



Effect of EDTA and NH_4Cl additives on electrodeposition of Zn–Ni films from choline chloride-based ionic liquid

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Abstract: Two additives of ethylene diamine tetraacetic acid (EDTA) and ammonium chloride (NH_4Cl) were separately used in the electrodeposition of Zn–Ni alloy films from a deep eutectic solvent. The effects of these two additives on electrodeposition behavior, composition, morphology, and corrosion performance of the Zn–Ni alloys were investigated. The electrodeposition behaviors of Zn–Ni alloy revealed by the cyclic voltammetry show that the addition of EDTA to the Zn–Ni electrolyte enhances the Zn incorporation into the alloy film while the addition of NH_4Cl produces an opposite effect by suppressing Zn incorporation into the film. With an increase of EDTA concentration in the electrolyte, the Zn content of the Zn–Ni films increases, while the grain size of the deposits and the current efficiency of the plating process decrease. The increase of NH_4Cl concentration in the electrolyte would significantly refine the grain size of the electrodeposited Zn–Ni films, reduce the Zn content and increase the cathodic current efficiency. The corrosion testing indicates that the barrier corrosion resistances of Zn–Ni films electrodeposited from NH_4Cl containing electrolytes are superior to those electrodeposited from EDTA-containing electrolytes, which in turn are superior to those electrodeposited from additive-free electrolytes.

Key words: additive; EDTA; NH_4Cl ; deep eutectic solvent; corrosion resistance

1 Introduction

The electrodeposition of Zn and its alloys has been widely used for corrosion protection of active metal substrates from aggressive corrosive environments [1]. Among potential Zn alloys, Zn–Ni alloy coatings have attracted much attention because they possess high corrosion resistance, thermal stability and better mechanical properties in comparison with pure Zn and many Zn alloy coatings [2–11]. They are used in many applications such as aerospace, oil, gas and automotive industries, and electrical and electronic components.

The success of electroplating depends to a large extent on the type of addition agents introduced in the plating electrolytes. Additives are often introduced into the Zn–Ni electroplating bath to control the deposition rate, crystallization mechanism, leveling and brightness of the Zn–Ni deposits with the purpose of obtaining bright, compact and grain refined high corrosion resistant coatings [12,13]. In addition, additives can change metal

ion speciation in the electrolyte, consequently altering the electrodeposition characteristics of the Zn–Ni alloy. Thus, additives can influence the alloy electrodeposition behavior such that the grain size and alloy chemical composition can be tailored to meet various requirements [12]. Depending on the nature of additives used, they can form complexes with metal ions, making the reduction of such metals more difficult, or they can inhibit metal nucleation by adsorbing on the electrode surface [13]. Thus, with proper selection of complexing agents during Zn–Ni electrodeposition, it is possible to make reduction of either Ni (II) ions or Zn (II) ions difficult, thereby influencing alloy composition and morphology [14].

The electrodeposition of Zn and its alloys has been generally performed in aqueous electrolytes with a wide range of additives [15–18]. There are a couple of papers on controlling of the alloy composition and grain morphology using additives during Zn alloys electrodeposition from aqueous electrolytes. SOARES et al [19] used aqueous NH_4Cl bath with gelatin to electrodeposit Zn–Ni alloy and found that the amount of

Zn content in the Zn–Ni films increased from 86% to 90% and current efficiency was observed to increase from 84% to 94%. KARWAS and HEPEL [20] studied the effect of boric acid on Zn–Co alloy electrodeposition from a sulphate bath containing NH_4Cl and found that the additive of boric acid accelerated Zn deposition and hindered Co deposition. KELLY and WEST [21] found that the polyethoxylated additives inhibit the electrodeposition of Zn during the first stages of nucleation process.

Room temperature ionic liquids (RTILs) are viable alternatives to aqueous electrolytes for metal/alloy electrodeposition due to their negligible vapor pressures at elevated temperatures, good ionic conductivities, good thermal stability and wide electrochemical windows [22,23]. Mixtures of quaternary ammonium salts, in particular choline chloride, with hydrogen bond donors like amide alcohol and carboxylic acid which are known as deep eutectic solvents (DES) [24,25] can be alternative ionic solvents. These DES liquids have the same advantages of RTILs but they are cheap and moisture stable [24,25]. Choline chloride-based DES has been successfully assessed for electrodeposition of different metals and alloys [26–31] on different substrates producing films that are completely different from those obtained from aqueous electrolytes. Electrodeposition of Zn–Ni alloys from deep eutectic solvents in the absence of additives demonstrated by YANG et al [18] and FASHU et al [26] have showed the influence of electrodeposition conditions on Zn–Ni alloy electrodeposition from a DES. Studies on the effect of Zn–Ni plating bath additives on electrodeposition and deposit properties during electrodeposition from ionic liquids are scarce. The presence of chelating ligands like amino carboxylic hexamethylene tetraacetic (HMTA), ethylene diamine tetraacetic acid (EDTA), nitrilotriacetic (NTA) and ammonium chloride (NH_4Cl) in the Zn–Ni electrolyte can bind either Ni (II) ions or Zn (II) ions in stable complexes, thus affecting the electrodeposited alloy composition and morphology. The objective of this study is to analyze the electrodeposition of Zn–Ni alloys from a choline chloride–urea eutectic-based ionic liquid that contains either EDTA or NH_4Cl as additives. The influences of these additives on the Zn–Ni films composition, morphology and resulting corrosion behavior were investigated and compared.

2 Experimental

2.1 Electrolyte preparation and electrochemical testing

Choline chloride (ChCl) ($\text{HOC}_2\text{H}_4\text{N}(\text{CH}_3)_3\text{Cl}$) (Aldrich, 99%) was dried at 60 °C for 24 h in an oven

