Short Communication

A Novel Waterborne Epoxy Coating with Anticorrosion Properties on Rusty Steel

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This paper reports the synthesis of waterborne epoxy phosphate emulsion (WEP) through the reaction between epoxy resin E44 and phosphoric acid and ammonia neutralization. Synthesized WEP was characterized by FTIR for the confirmation of reaction between epoxy groups and phosphoric acid and SEM for morphology. WEP acted as a modifier in two-component epoxy anticorrosion coating on rusty steel substrate. The anticorrosion properties of the coating on rusty steel were investigated by electrochemical impedance spectroscopy (EIS) and Tafel polarization curve. Tafel polarization curve revealed that waterborne epoxy coating containing WEP had better protection ability which is clearly reflected by the protection efficiency (96.6%). EIS study also showed the higher impedance value for WEP containing coating as compared to pure waterborne epoxy coating.

1. INTRODUCTION

In recent decades, water-based coatings are preferred due to the strict environmental regulations and their perfect chemical resistance [1–5]. Waterborne epoxy resins have high electrical resistance, outstanding adhesion to various substrates, good toughness as well as durability at high and low temperatures, and thus they have been widely used in the field of coatings [6–9]. However, the application of waterborne epoxy coatings is limited in the field of metal corrosion. Thus, corrosion

inhibitors have been added into the resin matrix to improve the anticorrosion property of waterborne epoxy coatings [10–13].

Functional phosphate compounds as important kind surfactants and functional monomers can form dense phosphate film on the metal surface, which has outstanding corrosion resistance and adhesion to the metal substrate. In recent decades, many researchers have reported on phosphate-modified polymer as corrosion protective coatings [14–18]. Lin et al. successfully synthesized an acrylic emulsion containing phosphate acrylate monomer and it can be seen from EIS test that acrylic emulsion containing phosphate acrylate monomer had good anticorrosion properties [19]. González et al. synthesized phosphate-type (meth)acrylates (PMC) emulsion via emulsion polymerization and it could strongly enhance adhesive and corrosion protective properties of PMC coating [20].

As reported in the literature, for better anticorrosive performance, coatings should be well adhered on the metallic substrate, so the rust on the surface of steel piece and hull must be removed thoroughly before painting by sand blasting or degreasing [21]. However, the cost of sand blasting and degreasing are more than half of the total construction and the level of sand blasting surface treatment must be above Sa2.5. In addition, sanded blasting cannot be performed at the corner points and concave points of steel pieces but remove rust by handwork. Therefore, it is important to develop a high efficiency anticorrosive coating which can be applied in moist, oil or rusty conditions.

Recently, there are number of industrial rust painting products having stability, transformation and permeation [22]. For example, Beijing Yanshan Petrochemical Corporation developed JTS low surface treatment material items, which can paint on steel with rust, water, oil or old coating [23]. Waterborne over-rust coating becomes a new research direction which can be directly coated on the steel surface with rust.

The present article reports the synthesis of epoxy phosphate emulsion (WEP) by the reaction of bisphenol A epoxy resin with phosphoric acid. The WEP emulsion was used to modify the waterborne epoxy, and modified waterborne epoxy were used as coating material. The syntheses, characterization as well as the anticorrosive properties of the waterborne modified epoxy coatings were investigated.

2. EXPERIMENTAL

2.1 Materials

Phosphoric acid (85%), triethylamine, concentrated HCl, acetone, ethanol and sodium chloride were purchased from Aladdin Industrial Corporation, and were used without further purification. Bisphenol A epoxy resin E44 was provided by Northwest Yongxin Paint & Coatings Co., Ltd.. Waterborne epoxy resin (EP-AB-W53) and curing agent (HGA-AB-20) was purchased from Zhejiang Business Development New Materials Co., Ltd. The Q235 steel electrode was selected for anticorrosion test. The electrode surface was gradually abraded with SiC abrasive paper up to 1500 grit, then rinsed with distilled water and dried in air, eventually formed rust spot on the surface.

