CORROSION PROTECTION OF CARBON STEEL USING ZIRCONIUM OXIDE/SILANE PRETREATMENT AND POWDER COATING

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Abstract. A new generation of metal pretreatments based on nanosized zirconium oxide or ogranosilane film has been investigated recently as an alternative method to phosphatation. In this paper, ZrO_2/silane composite film on carbon steel was prepared and characterized by field emission scanning electron microscopy, energy dispersive X-ray spectrum and electrochemical measurements. The effect of ZrO_2/silane surface treatment on the corrosion protection properties of powder coating was studied by spraying salt and adhesion measurement. The results showed that ZrO_2 was rapidly precipitated on the steel surface in the first minute of immersion. ZrO_2/silane film was formed after 4 minutes of immersion and gave the best protective property. Powder coating on carbon steel with ZrO_2/silane pretreatment had equivalent protection performance like the powder coating with phosphate pretreatment. Besides of this, higher dryness and better wet adhesive value of ZrO_2/silane pretreatment were comparable to those of phosphate pretreatment.

Keywords: pretreatment, zirconium oxide/silane composite film, adhesion, salt spraying test.

Classification numbers: 2.4.4, 2.5.2, 2.5.3.

1. INTRODUCTION

Surface pretreatment of the steel substrate before painting has significant effect on coating adhesion and corrosion protection performance. Phosphate conversion coatings are the most commonly methods used in surface pretreatments for ferrous and non-ferrous metals [1]. However, phosphate conversion coatings are gradually replaced by various alternatives because

of several drawbacks from environmental, energy and process standpoints [1]. A promising emerging pretreatment technique is one of potential replacements for phosphating and one of them is the application of zirconium oxide on the surface by the sol-gel method or immersion in a hexafluorozirconic acid (H_2ZrF_6) solution [2–6]. Besides this, organosilanes are widely used by surface pretreatment to improve the adhesion of organic coatings [7–10].

A number of researches have studied the use of additives and treatment conditions to improve the protection properties of ZrO_2 conversion coatings [3, 5, 11]. The best ZrO_2 conversion films on steel substrate were obtained by the solution pH of 4 and 4.5. The thickness and quality of the films depended on concentration of solution and immersion time [3,11]. The anti-corrosion performance and microstructure of the nanoceramic reinforced ZrO_2 coatings on cold-rolled steel substrates were studied and the results showed that the immersion time and treatment temperature were strongly affected by the microstructure and corrosion resistance of the conversion coatings [3]. Presence of $MnSO_4$ at low concentration improved the corrosion performance of zirconium conversion coatings, but the adhesion of organic coating was decreased by applying on treated surface [12].

Hot-dip galvanized steel panels were treated by a zirconium nitrate/organosilane solution [13]. The distribution of silane over the surface was dependent on the type of used silane. The corrosion resistance of galvanized steel substrates was pre-treated by silane doped with zirconium nitrate [14, 15]. The presence of zirconium nitrate decreased porosity and conductivity of coating and increased thickness of coating, therefore the silane coating improved the barrier properties. In our previous work, carbon steel substrates were pretreated in H_2ZrF_6/silane solutions, at pH 4 and immersion time about 4 minutes [16]. Electrochemical impedance spectroscopy (EIS) results showed that the highest corrosion resistance was obtained by the sample treatment with solution at Zr and silane concentration of 50 ppm and 0.025 % (w/w), respectively. Energy dispersive X-ray spectrum (EDS) and Fourier transform infrared spectroscopy proved the presence of zirconium (about 2.05 %) and silicon (about 0.76 %) in the coating layer.

In this study, the electrochemical behavior of carbon steel surface treated in H_2ZrF_6/silane solution was investigated. The impact of immersion time on the morphology and the composition of ZrO_2/silane film was evaluated and the effect of ZrO_2/silane pretreatment on corrosion protection of powder coating was studied.

2. EXPERIMENTAL

2.1. Chemicals

Carbon steel was used by substrate with following compositions in wt%: C-0.1; Al-0.75; Si-0.19; Cu-2.11 and Fe. Zirconium fluoride (ZrF_4) was purchased from Sigma. Aminopropyl-triethoxy-silane (APS) was purchased from Merck. Na_2CO_3, NaOH were purchased from China. Zn-phosphate (ZCR-588) was purchased from Viet Quang company (Vietnam). Powder polyester coating was purchased from Akzonobel.

