

Corrosion Resistance of ZnNi/Nanosilica Alloy Coating on Carbon Steel

Nguyen Thi Thanh Huong, Le Ba Thang, Le Duc Bao, Truong Thi Nam and Nguyen Van Chien
Institute for Tropical Technology, Vietnam Academy of Science and Technology,
18, Hoang Quoc Viet, CauGiay, Hanoi, VIETNAM.

ARTICLE INFO

Article history:

Received: 29 July 2019;

Received in revised form:

27 August 2019;

Accepted: 7 September 2019;

Keywords

Composite Electrodeposition,
Corrosion Resistance,
SiO₂ Nanoparticles,
SEM.

ABSTRACT

In this paper, study on the electrodeposition of ZnNi/nanosilica alloy coating on carbon steel and influence of 5g/L nanosilica in the plating bath on some properties such as morphology, structure characteristics and corrosion resistance of the ZnNi/nanosilica coating were conducted. The results revealed that ZnNi/nanosilica composite coating contained 16.37 % Ni and 0.32 % Si. Only the phase $\gamma\text{Ni}_5\text{Zn}_{21}$ were observed in the ZnNi/nanosilica alloy coatings. The thickness of the ZnNi/nanosilica coating was 16.56 μm . The corrosion resistance on the ZnNi/nanosilica coating was evaluated by time for red rust appearing in salt fog test as 900 hours.

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1. Introduction

Electrodeposited ZnNi coatings have found extensive use for the corrosion protection of steel. They are effective in isolating to the substrate from environment and afford sacrificial protection to steel if damage occurs to the coatings. Electrodeposited Zn-Ni alloy coatings can obtain from other solutions [1-11], such as chloride solution containing amonichlorid, cyanide, sulphate or acetate.

ZnNi coating has been used to replace cadmium electrodeposite which is widely used in the automobile and aerospace industries because of its excellent corrosion resistance. Our work on ZnNi/nanosilica composite coating is aimed at replacing the cadmium coating with ZnNi/nanosilica alloy because this coating shows great promise from the corrosion resistance point of view. ZnNi/nanosilica coating may also find a wide range of advanced applications in marine industry, so we found it interesting to study this type of composite coating in 3% NaCl. The particles of SiO₂ are hydrophilic and hence incorporate hardly into the surface of cathode [2].

In this paper, codepositing nanosilica particles into the Zn-Ni alloy coating under direct current in order to improve the surface properties and the corrosion resistance in aggressive media is studied.

2. Experimental

SPHC steel specimens were cut into size 100 x 50 x 1.2 mm. Chemical composition of the SPHC steel sheet is in accordance with JIS G3131. The specimens were prepared by mechanically polishing with sandpaper 280, 400 and 600, degreasing, and acidic pickling.

The nanosilica powder (AEROSIL 200, Belgium) with average particle size of 15 nm and surface area of 200 m²/g was used as received without any pretreatment. Before electrodeposition, the nanoparticles were dispersed in the bath by sonication 20 kHz for 30 min. Particles with concentration of 5 g/L were maintained in an electrolytic bath in suspension by continuous magnetic stirring of 200 rpm for at least 24 hours before deposition.

Zn-Ni and ZnNi/nanosilica coatings were produced in a 20 liter bath containing 60 g/l ZnCl₂; 250 g/l NH₄Cl; 150 g/l NiCl₂; 20 g/l H₃BO₃; with and without 5g/l nanosilica with operating conditions: pH 5.6, current density 3A/dm², plating time 20 minutes and temperature 30°C, anode: Nickel.

The specimens were kept in a decicator at room temperature before surface analysis and corrosion tests.

The phase structure of coatings was studied using XRD. The surface morphology of treated specimens was investigated by means of SEM. In this study, the specimens were cut into 1 cm × 2 cm for XRD and 1 cm × 1 cm for the SEM analyses.

The corrosion behavior of the specimens was evaluated by polarization tests. Polarization tests were performed at a scan rate of 2 mV/s in 3.5% NaCl solution using a conventional three-electrode cell: specimen as a working electrode, saturated calomel electrode (SCE) as a reference electrode and a platinum counter electrode. All electrochemical experiments were performed using Bio-Logic VSP-300.

