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Surface pretreatment of Mg alloys prior to Al electroplating in TMPAC-AlCl₃ ionic liquids

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Abstract: It is difficult to directly electroplate Al on Mg alloys. The effects of pretreatment parameters on the corrosion resistance of films obtained on AZ31 Mg alloy surface were studied by using potentiodynamic polarization curves, to produce a compact interfacial layer as zinc-immersion deposition. After the substrate was pretreated under optimized conditions, aluminum was electrodeposited on AZ31 from TMPAC-AlCl₃ room temperature ionic liquids. The depositions were characterized by scanning electron microscope equipped with energy dispersion X-ray. The results show that the traditional pretreatment of Mg alloys was successfully used for the Al-electroplating process from TMPAC-AlCl₃ ionic liquids. The entire procedure includes alkaline cleaning, chemical pickling, surface activation (400 mL/L HF acid, 10 min), zinc-immersion (20 min) and anhydrous treatment. A relatively compact zinc-immersion film was prepared on the substrate surface. A silvery-colored satin aluminum deposition was obtained on AZ31 from TMPAC-AlCl₃ using direct current plating.

Key words: magnesium alloys; electroplating; pretreatment procedure; aluminum; ionic liquids

1 Introduction

Magnesium and its alloys as light metal (1.7 g/cm^2) with so many merits have been applied in plane, automobile and electric industries [1]. However, the material is generally known to have a poor corrosion resistance [2]. The current surface treatment methods of Mg alloy include chemical conversion film, anodic oxidation, organic coating, surface modification and metal deposition and so on. The metal plating has a low production value, and its operation temperature is room temperature. Aluminum possesses a good anti-corrosion property and excellent mechanical property. The electroplating of Al on Mg alloy would not only prevent substrate from corrosion, but also not markedly increase its mass [3]. Magnesium and its alloys, wherever possible, are extremely easy to be oxidated under the existence of oxygen. To the authors' experience, it is difficult to directly electroplate Al on Mg alloys. Therefore, the Al-electroplating process needs a compact intermediate layer deposited on Mg alloys. The surface activation and zinc immersion are two kinds of the traditional surface treatments used for Mg alloys. If they

were used for the entire Al-electroplating pretreatment process, it will have important practice significance. Even though the similar pretreatments have been used for the process [4–5], their processing technology or technical formula is more or less different from the present work.

The electrodeposition of Al from anhydrous electrolytes has been studied widely on various kinds of metal substrates [6]. It is hard to electroplate Al on magnesium alloys owing to their high chemical reactivity. The first report on the subject was published by CHANG et al in 2007 [3]. CHANG et al [3, 7] and ZHANG et al [8] plated aluminum and its alloys on Mg alloys from anhydrous electrolytes, such as [EMIm]Cl-AlCl₃ and AlCl₃-NaCl-KCl-MnCl₂. Those work exhibited an important significance to exploit a novel surface treatment technology used for Mg alloys. The TMPAC-AlCl₃ ionic liquids (ILs) have a low melting point of -75 °C as x(AlCl₃)=66.7%, good electrochemical and thermal stability [9], and a relatively cheap price [10]. Its electric conductivity is low [11], but can be improved by the addition of benzene [12]. The electrodeposition of Al from TMPAC-AlCl₃ was achieved on the W [10, 13, 14] and Al [13] substrate.

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To our knowledge, less report was published on the electroplating of Al on the Mg alloy substrate from TMPAC-AlCl₃ ionic liquids.

In the present work, both activation films and zinc-immersion depositions were prepared under different HF acid concentration, activation time and zinc-immersion time. The corrosion resistances were measured by potentiodynamic polarization curves. The AZ31 magnesium alloy was treated by the optimized And surface pretreatment. then aluminum was AZ31 electroplated on from trimethyl-phenylammonium chloride and anhydrous aluminum chloride (TMPAC-AlCl₃) quaternary ammonium room temperature ionic liquids mixed with benzene by direct current plating. The Al depositions were characterized.