before use. Urea (U), nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) (Aldrich, >99%) and zinc chloride (ZnCl_2) (Aldrich, >98%) were used. The eutectic mixture was produced at 70 °C until a homogeneous colorless liquid was formed by stirring the dried ChCl and the urea in a mole ratio of 1:2 (solvent). The base electrolyte was formed by adding analytical grade nickel chloride (0.45 mol/L $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.45Ni) and zinc chloride (0.05 mol/L ZnCl_2 , 0.05Zn) to the prepared solvent and stirring the mixture at 70 °C until a green homogeneous solution was obtained. Electrolyte solutions were prepared by adding appropriate quantities of EDTA and NH_4Cl to the prepared 0.45 mol/L Zn–0.05 mol/L Ni base electrolyte to produce electrolytes shown in Table 1, in which the components B–G are named as 0.45Zn–0.05Ni–0.01EDTA, 0.45Zn–0.05Ni–0.03EDTA, 0.45Zn–0.05Ni–0.045E, 0.45Zn–0.05Ni–0.6 NH_4Cl , 0.45Zn–0.05Ni–0.8 NH_4Cl and 0.45Zn–0.05Ni–1.0 NH_4Cl , respectively. The electrolytes were formed by continuous stirring at 70 °C until all the EDTA or NH_4Cl solutes have completely dissolved. Cyclic voltammetry experiments were carried out in a three-electrode system consisting of a platinum working electrode (1 cm^2), a platinum counter electrode and a silver reference electrode. The platinum electrodes were cleaned in nitric acid (HNO_3) before rinsing and drying in each measurement. The cyclic voltammetry experiments were performed at 70 °C with a scan rate of 10 mV/s.

Table 1 Electrolyte compositions

Component	$c(\text{EDTA})/$ ($\text{mol} \cdot \text{L}^{-1}$)	$c(\text{NH}_4\text{Cl})/$ ($\text{mol} \cdot \text{L}^{-1}$)	$c(\text{NiCl}_2 \cdot 6\text{H}_2\text{O})/$ ($\text{mol} \cdot \text{L}^{-1}$)	$c(\text{ZnCl}_2)/$ ($\text{mol} \cdot \text{L}^{-1}$)
A	–	–	0.05	0.45
B	0.010	–	0.05	0.45
C	0.030	–	0.05	0.45
D	0.045	–	0.05	0.45
E	–	0.6	0.05	0.45
F	–	0.8	0.05	0.45
G	–	1.0	0.05	0.45

2.2 Electrodeposition and coating characterization

For electrodeposition, a three-electrode cell with a nickel anode, a copper plate cathode and a quasi reference silver electrode was used. Zn–Ni coatings were prepared by potentiostatic electrodeposition from the prepared electrolytes (Table 1) at a stabilized bath temperature of 70 °C and a deposition voltage of –0.9 V on copper substrates with sizes of 2 $\text{cm} \times 5 \text{ cm}$. In order to electrodeposit films of the same thickness, the electrodeposition time was adjusted to obtain the same charge density of 2 C/cm^2 in all experiments. Before plating, the copper substrates were electrolytically

cleaned in an alkaline solution (0.61 mol/L $\text{H}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ + 0.47 mol/L Na_2CO_3 + 0.25 mol/L NaOH) and were then subsequently rinsed with ethanol and deionised water, and dried in air. The gap distance between the cathode and anode during electrodeposition was maintained at approximately 3 cm. After the electrodeposition of each film, the sample was thoroughly and simultaneously cleaned with ethanol and distilled water, and then dried in air. The chemical compositions and surface morphologies of the deposits were examined with an energy dispersive spectroscopy (EDS) analyzer integrated with a scanning electron microscope (SEM). Structural measurements of the investigated Zn–Ni coatings were conducted by X-ray diffraction (XRD) in thin film mode.

2.3 Corrosion resistance measurements

The corrosion protection performances of the Zn–Ni samples in a marine environment were studied by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. These electrochemical experiments were carried out at room temperature in an aerated 3.5% NaCl aqueous solution using a classic three-electrode cell with a platinum plate as a counter electrode and a saturated calomel electrode (SCE) as a reference. The electrodeposited Zn–Ni samples were used as working electrodes and their exposed surface areas were obtained by using insulating epoxy resin leaving an uncovered area of approximately 1 cm^2 . Before the EIS experiments, the samples were first immersed into the 3.5% NaCl solution for about 4 h to stabilize open-circuit potentials (OCPs). The EIS measurements were carried out in the frequency range between 100 kHz and 0.1 Hz with an amplitude of 10 mV superimposed AC signal and the corresponding Nyquist and Bode plots were obtained. Then, potentiodynamic curves were recorded by scanning from 250 mV below OCP upwards at a rate of 1 mV/s up to 250 mV above OCP. The corrosion potentials (ϕ_{corr}) and the corrosion current densities (J_{corr}) were calculated from the intersections of the cathodic and anodic Tafel curves extrapolated from the anodic and cathodic polarization curves.

3 Results and discussion

3.1 Cyclic voltammetry behaviors

Electrochemical behaviors of electrodeposition electrolytes in the presence and absence of additives were studied by cyclic voltammetry (Figs. 1 and 2). It is clear that the presence of additives causes some significant changes in the shape and position of the voltammograms, indicating that the presence of additives alters both the Zn/Ni deposition and stripping processes.

In general, the voltammetric behavior of the alloy states the characteristics of its components and the structure of the deposited phases with the height of the peaks giving some information about the quantity of the deposited phases. Some crossovers of current are experienced in many voltammograms as the potential becomes more negative and indicates the formation of stable growth centers on the substrate surface [32,33].

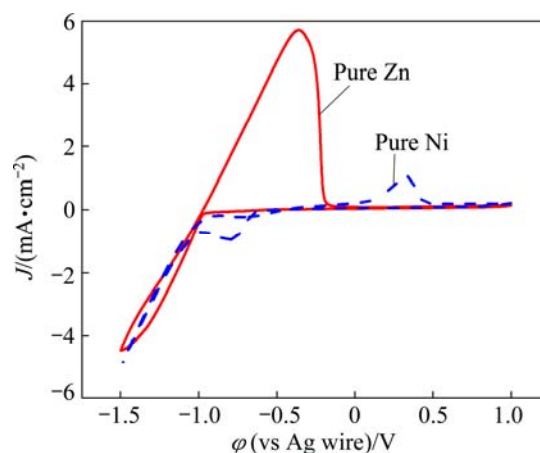


Fig. 1 Cyclic voltammograms of pure Zn and pure Ni at 70 °C with scan rate of 10 mV/s

3.1.1 Zn–Ni voltammetry in the absence of additives

For comparison, the voltammograms performed in the electrolyte free of additives and those of pure Zn and Ni are also presented here. The voltammograms of electrolytes of pure Zn and Ni are shown in Fig. 1. These voltammograms show that the reduction of Zn and Ni starts at potentials of approximately -1.01 and -0.59 V , respectively. In the reverse scan, a single Zn oxidation peak occurs at a potential of around -0.630 V and its width is broad as a consequence of the relatively high viscosity of the solvent used. Figure 2 shows the cyclic voltammograms obtained for the Zn–Ni additive-free electrolyte. Here, the reduction of Ni starts at a potential of approximately -0.51 V and the reduction of Zn starts at a potential of around -1.01 V . An analysis of the anodic process (Fig. 2(a)) indicates that two oxidation peaks are present and they correspond to the dissolution of the Zn–Ni alloy deposit. Ni is more stable than Zn [34]. Therefore, the more negative peak corresponds to the dissolution of Zn from the Zn-rich phase(s), and the more positive peak corresponds to the dissolution of the porous Ni matrix formed due to the preferential dissolution of Zn from the Zn-rich phases.

