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Citation	Journal of the Electrochemical Society, 158(9), D535-D540 https://doi.org/10.1149/1.3607426
Issue Date	2011-06-29
Doc URL	http://hdl.handle.net/2115/46930
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Type	article
File Information	JES158-9_D535-D540.pdf



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Effect of Copper Pretreatment on the Zincate Process and Subsequent Copper Electrodeposition of AZ31 Magnesium Alloy

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A small amount of Cu^{2+} ions was added to the activation bath used for pretreatment of the plating process of an AZ31 Mg alloy. In the activation process, a small amount of Cu was deposited at high density on the substrate surface accompanying Mg dissolution (Cu pretreatment). These Cu deposits acted as nucleation seeds for Zn deposition in the following zincate process and provided a uniform and dense Zn layer almost completely covering the substrate. The Cu layer electroplated on this zincated substrate showed considerable improvement in density and uniformity compared with those of the sample without Cu pretreatment. Cross-sectional SEM observation revealed that a less-defective interface between the Cu layer and substrate was obtained for the Cu-prepared sample. This structure also contributed to the improvement of adhesion strength. The mechanism of this improvement was investigated using electrochemical measurement and scanning electron microscopy observation with energy dispersive X-ray spectroscopy analysis.

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Manuscript submitted January 31, 2011; revised manuscript received April 22, 2011. Published June 29, 2011.

Owing to their superior strength, light weight and rich natural resources, Mg and its alloys are attractive materials in various applications. Unfortunately, the surface of Mg is easily covered with a thick oxide or hydroxide layer with a high electric resistance, which may not be suitable for some applications such as electronic devices. Therefore, it is important to establish a plating method that can produce functional coatings on Mg alloys such as corrosion-resistant and electrically conductive coatings with sufficient adhesion.

Since a thick passivation film is formed on Mg under an ambient atmosphere, pretreatment is necessary to remove the surface layer and to suppress its reformation prior to the plating process.¹⁻⁵ It is also important to obtain a uniform surface condition on Mg alloys for plating because intermetallic compounds such as Mg_xAl_y are formed at grain boundaries. Despite these difficulties, electroplating can provide potentially uniform coatings with good corrosion resistance for Mg alloys by using zincate pretreatment.⁶⁻¹¹ Application of zincate pretreatment to Mg alloys, however, has sometimes resulted in non-uniform Zn deposition, probably due to non-uniform dissolution of the substrate during the zincate process.¹¹ In the case of Al and its alloys, zincate pretreatment has also been optimized to obtain uniform Zn deposition. The effectiveness of various methods for reducing the influence of intermetallic compounds of Al alloys in an electroless plating process has been studied. These methods include etching treatment,¹² formation of a seed layer by using a dry process,¹³⁻¹⁷ and other techniques. Our group previously reported that addition of a small amount of Cu ions to the etching bath can dramatically improve the uniformity of Zn deposits on Al-Si alloys in the double zincate process because Cu deposits formed in the etching process acted as nucleation seeds for Zn deposition (Cu pretreatment).¹⁸ Since Cu pretreatment was effective for obtaining uniform Zn deposits on Al alloys, it was worth considering a similar method for zincate pretreatment of Mg alloys. Therefore, in this work, a Cu pretreatment was developed for an Mg alloy. For the Cu pretreatment an Mg alloy is immersed in an activation bath containing a low concentration of Cu^{2+} ions before the zincate process. The processes concerning with Cu^{2+} ions is proposed as follows. In this activation process, Mg dissolution and Cu deposition proceed as a substitution reaction. Fine Cu particles are deposited densely and uniformly, and there is little growth of the particles at the low concentration of Cu^{2+} ions in the activation bath. The Cu particles then act as nucleation sites for Zn deposition in the following zincate process. As a result, Zn is deposited densely and uniformly on the substrate to provide a suitable zincated surface for plating. In this study, the effect of Cu pretreatment on the zincate process of an AZ31 Mg alloy was investigated using scanning electron micros-

copy and electrochemical measurements. Cu was then electrodeposited on an AZ31 Mg alloy in an alkaline plating bath to examine the effect of Cu pretreatment on adhesion strength of the Cu plating layer. All processes used in this work were conducted under mild conditions using baths that did not contain any toxic chemicals.