2 Experimental

The trimethyl-phenyl-ammonium (TMPAC) of technical grade quality (>98%) was dried under vacuum at 100 °C for 24 h. All other reagents were of analytical grade. The acidic ionic liquid with the molar ratio of 2:1 was prepared by the slow addition of AlCl₃ to TMPAC at room temperature under a continuous magnetic bar stirring (the details were showed in Ref. [10]). The cathodes with dimensions of 40 mm×15 mm×3 mm were made of AZ31 magnesium alloys. The AZ31 samples were pretreated by the wet paper polishing, alkaline cleaning, chemical pickling, HF acid surface activation and zinc-immersion. And then they were fully cleaned with ethanol and toluene. Table 1 shows the details of the pretreatment procedure of magnesium alloy. The pure Al sheets with a purity of 99.9% used as anodes (20 mm× 20 mm×1 mm) were cleaned with acetone, fully rinsed with water, and then pickled in the 1 mol/L NaOH solution at 80 °C. Eventually, both the cathode and anode were immediately rinsed with ethanol and toluene,

 Table 1 Formulations and operation conditions of magnesium

 alloy pretreatment procedure

Procedure	Chemical agent and concentration	Procedure condition
Alkaline cleaning	50 g/L NaOH, 40 g/L Na ₂ CO ₃ , 10 g/L Na ₃ PO ₄ ·12H ₂ O	80 °C, 10 min
Chemical pickling	600 mL/L H ₃ PO ₄ (85%), 2 mL/L HNO ₃	90 s
Surface activation	400 mL/L HF (original concentration, 40%)	2–20 min
Zinc-immersion	30 g/L Zn ₂ SO ₄ ·7H ₂ O, 120 g/L Na ₄ P ₂ O ₇ ·10H ₂ O, 3 g/L LiF, 5 g/L Na ₂ CO ₃	pH 10–11, 80 °C, 5–40 min

respectively, before they were stored in a flask of toluene. In the ionic liquids with a benzene content of 50% (volume fraction), the Al plating was performed at 40-42 °C under an agitating speed of 200 r/min.

The morphology and components of cross-section or surface of depositions were examined on a scanning electron microscope equipped with an energy dispersion X-ray spectrometer (SEM-EDX, SSX-550, SHIMAZDU, Japan). The corrosion-resistances of samples were potentiodynamic investigated using polarization measurements in NaCl solution. A parallel team included three samples under the same conditions. All the measurements were performed in an ordinary three-electrode cell filled with 3.5% NaCl solution (mass fraction) at room temperature with an electrochemical workstation IM6e (ZAHNER, Germany). The working electrode was the films or depositions with an exposed surface area of 1 cm². The remainder was sealed with ethoxyline resin. The counter electrode and reference electrode were a platinum sheet and a saturated calomel electrode (SCE), respectively. The polarization resistance $(R_{\rm p})$ was calculated according to the polarization curves. The mean value and standard error of the parallel team were calculated.

3 Results and discussion

3.1 Surface pretreatment

It is necessary to achieve a compact activation film in the previous step of zinc immersion. The samples were obtained after reaction time of 10 min in HF activation solution with different concentrations. Their corrosion-resistant properties were tested by polarization curves in a 3.5% (mass fraction) NaCl solution. Figure 1 shows the polarization curves and the relationship curves between HF acid concentration and polarization resistance of activation films. The R_p of activation films increases with the increase of HF concentration. Table 2 shows the relative data of polarization curves from Fig. 1. From Fig. 1 and Table 2, as c(HF)=200 mL/L, the obtained activation film has a low R_p and a high corrosion current density (J_{corr}). As c(HF)=400 mL/L, R_p rises and J_{corr} decreases. It indicates that the activation film prepared c(HF)=400 mL/L has a more compact surface than the one at c(HF)=200 mL/L. With the increase of c(HF) from 400 mL/L to 800 mL/L, the J_{corr} slowly increases, and the mean R_p value has no significant increase considering the standard error (see Fig. 1(b)). In the present work, the HF volume concentration in activation solution was defined as 400 mL/L.