2.2 Synthesis of epoxy phosphate (WEP)

Epoxy phosphate was synthesized as earlier reported [24]. Phosphoric acid (7.69 g) was dissolved in 20 mL acetone, epoxy resin E44 (20 g, dissolved in 40 mL acetone) was added into the phosphoric acid solution dropwise (the molar ratio of phosphoric acid and epoxy group is 3 :2.5), then the mixture was stirred vigorous until the acid value remains unchanged (92.14 mg KOH/g). After that, triethylamine (11.90 g) and water were added into the solution dropwise. After complete of the reaction, acetone was removed through rotary evaporator, then we got the emulsion and solid content of the emulsion is 40 wt%.

2.3. Preparation of the epoxy phosphate modified epoxy coating

0.25 g epoxy phosphate emulsion (5 wt%) and 0.9 g curing agent were stirred with glass rod. Then 5 g epoxy resin emulsion dispersion was added to the mixture and the system was stirred at a high speed for 20 min. The liquid coating was applied onto the Q235 rusty steel surface with a 10# (50 μm) wire rod. Then coatings were cured at room temperature for 1 h and then baked them in vacuum oven at 80°C for 5 h. The coating thickness was 25±2 μm. For comparison, the pure epoxy coating was prepared in a similar way.

2.4 Characterizations

Fourier transform infrared (FTIR) spectra were performed on spectrometer (NICOLET 6700, Thermo) by collecting 32 scans at a spectral resolution of 4 cm^{-1}. The morphology of the coatings was examined using FEI Quanta FEG 250 scanning electron microscope (SEM).

The anticorrosion performances of coatings were evaluated on CHI-660E electrochemical system and aqueous 3.5 wt% NaCl was used as corrosive medium. Test system consisted of three electrodes (saturated calomel electrode (SCE) as reference electrode, platinum plate of 2.5 cm^2 as counter electrode and coated rusty steel was used as work electrode, respectively). Test frequency range was from 10^5 to 10^{-2} Hz and the amplitude of the sinusoidal voltage signal was from 20 to 50 mV for electrochemical impedance spectroscopy (EIS), All the samples were immersed in 3.5 wt% NaCl aqueous with the same time and then polarization curves were tested with scan rate of 0.5 mV/s, scan range was -200-200 mV vs. OCP.

3. RESULTS AND DISCUSSION

3.1 characterization of epoxy phosphate emulsion

Fig. 1 shows the FTIR spectra of epoxy resin and epoxy phosphate. The absorption peak at 915 cm^{-1} represented epoxy group. The peaks at 2965 cm^{-1} and 2870 cm^{-1} were assigned to the stretching vibrations of -CH$_2$, while the peak at 2925 cm^{-1} was the stretching mode of C-H. The peaks at 3045

cm^{-1}、1609 cm^{-1}、1575 cm^{-1}、1521 cm^{-1}、828 cm^{-1} corresponded to the C-H aromatic stretching. The peak at 3445 cm^{-1} corresponded to the O-H stretching vibration.

As can be seen from the FTIR spectra of epoxy phosphate, the absorption peak at 915 cm^{-1} of epoxy group disappeared, and there was a new peak at 1022 cm^{-1} of phosphate group observed which confirms the reaction occurs between epoxy groups and phosphoric acid.
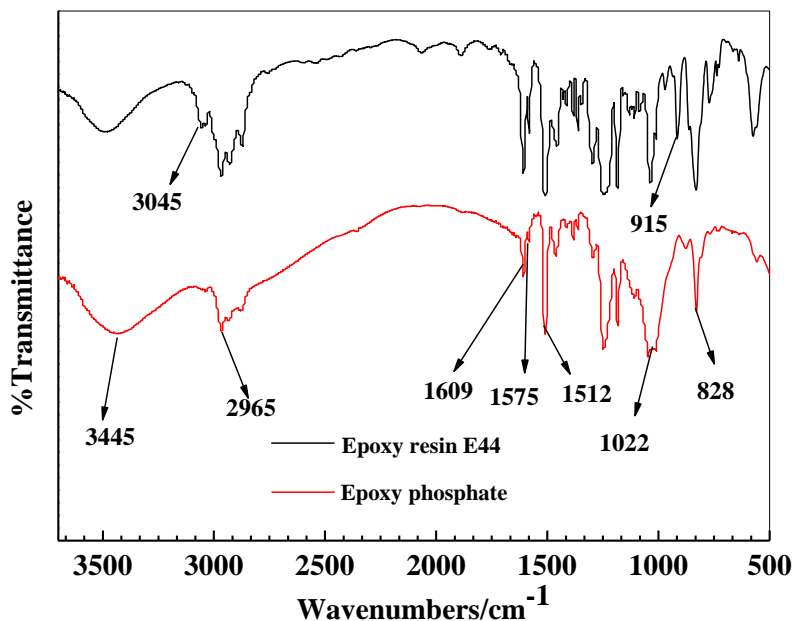