The salt spray testing of these treated samples was performed on Q-FOG CCT-600 according to the standard JIS H8502. The samples were exposed to 5 % NaCl fog in a salt spray chamber at 35 °C. The coverage of the sample surfaces by the white and red corrosion products was recorded.

3.Result and Riscussion

3.1. Distribution of nanosilica in plating solution

After dispersed nanosilica particles, the ZnNi/nanosilica plating solution (Figure 1) was stabilized for 24 hours under normal conditions. Before measured dispersion of nanosilica, the solution had conducted ultrasound in 30 minutes. The results are shown on Figure 2 and Table 1.

The size of nanosilica particles had a direct effect on the stability of the plating solution and on the strength of the ZnNi/nanosilica alloy coating. The size of nanosilica particles depended not only on the initial size of particle, but also on the dispersion conditions and the surface state of the particles.



Figure 1. The dispersion of nanosilica particles in water (1); in ZnNi/nanosilica plating solution (2); Zn-Ni plating solution without nanosilica (3).

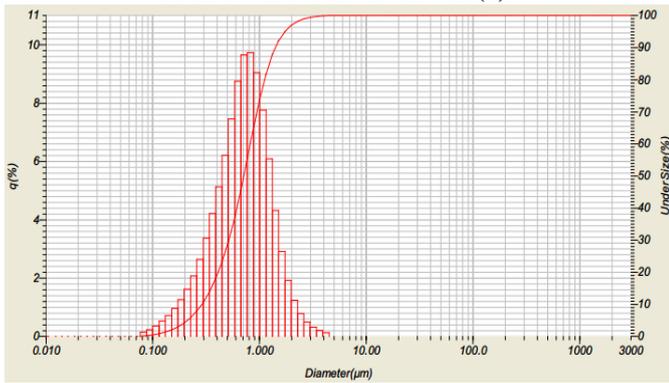


Figure 2. Distribution of nanosilica particles in ZnNi/nanosilica plating solution.

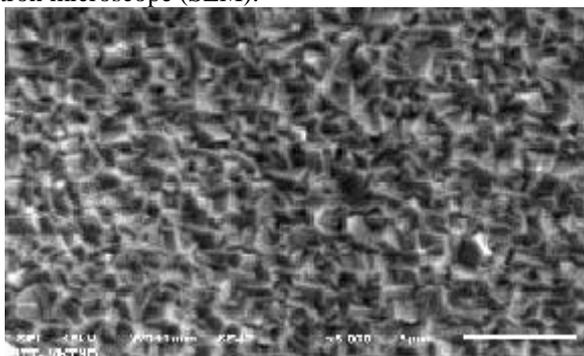
Table 1. Distribution of nanosilica particles in ZnNi/nanosilica plating solution.

The particle size (nm)	Percentage of the particle size (%)
87	0.140
150	1.948
172	2.902

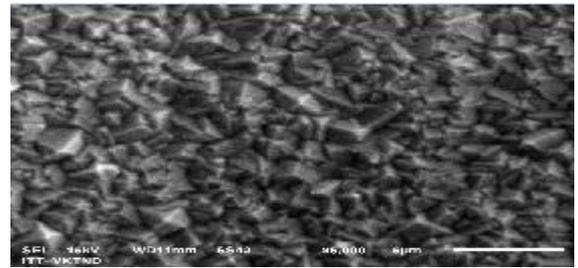
From Figure 2 and Table 1, the smallest particle size of nanosilica in the ZnNi/nanosilica solution was 87 nm. The size of nanosilica particles in the plating solution was larger than that of the nanosilica particles dispersed in water (58 nm). Because pH of the plating solution was low (pH ~ 5.6), so after the plating solution was dispersed nanosilica particles, these nanosilica particles were easily agglomerated to form bigger particles.

3.2. SEM Micrographs

Morphology of coatings was investigated by scanning electron microscope (SEM).



a. Zn-Ni.



b. ZnNi/nanosilica.

In Figure 3, these alloy coatings were plated as pyramid-shape crystal of the gamma phase. These crystals were fine and compact. The cross sectional thickness of the coating was about 16.56 µm (Figure 4).