Experimental

Specimens were prepared from a die-cast AZ31 Mg alloy sheet composed of 3.19 wt % Al, 0.81 wt % Zn, 0.334 wt % Mn, and bal. Mg. The testing specimens were cut into rectangular pieces of $10 \times 10 \times 7$ or $30 \times 30 \times 7$ mm in size. The specimens were embedded in epoxy resin, and the exposed area of 100 or 900 mm² was mechanically polished with SiC papers of 700, 1000, and 1500 grits. They were then cleaned with distilled water and dried with a stream of air. Bath compositions and operation conditions of the processes used in this study are shown in Table I. Milli-Q filtered water and analytical-grade chemicals were used for preparation of all baths. Specimens were subjected to a pickling bath, an activation bath with (Cu-prepared) or without (non-prepared) Cu^{2+} ions, and then a zincate bath, successively. Specimens were washed with distilled water after each treatment and immersed immediately in the next bath to avoid drying. A potentiostat/galvanostat (Ivium Technologies, model IviumStat) was employed for Cu electrodeposition by using a typical three-electrode system consisting of a working electrode (WE) of AZ31 Mg alloy, an Ag/AgCl reference electrode (RE) and a counter electrode (CE) of a Cu plate (99.99%). In this paper, electrode potential is presented as a value vs. Ag/AgCl-RE. Cu was electrodeposited in an alkaline plating bath with current density of -12 mA cm^{-2} under a stirring condition. All experiments were conducted at room temperature. Adhesion strength of the Cu electroplating layer to the substrate was measured by using a pull-off adhesion tester (Elcometer 106). Scanning electron microscopy (SEM) combined with energy dispersive X-ray spectroscopy (EDX, EDXS) (JEOL Co., model no. JSM-6500F) was used to observe the surface morphology and elemental composition of the coatings.

Results and Discussion

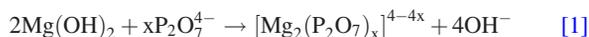
Cu pretreatment and zincate process.—In order to investigate the effects of Cu^{2+} ions in the activation process, SEM images were taken for samples immersed in the activation bath with or without Cu^{2+} ions as shown in Fig. 1. After the pickling process, the substrate surface was smooth as shown in Fig. 1a. The sample after activation in the bath without Cu^{2+} ions had a non-uniform film composed of Mg hydroxide and Mg fluoride on the surface as a dark area shown in Fig. 1b. In this activation process, an Mg hydroxide film that was formed through rinsing in distilled water after the pickling process was dissolved in the following reaction

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Table I. Bath compositions and operation conditions for the pretreatments and electrodeposition of Cu on the AZ31 Mg alloy.

Process	Bath composition	Concentration (g l ⁻¹)	Condition
Degrease	Ethanol	—	Rinse or ultrasonication
Pickling	HF + HCl	0.25 wt %	Room temp., 20 s
Activation	K ₄ P ₂ O ₇	86	Room temp., 120 s
	Na ₂ CO ₃	15	
Zincate pretreatment	KF	4.5	
	CuSO ₄ ·5H ₂ O	0 or 0.08	
	ZnSO ₄ ·7H ₂ O	46	pH 10.4
	K ₄ P ₂ O ₇	139	Room temp., 1000 s
	Na ₂ CO ₃	5	
Cu electrodeposition	KF	6	
	CuSO ₄ ·5H ₂ O	70	pH 13.5
	KNaC ₄ H ₄ O ₆ ·4H ₂ O	346	Stirring at 600 rpm
	NaOH	120	Room temp.
	H ₃ BO ₃	20	<i>I</i> _C = -12 mA cm ⁻² 3600 s



Dissolution of the Mg substrate and then formation and successive dissolution of a new Mg hydroxide film occurred. In this activation bath, a less-soluble Mg fluoride film that might suppress further dissolution of the substrate was also formed.⁹ The surface therefore showed a patchwork pattern of corrosion and protected areas as seen in Fig. 1b.

On the other hand, a quite uniform surface was obtained for the Cu-prepared sample as shown in Fig. 1c. Probably, Cu was deposited on the substrate after removal or thinning of the initial hydroxide film in reaction 1 and acted as charge transfer sites to accelerate the substrate dissolution as discussed below. Fast dissolution of Mg prevented accumulation of Mg hydroxide on the surface and thus provided a smooth and uniform surface condition as shown in Fig. 1c. Although the Cu deposits could not be detected by EDS analysis because of its small deposition mass, they acted as efficient catalysts

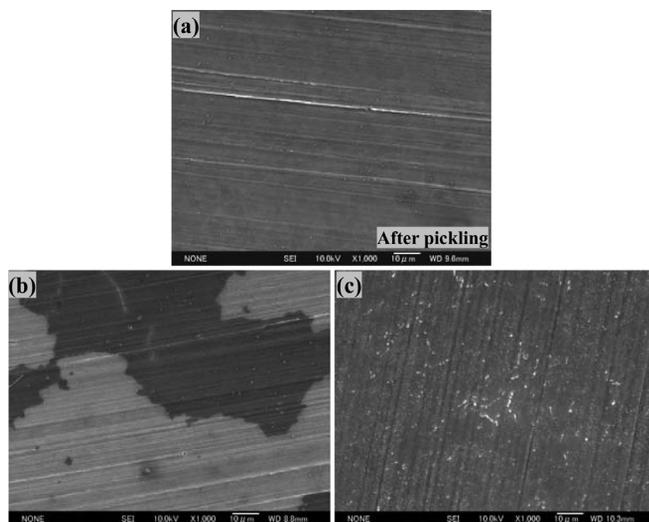


Figure 1. SEM images of the AZ31 Mg alloy after pickling treatment (a) and after activation in solutions without (b) and with (c) Cu²⁺ ions.