Figure 1. FTIR spectra of epoxy resin (E44) and epoxy phosphate

3.2. Corrosion resistance

EIS has been widely used for evaluating the corrosion resistance of epoxy coatings. The data of different coatings was presented in Bode plot and Nyquist format as shown in Fig. 2 (E_1, E_2 is pure epoxy coating and coating containing 5 wt. % epoxy phosphate, respectively). It is known that impedance modulus at low frequency represents the ability to impede the flow of current between anodic and cathodic areas, which is an appropriate parameter for characterizing the corrosion protection of coatings [25-28]. At low frequency region E_2 have higher impedance value than E_1 which may be due to the improved water barrier properties of epoxy phosphate coating.

At the beginning of immersion, E_1 coating had the $|Z|_{0.01\ Hz}$ value of $8.0 \times 10^4\ \Omega\ cm^2$. After 108 h of immersion, the $|Z|_{0.01\ Hz}$ value gradually decreased and stayed at $4.5 \times 10^4\ \Omega\ cm^2$. For E_2 coating the $|Z|_{0.01\ Hz}$ value gradually increased from $1.4 \times 10^5\ \Omega\ cm^2$ to $1.5 \times 10^6\ \Omega\ cm^2$, which may due to some kind dense film formation with immersion [29]. The $|Z|_{0.01\ Hz}$ value of E_2 coating was one order of magnitude higher compared with E_1 coating. On the other hand, the phase angle of E_2 coating was higher than E_1 coating in the whole immersion process. The EIS results indicated that the corrosion protection of the E_2 coating was better than E_1 coating.

In order to discuss the evolution of the anticorrosion properties of E_1 and E_2 coatings, EIS data were fitted by equivalent circuit, as shown in Fig. 3. The solution resistance was signed as R_s, the coating resistance and transfer resistance were signed as R_c and R_{ct}, respectively, and Q_c and Q_{dl} represent the coating capacitance and double-layer capacitance, respectively. In the stage of immersion, Nyquist plots of both E_1 and E_2 coatings showed two capacitance loop, so the equivalent circuit R(Q(R(QR)) (Fig. 3) was chosen for the fitting procedure [30]..
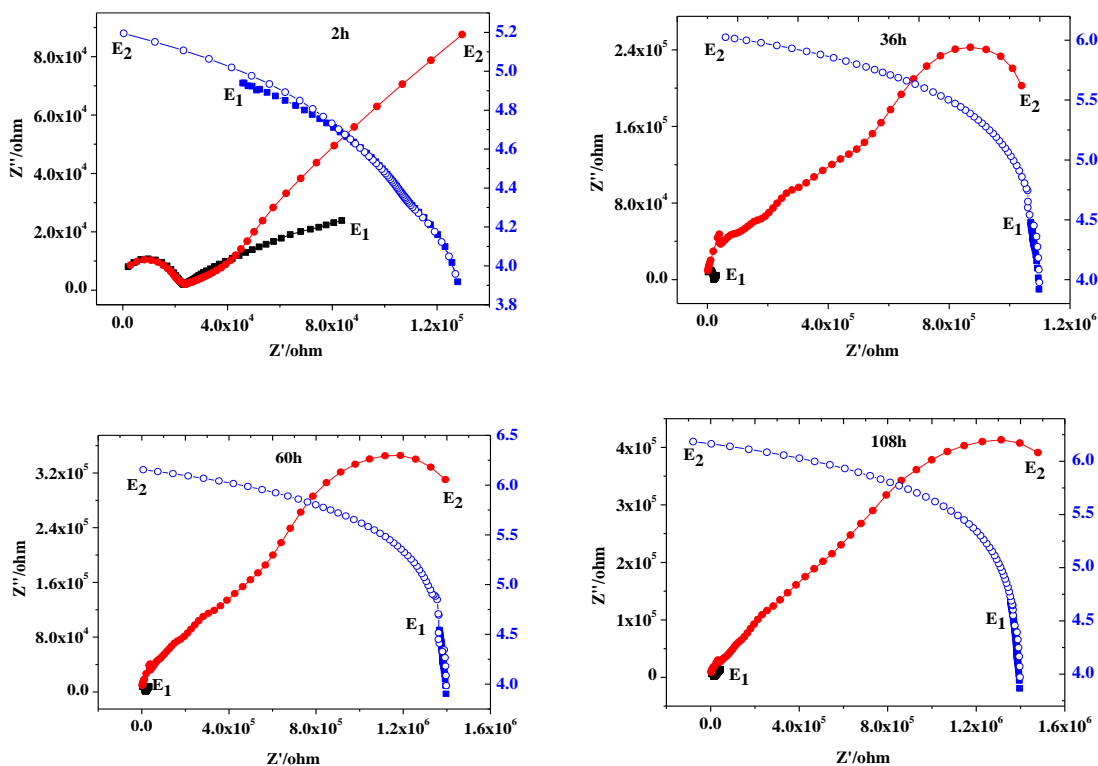

