

Effect of Deposition Potential on ZnNi Coating Corrosion Behaviour

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Abstract

ZnNi coatings were deposited using the electrochemical deposition method. In this study, the effect of potential electrodeposition on deposited properties, morphology, and size of ZnNi alloy nanoparticles was investigated in detail. The as-synthesized products were characterized by ZnNi coating properties is characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and electrochemical impedance spectroscopy (EIS). The result indicated that the electrodeposition processes of ZnNi were governed by a nucleation process controlled by diffusion. XRD results showed that the phase structure of both alloy and composite coatings was single ZnNi phase. Potential increase influences the larger crystal size and the surface of coating was compact and uniform, the R_{ct} increase, and greater the i_{corr} so that the possibility of corrosion is higher.

Keywords: corrosion test, ZnNi coating, electrodeposition, deposition potential

1. Introduction

Corrosion is a problem in transportation, building, and marine equipment that mainly use steel as its source [1,2]. Pure zinc coatings are widely used as sacrificial coatings to protect steel structures from corrosion as a replacement to cadmium coatings which has higher cost and high toxicity. To improve the corrosion resistance properties, Zn alloys were made with Fe, Cu, and Ni. Interest in ZnNi alloys has increased as its perform better as a sacrificial protections than Zn-Fe, Zn-Co, and Zn-Ni-Fe which also have potential as a sacrificial coatings [3]. ZnNi demonstrate higher corrosion protection and thermal stability to its properties that not easily oxidised making its easier to control the corrosion rate and formation of complex corrosion products that act as a barrier against diffusion of the corrosive environment thus preventing corrosion of the underlying coating layer [4].

Electrodeposition methods are commonly used as its more cost effective due to its single-step process and does not require expensive equipment, materials and processing methods. Electrodeposition method also offer larger coating surface areas with desired morphologies and control to the growth of kinetics on coating deposits [5].

Significant research efforts are made to investigate deposition ZnNi which is an anomalous codeposition, consisting in the preferable deposition of the less noble metal which affect the composition of the resulting alloy and its anti-corrosion properties. Products with more Zn deposits have lower corrosion resistance whereas product with more Ni deposits have better corrosion resistance [6]. In addition, ZnNi corrosion resistance behaviour has been investigated that the corrosion resistance and composition of the ZnNi alloy are affected by temperature, current density and ratio of in $[Zn^{2+}]/[Ni^{2+}]$ electrolyte [7]. The aim of the present work was to investigate the effect of different deposition potential of ZnNi coating on its phase structure and corrosion resistance properties.

2. Materials and Method

The material for the synthesis of ZnNi on copper wire is $ZnSO_4 \cdot 7H_2O$, $NiSO_4 \cdot 6H_2O$, H_3BO_3 , and Na_2SO_4 by electrodeposition method using Pt wire as counter electrode, Ag/AgCl (3 M) as reference electrode and copper wire as working electrode. Solutions were made as much as 25 mL with concentrations of $ZnSO_4 \cdot 7H_2O$ (57.5 g/L), $NiSO_4 \cdot 6H_2O$ (52.5 g/L), H_3BO_3 (9.3 g/L) and Na_2SO_4 (56.8 g/L). The deposition time is set at 30 minutes with

voltage variations of -1.25 V, -1.4 V, and -1.5 V on copper wire substrates (diameter 4 mm). ZnNi that has been deposited then washed with aquades. SEM-EDX characterization was carried out to determine the morphology of the deposited sample and the composition of ZnNi formed, characterization with XRD for the ZnNi identification process, EIS testing using 0.1 M KCl solution with a frequency range of 100 KHz – 1 Hz and corrosion test with HCl 0.1 M scan rate 10 mV/s.

3. Results and Discussion

The phase structure of coatings was studied using XRD. The ZnNi diffraction pattern in Fig. 1 shows a significant peak at 43.32° which indicates a single ZnNi phase [8–10]. The morphology of these coatings plated in different potentials is presented in Fig. 2, further that the Zn–Ni alloy exhibits a uniform.

