

An Electrodeposition Method for Preparing (Cu-Ni)/(Ni-Cu) Multilayers on Magnesium Alloy from Ionic Liquid

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ABSTRACT

A single bath of ionic liquid electrodeposition method has been developed for the preparation of (Cu-Ni)/(Ni-Cu) multilayers on AZ91D magnesium alloy. The technique has been used to make multilayers with a composition of (53.23at.%Cu-46.77at.%Ni)/(92.47at.%Ni-7.53at.%Cu) in a cycle of composition. The composition and thickness of the multilayers can be controlled by varying the electroplating current density and time. A uniform, smooth and dense nanocrystalline (Cu-Ni)/(Ni-Cu) multilayers exhibited an excellent corrosion protection due to the electrochemical synergistic effect between the (Cu-Ni)/(Ni-Cu) multilayers. The surface morphology, cross-section morphology and corrosion behaviors of the multilayers are discussed.

Keywords: ionic liquid, electrodeposition, multilayers, magnesium alloy.

1 INTRODUCTION

Magnesium (Mg) alloys with high strength/weight ratio, good recyclability and important mechanical properties become an excellent candidate material in automotive and lightweight engineering. The high chemical reactivity and poor corrosion resistance associated with Mg alloys especially in humid atmosphere, however, have been limiting their widespread applications. To extend their application, various surface treatments such as anodic or micro-arc oxidation, physical vapor deposition (PVD), electroless plating, electrodeposition, organic coatings, etc. have been used, which not only improve their corrosion resistance, but also improve their wear resistance and decorative appearance. Multilayered coatings exhibit better corrosion resistance than the single layer counterparts owing to the reduction in interconnecting pores and defects within the coating structure. In general, two techniques are normally adopted for electrodeposition of multilayers according to the published research reports: ① dual-bath; and ② single-bath electrodeposition. In terms of dual-bath electrodeposition technique, a substrate is moved between two plating baths containing expected arbitrary composition and a layer is deposited alternately from each bath to build up the multilayer. This operation incurs an undesirable mechanical complexity and production cost, compared to the single-bath method. The single-bath technique is an ideal method to

manufacture multilayer products given its simple operational procedures, build-up of nearly unlimited number of individual layers. In the present work, we report a single-bath electrodeposition method using a deep eutectic ionic liquid (IL) containing a mixture of choline chloride (ChCl) and urea in a 1:2 mole ratio, to deposit multilayered Ni-Cu alloy deposits on AZ91D Mg alloy for corrosion protection and the conductive requirement.

2 MATERIALS AND METHODS

The nominal chemical compositions of AZ91D Mg alloy (wt.%) substrate used are as follows: 8.5-9.5%Al; 0.45-0.90%Zn; 0.17-0.4%Mn; $\leq 0.05\%$ Si; $\leq 0.025\%$ Cu; $\leq 0.001\%$ Ni; $\leq 0.004\%$ Fe; balance Mg. The samples were machined into a size of 20 mm \times 10 mm \times 5 mm, mechanically polished using SiC papers with 2000 grit (2.0 \sim 1.5 μ m), cleaned with deionized water, degreased ultrasonically in acetone for 10 min and then dried in air. A 1:2 ChCl-urea IL containing the mixture of 0.6 M NiCl₂·6H₂O, 0.03 M CuCl₂·2H₂O and 0.2 M NH₂CH₂COOH was used as the electrodeposition bath and designated as "Ni-Cu bath".

Cyclic voltammetry (CV) tests were carried out by a PARSTAT 2273 with a three-electrode-cell system to obtain the information related to the redox potentials in the IL baths at 50°C. A pure copper wire with a diameter of 0.5 mm was used as a working electrode after cleaned in 40% HNO₃ solution, whereas an Ag wire was used as a reference electrode. The counter electrode was a pair of parallel Ni plate (50mm \times 25mm \times 3mm) which was also immersed in the IL bath directly. The voltage was initially swept from the open circuit potential (E_{OC}) of the Cu wire, namely the initial potential vs. open circuit potential is zero voltage, to the negative potential -1.5 V_{Ag} (Ag wire as reference electrode), then the scan is reversed to a positive potential of +0.5 V_{Ag}, and finally the voltage is swept back to E_{OC} at a voltage scan rate of 10 mV/s.