Figure 2. EIS curves of E_1 and E_2 immersed in 3.5% NaCl solution with different time
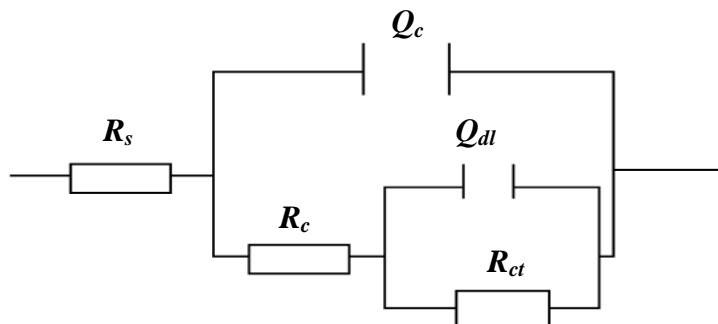

Figure 3. Equivalent circuits used to fit the EIS data.

Fig.4 shows coating resistance (R_c) and transfer resistance (R_{ct}) of E_1 and E_2 coatings. Generally, R_c decreases with the immersion time as a smaller number of H_2O, O_2 and Cl^- molecules penetrated into the coatings [31]. The R_c value of E_1 coating decreased from the initial value of 2.1×10^5 Ω cm^2 to a steady value of 1.3×10^4 Ω cm^2 after 108 h immersion. For the E_2 coating, the R_c value

decreased from the initial vale $2.3 \times 10^5 \, \Omega \, cm^2$ to a steady value of $2.1 \times 10^4 \, \Omega \, cm^2$ after 36 h immersion, however, the value increased to $2.3 \times 10^{10} \, \Omega \, cm^2$ at 60 h , and remained at this level till 108 h.

Generally, R_{ct} is a parameter of the resistance to electron transfer across a metal surface and is inversely proportional to the corrosion rate. The R_{ct} of E_1 coating fluctuated and stabilized at about $1.0 \times 10^4 \, \Omega \, cm^2$ during 108 h of immersion. The R_{ct} of E_2 coating did not emerge during 108 h immersion, indicating that the addition of WEP could improve the barrier protection of epoxy coating.
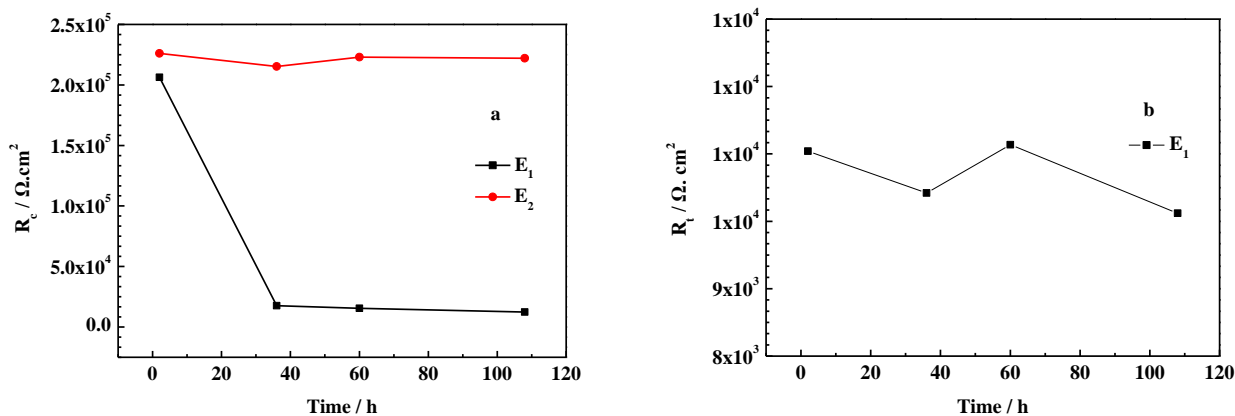