The samples were obtained after different reaction time (t) in 400 mL/L HF activation solution. Figure 2 shows the polarization curves and the relationship curves between reaction time and polarization resistance of



Fig. 1 Polarization curves (a) and relationship curve (b) between HF acid concentration and polarization impedance of acid activation films

Table 2Relative parameters on polarization curves ofactivation films from Fig. 1

HF acid concentration/ (mL·L ⁻¹)	$b_{\rm c}$	b_{a}	$\varphi_{\rm corr}/{ m V}$	$J_{ m corr}/$ ($\mu m A \cdot m cm^{-2}$)	$R_{\rm p}/$ (k Ω ·cm ²)
200	149	37.6	-1.143	131	0.099
400	225	13.7	-1.318	5.97	0.88
600	154	39	-1.171	8.19	1.65
800	191	52.2	-1.27	13.3	1.33

activation films. Table 3 shows the relative data of polarization curves from Fig. 2. The R_p of activation films rapidly increases with the prolonged time *t*. After 10 min, R_p increases slowly. Considering the standard error of the mean R_p value, there is no significant difference for the samples' resistance beyond 10 min (see Fig. 2(b)). In the present work, the activation time was defined as 10 min in the 400 mL/L HF acid solution.

The samples were obtained after different reaction time (t) in the zinc-immersion solution. Figure 3 shows the polarization curves and the relationship curves between reaction time and polarization resistance of zinc-immersion depositions. Table 4 shows the relative data of polarization curves obtained from Fig. 3. The Rof zinc depositions rapidly increases with the reaction



Fig. 2 Polarization curves (a) and relationship curve (b) between reaction time and polarization resistance of HF activation films

Table 3 Relative parameters on polarization curves ofactivation films from Fig. 2

Time/ min	$b_{\rm c}$	b _a	$\varphi_{\rm corr}/{ m V}$	$J_{\rm corr}/$ ($\mu {\rm A} \cdot {\rm cm}^{-2}$)	$R_{\rm p}/$ (k Ω ·cm ²)
2	109	46	-1.236	47.3	0.297
4	219	59.1	-1.219	61.5	0.329
6	138	44.1	-1.23	29.1	0.499
8	136	43.4	-1.23	28.7	0.498
10	84.3	135	-1.239	2.38	0.93
15	171	45.6	-1.223	16.1	0.96
20	201	65.9	-1.263	20.2	1.06

time *t*. After 10 min, R_p increases slowly. Considering the standard error, R_p is of no significant difference when *t* is longer than 10 min (see Fig. 3). As *t*=20 min, the zinc-immersion process has a good repetition owing to a narrow distribution of the mean R_p value and its standard error. It is steadier than the samples prepared below 20 min and at 40 min. In short, it is sufficient to obtain a compact zinc deposition beyond 10 min. In the present work, the zinc-immersion time was defined as 20 min.

The zinc deposition was prepared after 20 min on AZ31 substrate. The SEM image of its surface and the



Fig. 3 Polarization curves (a) and relationship curves (b) between reaction time and polarization impedance of zinc-immersion

Table 4 Relative parameters on polarization curves ofzinc-immersion depositions from Fig. 3

Time/ min	$b_{\rm c}$	b_{a}	$\varphi_{\rm corr}/{ m V}$	$J_{ m corr}/$ ($\mu A \cdot m cm^{-2}$)	$R_{\rm p}/$ (k Ω ·cm ²)
5	138	94.2	-1.208	94.2	0.26
10	64.4	29.6	-1.124	7.81	1.12
15	72.3	57.1	-1.147	14.4	0.96
20	78.2	133	-1.168	23	0.93
40	153	46	-1.119	9.93	1.54

backscattered electron image of its cross-section are shown in Fig. 4. The zinc layer is porous. The layer is lighter than Mg substrate due to the higher atomic number of zinc than that of magnesium in the backscattered electron image (see Fig. 4(b)). The white-colored zinc-immersion film has a thickness of 1 μ m and exists on the AZ31 substrate surface.

