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Electrodeposition and Corrosion Behavior of Zinc-Nickel Films Obtained From Acid Solutions: Effects of TEOS as Additive

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Zinc-nickel composite film has been electrodeposited on carbon steel surface via adding tetraethylorthosilicate (TEOS) in electrolating solution. X-ray diffraction (XRD) and scanning electron microscopy (SEM) results showed that the phase and surface morphology of zinc-nickel films could be changed with varying the concentration of TEOS in electroplating bath. Polarization curves and electrochemical impedance spectroscopy (EIS) results indicated that the films obtained with the TEOS addition possessed better corrosion resistance. Open circuit potential (OCP) results indicated that the film obtained at 0.005 M of TEOS still showed cathodic protection ability to the substrate after immersion in 3.5 wt% sodium chloride solution for hundreds of hours. This can be attributed to the optimizational effect with suitable concentration of TEOS to be added in electrolating bath. The results indicated that TEOS may act as an additive to be used in surface coating technology.

Keywords: Zinc-nickel; TEOS; Electrodeposition; Corrosion

1. INTRODUCTION

Cathodic protection against the corrosion of steel or other metal substrates by electrodeposition has been extensively studied due to its importance in surface coating industry [1-3]. Zn alloys are common materials used for metal protection since they have high protective capacity against corrosion compared with pure zinc. The addition of further elements, such as Fe, Co and Ni, can modify the corrosion rate and maintain sacrificial protection [4-6]. Among these alloys studied, zinc-nickel coatings prepared by electrodeposition were the most successful for they possessed higher corrosion resistance and better mechanical characteristics and have been shown to be effective substitutes for toxic cadmium coatings [7]. It has been reported that zinc-nickel coating with the amount of nickel varying between 8% and 14% provided superior corrosion resistance compared with unalloyed zinc

[8]. Lower nickel content leads to lower barrier properties and the coating with a higher nickel content has no longer sacrificial with respect to the steel substrate [4]

Many factors can influence the microstructure and morphology of zinc-nickel coating obtained by electrodeposition. Several studies have investigated the influence of bath composition, cathode current density, temperature and bath agitation on the characteristics of zinc-nickel coating [7, 9-13]. Among these, additive is an important factor for electrodeposition to improve the microstructure and morphology of deposits. It is well known that the addition of small amounts of some substances in the plating bath leads to significant changes in the properties and morphology of the resulting deposit [14]. Additives may have the ability of modify nucleation process and structure, wetting, brighten and increase film thickness [15-19]. Several studies have investigated the influence of additives in the electrolysis bath on the zinc-nickel alloy properties such as microstructure, morphology, as well as corrosion resistance [1, 20-23].

Tetraethoxysilane [TEOS, $Si(OC_2H_5)_4$] is an organofunctional hybrid organic–inorganic chemical. It is commonly used as a coupling agent for adhesion between organic and inorganic materials, such as glass fiber-reinforced polymeric composites [24]. Recent studies have shown that the films based on TEOS obtained by the sol–gel, electrodeposition and spraying methods can be used for corrosion resistance [25-27]. In previous studies, we have used TEOS to fabricate zinc/silicon dioxide composite film in zinc nitrate solution by electrodeposition method. It was found that the addition of TEOS could make the composite film much smoother and the corrosion resistance of the composite film improved [28]. In this present paper, the influence of TEOS on the electrodeposition of zinc–nickel coatings was investigated. The aim of present work is to fabricate zinc–nickel coatings by electrodeposition using TEOS as additive and to determine the effect of TEOS on the microstructure and anticorrosion properties of the resultant coating. This was achieved by using scanning electron microscope (SEM), X-ray diffraction (XRD) and the anticorrosion characterization is examined by open circuit potential (OCP), polarization curves and electrochemical impedance spectroscopy (EIS).

2. EXPERIMENTAL

2.1. Raw materials

All the chemicals were analytical pure and used as purchased without any purification. The water used was distilled water.

