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Corrosion Behavior of Oxyacetylene Flame Sprayed Zn-Ni Composites Coating with Spray-dried Agglomerating Powders in Natural Seawater

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In this paper, three different nickel content agglomerated Zn-Ni powders were prepared by spray-dried method, then Zn-Ni composites coating was deposited by oxyacetylene flame spraying method. The anti-corrosion performance of Zn-Ni composites coating in seawater was examined by potentiodynamic polarization and electrochemical impedance methods, together with the analysis of SEM, EDS and XRD. The results show that the thickness of Zn-Ni composite coatings prepared by thermal spraying process is about 300μm. Zinc was consumed first as it is immersed in seawater. The attachment of corrosion products on the coating surface and the formation of nickel-rich layer below the product film can slow down the corrosion rate of coating. With the nickel content increasing, the corrosion potential E_{corr} of coating becomes more positive. When the nickel content is too high, micro-cell corrosion will occur and have a negative influence on the coating. The corrosion products, accumulated within the coating, have a significant impact on the anti-corrosion performance of coating and decrease the corrosion current continuously. The presence of nickel can prevent the dense $Zn(OH)_2$ from being converted into the loose ZnO. The anti-corrosion performance of the coating with 20wt% Ni is the best. The stable corrosion current I_{corr} of the coatings range from $1.24\mu A/cm^2$ to $1.87\mu A/cm^2$, while the stable corrosion potential E_{corr} range from -0.98V to -0.95V. The Zn-Ni coatings meet the requirements of the cathodic protection. It can be concluded from above analysis that Zn-Ni coating can serve as low potential cathodic coating for steel substrate and has a long life period.

Keywords: Oxyacetylene flame spraying, Agglomerating Powder, Zn-Ni coating, Corrosion resistance

1. INTRODUCTION

The corrosion behavior of metals results in enormous economic losses and consumption of resources, including materials degradation, accident and injury to people. So the research of metal corrosion and protection is of great significance in every aspects of society [1]. There are many methods developed to prevent corrosion such as cathodic protection, inorganic coatings, organic coatings and inhibitors. Each type of methods has its features and scope of application. Metallic coating, as an economic and convenient anti-corrosion method, has been widely used to protect metal structure from corrosion at atmospheric environment. There are two basic functions for metallic coating, one is barrier effect, another is cathodic protection. Ideally, a metallic coating must be self-passivation and has a potential lower than substrate, this can make the coating long life circle and high protecting efficiency [2]. At the same time, the potential of coating materials shound not be too negative, otherwise hydrogen embrittlement will happen to substrate. Dacrolon coating is one of such coatings, chromium can accelerate the passivation of zinc then prevent the coating from further consumption. For this reason, the Dacrolon coating had been widely used in automobile industry. Unfortunately, Dacrolon will be prohibited in recently future by most of the government in the world for the poison of hexvalent chromium ion [3]. Researchers are now looking for a new self-passivation coating system for alternatives. But most of the metallic coating can have only one function, either barrier effect or cathodic protection [4-6].

Zinc has a good cathodic protection effect, but has a limited barrier effect in marine environment. People found that the corrosion resistance of zinc coatings can be remarkedly improved by alloying with more noble metals such as Sn, Co and Ni. The nickel zinc alloy is very expensive because it is not easy to prepare nickel zinc alloy through metallurgy for the large melting point difference between nickle and zinc.

Zinc-nickel alloy used as low potential corrosion-resistant alloy, is usually coated by electroplating methods because of difficult in preparing Zn-Ni alloy by fusion metallurgy. However, electroplating process is much complicated, The plating solution will also pollute environment, it is not suitable for on-site operation [7-9]. Some researchers had tried PVD Zn-Ni coating, but also get an unsatisfied result [10]. A possible way to get Zn-Ni alloy coating is thermal spraying. The zinc cannot be flame sprayed directly because the boiling point of zinc is about 900℃ which will lead to evaporation of zinc. At such a high temperature, oxidation also will occur to zinc. While for nickel particle, the melting point is about 1450℃, it will not melt during thermal spraying. So the nickel zinc composites coating can be flame sprayed by agglomerated nickel around zinc particles.

In present work, different Zn-Ni alloy coating is prepared by oxyacetylene flame spraying method with spray-dried agglomerated Zn-Ni powders, and a preliminary study of the barrier and sacrificial corrosion properties Zn-Ni alloy coating is studied by electrochemical test. The mechanism of anticorrosion of Zn-Ni composites coating is also examined.

2. EXPERIMENTAL METHODS

A commercial nickel powder is provided by Shijiazhuang Gaogong Powder company, the purity is 99.9%. A commercial zinc powder is provided by Zhoucheng Powder company, the purity is 99.7%. The nickel and zinc powder were observed under SEM (XL-30 Environmental Scanning Electronic Microscope, manufactured by Philips, Netherland), and the morphology is shown in Fig. 1.

and Fig. 2.. The shape of zinc powder is quasi-spherical with size distribution from 5 um to 50um. The shape of most nickel powder is irregular with size distribution from 1 um to 20um, part of the nickel powder is quasi-spherical. No oxidation can be found on the surface of both powders. The nickel and zinc powder are mechanically mixed on a screen vibrator for 0.5hour with the following nickel content: 10%, 20% and 30%, then agglomerated using a spray drying tower as shown in Fig. 3.. The principal of spray drying is as follows: Cool air is heated in the heater, then transfer to the drier tower by wind machine. Simultaneously, slurry is pumping to centrifugal atomizing disk lying at the top of the drier cabinet. The slurry then is thrown out by centrifugal force and form spherical droplet in the drier. Droplet mixed with hot air in the drier sufficiently, and the water of droplet is evaporated off quickly.

