

INFLUENCE OF NICKEL CONCENTRATION ON THE CHARACTERISTICS OF THE ELECTROPLATING Zn-Ni ALLOY

Bui Thi Thanh Huyen, Le Viet Dai, Ngo Thi Minh Thuy, Hoang Thi Bich Thuy*

School of Chemical Engineering, Hanoi University of Science and Technology, 1 Dai Co Viet, Hai Ba Trung, Ha Noi

*Email: thuy.hoangthibich1@hust.edu.vn

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ABSTRACT

Zn-Ni alloy electroplating behaves as anodic coating but has better mechanical properties in comparison with pure Zn coatings. Hence, Zn-Ni coating is accepted as an environmentally friendly alternative to cadmium coatings which is very toxic during producing and use. In this paper, Zn-Ni alloys were electrodeposited from sulfate electrolyte baths at various ratios of Ni^{2+}/Zn^{2+} . Influences of nickel concentration on the plating process were investigated. The composition, morphology and structural properties of the thin films were analyzed by scanning electron microscope (SEM), energy-dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) measurements. Electrochemical behaviour of the plated thin films was characterized by open circuit potential and potentiodynamic polarization curves. It was seen that the optimum condition for Zn-Ni electroplating was at temperature of 50 °C, current density of 5 A/dm², anode - cathode distance of 2.5 cm with stirring. Current efficiency of the plating process and characteristics of the Zn-Ni alloy coatings depended much on the nickel concentration in the plating bath. The best properties were found for the electroplated alloy coating with nickel content in the range of 12 - 14 %.

Keywords: Zn-Ni coating, Zn-Ni alloy, electroplating, cadmium coating substitution.

1. INTRODUCTION

Sacrificial metallic coatings, such as those based on Zn and Cd are used to protect steel components against corrosion. Zinc is used in automotive applications, but Cd coatings are at present used in defense and aerospace industries owing to its superior sacrificial protection capabilities. Growing environmental and health concerns led to the formation of stringent regulations, which has limited the use of Cd in any form, since Cd plating bath is cyanide based and Cd compounds are carcinogenic [1, 2]. Thin pure Zn coating shows very poor corrosion resistance. These limitations have led to the development of environmental friendly Zn based alloy coatings. Zinc alloys are able to provide higher corrosion resistance than that of pure zinc. This is obtained by alloying Zn with more noble metals of in the iron group (Ni, Co and Fe). Recently electrodeposited Zn-Ni alloy coatings have attracted a great deal of attention because

they can offer a higher degree of corrosion resistance and mechanical properties e.g. micro-hardness, wear resistance, ductility, strength, decorative properties... etc, than pure zinc coating [3, 4]. Of all Zn based alloy coatings namely Zn-Ni, Zn-Fe, Zn-Co, Zn-Al and Zn-Fe-Co, coatings Zn-Ni alloys have been found to be the most attractive one to replace Cd because of its superior corrosion resistance, hardness thermal stability and wear resistance [1, 4, 5]. It is clear that Zn-Ni alloys can be considered as the best alternative for Cd and Zn coatings [1 - 5].

It is found that the characteristics of the deposited coating depend on the applied voltage, current density, pH, bath composition, additives and temperature etc. The phases and microstructure of the surface of the deposited Zn-Ni alloys were other important characteristics which controls the corrosion resistance and other mechanical properties [3]. In this study, the effects of nickel concentration on the plating process were investigated. The composition, morphology and structural properties of the thin films were analyzed by SEM, EDX and XRD measurements. Electrochemical behaviour of the plated thin films was characterized by open circuit potential and potentiodynamic polarization curves.

2. EXPERIMENTAL AND METHODS

2.1. Materials and solutions

The test samples were made of carbon steel with thickness of 0.8mm. The working electrode for electrochemical measurements had area of 1cm^2 and the rest of the surface was covered by epoxy. Before each test, specimens were mechanically ground down to 1000 grit abrasive SiC paper, then degreased with soap and rinsed in distilled water, after that were dried by blotting paper with alcohol.

The electrodeposited electrolytes were prepared with analytical grade and distilled water. The solution composition and operating condition of plating process are illustrated in table 1.

Table 1. The solution composition and operating condition of plating process.

Solution composition		Operating condition of plating process
Composition	Concentration (M)	
ZnSO ₄	0.5	Current density: 5 A/dm ²
Na ₂ SO ₄	1	Speed stirring: 500 rpm
H ₃ BO ₃	0.3	Anode - cathode distance: 2.5 cm
NiSO ₄	1.5 ÷ 0.25	pH: 3
Ni ²⁺ : Zn ²⁺	3 : 1 (sample S.1)	Operating temperature: 50 °C
	2 : 1 (sample S.2)	Electrolysis time: 20 minutes
	1 : 1 (sample S.3)	Anode: Mixed metal oxide titanium anodes
	0.5 : 1 (sample S.4)	Cathode: Steel substrate

After plating process, the working electrodes were lifted off the plating solution, rinsed by tap water and distilled water, and then dried at 80 °C in the range of ten to fifteen minutes.