The substrate used in this experiment was made of carbon steel with the composition of 0.1 wt% C, 0.4 wt% Mn, 0.12 wt% Si, 0.02 wt% S, 0.05 wt% P, and remainder Fe. In order to match the sample geometry to the specific experimental requirements, two types of samples were applied. Steel rods mounted with epoxy resin were used for the electrochemical measurements, maintaining a constant exposed area (0.196 cm^2) throughout the experiments. The substrates used for XRD, SEM and energy dispersive spectrometer (EDS) characterization were steel flakes (0.2 cm^2). Prior to film deposition, steels were polished using emery paper (1200 grits). Then, all samples were sonicated in acetone, ethanol, clean water, and finally dried at room temperature.

2.2. Preparation of zinc-nickel coating

Zinc-nickel coating were electrochemically deposited onto carbon steel substrates from a weak acid bath. The bath contained 0.1 mol L^{-1} zinc chloride ($ZnCl_2$), 0.1 mol L^{-1} nickel chloride ($NiCl_2$), 3.0 mol L^{-1} ammonium chloride (NH_4Cl), 0~0.01 mol L^{-1} TEOS, 0.05 mol L^{-1} hydrochloric acid (HCl) and 0.02 mol L^{-1} boric acid (H_3BO_3). All deposition experiments were carried out at room temperature (about 25 ^oC) in a 100 mL glass single-compartment cell. A platinum-niobium wire (~3 cm^{-2}) and a standard calomel electrode (SCE) were employed as auxiliary and reference electrodes, respectively. Current density used for electrodeposition was 10 mA cm^{-2}. Stirring rates were 300 rpm. Prior to electrodeposition, TEOS was added in the bath and stirred for 30 min to hydrolyze completely.

2.3. Characterization

The phase content was determined by XRD with a diffractometer (D8 Advance, Rruker Corporation) using monochromeatized Cu K_α radiation at a scanning speed of 1.2 ^{o} min^{-1}. The surface morphologies and chemical composition of the deposited films were studied using a scanning electron microscope (XL-30, Philips), which was coupled with an energy dispersive spectrometer (EDAX company).

2.4 Electrochemical measurements

All the electrochemical experiments, including electrodeposition, polarization curves and EIS, were carried out by a computer-controlled electrochemical system (PARSTAT 2273， PAR). Polarization curves were recorded at a sweep rate of 1 mV s^{-1}. Sodium chloride (NaCl) solution (3.5 wt%) was used as the electrolyte. EIS experiments were carried out at the frequencies of 10^5 Hz to 10^{-2} Hz at open circuit potential where the amplitude of the perturbation voltage was 5 mV. All the experiments were carried out at room temperature and the test samples were immersed in 3.5 wt% sodium chloride solution for a long time (30 min) to ensure stability of open circuit potential.

3. RESULTS AND DISCUSSION

3.1. SEM and XRD characterizations

In Figure 1 the morphology of the zinc-nickel coatings deposited with 10 mA cm^{-2} at different concentrations of TEOS: 0, 0.005 and 0.01 mol L^{-1}, are compared. It can be seen that deposits obtained from the bath without TEOS (bath-I) shows homogeneous morphology with grains of size ~2 μm. In the presence of 0.005 mol L^{-1} TEOS (bath-II), the grain size of deposit is reduced, with more refined grains (approximately 1 μm). However, when the bath containing 0.01 M of TEOS (bath -III), the deposit obtained is less compact with no well defined corners. This finding suggesting that, in the presence of higher concentration of TEOS, the crystal growth rate is lower. This examination of the deposits using SEM indicated that both the morphology and grain size are affected by the presence and concentration of TEOS.