Figure 4. Changes of R_c (a) and R_{ct} (b) curves as a function of immersion times.

Fig. 5 shows the polarization Tafel curves of E_1 and E_2 coatings immersed in 3.5 wt% NaCl solution for 108 h. Corrosion parameters like corrosion density (i_{corr}), corrosion potential (E_{corr}), corrosion resistance (R_p), anodic Tafel slope (b_a), and cathodic Tafel slope (b_c) were calculated by Tafel extrapolation method and summarized in Table 1. E_2 coating showed lower current density i_{corr} (0.22 $\mu A \, cm^{-2}$) and higher corrosion potential E_{corr} (-0.50 V) compared with E_1 coating. Furthermore, the polarization resistance R_p of E_2 coating (1687 $K\Omega \, cm^2$) was much higher than E_1 coating (42.5 $K\Omega$ cm^2), which indicated that E_2 coating improved the corrosion resistance of the rusty Q235 steel.
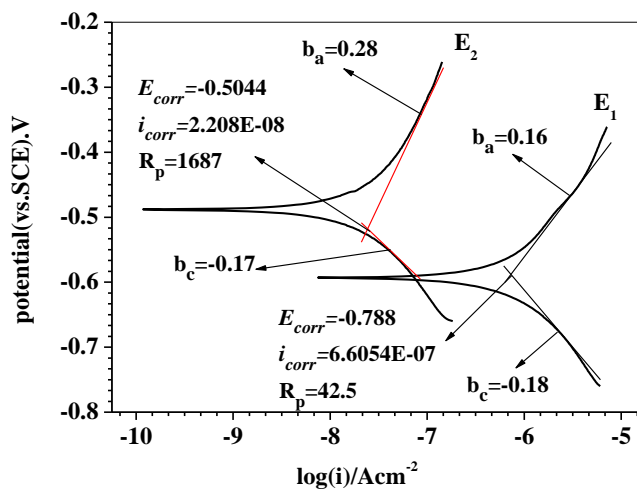

Figure 5. Tafel curves of E_1 and E_2 immersed in 3.5 wt% NaCl solution for 108 h

Table 1. Corrosion parameters of E_1 and E_2 in 3.5 wt% NaCl solution for 108 h

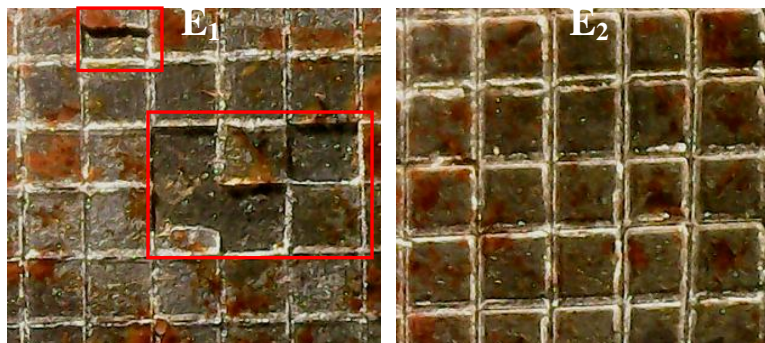| Samples	E_{corr} (V, vs. SCE)	i_{corr} (A cm^{-2})*10^7	b_a (V/dec)	b_c (V/dec)	R_p (KΩ cm^2)	η%
E_1	-0.58	6.61	0.16	-0.18	42.5	—
E_2	-0.50	0.22	0.28	-0.17	1687	96.66

