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Author(s)	Ueda, Mikito; Tabei, Yasushi; Ohtsuka, Toshiaki
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Surface finishing of Mg alloys by Al electroplating in AlCl₃-EMIC ionic liquid

Mikito Ueda, Yasushi Tabei, and Toshiaki Ohtsuka

Graduate school of engineering Hokkaido University
Kita-13, Nishi-8, Kita-ku, Sapporo, Hokkaido 060-8628 Japan

In order to improve the corrosion resistance of Mg and its alloys, Al layer was electrodeposited on their surface from aluminum chloride-1-ethyl-3-methylimidazolium chloride ionic liquid (AlCl₃-EMIC). Mirror-like Al surface can be electroplated in AlCl₃-EMIC ionic liquid by pulse electrolysis at 323 K, though Al layer was not dense and homogeneous. A dense and flat Al layer was successfully electroplated on Mg alloys in the AlCl₃-EMIC ionic liquid at lower temperature of 283 K.

Introduction

Magnesium alloys recently have a great attention and are expected to be future materials due to good mechanical properties and applications in various fields of auto-mobile, aerospace, and mobile phone etc. (1). These alloys, however, have poor corrosion resistance, which restricts the usage of alloys. For the corrosion protection, several surface treatments have been applied such as chemical conversion, anodization, organic coating, metal coating, etc. (2,3). Reports about conversion coating concluded that these coatings are not protective enough yet for the corrosion (4,5). Anodization treatment is a popular process which improves the corrosion resistance of Mg and its alloys. Nevertheless, this oxide layer produced is generally nonconductive and rather rough, and therefore the treatment needs another surface finish process on the oxide layer (6,7). A conductive coating has a great advantage of great interest to accurate instrument field because of its low resistivity.

There are several studies on electroplating aluminum (Al) or Al alloys layered on Mg and its alloys (8,9). Electroplating of Al on Mg substrate has some merits as the following: (a) Al is a lightweight metal, the same as Mg. (b) An electrochemical potential of Al is close to that of Mg. It is supposed that Al is relatively easy to be electrodeposited on Mg or Mg alloys compared with other metals, such as Ni and Cu. (c) Al coating on the plates could be recycled well because Al is a primary alloy element for the AZ series Mg alloys widely used.

We aim in this paper, establishment of direct electroplating of Al onto Mg alloys in ionic liquid. The electroplating is one of the simple processes and functional plating may be easily produced. In our previous study, electroplating of Al on Mg and its alloys from AlCl₃-NaCl-KCl molten salt was carried out. The Al layer electroplated, however, was very rough and exhibited low adherence. It has been supposed that relatively high temperature (423 K) of the molten salt brought about exchange between Al ion and metallic Mg. In this paper, we report the electroplating of Al on Mg and its alloy from

AlCl₃-EMIC ionic liquid at the lower temperature of 323 K and 283 K. Surface morphology of the Al deposits and interfacial structure between the Al layer and the substrates are also reported.

Experimental

Aluminum chloride (AlCl₃, Soekawa chemical, 99.99% pure) and 1-ethyl-3-methylimidazoliumchloride (EMIC, Kanto-Kagaku, 99.5% pure) were used as received. All chemicals were handled under argon atmosphere in a glove box. A Pyrex glass cell was used for the electrochemical measurements and electrodeposition. A mixture of 67 mol% AlCl₃-33 mol% EMIC of 80 ml volume was prepared in the cell. After the preparation, aluminum chips were immersed in the ionic liquid for 2 days to remove impurities. Pure Mg and magnesium alloy plates of AZ91 and AZ121 with surface area of 3 cm² were used as the working electrode. The composition of magnesium alloys is shown in Table.1. A pure aluminum plate (Niraco, 99.99%) was used as a counter electrode and a pure aluminum wire (Niraco, 99.98%, φ=0.5 mm) inserted in a small Pyrex glass tube filled with the AlCl₃-EMIC ionic liquid was used as a reference electrode. Electrochemical measurements were carried out with the potentiostat, HAG-3010, Hokuto-Denko, in the glove box.

Electroplating of Al were carried out on the pure Mg or Mg alloys electrode at constant current density of 1.7 mAcm⁻² in the ionic liquid at 323 K and 283 K. Electroplating by current pulse was also carried out with agitation of 500 rpm by a magnetic stirrer. All the Electroplating process was done with a constant charge density of 7 Ccm⁻². The composition, surface morphologies and cross-section of electroplating film were observed by scanning electron microscopy (SEM. JEOL JXA-8900M).