The processing of powder preparation is as follows, the slurry of zinc and nickel power in solvent of ethanol with dispersant and organic binder. The slurry must be stirred to form a suspension solution. The slurry must be spray in half an hour from sedimentation of powders, and the parameter of spray-drying was listed in Tab.1 The agglomerated powder were dried in a drying cabinet for half an hour under the temperature of 100℃, then powder with diameter of 45-150μm were sieved for preparing coating.

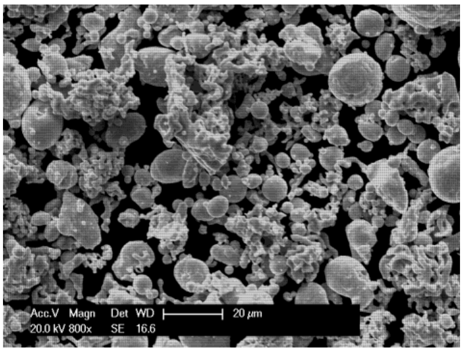


Figure 1. ESEM morphology of nickel powder

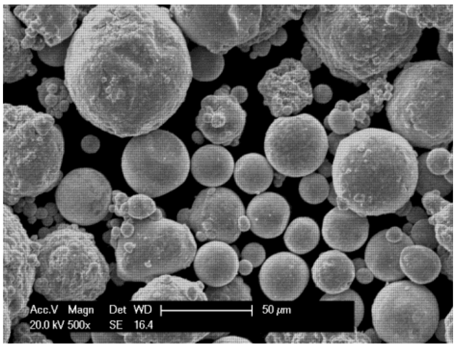


Figure 2. ESEM morphology of zinc powder

Before spray, the substrate is sand blasted by alumina for 15 minutes, with the air pressure about 0.5MPa. This can improve the bonding strength of the coating and substrate by coherence. The substrate used here is Q235 steel. The substrate is preheated to about 90 ℃ to avoid the effect of moisture and the difference of expansion ratio. The equipment used for coatings preparation is SHF-E2000 Oxygen Acetylene Flame Spray machine [11, 12] (Fig. 4). The pressure of oxygen is 0.6 MPa, the pressure of acetylene is 0.1MPa, the volume ratio of oxygen to acetylene is l:1.2, volume ratio of oxygen to acetylene is l:1.2 for preheating gas. Three kinds of coatings are prepared according to the powders. A self-designed G10-100 syphonaged spray gun is used for sample preparation. The powder is syphonaged into the spray gun from a coaxial powder feeding pipe. The highest temperature of the powder travels from the feeding pipe to the substrate is about 1000℃.

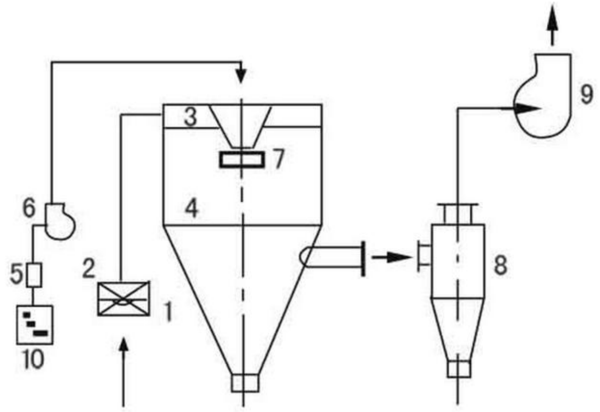


Figure 3. The sketch photo of Spray Drying installation. 1-Air filter; 2-heater; 3-hot air distributer; 4-drying chamber； 5-purifier; 6-pumping; 7-nozzle； 8-cyclone seperator； 9-fan； 10-liquid feeding duct

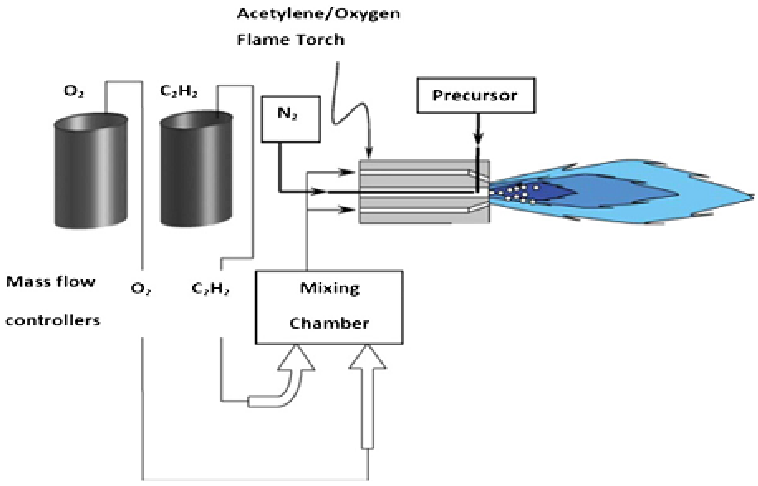


Figure 4. Schematic diagram of oxyacetylene flame setup

Table 1. Processing parameter of spray-dried process

Inlet temperature/℃	Outlet temperature/℃	Feeding rate/ml·s-1	Rotation speed of atomization plate/r·min-1
160	45	6-6.5	17000

