Evaluating the anti-corrosion behavior of hybrid zirconium-polyethyleneimine layer by mean of electrochemical method

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Abstract. Zirconia conversion coating as an eco-friendly treatment technology is the most promising method of replacing traditional phosphating technology. A new kind of zirconia/polyethyleneimine composite coating was fabricated on carbon steel. Potentiodynamic polarization, electrochemical impedance spectroscopy and salt spray test analyses were used to evaluate the corrosion behavior of samples in 3.5wt% NaCl solution. Scanning electron microscope was used to characterize the surface morphology of the samples. Results showed that zirconia coating after polyethyleneimine (PEI) treatment generated a protective layer through combination of physisorption and chemisorption, which enabled the new composite coating to perform much better than single zirconia coating. The zirconium-polyethyleneimine layer demonstrated the best anti-corrosion performance with the lowest corrosion current and highest polarization resistance. Overall, this study established a promising anticorrosion method involving the production of zirconia coating as an interlayer prior to forming PEI coating on a substrate.

1. Introduction

Pretreatment as a key process of corrosion protection directly effects the anti-corrosion resistance and adhesion of steel substrate with coating. The phosphating technology was commonly used to improve the coating’s adhesion in the past, due to high corrosion resistance and cost-effectiveness, which was widely popular in the fields of automobile, ship, aerospace and others[1-4]. However, phosphating technology could lead eutrophication of the freshwater lakes and reservoir. Phosphate-rich waste water was also harmful to groundwater. Hence, phosphating replacing process of coating pretreatment was focus of attention[5-7].

Pretreatment technology with the hexafluorozirconic acid solution seems like a promising phosphating replacing process, zirconium-based conversion coating have excellent anti-corrosion resistance[5,8-13]. In comparison with the traditional phosphating technology, zirconium treatment technology simplifies the production process significantly, and reduces energy consumption and environmental pollution[14-19]. Zirconium-based conversion coating is prone to rust for long stay in the air, due to the nature of thin coating along with micro-cracks. Use of zirconium-based coating is greatly limited for the flash rust of steel work. Further, treatment is indispensable for a single zirconium-based coating, which prevents flash rust during temporary storage[14,18].

In various pretreatment technologies, polymer coating is a simple and effective method to restrain the substrate from rapid corrosion[20-23]. Specifically, organic molecules can adsorb on the metal surface and form a protective layer. Owing to the multiple adsorption sites, the adsorption of the polymer compound
is stronger than the monomer substance\cite{24,25}. Polymer has been used frequently in zirconium-based coatings in order to further elevate the quality of coating, adding polymer in zirconium-based coating enhanced anti-corrosion property, especially when flaws occurred through the film.

Gao\cite{26} investigated the corrosion inhibition property of quaternized PEI (QPEI) for low carbon steel in sulfuric acid and inhibition mechanism. It was found that QPEI possessed excellent corrosion inhibition action. QPEI could form a protective layer on the surface of low carbon steel with physisorptions and chemisorptions. Schweinsberg\cite{27} employed potentiodynamic and in situ surface-enhanced Raman scattering (SERS) techniques to study the adsorption and inhibitive effects of polyvinylpyrrolidone (PVP) and polyethylenimine (PEI) on copper in H2SO4 at 30 °C. It confirmed that the adsorption between steel and PEI was most probably caused by nitrogen atoms. Niknahad\cite{28} has studied the effect of mixture of hexafluorozirconic-acid (Zr), polyacrylic-acid (PAA) and polyacrylamide (PAM) pretreatment on the properties of aluminium substrate. It displayed that the corrosion protection performance of the PAA/PAM/Zr pretreatment improved dramatically compared to the PAA/Zr treatment. Finsgar\cite{25} studied the effect of PEI as a corrosion inhibitor on ASTM 420 stainless steel in 3 wt% NaCl solution. A dense PEI layer not only hold back the diffusion of ionic species from the film effectively, but also protect substrate from destructing by chlorine from the salt water. PEI as a nice corrosion inhibitor could reduce the corrosion of low carbon steel in a broad range of phosphoric acid solutions. Both polymers delay corrosion rate of the anode and cathode, especially for anodic reactions\cite{29}. In brief, PEI as an inhibitor could enhance the anti-corrosion resistance of metal.