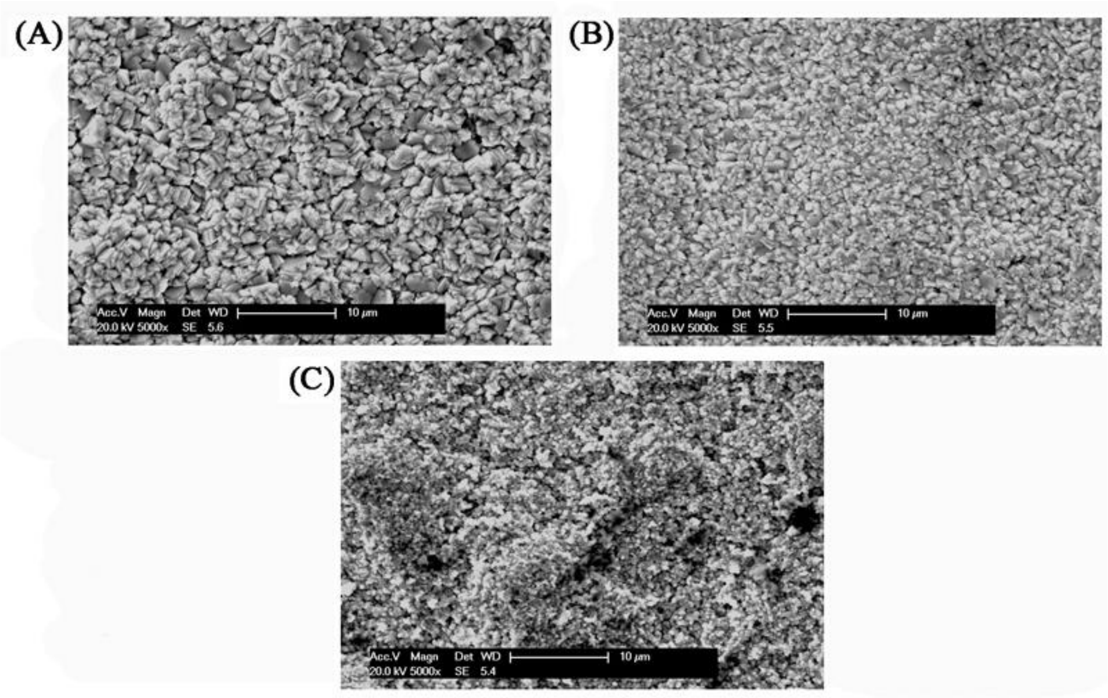

Figure 1. SEM images of the composite films deposited in the solution containing different concentrations of TEOS: (A) 0 M, (B) 0.005 M, (C) 0.01 M.

Some researches indicated that the additive in the bath may adsorb on the surface of the substrate, thus limiting the initial grain growth [1, 29]. For TEOS, it can hydrolysis in solution as the following equation:

$$Si(OCH_3)_4 + nH_2O \rightarrow Si(OCH_3)_{4-n}(OH)_n + nCH_3OH \qquad (1)$$

The −Si−OH group may adsorb on the electrode surface to limit the deposition of metal. Besides, there are strong hydrogen bonds between −Si−OH groups and so make zinc and nickel ions difficult to get electron at the surface of electrode. For these reasons, the grain size of the deposits obtained in bath II and III decreased.

The typical cross-section shows the thickness of zinc-nickel coating is less than 100 μm (Figure 2). EDS analysis reveals the composition of about 6~9 wt.% nickel in zinc-nickel alloy coatings with the concentration of TEOS increasing from 0 to 0.01 mol L^{-1}.

Figure 3a-c show typical XRD patterns of zinc-nickel deposits on steel substrates. It is known that electrodeposited zinc-nickel alloys exhibit three main phases: α-phase, a solid solution of zinc in nickel with an equilibrium solubility of about 30% Zn; γ-phase, an intermediate phase with a composition Ni_5Zn_{21}; η-phase, a solid solution of nickel in zinc with a very low amount of nickel [22]. The results show that the coatings deposited at TEOS's concentration of 0 and 0.005 mol L^{-1} show biphasic structures comprised of the γ-phase structure and the hexagonal phase of zinc. Some researches have described the same composition under higher stirring rates and current density [4, 22].