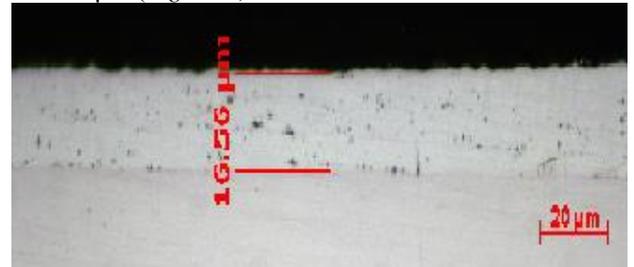


Figure 4. Thickness of the coating ZnNi/nanosilica.

3.3. EDX analysis

In order to determine the presence of nanosilica in the alloy coating, EDX analysis was performed on Zn-Ni and ZnNi/nanosilica alloy plating samples in Figures 5 and 6.

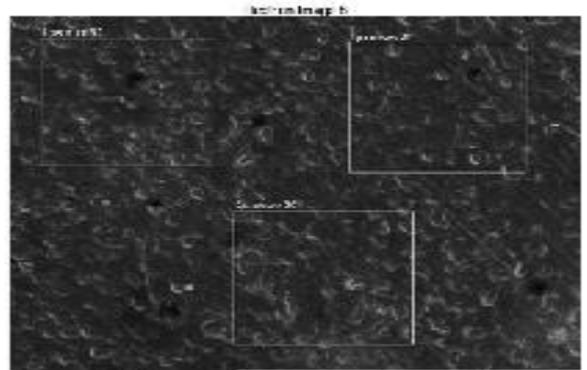
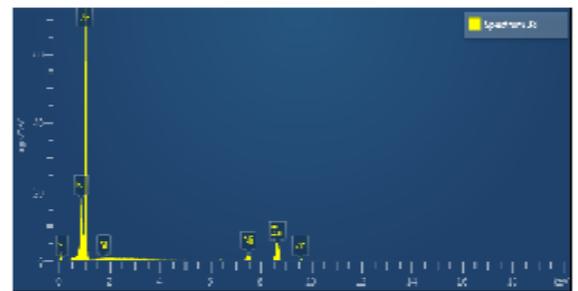
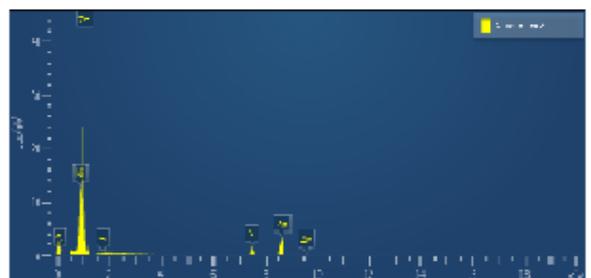


Figure 5. EDX scattering spectrum of the Zn-Ni coating.



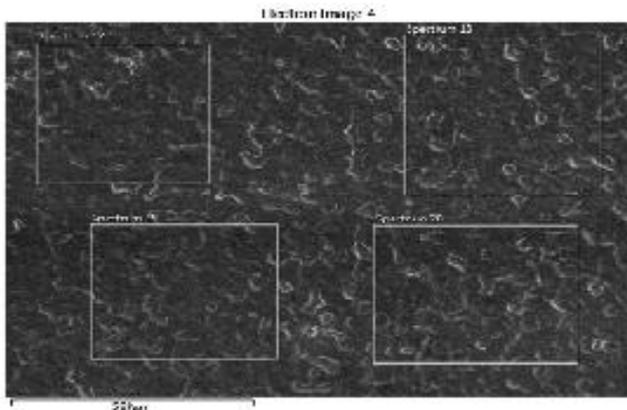


Figure 6. EDX scattering spectrum of the ZnNi/nanosilica coating.

The results of EDX analysis in Table 2 show that the Si element was absent in the Zn-Ni coating, but present in the ZnNi/nanosilica coating with an Si content of 0.32 %, revealed a higher percentage of Ni in the deposit. The nanosilica had been successfully combined to form the ZnNi/nanosilica alloy coating.

Table 2. Content of Zn, Ni and Si of the coatings.