Figure 6. The adhesion test result of E_1 and E_2 coatings

Adhesion can evaluate coating resistance divorced from matrix, according to GB/T 9286-1998 the adhesion of E_1 and E_2 coatings were tested, and the results showed in Fig. 6. It can be seen from the pictures that there was much falling from E_1 coating while E_2 coating was still complete. The resulted showed that E_2 coating containing WEP can improve the adhesion to rusty steel matrix. The good adhesion to rusty steel matrix of E_2 coating confirmed that WEP had strong chemical bonds with the rusty steel, which could form a dense film on the surface of steel.
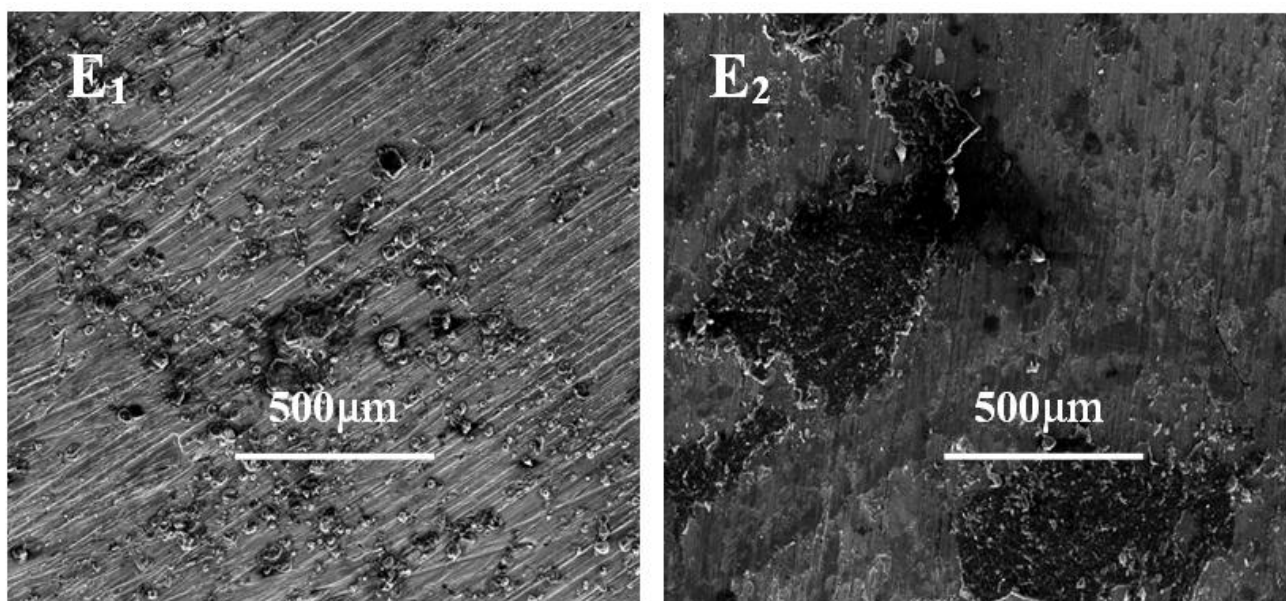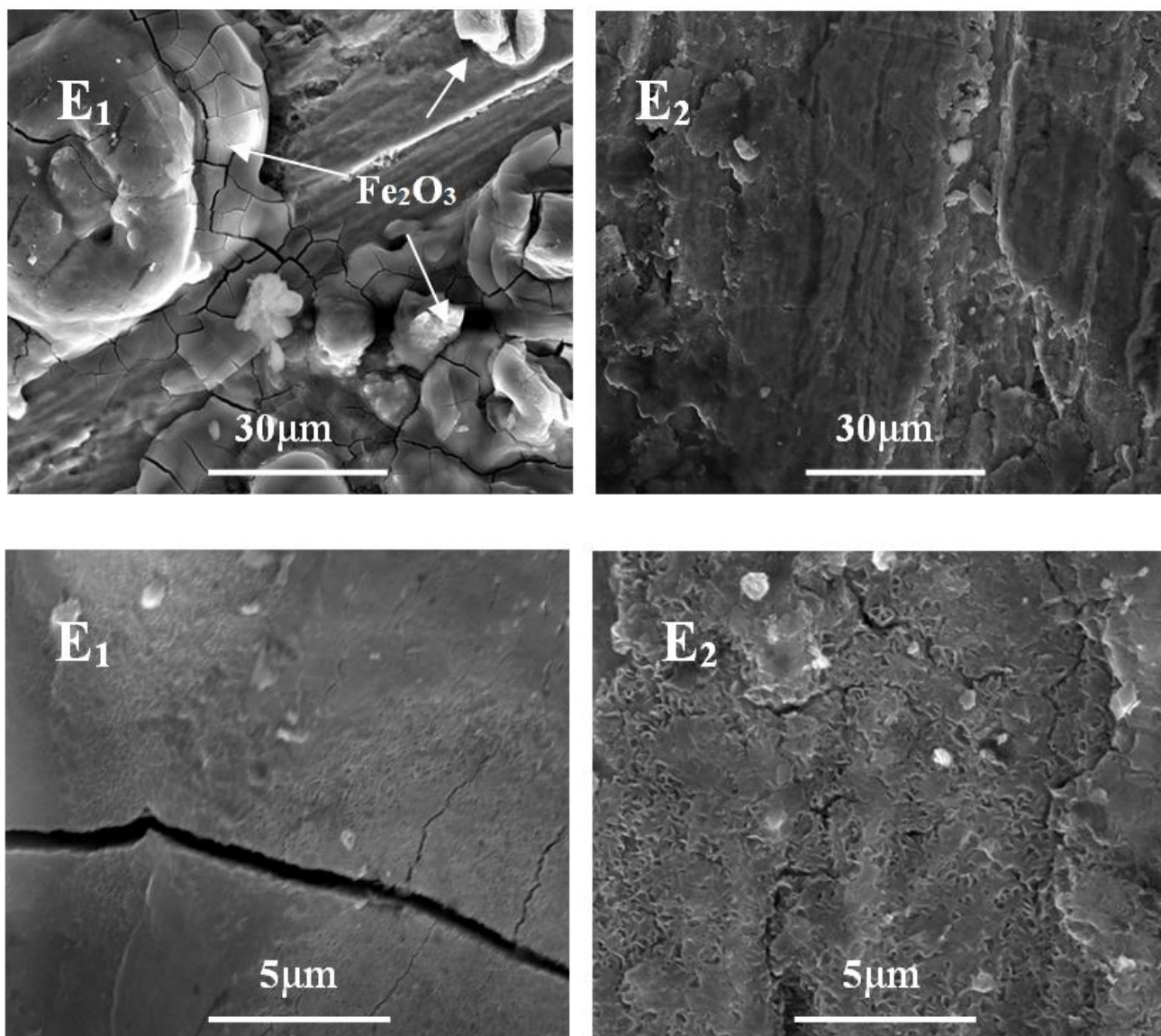
Figure 7. The SEM images of E_1 and E_2 coatings