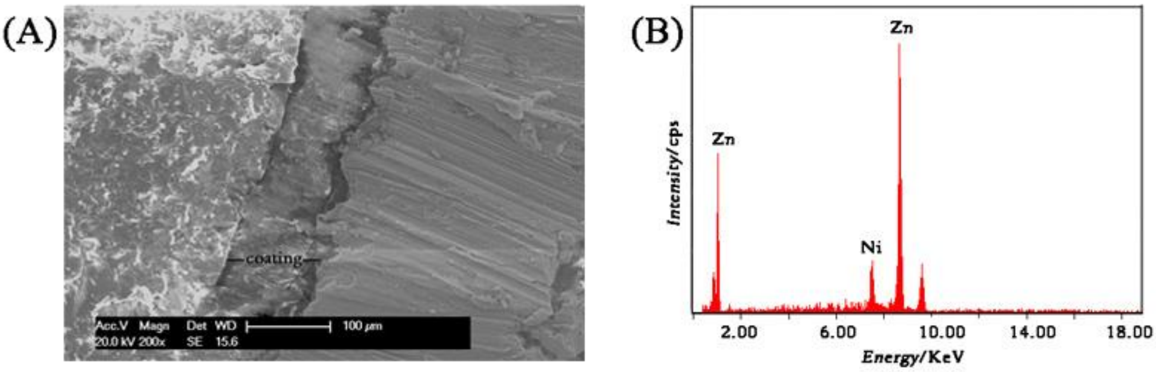

Figure 2. The cross-section (A) and EDS (B) of zinc-nickel coating deposited in the solution containing 0.005 M of TEOS.

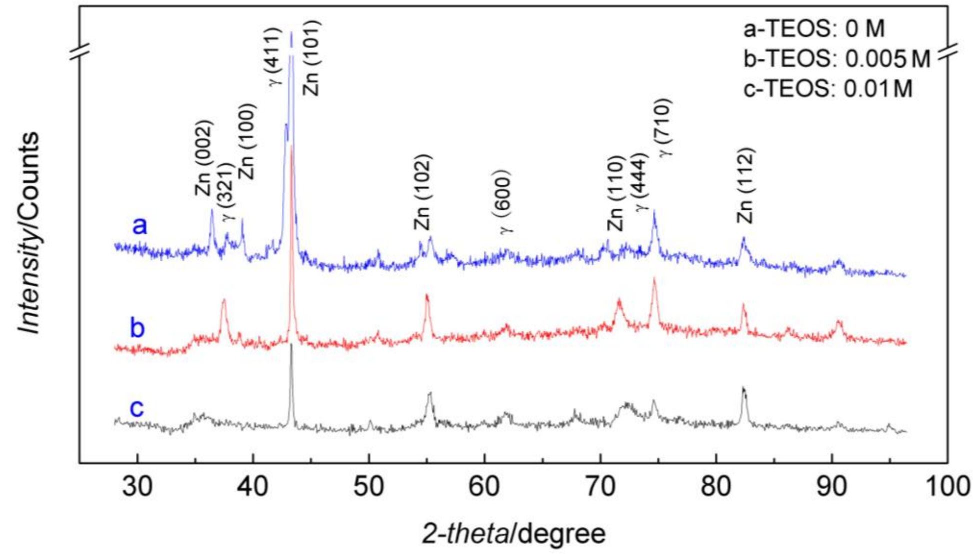

Figure 3. XRD patterns of the composite films fabricated by adding different concentrations of TEOS: (a) 0 M, (b) 0.005 M, (c) 0.01 M.

The formation of crystalline γ-phase is related to the presence of high amount of zinc in the bath. Other authors reported that from deposition baths with similar nickel and zinc contents, the nickel rich α-phase is present [22]. However, the α-phase is not observed in present diffractograms although the bath we used has the same nickel and zinc contents. When the bath has 0.01 mol L^{-1} of TEOS, marked decreases on Zn (0 0 2) and γ (3 2 1) plane intensities is found. The hindrance of the development of planes can be attributed to an increase of the surface energy of this plane in these conditions [30]. The result indicates that TEOS can act as a structure modifier to change the structure of the deposit.

The analysis of the deposit by SEM and XRD techniques help to understand effect of existence of TEOS on morphology and microstructure changes of zinc-nickel deposit. The addition of TEOS in the bath influences grain size, surface roughness and the change of structures and these changes may influence the corrosion performance of the coatings.

