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Effects of Electrolyte pH on the Electrodeposition of Nickel on Zincated Aluminium Surfaces

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A nickel coating was successfully deposited on zincated aluminium by electrodeposition. A detailed study was made on the effect of the pH of electrolytes containing 0.1 M nickel sulphate ($NiSO_4$) by cyclic voltammetry (CV). A constant potential of -0.8 V (pH 2), -1.1 V (pH 6) and -1.5V (pH 10) was chosen from different regions of each CV for the deposition of nickel using chronoamperometry (CA). The surface morphology, chemical composition and crystallographic structure of the nickel coating were investigated by field emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDAX) and X-ray diffraction (XRD), respectively. The adhesion strength of the nickel coating was analysed using Scotch® tape. It was found that the nucleation potential for nickel deposition on zincated aluminium increased with increasing electrolyte pH. Notably, pH 2 produced the highest current during the deposition of nickel as compared to pH 6 and pH 10, due to the simultaneous hydrogen evolution reaction (HER). Because of HER, a lot of pits were present on the zincated aluminium surface and only a few nickel particles were formed, as shown in FESEM images. Meanwhile, deposition using a pH 6 solution (without HER) produced an almost fully-covered nickel coating with uniform nodular morphology. However, when the pH 10 solution was used, the coating morphology appeared as cauliflower-like agglomerates with less surface coverage. EDAX analysis showed that the nickel coating deposited at pH 6 had the highest nickel content with 73.63 wt%. XRD analysis indicated that all nickel deposits had a cubic crystalline structure. Nickel deposited with the pH 6 solution was the most well-adhered coating. Thus, electrolyte pH has a strong influence on the deposition of nickel on a zincated aluminium surface.

Key words: Zincated Aluminium; nickel coating; electrodeposition; electrolyte pH

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Aluminium is the material of choice for many technological applications, such as aerospace, automotive and light rail, as well as for decorative purposes because of its light weight, excellent workability, corrosion resistance, good appearance and recyclability [1-4]. However, the relatively poor surface properties of this material represent a serious barrier to its wider application. Therefore, it is necessary to improve its surface properties using suitable functional surface coatings which can provide adequate protection against wear and corrosion. To overcome this problem, nickel may be used as an underlayer coating on zincated aluminium surfaces to enhance corrosion resistance and increase the adhesion of other coatings [5] to the aluminium substrate. A general formulated nickel electrolyte solution such as nickel sulphate or nickel chloride was proposed in 1916 [2] and this nickel electrolyte solution is still used today because it is easy to control, cheap to operate and can produce a range of functional and decorative nickel finishes [6].

The technique used for nickel coating in this work was electrodeposition. The electrodeposition technique is of interest to industry because it boasts a faster deposition rate and requires less maintenance compared to other methods. The nature of electrode reactions, nucleation mechanisms and growth of the coatings can be determined by investigating cyclic voltammetric behaviour [6,7]. There is a great interest in understanding the electrochemical process of nickel nucleation mechanisms on zincated aluminium surfaces by studying the current density-potential peak as it appears in a cyclic voltammogram. It is important to identify the nickel electrodeposition mechanisms from electrochemical information recorded by the cyclic voltammogram in order to produce the desired nickel coating. Although the literature on nickel electrodeposition is voluminous, this study focuses on the effect of the pH of nickel electrolyte solutions on the production of nickel coatings.

EXPERIMENTAL

Chemicals and Materials

A zincated aluminium substrate (2 cm x 2 cm with 0.1 cm) [8], nickel sulphate ($NiSO_4$), sulfuric acid (H_2SO_4), sodium hydroxide (NaOH) and sodium citrate (C_6H_5 $Na_3O_7.2H_2O$) were supplied by R&M Chemicals. A silver-silver chloride (Ag/AgCl) electrode and a platinum rod (Pt) electrode were procured from Metrohm (Malaysia). All chemicals were of analytical grade and used as received.

Preparation of Nickel Underlayer Coating from Electrolytes at Different pH

The substrate for nickel deposition was zincated aluminium, measuring 2 cm x 2 cm with 0.1 cm thickness. Prior to deposition, 0.1 M nickel sulphate ($NiSO_4$) electrolyte solutions of different pH (2, 6 and 10) were prepared. The pH 2 solution was adjusted by adding diluted sulfuric acid, H_2SO_4, while a small amount of diluted 0.01 M sodium hydroxide, NaOH was added to adjust the solution to pH 6, and the pH was adjusted to 10 by adding 0.1 M NaOH solution with the presence of 0.1 M sodium citrate (C_6H_5 $Na_3O_7.2H_2O$). The sodium citrate was used as a complexing agent for stabilizing nickel ions in alkaline solution.

A standard three-electrode cell was set up with the zincated aluminium sample as the working electrode, Ag/AgCl as the reference electrode and a platinum rod as the counter electrode. All three electrodes were immersed in a glass cell containing electrolyte solution with an exposed area of 2 cm^2 on the upward-facing treated zincated aluminium sample. Electrochemical experiments were controlled using a Autolab Potentiostat (Aut302 FRA2) interface with a PC running NOVA software. All experiments were conducted at 25 °C.