The pretreatment processes of AZ91D Mg alloy substrate were as follows: ① alkaline cleaning \rightarrow ② acid pickling \rightarrow ③ activation \rightarrow ④ Zn immersion \rightarrow ⑤ Cu preplating. The samples were thoroughly rinsed with distilled water after each step. Cu preplating was carried out in an aqueous pyrophosphate based solution by a two-step galvanostatic method including a strike by 50 mA/cm² for 1 min and immediately followed by 15 mA/cm² for 30 min. The

detailed processes flow, solution compositions and operating conditions of the pretreatments can be referred to our previous work [1]. A multilayers with a duplicate composition of (53.23at.%Cu-46.77at.%Ni)/(92.47at.%Ni-7.53at.%Cu), namely a cycle of composition, and including three such cycles in the multilayers was produced. The current waveform employed for producing such a multilayers coating are illustrated in Fig.1. The current waveform represented in (a) was used to produce a (53.23at.%Cu-46.77at.%Ni) alloy sublayer, whereas that presented in (b) was used to produce a (92.47at.%Ni-7.53at.%Cu) alloy sublayer.

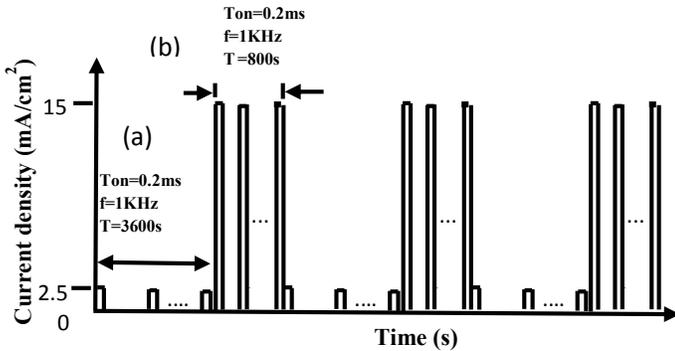


Fig.1: The current waveform used for electrodeposition.

3 RESULTS AND DISCUSSION

3.1. Cyclic Voltammetry(CV)

The CV curve obtained in the “Ni-Cu bath” is illustrated in Fig.2. It is shown that the reduction current rapidly increases when the voltage forward sweep to near -0.75V. This indicates that Ni ions begin to be reduced from the “Ni-Cu bath”. It can be found from Fig.2 that a single Ni-Cu alloy deposit with different content of Cu can be obtained from the “Ni-Cu bath” by varying the electrodeposition potential or current density. Therefore, the composition-modulated Ni-Cu multilayers with different thickness of sublayer can also

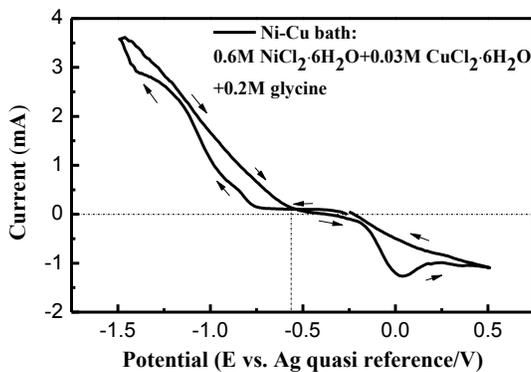


Fig.2: Cyclic voltammograms of “Ni-Cu bath” obtained on the Cu wire electrode at 50°C.

be achieved by controlling the current density and electrodeposition time.

3.2 Multilayers on AZ91D Magnesium Alloy

One sublayer with a composition of (53.23at.%Cu-46.77at.%Ni), hereinafter we designated it as (Ni-Cu)₁ sublayer, was deposited at average current density 0.5 A/cm²; the other sublayer with a composition of (92.47at.%Ni-7.53at.%Cu), hereinafter we designated it as (Ni-Cu)₂ sublayer, was deposited at average current density 3 mA/cm² as shown in Fig.1. The deposition time was 3600 s for (Ni-Cu)₁ sublayers and 800 s for (Ni-Cu)₂ sublayers respectively. The benefits by using pulse current to deposit dense and uniform multilayers without cracks have been reported and discussed in the early research works [2-3]. The image and EDS line scanning profile of the (Ni-Cu)₁ / (Ni-Cu)₂ multilayers are shown respectively in Fig.3a and 3b.

