



THE INFLUENCE OF ZrO₂/SILANE PRETREATMENT ON CORROSION RESISTANCE OF POWDER COATING

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ABSTRACT

Carbon steel was treated by immersion in silane doped hexafluorozirconic acid solution. Treated surface was characterized by field emission scanning electron microscopy (FE-SEM) and electrochemical methods. The effect of ZrO₂/silane pretreatment on the protective properties of powder coating was studied by adhesion measurement and electrochemical impedance spectroscopy (EIS). The obtained results showed that the morphology and electrochemical characteristics of ZrO₂/silane film depend on solution pH. Surface morphology was uniform and compact at solution pH = 4. The best corrosion performance was obtained with the film formed in solution with pH and immersion time of 4 and 4 mins, respectively. The ZrO₂/silane pretreatment significantly improved adhesion and corrosion resistance of powder coating on carbon steel.

Keywords: pretreatment, silane doped hexafluorozirconic acid, adhesion, EIS.

1. INTRODUCTION

Surface pretreatments by phosphate are used on metal substrates before application of organic paints for better adhesion and improved corrosion protection. However, phosphate conversion coatings are being replaced because of several drawbacks from environmental, energy and process points of view [1]. Zr-based convention or organosilane pretreatment have been studying as an environment friendly replacement [1–7]. The effect of Zr-based convention is expressed in which increasing surface donor properties of the steel substrate leads to increment of work of adhesion of the organic coating to the steel surface due to attribution to formation of oxide–hydroxide of zirconium and adsorbed fluoride ion on the mild steel surface [2, 6]. The strength of the silane technology lies in its universal applicability. It can be used in

almost any metal-paint combination. It has also been demonstrated that silane films can protect against various different forms of corrosion, including many forms of localized corrosion [7].

Optimizing the solution to reach better conversion coating has been studied. For Zr based coating, the thickness of conversion layer increased, uniformity decreased when immersion time increased. The best coating was gained at solution pH =4 or 4,5 [4, 5, 8–10]. Studying the effect of immersion time on the properties of nano size zirconium oxide coating on CT3 steel showed that the ZrO_2 film was uniform with the immersion time of 4 minutes [10]. For silane pretreatment, deposition from solution is very fast and the thickness of the film remains virtually unchanged, even if the immersion time is varied between 30 s to 30 mins [7]. Pretreatment from pH 4 silane solution promoted thinner and more homogeneously distributed coatings than pH 6 solution [11]. Influence of the pH of an aminosilane based pre-treatment on adhesion strength and durability via single lap shear tests was studied [3]. Although the joints pretreated at pH 10.6 had better durability than at pH 4.6, important result is that aminosilane treatments at pH 4.6 also improved the wet durability of joints [3].

A combination of Zr based and silane based pretreatment on galvanised steel substrates in different ways has been performed recently. The combined layer is in general better than that of each component [12–14]. Studying the influence of silane concentrate on surface morphology and composition of zirconium oxide/silane pretreatment film was conducted. The results indicated that zirconium and silicon were found in the formed coating and the homogenous morphology was gained with the silane concentrate of 0.025 % (w/w) [15]. This paper investigated the effect of solution pH on surface morphology and electrochemical characteristics of zirconium oxide/silane pretreatment film. At the same time, corrosion performance and adhesion of powder coating with or without the pretreatment were also studied.

2. EXPERIMENTAL

Hexafluorozirconic acid solution, containing 50 ppm Zr^{4+} was prepared by dissolving of ZrF_4 (Sigma) in HF in distilled water. Aminopropyl-triethoxy-silane (APS-Merck) was added to H_2ZrF_6 solution with concentration of 0.025 % (v/v). The pH of solutions was adjusted to 2, 4 or 6 ± 0.05 by H_2SO_4 or NaOH solution (China).

The CT3 sheets ($100 \times 75 \times 1$) mm were abraded with SiC polishing paper, cleaned with distilled water, ethanol and immersed in silane doped hexafluorozirconic acid solution at pH = 2, 4, and 6 for time of 4 minutes [10]; cleaned with distilled water, dried in hot air (70 ± 3 °C).

Powder polyester coating (Akzonobel) was applied on the untreated and treated steel surface by spray method. The coatings were dried at 190 °C for 10 mins. The thickness of coatings were 60 ± 5 μm .

The morphology of ZrO_2 /silane films was investigated by a field emission scanning electron microscopy (FE-SEM), Jeol 7401F. The adhesion strength of the coatings was determined according to ASTM D4541 by a PosiTest AT-M with 20 mm dollies. All tests were repeated three times to ensure the measurements repeatability.