2.2. Fabrication of ZrO_2/silane film and zinc phosphate film on steel substrate

Hexafluorozirconic acid solution (H_2ZrF_6), containing 50 ppm Zr^{4+} was prepared by dissoluting ZrF_4 in HF with distilled water. APS was added to H_2ZrF_6 with silane concentration of 0.025 %. The pH of treatment solutions was adjusted to 4±0.05 by 0.1 % NaOH solution.

Carbon steel sheets ($100 \times 75 \times 1$ mm) were abraded with SiC polishing paper, cleaned by distilled water and ethanol. After that, the sheets were immersed in hexafluorozirconic acid solution by variable times between 1 and 6 minutes, cleaned by distilled water and dried in hot air (70 ± 3 ^{o}C) [17].

For phosphate treatment, the samples after polished and cleaned were immersed in 5 % zinc phosphate solution with 0.02 % accelerator for 20 minute, cleaned by distilled water and dried in hot air.

2.3. Preparation of powder coating

Powder coating was applied on the untreated and treated steel surface by spraying method. The coatings were dried at 190 ^{o}C for 10 min. The thickness of coatings was 60 ± 5 µm.

2.4. Characterization of conversion film

For open circuit potential (OCP) measurement a three-electrode cell was used by a platinum auxiliary electrode and a saturated calomel reference electrode (SCE). A working electrode was carbon steel immersed in H_2ZrF_6/silane solution. The measurement was performed by using an Autolab PGSTAT 204N device. The morphology and composition of ZrO_2/silane conversion film were investigated by field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray spectrum (EDS) on a Jeol 7401F device.

2.5. Adhesion test

The adhesion strength of the coatings was determined according to ASTM D4541 by a PosiTest digital Pull-Off adhesion tester (DeFelsko) with 20 mm dollies. The measurements were conducted before (dry pull-off strength) and after every 15 days immersed in the 3.5 % NaCl solution. The experiments involved pulling dollies affixed with a 2-part AralditTM Epoxy adhesive away from the coated substrate. The maximum force by which the dolly lifts the coating from the steel plate was recorded as a measure of the bond strength between the coating and the substrate. All tests were repeated three times to ensure the measurements repeatability.

2.6. Salt spraying test

Corrosion resistance of powder coatings was investigated by the salt spraying test used Q-FOG CCT 600 chamber according to ASTM D1654. The samples were scratched before tested. Two cuts were made in the film with each about 50 mm long that intersects were near their middle with an angle of approximately 45°. Three samples of each system were tested.

3. RESULTS AND DISCUSSION

3.1. Study on the formation of ZrO_2/silane film

3.1.1. Electrochemical behavior of the steel sample in treatment solution

The variation of OCP of steel sample in the H_2ZrF_6/silane solution is presented in Fig. 1. It was observed that the OCP of steel electrode was moved toward more positive values during first 4 minutes of immersion, then the OCP of electrode was stable with immersion time. This