Characterization of Nickel Underlayer Coatings

The surface morphology, elemental composition and crystallographic structure of the deposited nickel films were examined by field emission scanning electron microscopy (FESEM Carls Zeiss SMT Supro 40VP), Energy Dispersive X-Ray spectroscopy (EDX) and Thin Film X-Ray diffraction (TF-XRD), respectively. Additionally, the adhesion of nickel coatings to the substrate was analysed using the Scotch® tape test.

RESULTS AND DISCUSSION

Electrodeposition of Nickel Underlayer on Zincated Aluminium

Initially, cyclic voltammetry (CV) experiments were conducted in order to evaluate the deposition and dissolution processes of nickel on the zincated aluminium surface. The CV analysis was performed with the three-electrode electrochemical cell over a range of 0 V to -2.0 V with a 100 mV/s scanning rate at 25 ˚C. The value of the vertex potential was limited to -2.0 V in order to reduce the HER which occurred predominantly. These CV studies were performed using a 0.1 M $NiSO_4$ electrolyte solution followed by chronoamperometric experiments for nickel deposition. The effects of the pH (at pH 2, 6 and 10) of the electrolyte solutions on the formation of the nickel coating were investigated.

The effects of pH on the cyclic voltammetry analysis of zincated aluminium substrate in Ni (II) solutions are shown in Figure 1. From the voltammograms, it was observed that the shapes and patterns of the CVs were not similar. The reduction or nucleation of nickel ion species in the pH 2 electrolyte solution occurred at about -0.6 V, while for the pH 6 and pH 10 solutions it occurred at about -0.9 V and -1.2 V, respectively. A higher applied potential was needed for the reduction of nickel ions from the pH 10 electrolyte solution compared to the pH 2 and pH 6 solutions due to the large current or energy required to break down the complex bonding between nickel and citrate before nickel ions may be reduced. The current density slowly increased between -0.6 V to -0.7 V for pH 2, -0.9 V to -1.0 V for pH 6 and -1.2 V to -1.4 V for the pH 10 solution, indicating the nucleation of electroactive species (nickel) on the working electrode. This process is known as electron transfer. The cathodic current density increased during the forward scan toward negative potentials. The drastic increases of cathodic current density between -0.7 V to -0.9 V (pH 2), -1.0 V to -1.2 V (pH6) and -1.4 V to -1.6 V (pH 10) correspond to the further nucleation and growth of stable nickel nuclei on the zincated aluminium electrode. All these processes were controlled by electron transfer and mass transport. The reaction responsible for cathodic current is:

$$Ni^{2+} + 2e^{-} \rightarrow Ni \qquad (1)$$

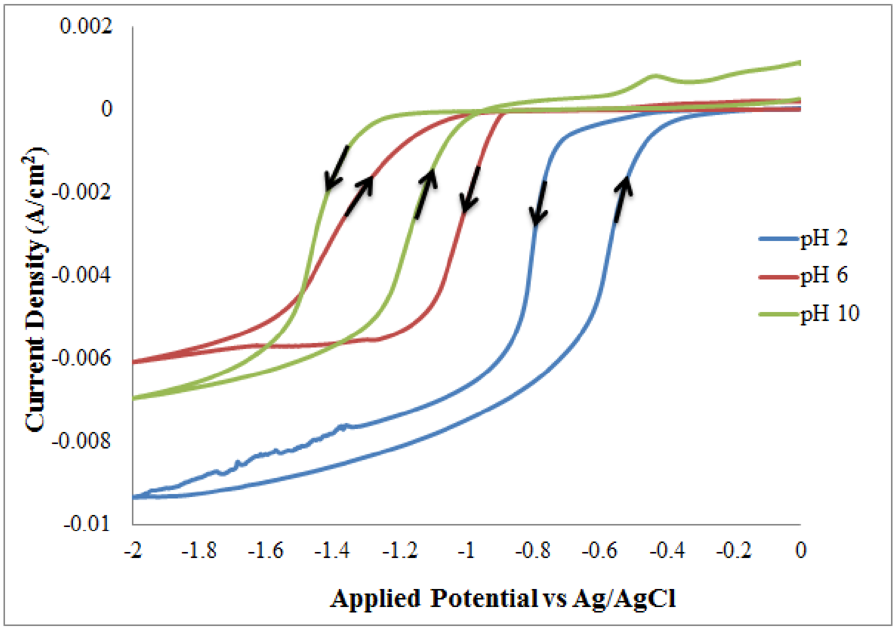

Figure 1. Cyclic voltammograms of zincated aluminium substrates in solutions containing 0.1 M $NiSO_4$ + diluted H_2SO_4 solution (pH 2), 0.1 M $NiSO_4$ + 0.01 M NaOH + C_6H_5 $Na_3O_7.2H_2O$ solution (pH 6) and in 0.1 M $NiSO_4$ + 0.1 M NaOH + C_6H_5 $Na_3O_7.2H_2O$ solution (pH 10) at 25 ˚C. Scan Rate: 100 mV/s. The arrows indicate the direction of the scan cycle.