3.1.2 Zn–Ni voltammetry in the presence of EDTA additive

To study the influence of the concentration of EDTA in the electrolyte on the Zn–Ni electrodeposition behaviour, cyclic voltammetry of electrolytes with different concentrations of EDTA (Table 1) was

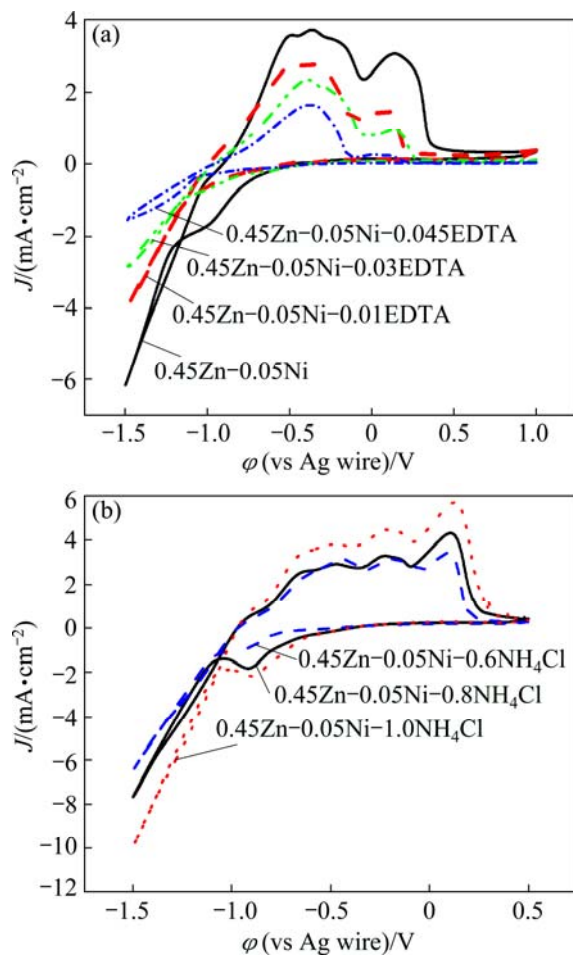


Fig. 2 Cyclic voltammograms of 0.45Zn–0.05Ni electrolytes in the presence of different concentrations EDTA (a) and NH_4Cl (b) performed at 70 °C with scan rate of 10 mV/s

performed. The voltammograms of Zn–Ni electrolytes containing different EDTA concentrations are shown in Fig. 2(a). These voltammograms show that the current density is significantly reduced with an increase in EDTA concentration in the electrolytic bath. This effect may be related to the decrease in conductivity of the electrolytes with the increase in electrolyte EDTA concentration, as shown in Fig. 3(a). Figure 2(a) shows that the onset potential for Ni reduction increases cathodically with the increase in EDTA concentration, from –0.51 V for EDTA-free electrolyte, –0.65 V for 0.01 mol/L EDTA-containing electrolyte, –0.67 V for 0.03 mol/L EDTA-containing electrolyte, and up to –0.7 V for 0.045 mol/L EDTA-containing electrolyte, whilst that of Zn is almost constant at –1.01 V in all cases. This blocking effect caused by EDTA to Ni reduction brings the reduction potentials of Zn and Ni closer to each other, making it more favorable for the incorporation of more Zn into the Zn–Ni alloy deposit. There are two clear anodic peaks in each voltammogram and they are associated with the dissolution of Zn and Ni from the Zn–Ni

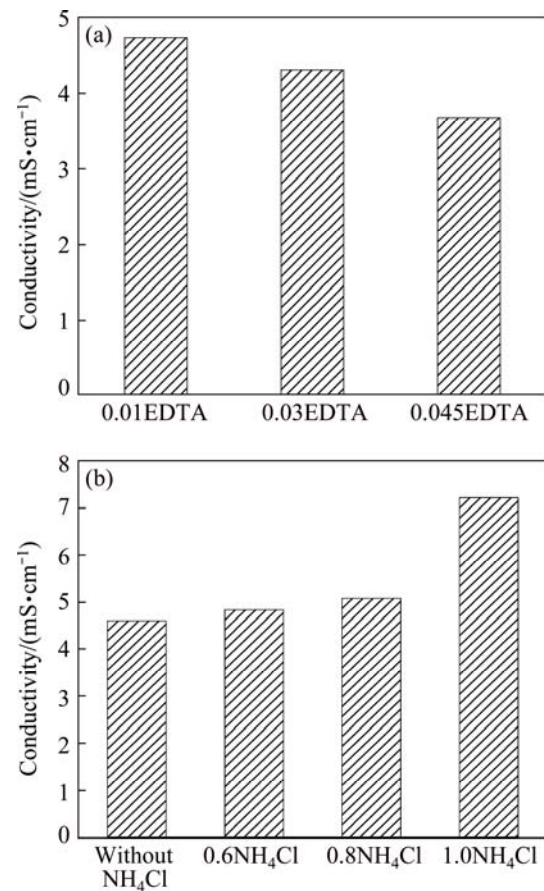


Fig. 3 Conductivities of 0.45Zn–0.05Ni electrolytes containing EDTA (a) and NH_4Cl (b) at 70 °C

electrodeposited film. The more positive anodic peaks are attributed to oxidation of Ni species and the more negative anodic oxidation peaks to the oxidation of Zn species. The more positive deposition and dissolution potentials for Ni in comparison with Zn are simple due to the fact that Ni is relatively noble for redox reaction with respect to Zn [34]. Figure 2(a) shows that the intensity of the anodic peaks related to Ni drastically reduces as the EDTA concentration in electrolyte is increased from 0 to 0.045 mol/L. This is another confirmation that the EDTA additive strongly hinders Ni deposition. As the peak corresponding to Ni diminishes, the peak corresponding to Zn increases and becomes sharp, showing that the quantity of deposited Zn phase becomes higher than that of Ni.