result can be explained by the formation of ZrO$_2$/silane film on the steel surface [15]. The ZrO$_2$/silane film was formed rapidly during first 4 minntes of immersion and was stable for up to 6 minutes. By this time, the ZrO$_2$/silane film was probably covered by the whole steel surface, therefore the properties of the ZrO$_2$/silane film did not change.
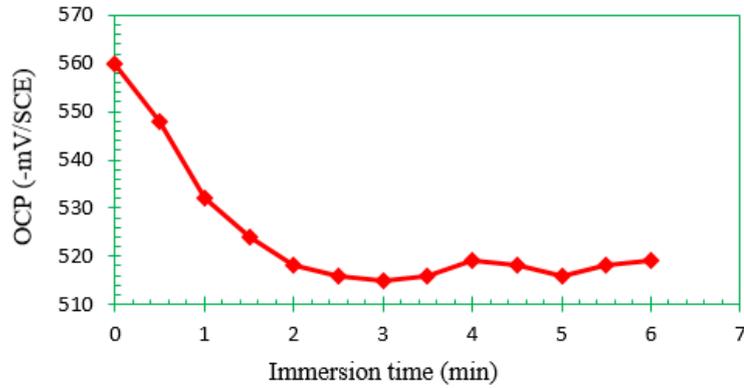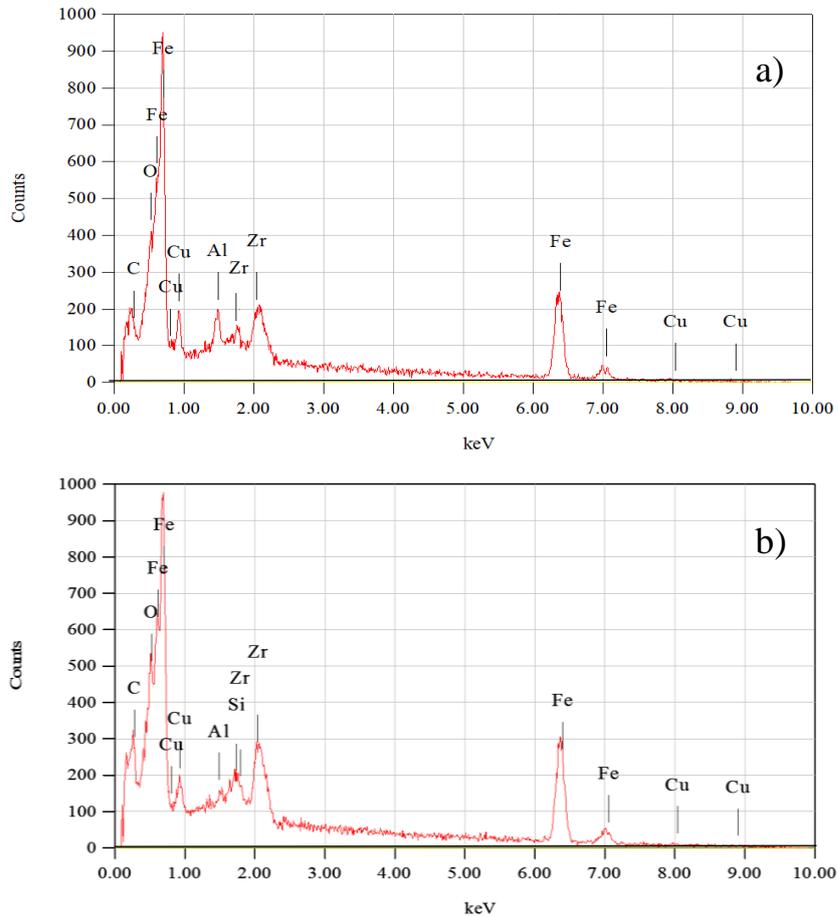

Figure 1. Variation of OCP with immersion time.

Figure 2. EDS spectrum of steel surface after first 4 minutes of immersion in H$_2$ZrF$_6$ solution (a) and in H$_2$ZrF$_6$/silane solution (b).

3.1.2.Composition and morphology of conversion coating

Figure 2 shows the EDS spectrum of the steel surface after 4 minutes of immersion in H_2ZrF_6 solution and H_2ZrF_6/silane solution. The spectrum was observed the presence of Zr and Si in the conversion film for H_2ZrF_6/silane solution and the presence of Zr for H_2ZrF_6 solution. The increase of the Zr concentration together with the O amount in the film suggested that Zr was mainly present in the form of oxide/hydroxide. The results proved that most of the Zrs were present by the form of ZrO_2 [18]. T. Lostak et al. used various electrochemical and surface analytical methods to investigate the chemical composition of Zr-based layer. The results showed that the main component was ZrO_2 [19]. This result demonstrated the formation of zirconium oxide and silane on conversion film [16]. High peaks were detected and most of which were the substrates because the coating was very thin [2]. In addition, some aluminium and copper were detected with small peaks. This can be explained by the substrate inclusion [2].

The variation of Zr and Si contents in the conversion film with immersion time is shown in Figure 3. The formation of ZrO_2 on steel surface was very fast, while the formation silane was very slow in a first minute. When the steel surface was immersed in H_2ZrF_6/silane solution, the electrochemical reaction occurred. Metal was oxidized and dissolved into solution by the anode reaction ($Me \rightarrow Me^{2+} + 2e$). H^+ ion was reduced by the cathodic reaction and leaded to the increase of pH on the metal surface ($2H^+ + 2e \rightarrow H_2\uparrow$). As a result, H_2ZrF_6 was hydrated to ZrO_2 on the metal surface by electrochemical reaction [3]:

$$H_2ZrF_6 + Fe + 2H_2O \rightarrow ZrO_2\downarrow + 4H^+ + 6F^- + H_2\uparrow \tag{1}$$
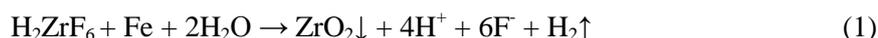
The rapid electrochemical reaction to form ZrO_2 at the initial stage inhibited formation of silane film on the metal surface. The thicker ZrO_2 film became, the easier electrochemical reaction slowed down and the formation of covalent bonds between the silane and the metal surface became [7]:

$$Me\text{-}O\text{-}H + H\text{-}O\text{-}Si \leftrightarrow Me\text{-}O\text{-}Si + H_2O \tag{2}$$

$$Si\text{-}O\text{-}H + H\text{-}O\text{-}Si \leftrightarrow Si\text{-}O\text{-}Si + H_2O \tag{3}$$

when the immersion time was increased from 1 min to 4 mins, the presence of Zr and Si proved that ZrO_2/silane film was formed on steel surface [16]. After 4 mins of immersion, the Si content increased gradually but the Zr content did not nearly change. This indicated that the formation of ZrO_2 was almost unchanged and silane film increased continuously until 6 minutes of immersion.
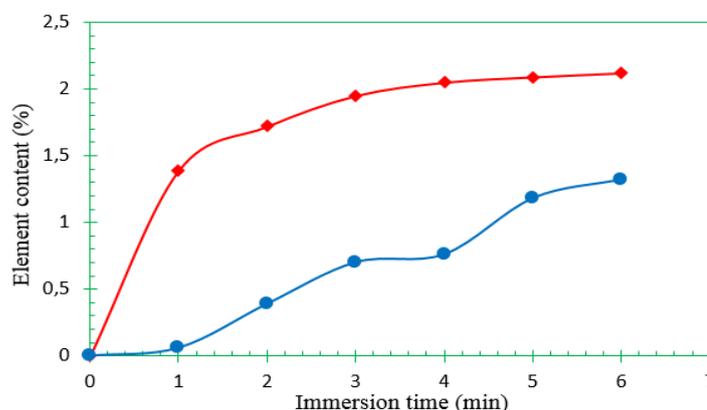

Figure 3. Variation of Zr (♦) and Si (●) content in the conversion film with immersion time.

Figure 4 shows FE-SEM images of ZrO_2/silane film after different immersion times and ZrO_2 film after 4 minutes of immersion. It was observed that ZrO_2/silane film was more homogenous and compact than ZrO_2 film after 4 minutes of immersion (Fig 4b,d). This may be explained by the competition in the process of coating formation, which silane was tended to concentrate around ZrO_2- rich islands along the surface [13]. This result is consistent with the conclusion of Trabelsi W. et al, in which the surface morphology of galvanised substrates were pretreated with silane solutions doped with zirconium nitrate [15].
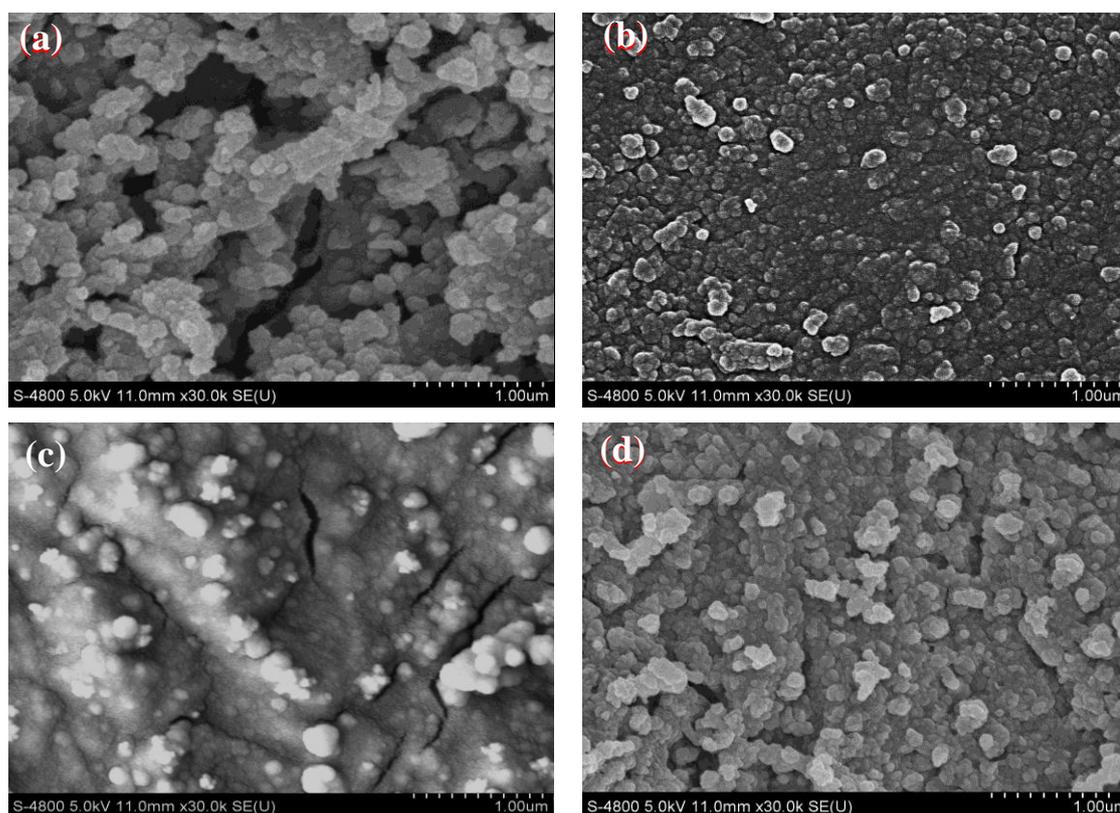