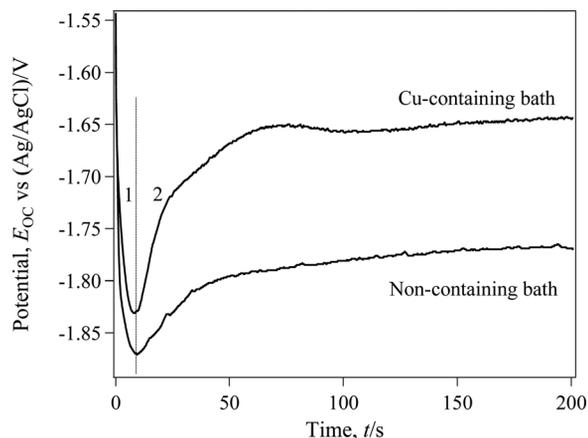


Figure 2. Change in EOC, E_{OC} , of the AZ31 Mg alloy during the activation process in baths with and without Cu²⁺ ions.

for electrochemical reaction on the substrate, resulting in a dramatic effect on surface conditioning.

The open circuit potential, E_{OC} , of the specimens immersed in the activation baths with and without Cu²⁺ ions is shown in Fig. 2. The curve measured for the non-prepared sample can be divided into two stages. The steep drop of E_{OC} within 10 s in the first stage suggests rapid dissolution of the hydroxide film described by reaction 1 and initiation of the dissolution reaction of the Mg substrate. The shift of E_{OC} in the noble direction and successive slow transition to a steady potential in the second stage is mainly attributed to the process of surface covering with Mg hydroxide and Mg fluoride films as mentioned above. Although these films suppressed the dissolution reaction of the substrate, E_{OC} remained less-noble due to continuous dissolution of the Mg substrate and low charge transfer efficiency via these films.

On the other hand, E_{OC} of the Cu-prepared sample shows noble potential compared with that of the non-prepared sample. The difference between the two curves can be explained by the model illustrated in Fig. 3. In the activation bath, dissolution of the surface

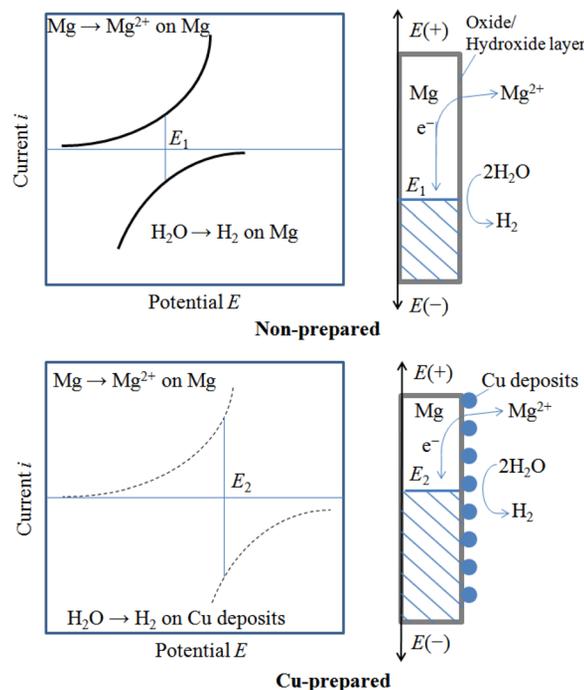


Figure 3. (Color online) Schematic representation of mixed potential of the AZ31 Mg alloy during the activation process (E_1) and Cu preparation process (E_2).

hydroxide film promotes oxidation of the Mg substrate to form an oxide/hydroxide film and dissolution of Mg through the film. This oxidation process leaves electrons in the electrode to cause a shift of E_{OC} in the less-noble direction and promotes H_2 gas evolution. A considerably less-noble E_{OC} in a steady state at about -1.8 V in the activation bath without Cu^{2+} ions indicates a less-active surface of the specimen for H_2 gas evolution reaction. Mg is a base metal and its surface is easily oxidized to be covered with a thick hydroxide layer in aqueous solution, which disturbs electron transfer and combination of adsorbed H atoms to form H_2 molecules. On the other hand, in the activation bath containing Cu^{2+} ions, decrease of E_{OC} causes not only H_2 gas evolution but also Cu deposition on the substrate. Since the electrochemical activity of Cu is considerably higher than that of Mg, a small amount of Cu deposition on the Mg substrate greatly increases the efficiency of H_2 gas evolution, even at smaller overpotential. A relatively noble E_{OC} also accelerates dissolution of the Mg substrate. As a result, H_2 gas evolution and Mg dissolution become noticeable in the activation bath containing Cu^{2+} ions.

