A fast, low temperature zinc phosphate coating on steel accelerated by graphene oxide

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ABSTRACT

Graphene oxide (GO) is used to accelerate zinc phosphating process on steel. The effect of GO on microstructure and corrosion resistance of phosphate coating is investigated. Experiments show that GO sheets can act as sedimentary beds at the initial stage of phosphating process, which can capture metal ions and thus favor the nucleation of phosphate crystals. When the concentration of GO is optimized to be 1.2 g/L, the phosphate coating possesses the most uniform and compact structure and achieves the strongest corrosion resistance. Results demonstrate that GO can effectively accelerate phosphating process and enhance corrosion resistance of phosphate coating.

1. Introduction

Steel, as the most widely used engineering material in the world, its corrosion protection is of great significance. Many effective ways have thus been developed to improve corrosion resistance of steel [1–6]. Phosphate coating, for example, is one of the most widely used pre-treatment of steel due to its economy, quick operation combined with wear resistance and lubricative properties [7]. Moreover, phosphate coating can not only provide resistance barrier to corrosion but also enhance the adhesion of organic top coating, which is of great interest in industrial applications.

Apart from the advantages of phosphate coating, traditional phosphating process is time-consuming and under relatively high temperature such as 90–98 °C [8,9], which account for enormous energy consumption. Thus, accelerator is generally adopted to speed up phosphating process and lower operating temperature. Traditional accelerators such as nitrides, nitrates and chlorates [10] can effectively enhance the performance of phosphate coating but are harmful to human health [11] and environment [12]. Different attempts have thus been carried out to develop new accelerators [10–14]. Besides, more effective ways are still highly needed to upgrade traditional phosphating industry.

Graphene oxide (GO) contains various oxygenated functional groups, and thus shows excellent compatibility with base materials [15]. Researches prove that GO can greatly enhance the corrosion inhibitive ability of coatings due to its special 2D nano-plate structure and excellent impermeability to ions and gases [4,16–23]. However, in most of the reported works, GO or functionalized GO was directly used as pigment of organic coating [16,22,24–31], where the dispersibility of GO in base resin was the main hindrance that limited its practical applications. Besides, these investigations also included complicated modification or functionalization process of GO. To the best of our knowledge, using GO to accelerate phosphating process and then simultaneously introducing GO into the phosphate coating have not yet been reported.

Herein, experiments are designed to investigate the possibility of GO as a new effective phosphating accelerator. GO aqueous dispersion is directly added into traditional phosphating bath to prepare phosphate coating co-deposited with GO sheets on steel. Scanning electron microscopy (SEM), X-ray diffraction (XRD) analysis are employed to investigate the morphology and phase composition of phosphate coating. The mechanism of accelerating phosphating process by GO is proposed based on the above observations. Electrochemical measurements, including potentiodynamic polarization and electrochemical impedance spectroscopy (EIS), are then used to evaluate the corrosion inhibitive properties of phosphate coating.

2. Experimental

2.1. Preparation of phosphate coating

GO dispersion was prepared according to our previous report [32]. Steel specimens, with the dimension of 10mm × 10mm × 1mm, were directly cut from commercially available Q235 steel with the chemical

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Table 1
Chemical composition of Q235 steel.

Element	C	Si	S	P	Mn	Fe
Content (wt.%)	≤ 0.22	≤ 0.35	≤ 0.05	≤ 0.05	≤ 1.40	Balance

Table 2
Chemical composition of phosphating bath and operating conditions.

Chemical composition	Concentration	Operating conditions	
$Zn(H_2PO_4)_2$	55 g/L	Temperature	40 °C
$Zn(NO_3)_2$	60 g/L	Time	20 min
H_3PO_4	8 g/L		
GO	0–3.6 g/L		

composition as shown in Table 1. The specimens were first carefully ground by abrasive paper to remove rust and oxides, and then degreased in 10.0 wt.% NaOH at 40 °C for 10 min. After that, the degreased specimens were washed by de-ionized water and then subjected to phosphating bath with the composition as listed in Table 2. The phosphating temperature was 40 °C and the time duration was 20 min. Finally, specimens deposited with phosphate coating were washed by de-ionized water and dried by blowing air at room temperature.

2.2. Characterization of phosphate coating

The surface microstructure of phosphate coating were investigated by Zeiss Merlin SEM. XRD analysis of phosphate coating was carried out on Bruker D8 ADVANCE diffractometer with Cu Kα radiation generator.

The phosphate coating mass per unit area (MPA) was calculated according to the equation MPA $= (M_1 - M_2)/S$, where M_1 and M_2 were the mass of specimen before and after phosphate coating being eliminated, and S was surface area of the coated specimen. In order to calculate the mass of phosphate coating deposited on steel surface, the coated specimen was first immersed in specially made solution [33] at 70 °C for 5 min to completely dissolve the phosphate coating and leave behind the bare steel substrate. The mass, before and after the dissolving process, was then measured and marked as M_1 and M_2.