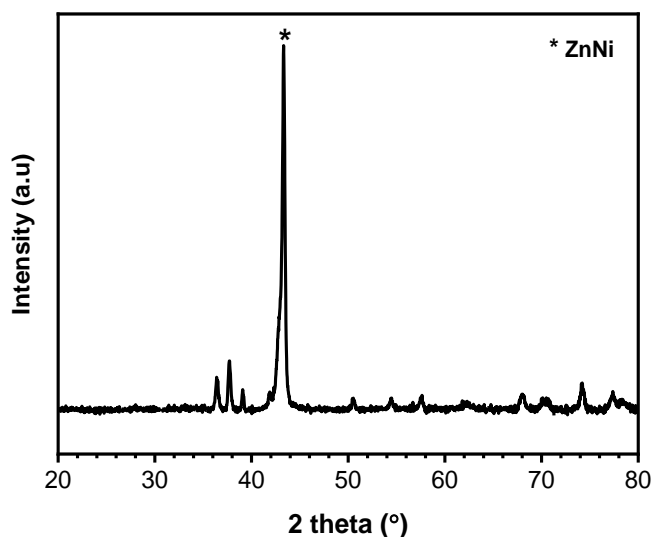


Figure 1. XRD pattern of ZnNi sample.

ZnNi samples synthesized at -1.25 V and -1.4 V have a branched round shape with a size of $\pm 0.6 - 1.1 \mu\text{m}$ and at -1.4 V the particle size formed larger. When increased to -1.5 V, ZnNi is shaped like a porous hexagonal crystal with a larger size of $\pm 2.1 - 3 \mu\text{m}$. In this case it shows that an increase in the depository potential in the negative direction causes the particle size to get bigger and the resulting morphological changes [11]. The voltage used at the time of deposition will affect the morphology of the resulting sediment where higher potential will produce a denser and denser precipitate while at a lower level it will be looser and porous [12].

The EDX analysis in Table 1 shows that the element compositions of the composite are Zn and Ni. The EDX characterization of ZnNi with different deposition potential ZnNi has been shown in Fig. 2. The ratio of Zn/Ni that formed in copper wire is shown in Table 1. %wt. Ni

increases with the increase in negative deposition potential used, same as the previous study conducted by Faid 2017 where the %wt. of nickel increased with the increase in the negative deposition voltage used [13].