In order to investigate the effect of Cu pretreatment on Zn deposition in the zincate process, SEM images were taken for samples at different zincating times as shown in Fig. 4. From these images, it is clear that the zincate process was initiated with nucleation followed by growth of Zn deposits. For example, the non-prepared sample after 30-s immersion shows initiation of Zn nucleation on the surface as seen in Fig. 4a. It is also observed that nucleation occurred preferentially at the grain boundary of the substrate as shown by an arrow. After 300 s, the Zn particles increased in number and size and were deposited preferentially on the grain boundary as shown in Fig. 4b. After 1000 s, Zn particles grew continuously and became connected to each other as seen in Fig. 4c. However, the Zn layer did not completely cover the substrate, probably due to the low density of the initial nucleation and rather slow deposition rate of Zn, which enabled growth of individual Zn particles.

A considerable number of Zn particles were observed on the Cu-prepared sample after zincating for 30 s as shown in Fig. 4d. After 300 s, all Zn particles had grown and the density of Zn particles was considerably higher than that of the non-prepared sample as can be seen from a comparison of Fig. 4e with Fig. 4b. After 1000 s, a compact and dense Zn layer almost completely covered the substrate as shown in Fig. 4f. Although Zn was deposited along the grain boundary, further Zn deposition proceeded on the whole surface. This improvement in Zn deposition is possibly due to the formation of dense Cu seeds on the substrate, and these Cu seeds act as a catalyst for Zn deposition, leading to rapid and dense Zn deposition. This mechanism will be further discussed later.

The effect of Cu pretreatment on formation of a Zn layer was also confirmed by the time-transition of open circuit potential, E_{OC} , during the zincate process as shown in Fig. 5. In these traces, initial drop of E_{OC} corresponds to rapid dissolution of the substrate, and the following increase in E_{OC} and successive slow approach to a steady potential at ca. -1.3 V corresponds to Zn deposition and completion of the zincate process. The steady potential was slightly less noble than the EOC of a Zn plate at -1.25 V measured in the same bath. This indicates that dissolution reaction of the Mg substrate continues slowly beneath the Zn deposits, especially in the case of a non-prepared sample, or that EOC of the zincate layer differs slightly from that of a Zn plate. The noticeable difference between the non-prepared sample and the Cu-prepared sample is the noble E_{OC} and faster Zn deposition process for the latter, which can be attributed to the catalytic function of Cu seeds for substitution reaction of Mg dissolution and Zn deposition. Electrons formed by the Mg dissolution reaction transfer efficiently to Zn^{2+} ions via Cu seeds, resulting in noble E_{OC} which promoted Mg dissolution and thus rapid Zn deposition on Cu seeds with high density. In conclusion, a small amount of Cu deposits not only increases the deposition rate but also improves uniformity of Zn deposits on an AZ31 Mg alloy.

