode cell, with titanium and a commercial Ag/AgCl electrode acting as counter and reference electrodes, respectively. After deposition, the films were immersed in distilled water and ethanol in order to remove ions from solution and dried for 1 h at 60ºC.
Coated and uncoated coupons were analysed by linear polarization technique (LPR) and electrochemical impedance spectroscopy (EIS) using the afore mentioned potentiostat and three-electrode cell in a solution of NaCl 3,5%. On the first analysis, the open circuit potential (OCP) was measured during 300 s, then the potential was varied from -10 mV to +10 mV regarding the OCP, with a scan rate of 0,33 mV/s and increments of 1,00 mV. The polarization resistance (R_P) was determined by the slope of the obtained E x I curve. EIS measurements were taken after 15 min of immersion, applying a sinusoidal wave with a perturbation of 10 mV, and frequencies ranged from 10^5 Hz to 0,01 Hz. The topography was analysed by optical microscopy using a Zeiss-Smart Zoom 5.

Results and discussion

Optical microscopy images showed no distinction between the films' morfology obtained for different surface treatments. Figure 1 presents a representative area of the deposited films, showing a highly porous structure (Figure 1 (b)), opaque and white coloured. Since the optical microscopy analysis shows no difference between the deposited films, only one figure is presented.
In order to obtain an estimate value for film thickness, 3D imaging tool from Smart Zoom 5 optical microscope was employed. Even though it is not a standard procedure, as described by ASTM B487-85 (Standard Test Method for Measurement of Metal and Oxide Coating Thickness by Microscopical Examination of Cross Section), the method uses different focal planes to obtain an estimate value of topology parameters, including the height difference between two surfaces. As it can be pointed out by Figure 2, the obtained film has thickness in the micrometre range, similarly to the ones obtained in literature (1)(4)(7)(10).

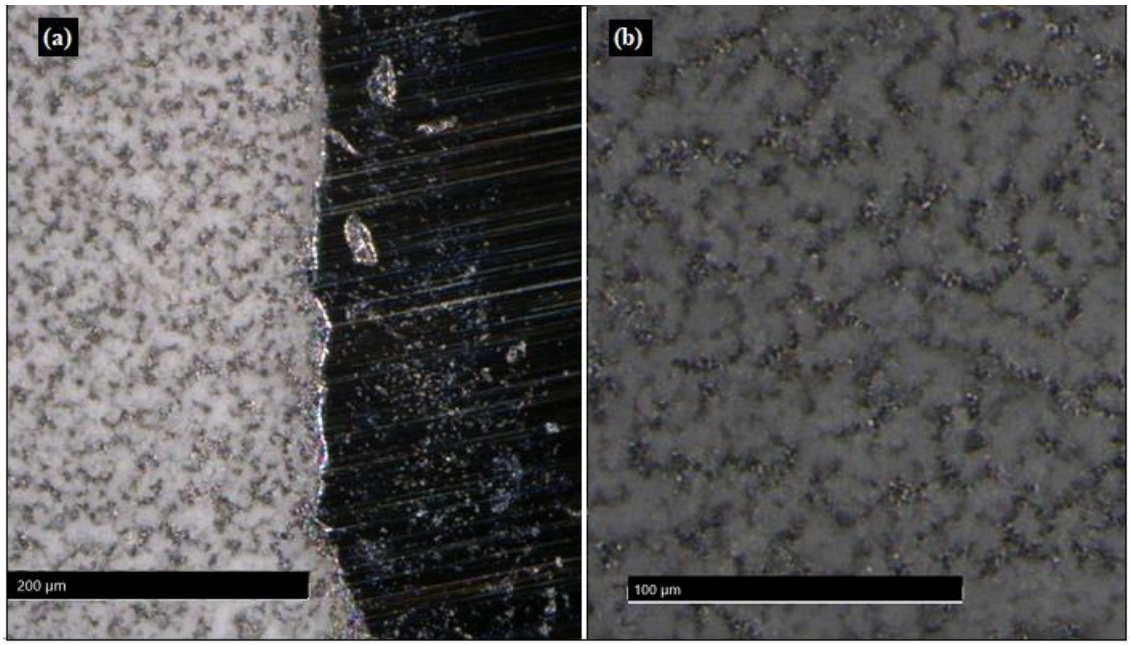

Figure 1 – Optical microscopy of silica film deposited on carbon steel coupons, where (a) represents an upper view of film edge and (b) a higher magnification of electrodeposited film.