3.2 Corrosion tests

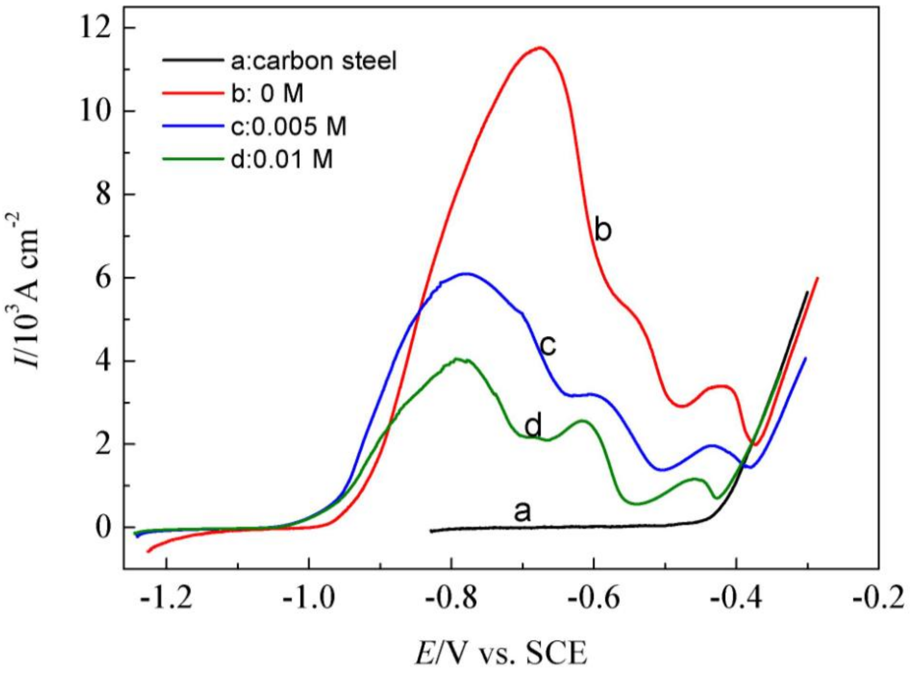

Figure 4. Polarization curves of zinc-nickel coatings with the addition of different concentrations of TEOS (a, carbon steel; b, 0 M; c, 0.005 M; d, 0.01 M).

The potentiodynamic polarization curves for electrodeposited zinc-nickel composite films are presented in Figure 4. It can be observed in Figure 4 that the three curves show similar profile. Curve (a) is presented for reference as the steel substrate. The first current peak is attributed to the dissolution of the zinc phase in the zinc-nickel alloy [11]. The remaining phase shows a higher corrosion resistance. The two left peaks are attributed to γ and nickel rich phases. Dezincification leads to the formation of an improved barrier layer which reduces the rate of anodic dissolution. Initially, the zinc corrodes completely, its dissolution peak is high but nickel dissolution peak is low because zinc is deposited with higher content and nickel with lower. Then the steel dissolves through the pores or microcracks in the zinc-nickel coatings, corresponding to the increase of current at about□ -400 mV (vs SCE). Compared with the coating deposited in bath I, other coatings have the lower current density. This indicates the addition of TEOS can improve the corrosion resistance of zinc-nickel coatings. This can be attributed to the refined grain size and the change of structures.

In order to evaluate the long time protection behavior of the three electrodeposited coatings, the evolution of OCP and EIS with respect to the immersion time in the 3.5 wt% sodium chloride solution were studied.