The corrosion resistances of the electrodeposited Zn-Ni alloy coatings were investigated in 3.5 % NaCl solution.

2.2. Methods

Surface morphology of electrodeposited Zn-Ni alloy coating were observed by scanning electron microscope (SEM) and compositions of the alloys were analyzed by energy dispersive spectrometer using X-ray (EDX) with JEOL 6490, Jed 2300 (Japan).

The current efficiency of electrodeposited alloy coating was calculated as follow:

$$H = \frac{M \times 100}{q_{\text{alloy}} \times Q}, \quad \% \quad (1) \quad q_{\text{alloy}} = \frac{q_1 \times q_2}{q_1 \times f_1 + q_2 \times f_2}, \quad \text{g/Ah} \quad (2)$$

where: M is electrodeposited alloy coating weight, g; Q is the quantity of electricity passed through the electrolytic tank determined by the copper meter, Ah; q_{alloy} is electrochemical equivalent of alloy, g/Ah; q_1, q_2 is electrochemical equivalent of metal 1 and metal 2 in the alloy, g/Ah; f_1, f_2 is the content of metal 1 and metal 2 in electrodeposited coating, %.

The average thickness of electrodeposited Zn-Ni alloy coatings (δ) was calculated as equation:

$$\delta = 10^4(G_1 - G)/\gamma_{\text{alloy}}S, \quad \mu\text{m} \quad (3) \quad \frac{1}{\gamma_{\text{alloy}}} = \frac{f_1}{\gamma_1} + \frac{f_2}{\gamma_2}, \quad \text{cm}^3/\text{g} \quad (4)$$

Where: G and G_1 is the mass of the object before and after the plating, g; γ_{alloy} is the density of the alloy plating, g/cm³; S = surface area of the plated part, cm². 10^4 is conversion coefficient from cm of μm ; γ_1, γ_2 respectively is the density of the metal 1 and metal 2, g/cm³.

The corrosion resistances of the electrodeposited Zn-Ni alloy coatings were investigated by electrochemical methods in 3.5 % NaCl solution. The corrosion potentials of electrodeposited Zn-Ni coating alloy were recorded at various times (from 0 to 4 weeks). Polarization curves were measured by potentiodynamic technique. The working electrode potentials were scanned from -0.25 V to +0.5 V versus open circuit potential with scanning rate of 5mV/s. Determination of the corrosion current is based on Tafel extrapolation method. All the electrochemical tests with conventional three-electrode cell were carried out by Autolab PGSTAT 302N (Netherlands). A platinum mesh and SCE were the counter-electrode and the reference-electrode respectively.

3. RESULTS AND DICUSSIONS

3.1. Influence of nickel concentration on the surface morphologies and thickness of the electroplating Zn-Ni alloy

SEM images of electrodeposited Zn-Ni alloy coatings with different solution are illustrated in figure 1.

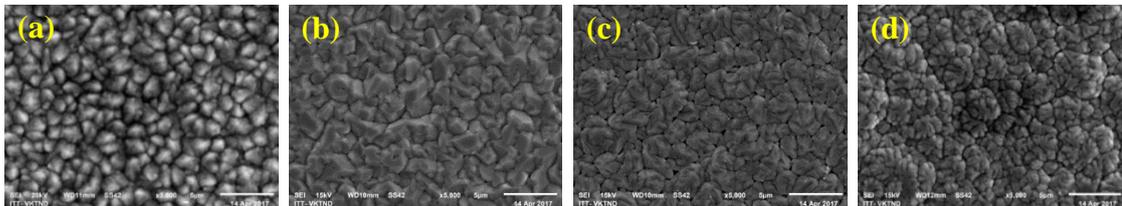


Figure 1. SEM images of electrodeposited Zn-Ni alloy coatings: (a) S.1; (b) S.2; (c) S.3 and (d) S.4 sample.

SEM images showed that surface morphologies were different at the electroplating sample with various nickel concentration. It could be seen in Fig. 1a and 1b, the crystals of Zn-Ni coating (sample S.1 and S.2) developed pyramidal orientation similar to nickel plating layer with high nickel concentration in bath solution. The sample S.3 and S.4 crystal was slightly finer and formed crystal-shaped flower closely resembles a zinc coating (Fig. 1c and 1d).

The EDX analysis results, current efficiency and thickness of electrodeposited Zn-Ni alloy coatings are reported in table 2. The EDX results showed that the composition of electroplating alloy coating involving in zinc and nickel with nickel content reduced from 14.48 % to 10.73 % when the Ni^{2+}/Zn^{2+} ratio in the plating solution was decreased from 3 (S.1) to 0.5 (S.4).