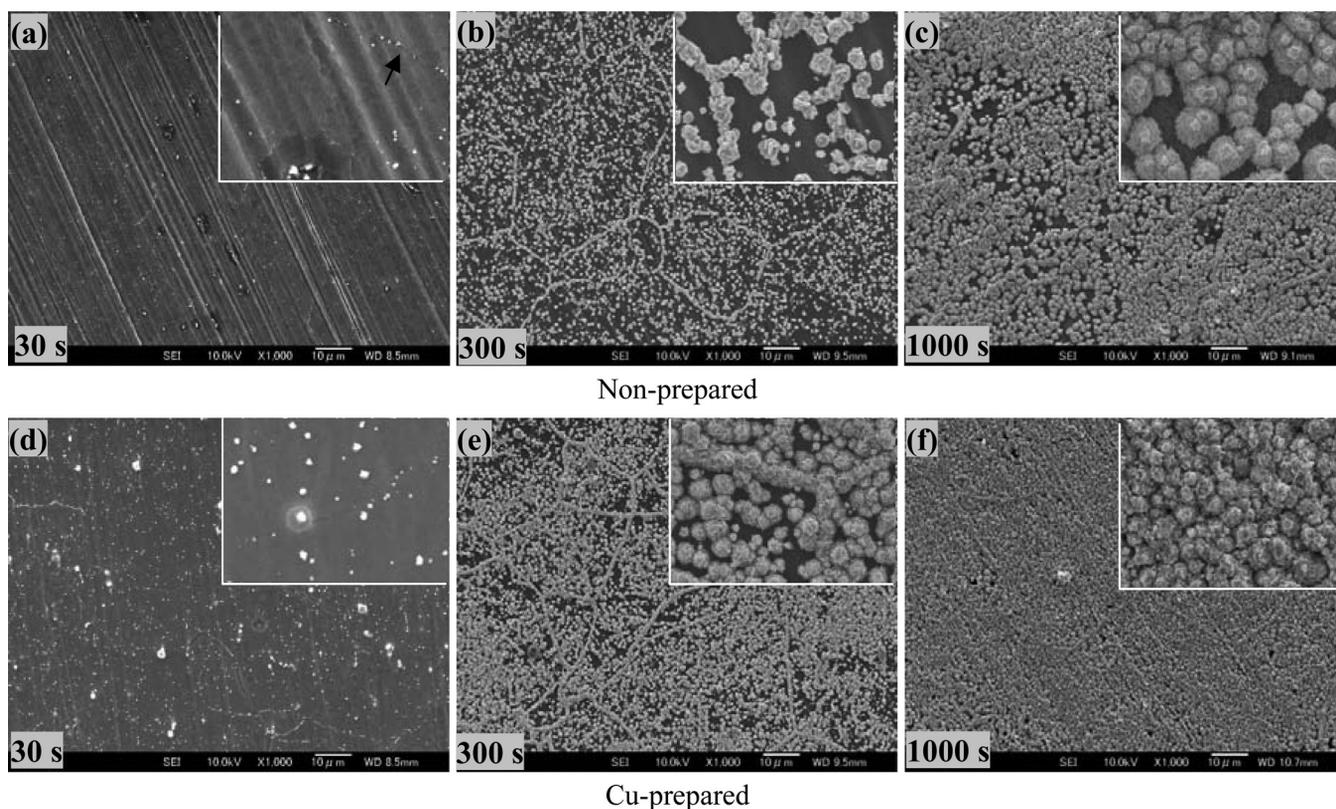


Figure 4. SEM images of non-prepared (a,b,c) and Cu-prepared (d,e,f) AZ31 Mg alloy samples after zincate pretreatment for different times. Magnified ($\times 5$) images of each surface are superimposed at the upper-right in each image.

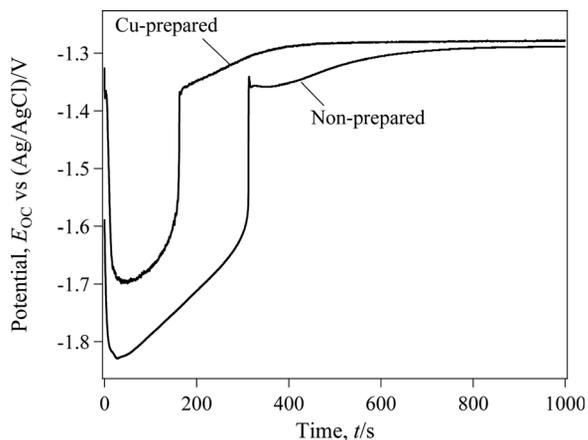


Figure 5. Changes in EOC, E_{OC} , of non-prepared and Cu-prepared AZ31 Mg alloy samples during the zincate process.

Electrodeposition of copper.—In order to investigate the effect of Cu pretreatment on the plating process, Cu was electrodeposited on samples prepared with and without Cu pretreatment and the surfaces of the Cu layers were observed by using SEM as shown in Fig. 6. From these images, it is evident that the morphology of the Cu layer was strongly influenced by Cu pretreatment. For example, undulation of the surface of the Cu layer formed on the non-prepared sample shown in Fig. 6a reflects the morphology of Zn deposits shown in Fig. 4c. Defects on the Cu layer surface shown by arrows are thought to be induced by non-uniform deposition of the Zn layer on the substrate. The cross-sectional SEM image shown in Fig. 6c also indicates the existence of defects between the Cu layer and substrate and voids in the Cu layer. Results of EDS line analysis shown in Fig. 6e reflect such a structure, i.e., the Zn signal was distributed at the interface between the Cu layer and substrate and the Cu signal gradually increased from the Zn layer to a steady value of the Cu layer. This indicates that some of the substrate was not covered with the Zn layer as seen in Fig. 4c and that Cu expanded to this area from Cu deposits at the initial stage of Cu electrodeposition. This process caused formation of voids at the interface and lessened the adhesion strength of the plating layer as discussed later.