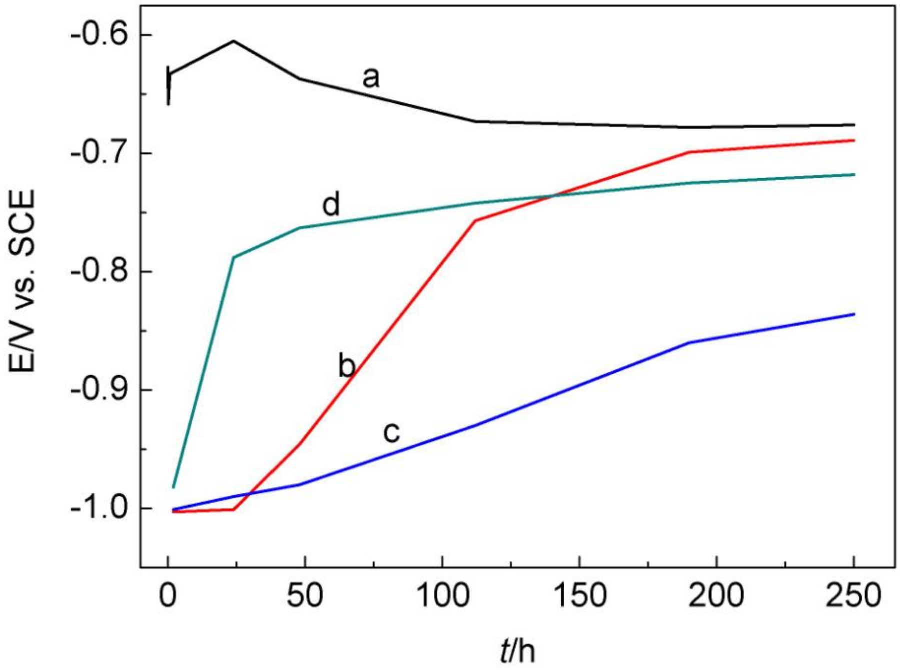

Figure 5. OCP versus times for the coatings deposited in the solution containing different concentrations of TEOS: (a, carbon steel; b, 0; c, 0.005 M; d, 0.01 M).

It can be seen in Figure 5 that all of the zinc-nickel coatings present a corrosion potential lower than steel. With increasing immersion time, all the OCP tend towards nobler values. The shift of the OCP towards more positive values is consistent with the biphasic structure of the coating, comprised of the hexagonal phase of zinc and γ phase [4]. It indicates a progressive decrease in the sacrificial properties of the zinc-nickel coating. This change is the result of the dissolution of the zinc from the coating and the accumulation on the surface of electrode. However, there are several differences in OCP behavior depending on the concentration of TEOS in electrodeposition bath. At longer immersion times 250 h the OCP value is close to that of steel, although still lower than it, for the coating deposited with 0 and 0.01 mol L^{-1} TEOS. But the coating deposited with 0.005 mol L^{-1} TEOS, has an OCP value of −834 mV, still about 150 mV more negative than the steel, −678 mV. This indicates the coating still has cathodic protection ability to the substrate.

Electrochemical impedance spectroscopy (EIS) is a well known powerful, non-destructive electrochemical technique for characterizing electrochemical reactions at the metal/electrolyte interface and the formation of corrosion products [31]. Herein, EIS are recorded at the open circuit potential after 2, 48, 112 and 250 h to monitor the change of the zinc-nickel coating in 3.5 wt% sodium chloride solutions.