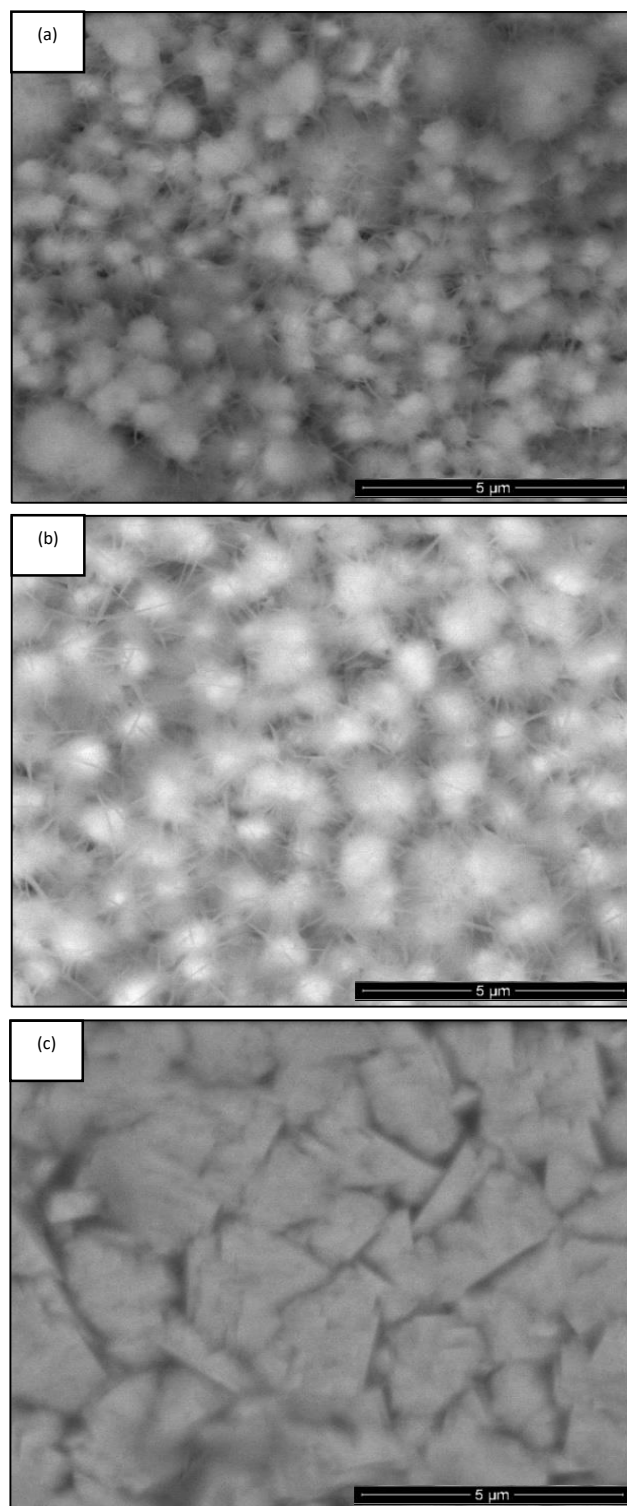


Figure 2. Morphology of ZnNi with different deposition potential: (a) -1.25 V, (b) -1.4 V, and (c) -1.5 V.

Table 1. The ratio of Zn and Ni wt.% with different deposition potential of ZnNi.

Deposition potential of ZnNi (V)	Zn (wt.%)	Ni (wt.%)
- 1.25 V	91.44 %	8.55 %
- 1.40 V	91.05 %	8.94 %
- 1.50 V	91.34 %	8.65 %

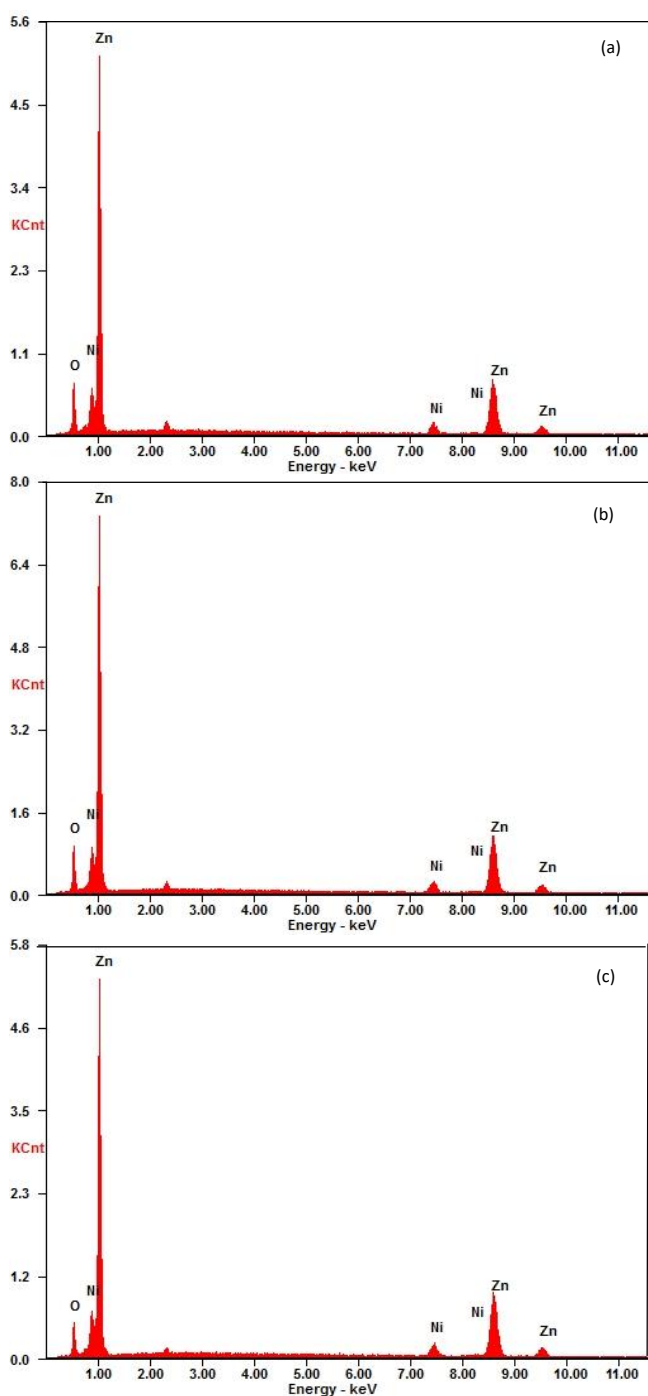
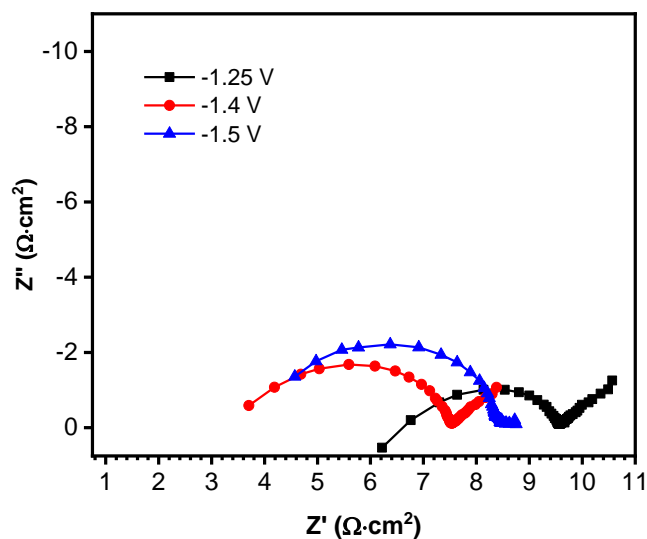
**Figure 2.** EDX spectrum of ZnNi with different deposition potential (a) -1.25 V, (b) -1.4 V, and (c) -1.5 V