3.1.3 Zn–Ni voltammetry in the presence of NH_4Cl additive

Figure 2(b) presents the influence of electrolyte NH_4Cl additive concentration on Zn–Ni electrodeposition behaviors. It can be seen that with the increase in NH_4Cl additive concentration, the shape and position of the voltammograms change in two ways: 1) the onset of reduction of Zn was significantly shifted to negative values whilst that of reduction of Ni was almost constant

at a potential of around -0.59 V; 2) the current density increases. The increase in current density with the increase in electrolyte NH_4Cl additive concentration is likely to be due to increase in electrolyte conductivity as shown in Fig. 3(b). The shifting of the onset of Zn deposition to more negative values shows that NH_4Cl additive suppresses Zn deposition and incorporation into the Zn–Ni alloy film. During the anodic scan in the voltammograms, many anodic peaks were observed corresponding to the dissolution of Zn and Ni from different phases of the Zn–Ni alloy. Figure 2(b) shows that the intensity of the anodic peak related to Zn (more negative) drastically reduces while that related to Ni (more positive) increases as the electrolyte NH_4Cl concentration is increased from 0.8 to 1.0 mol/L. This is another confirmation that the NH_4Cl additive strongly suppresses the Zn deposition.

3.2 Potentiostatic electrodeposition

The conductivities of the Zn–Ni electrolytes decrease with the increase in EDTA concentration and increase with the increase in NH_4Cl concentration as shown in Figs. 3(a) and (b). This is corroborated by the electrodeposition current (I)–time (t) curves shown in Figs. 4(a) and (b) which show a decrease in electrodeposition currents with an increase in EDTA concentration and an increase in electrodeposition currents with an increase in NH_4Cl electrolyte concentration. Since the electrodeposition current decreases with the increase in EDTA concentration, hence it is essential to optimize the EDTA concentration producing the required film composition while allowing the deposition to proceed at acceptable rates. The cathodic current efficiency (CCE) was calculated using the mass gained, the charge transferred and the average chemical composition of the deposit [36]. The mass of the coatings as a result of the mass difference of specimens before and after electrodeposition was measured by an electronic balance with a precision of 0.1 mg. The current efficiencies (η), for Zn–Ni alloy electrodeposition using EDTA or NH_4Cl electrolyte in Table 1 at -0.9 V were calculated on the basis of the Faraday's law using a method described in Ref. [36], which is stated as

$$\eta = \left(\frac{m_e}{m_t} \right) \times 100\% \quad (1)$$

where m_e is the experimentally obtained mass of the deposit and m_t is the theoretical deposit mass given by the Faraday's law.

The variable m_t is obtained using the following Faraday equation:

$$m_t = \frac{Mit}{zF} \quad (2)$$

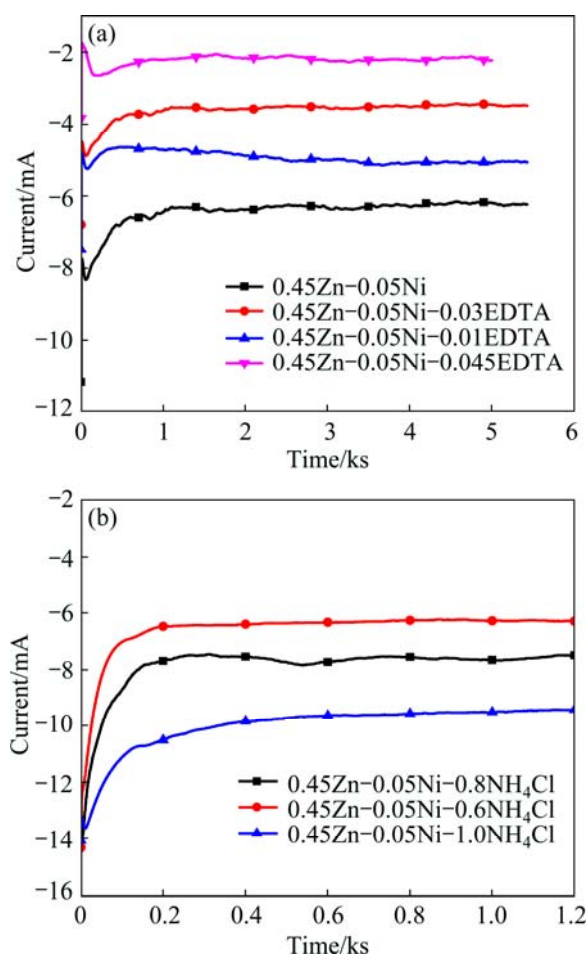


Fig. 4 Effect of additive concentration on deposition current in plating process from EDTA-containing (a) and NH_4Cl -containing (b) electrolytes at 70 °C and -0.9 V

where M is the relative atomic mass of the alloy, I is the current of electrodeposition, t is the time of electrodeposition, z is the number of electrons exchanged, and F is the Faraday constant (96485 C/mol).

Thus,

$$\eta = \frac{m_e F}{It} \sum \frac{z_i w_i}{M_i} \times 100\% \quad (3)$$

where w_i is the mass fraction of the element in the alloy deposit, z_i is the number of electrons transferred per atom of each metal (It is 2 in this case).

Figures 5(a) and (b) show the effects of EDTA or NH_4Cl concentration on cathodic current efficiency. The cathodic current efficiency for electrodeposition decreases with the increase in EDTA concentration and increases with the increase in NH_4Cl concentration. The decrease in current efficiency with the increase in EDTA concentration is likely to be due to the dissociation of the additive and incorporation of components into the film, whilst the increase in current efficiency with the increase in NH_4Cl concentration may be related to the increase in electrolyte conductivity.