The corrosion inhibitive ability of phosphate coating was analyzed by potentiodynamic polarization and EIS measurement using a standard three-electrode system. Saturated Ag/AgCl electrode, graphite electrode and specimens were adopted as reference electrode, counter electrode and working electrode, respectively. All measurements were conducted in 3.5% NaCl solution using the electrochemical workstation (PGSTAT 302N, Metrohm AG, Switzerland). The EIS was carried out at open circuit potential (OCP) in the frequency range from100 kHz to 10 mHz with the amplitude of 10 mV. The time waiting for the stable OCP was set to be 600 s prior to EIS measurement. Zview software (Version 3.1) was used to analyze EIS results. The potentiodynamic polarization was performed following EIS measurement to obtain the polarization curves. The sweeping range of potential was −0.15 V below OCP to 0.15 V above OCP and the potential scan rate was 1 mV/s. The electrochemical parameters, corrosion potential and corrosion current density, were obtained from Tafel extrapolation method using the attached program of electrochemical workstation. All the measurements were performed 5 times and average values were adopted.

3. Results

Phosphate coatings are fabricated by immersing steel plates in phosphating bath with different content of GO at 40 °C for 20 min. The GO content in phosphating bath is 0 g/L, 0.6 g/L, 1.2 g/L, 2.4 g/L, and 3.6 g/L, respectively. And the specimens are denoted as BP, GP-0.6, GP-1.2, GP-2.4, and GP-3.6, respectively.
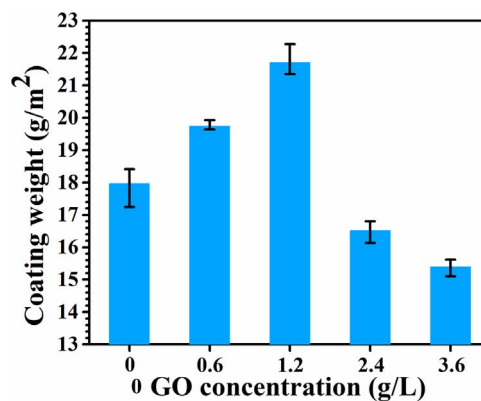

Fig. 1. Variations of phosphate coating mass per unit area versus GO concentration in phosphating bath, the values are of the average of five different measurements.

3.1. Evaluation of phosphate coating mass per unit area

As shown in Fig. 1, MPA is measured to evaluate the effect of GO content on the deposition of phosphate coating. All measurements are repeated for five times and averaged, and the standard deviation range is between 0.9% and 4.1%, as shown as the error bar in Fig. 1. It can be seen that GO would affect the phosphating process, resulting in the formation of phosphate coating with different MPA. The MPA for BP is 17.97 g/m². As GO is added into phosphating bath, the MPA first increases until the maximum value of 21.70 g/m² at the content of 1.2 g/L GO. While GO content exceeds to 1.2 g/L, the MPA, in turn, drops down. The values for GP-2.4 and GP-3.6 decrease to be 16.52 g/m² and 15.40 g/m², respectively.

3.2. XRD characterization

XRD is used to characterize the phase composition of the phosphate coating. The XRD spectra of coatings obtained with and without GO in phosphating bath are displayed in Fig. 2. It can be seen that all phosphate coatings are mainly consisted of $Zn_3(PO_4)_2 \cdot 4H_2O$ (hopeite, JCPD file #37-0465). Although $Zn_2Fe(PO_4)_2 \cdot 4H_2O$ (phosphophyllite, JCPD file #29-1427) can also be identified, the peak intensities are weak. In addition, the peak intensities of $Zn_2Fe(PO_4)_2 \cdot 4H_2O$ decrease with the increasing content of GO, as depicted by black blocks in Fig. 2. Particularly, the peak of $Zn_2Fe(PO_4)_2 \cdot 4H_2O$ can hardly be observed for GP-3.6. Thus, the observations prove that the addition of GO does not change phase composition of phosphate coating but can influence the preferential growing orientation of phosphate crystals. And adding GO into phosphating bath prefers the growing of hopeit rather than the growing of phosphophyllite.
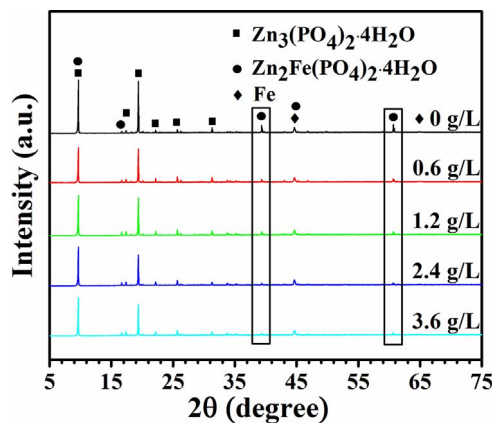

Fig. 2. XRD patterns of phosphate coatings obtained from phosphating bath with different content of GO.