Figure 4. FE-SEM images steel surface after different immersion time in H_2ZrF_6/silane solution:
1 min (a), 4 min (b), 6 min (c) and after 4 mins of immersion in H_2ZrF_6 solution (d).

Figure 4a also indicates that the ZrO_2/silane structure was not compact after a minute of immersion. This time, the film had been formed on the steel subtrate. The film was consisted mostly of ZrO_2 but very little of Si (as data from Figure 3). Therefore the surface morphology in Figure 4a is similar to that in Figure 4d (only ZrO_2) although it is more porous and incomplete. After 6 minutes of immersion, as discussed above, silane was formed except ZrO_2. Therefore the surface morphology is more characteristic of silane (Fig. 4c). The crack formed in the film can be caused by non-uniform film thickness or the dehydration of conversion coating after drying [3].

3.2. Performance of powder coatings on steel surface treated with H_2ZrF_6/silane solution

Powder coatings were applied on steel surface with ZrO_2/silane conversion film, ZrO_2 conversion film and phosphate treatment. The immersion time was 4 minutes. The performance of full coatings was evaluated by adhesion measurement and salt spraying test.

3.2.1.Adhesion testing

Adhesion strength of powder coatings immersed by 3.5 % NaCl solution was depicted in Figure 5. The adhesion strengths of coatings before immersed in NaCl solution were different. The dry adhesion of coating layer of treatment on surface treated with ZrO_2 was higher than that of without treatment but lower than that of treatment with ZrO_2/silane and phosphate treatment. The highest adhesion was obtained by the coating with ZrO_2/silane treatment.
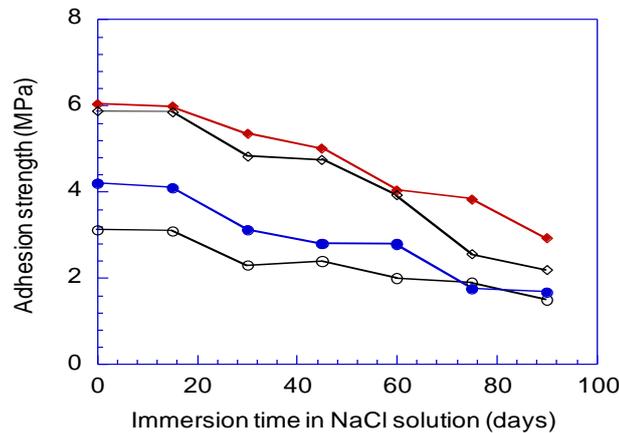

Figure 5. The variation of adhesion strength of powder coating on carbon steel without (o) treatment, with (●) ZrO_2 treatment, with (♦) ZrO_2/silane treatment and with (◊) zinc phosphate treatment during immersion time in NaCl solution.