In this paper, PEI was used to further enhance the corrosion resistance of zirconium-based coating. The hybrid coatings of Zr and PEI were fabricated, and its anti-corrosion behavior was investigated by means of electrochemical methods. Zirconium-based conversion coating using PEI pretreatment obviously enhanced the anti-corrosion resistance. The hybrid coatings of Zr and PEI seems like a promising phosphating replacing process.

2. Experiment procedure

2.1 Experiment materials
The substrate material is Q235 steel sheet, which was cut into a dimension of 5 cm×5 cm. Then Q235 steel sheet was degreased with the mixture solution of Na2CO3 and Na3PO4. All of grease was removed from the substrate surface, then substrate sheets were cleaned with distilled water and proceed to next step.

2.2 Specimens preparation
Zirconium-based conversion coating was prepared by dipping in 0.5 ‰ hexafluorozirconic acid solution at 30 °C for 15 min, ammonia was used to adjust pH 4.6. The solution of 0.3 wt.% PEI was chosen to fabricated PEI coating. The hybrid PEI/Zr coatings were fabricated in turn, firstly immersed in PEI solution for 5 min and following in hexafluorozirconic acid solution for 15 min. Afterwards, the hybrid Zr/PEI coatings was obtained by dipping in turn, in hexafluorozirconic acid solution for 15 min and in PEI solution for 5 min. Finally, the coating was cleaned by distilled water and dried naturally. The procedure for preparing both kinds of composite coatings is illustrated in figure 1.
2.3. Scanning electron microscopes (SEM)

The morphology of coatings were characterized using a scanning electron microscope. The scanning voltage of electron gun was 5 kV and the current was about 40 mA.

2.4. Electrochemical test

Electrochemical corrosion property was investigated using an electrochemical workstation (Corrtest CS350). Corrosion resistance of coatings was evaluated by means of potentiodynamic polarization tests and electrochemical impedance spectrum. All electrochemical tests were measured by three electrodes system in 3.5 wt % NaCl solution at room temperature, which was consisted of a saturated calomel electrode as reference, a platinum-wire electrode as counter electrode and a working electrode, the conversion coating on carbon steel as working electrode with an exposed surface of 1 cm² to contact the electrolyte solution. The working electrode was immersed in the test solution until the system open circuit potential was stable before measurement. EIS measurements were carried out from 100 kHz to 10 mHz, accompanying 5 mV amplitude perturbation. EIS data were presented as Nyquist plots. The plot fitting was implemented using ZSimpWin software. All dynamic potential scanning experiments were set at the relatively open circuit potential of plus or minus 1 V at scanning velocity of 5 mV·s⁻¹. All of tests were performed in the same condition.

3. Results and discussions

3.1. Morphology of the coatings

The morphology of the coating of PEI, Zr, PEI/Zr and Zr/PEI was characterized using the SEM. The micrographs were shown in figure 2. The exposed micro-cracks could be obviously observed in the picture of Zr coating. The PEI coating is a thin layer of organic film along with tiny cracks. The PEI/Zr coating and Zr/PEI coating presented uniform layer on the surface, no crack was presented, which might act as a barrier to retard corrosion substances from penetrating into matrix. The hybrid coatings provide a tight protective layer on the steel sheet.
3.2. Polarization curves and EIS measurement

Figure 3 indicates Nyquist plots and Bode plot of PEI coating, Zr coating, PEI/Zr coating, and Zr/PEI coating. The appearance of the coatings in the Nyquist plots consisted mainly of capacitive loop, which manifests that a double layer existed between the coating and electrolyte interface. Electrochemical process was demonstrated in the semicircle of high-frequency region which exposed the coating property generally. Meanwhile, the semicircle in the low-frequency region involved with mass transport processes disclosing the information between the coating and the substrate interface[6,30].

The Nyquist plot of Zr coating had a diffusive character in the low-frequency region as shown in figure 3a. This finding indicated that Zr coating underwent a diffusive process, which was probably attributed to trifle corrosion medium penetrating the interface of the coating. The Nyquist plot of PEI coating presented the appearance of a shrink tail in the low-frequency region, which show that the electrolyte penetrated into the defects of PEI coating. At this stage, the dissolution rate of the coating increased by mean of adsorbed chloride ions, and the layer became thinner, that resulted in increased anodic polarization current density, Subsequently, the ions from coating quickly entered the solution[13,31]. These findings were probably attributed to the coating defect.

