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ORIGINAL PAPER

Al electroplating on the AZ121 Mg alloy in an EMIC–$AlCl_3$ ionic liquid containing ethylene glycol

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Abstract To improve the corrosion resistance of Mg alloys, an Al layer was electrodeposited on the Mg surface from an ionic liquid of 1-ethyl-3-methylimidazolium chloride (EMIC) and aluminum chloride ($AlCl_3$) at 283 K. A smooth surfaced Al electrodeposit can be electroplated in the $AlCl_3$–EMIC ionic liquid by pulse electrolysis at 6.7 Hz and a duty ratio of 0.67. A denser and flatter Al layer was successfully electroplated on AZ121 substrate at the lower temperature of 283 K in an $AlCl_3$–EMIC ionic liquid with 0.1 M ethylene glycol added.

Keywords Al electroplating · EMIC–$AlCl_3$ ionic liquid · Mg alloy · Ethylene glycol

Introduction

Recently, magnesium alloys have attracted much attention and are considered to have potential as future materials due to the attractive mechanical properties and lightness in the fields of automobiles, aerospace, mobile phones, and others [1]. These alloys have poor corrosion resistance which restricts the usage, however. For corrosion protection, surface treatments have been proposed including chemical conversion, anodization, organic coating, metal coating, and others [2, 3]. Reports investigating conversion coating have concluded that these coatings are not sufficiently protective against corrosion at present [4, 5]. Anodization is a commonly applied process which improves the corrosion resistance of Mg and its alloys; however, the oxide layer produced is generally nonconductive and uneven [6, 7], and therefore, anodization treatments need further surface finishing processes on the deposited oxide layer. A conductive coating has great advantages and is of great interest in precision instrument manufacture because of its low resistivity.

Studies have reported on electroplating of aluminum or Al alloy layers on Mg and its alloys [8, 9], and on zincate-treated Mg alloys [10]. Electroplating of Al on an Mg substrate offers advantages such as: (1) Al is also a light-weight metal like Mg. (2) The standard electrode potential of Al is close to that of Mg and it may be hypothesized that Al is relatively easily electrodeposited on Mg or Mg alloys, compared with other metals such as Ni and Cu. (3) The Al coated on components could be recycled as Al is a primary alloying element for the widely used AZ series of Mg alloys.

This paper proposes a direct method of electroplating Al onto Mg alloys in $AlCl_3$–1-ethyl-3-methylimidazolium chloride (EMIC) ionic liquids. Electroplating is a straightforward commonly used process and plating may be simply carried out. A previous study reported electroplating of Al on Mg and its alloys from $AlCl_3$–NaCl–KCl molten salts; however, the electroplated Al layer was very uneven and exhibited low adherence [11]. It was suggested that the relatively high temperature (423 K) of the molten salts brought about an exchange between Al ions and metallic Mg. To inhibit the exchange reaction, a lower temperature for the electroplating was studied, and a lower optimum temperature of 283 K was determined in our previous study [11]. This paper investigates the effect of frequency in pulse electrolysis and the effect of ethylene glycol addition on the formation of a smooth Al electroplating on Mg alloys.

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Experimental

Aluminum chloride ($AlCl_3$, Soekawa Chemical, 99.99 %) and 1-ethyl-3-methylimidazolium chloride (EMIC, Merck, 98 %) were used as received. All chemicals were handled under an argon atmosphere in a glove box. A Pyrex glass cell was used for the electrochemical measurements and electrodeposition. A mixture of 67 mol% $AlCl_3$–33 mol% EMIC, volume 80 ml, was prepared in the cell. After the preparation, aluminum chips were immersed in the ionic liquid for 2 days to remove impurities.

Electrical conductivity was calculated from the electrical resistance at a high-frequency limit in impedance measurements. Mixtures of 33 mol% EMIC–$AlCl_3$ ionic liquid with or without ethylene glycol (EG) additive were kept at 283 K in Pyrex glass cell. Glassy carbon (GC, Tokai carbon, GC-20) plates of 1 cm^2 were used as the working and counter electrodes. The electrodes were set in the cell with an inter-electrode distance of 15 mm, Al wire (Niraco, 99.99 %, φ=0.5 mm) was used as a reference electrode. Impedance measurements were carried out using AC voltage with an amplitude of 15 mV and at frequencies from 1 Hz to 20 kHz.

