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Effect of graphene on corrosion resistance of waterborne inorganic zinc-rich coatings

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ABSTRACT

The effect of graphene nanosheets on corrosion resistance of waterborne inorganic zinc-rich coatings was investigated in the paper. Coatings were applied on the carbon steel panels with different composition of zinc and graphene. The anticorrosion properties of the waterborne inorganic zinc-rich coatings were investigated by DC polarization technique and electrochemical impedance spectroscopy (EIS). The results showed that the addition of graphene improved the effective zinc content and the cathodic protection of the coating due to the electrical conductivity of the graphene. The coating with 2 wt% graphene maintained cathodic protection for 40 days. XPS results showed that $Zn_5(OH)_8Cl_2$ was the main corrosion products on the surface of the coating and graphene greatly improved the corrosion rate of the zinc particles.

1. Introduction

Shop primer, known as metal pretreatment primer, is utilized for the temporary protection of carbon steel from cutting, welding or corrosion. So far, zinc-rich coatings including organic epoxy zinc-rich coating and inorganic potassium silicate zinc-rich coating [1] are effective ways to protect steel structures against corrosion in the steel industry [2,3]. In the zinc rich coatings, zinc particles provide a cathodic protection of the carbon steel, protecting the carbon steel with sacrificial galvanic protection [4]. Then, the corrosion products of zinc powder will gradually deposit to form a layer of protective film on the steel, which may seal the pores in the primer and improve barrier properties [5–8].

Several efforts are being done to improve the anticorrosive properties of zinc rich coatings. Jagtap believed that 15 wt% zinc oxide could improve the anticorrosion properties of the zinc-rich coating [9,10]. Y. Cubides [11] found that carbon nanotube can improve the corrosion protection and N. Arianpouya [12] found that PU/Zn/OMMT nanocomposite coatings exhibit excellent corrosion protection effect and the barrier properties of the coating are greatly improved. At present, the effect of waterborne zinc rich coating has almost been comparable with the performance of solvent coatings [13,14]. Waterborne inorganic zinc-rich coatings has many features, including low VOC, fast drying, good rust resistance, weld ability, high mechanical performances [15] low maintenance cost and safety [16–19].

In order to ensure a good electrical contact between zinc particles and cathodic protection of carbon steel substrate, a high pigment concentration of 92 wt% zinc is required in the dry film [20]. However, excessive zinc content in the coating weakens the adhesion of the film and zinc oxide dust produced in welding is harmful to the health of workers. It is also important to point out the need of decrease of zinc in coatings, which help to save materials and energy [12].

Therefore, graphene is used to reduce the amount of zinc, and the addition of flake pigments has a positive effect on the properties of zinc-rich coatings [11,12].

Graphene has gained relevance in many applications [21], for its

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good mechanical and thermal stability [22,23], low chemical reactivity [24], gas impermeability [25], and good barrier property [25–27]. Because of these properties, graphene is gaining scientists' attention for preparing anti-corrosion coatings. Several groups have demonstrated the effectiveness of graphene as oxidation resistive [28,29] and corrosion inhibitive coatings [30,31]. Arun S. Kousalya [28] found an effective oxidation barrier coating with graphene. However, this kind of coating only provides the barrier protection and the electrical conductivity of graphene is not used effectively. What's more, there's little research of graphene on the waterborne inorganic zinc-rich coating.

In our work, we show that the composite coating has much better corrosion protection properties than pure zinc rich coatings.

2. Experiment

2.1. Material preparation

According to ASTM D 609, the carbon steel plate used as a metal substrate is sandblasted to Sa2 1/2 and cut to a size of $10 \times 15 \times 0.4\ \text{cm}^3$ for EIS measurement.

Aqueous solution of potassium silicate was provided by Xingtai Ocean Chemical Company. 30 wt% colloidal solution of nano-silica AJN-830 with a particle size of 5–10 nm were purchased from Dali Zhongfa Company. Zinc dust (1#) with an average particle size of 5–10 μm was offered by Changsha Resucerial New Material Company. Graphene nanoplatelets (8–10 layers) were sourced from the Suzhou Geruifeng Nanotechnology limited company (China).