The coatings on the surface of the electrode were removed after immersion in 3.5 wt. % NaCl solution 108 h, then the surface of the carbon steel was observed and analyzed by electron microscope scanning (SEM) as showed in Fig. 7. The microstructure on the surface of the rusty Q235 steel under E_2 coating more uniform than the surface of the rusty Q235 steel under E_1 coating and there was no obvious Fe_2O_3 particles observed on the surface of the rusty steel under E_2 coating. However, the iron oxide particles were observed on the surface of the rusty steel under E_1 coating after 108 h. These results indicate that WEP could form covalent bond [24], and well adhered on the rust metal surface. Therefore, the coating containing WEP can prevent the rusty metal from further corrosion.
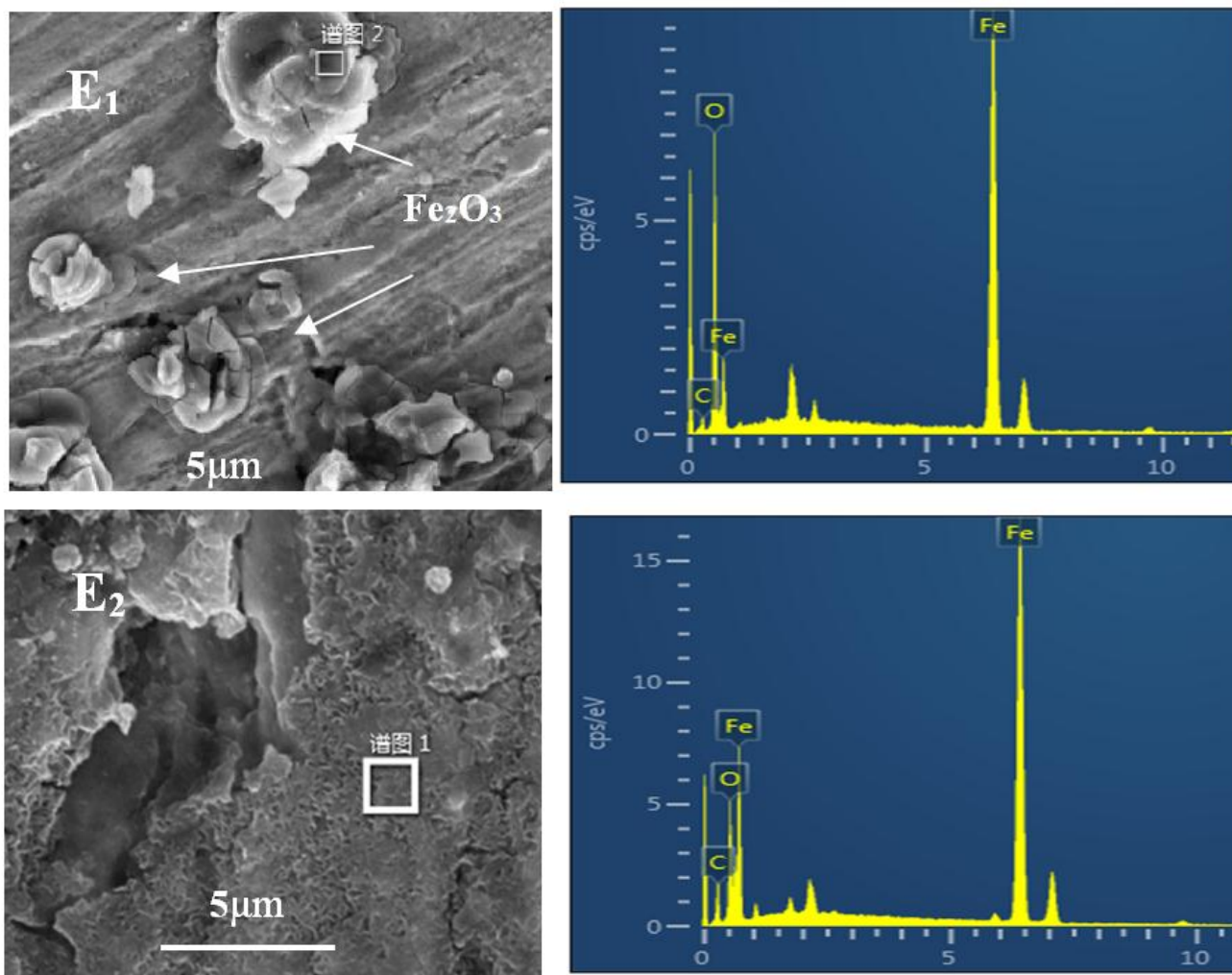
Figure 8. The EDS of E_1 and E_2 coatings

In order to explore the main composition of the carbon steel surface, energy spectrum analysis (EDS) was made to analysis the electrode surface of E_1 and E_2 after 108 h immersion in 3.5 wt% NaCl solution as shown in Fig. 8. Compared to E_2 steel, the content of oxygen on the surface of E_1 rusty steel increased, and there was large number of Fe_2O_3 particles on the surface of the rusty steel. This result indicates that WEP could enhance the interface bonding, lessen the interface defects between the rusty steel and the waterborne epoxy resin coating and prevent the rusty steel from further oxidation.

4. CONCLUSIONS

Synthesized WEP emulsion was to investigate corrosion resistance of waterborne epoxy coating to the rusty metal substrate. FTIR spectra showed that the WEP emulsion was prepared successfully. EIS and Tafel measurements revealed that the addition of epoxy phosphate (5 wt%) into waterborne epoxy remarkably improved corrosion protection compared with pure waterborne epoxy coating by showing higher impedance value and inhibition efficiency.

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