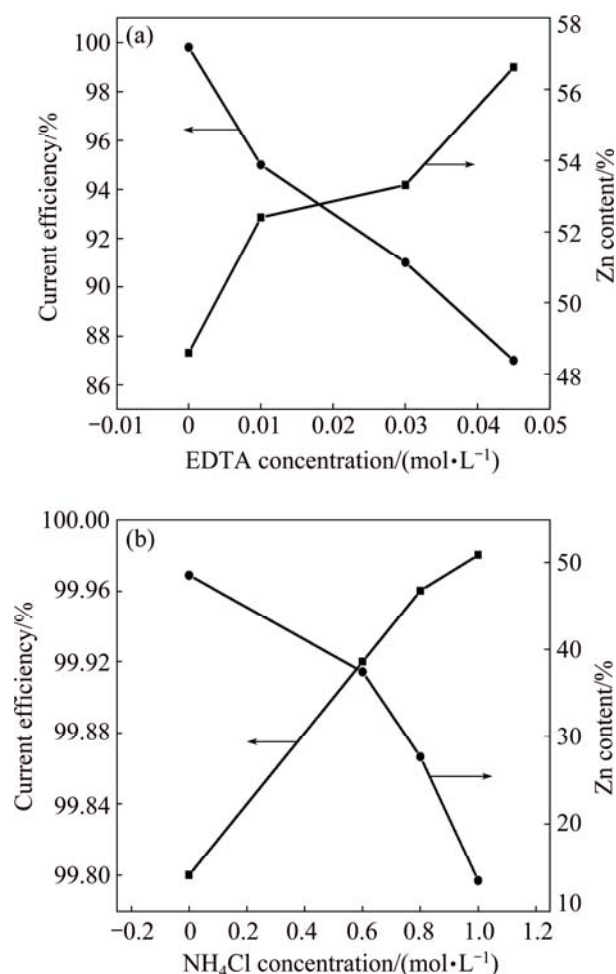


Fig. 5 Effect of EDTA (a) and NH₄Cl (b) concentration on cathodic current efficiency and Zn content in films

3.3 Morphology and chemical compositions

To evaluate the variations in chemical composition of the films with EDTA or NH₄Cl concentration, the variations of Zn content (balance Ni) with EDTA or NH₄Cl concentration for Zn–Ni electrodeposits electrodeposited at -0.9 V are shown in Figs. 5(a) and (b), respectively. It is evident in all cases that the Zn content in the Zn–Ni alloy deposits is less than that in the electrolyte. This shows that in all cases the Zn–Ni electrodeposition follows the normal type of co-deposition. For EDTA-containing electrolytes the Zn content significantly increases with the increase in EDTA concentration, whilst for NH₄Cl-containing electrolytes the Zn content is suppressed with the increase of NH₄Cl concentration. These results corroborate well with the observations from the voltammograms of these electrolytes in Section 3.1. It is shown that the increase of EDTA concentration enhances the deposit Zn content, whilst the increase of NH₄Cl concentration suppresses the deposit Zn content. The results indicate that the Zn content increases with the increase in EDTA

concentration, which is in strong agreement with that obtained by ROEV et al [34] in aqueous solutions containing amino complexing agents.

Visual inspections of the Zn–Ni films showed that all the films were smooth and shiny. The films produced from NH₄Cl-containing electrolytes were bright. The surface morphology of the Zn–Ni films obtained from an additive-free electrolyte at a potential of -0.9 V and a temperature of 70 °C is illustrated Fig. 6(a). The variations of the surface morphologies of Zn–Ni films obtained from additive-containing electrolytes at a potential of -0.9 V and 70 °C are illustrated in Figs. 6(b)–(d) and Fig. 7. The coatings produced under these conditions were generally compact, smooth, and adherent to the substrate. From these figures, it can be seen that with the increase of the EDTA or the NH₄Cl concentration in electrolytes, the morphologies of the Zn–Ni coatings generally evolve from coarse grains to fine grains. With the increase of EDTA concentration, some fine grains also agglomerate to form some clusters which disperse into the whole microstructure (Figs. 6(b)–(d)). Comparisons of Fig. 6 with Fig. 7 show that both NH₄Cl and EDTA additives are good grain refiners, and NH₄Cl is a more effective grain refiner than EDTA.

3.4 Crystal structure of deposits

Figures 8(a) and (b) show the XRD patterns of the Zn–Ni alloy coatings obtained from different electrolytes with EDTA or NH₄Cl additive, respectively. All the coatings obtained consist of α -phase, i.e., a solid solution of Zn in a Ni matrix with a structure similar to polycrystalline Ni. The peak position corresponds to that of pure Ni with orientations of (1 1 1), (2 0 0) and (2 2 0). With increase of Zn content (Fig. 8(a)) in the films, the peak assigned to (1 1 1) shifts to a lower angle and broadens while the peaks for (2 0 0) and (2 2 0) weaken and disappear. This is because Zn forms a substitutional solid solution by replacing the Ni atom in the FCC lattice, expanding the Ni lattice. Thus, the lowering of diffraction angles due to the larger lattice parameter of α -Zn–Ni compared with that of pure Ni and the broadening of the peak are attributed to the reduction in grain size with the increase in Zn content [18]. Thus, Fig. 8 shows that the (111) peaks from EDTA-based electrolyte (higher Zn content deposits) are broader and less intense than those from NH₄Cl-based electrolyte (lower Zn content deposits). A similar behavior in the Zn–Ni alloy phase composition was reported previously [30] and it is in agreement with the Zn–Ni phase diagram. FRATESI and ROVENTI [36] observed that when the Ni content in the Zn–Ni coating was greater than 50%, the α -Zn–Ni phase dominated. In addition,