Coatings	Zn-Ni	Zn-Ni-SiO ₂
Elements, % weight		
Ni	14.41	16.37
Zn	85.59	83.32
Si	0	0.32

3.4. FTIR analysis

In order to determine the presence of nanosilica in the alloy coating, the infrared spectra of Zn-Ni and ZnNi/nanosilica alloy coatings were investigated. Nanosilica was also analyzed by FTIR to determine the range of the wave characteristic of nanosilica. The result was as follows:

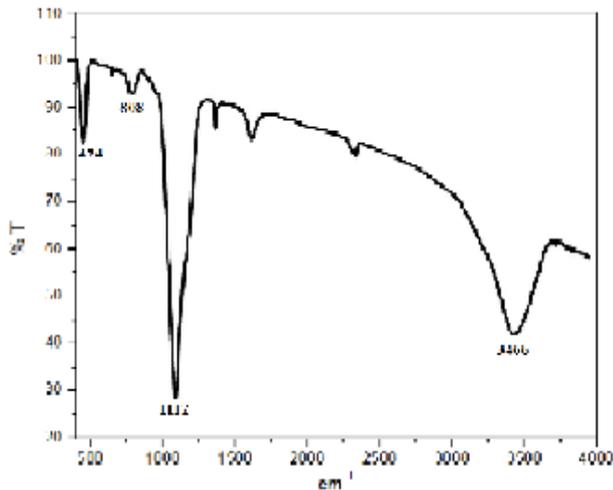


Figure 7. IR spectra of nanosilica

In Figure 7, the characteristic peak for silica functional groups appeared in the IR spectra 3000- 3750 cm⁻¹ that corresponded to the valence oscillation of the OH group and water in the sample. Peaks sharp, with a strong intensity of about 1112 cm⁻¹, a weak at 808 cm⁻¹ and a strong at 474 cm⁻¹ corresponded to the asymmetric valence oscillation, the symmetric valence oscillation and the deformation oscillation of the Si-O. The FTIR measurement was used to determine the absorption bands that characterized the oscillations of the Si-O. Based on this result, the presence of silica was determined. The FTIR analysis results of the alloy coatings are shown in Figure 8.

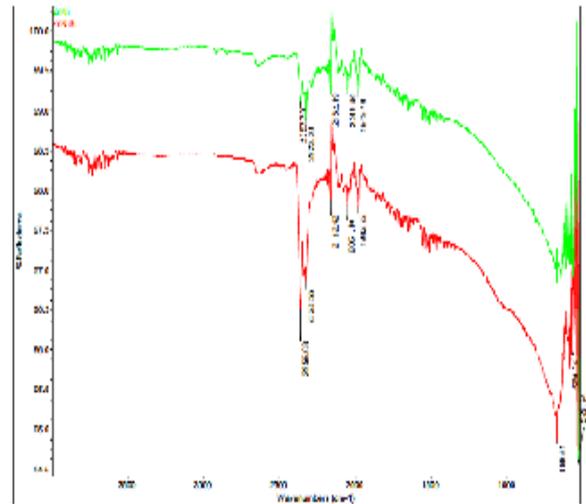


Figure 8. FTIR spectra of the Zn-Ni and ZnNi/nanosilica coatings.

The result of IR measurement of the ZnNi/nanosilica coating showed the absorption peaks around the 1112 cm⁻¹ and 808 cm⁻¹ wavenumbers that was the oscillation of the Si-O. In the ZnNi/nanosilica alloy coating, silicon bonding groups appeared. Whereas there was not the oscillation of the Si-O in the Zn-Ni alloy coatings. The nanosilica had been successfully codeposited to form the ZnNi/nanosilica alloy coating.

3.5. XRD analysis

The X-ray diffraction results are presented in Figure 9. There was not significant changes in phase compositions when nanosilica particles were added. Only the phase γ Ni₅Zn₂₁ were observed in the Zn-Ni and ZnNi/nanosilica alloy coatings.