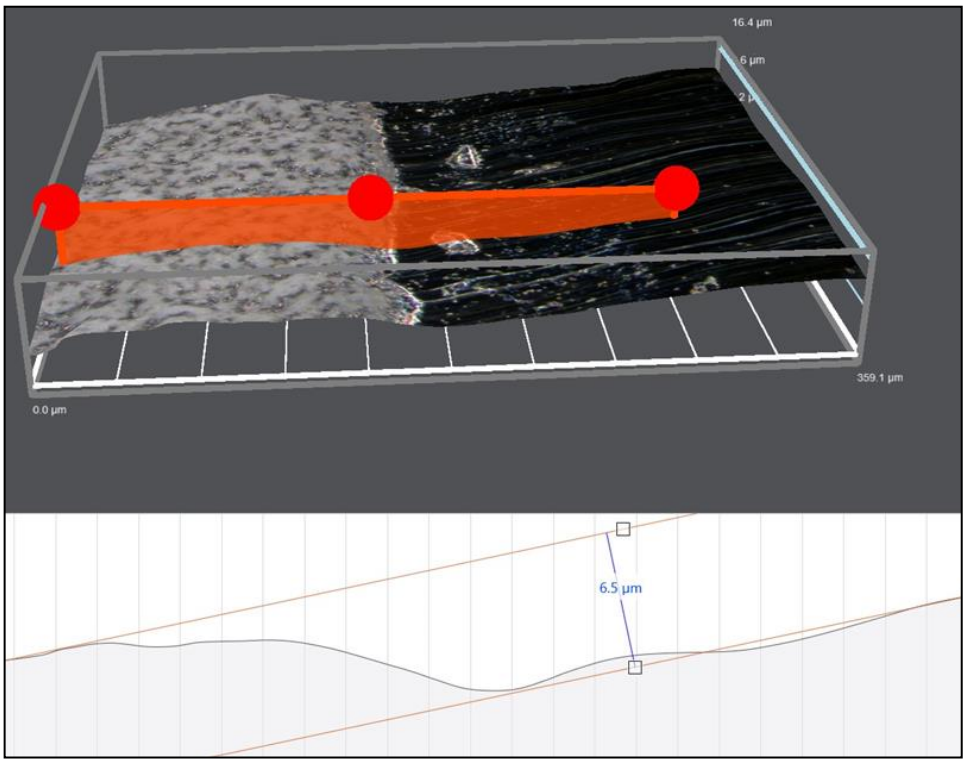

Figure 2 – 3D image of film edge and thickness obtained by Zeiss Smart Zoom 5.

As part of the characterization process, the roughness factor RA was measured for each sample and its replicates. As shown in Figure 3, the samples abraded with higher emery paper degree (P02 and P04) have lower average RA value. However, it is important to point out that even though P04 was sanded with a 1200 emery paper, its roughness is not statistically different from the ones abraded with a 600 emery paper. It is possible to suggest that the

higher roughness value of P04 is due to the ultrasonic bath in NaOH 2,5%, which is able to create thin protective oxide layers on carbon steel's surface. However, further tests are necessary to confirm such hypothesis.