The corrosion resistance of coatings was assessed by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization measurements in the solution of NaCl 3.5 % (w/w). A three-electrode cell (AutoLAB PGSTAT 204N) was used with a platinum auxiliary electrode, a saturated calomel reference electrode (SCE) and treated steels as working electrodes. EIS method was also used to evaluate the effect of different treatment on corrosion resistance of powder coatings.

3. RESULTS AND DISCUSSION

3.1. Influence of solution pH on surface morphology and anti-corrosive characteristics

3.1.1. Influence of solution pH on surface morphology

Figure 1 shows FE-SEM images of ZrO_2 /silane film at different solution pH. It was observed surface microstructure was uniform and compact with the treatment at pH 4 (Fig. 1b). This result was due to the ZrO_2 /silane deposition on the surface at the best conditions with both ZrO_2 and silane components [10, 11]. As mentioned, the presence of zirconium and silicon in the coating was proved [15]. Moreover, both ZrO_2 and silane tend to deposit on steel substrate during immersion. So they competed to each other to form the ZrO_2 /silane film. As a result, surface morphology was uniform and compact. In very low pH, the coating could be dissolved in conversion solution and the resulting thin ZrO_2 film [4]. On the contrary, it may be because at pH = 6 (higher alkalinity) leading to the lower anodic reaction rate. It meant that the cathodic reaction rate was also not high enough to increase the interface pH for Zr oxide/hydroxide precipitation [9]. In both cases, pH = 2 or 6, ZrO_2 film formed was not as completely as pH = 4. However, silane film formation was similar to that of pH = 4. As a result, surface morphology was characteristic of silane (Fig. 1a, c).

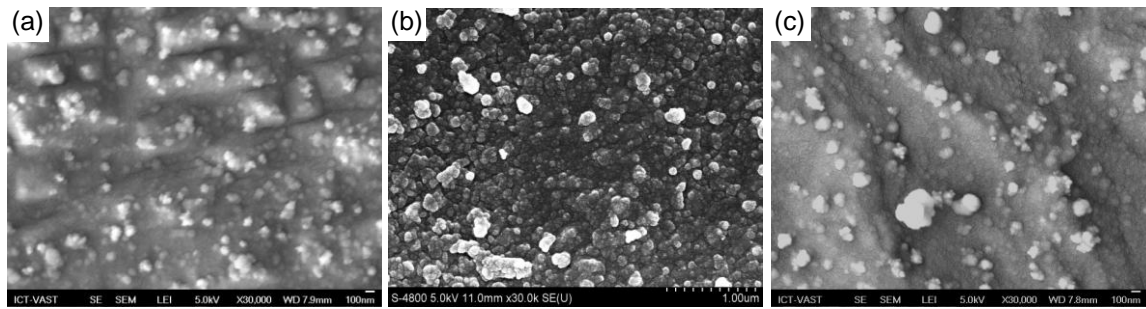


Figure 1. FE-SEM images of steel surface after treatment: pH = 2 (a); pH = 4 (b) and pH = 6 (c).

3.1.2. Influence of solution pH on anti-corrosive characteristics

Nyquist plots and polarization curves of treated samples with different solution pHs are shown in Figure 2.

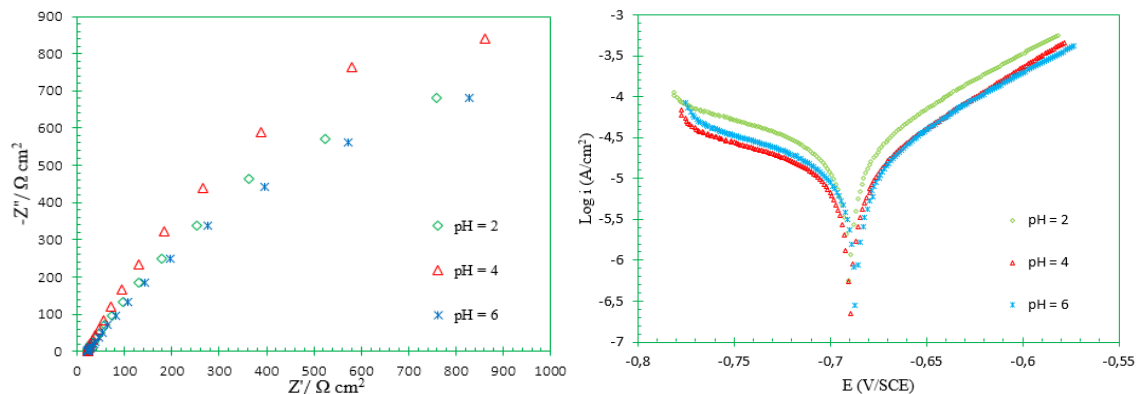


Figure 2. Nyquist plots and polarization curves of treated samples in different solution pHs.