Table 2. The EDX analysis results, current efficiency and thickness of electrodeposited Zn-Ni alloy coatings.

Sample	Element content (wt. %)			Current efficiency (%)	Thickness δ (μm)
	Ni	Zn	Total		
S.1	14.41	85.59	100	91.98	25.61
S.2	12.47	87.53	100	93.55	26.12
S.3	11.91	88.09	100	94.35	26.84
S.4	10.73	89.27	100	95.02	28.05

The current efficiency and thickness of electrodeposited Zn-Ni alloy coatings increased with the decrease in nickel content in the plating coating. This can be explained as follow: Due to the over-potential of hydrogen on nickel is small, hydrogen is easily discharged and resulting in low electroplating efficiency. Therefore, as the higher the nickel content in the alloy coating, the higher the amount of hydrogen released, leading to the lower current efficiency. It could be seen that the thickness of electrodeposited Zn-Ni alloy coatings insignificantly changed (maximum 2.44 μm) within investigated samples.

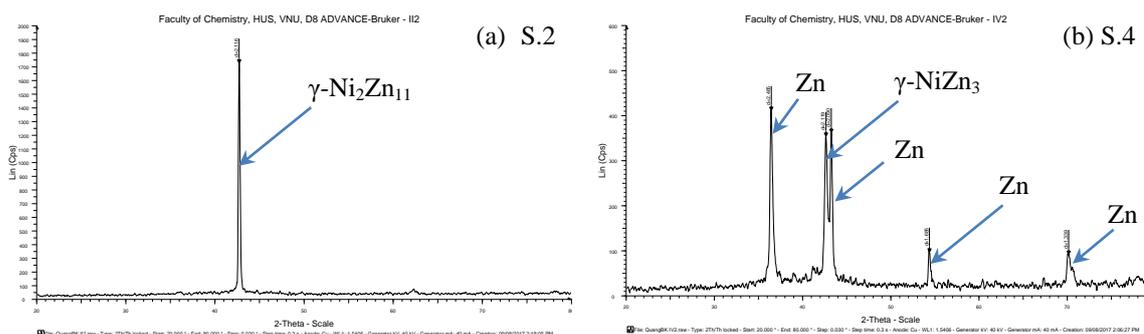


Figure 2. XRD diagram of S.2 and S.4 sample

It can be seen the differences between surface structures of S.2 (single phase) and S.4 (multi-phases) sample (Fig. 2). For high nickel, sample S.2 with Ni^{2+}/Zn^{2+} ratio of 2, the coating consists of $\gamma-Ni_2Zn_{11}$ with cubic structure. By decreasing this ratio to 0.5 (sample S.4), the mixture of Zn hexagonal structure and $\gamma-NiZn_3$ orthorhombic structure appeared in the deposit. This means that the phases in the Zn-Ni alloys have varied with nickel concentration. According

to previous studies [4], Zn-Ni coatings with single Ni₅Zn₂₁ γ phase structure and Ni content in range of 10 ÷ 14 wt.% have shown five times better corrosion resistant compared to pure Zn. Coatings of less than 10 wt.% Ni were a mixture of different phases. Most of the literatures describing corrosion testing of Zn-Ni alloy coatings have concluded that the best corrosion resistance was obtained when the coatings consisted of only the phase [4-6]. This implies that the Ni²⁺/Zn²⁺ ratio in the plating solution or nickel content in Zn-Ni alloy coating has affected on surface structure of the electrodepositing Zn-Ni alloy. The result showed that S.2 sample (with Ni²⁺/Zn²⁺ ratio = 2) can has higher corrosion resistance than S.4 sample (Ni²⁺/Zn²⁺ ratio = 0.5).

2.3. Influence of nickel concentration on corrosion resistance of the electroplating Zn-Ni alloy

Figure 3 illustrates the dependence of corrosion potential of the electroplating Zn-Ni alloy in 3.5 % NaCl solution on immersion time.

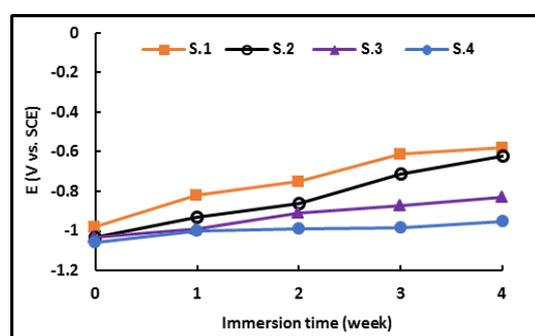


Figure 3. The dependence of corrosion potential of the electroplating Zn-Ni alloy in 3.5 % NaCl solution on immersion time