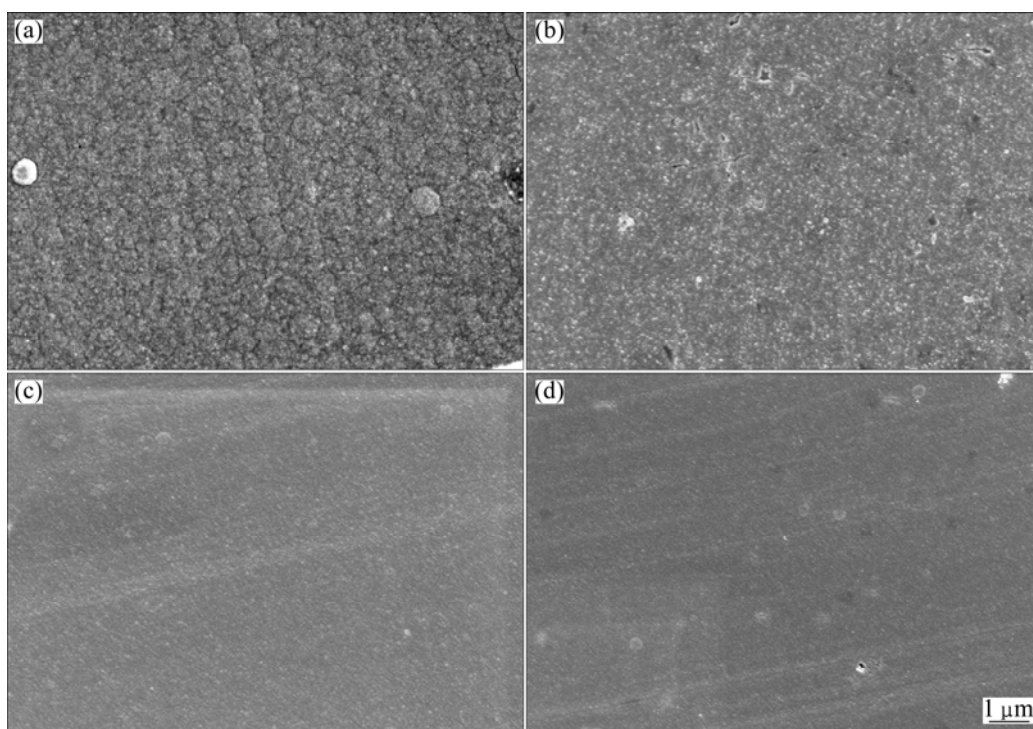


Fig. 6 SEM images of Zn–Ni films electrodeposited at -0.9 V in $0.45\text{Zn}-0.05\text{Ni}$ electrolyte without additive (a) and with 0.01 mol/L (b), 0.03 mol/L (c) and 0.045 mol/L (d) of EDTA, respectively

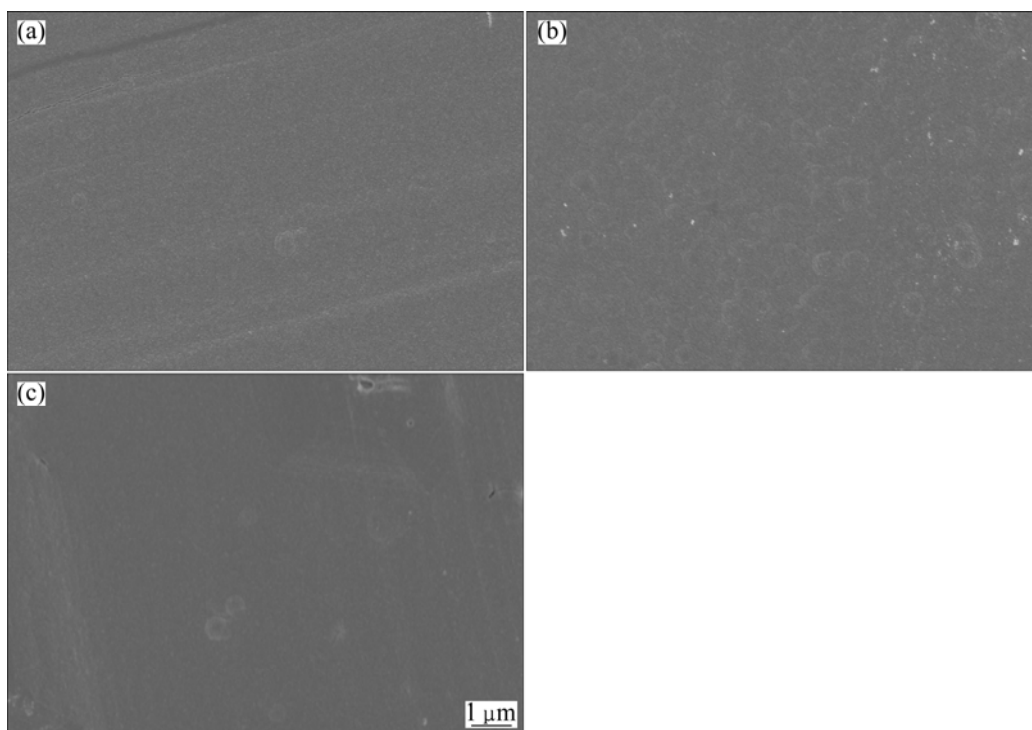


Fig. 7 SEM images of Zn–Ni films electrodeposited at -0.9 V in $0.45\text{Zn}-0.05\text{Ni}$ electrolyte with 0.6 mol/L (a), 0.8 mol/L (b) and 1.0 mol/L (c) NH_4Cl , respectively

ALFANTAZI et al [37,38] observed that the α -phase is the only phase present in Zn–Ni coatings with the Ni content of 63%. YANG et al [18] also observed that

during Zn–Ni deposition from deep eutectic solvents, α -Zn–Ni is the only phase present in Zn–Ni coatings due to the presence of high Ni content in films.

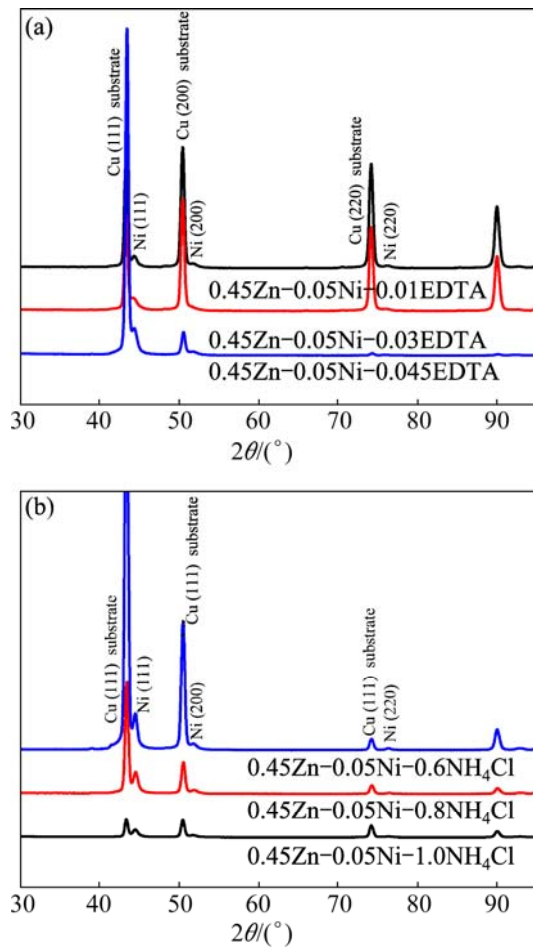


Fig. 8 XRD patterns of Zn–Ni films electrodeposited at -0.9 V in EDTA-containing electrolytes (a) and NH_4Cl -containing electrolytes (b) at 70°C