For Nyquist plots, one time-constant semicircle equivalent circuit models were made. This signifies that the same fundamental phenomena could have occurred in all these coatings but over a different effective area in each case [4]. The appearance of a single semicircle in the Nyquist plots of the coated samples showed that the corrosion process of these coatings involved a single time constant indicating the existence of a double layer at the coating-electrolyte interface. The electrical circuit equal to the electrode-electrolyte for the treated samples is shown in Figure 3 (using Nova 2.0 software). In this figure, R_s represents solution resistance, R_p represents polarization resistance at coated metal-electrolyte interface and CPE represents non-ideal double layer capacitance. The capacitor from CPE was determined from the formula [4]:

$$C = (Y_0 \times R_p^{1-n})^{\frac{1}{n}}$$

Tafel extrapolation method was used to determine the corrosion potential and the current density.

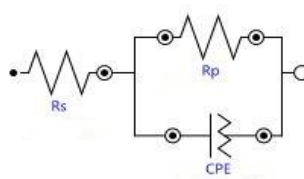


Figure 3. Electrical circuit used to simulate the EIS results.

The archived results are shown in Table 1. It was observed that conversion coating at solution pH = 4 showed the best anti-corrosion performance (the highest $R_p = 9112 \Omega.cm^2$ or the lowest $J_{corr} = 5.3 \mu A/cm^2$). This result could be explained as the ZrO_2 /silane deposition on the steel substrate at the best conditions with both ZrO_2 and silane components [10, 14]. The resistance values of the films at solution pH = 2 ($R_p = 7517 \Omega.cm^2$) or 6 ($R_p = 7832 \Omega.cm^2$) were lower than that at pH = 4 due to the fact that in these conditions, the thin ZrO_2 film could not sufficiently protect the substrate [4]. The film was mainly formed by silane. As a result, the Si/Zr ratio in both cases of pH = 2 or 6 was higher than that at pH = 4. Montemor M. F. et al. indicated that the pre-treatment that led to a higher Si/Zr atomic ratio was the one that revealed the worse corrosion performance [11]. This was explained why the conversion coating at pH = 4 showed the best anti-corrosion performance.

Table 1. Obtained data from EIS fit and Tafel extrapolation in different solution pH.

Parameters	Solution pH = 2	Solution pH = 4	Solution pH = 6
$R_p \pm \% (\Omega.cm^2)$	7517 ± 4.39	9112 ± 3.06	7832 ± 3.69
$C (\mu F/cm^2)$	359	327	365
$E (mV/SCE)$	- 689.3	- 691.1	- 686.7
$J_{corr} (\mu A/cm^2)$	7.9	5.3	7.8

3.2. Adhesion strength of organic coated samples

Adhesion force depends on both the behavior of the underside of the paint film and the properties of the top side of steel or, in this case, on ZrO_2 /silane pretreatments. In this work, dry adhesion values of powder coatings on bare and conversion coated steel samples are shown in Table 2. The bonding strengths were approximately 5.24, 6.04 and 5.44 MPa for ZrO_2 /silane

pretreatment at pH = 2, 4 and 6, respectively while the result for bare steel was about 3.04 MPa. It was seen that the pretreatment with ZrO₂/silane improves the adhesion of the coating by about 1.7 to 2 times compared to without pretreatment. This was due to the ZrO₂ film was firmly precipitated to the steel substrate and thanks to the couple agent of silane. The conversion coating includes metal oxides which could cause a very strong electrostatic attraction between the polar groups of the paint and the pretreated metal surface [9]. Under better conditions to form the coating as discussed in Table 1, the adhesions were also higher, respectively. At solution pH = 4, the highest adhesion to the treated sample was probably due to the best ZrO₂ film formation, which also produced the best ZrO₂/silane film.

Table 2. The results of adhesion test with pull-off method.

Parameters	untreated	pH = 2	pH = 4	pH = 6
Bond strength values (MPa)	3.04 ± 0.23	5.24 ± 0.36	6.04 ± 0.59	5.44 ± 0.41

3.3. Corrosion performance of organic coated samples

EIS studies were conducted to compare the corrosion protection behavior of full paints with pretreatment by ZrO₂/silane conversion coatings at pH = 2, 4, and 6. The samples were exposed to a 3.5 % NaCl solution and periodically tested for 90 days. The EIS spectra from the first day of immersion are shown in Figure 4a. The presence of typical semicircles in the Nyquist plot of the impedance data indicated the presence of electrochemical reactions and showed that the paint system was very protective. As we know, the diameter of the arc can be viewed as the total resistance of full coating. It was shown that treated samples exhibited significantly higher durability than untreated sample. The best corrosion performance was gained with sample pretreated in pH 4 solution. The best anti-corrosive ZrO₂/silane conversion coating effect and highest adhesion bonding could explain for this result. The impedance data at immersion time of 60 days for samples are presented in Figure 4b. The low frequency impedance values of the all treated samples were decline, but different. Sample treated at pH = 4 was decreased of about 1.75 times while samples treated at pH = 2 or 6 were decreased approximately by 3 times. On the other hand, the impedance spectra of untreated sample showed that, corrosion had occurred on the steel substrate.