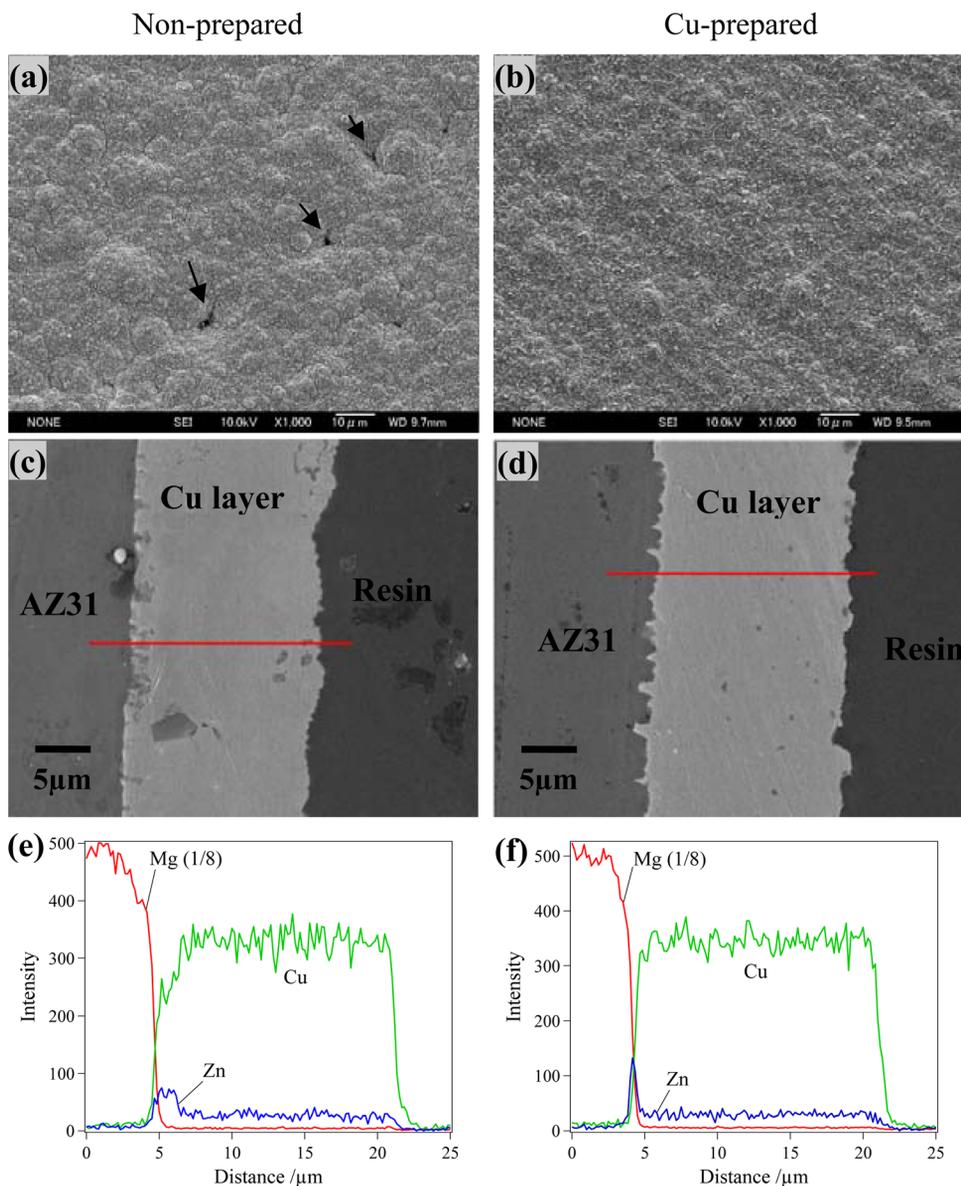


Figure 6. (Color online) SEM images of non-prepared (a,c) and Cu-prepared (b,d) AZ31 Mg alloy surfaces after Cu electrodeposition. (c,d) Cross-sectional images. (e,f) EDS line analysis at the lines shown in Fig. c and d.

On the other hand, in the case of the Cu-prepared sample shown in Fig. 6b, a smooth and dense Cu surface without defects was obtained on the dense and uniform Zn layer shown in Fig. 4d. This compact structure was also confirmed from a cross-sectional SEM image shown in Fig. 6d, i.e., a Cu layer with few defects and a uniform thickness of about 15 μm was formed. Defects or voids were not observed at the interface between the Cu layer and the substrate. An irregular structure of the interface containing pores on the substrate was induced by the acceleration of substrate dissolution due to Cu pretreatment in the activation process. Cu deposition in the pores was confirmed by a cross-sectional SEM image, and this may have contributed to the better adhesion strength of the Cu plating layer as discussed later. In the results of EDS line analysis shown in Fig. 6f, the Zn signal of the Cu-prepared sample shows a sharp peak and the Cu signal rapidly increases to a steady value of the Cu layer. These results confirm that the Cu pretreatment resulted in formation of a compact and dense Zn layer on the substrate and enables formation of a Cu layer with few defects and uniform thickness.