3.2 Electrodeposition of Al

The silvery-colored satin Al layer was constantcurrent electrodeposited on AZ31 with a zinc deposition from the TMPAC-AlCl₃ ionic liquids mixed with benzene with a volume content of 50%. The depositions



Fig. 4 SEM images of zinc-immersion film (a) obtained after 20 min and its cross-section (b)

were prepared at 5.8 mA/cm² for 60 min, at 12.3 mA/cm² for 60 min, and at 12.3 mA/cm² for 120 min, respectively. Their SEM images and EDX analysis are shown in Fig. 5. The Al layer has a bulk grain microstructure prepared at a low current density ($J=5.8 \text{ mA/cm}^2$) (Fig. 5(a)). Nevertheless, it has a spherical grain structure at relatively high current density ($J=12.3 \text{ mA/cm}^2$), as shown in Fig. 5(b). In Fig. 5(a), there are many pinholes in Al layer, which results in the less compact surface. The Al deposition with spherical equiaxed grains is more compact than that with bulk grains. It is quite different for the microstructures obtained at high and low current. The nucleation rate of a new grain increases more rapidly than its growing rate as the current density rises. At a relatively high current density, the nucleation rate controls the growth of Al deposition. It promotes the formation of the equiaxed crystal grains with spherical shape [15]. Thanks to no pore and crack, the deposition (Fig. 5(b)) is more smooth and compact than that shown in Fig. 5(a). The grains grow fully and their size increases with the rising of deposition time (see Figs. 5(b) and (c)). The EDX analysis of this layer (Fig. 5(b)) shows that the as-deposited layer consists of Al (Fig. 5(d)).

The deposition was prepared at 12.3 mA/cm² for 120 min on AZ31 substrate. The SEM image and linear composition analysis of its cross-section are shown in Fig. 6. The Al layer is uniformly deposited on the substrate (Fig. 6(a)). A close bonding among Al, zinc and the substrate is beneficial to protect the AZ31 Mg



Fig. 5 SEM images of as-deposited Al depositions on AZ31 magnesium alloy surface obtained at 5.8 mA/cm² for 60 min (a), 12.3 mA/cm² for 60 min (b) and 12.3 mA/cm² for 120 min (c) and EDX spectrum (d)



Fig. 6 SEM image (a) and linear composition distribution (b) of as-deposited Al deposition cross-section on AZ31 obtained at 12.3 mA/cm^2 for 120 min

alloy substrate. According to the black arrow direction in Fig. 6(a), the linear analysis was obtained (Fig. 6(b)). It indicates that the Al layer has a thickness of about 13 μ m. A white-colored zinc-immersion layer exists between the Al deposition and Mg alloy substrate.

4 Conclusions

1) A compact activation film on AZ31 Mg alloy surface was obtained within 10 min in 400 mL/L HF acid solution. Then, a relatively compact zinc film is prepared after immersion for 20 min. Those optimized pretreatments were successfully used for Al-electroplating process from TMPAC-AlCl₃ ionic liquid.

2) A compact silvery-colored satin Al layer with spherical-shape equiaxed grains was electroplated at constant current 12.3 mA/cm² from TMPAC-AlCl₃ ionic liquid with 50% content benzene.

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AZ31镁合金离子液体镀铝前处理

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摘 要:通过优化镁合金活化及浸锌前处理工艺,在前处理后的镁合金AZ31表面上实施电镀铝。采用SEM/EDX 以及极化曲线等手段对镁合金表面上的膜层或镀层进行表征。结果表明,可用于离子液体电镀铝的镁合金前处理 工序为碱洗、酸洗、HF活化(400 mL/L 40% HF, 10 min)、浸锌(20 min)、除水工序。通过该工序,可在镁合金表面上获得致密的浸锌层。采用TMPAC-AlCl₃离子液体直流电镀铝,可获得致密的银白色电镀铝层。 关键词:镁合金;电镀铝;前处理;浸锌;离子液体

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