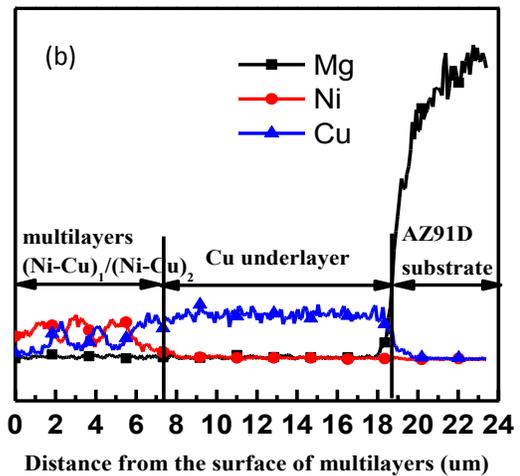
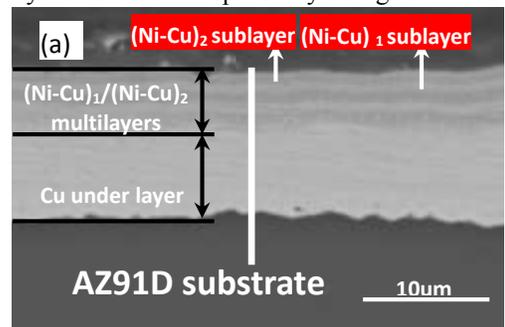


Fig.3: (a) Cross-section morphology; and (b) EDS line scanning profile of (Ni-Cu)₁ / (Ni-Cu)₂ multilayers electrodeposited from “Ni-Cu bath”.

Fig.3a shows the multilayer is uniformly bonded to Cu under-layer without any cracks. Moreover, the Cu under-layer is also closely bonded to the AZ91D Mg alloy substrate between Cu under-layer and AZ91D substrate. It is indicated that there is an excellent adhesion between the multilayers, Cu under-layer and the AZ91D Mg alloy substrate. Fig.3b shows the average thicknesses of the (Ni-Cu)₁ / (Ni-Cu)₂ multilayers and the Cu under-layer are about 8 µm and 10 µm respectively. In addition, the average thickness of individual

(Ni-Cu)₁ and (Ni-Cu)₂ sublayer is about 1 μ m and 1.5 μ m respectively. The periodic fluctuation of Ni and Cu content shown in Fig.3b is completely corresponded to the periodic layered structure in Fig.3a.

3.3 Corrosion Behaviors of (Ni-Cu)₁ / (Ni-Cu)₂ Multilayers

The potentiodynamic polarization (PD) curves of bare AZ91D substrate, Cu under-layer and (Ni-Cu)₁ / (Ni-Cu)₂ multilayers in 3.5wt.% NaCl solution at room temperature without stirring are shown in Fig.4. It is shown that the bare AZ91D substrate has the least noble E_{corr} of -1.502 V_{SCE} and the highest I_{corr} of 4.039×10^{-6} A/cm²; the E_{corr} of Cu under-layer shifts nobly to -0.203 V_{SCE}, and its I_{corr} decreases to 1.735×10^{-6} A/cm². This implies that the Cu under-layer can significantly improve the corrosion resistance of AZ91D substrate. In contrast, the (Ni-Cu)₁ / (Ni-Cu)₂ multilayers demonstrate a little more negative E_{corr} of -0.278 V_{SCE} than the Cu under-layer due to the existence of outermost (Ni-Cu)₂ sublayer. However, its corrosion current I_{corr} of 5.47×10^{-7} A/cm² is lower than the I_{corr} of 1.735×10^{-6} A/cm² of Cu under-layer and was nearly one orders of magnitude lower than that of the bare AZ91D substrate. These results show that the multilayers can significantly enhance the corrosion resistance of AZ91D substrate.

The (Ni-Cu)₁ / (Ni-Cu)₂ multilayers exists a typical passivation characteristic in the potential range from -0.2 V_{SCE} to -0.1 V_{SCE} in the anodic branch of its PD curve as shown in Fig.4. It is indicated that a passive film was formed on the surface of (Ni-Cu)₁ / (Ni-Cu)₂ multilayers in the

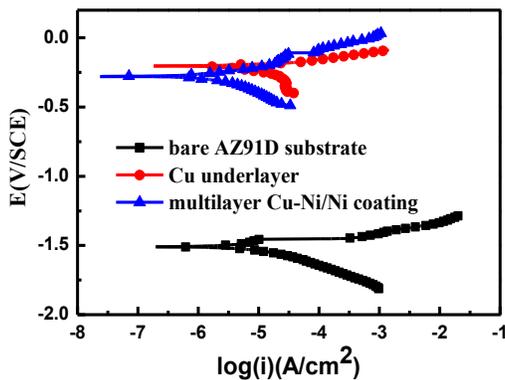


Fig.4: PD curves of bare AZ91D substrate, Cu underlayer and (Ni-Cu)₁ / (Ni-Cu)₂ multilayers in 3.5wt.% NaCl solution at room temperature without stirring.