However, when the applied potential was more than -1.4 V for pH 2, a lot of bubbles were observed at the zincated aluminium surface indicating the HER. On the other hand, from -1.8 V to 2.0 V for the pH 6 and pH 10 solutions, HER dominated the reaction as in (2).

$$2H^{+} + 2e^{-} \rightarrow H_2 \qquad (2)$$

On the reverse scan, nucleation and growth of electroactive species still occurred when the current density was in the cathodic direction. However, when the potential became less negative at -1.0 V, the current (above 0 mA/cm^2) gradually became anodic. In the anodic direction, the oxidation of deposited nickel results in a potential close to the Ni/Ni^{2+} equilibrium potential. During the anodic scan, it was possible to observe that one stripping peak (a dissolution peak) was detected at -0.5 V for the pH 10 reaction. The stripping peak formed was low because the dissolution charge was very low, where nickel was oxidized back to nickel ions during the reverse scan [5,6,7] according to reaction (3). Besides that, with the presence of a complexing agent (sodium citrate) in the bath solution, the voltametric profile showed a more complex form with the anodic peak [8].

$$Ni \rightarrow Ni^{2+} + 2e^{-} \qquad (3)$$

Since the focus of this study was the electrodeposition of nickel, we only look at the cathodic reaction of nickel (II). A potential at different regions in the CVs (i.e.: -0.8 V (pH 2); -1.1 V (pH 6) and -1.5V (pH 10)) was selected for each pH solution for nickel deposition.

During electrodeposition, the current flow results from faradaic and non-faradaic processes. A faradaic process involves the transfer of electrons across the electrode-electrolyte interface, while a non-faradaic process involves charging current at the interface where the species in the electrolyte may adsorb or desorb on/from the electrode surface, an example being a double layer without the transfer of electrons. Figure 2 shows the current-time (I-t) transients or chronoamperometric curves for the electrodeposition process of nickel for 900 s.

From the figure, it was found that the current time transient trends varied in current density. The chronoamperometric (CA) curve of the electrodeposition process for nickel at pH 2 shows that a non-faradaic process occurred rapidly at a current density of –0.005 A/cm^2 to -0.006 A/cm^2 for the first 250 s. After that, a faradaic process occurred constantly at -0.007 A/cm^2 until the end of the electrodeposition process. The current density for the CA curve for pH 2 was higher; this may be due to other simultaneous reactions that occurred, such as the HER. Meanwhile, the CA curve for pH 6 using an applied potential of -1.1 V showed a non-faradaic process starting to occur from

-0.005 A/cm^2 to -0.0055 A/cm^2 for the first 10 s. After that, it was observed that the current density rose almost to -0.006 A/cm^2, indicating a faradaic process. For longer deposition times until 900 s, the current density tended to be a steady-state value when the cathodic surface was saturated with nickel [9]. The reactions occurring on the surface of the coating showed a certain state of equilibrium. After the system reached an equilibrium state, the current density was maintained at a constant value. Thus, this phenomenon confirmed that nickel underlayer electrodeposition on zincated aluminium displayed a typical three-dimensional nucleation process [10]. At pH 10, it was observed that the current density of the electrodeposition process at -1.5 V was very low and a non-uniform CA curve was observed. This was because the charge transfer process was not enough to complete the coating within the 900 s deposition time. It can be seen that the increase of pH in electrolyte solutions leads to a shift of the current density to lower values. This action may be due to the blocking of the cathode surface by hydroxides that form as a result of strong alkalization of the electrolyte near the cathode surface.