In the voltammetry, the GC electrode and a pure Al plate (Niraco, 99.99 %) electrode were used as the working and counter electrodes, respectively. The voltammogram was measured at a potential range from 0.8 to -0.6 V vs. Al/Al (III) reference electrode with a scan rate of 1.0×10^{-2} V s^{-1} in the ionic liquid.

In the electroplating experiments, the magnesium alloy specimen was AZ121 composed of 12.4 Al, 0.84 Zn, 0.18 Mn, 0.01 Si, 0.003 Cu, 0.001 Ni, and 0.001 Fe, all in wt.%, and used as a working electrode with a surface area of 3 cm^2. A pure aluminum plate (Niraco, 99.99 %) was used as a counter electrode and a pure aluminum wire (Niraco, 99.99 %, φ=0.5 mm) inserted in a small Pyrex glass tube filled with the $AlCl_3$–EMIC ionic liquid was the reference electrode. All electrochemical measurements were carried out with the potentiostat (Iviumstat, Ivium Technologies) in a glove box under a pure argon gas atmosphere. Electroplating of the Al by current pulses were carried out on the AZ121 alloy electrode at a constant current density of 1.7 mA cm^{-2} in the ionic liquid at 283 K. The pulse frequencies were from 0.67 to 111 Hz with a duty ratio of 0.67. Here, the duty ratio (t_{on}/t_{total}) is defined as the ratio of the duration of on-time for the cathodic current (t_{on}) and the sum of the durations of the on- and off-times (t_{total}). All the electroplating processes were performed with a constant charge density of 20 Ccm^{-2}. The EG additive concentration was from 0.1 to 0.5 mol l^{-1} in the ionic liquid. The surface morphologies and cross-sections of electroplated films were observed by scanning electron microscopy (SEM, JEOL JSM-6510MA).

Results and discussion

Voltammogram measurements

The voltammograms in the ionic liquid are shown in Fig. 1; here, the potential is scanned from 0.8 to -0.6 V at a sweep rate of 1×10^{-2} V s^{-1} on the glassy carbon electrode in the 33 mol% EMIC–$AlCl_3$ at 283 K, and the measurements at 278 and 298 K are also shown for comparison. All voltammograms indicate an increase in cathodic current at potentials more negative than -0.05 V. In the reverse scan, anodic currents were observed from -0.1 V. The cathodic and anodic currents correspond to Al deposition and dissolution reactions, and as the amounts of electricity of Al deposition and dissolution are very similar at every temperature, it may be concluded that the electrodeposition and dissolution for Al in the EMIC–$AlCl_3$ ionic liquid are reversible.

From the voltammograms, the cathodic currents for the Al electrodeposition increase with a rise in temperature, and the anodic currents also increase with temperature. The decrease in current density with lower temperature is possibly due to the decrease in electrical conductivity of ionic liquid at the lower temperature. The starting potential for the Al electrodeposition shifts to more negative potentials with decreases in temperature, showing that large overpotentials are needed for Al electrodeposition at lower temperatures.

Current pulse electroplating

To investigate optimum pulse conditions, current pulse electroplating of Al was carried out by an applied cathodic current density of 1.7 mA cm^{-2} with pulse frequencies from 0.67 to 111 Hz and a duty ratio of 0.67 on substrates of

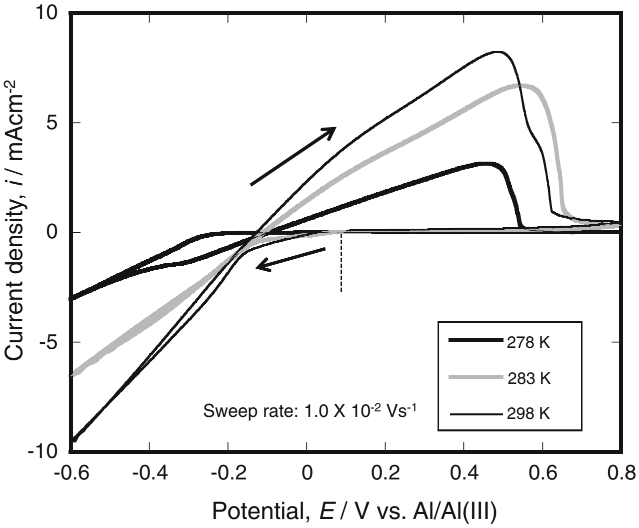

Fig. 1 Voltammograms on the GC electrode in 33 mol% EMIC–$AlCl_3$ at 278, 283, and 298 K