Table I Composition of AZ91 and AZ121 alloys.

	Al	Zn	Mn	Si	Cu	Ni	Fe	Mg
AZ91	9.1	0.72	0.24	0.01	0.003	0.001	0.002	Bal.
AZ121	12.4	0.84	0.18	0.01	0.003	0.001	0.001	Bal.

Results

Constant current electrolysis for electroplating of Al at 323 K

Electroplating of Al was carried out by applied cathodic current density of 1.7 mAcm⁻² on the substrates of pure Mg and the Mg alloys. Al deposit was black-gray on pure Mg substrate and silver-gray on AZ91 and AZ121 alloy at 323 K. The appearance of Al deposit on pure Mg was rough with low adhesion. Al deposit on AZ91 and AZ121 alloys were relatively smooth, however, needle-like deposits were observed on the edge part of the alloy specimens. Figure 1 shows the SEM images of the electrodeposits formed on (a) pure Mg, (b) AZ91 and (c) AZ121 substrate with current density of 3.3 mAcm⁻² at 323 K. Many cracks were observed on the Al deposit layer formed on pure Mg and dendrite shapes on Al deposits layer on AZ91 and AZ121.

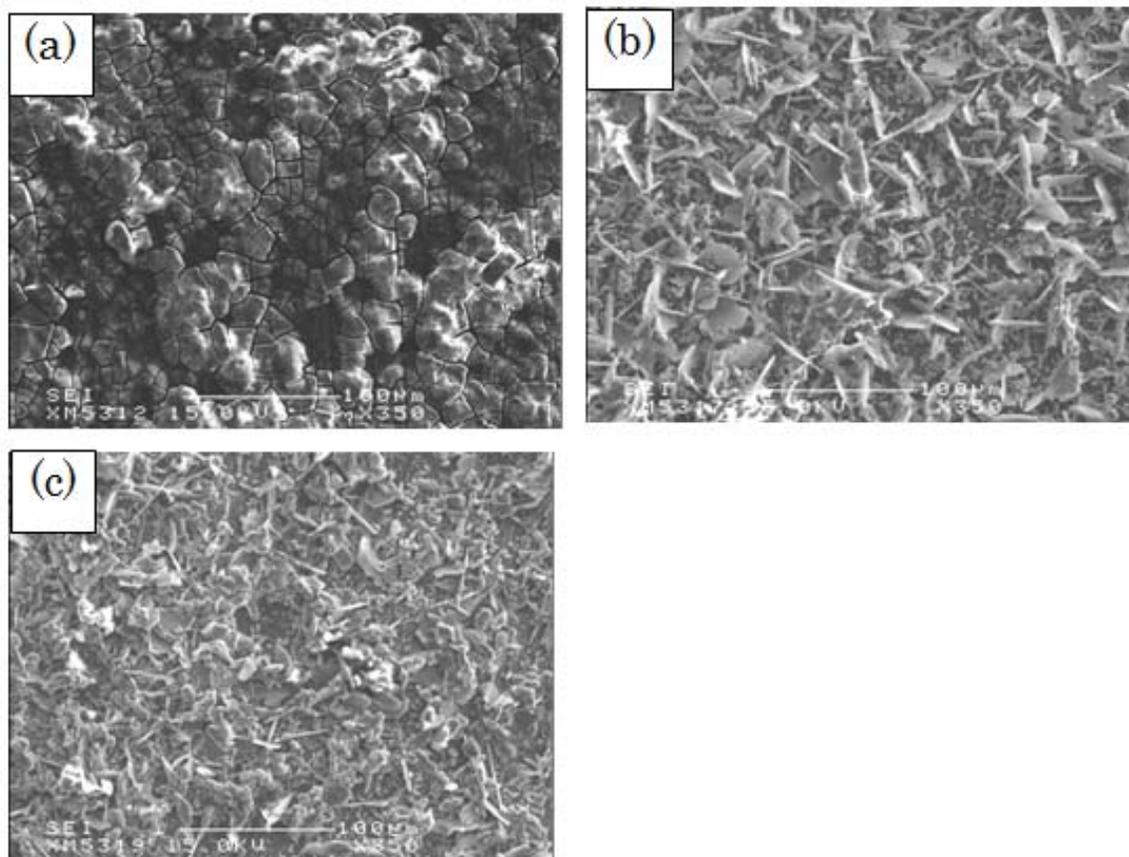


Figure 1. SEM image of surface of Al electroplating on (a) pure Mg, (b) AZ91, and (c) AZ121 at 323K.