Figure 7 shows the time-transitions of the electrodeposition potential, E_{ED} , on Zn-coated AZ31 Mg alloy samples prepared with and without Cu pretreatment during galvanostatic Cu electrodeposition. In the case of the Cu-prepared sample, E_{ED} initially decreased and then increased rapidly from a less-noble potential to about -1.0 V within ca. 110 s and then increased slowly thereafter. This rapid potential shift at the initial stage indicates that Cu nucleation proceeded rapidly on the Zn layer which completely covered the substrate and then Cu electrodeposition continued on the Cu deposits. Electrodeposition for the initial 110 s corresponds to 0.46 μm of Cu layer calculated simply from the Cu layer thickness of 15 μm for 3.6-ks electrodeposition, and this initial thickness seems to be sufficient to cover the substrate shown in Fig. 6d. From the fact that Cu was electrodeposited in the pits on the substrate, it is reasonable to assume that some of the Zn layer dissolved chemically or was removed from the surface to provide an ionic path for Cu^{2+} to reach these pits for electrodeposition in the initial stage.

In the case of the non-prepared sample, initial E_{ED} was considerably less noble than that of the Cu-prepared sample. Since Cu was electrodeposited only on electro-conductive Zn particles in the initial stage, incomplete Zn coverage on the non-prepared sample resulted in higher overpotential for Cu electrodeposition occurring on fewer Cu particles, and a longer electrodeposition period was necessary for almost complete coverage of the substrate with a Cu layer. As shown in Fig. 7, 500 s was needed to cover the substrate with the initial Cu layer. The thickness of this initial Cu layer is estimated to be about 2.1 μm from the simple calculation described

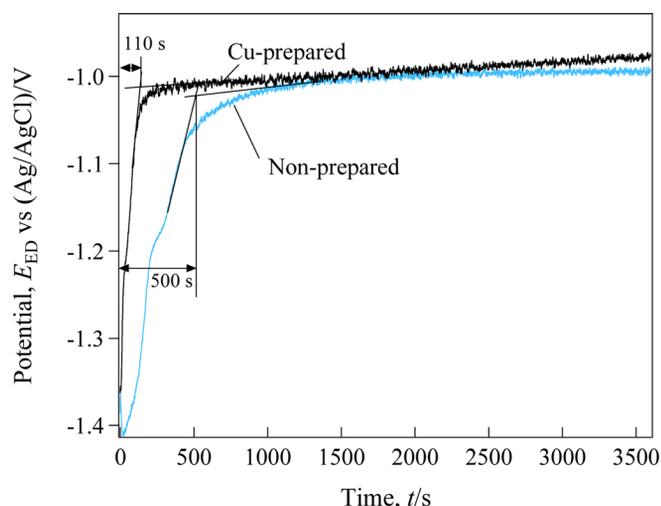


Figure 7. (Color online) Potential-time transitions of non-prepared and Cu-prepared AZ31 Mg alloy samples during galvanostatic electrodeposition of Cu at -12 mA cm^{-2} .

Table II. Adhesion strength of the Cu plating layer deposited on the Zn-coated AZ31 Mg alloy measured by a pull-off test. Values are averaged data of three runs for each condition.

Preparation	Cu-prepared	Non-prepared
Adhesion strength (MPa)	14	9

above, and this thickness also seems to be comparable to the defective Cu deposits at the interface shown in Fig. 6c. After 1000 s, E_{ED} remained at almost the same value as that of the Cu-prepared sample.

Adhesion tests.—Results of test of adhesion strength of the Cu electroplating layer to the substrate are summarized in Table II. Better adhesion strength was always obtained for the Cu-prepared samples. From the results described in the previous subsections, it is proposed that improvement in adhesion strength due to Cu pretreatment is provided by dense Cu seeds on the substrate, which enable dense and compact Zn deposition followed by Cu electrodeposition with few defects, due to the defect-less interface structure between the substrate and Cu layer and also due to the anchor effect provided by irregular dissolution trace of the substrate and complementary Cu deposition to it. In the case of the non-prepared sample, adhesion was always weak due to a defective interface and less-compact Cu layer. Figure 8 shows photos of non-prepared and Cu-prepared samples after the pull-off adhesion test. For the non-prepared sample, the Cu electrodeposited layer was easily detached from the substrate. On the other hand, for the Cu-prepared sample, only a small area of the Cu layer was detached from the substrate, as shown by an arrow.