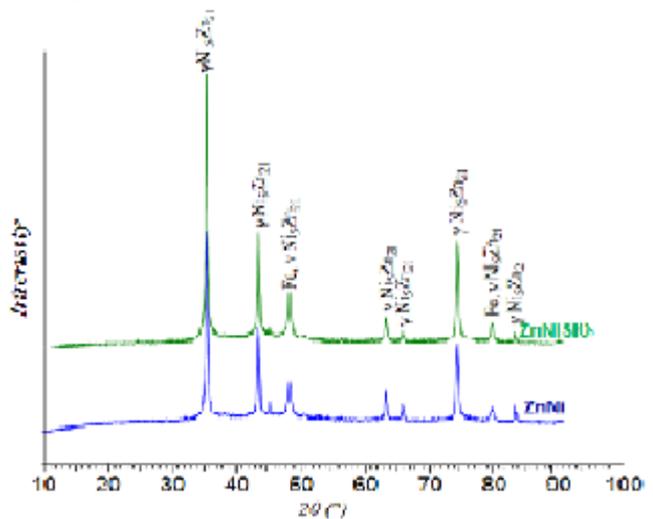


Figure 9. X-ray diffractograms for Zn-Ni (a) and ZnNi/nanosilica (b) coatings electroplated at 3 A/dm² for 20 min

3.5. The polarization curves of Zn-Ni and ZnNi/nanosilica

Figure 10 shows the potentiodynamic polarization curves of Zn-Ni and ZnNi/nanosilica alloys were measured in a 3.5% NaCl solution. The corrosion potential and the corrosion current of the alloy coatings could be calculated from the polarization curves by Tafel extrapolation. The results are shown in Table 3.

Table 3. Potentiodynamic polarization data

Samples	E _{corr} , mV/SCE	i _{corr} , A/cm ²
Zn-Ni	- 740	1.75×10 ⁻⁶
ZnNi/nanosilica	- 720	1.70×10 ⁻⁶

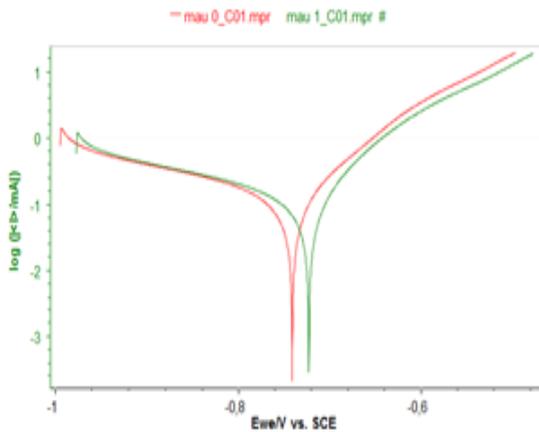


Figure 10. Polarization curves of the samples: Zn-Ni (0) và ZnNi/nanosilica (1).

In the potentiodynamic polarization, the Zn-Ni (0) and ZnNi/nanosilica (1) coatings were polarized around its open circuit potential OCP (-250 mV to $+250$ mV/SCE vs. OCP) by a direct current (DC) signal at a scan rate of 2 mVs $^{-1}$. Figure 10 presents the polarization curves of 2 alloy coatings after 30 minutes of immersion in 3.5 % NaCl solution. The corrosion current (i_{corr}) values of steel substrate were deduced

from these polarization curves. Table 3 presents the values of E_{corr} and i_{corr} for 2 these coatings. As can be seen in this table, the presence of nanosilica in Zn-Ni alloy coating did not reduce its corrosion current.

3.6. Salt fog test

The images of the alloy coatings tested in salt spray chamber at different times are shown in Figure 11.

Table 4 represents time for red rust appearing on the surface of the alloy coatings during salt spray exposure.

Table 4. Time for rust appearing

Samples	Time for red rust appearing (hours)
Zn-Ni	600
Zn-Ni-SiO ₂	900

Figure 11 shows the surface of coatings before and after exposure to salt spray. As seen in figure 11, after 96 hours of exposure to salt spray, the surface of all coatings was covered by white rust. After 600 hours of exposure to salt spray, there were the red rust over the surface of Zn-Ni coatings. The presence of red rust could not be observed in ZnNi/nanosilica coatings. Until 900 hours of exposure to salt spray, the red rust could be observed for ZnNi/nanosilica coatings. The corrosion resistance of the alloy coatings decreased in the order: ZnNi/nanosilica > Zn-Ni.