3.5 Corrosion tests

3.5.1 Potentiodynamic polarization studies

The potentiodynamic polarization curves of prepared Zn–Ni films performed in aerated 3.5% NaCl solution at room temperature are shown in Fig. 9. The corrosion current densities (J_{corr}) and corrosion potentials (ϕ_{corr}) of the Zn–Ni coatings were calculated from the intercepts of the Tafel slopes by extrapolation and their values are given in Table 2, where the capital letters represent the electrolytes from which the films were electrodeposited. The corrosion potential is an indication of the corrosive activity of the deposit in a corrosive environment. It is worth noting that corrosion resistances of coatings are generally related to their morphologies and phase compositions, as well as their chemical compositions [39]. Since all the electrodeposited Zn–Ni coatings have a similar phase composition, i.e. a single α -Zn–Ni phase structure, so surface morphology and chemical composition are the main factors affecting their corrosion performances. Here, it is generally observed that the corrosion potential of the electrodeposits increases with increase in Zn content of the deposit films

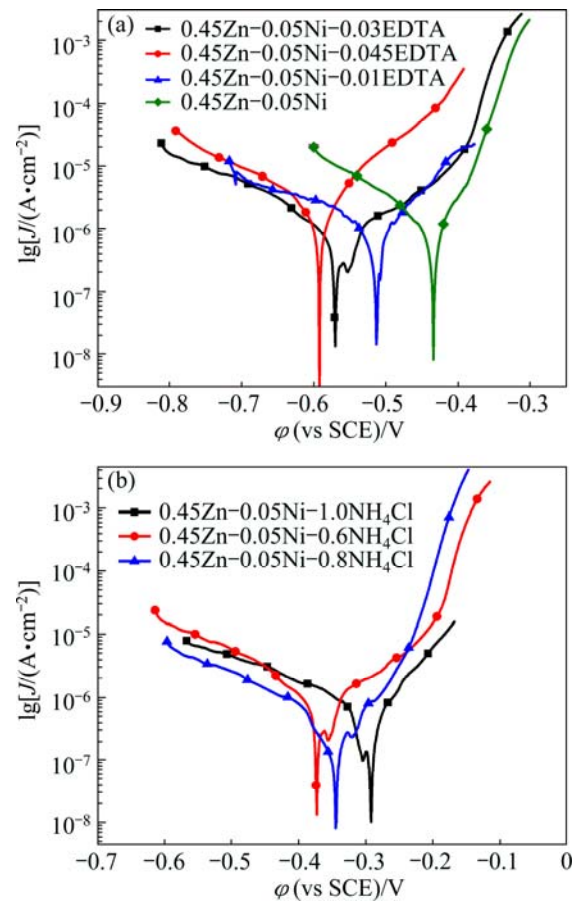


Fig. 9 Potentiodynamic polarization curves of Zn–Ni films electrodeposited at -0.9 V in EDTA-containing (a) and NH_4Cl -containing (b) electrolytes at 70°C

Table 2 Corrosion data of samples as shown in Table 1 derived from Figs. 9 and 10

Film	$\phi_{\text{corr}}/$ mV	$J_{\text{corr}}/$ ($\mu\text{A}\cdot\text{cm}^{-2}$)	$R_s/$ ($\Omega\cdot\text{cm}^2$)	$R_p/$ ($\Omega\cdot\text{cm}^2$)	CPE/ ($\mu\text{F}\cdot\text{cm}^{-2}$)
A	−435	1.026	3.146	8093	7.41
B	−512	0.674	4.753	18895	6.34
C	−567	0.761	3.246	40778	2.15
D	−593	0.986	5.74	71621	16.45
E	−376	0.516	5.851	65265	9.69
F	−332	0.356	3.83	96693	4.74
G	−268	0.225	3.776	21020	5.11

(Table 2) and the corrosion rate increases with increase in corrosion potentials. Table 2 shows that ϕ_{corr} is shifted negatively with an increase in EDTA concentration and this is due to an increase in Zn content of the electrodeposited Zn–Ni films. With an increase in EDTA concentration, the corrosion current density slightly increases in spite of large decrease in corrosion potential and this is mainly attributed to the refinement of grain at high EDTA concentrations. The Zn–Ni alloys

electrodeposited from NH_4Cl are characterized by the lowest corrosion current density and the highest corrosion potential, and their corrosion resistance is improved with an increase in NH_4Cl concentration. Lowering of corrosion current density with the increase in NH_4Cl concentration is likely to be due to both grain refinement and increase of corrosion potential. Thus, Zn–Ni alloys electrodeposited in the NH_4Cl -containing bath exhibited superior barrier corrosion resistance to those in EDTA-containing bath.

3.5.2 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is a useful technique for evaluating the corrosion resistance of the coatings and it gives information about the nature of the coatings. EIS studies have been performed in a 3.5% NaCl solution to evaluate the corrosion resistance behavior of the Zn–Ni films. The Nyquist impedance and Bode plots measured for Zn–Ni coatings electrodeposited in EDTA-containing and NH_4Cl -containing electrolytes are shown in Figs. 10 and 11, respectively. In the Nyquist plots the polarization resistance approximately corresponds to the size of the semicircle [39,40]. The corrosion resistances of the present Zn–Ni coatings can be explained by a simple

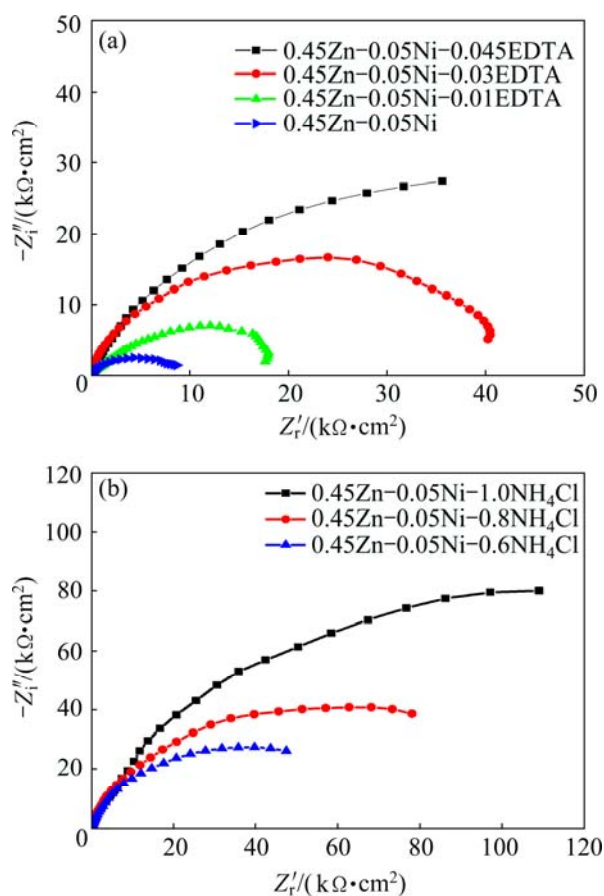


Fig. 10 Nyquist plots of Zn–Ni films electrodeposited at –0.9 V in EDTA-containing (a) and NH_4Cl -containing (b) electrolytes at 70 °C