The coating process for the AZ31 Mg alloy prepared with or without Cu pretreatment is schematically represented in Fig. 9. In the case of the non-prepared sample, the preformed corrosion layer partly dissolved in the activation process and a non-uniform Zn layer was formed on it in the following zincate process. Density of Zn nucleation was low and Zn particles became large compared with those of the Cu-prepared sample. In the Cu electroplating process, Cu was deposited only on the Zn particles with low density, resulting in formation of voids or a defective interface between the Cu layer and the substrate and a defective Cu layer itself with an uneven surface. On the other hand, for the Cu-prepared sample, dense Cu deposits were formed in the activation bath containing a small amount of Cu^{2+} ions. These Cu deposits acted as catalysts for Zn deposition in the zincate process, and thus a compact Zn layer almost completely covered the substrate. Cu was then electrodeposited on this Zn layer with few defects at the interface and in the film itself. This plating film also showed improvement in adhesion strength.

In conclusion, Cu pretreatment applied to the plating process on an AZ31 Mg alloy improves the quality and adhesion strength of the Cu electroplating layer. It is also expected that the Cu-deposited Mg alloy can be used as a substrate for Ni electrodeposition in acidic plating baths to obtain a corrosion-protective Ni/Cu coating.

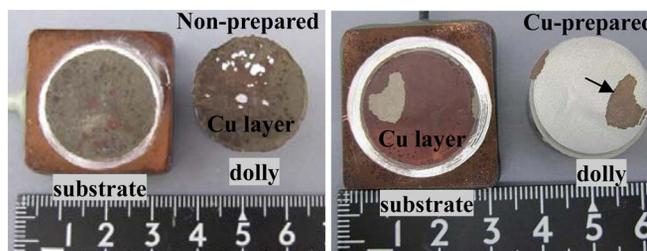


Figure 8. (Color online) Photos of non-prepared and Cu-prepared AZ31 Mg alloy samples after the pull-off adhesion test.

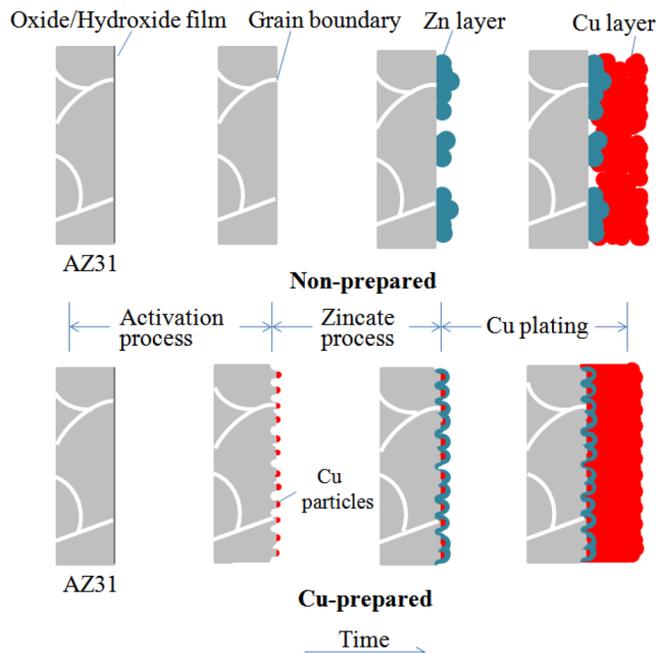


Figure 9. (Color online) Schematic representation of coating formation on non-prepared and Cu-prepared AZ31 Mg alloy samples during the activation, zincate and Cu electroplating processes.

Conclusions

In this study, effects of Cu^{2+} ions in the activation bath on the following zincate process of an AZ31 Mg alloy and on the Cu electrodeposition were investigated, and the following results were obtained:

1. A small amount of Cu was deposited uniformly and densely on the Mg alloy as a substitution reaction of Mg dissolution in the activation bath containing a low concentration of Cu^{2+} ions. These Cu deposits greatly increased the electrochemical activity of the Mg alloy and promoted Mg dissolution to provide a uniform substrate suitable for subsequent treatment.

2. Cu deposition on the Mg alloy greatly improved the uniformity and density of Zn deposition in the following zincate process. This effect was provided by Cu deposits that acted as nucleation sites for Zn deposition, resulting in the formation of a dense Zn deposition layer entirely covering the substrate.

3. Nucleation of Zn deposition in the zincate process was initiated preferentially at the grain boundary on the AZ31 Mg alloy and caused non-uniform Zn deposition on a sample without Cu pretreatment. In the case of a Cu-prepared sample, however, further Zn deposition proceeded on the surface other than the grain boundary and thus the deposition at the grain boundary was insignificant.

4. A smooth dense Cu layer with few defects was electrodeposited on the Zn-coated AZ31 Mg alloy pretreated with Cu, and the adhesion strength of this Cu plating layer was considerably improved compared with that of the non-prepared sample.

Acknowledgments

This work was supported by the Global COE Program (Project No. B01: Catalysis as the Basis for Innovation in Materials Science) from the Ministry of Education, Culture, Sports, Science and Technology, Japan and also supported in part by the Light Metal Educational Foundation.

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