Fig. 3 shows the bottleneck of the sample interpreted with the Nyquist plot. The resistance results in samples deposited at voltages of -1.25 V, -1.4 V and -1.5 V were 2.4547 Ω , 3.6478 Ω and 4.395 Ω , respectively. This shows that as the negative deposition voltage used, the resistance will be higher. This increase in resistance occurs due to higher nickel levels with the more negative the deposition voltage used [13]. Nickel has a higher reduction stress than zinc so the greater the middleman used, the more likely nickel is to deposition which results in higher nickel levels [14].

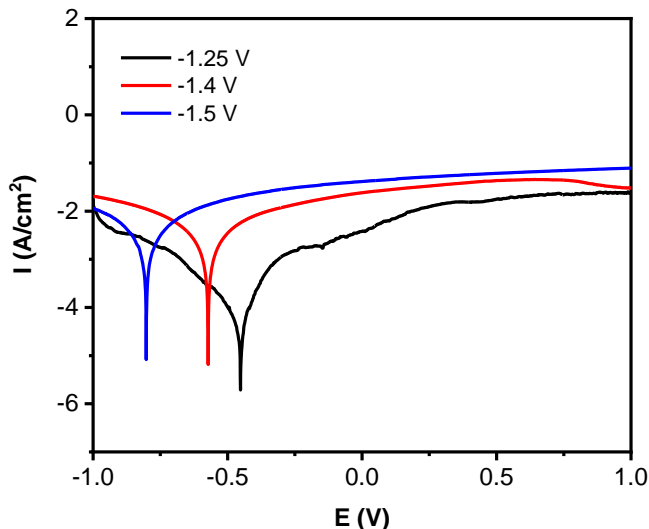
**Figure 3.** Nyquist plot of ZnNi samples.**Table 2.** Impedance of ZnNi samples.

Deposition potential of ZnNi (V)	R_p (Ω)
-1.25	2.4547
-1.40	3.6478
-1.50	4.3935

Fig. 4 shows the Tafel curves measured for the ZnNi alloy. The corrosion potentials and corrosion currents calculated from Tafel plots, the corrosion potential E_{corr} , the polarization resistance R_p , and corrosion current i_{corr} . Values were determined from this figure and cited in Table 3. The i_{corr} value shows the more negative the deposition potential, the greater the i_{corr} value so that the possibility of corrosion is higher [15]. The ZnNi -1.25 V have better corrosion resistance than that of ZnNi -1.4 V and -1.5 V, the corrosion potential increased with the increase of nickel content. This is due to the increasing nickel content so that the resistance will be greater [13].

Table 3. Corrosion parameters.

Deposition potential of ZnNi (V)	E_{OCP} (V)	E_{corr} (V)
-1.25 V	-0.074588	-0.45827
-1.40 V	-0.60175	-0.57402
-1.50 V	-0.81678	-0.80246

**Figure 4.** Potentiodynamic polarization of ZnNi samples.

4. Conclusion

The deposition stress used when synthesizing ZnNi coating for anti-corrosion affects the level of nickel in the deposition result. At a voltage of -1.5 V the nickel content is higher than the result with a voltage deposition of -1.25 V. Samples with higher nickel content show better resistance and corrosion resistance results in the sample.

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