Current pulse electrolysis at 323 K

The current pulse electrolysis is expected to inhibit dendrite growth of Al electroplated. For the pulse, the parameters were controlled, as illustrated in Figure 2; the duration of on-time cathodic current (t_1), the duration of off-time (t_2), frequency ($1/T$).

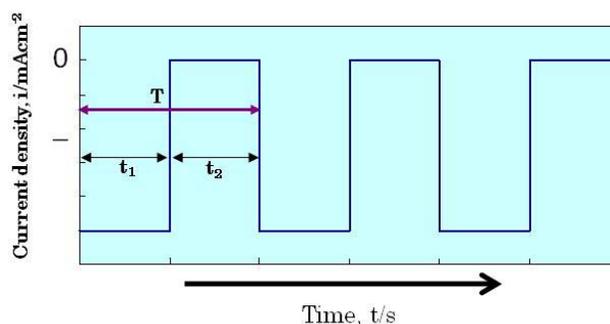


Figure 2. Illustration of parameters for current pulse electrolysis.

The exact condition of the current pulse electrolysis is the following; an applied current density of 1.7 mAcm^{-2} during the on-time, and a frequency of 0.67 Hz, a duty ratio (t_1/T) of 0.67. The Al layer deposited by current pulse electrolysis reveals silver-gray in color on all the substrates, especially the Al layer on AZ121, which has a mirror-like appearance. The deposit surface is relatively rough on pure Mg, while very flat surface is observed on AZ91 and AZ121. However, Al layer on AZ91 and AZ121 have some nodules of about 1 μm . Figure 3 shows the SEM images of the electrodeposits formed on the three substrates by the pulse electrolysis at 323 K. The Al layers deposited on all the substrates were dense and covered on the whole surface. As shown in Fig. 3(a), electrodeposit with particle size of 1-5 μm was observed along with polishing scars and small cracks. On the other hand, very fine and smooth surface of Al layers were found on AZ91 and AZ121 in Fig. 3(b) and (c). However, very small cracking occurred at the part of swelling.