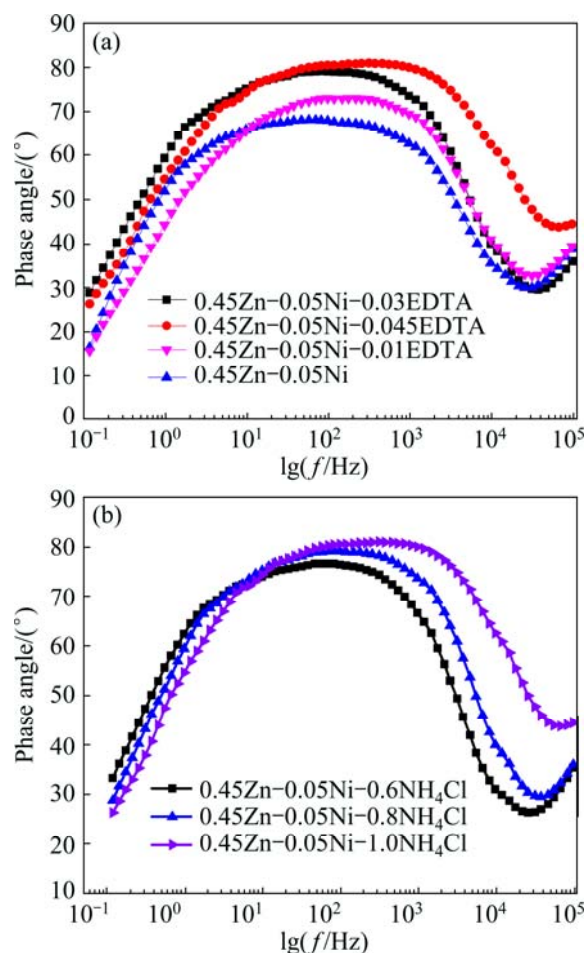


Fig. 11 Bode plots (phase angle vs $\lg f$) of Zn–Ni films electrodeposited at –0.9 V in EDTA-containing (a) and NH_4Cl -containing (b) electrolytes and 70 °C

Randles circuit [37]. The equivalent circuit is also presented in Fig. 12, where R_s is the solution resistance, R_p is the polarization resistance (also known as charge transfer resistance) and CPE is the constant phase element. Using this equivalent circuit model, all measured impedance values were fitted with the aid of Z-view software. Goodness of fitting was at a high level. Extracted fitted data from the equivalent circuit are shown in Table 2. R_s values are determined by the conductance of the 3.5% NaCl solution and the solution resistances of all coatings show no significant difference. According to Table 2, the corrosion resistance of the coatings increases with the increase in EDTA or NH_4Cl concentration, and corrosion resistance of the coatings in NH_4Cl electrolyte is superior to that in EDTA electrolyte. As seen in the Bode curves (Figs. 11(a) and (b)), the phase angle also increases with the increase in EDTA or NH_4Cl concentration. All these impedance results are consistent with the potentiodynamic polarization studies (Figs. 10(a) and (b)) and show that the Zn–Ni films obtained from higher concentration NH_4Cl electrolyte have the best corrosion resistance.

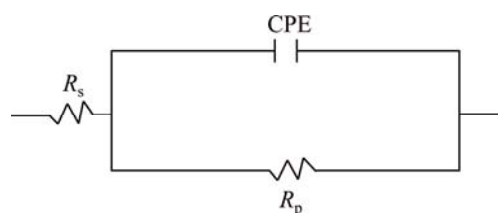


Fig. 12 Equivalent circuit used for fitting impedance spectra data

4 Conclusions

1) Cyclic voltammetry results showed that the addition of EDTA to the Zn–Ni electrolyte enhances Zn incorporation into the Zn–Ni film whilst the addition of NH_4Cl to the electrolyte produces an opposite effect of suppressing Zn incorporation into the film.

2) Increasing the EDTA concentration can increase the Zn content of Zn–Ni film, reduce the grain size of the deposits and decrease the current efficiency. The increase of NH_4Cl concentration will significantly refine the electrodeposited Zn–Ni film morphology, reduce the Zn content and increase the cathodic current efficiency.

3) The corrosion resistances showed that the barrier corrosion resistances of Zn–Ni films electrodeposited in NH_4Cl -containing electrolytes were superior to those electrodeposited in EDTA-containing electrolytes, which in turn were superior to that electrodeposited from an additive-free electrolyte.

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EDTA 和 NH_4Cl 添加剂对氯化胆碱基离子液体中电沉积 Zn–Ni 薄膜的影响

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摘要: 在低共熔溶剂中添加乙二胺四乙酸 (EDTA) 和氯化铵 2 种添加剂电沉积制备 Zn–Ni 合金镀层。研究添加剂对合金电沉积行为、成分、形貌和腐蚀性能的影响。循环伏安测试表明, EDTA 的加入可以促进 Zn 进入 Zn–Ni 镀层中, 而氯化铵起抑制 Zn 还原的作用。随着 EDTA 含量的增加, 镀层中的 Zn 含量增加, 但镀层的晶粒尺寸和电流效率降低。氯化铵浓度的增大能够有效地降低镀层的晶粒尺寸和 Zn 的含量, 提高阴极电流效率。腐蚀实验表明, 从含有氯化铵的镀液中得到的 Zn–Ni 镀层比从含有 EDTA 的镀液中得到的镀层具有更高的耐腐蚀性能。此外, 添加剂的加入提高了镀层的耐腐蚀性能。

关键词: 添加剂; 乙二胺四乙酸(EDTA); 氯化铵(NH_4Cl); 低共熔溶剂; 耐腐蚀性能

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