As sprayed coating are cut through the cross-section. Microstructural characteristics of corroded surfaces were observed with optical microscope (ZEISS PRIMOSTAR-3-iCAM, German) and scanning electron microscope (SEM). Chemical analyses were carried out with energy-dispersive X-ray spectroscopy (EDX).

Samples preparation for electrochemical test: As sprayed coatings are cut into pieces with size of 20mm x 20mm, welded with copper lead, sealed with epoxy resin with 10mm*10mm area as working face, distilled with acetone, water and ethyl according to priority after dried with an air drier.

Electrochemical tests are carried out in a conventional three electrodes system with Par 2273 Potentiostat Electrochemistry Workstation (Ametek company, America), SCE as a reference electrode, Pt electrode as a counter electrode, natural seawater (from Maidao corrosion test site of China Corrosion Association) as the electrolyte. The scanning rate for potential dynamic test is 0.4mV/s; a sinusoidal potential of 10mV in amplitude is used for electrochemical impedance test, the frequency ranges from 100kHZ to 10mHZ. All electrochemical data are collected after the potential become stable. The surface morphology of coating after 60 days' immersion is examined by ESEM.

Scanning Electron Microscopy (SEM) was used in work for high magnification imaging and elemental analysis. A Philips-30 scanning electron microscope equipped with an energy dispersive spectrometer (EDS) was used for the analysis. The accelerating voltage and current in the measurements were 15 kV and 12 nA, respectively, and the resolution of the instrument was 3.5 nm (35 kV).

X-Ray diffraction (XRD) was used to investigate the bulk phases present in the sample and to determine the phase transformations during the flame spray. The XRD diffractograms presented in this study were recorded on a Bruke D8 advanced diffractometer employing Cu Kα radiation ($\lambda = 1.5406$ Å, 40 kV, 30 mA) at 0.020° intervals in the range $5° \leq 2\theta \leq 90°$ with 1s count accumulation per step. Diffraction patterns were assigned using the PDF database supplied by the International Centre for Diffraction Data (PDF2- Diffraction Database File).

3. RESULTS AND ANALYSIS

3.1 Character of agglomerated powder

The agglomerated powders of different nickel content have some different characters (Fig. 5). Some of the particle is quasi-spherical, it is zinc powder without nickel covering on it. It can be seen that not all zinc powder are covered by nickel, and not all nickel powder are stick to zinc powder. Obviously, the ratio of covered zinc powder increase with the increase of nickel content. This character of powder determines that the nickel particle will not melt during spraying, but the nickel covering on the zinc can prevent oxidation during thermal spray procedure.

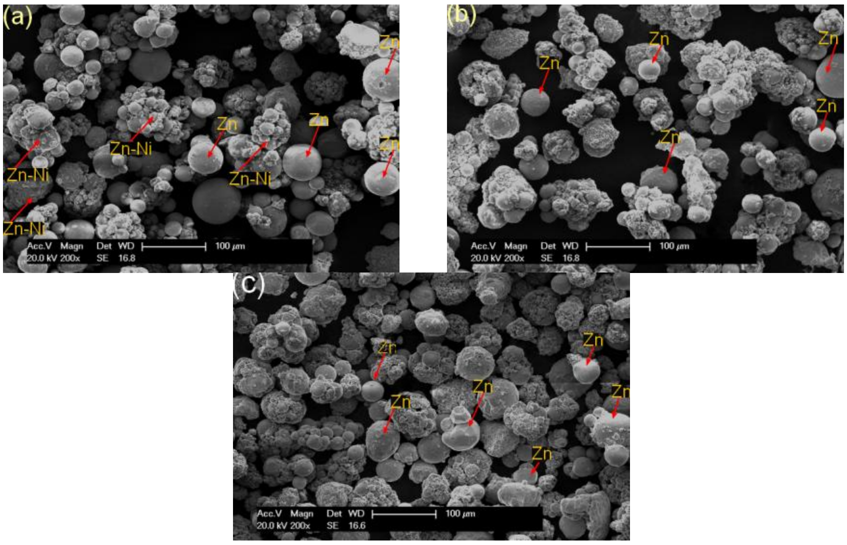


Figure 5. ESEM morphology of agglomerated zinc nickel powder, a) 10% nickel; b) 20%; a) 30% nickel

3.2 Character of Zn-Ni composite coating

The cross-section morphology of different coatings is shown in Fig. 6. It can be seen from the picture that the weight content of nickel in coating are not consistence to the content in powder for each samples. The content of nickel increases as the nickel content increases in powders. The nickel particles are dispersed in the coatings. No nickel zinc alloy phase are found in XRD spectrum (Fig. 7). Also there is no oxide phase is observed by XRD. The nickel particle did not deform during thermal spraying.