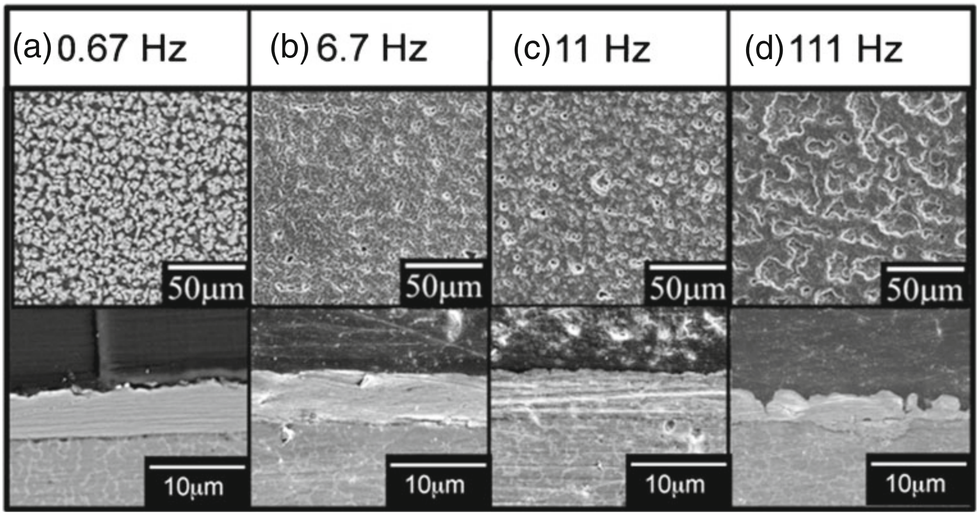

Fig. 2 Surface and cross-sectional SEM images of Al electroplating on a AZ121 alloy formed from 33 mol% EMIC–$AlCl_3$ ionic liquid by pulse frequency of **a** 0.67 Hz, **b** 6.7 Hz, **c** 11 Hz, and **d** 111 Hz at 283 K

AZ121 alloy. Figure 2 shows SEM images of the surfaces and cross-sections of the electrodeposits formed at (a) 0.67 Hz, (b) 6.7 Hz, (c) 11 Hz, and (d) 111 Hz at 283 K.

The Al deposits on the AZ121 alloy are all silver grey. From the surface images, the Al deposits on the AZ121 alloy were relatively smooth at the frequency of 6.7 Hz, there were needle-like Al deposits at 0.67 Hz and nodule-like Al deposits at 11 and 111 Hz. The cross-sectional images show that the Al layers were nearly flat at 0.67, 6.7, and 11 Hz, the 111 Hz cross-section shows an uneven Al layer with asperity of about 5 μm.

Generally, it is difficult to form Al layers with flat surfaces by constant current electrolysis due to Al dendrite growth. Therefore, to protect against dendrite growth, pulse electrolysis is commonly used for such plating. When the AZ121 substrate is immersed in the EMIC–$AlCl_3$ ionic liquid, an exchange reaction between Al(III) ions and Mg atoms from the substrate occurs immediately. Because of this exchange reaction, and when the duration of the current off (t_{off}) pulse in the electrolysis is relatively long in the initial stage of the electroplating, no dense electroplated layer is obtained. However, when t_{off} is short in the pulse electrolysis, the exchange reaction is inhibited in the initial stage of the electroplating, and uniform growth of the plating layer becomes difficult after the initial stage.