corrosive medium. When the corrosive medium penetrates through the outmost (Ni-Cu)₂ sublayer and reaches the next (Ni-Cu)₁ sublayer in the multilayers, the (Ni-Cu)₂ sublayer with more negative corrosion potential would be corroded as a sacrificial anode and the (Ni-Cu)₁ sublayer with more positive corrosion potential would be protected as a cathode. Furthermore, if the corrosive medium penetrates through the (Ni-Cu)₁ / (Ni-Cu)₂ multilayers and reaches the Cu under-

layer, the multilayers will act as a sacrificial anode and the Cu under-layer will be protected as a cathode because the E_{corr} of Cu under-layer is more positive than that of the multilayers as shown in Fig.4. The variations of E_{OCP} of (Ni-Cu)₁/(Ni-Cu)₂ multilayers deposited on AZ91D Mg alloy with different immersion time in 3.5wt.% NaCl solution at room temperature are shown in Fig.5. It is shown that the curve of E_{OCP} can be divided into four stages. During the first stage (1-12 h), the E_{OCP} value rapidly increases from -0.6 to -0.12 VSCE, indicating that a passive film begins to form on the outmost surface of the multilayers. During the second stage (12-24 h), the E_{OCP} value decreases from -0.12 to -0.195 V_{SCE} and tends to a steady value, indicating that the passive film has already covered the whole test area. During the third stage (24 – 204 h), the E_{OCP} value fluctuates over a range from -0.19 to -0.24 VSCE. This stage can be ascribed to that the passive film may be broken down occasionally in some locations and the synergistic effect of (Ni-Cu)₁ / (Ni-Cu)₂ multilayers come into play for protecting the substrate. During the final stage (after 204 h), the E_{OCP} value drops dramatically to -1.4 V_{SCE}, indicating that the protection of (Ni-Cu)₁/(Ni-Cu)₂ multilayers and Cu under-layer for the AZ91D substrate is completely destroyed.

Fig.6 shows the results of electrochemical impedance spectroscopy (EIS) measurement on (Ni-Cu)₁ / (Ni-Cu)₂ multilayers corresponding to the E_{OCP} test. It can be clearly found from the Nyquist plots in Fig.6a (partial enlarged drawing indicated by the circle in Fig.6b) and Fig.6b that the polarization is a typical combination of kinetic and diffusion processes. The characteristics of Warburg impedance are obviously seen when the immersion time is 1 h and 3 h respectively. The diffusion process become the predominant

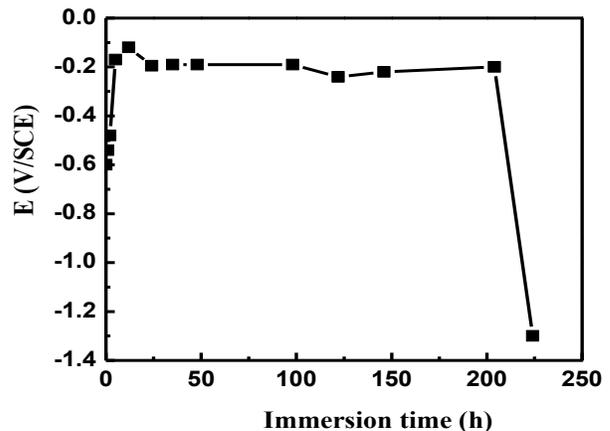


Fig.5. Variations of E_{OCP} of the multilayers of Ni-Cu alloy deposits on AZ91D magnesium alloy with immersion time in 3.5wt.% NaCl solution at room temperature.

process after the immersion time is greater than or equal to 12 hours and till about 204 hours. This means that the impedance of charge transfer are much smaller than the solution resistance and Warburg impedance. Fig.6c and Fig.6d show the Bode plots in which the variation of