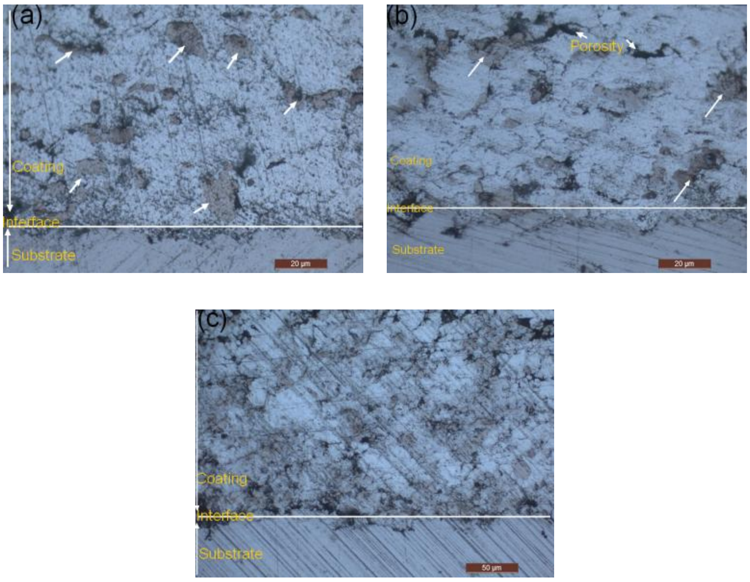


Figure 6. OM morphology of composite zinc nickel coating on steel substrate, a) 10% nickel; b) 20%; a) 30% nickel

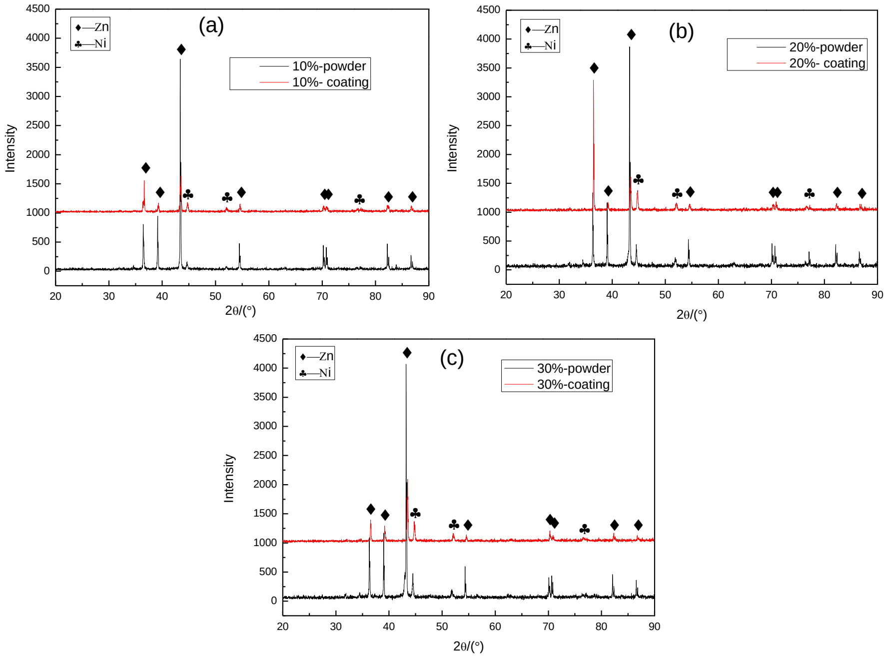


Figure 7. Comparison of XRD spectrum of agglomerated zinc nickel powder and zinc nickel composites coating, b) 10% nickel; b) 20%; c) 30% nickel

The spraying temperature is over 1000℃ but lower than 1455℃. The porosity of three kinds of coatings is about 3.8%, 4.5% and 6.6% respectively. Porosity of coating is strongly influenced by deformation of feeding particles, as the content of the nickel increases, the undeformed particles increases, then the porosity degree increases. It can be inferred that there are no oxidation and phase transformation during the spraying process by comparing the XRD spectrum of powders and corresponding coating.

3.3 Corrosion morphology and products of Zn-Ni coating

The cross-section morphology of different coatings shows that after 60 days' immersion, most of the pores are filled up with corrosion products (Fig. 8). The coating contains mainly zinc and nickel element before immersion (Fig. 7), it means that the covering of nickel prevent the zinc from oxidation. After 60 days immersion, the products on the surface is mainly ZnO, $Zn(OH)_2$ and $ZnCl_2$• $4Zn(OH)_2$ (Fig. 9). Zinc and nickel can also be detected by XRD spectrum that the thickness of the corrosion products is not enough to cover the information of substrate [13, 14]. The enrichment of nickel can be detected by comparing the height ratio of nickel peak to zinc peak after a period immersion.