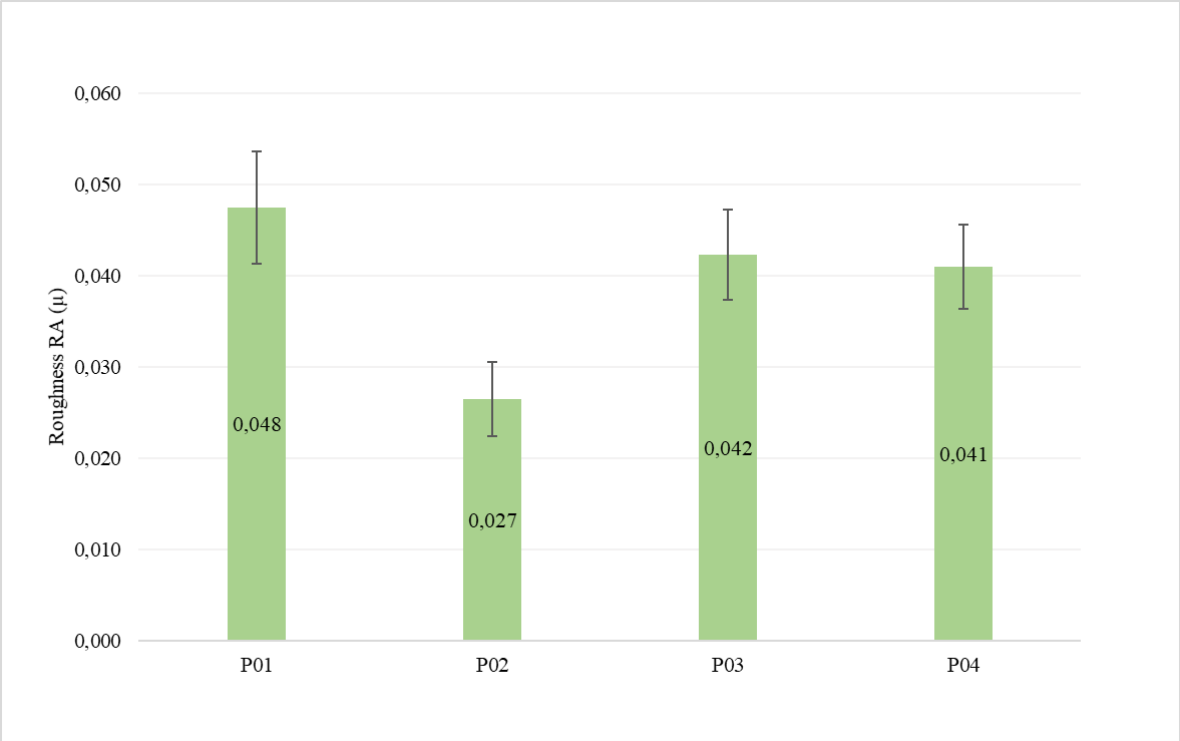

Figure 3 – Average roughness factor RA and standard deviation for each sample.

Unlike the coupons only cleaned with ethanol, the ones bathed in NaOH solution, whenever immersed in the deposition solution prior to the application of the cathodic potential, had a positive open circuit potential (OCP) around +0,1 V vs. Ag/AgCl. Such potential slowly reaches 0,0 V vs. Ag/AgCl and then rapidly decreases to even more cathodic potentials, stabilizing around -0,4 V vs. Ag/AgCl. The authors also noticed that, if the deposition potential (-1,2 V vs. Ag/AgCl) is applied right after the immersion of the coupon, the resulting film would present flake-off regions. On the other hand, the application of deposition potential after 1 min of stabilization, the film presented good coverage and no flake-off region.

Linear polarization resistances were measured before and after film deposition, as shown in Figure 4. All coated coupons presented higher polarization resistances (R_P) than uncoated species, indicating a certain level of protection granted by the film. However, coupons that were abraded with 1200 emery papers (P02 and P04) showed even higher average values of R_P (85333 Ω cm^2 and 76610 Ω cm^2) than the ones abraded with 600 emery paper (36113 Ω cm^2 and 20934 Ω cm^2), independently of ultrasonic alkaline bath. As a matter of fact, the comparison of R_P with and without alkaline bath, under the same degree of emery paper (P01-P03 and P02-P04), showed no statistical difference what so ever. Such fact indicates that either the alkaline ultrasonic bath has no effect on the corrosion protection or the chosen alkaline solution is inefficient.

The results of LPR (Figure 4) are consistent with the results showed in Figure 5, which points out the average impedance module at 0,1 Hz for each surface preparation procedure, after 15

minutes of immersion in NaCl 3,5%. Since stabilization time is low, frequencies as low as 0,01 Hz could not be applied to analyse corrosion effects, due to the presence of errors.