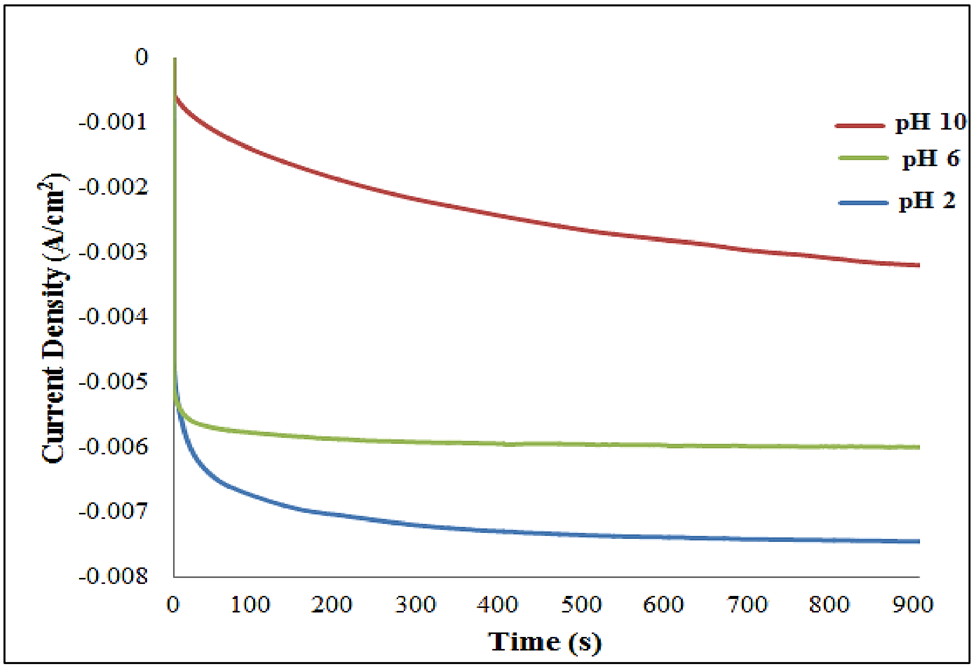

Figure 2. Chronoamperometric curves of the electrodeposition process of nickel on zincated aluminium surface with different electrolyte solutions, pH 2, pH 6 and pH 10 at 25 °C for 900 s.

Characterization of Nickel Coatings on Zincated Aluminium

Figure 3 shows the morphology of the nickel coating after electrodeposition from 0.1 M $NiSO_4$ solution at 900 s with various electrolyte pH solutions [deposited at -0.8 V (pH 2); -1.1 V (pH 6) and -1.5 V (pH 10)].

From these images, it was found that the surface morphologies of nickel-coated zincated aluminium prepared under different pH conditions were significantly different. White spots of nickel particles were less common on the surface and round pits as well as non-homogeneously small nuclei were formed with pH 2 nickel solution. The reverse zincated aluminium surface was found to be the original etched aluminium. This is due to dissolution of zinc from the aluminium surface as this deposition was done in acidic solution [11]. However, the nucleation behaviour of the microstructure was totally different at pH 6 where nodular morphology with a uniform coating was formed on the zincated aluminium surface, with almost 90% coverage. With a bath solution of pH 10, the nodular morphology changed to cauliflower-like agglomerates on the zincated aluminium surface, as shown in Figure 3(c), in agreement with a previous study by Khorsand et al. [12]. It is also explicitly observed that the deposition coverage was discontinued and underneath zincated aluminium surface as can be seen between the deposition of nickel (Figure 3(c)). This might because Ni^{2+} ions were in competition with hydroxide ions (OH^-) during the reduction when the pH 10 solution was used.