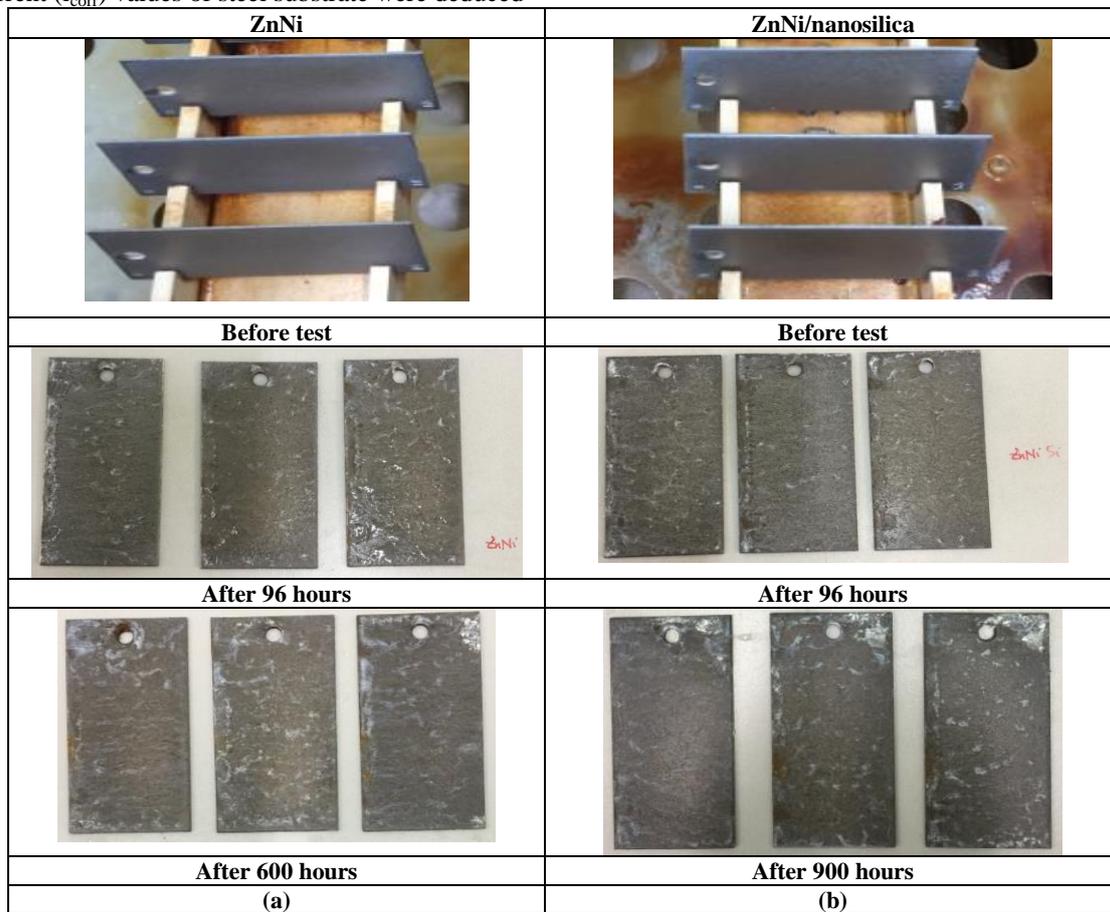


Figure 11. Surface appearance of prepared coatings before and after exposure to salt spray: (a) Zn-Ni coatings. b) ZnNi/nanosilica coatings.

4. Conclusions

1. Nanosilica was codeposited successfully to form ZnNi/nanosilica coating.
2. The thickness of the ZnNi/nanosilica coating was 16.56 μm .
3. The ZnNi/nanosilica coating contained 83.32% Zn, 16.37% Ni and 0.32% Si. Only the phase $\gamma\text{Ni}_5\text{Zn}_{21}$ were observed in the ZnNi/nanosilica alloy coatings.

4. On the ZnNi/nanosilica samples, red rust appeared after 900 hours of salt fog exposure.

Data Availability

The figures and tables data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgment

This work was financial supported by the Vietnam Academy of Science and Technology (VAST03.02/19-20).

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