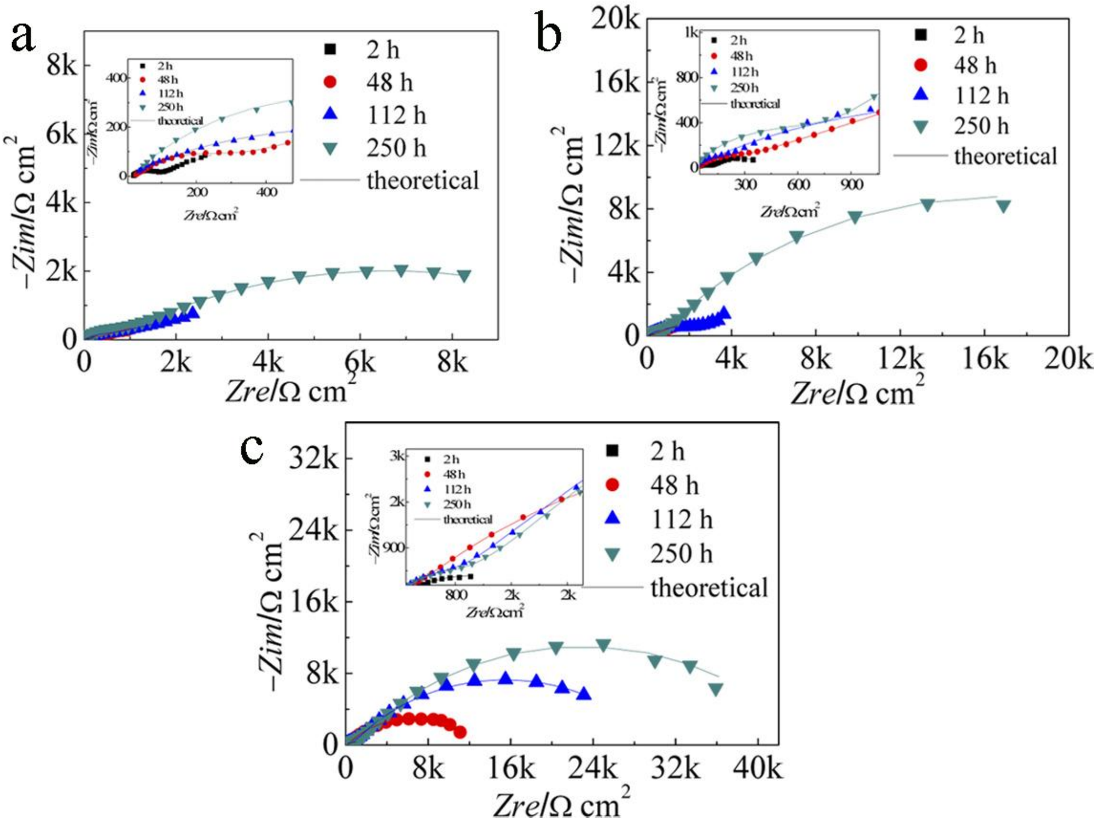

Figure 6. Representative Nyquist diagrams for the coatings deposited at different concentrations of TEOS: (a) 0 M, (b) 0.005 M, (c) 0.01 M.

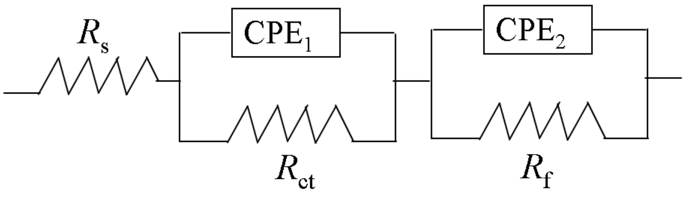

Figure 7. Equivalent circuit used for fitting the impedance data of the zinc-nickel coatings.

Figure 6 shows the impedance spectra in 3.5 wt% sodium chloride solution as a function of time. As shown in Figure 6, it is remarkable that all the diameters of semicircles in three EIS schemes increase with the exposure period from 2 to 250 h, which suggests the increase in the charge transfer resistance of the corrosion film resistance with time. The EIS for different exposure times were fitted to circuit parameters in the computer program. Figure 7 shows the corresponding equivalent circuit, which can be satisfactorily used for fitting the EIS obtained at different exposure times. The changes of R_{ct} for the three coatings are listed in Figure 8. It is obviously that the R_{ct} of the three coatings improved as the time increased. Both of the coating obtained from bath II and III have higher R_{ct} values after immersion in the sodium chloride solution for 250 h. As mentioned above, this can be attributed to the dissolution of the zinc phase in the coatings and the nickel rich phase left. Another possibly reason is the corrosion product assembled on the electrode surface. This can be easily concluded from Figure 9. In Figure 9, the surface appearance of the three coatings on carbon steel after 250 h of immersion in 3.5 wt% sodium chloride solution is shown.