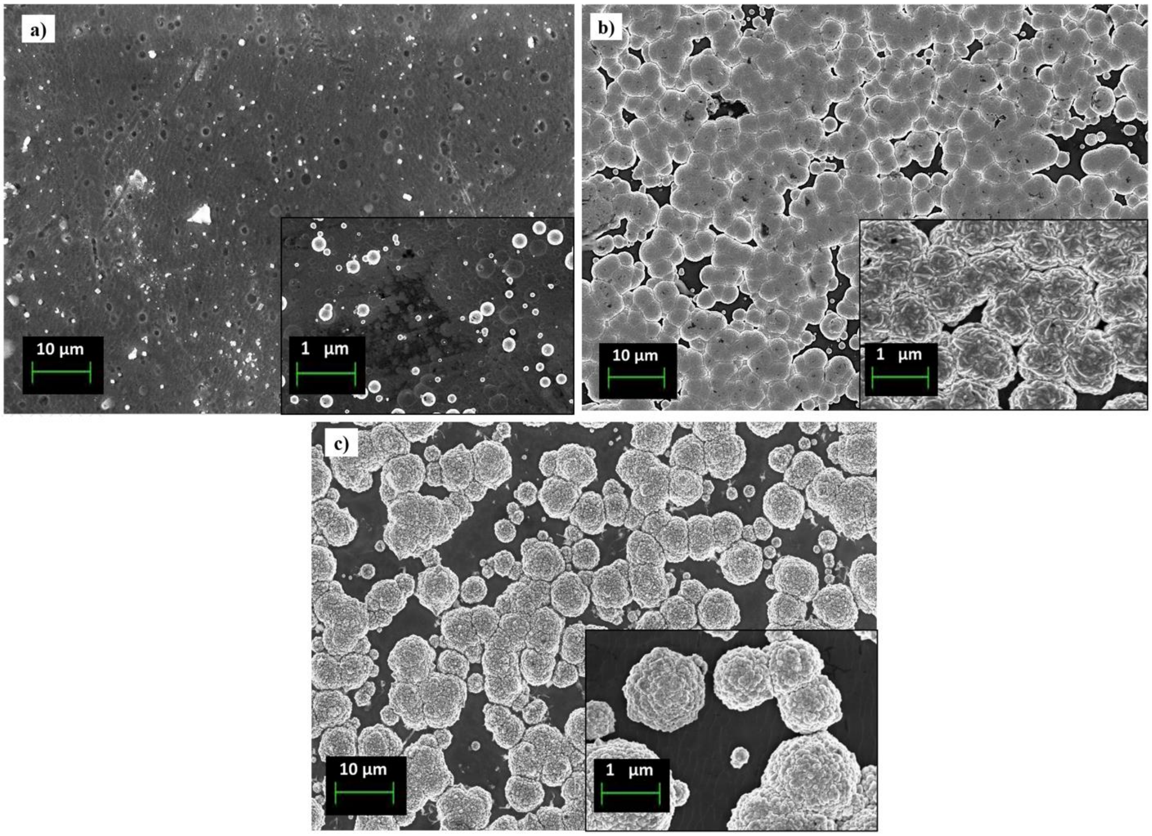

Figure 3. FESEM images of nickel coated on zincated aluminium substrates from (a) 0.1 M $NiSO_4$ + H_2SO_4 solution (pH 2), (b) 0.1 M $NiSO_4$ + 0.01 M NaOH + C_6H_5 $Na_3O_7.2H_2O$ solution (pH 6) and (c) 0.1 M $NiSO_4$ + 0.1 M NaOH + C_6H_5 $Na_3O_7.2H_2O$ solution (pH 10) at 25 $^{\circ}$C. Magnification: 5000x and 10000x (insert images)

In this study, the growth of nickel particles on zincated aluminium was measured manually based on the FESEM micrographs in Figure 3. Therefore, in order to observe the effect of pH on the growth of nickel particles, the length of one side of the coating particles was measured. From Figure 3, the FESEM micrographs were divided into four quadrants and in each quadrant, ten nickel particles were selected [13]. The lengths of the selected nickel particles were then measured, and the average length of the nickel particles from each quadrant were recorded. Figure 4 shows a graph of the size of the nickel particles deposited with electrolytes at different pH. The result showed an increase in the nickel particle size from 0.09 µm to 0.8 µm to 1.7 µm as the electrolyte pH increased from pH 2 to pH 6 to pH 10, respectively.

Figure 5 shows EDAX spectra of the nickel coatings as a function of the pH of the electrolyte solutions, while the elemental compositions of the nickel coatings by EDAX analysis are summarized in Table 1.

The highest percentage of nickel (Ni) deposited on a zincated aluminium surface was obtained with the pH 6 solution at -1.1 V deposition potential with 73.63 wt.%. The zinc (Zn) peak was also detected with 2.34 wt. % for pH 6 and 1.53 wt.% for pH 10, which comes from the zincated aluminium surface itself. The wt. % for aluminium (Al) was very high at pH 2 with 94.99 wt.% and only a small Ni peak was observed, indicating only a small amount of Ni was present while Zn was not detected, perhaps due to dissolution. The lower wt. % of Ni and Zn on the zincated aluminium surface due to the HER occurring in competition with the reduction of nickel and dissolution of Zn metal to Zn^{2+} ions during electrodeposition. Besides this, oxygen was still detected by EDAX for all nickel coatings. The remaining oxygen cannot be excluded because nickel itself can oxidize by air in the presence of moisture and it is also due to reaction with hydroxide ions, OH^-. The highest oxygen content was found to be 5.04 wt.% for deposition at pH 10.

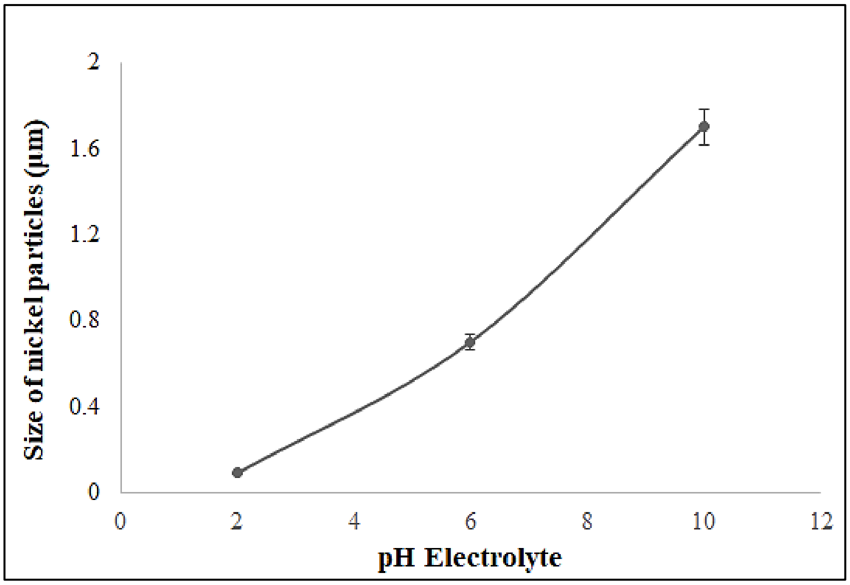

Figure 4. Analysis of the size of nickel particles deposited on zincated aluminium substrates with (a) 0.1 M $NiSO_4$ + H_2SO_4 solution (pH 2), (b) 0.1 M $NiSO_4$ + 0.01 M NaOH + C_6H_5 $Na_3O_7.2H_2O$ solution (pH 6) and (c) 0.1 M $NiSO_4$ + 0.1 M NaOH + C_6H_5 $Na_3O_7.2H_2O$ solution (pH 10) at 25 ˚C.