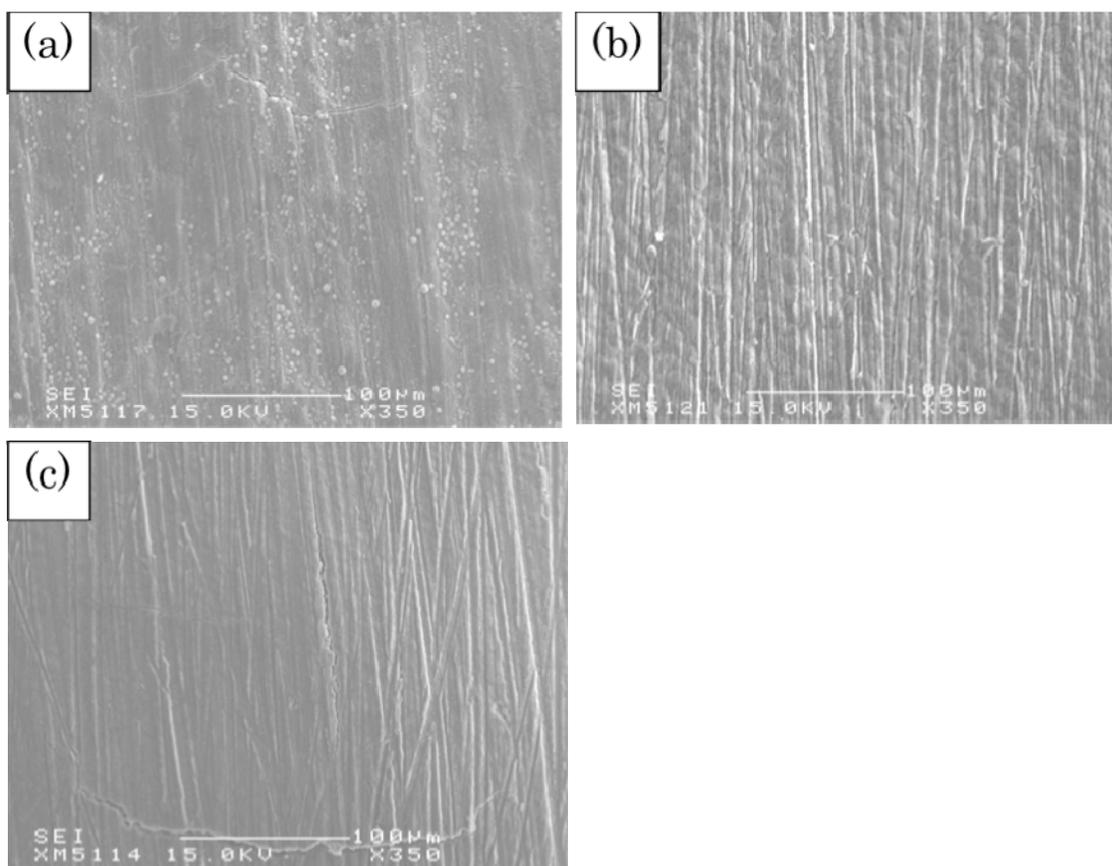


Figure 3. SEM image of surface of Al electroplating on (a) pure Mg, (b) AZ91, and (c) AZ121 at 283K.

Cross-sectional SEM and EDS analysis was done to pursue the reason of the swelling. Elemental mapping images by EDS on the cross-section at the part of nodule of the Al layer electrodeposited by current pulse electrolysis are shown in Figure 4, where electrolysis condition is the following; an applied current density of 1.7 mAcm^{-2} , a frequency of 0.67 Hz, and a duty ratio of 0.67. The thickness of Al layer was about 10-15 μm . It was clearly seen that there were many pores in the Al layer and also this layer had low adherence on the substrate. Comparing with Figures 4(a) and (b), the porous part on

substrate in Figures 4(a) corresponds with the electroplating layer of Al. Figures 4(c) and (d) show that the Al layer included oxygen. The oxygen was also detected between the Al layer and the substrate at the point of crack.