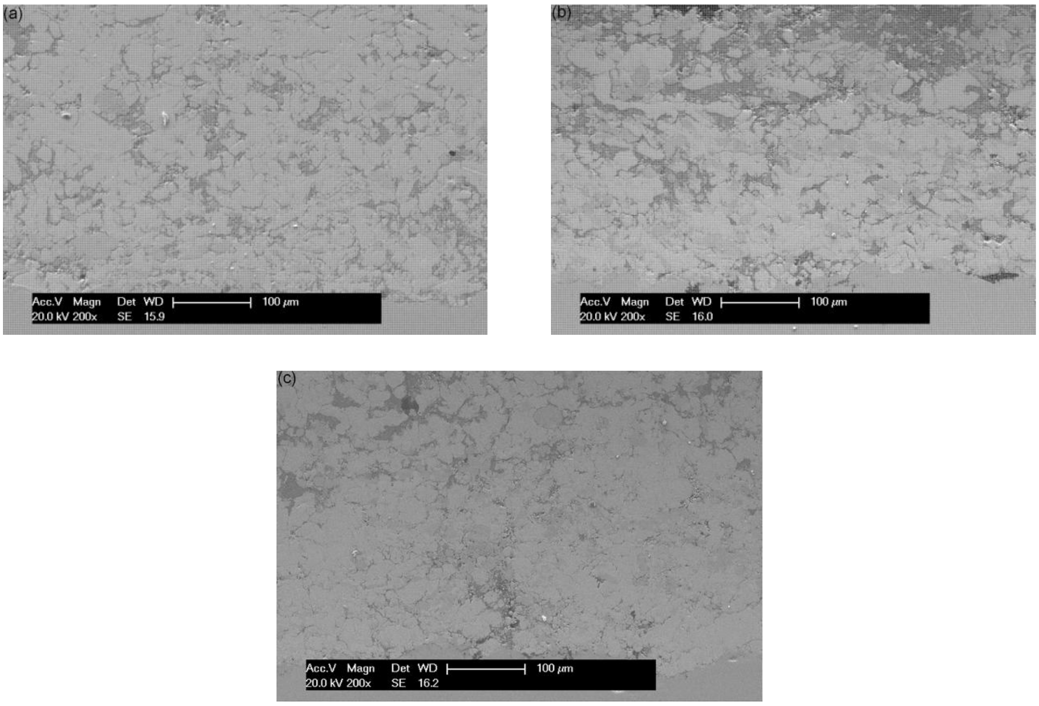


Figure 8. OM morphology of composite zinc nickel coating on steel substrate, a) 10% nickel; b) 20%; a) 30% nickel

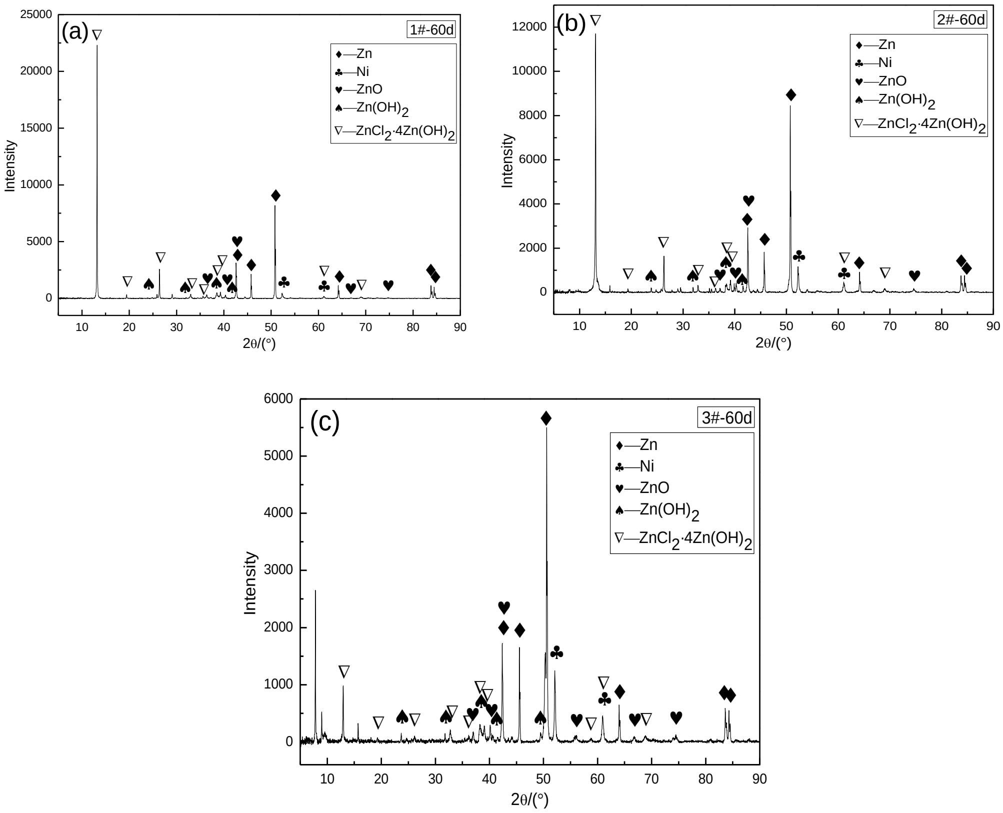


Figure 9. XRD spectrum of agglomerated zinc nickel powder and zinc nickel composites coating, b) 10% nickel; b) 20%; c) 30% nickel