From the cross-sectional images of the specimens, the frequencies of 0.67, 6.7, and 11 Hz with duty ratio 0.67 are satisfactory as growth conditions for the plated layer. From

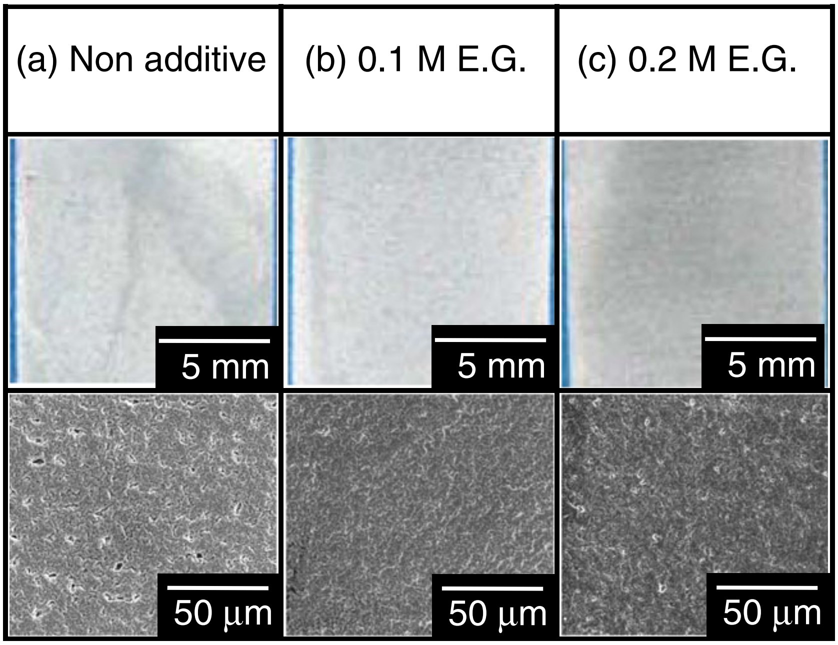

Fig. 3 SEM images of Al electroplating on a AZ121 alloy obtained at 283 K from **a** 33 mol% EMIC–$AlCl_3$ ionic liquid, **b** the melt containing 0.1 M ethylene glycol, and **c** the ionic liquid containing 0.2 M ethylene glycol

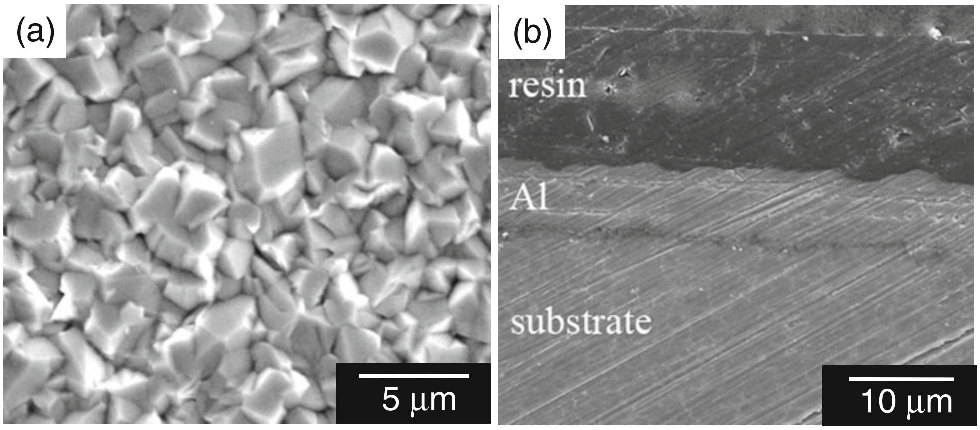

Fig. 4 SEM image of Al electroplating on AZ121 obtained from 33 mol% EMIC–$AlCl_3$ containing 0.1 M EG at 283 K. **a** Surface image and **b** cross-sectional image

the surface images of the Al-plated surface, a more uniform surface is formed by 6.7 Hz pulses, and therefore the frequency of 6.7 Hz was determined as the optimum pulse frequency here.