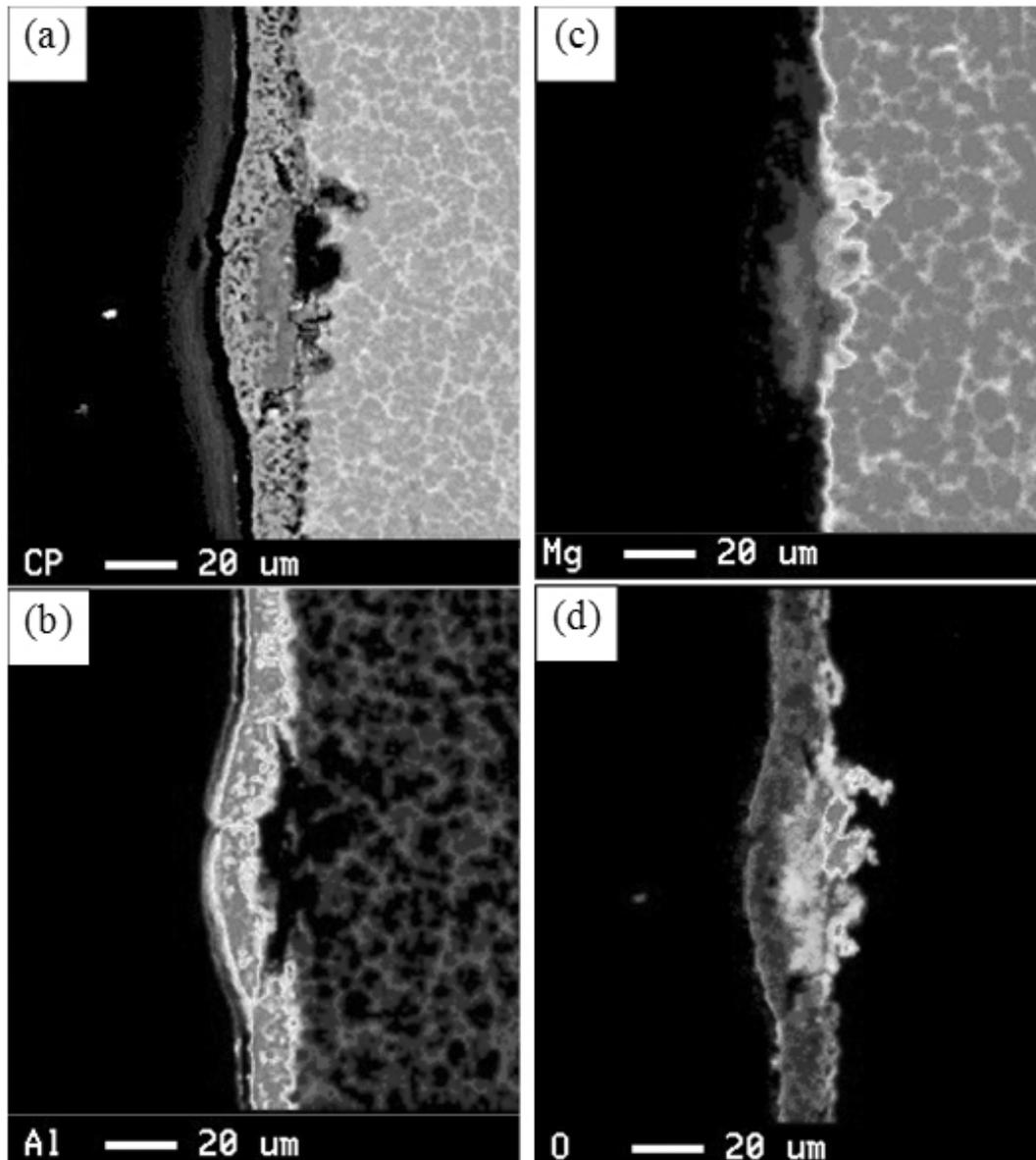


Figure 4. Cross-sectional SEM image and EDS mapping image of the electrodeposit on AZ121 alloy by pulse electrolysis at 323 K.

Al electrodeposition at 283 K

To examine the influence of the temperature of the electrolyte for electroplating of Al, constant current electrolysis and the current pulse electrolysis were carried out at the electrolyte temperature of 283 K. Condition of cathodic current density applied for the constant current electrolysis was 1.7 mAcm^{-2} as same as in the case of 323 K. The Al layers formed on all the substrates by the constant current electrolysis were not homogeneous and not entirely covered, while that by the current pulse electrolysis were

successfully electroplated. The condition of current pulse electrolysis was the following; an applied current density of 1.7 mAcm^{-2} , a frequency of 0.67 Hz, and a duty ratio of 0.67. The Al layer on pure Mg had a silver-white color and relatively flat appearance. The Al layer on AZ91 and AZ121 also were silver-white and some part of the surface was mirror-like. In particular, a mirror-like area of the Al surface on AZ121 was about 2/3. The cross-sectional SEM images of Al layers deposited by the current pulse electrolysis on each substrate are shown in Figure 5. In the Al layer on pure Mg and AZ91, small vacant space was observed between the plating layer and the substrate in addition to adherent part of the plating layer in Figure 5 (a) and (b). The Al layer on AZ121 was uniformly electrodeposited and there is no vacant space between electroplating layer and substrate.

