Corrosion Resistance Improvement of Galvanised Steel by Doped Silane Pre-Treatments

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ABSTRACT: In this paper, galvanised steel substrates were pre-treated in γ-(2,3-epoxypropoxy) propytrimethoxy silane solutions containing salts ((NH4)2TiF6, K2ZrF6 and NaVO3) and SiO2. The surface microstructures of the coated substrates were evaluated by scanning electron microscopy (SEM). The anti-corrosion performance of the modified silane film applied on galvanised steel substrates was evaluated by potentiodynamic polarization (Tafel) and electrochemical impedance spectroscopy (EIS). The electrochemical results revealed that the addition of salts ( (NH4)2TiF6, K2ZrF6 and NaVO3) may produced a more stable and protective fluoride combined with their oxides in the silane layer. The results also revealed that the addition of the SiO2 nanoparticles reinforces the barrier properties of the silane films and imparts its corrosion inhibition ability.

1. INTRODUCTION

Different additives have been used in the modification of silane films for improvement of their anti-corrosion properties in literatures (Shchukin, 2004, Kasten, 2006, Liu, 2006 Phani, 2005 and Pepe, 2001). Corrosion inhibitors, nanoparticle fillers, are doped into the silane coatings to enhance their corrosion resistant performance.

The modification of silane films with rare earth and nanoparticles has been successfully investigated (Palanivel, 2003, Ferreira, 2004, Behzadnasab, 2011, Palomino, 2007 and Montemor 2009), but the modification of silane film with nanopartiles and the salts like (NH4)2TiF6, K2ZrF6 or NaVO3 has not been reported. This work investigated properties of the surface film prepared by the solution with the addition of (NH4)2TiF6, K2ZrF6, NaVO3 and SiO2 nanoparticles combined with silane. Different combinations of the additives were tested and their effects on the corrosion resistance of silane film was analyzed.
2. EXPERIMENTAL DETAILS

The \(\gamma\)-(2,3-epoxypropoxy)propytrimethoxy silane (Sinoreagent product) solutions were prepared by dissolving 10\% (v/v) of silane in methanol (22.5\%, v/v) and deionized water (67.5\%, v/v). The silane solution was stirred for 1 h and was kept for 24 hours before use.

The silica nanoparticles (purity \(\geq\)99.8\% and an average diameter of 30–40 nm, were ultrasonically dispersed in electrolyte solution solutions (0.072 wt.% \((\text{NH}_4)_2\text{TiF}_6\), 0.02 wt.% \(\text{K}_2\text{ZrF}_6\) and 0.075 wt.% \(\text{NaVO}_3\)) and the concentration of nano SiO\(_2\) was controlled in 250 ppm. Then this aqueous dispersion the preparation of the silane solution as the ratio of 1: x. Furthermore, doped silane solution only with inorganic salt but without SiO\(_2\) nanoparticles also prepared.

3. RESULTS AND DISCUSSION

The barrier properties of the silane films applied on galvanised steel substrates was Evaluated via EIS and polarization curves in 3.5 wt.% NaCl solution. EIS is a powerful and non-destructive electrochemical technique to affirm electrochemical reactions and investigating corrosion behaviors at the electrode/electrolyte interface. As showed in Figure 1.a, the impedance of silane film shows one order of magnitude increase to blank galvanized steel, and the impedance of doped silane films show bigger impedance than undoped silane films. The impedance value increases in the order blank galvanized steel < silane < silane+salts < silane+salts+SiO\(_2\). What’s more, the phase angle curve for all specimens originates the presence of a new time constant at higher frequencies (showed in Figure 1.b), which describes the behavior of a protective barrier formed on the surface of the substrates. It may be contributed by oxidation film formed on the surface of galvanized steel specimen in NaCl salt solution.

Figure 1. EIS Bode plots obtained on the different specimens during immersion in 3.5\% NaCl solution.
The corrosion behavior of coating can also be studied by polarization curves in corrosive media that yield specific data on the behavior of the coating system. Figure 2 shows the polarization curves of galvanized steel and silane film specimens in 3.5 wt.% NaCl solution. It is obvious see from Figure 2 that silane films specimens have lower corrosion current density compare with galvanized steel specimens, indicating silane films contribute strongly on the corrosion barrier.
Moreover, it is evident that the doped silane films show a better corrosion resistance than undoped silane film.

The microstructures of different specimens after polarization test were showed in Figure 3. Figure 3.(a) shows that the surface of galvanized steel formed an argenteous layer after polarization test, it’s may formed by the oxide of zinc, but the zinc oxide layer may not enough compact to prevent further corrosion. Figure 3.(b) shows that the silane film are partly fall off the substrate and deposit on the film surface, and the small rounded protuberances on the galvanized steel surface were disappeared during corrosion process by polarization test. Figure 3.(c) is the microstructure of silane film modified with salts after polarization test in 3.5 wt% NaCl, the microstructure of the layer is uniform and compact. From Figure 3.(d) it can see that the distribution of SiO$_2$ nanoparticles on the film surface are more dispersed than Figure 3.(c), and this may contribute to the higher compactness of doped silane layer.

In this work, the electrochemical results indicated that the addition of salts ((NH$_4$)$_2$TiF$_6$, K$_2$ZrF$_6$ and NaVO$_3$) may produced a more stable and protective fluoride combined with their oxides in the silane layer, and they are highly effective in the inhibition of the corrosion processes starting at defects. The addition of SiO$_2$ nanoparticles can combine with the formation of -Si-O-Si-, it may improve the structural strength and reduce the porosity of the silane layer producing a more stable and protective layer.

4. CONCLUSIONS

1. The addition of salts ((NH$_4$)$_2$TiF$_6$, K$_2$ZrF$_6$ and NaVO$_3$) to silane film has marked effects on the corrosion activity. These salts may produce a more stable and protective fluoride combined with their oxides in the silane layer, and they are highly effective in the inhibition of the corrosion processes starting at defects.
2. The addition of salts and SiO$_2$ can improve the density of silane layer, lower amount of free chlorides available for disruption of this protective film.

ACKNOWLEDGEMENTS

This paper is financially supported by Project of Coordinative Innovation for Manufacturing-Studying-Research of Nantong Municipal (No.BC2014010), the Natural Science Foundation of China 50571059 and 50615024 and the State Key Laboratory of Development and Application Technology of Automotive Steel (Bao. Steel).
REFERENCES