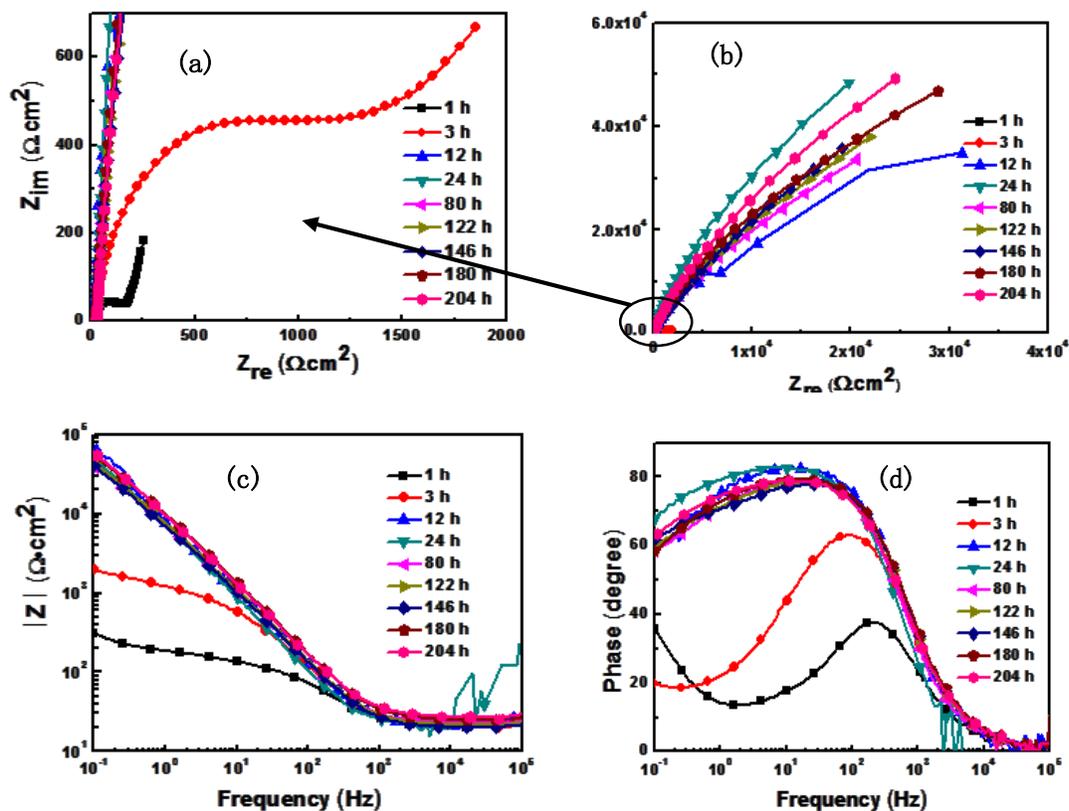


Fig.6: The results of EIS measurement of $(\text{Ni-Cu})_1 / (\text{Ni-Cu})_2$ multilayers deposited on AZ91D magnesium alloy as a function of immersion time in 3.5wt.% NaCl solution at room temperature. (a) and (b) are Nyquist plots; (c) and (d) are Bode plots.

impedance is very small and the synergistic effect of $(\text{Ni-Cu})_1 / (\text{Ni-Cu})_2$ multilayers come into play for protecting the substrate during this period of time corresponding to the third stage in the OCP test. However, the $(\text{Ni-Cu})_1 / (\text{Ni-Cu})_2$ multilayers and Cu under-layer were eaten through after the immersion time is greater than 204 h. These results indicate that the $(\text{Ni-Cu})_1 / (\text{Ni-Cu})_2$ multilayers can protect the AZ91D Mg alloy substrate from corrosion lasting for at least 200 h in 3.5wt.% NaCl solution at room temperature due to its synergistic effect of protection between sublayers.

4 SUMMARY

Cyclic voltammetry studies reveal that the Cu content in the Ni-Cu alloy deposits can be adjusted according to the requirements. The study on the morphologies of surface and cross-section of the alloy deposits and the corrosion behaviors of electrodeposited multilayers demonstrate that the periodic fluctuation of Ni and Cu content in the EDS line scanning profile corresponds to the designed periodic layer structure. It is feasible to change the thickness of the individual alloy sublayer over a range from nanometer to micrometer by modifying the deposition time of each

sublayer. A uniform, smooth and dense nanocrystalline $(\text{Ni-Cu})_1 / (\text{Ni-Cu})_2$ multilayers protects AZ91D Mg alloy substrate from corrosion lasting for at least 200 h in 3.5wt.% NaCl solution at room temperature due to the electrochemical synergistic effect between the $(\text{Ni-Cu})_1 / (\text{Ni-Cu})_2$ sublayers with various electrode potential.

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