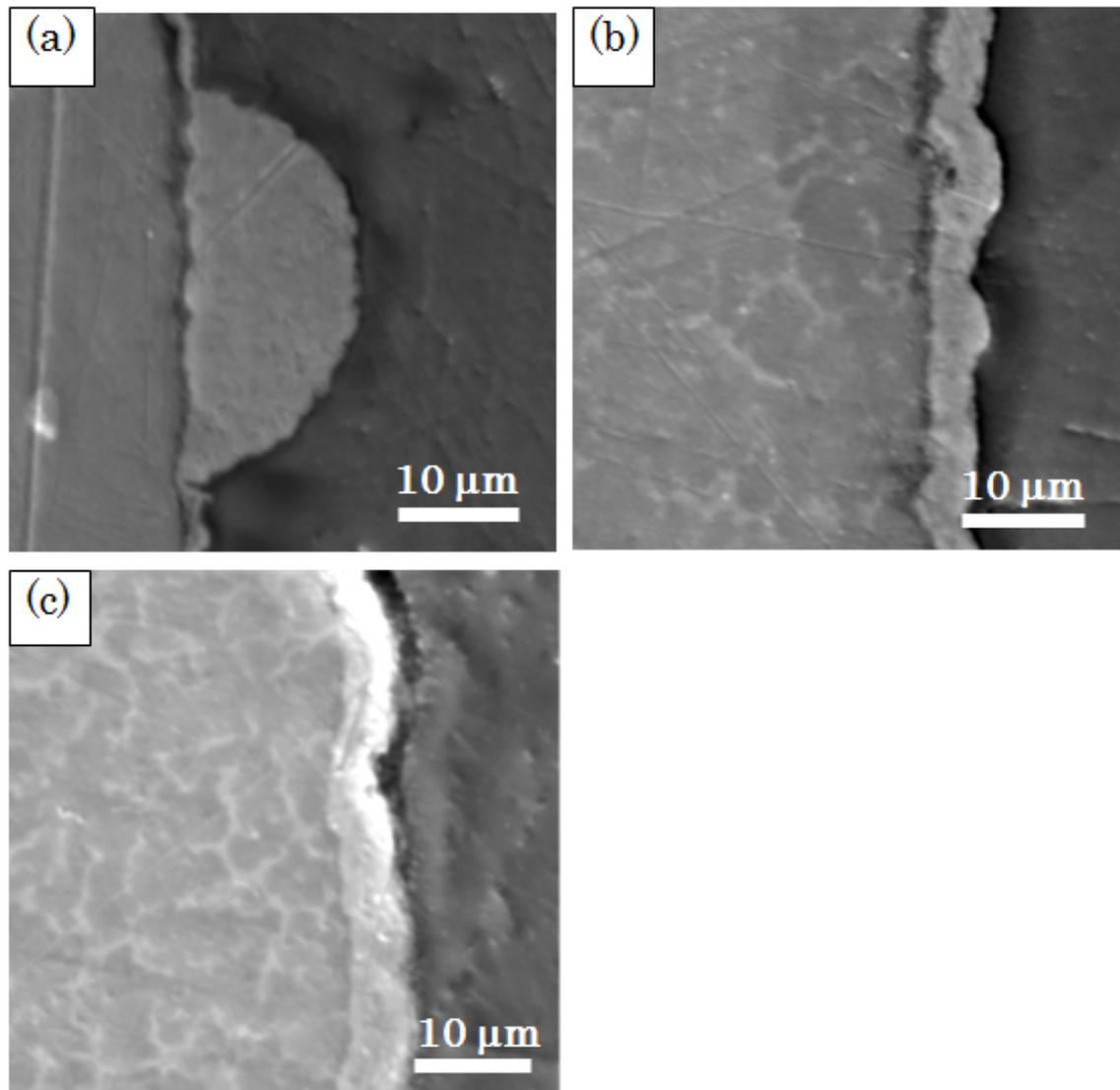


Figure 5. Cross-sectional SEM images of the Al electroplating on (a) pure Mg, (b) AZ91 and (c) AZ121 alloys by pulse electrolysis at 283 K.

Discussion

Comparing the current pulse electrolysis with the constant current electrolysis, the surface appearance and morphology of Al layer on each substrate were much improved, probably because the number of nuclei of Al increased by the pulse electrolysis.

It is known that AZ series of Mg alloys consist of two phases one of which is Mg solid solution phase (α -phase) and another intermetallic phase (γ -phase, $Mg_{17}Al_{12}$). The bright area in Figures 4(a) and (b) may consist of α -phase and the gray and dark areas of γ -phase. Since the α -phase is believed to be more dissolvable in $AlCl_3$ -EMIC ionic liquid, Al may be easily deposited on β -phase. Mg is assumed to preferentially dissolve from α -phase when Mg alloy immerses in the ionic liquid. This may lead to low adherent Al electroplating and thus introduce many small vacant spaces between the Al layer and substrate. When moisture penetrates through cracks or pinholes in the Al layer after removal from the dry ionic liquid, Mg oxide may be formed at interface between the Al layer and substrate as shown in Figures 4 (c) and (d).

The Al layers formed on all the substrates by the constant current electrolysis were not homogeneous and not covered over whole surface at 323 K as previously mentioned. When the current pulse electrolysis was adopted, the surface appearance and morphology of Al layer was dramatically improved at 323 K, compared with the constant current electrolysis. The Al layer formed by current pulse electrolysis comprised of Al particles with various sizes. The large distribution of the particle sizes may result from a large number of nuclei of Al generated on the substrate due to the pulse electrolysis and agitation. The adhesion of Al layers on each substrate at 283K was also enhanced, probably because exchange reaction between Al ion in ionic liquid to metallic Al and Mg substrate to Mg ion during the immersion before the electrolysis becomes more moderate.

Conclusion

The electroplating of Al on pure Mg and Mg alloys was surveyed in $AlCl_3$ -EMIC ionic liquid at 323 K and 283 K.

- (1) When constant current electrolysis was applied, Al layer electrodeposited on the three substrates at 323 K were dendrite shaped with low adherence.
- (2) When pulse current electrolysis was applied at 323 K, the surface flatness and adherence were improved. The Al layer on AZ121 revealed mirror-like surface appearance, although the adhesion strength of the Al layers was not enough large.
- (3) The adhesion of Al layers on all the substrates were much enhanced at lower temperature of 283 K by the pulse current electrolysis. Preparation of adherent, flat, and dense Al layer was achieved on AZ121 at the temperature.

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