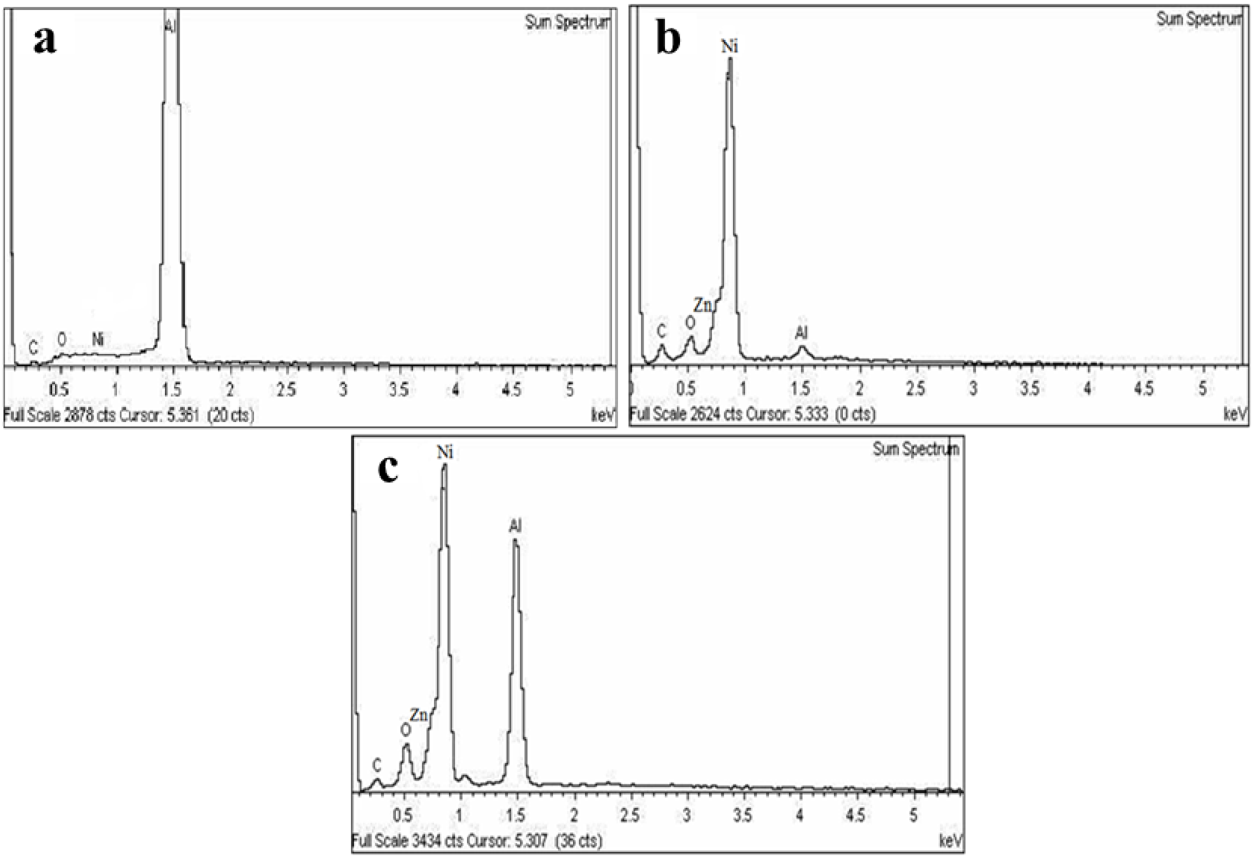

Figure 5. EDAX spectra of nickel coatings prepared with various electrolyte solutions at (a) pH 2, (b) pH 6 and (c) pH 10.

Table 1. The elemental compositions of nickel underlayers on treated zincated aluminium surfaces with different electrolyte solutions

Nickel underlayer	**Surface Composition (Weight%)**				
	Ni	**Zn**	**Al**	**O**	**C**
pH 2	2.04	0.00	94.99	0.62	2.35
pH 6	73.63	2.34	19.99	3.03	1.01
pH 10	66.16	1.53	23.52	5.04	3.75