After 14 days of immersion, the values of adhesion strengths of all coatings were nearly the same. When the immersion time was increased from 14 days to 90 days, the adhesion strengths of all coatings were decreased dramatically. However, the adhesion strength of sample with ZrO_2/silane treatment remained about 3 MPa and was higher than that of other samples. This result indicated that the presence of silane enhanced the effect of ZrO_2 treatment on the adhesion of powder coating. The adhesion of ZrO_2/silane treatment was higher than that of zinc phosphate treatment.

3.2.2.Salt spray test

Figure 6 presents images of coating samples after 400 hours exposed to salt spraying test. The determinations of rust creep from scratch of coatings and rating numbers were presented in Table 1.

Table 1. Corrosions at scratches of coatings after 400 h exposed to salt spraying test.

No.	Samples	Rust creep from scribe	Rating number
1	Powder coating without treatment	2.04 mm	6
2	Powder coating with ZrO_2 treatment	1.47 mm	7
3	Powder coating with ZrO_2/silane treatment	0.89 mm	8
4	Powder coating with zinc phosphate treatment	0.94 mm	8

Table 1 shows that the rust creeps of powder coatings with ZrO_2/silane treatment and zinc

phosphate treatment were lower than that of powder coatings without treatment or with ZrO_2 treatment. The rating numbers of powder coatings with ZrO_2/silane treatment and zinc phosphate treatment were 8 while that of powder coating with ZrO_2 treatment and without treatment were 7 and 6, respectively. The results showed that the ZrO_2/silane treatment enhanced corrosion resistance of powder coatings on steel surface.
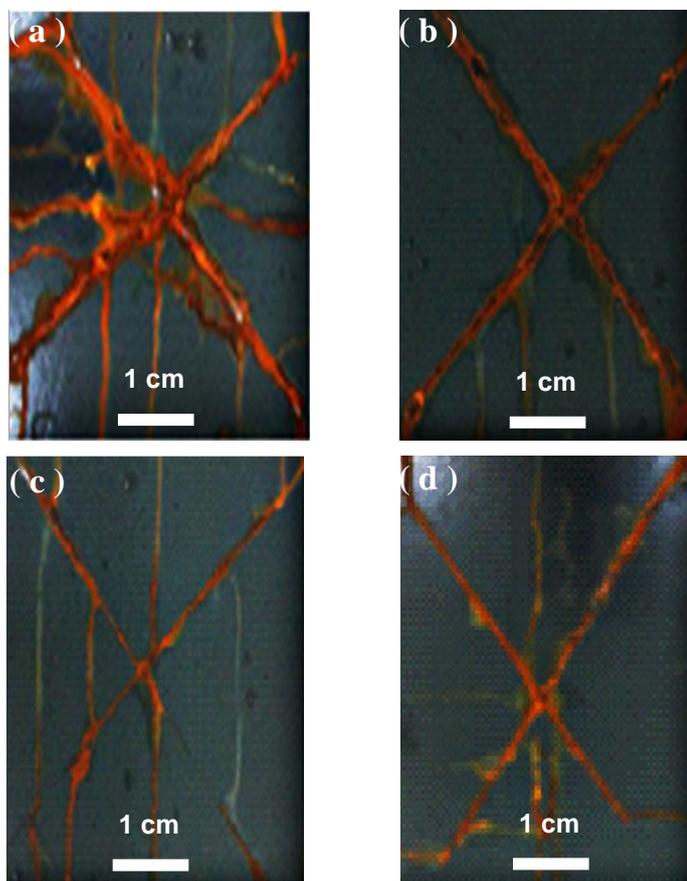

Figure 6. Images of powder coating on steel without treatment (a), with ZrO_2 treatment (b), with ZrO_2/silane treatment (c) and with zinc phosphate treatment (d) after 400 h exposed to salt spraying test.

4. CONCLUSIONS

The ZrO_2/silane composite film with predominant content of ZrO_2 was formed on steel surface during a first minute of immersion. The best ZrO_2/silane conversion film was formed after 4 minutes of immersion. The presence of silane enhanced surface morphology of ZrO_2 conversion film. The effect of ZrO_2/silane treatment of both of dry and wet adhesion of powder coating was higher for than that of zinc phosphate treatment. Moreover, protection performance of powder coating on steel substrate with ZrO_2/silane pretreatment was slightly higher than that of powder coating on steel with zinc phosphate pretreatment.

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