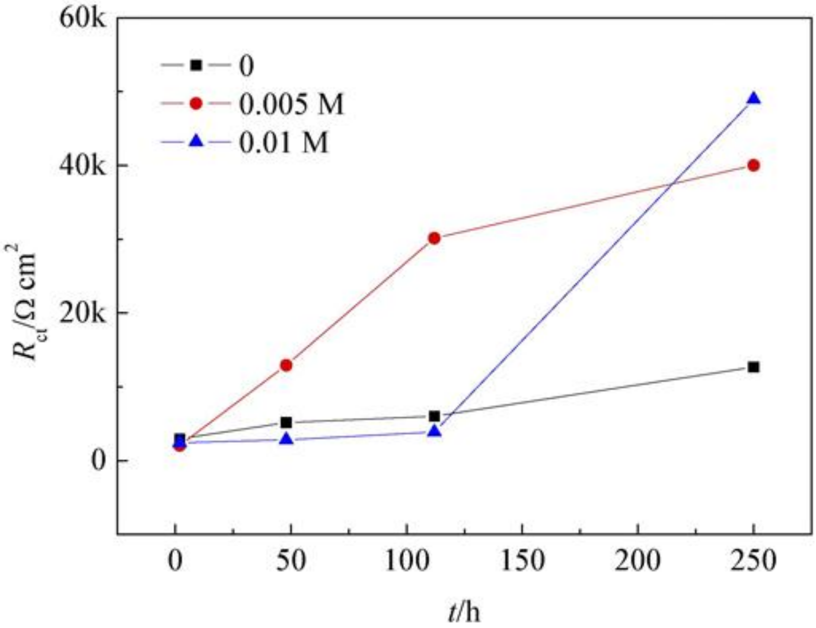

Figure 8. The change of R_{ct} for the coatings deposited at different concentrations of TEOS: 0 M, 0.005 M and 0.01 M.

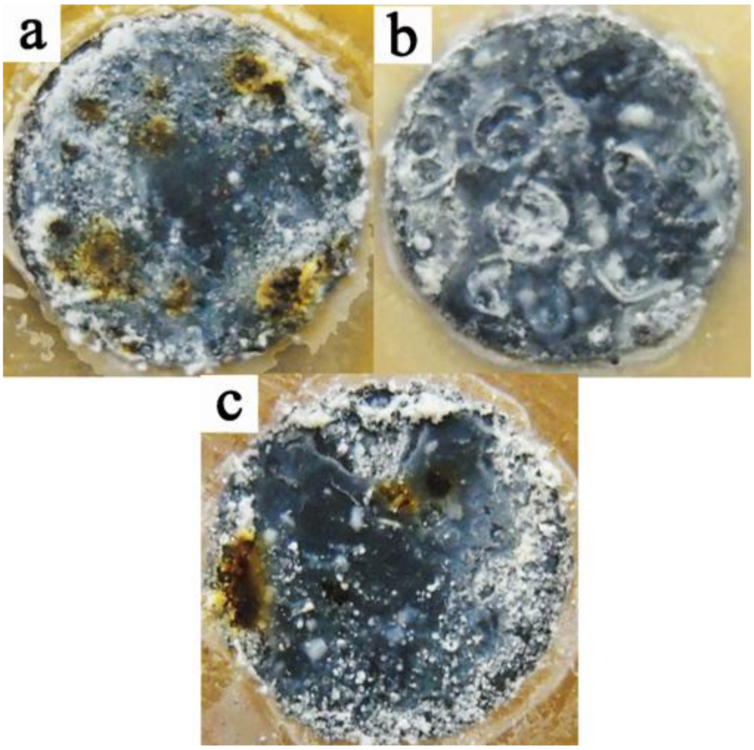

Figure 9. The images of zinc-nickel coatings on carbon steel deposited at different concentrations of TEOS after 250 h of immersion in 3.5 wt% sodium chloride solution ((a), 0 M; (b), 0.005 M; (c), 0.01 M).

There are white and brown corrosion products on the coating deposited with 0 and 0.01 mol $L^{\square 1}$ TEOS. The white product is zinc corrosion product, which including ZnO, $Zn(OH)_2$ et al. The brown product is steel corrosion product, which means the coating is broken. However, the coating deposited with 0.005 M of TEOS has only white corrosion products. This indicates that the coating still has the protection ability to the substrate. This result is in accordance with the OCP results.

4. CONCLUSIONS

Zinc-nickel composite coatings were fabricated on carbon steel substrate from the mixed solution containing different concentrations of TEOS by electrodeposition method. The composite film had different phases and surface morphologies when different concentrations of TEOS were added in solutions. Corrosion measurement results indicated that the film obtained at the TEOS concentration of 0.005 M still showed cathodic protection ability to the substrate after immersion in 3.5 wt% sodium chloride solution for hundreds of hours. This can be attributed to the compact surface and the proper component of nickel in the composite film. The results indicate that TEOS may act as an additive to be used in surface coating industry.

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