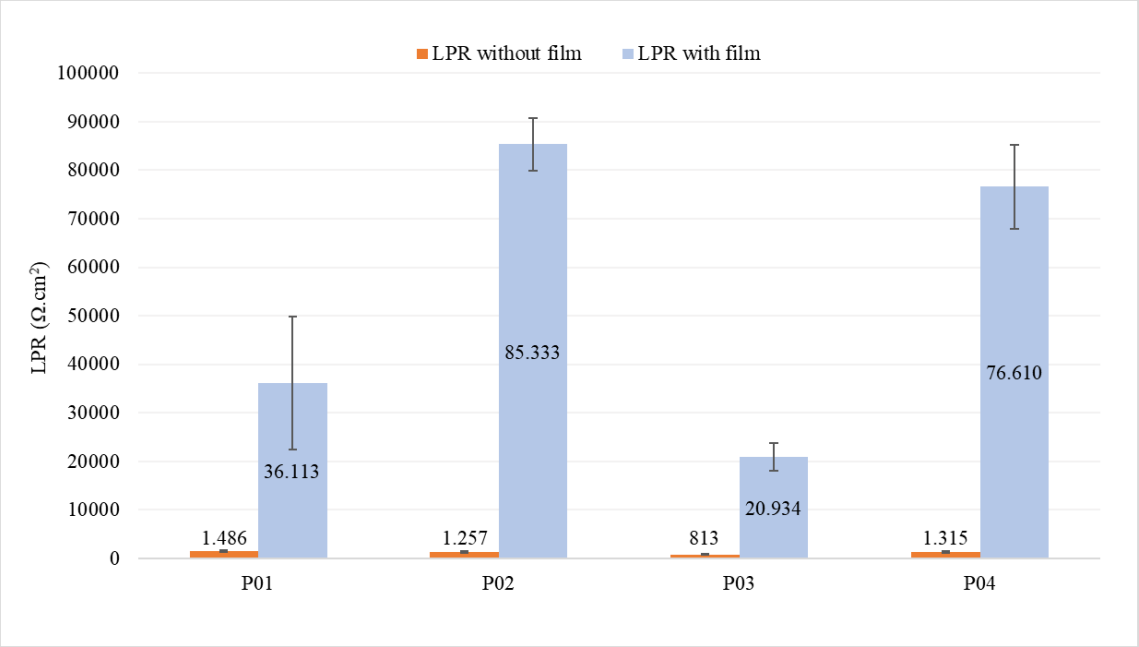

Figure 4 – Linear polarization resistance and standard deviations for carbon steel coupons with and without silica film.

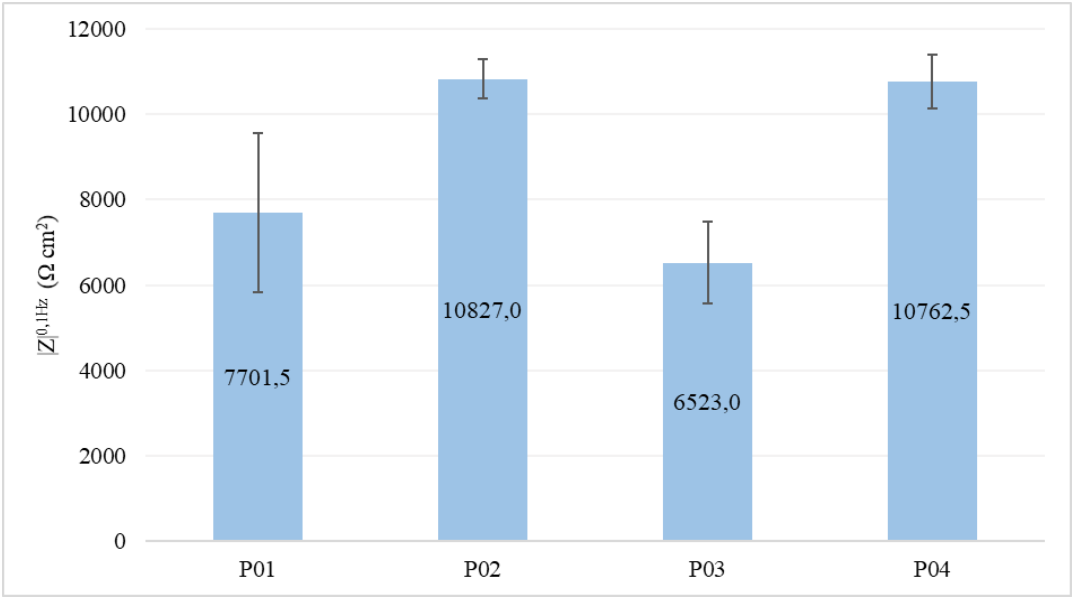

Figure 5 – Average values of impedance module at the frequency of 0,1 Hz for each surface preparation procedure and its standard deviation.

Conclusions

The present work evaluated the effect of surface preparation of carbon steel on its corrosion behaviour after electrodeposition of a silica film. In order to do so, four different preparation procedures were designed combining two sets of emery paper (600 and 1200) and the presence or not of alkaline ultrasonic cleaning. All the surface preparations provided films with a certain degree of corrosion protection, when compared to the bare metal. Beyond that, higher degree of emery paper produced films more prone to resist corrosion. On the other hand, the alkaline treatment has not shown statistical significance on the results, considering the parameters and solutions applied to this research. Therefore, such evaluation may represent a guide of great importance when deciding how to prepare the surface prior to deposition of sol-gel films.

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