3.4 Potentiadynamic polarization of Zn-Ni coating

It can be seen from the polarization curve as shown in Fig. 10 that there is no passivation potential region. The Tafel slope is much small for the corrosion reaction of zinc. This phenomenon indicates that the coating has no passivation effect. The Tafel extrapolation method is used to measure uniform corrosion rates. The Tafel slopes, being the slopes of the straight line portion of the semi-logarithmic polarization curve on both anodic and cathodic regions, are extrapolated until they intersect. The corrosion rate calculated by above method is shown in Fig. 11, it also can be seen from the corrosion rate and the resistance module that the corrosion resistance of the coating becomes large and the corrosion rate become smaller. This is a typical phenomenon for zinc base coating in seawater environment [15, 16]. The corrosion products of zinc block the pores of the coating and form a barrier layer on the surface of the coating, which makes the samples have lower corrosion rate. The stable corrosion current I_{corr} of the coatings range from 1.24μA/cm^2 to 1.87μA/cm^2, The 20% nickel coating has the most stable corrosion rate and lowest corrosion rate.

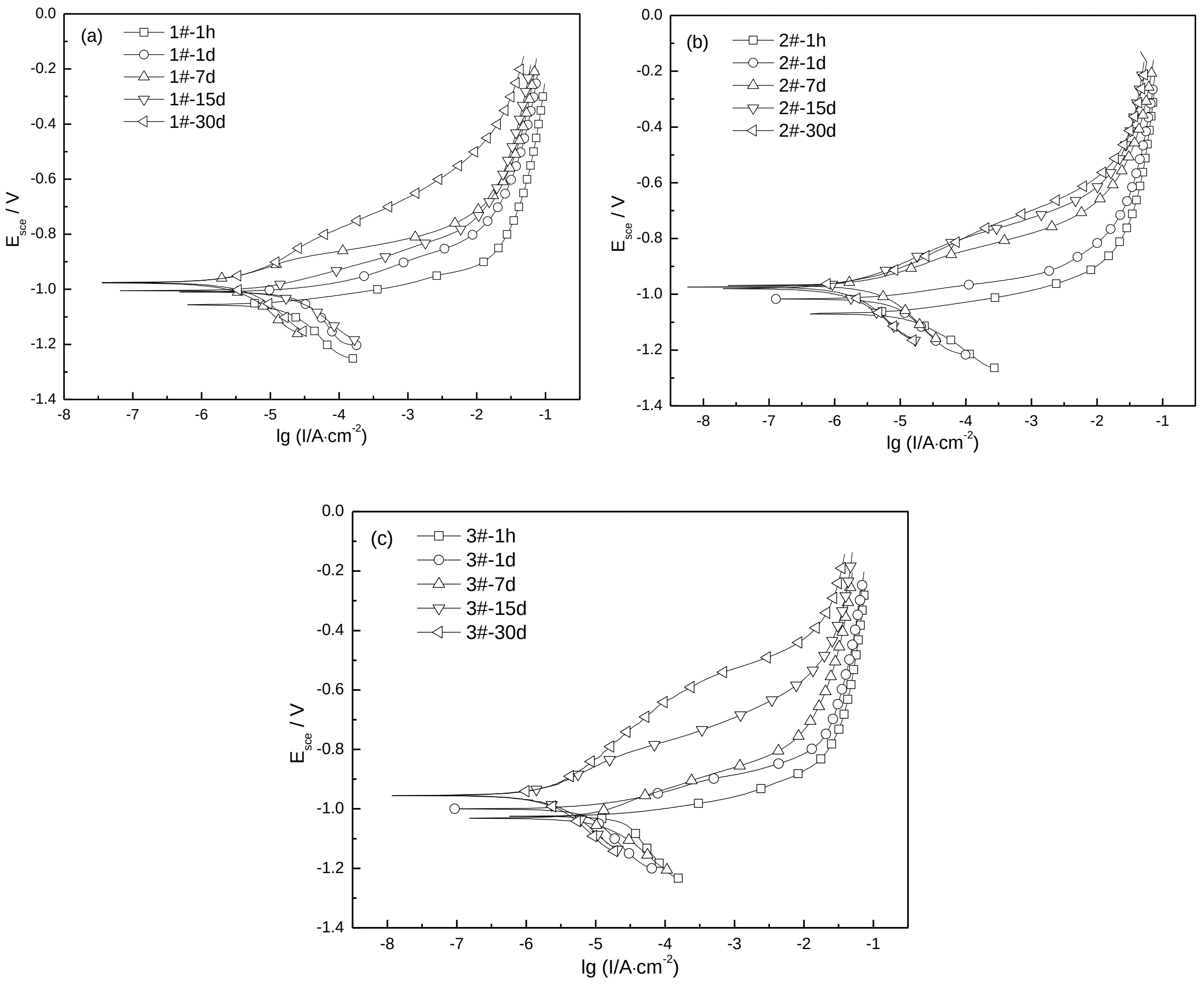


Figure 10. Variation of potentialdynamic polarization curve of composites zinc nickel coating in seawater with time, a) 10% nickel; b) 20%; c) 30% nickel