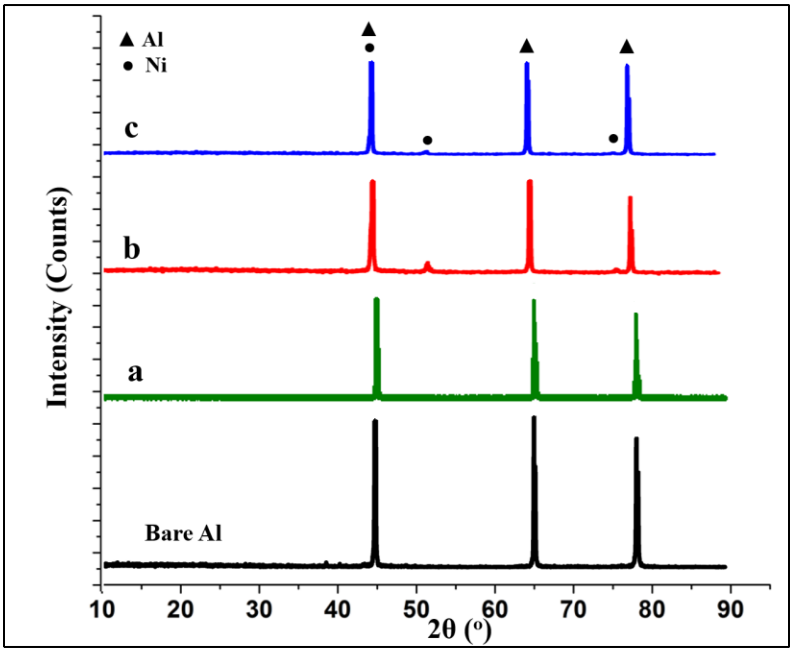

Figure 6. XRD patterns of nickel coated on zincated aluminium substrate after electrodeposition for 900 s from (a) 0.1 M $NiSO_4$ + H_2SO_4 solution (pH 2) at -0.8 V, (b) 0.1 M $NiSO_4$ + 0.01 M NaOH + C_6H_5 $Na_3O_7.2H_2O$ solution (pH 6) at -1.1 V, (c) 0.1 M $NiSO_4$ + 0.1 M NaOH + C_6H_5 $Na_3O_7.2H_2O$ solution (pH 10) at -1.5 V with Bare Al for comparison.

Figure 6 depicts typical X-ray diffraction patterns for nickel coatings formed on zincated aluminium surfaces after 900 s of electrodeposition at 25 ˚C. The results revealed that nickel had a cubic crystalline structure, with a strong (111) diffraction that overlay with the aluminium peak, in addition to (200) and (220) peaks with relatively low intensities for pH 6 and pH 10 only. This means that most of the nickel crystallites were oriented parallel to the (111) plane. Two major peaks were observed for pH 6 and 10, which were attributed to the (111), (200) and (220) planes of nickel. The position of 2θ values was compared with the database reference pattern for nickel (reference code: 00-004-0850) and these nickel values matched the standard reference pattern at 44.05°, 51.84° and 76.37°. Meanwhile, nickel crystallite structure was not detected by XRD at pH 2 probably due to the fairly low content of nickel present, and thus only aluminium peaks were observed at 44.74°, 65.14° and 78.23°.

The nickel coating formed on zincated aluminium was observed visually, as shown in Figure 7. It is clear that there was no coating on the zincated aluminium surface used with the pH 2 solution. The exposed zincated aluminium surface (2 cm^2 in solution during the electrodeposition process) was the same as the original bare aluminium surface with no coating apparent. However, a very bright light-yellow coating uniformly covered the zincated aluminium surface used with the pH 6 solution (Figure 6 (b)). The nickel coating obtained from the pH 10 solution showed a dark-brown colour coating that covered the entire exposed surface. Nevertheless, the nickel coating obtained with the pH 10 solution had not adhered very well to the substrate

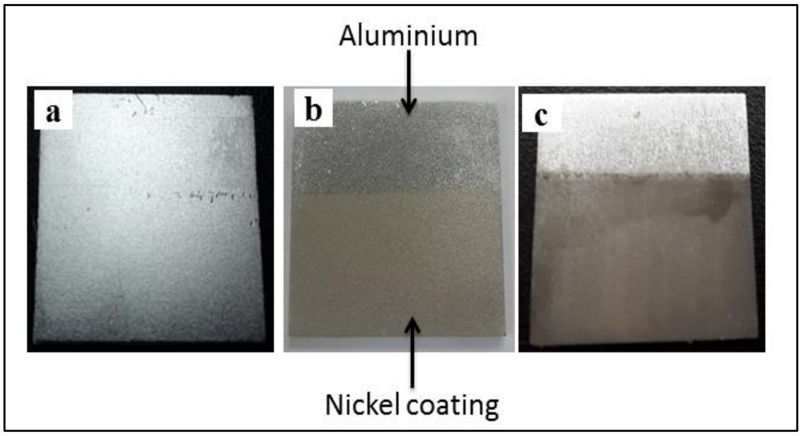

Figure 7: Visual observation of nickel coatings prepared from (a) 0.1 M $NiSO_4$ + H_2SO_4 solution (pH 2) at -0.8 V, (b) 0.1 M $NiSO_4$ + 0.01 M NaOH + C_6H_5 $Na_3O_7.2H_2O$ solution (pH 6) at -1.1 V and (c) 0.1 M $NiSO_4$ + 0.1 M NaOH + C_6H_5 $Na_3O_7.2H_2O$ solution (pH 10) at -1.5 V.