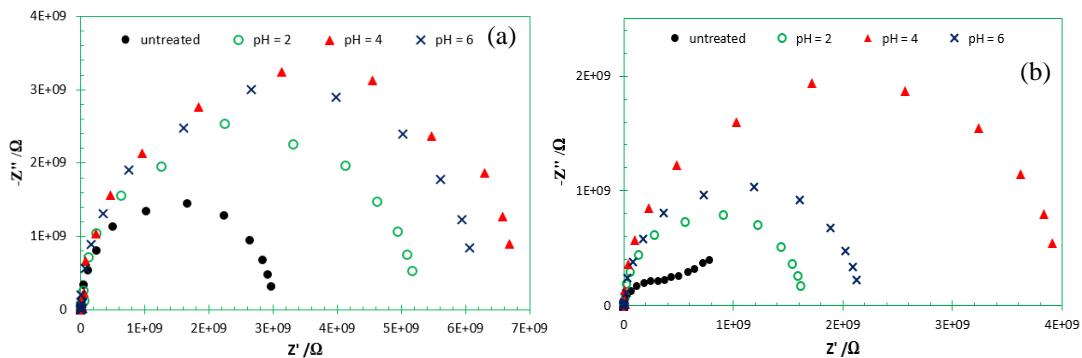


Figure 4. Nyquist plots of samples without (●) and with pretreatment at solution pH = 2 (○), 4 (△), 6 (×).

Impedance module of coating system at low frequency ($|Z|_{10\text{mHz}}$) is believed to be an appropriate indication of coating total resistance [9]. In other words, $|Z|_{10\text{mHz}}$ characterizes

corrosion resistance of full paint against the immersion time. The trend of $|Z|_{10\text{mHz}}$ values of the samples is shown in Figure 5.

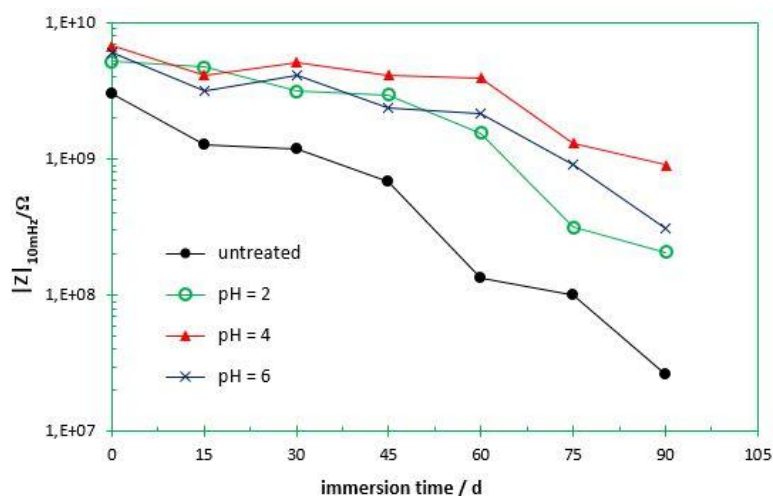


Figure 5. Trends of impedance magnitude $|Z|$ at 10 mHz for fully painted steel samples.

It can be seen that total impedance attenuation was greatest for untreated sample and minimal for sample treated at pH = 4, which compared with samples treated at pH = 2 or 6. After 90 days in saline, the impedance magnitude of untreated samples were reduced about 100 times while the treated samples at pH = 2, 4 and 6 were reduced by 25, 7.5 and 20 times, respectively. This indicates the penetration of the water and ionic species from the electrolyte into coatings. Different degree of decline might be associated with the surface properties of the treated steel. The pretreatment, which gave higher corrosion resistance and higher adhesion, would improve better corrosion performance in an organic coated system. This result proves that $\text{ZrO}_2/\text{silane}$ conversion coating pretreatment does not only enhance the coating performance but also maintain its higher durability.

4. CONCLUSIONS

Steel surface pretreatment in silane doped hexafluorozirconic acid solution has been investigated with optimizing solution pH. Surface morphology was uniform and compact with treatment at pH = 4. From the EIS results and potentiodynamic polarization tests it was deduced that the surface pretreated at pH = 4 had better corrosion resistance than that at pH = 2 or 6. Pull off testing indicated that the adhesion between the treated steel substrate and the organic coating was improved by 1.7 to 2 times compared to without treatment. EIS results of samples revealed that $\text{ZrO}_2/\text{silane}$ pretreatment can improve long time corrosion performance of fully coated systems.

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