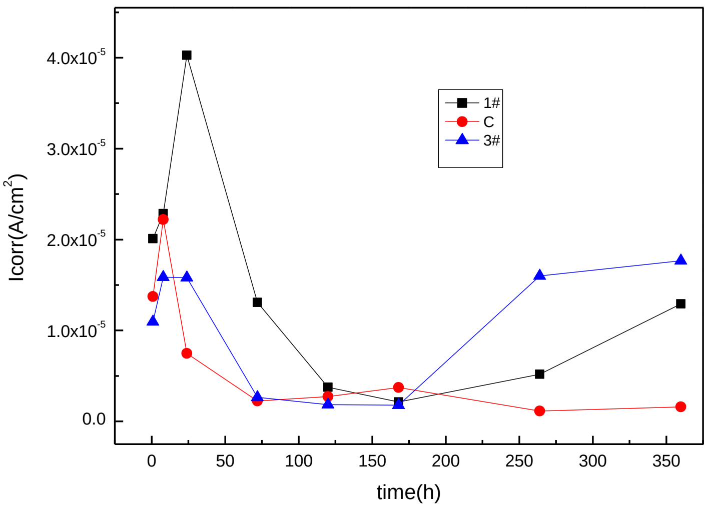
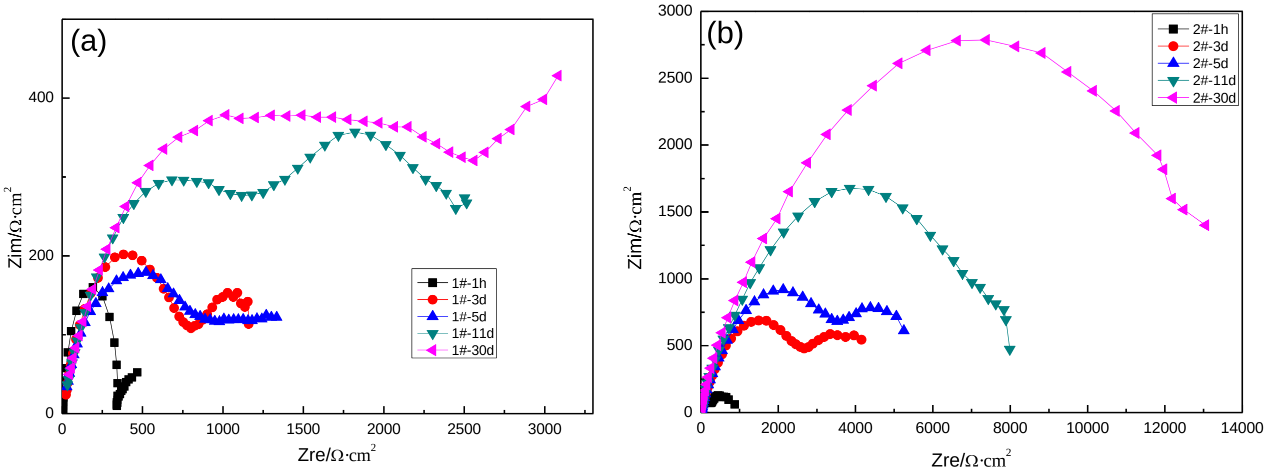


Figure 11. Corrosion rate of composites zinc nickel coating in seawater with time

3.5 Electrochemical impedance of of Zn-Ni coatings

The Nyquist plots of different samples in seawater are shown in Fig. 12. For all coatings, there are two time constant at first 15days, so all the structure of coating can be expressed as a equivalent circuit as shown in Fig. 12. R_s is solution resistance, Q_c is capacitance of coating, R_c is coating resistance, Q_{dl} is capacitance of coating, R_t charge transfer resistance. It can be seen from the simulation that the equivalent circuit can express the structure and reaction occurred on the coating ideally.

The semi-circle of each types of coating is severely flattened, which means that there are two time constants for each type of samples, one time constant corresponding to electrochemical reaction, another time constant corresponding to corrosion products. The resistance of Zn-Ni coating increases as immersion time increases. The corrosion products accumulated on the surface increases the barrier effect and slow down the dissolving rate of zinc. At the same immersion time, the 20% nickel coating has the largest corrosion resistance. The R_c and R_t both increase as immersion time increases. R_c is the barrier effect induced by corrosion product, and R_t is the charge transfer resistance of electrode.