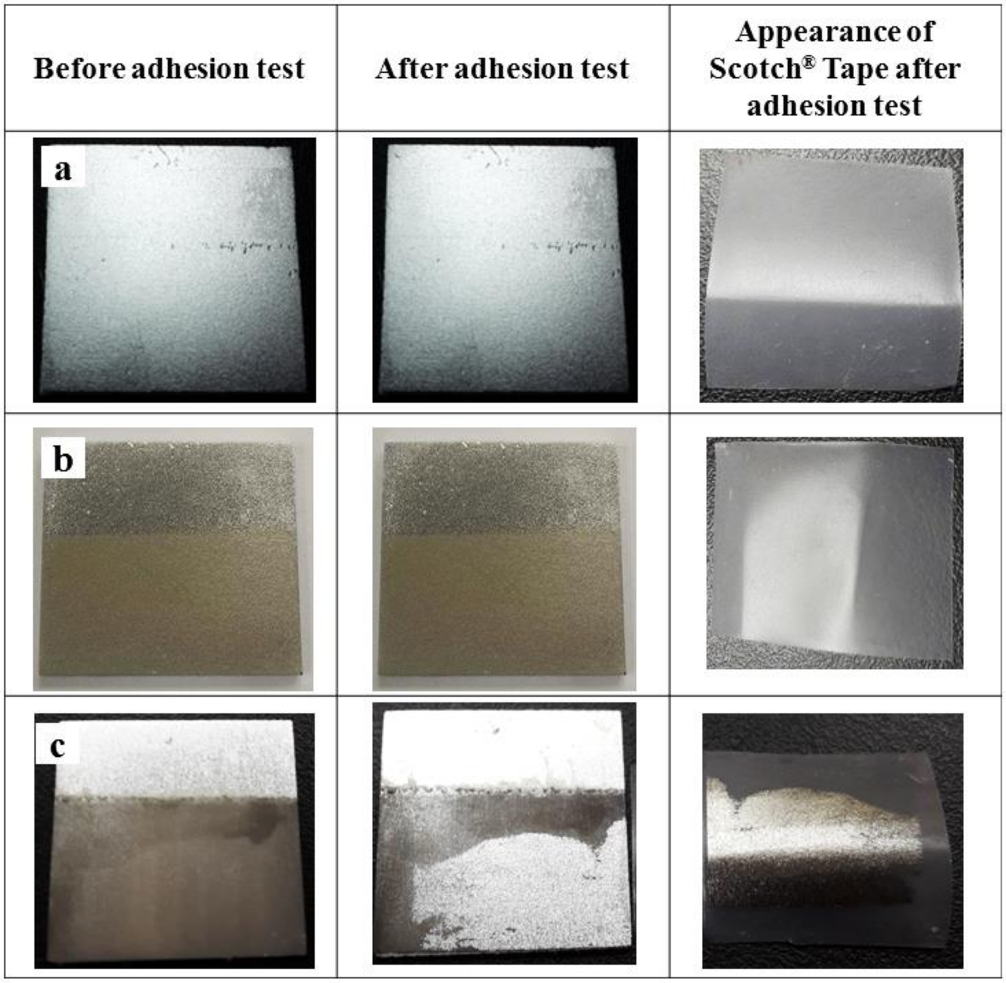

Figure 8: Visual observations of nickel coatings prepared from (a) pH 2, (b) pH 6 and (c) pH 10 solutions for before and after removal by Scotch® tape.

compared to the coating obtained with the pH 6 solution. This might be due to the formation of loose nickel hydroxide ($Ni(OH)_2$) deposits due to the highly alkaline bath solution.

The adhesion properties of nickel coatings are critical as they greatly affect long-term performance. A nickel coating as an underlayer or a top coating must be well-adhered to the substrate for any application. Figure 8 shows the nickel coatings prepared from various electrolyte solutions at different pH before and after the adhesion tape test. There was no pulled-off area observed for the nickel coating prepared using pH 2 solution as shown in Figure 8(a)after the adhesion test using Scotch® tape on the exposed zincated aluminium surface. This is because the sample itself had returned to its original bare aluminium surface due to the dissolution process of metals in strong acidic environments. This is strongly supported by the FESEM and EDAX analysis results. However, for the nickel coating formed using the pH 6 solution (Figure8(b)), the Scotch® tape was clear, indicating the nickel coating had strongly adhered to the zincated aluminium surface, and thus had passed the adhesion test. Besides this, the nickel coating on the zincated aluminium surface was not removed even by rubbing the coating with tissue after the electrodeposition process. In contrast, the nickel coating prepared from the pH 10 solution was easily flaked off from the zincated aluminium surface when the Scotch® tape was pulled off as shown in Figure 8(c), which implied a weak adhesion of the coating to the substrate. A large area of the coating was removed by the tape and only a small part remained intact on the electrode surface.

CONCLUSION

Nickel coatings were successfully produced on zincated aluminium surfaces by electrodeposition using a pH 6 solution containing Ni(II) by applying a constant potential of -1.1 V for 900 s. The pH of the electrolyte solution significantly affected the formation of the nickel coating on the zincated aluminium surface. From the results obtained, it can be summarized that the nickel coating deposited on the zincated aluminium surface at pH 6 was highly adherent and compact compared to the coating formed using pH 2 and pH 10 solutions, as it was strongly bound to the zincated aluminium surface. This coating also had a good appearance with uniform surface morphology and the highest nickel composition at 73.63 wt. %.

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Conflict of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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