It can be seen that the corrosion potential of all sample trended to shift to positive direction in immersion time to 4 weeks. The corrosion potentials moving towards the positive side may be due to the solubilization process of anode producing protective products. The product of zinc corrosion in zinc-nickel alloy coatings usually existed in the form of zinc chloride hydroxide (Zn₅OH₈Cl₂·H₂O - simonkolleite) which more stable than the pure zinc coating (ZnO) [1]. In addition, the nickel corrosion in the coating produced a passive nickel forms that reduced the rate of corrosion. Therefore, the corrosion potential of the electroplating layer

becomes more positive when nickel content increased. As the fact that the most positive corrosion potential appeared at S.1 sample (Ni²⁺/Zn²⁺ ratio = 3) and the most negative value obtained at S.4 sample (Ni²⁺/Zn²⁺ ratio = 0.5).

Influence of nickel concentrations on polarization curve of the electroplating Zn-Ni alloys in 3.5% NaCl solution are shown in Figure 4.

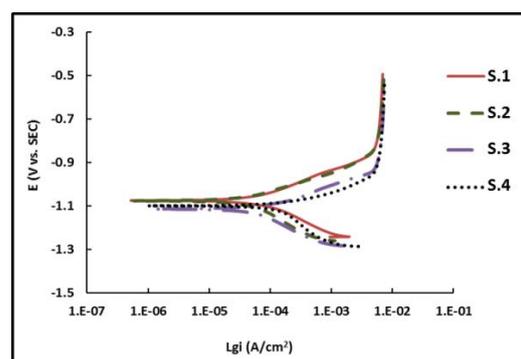


Figure 4. Polarization curve of the electroplating Zn-Ni alloy coating with the different nickel concentrations of bath solution in 3.5 % NaCl solution.

Table 3. Corrosion parameters of electrodepositing Zn-Ni alloy coatings on mild steel

Sample	E _c (V vs. SCE)	i _c (μA/cm ²)	β _A (V/dec)	β _C (V/dec)
S.1	-1.076	58.09	0.1338	0.1037
S.2	-1.076	40.37	0.0840	0.1681
S.3	-1.113	61.33	0.1409	0.1016
S.4	-1.110	128.85	0.0677	0.2187

E_c: corrosion potential

i_c: corrosion current density

β_A and β_C is anodic and cathodic Tafel slopes

Figure 4 showed that the anodic dissolution of the electrodeposited Zn-Ni alloy coatings occurred firstly with zinc dissolve and then nickel dissolved at passive current density of about 10^{-2} A/cm². The nickel content decreased from 14.48 % (at S.1 sample) to 10.73 % (at S.4 sample), corrosion potential of electrodeposited Zn-Ni alloy coating shifted toward to more negative direction (a little) and generally both anodic and cathodic braches of the curves shifted to the higher current density direction. Therefore, the nickel content in the coating (or Ni²⁺/Zn²⁺ ratio in the plating solution) may affect on the protection ability of the coating for mild steel substrate in NaCl solution.

The values of E_c , i_c , anodic and cathodic Tafel slopes obtained by the Tafel extrapolation method from polarization curves are listed in Table 3. The nickel content decreased, the corrosion current density increased. The S.1, S.2, S.3 samples supplied better corrosion protection than S.4 sample and the S.2 was the best coating among them. The corrosion protection of electrodeposited Zn-Ni alloy coating increased with the increase of nickel content, due to the change in surface structure of coating and the corrosion dissolve products of the layer in NaCl solution. According to [7], when nickel content of the electroplating coating in the range 12 ÷ 14 %, structure of Zn-Ni alloy coating changes from η phase to γ and δ phase which have a higher corrosion resistance than the former. The corrosion test results confirmed the discussion of morphological and surface structure results.

The data of Table 2 and Table 3 indicated that the corrosion resistance of electrodeposited Zn-Ni alloy coating was significantly affected by the nickel content in the coating when the thickness of the coating change slightly. It is attributed to phase structure of the alloy coatings with nickel content in the range of 12 ÷ 14 % supply the best corrosion resistance.

4. CONCLUSIONS

The morphology and structure surface of the electrodeposited Zn-Ni alloy coating depended on nickel concentration the plating bath. The Zn-Ni coatings with high nickel content, the crystals develop pyramidal orientation and the surface structures were single phase; the coatings with lower nickel content, the crystals were slightly finer and formed crystal-shaped flower and the surface structures were multi-phase.

Current efficiency of the plating process of Zn-Ni alloy was relatively high (> 85 %) and the value increased with the increase in nickel content in the coating.

The Ni content had a major effect on the protection performance of the coatings. The corrosion resistance of the coating increased with the increase of nickel content in the coating. The electroplated alloy coating with the nickel content in the range of around 12 ÷ 14 % (correspond to Ni²⁺/Zn²⁺ ratio in the solution from 3 to 2) provides the best corrosion resistance behavior.

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