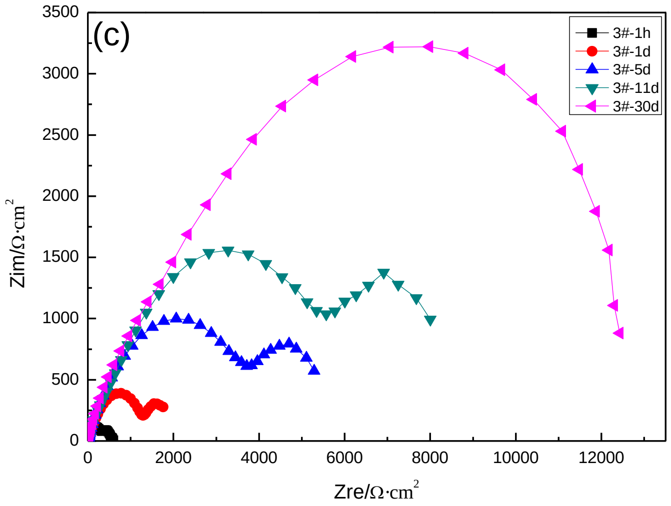


Figure 12. Variation of electrochemical impediance of composites zinc nickel coating in seawater with time, a) 10% nickel; b) 20%; c) 30% nickel

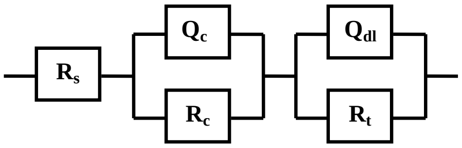


Figure 13. Equivalent circuit of Zn-Ni composite coatings in seawater

4. DISCUSSION

The potential of different coatings become positive abruptly as immersion time increases, then drop gradually to a stable value. The reason of potential increase is because that the formation of corrosion products and the enrichment of nickel in the corrosion product. Apparently [17], nickel seldom dissolves in seawater under open circuit potential, especially when it attaches to negative metal such as zinc. Then after a certain period, the potential become positive. Finally, the potential of 30% nickel is the most positive among three samples. Further information is needed to judge the effect of nickel on corrosion potential, and there is not a linear relation between corrosion potential and nickel content in coatings, neither between corrosion potential and nickel content. The nickel has two aspects effect on corrosion rate of Zn-Ni composites coating, nickel can prevent corrosion products of $Zn(OH)_2$ from converting to ZnO. $Zn(OH)_2$ and $ZnCl_2$• $4Zn(OH)_2$ is much more compact than ZnO, which can prevent corrosion medium from permeating to the substrate. The corrosion products of pure Zn is mostly ZnO, numerous studies[18,19] had indicated that ZnNi coating has a much higher anti-corrosion performance than pure zinc coating mainly due to the type of products. The EIS results can also validate this conclusion, The R_c and R_t both increase as immersion time increases. R_c is the barrier effect induced by corrosion product, and R_t is the charge transfer resistance of electrode. The nickel can also inhibit the cathodic reaction. Reduction potential of oxygen on nickel is much higher than on zinc, so the reaction rate of oxygen reduction will be hold back by addition of nickel in zinc coating. At the same time, the potential of nickel is much higher than that of zinc, micro corrosion cell effect will lead a main role if the nickel content is too high. According to previous studies, for zinc nickel alloy coating, the maximum nickel content is about 15%. The anti-corrosion performance of nickel zinc alloy coating will decrease as the nickel content increase in the alloy. It is also true for Zn-Ni composites coating, it can be inferred that the 20% nickel content coating has the best anti-corrosion performance and longest corrosion life under the same thickness. While the 30% nickel coating is not so good as 20% nickel coating.

Through above analysis, a two stages reaction mechanisms can be proposed for corrosion behavior occurred on the surface of Zn-Ni composites coating, it can be written as follows:

1) First stage:

Anodic reaction:

$$Zn+2H_2O\rightarrow Zn(OH)_2+2H^++2e \qquad (1)$$

$$Zn(OH)_2\rightarrow ZnO+H_2O \qquad (2)$$

Cathodic reaction:

$$O2+H_2O+4e\rightarrow 4H_2O \qquad (3)$$

2) Second stage

$$5ZnO+ 4H_2O+2Cl^-\rightarrow ZnCl_2\cdot 4Zn(OH)_2 \qquad (4)$$

5. CONCLUSIONS

From above analysis, the following conclusion can be drawn: he results show that the thickness of Zn-Ni composite coatings prepared by thermal spraying process is about 300μm. Zinc was consumed first as it is immersed in seawater. The attachment of corrosion products on the coating surface and the formation of nickel-rich layer below the product film can slow down the corrosion rate of coating. With the nickel content increasing, the corrosion potential E_{corr} of coating becomes more positive. The nickel can enhance the stable potential of coating and decrease the corrosion electromotive force. When the nickel content is too high, micro-cell corrosion will occur and have a negative influence on the coating. The corrosion products, accumulated within the coating, have a significant impact on the anti-corrosion of coating and decrease the corrosion current continuously. The presence of nickel can play a role that restrain the dense $Zn(OH)_2$ to be converted into the loose ZnO. The anti-corrosion properties of the coating with 20wt% Ni is best. The stable corrosion current I_{corr} of the coatings range from $1.24\mu A/cm^2$ to $1.87\mu A/cm^2$, while the stable corrosion potential E_{corr} range from -0.98V to -0.95V. The Zn-Ni coatings meet the requirements of the cathodic protection. It can be concluded from above analysis that Zn-Ni coating can serve as low potential cathodic coating for steel substrate and has a long life period.

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