According to the principle of impedance, the corrosion resistance is proportional to the diameter of
a semicircle in the Nyquist plots\cite{24,32}. In this work, the radius of the impedance spectrum increased, showing that the conduction of resistance charge increased, the corrosion rate decreased, and the corrosion resistance of coating was superior\cite{6}. The corresponding Bode plots displayed in the figure 3b were consistent with the results of the Nyquist plots. With reference to the Bode plot, two time constants can be observed clearly in PEI coating. The second time constant occurred, because the corrosive media tend to extend inward to the substrate/coating interface through the crack.

The corresponding mathematical physical model was determined according to the characteristics of impedance spectrum and related electrochemical experience. The least square method was used to fit the established model with ZSimpWin software, and the parameter values of each equivalent element in the mathematical model were obtained. The corresponding equivalent circuit is shown in figure 4. The maximum error in the simulated data is less than 10\% for both \( Z' \) and \( Z'' \). However, the frequency response characteristics of the double layer capacitors of all specimens were mismatched with the pure capacitance due to surface roughness, active sites, and inhomogeneous solids. This phenomenon is called the dispersion effect. Therefore, the capacitance C is always replaced by a constant phase element (CPE), which is expressed as following\cite{11,33,34}:

\[
Z_{CPE} = \frac{1}{Y_0(j\omega)^n}
\]

Where \( Y_0 \) always takes a positive value, \( j \) is a complex operator (-1)\(^{1/2} \), \( \omega \) is the angular frequency, and \( n \) is an empirical exponent that is applied to describe the surface roughness. When \( n=1 \), CPE becomes ideal capacitor C; \( n=0 \), CPE reverts to resistance R; \( n=-1 \), CPE is an inductive L\cite{33,34}.

\( R_s \) is the resistance between working and reference electrode. \( Q \) represents capacitance of the coating. \( R_{ct} \) is the transfer resistance. In terms of bare metal, when the frequency is close to zero, the \( R_p \) value can be defined as the intercept of the experimental impedance data along with the real axis of the Nyquist plot. The value of the \( R_{ct} \) is the diameter of the Nyquist semicircle along the real axis for a simple circuit. In the simplest case, these two values can be considered identical\cite{35}.

Polarization resistance values obtained from EIS are summarized in table 1. The corrosion resistance was determined using the diameter of semicircle. The improvement in impedance was observed in the case of coupons with PEI treatments. The zirconium specimen coated with PEI coating showed the best anticorrosion property in contrast with other specimens, which provided a good protection for the substrate. This property can be attributed to the relative barrier properties of dense composite coating formed on the surface.

Figure 4. Equivalent electrical circuit used to simulate the EIS results of all coatings.
Table 1. Fitting parameters of EIS for different coatings measured in 3.5 wt.% NaCl solution.

| Sample  | $R_s/\Omega$ | $Y_0/\Omega\cdot s^n$ | $n_c$ | $R_c/\Omega$ | $Y_{dl}/\Omega\cdot s^n$ | $n_{dl}$ | $R_{ct}/\Omega$ | $\chi^2$ |
|---------|--------------|------------------------|-------|--------------|------------------------|----------|----------------|--------|
| PEI     | 1.604        | $6.125\times10^{-4}$   | 0.8218| 41.5         | $4.47\times10^{-4}$   | 0.9016   | 260.3          | 8.5$\times10^{-3}$ |
| Zr      | 3.322        | $1.836\times10^{-4}$   | 0.6383| 4.505        | $7.237\times10^{-4}$ | 0.7123   | 514            | 9.14$\times10^{-4}$ |
| PEI/Zr  | 2.912        | $9.447\times10^{-4}$   | 0.6696| 31.75        | $6.908\times10^{-4}$ | 0.6713   | 667.4          | 6.23$\times10^{-4}$ |
| Zr/PEI  | 4.134        | $2.883\times10^{-4}$   | 0.6509| 26.14        | $2.3\times10^{-4}$   | 0.804    | 732.7          | 4.07$\times10^{-4}$ |