2.2. Preparation of coating

Potassium silicate was heated to 55 °C and then nano-silica colloidal solution was added until the molar ratio of SiO2/K2O was 6: 1, stirring for 2 h, and ultrasound for 1 h. The mixed solution is the modified potassium silicate solution. Paints were made up of the modified potassium silicate solution serving as binder, zinc dust and graphene serving as antirust filler. The coating was sprayed on the steel plate and dried at room temperature at 40% air humidity for 5 min and solidified for 7 days. The thickness of the coatings was between 40 μm and 50 μm. Table 1 shows the characteristics of the coatings.

2.3. Electrochemical measurements

Electrochemical measurements were conducted in CHI760E electrochemical workstation. Samples were embedded with epoxy resin in order to obtain a well-defined surface of $23.7\ \text{cm}^2$. The coated sample as the working electrodes, a saturated calomel electrode (SCE) as the reference electrode, and the stainless-steel mesh with large area as the counter electrode was used for the measurements of open circuit potential (OCP) electrochemical impedance spectroscopy (EIS), and DC polarization technique. The setup was placed in a faraday cage. DC polarization curve were performed at a potential scan rate of $0.001\ \text{V s}^{-1}$. A 10-mv perturbation signal was applied to the coating and the EIS was collected at the open circuit potential with the frequency ranging from 10^5 Hz to 0.01 Hz. Zsimpwin software was used to fit EIS data. All electrochemical measurements were performed in the 3.5 wt% NaCl electrolyte on carbon steel panels coated with different coatings at different exposure times.

3. Results and discussion (low zinc content)

3.1. Morphology and structure of the coatings

Fig. 1 shows SEM images for G1 & G5 (the morphologies of G2, G3, G4 & G5 are similar to each other). The surface of the sample G5 is very smooth and there's no spherical zinc particles on the surface of the coating (Fig. 1B). This shows that the zinc powder disperses unevenly. The sedimentation rate of the zinc powder which is much higher than that of the graphene. The sedimentation rate can be estimated by Stockes settlement formula:

$$\omega = \frac{g * d^2 * (\rho_d - \rho)}{18 * \mu}$$

where ω is sedimentation rate; g is acceleration of gravity; d is the particle size of zinc powder; ρ_d is the density of zinc; ρ is the density of solution and μ is the viscosity of solution. The sedimentation rate of graphene is so slow that settlement of graphene is considered not to occur before the coating solidification. The coating can be divided into two pieces (Fig. 2): the upper layer with high modulus potassium silicate as binder and graphene as filler; the lower layer with high modulus potassium silicate, graphene and zinc particles. The upper layer prevents water from penetration and corrosion products from dissolution while the lower layer contributes to the conductive network between zinc powder.

3.2. Corrosion rate of the coatings

Fig. 3 shows the Tafel plots of G1, G2, G3, G4 and G5 when the samples have been immersed in 3.5 wt% NaCl solution for 24 h. The corrosion current of the sample G3 is higher than the sample G1 & G2. This means that only 30phr of zinc powder begin to react under the action of graphene. However, the mixed corrosion potential of the coating G3 is still at −0.6 V (Vs SCE), revealing there's no cathodic protection. A marked change of Tafel plot has taken place when the addition of graphene reaches 1.5 wt%. Compared with the blank sample G1, the corrosion potential of the sample G4 and G5 are stay at −1.0–1.2 V (Vs SCE) while the electrode of Fe oxidation equals −0.76 V (Vs SCE), so that the conditions of the sacrificial anode cathodic protection are satisfied. The corrosion current density, I_{corr} of coatings increase with the amount of graphene. This

Table 1
Characteristics of the dry coatings.

	Sample	Zinc dust g	Binder g	Graphene content to zinc dust wt%
low Zn content	G1	30	7.5	0
	G2	30	7.5	0.5
	G3	30	7.5	1
	G4	30	7.5	1.5
	G5	30	7.5	2
high Zn content	P1	60	7.5	0
	P2	60	7.5	2