EG addition to EMIC–$AlCl_3$

To investigate the effect of additives to the electrolyte for electroplating of Al at the optimum pulse condition, EMIC–$AlCl_3$ ionic liquids containing 0.1 or 0.2 mol dm^{-3}(M) of EG were investigated at the electrolyte temperature of 283 K. Surface photos and SEM images of Al electroplated in EMIC–$AlCl_3$ ionic liquid and in EMIC–$AlCl_3$ containing 0.1 and 0.2 M EG are shown in Fig. 3. The surface obtained from the EMIC–$AlCl_3$ ionic liquid alone shows unevenness in the surface photo with cavities of about 5 μm in the SEM image. By adding 0.1 M EG, there is a very flat surface of the Al plating in the photo and no cavities are observed on the surface in the SEM image. By adding 0.2 M EG, a flatter Al-plated surface than without additive in the EMIC–$AlCl_3$ ionic liquid in the surface photo and cavities of about 1 μm are observed on the surface in the SEM image. On the basis of these results, it was determined that the EMIC–$AlCl_3$ ionic liquid containing 0.1 M EG is the better concentration for achieving surface flatness in Al electroplating.

Enlarged surface and cross-sectional SEM images of electroplated Al in the EMIC–$AlCl_3$ ionic liquid containing 0.1 M EG are shown in Fig. 4. The surface SEM image shows Al electrodeposits of about 2 μm grain size which are packed closely. The cross-sectional image shows a dense Al layer with no void space with the AZ121 substrate and the thickness of the Al layer is about 12 μm.

The effect of the EG additive on the EMIC–$AlCl_3$ ionic liquid is discussed as follows. Generally, polyethylene glycol (PEG) is used as a smoothing agent in electroplating in aqueous solutions. The PEG in the solution is known to adsorb oxygen containing lone-pair electrons to active sites of the top of the electrodeposit, and this results in the formation of a flat surface without dendrite growth. However, the EG in this study has no oxygen containing lone-pair electrons, and its adsorption on the electrodeposited surface would be very low. Therefore, the improvement in surface flatness is probably not due to adsorption of EG molecule on the Al electrodeposit. To investigate the conductivity changes, impedance measurements were carried out for several concentrations of EG in the EMIC–$AlCl_3$ ionic liquid. The electrical conductivities were calculated by impedance values from a high-frequency-limit electrode with a cell constant which was measured by 1 mol kg^{-1} potassium chloride solution at 283 K. The electrical conductivity is shown as a function of the concentration of EG in Fig. 5. Here, there is an almost linear relation between the electric conductivity and the EG concentration with the electric conductivity exhibiting the highest value for the EMIC–$AlCl_3$ ionic liquid without additive. Therefore, EG may be surmised to decrease the electric conductivity, and the decrease in the rate of electroplating may contribute to inhibit oriented growth of the Al electrodeposit.

Taken together, the results suggest that an optimum formation technique for electroplating very flat layers of Al on AZ121 alloy may be a combination of the low temperature

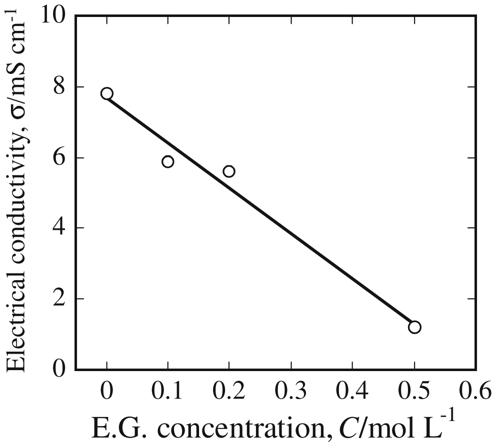

Fig. 5 Relationship between electric conductivity and ethylene glycol concentration at 283 K

of 283 K, a pulse frequency of 6.7 Hz, a duty ratio of 0.67, and a current density of 1.7 mA cm^{-2} in an EMIC–$AlCl_3$ ionic liquid containing 0.1 M EG.

Conclusions

The deposition of a more smooth electroplated layer of Al on AZ121 alloy was investigated in $AlCl_3$–EMIC ionic liquid at 283 K.

First, pulse current electrolysis, with a pulse frequency of 6.7 Hz was determined as optimum for the electroplating condition at 1.7 mA cm^{-2} and a duty ratio of 0.67 at 283 K.

Second, preparation of a mirror-like surface and a dense Al layer was achieved by addition of 0.1 M EG to the $AlCl_3$–EMIC ionic liquid with the electrolysis conditions described above.

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