The polarization curves were measured after impedance spectrum test. Figure 5 shows the potentiodynamic polarization curves. According to the polarization curves, the corrosion current density and corrosion rate of different specimens were fitted in the Tafel method. The electrochemical parameters of the corresponding specimens were listed in Table 2. The $E_{corr}$ values of the PEI coating, Zr coating, PEI/Zr coating and Zr/PEI coating changed, which were approximately $-0.69803$ V, $-0.67707$ V, $-0.65514$ V, and $-0.65007$ V respectively. Zr/PEI coating presented superior corrosion potential value than others. Based on the results of polarization curves, Zr/PEI coating has stronger thermodynamic stability than the others. The uniform coating acted as a barrier to inhibit the electrolyte to the substrate, led to the $E_{corr}$ toward positive side change and decreased the corrosion current. The corrosion current of the Zr/PEI coating was inferior to that of bare Zr coating. This phenomenon occurred because the composite coating adhered onto the surface and thus served as an effective barrier against the attack of chloride ions from solution. This result was consistent with that of EIS analysis. Both of potentiodynamic polarization and EIS test results demonstrated that the nice corrosion resistance of the composite coating was attributed to the hybrid coating of the Zr and PEI.

Figure 5. Potentiodynamic polarization curves of different coatings measured in 3.5 wt% NaCl solution at room temperature.

Table 2. Polarization parameters and corrosion rate for coatings treated in different concentrations of PEI in 3.5 wt% NaCl solution at room temperature.

| Sample   | $E_{corr}$/V (vs SCE) | $I_{corr}$/μA·cm$^{-2}$ | $r_{corr}$ /mm·a$^{-1}$ |
|----------|------------------------|-------------------------|-------------------------|
| PEI coating | -0.69803               | 28.055                  | 0.32747                 |
| Zr coating | -0.67707               | 20.043                  | 0.23394                 |
4. Discussions
Owing to some cracks that appeared on the coating, the individual Zr coating presented poorer corrosion resistance than PEI coating. The many cracks of Zr coating were completely covered by the PEI coating after PEI treatment. Polyethyleneimine, as a kind of water-soluble polyamine corrosion inhibitor, is available to form a layer on the metal through physisorptions and chemisorptions. The protective layer was formed by combination of two kinds of adsorption\(^{26,28}\). Physical adsorption can be carried out by a positively charged nitrogen atom and a negatively charged metal surface\(^{22}\). From the perspective of chemical, the nitrogen atoms of PEI molecule, as strong electron donors, could provide organic adsorption with active centers. By donor–acceptor interactions, the adsorption of polymer can make use of the electrons of the organics and vacant d-orbital of the metal surface atoms resulting in \(\pi-d\) complexes\(^{25,28,36}\).

When the Zr coated specimen with cracks was immersed in PEI solution, PEI molecules infiltrated into the substrate and formed a protective layer by adsorption, which can compensate for the defect of Zr coating\(^{25}\). Similarly, the PEI-coated specimen was dipped in hexafluorozirconic-acid, and nanoceramic metal oxide particles from hexafluorozirconic-acid can fill into the cracks of PEI coating, generating a favorable protective coating. Thus, the bilayers make the surface of the coating more compact, performing excellent corrosion resistance with two kinds of functions. Moreover, PEI molecules with many active sites can act together and form a high effective protective layer together with Zr coating to block chloride from eroding in the brine\(^{25,33}\). The composite coatings increased the coating’s surface coverage and compactness, reduced the porosity and enhance the substrate’s corrosion resistance. The procedure for preparing both kinds of composite coatings is illustrated in figure 1. Overall, based on the above mechanism, zirconium/polyethyleneimine composite coatings showed excellent anticorrosion behavior on steel surface in 3.5 wt% NaCl solution.

5. Conclusions
According to the results of polarization curves and EIS, the specimen pretreated in PEI solution had better corrosion resistance compared with untreated specimens. PEI coating could generate a protective layer through combination of physisorptions and chemisorptions, which made the hybrid layer perform noble anti-corrosion property.

The surface could form a more dense film after PEI treatment by observing SEM, which can protect the substrate from corrosion. Electrochemical tests also proved that the pretreated specimen could effectively enhance the corrosion resistance of the matrix.

The Zr-based conversion coating acted as an interlayer prior to the PEI on a substrate, which was a promising way to improve the anti-corrosion performance of a substrate.

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