Adhesivity of Al Electroplated Films on Mg-Al-Zn Alloys with an Al-Mg Intermetallic Compound Focus

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ABSTRACT

To clarify the relationship between adhesive strength of Al electroplating film and Mg alloy substrate, the amounts of γ-phase (Mg21Al12) and α-phase (Mg solid solution phase) in Mg alloy surface was investigated. Al electroplating film on Mg alloy was formed by current pulse electrolysis in AlCl3-1-ethyle-3-methylimidazolium chloride mixture ionic liquid at 283 K. It was found that the adhesive strength was affected by the ratio of γ-phase in the Mg alloys and it increased with increasing ratios of γ-phase on the Mg alloy surface. The results suggest that the adhesive strength of the electrodeposits on the γ-phase is stronger than that of the α-phase due to little oxide formation on the γ-phase.

Keywords : Ionic Liquid, Al Electroplating, Mg Alloys, Adhesive Strength

1. Introduction

Recently Mg alloys have attracted attention in the fields of automobile, aerospace, and electronic devices, due to the light weight, high specific strength, excellent electrical conductivity, and electromagnetic shielding properties. However Mg alloys have poor corrosion resistance in atmospheric environments. Commonly, chemical conversion or anodizing processes are applied to improve the corrosion resistance of Mg alloys, and as the treated surfaces possess insulting properties, the use of Mg alloys in electronic components is limited. A conductive coating would offer great advantages and be of great interest in precision instrument manufacture. Electroplating offers many advantages in developing conductive coatings; low cost, rapid processing, and simple control of the film thickness. Electroplating of Al on Mg substrates also has many advantages such as good corrosion resistance, inhibition of galvanic corrosion between Mg and Al, and good recycling characteristics.

Electrodeposition of Al does not occur in aqueous solutions because decomposition of water occurs preferentially to Al electrodeposition, and ionic liquids at room temperature have been the medium for electrodeposition of Al. Ionic liquids offer attractive features such as low vapor pressure, good ionic conductivity, and a wide electrochemical potential window in the ionic liquids. The electrodeposition of metallic Al coatings from AlCl3-1-ethyle-3-methylimidazolium chloride (AlCl3-EMIC) has been proposed as a new method to provide protective Mg alloys.

Electroplating of Al on Mg alloys results in poor adhesion because of the exchange reaction between Al(III) in the electrolyte and Mg atoms from the substrate, and the reaction starts immediately when the Mg alloys are immersed in the electrolyte. The Al deposit formed by the exchange reaction has a sponge-like morphology and very poor adhesion. This exchange reaction is greatly promoted at higher temperatures.

In previous study, the optimum temperature for the electrolyte to inhibit the exchange reaction was determined to be 283 K. At this temperature, pulse current electrolysis ensured the formation of dense Al electrodeposits. In that study, a reasonably good Al electroplated film was formed on AZ121 (12 mass% Al, 1 mass% Zn) alloy. However on AZ31 (3% Al, 1% Zn), AZ61 (6% Al, 1% Zn), and AZ91 (9% Al, 1% Zn), only relatively poorly adhesive films were formed. Further, the previous study showed that adhesion strength of Al plating film on AZ91 is stronger than that of the film on AZ31, suggesting that the adhesive strength may depend on the Al concentration in the AZ alloys.

In further investigation, it was found that substrate structure is more closely related to the adhesive strength of Al electroplating film to AZ alloy substrates than the Al concentration in AZ alloys. In this paper, we report the adhesive strength of electroplating of Al on pure Mg, AZ31, AZ61, AZ91, and AZ121 and discuss the relationship between the adhesive strength and composition of the substrates.

2. Experimental

Anhydrous aluminum chloride (AlCl3, Kanto chemical, 98% pure) and 1-ethyle-3-methylimidazolium chloride (EMIC, MERCK, 98% pure) were used as received. The electrolyte was prepared by mixing AlCl3 and EMIC at a molar ratio of 2:1 in an Ar atmosphere glove box. Impurities in the electrolyte were removed by immersion of pure Al wire in the electrolyte for 2 days.

In the study, pure Mg (Nilaco, 99.9%), AZ31 (3 mass% Al, 1 mass% Zn), AZ61 (6 mass% Al, 1 mass% Zn), AZ91 (9 mass% Al, 1 mass% Zn), and AZ121 (12 mass% Al, 1 mass% Zn) alloys were used. The AZ series of alloys were supplied by Toyota Motor Corporation. All of the specimens were used as working electrodes, with a surface area of 7 cm², and with a pure Al plate used as the counter electrode. Pure Al wire was used as the reference electrode. Prior to the electrodeposition, the specimen substrates were polished and ultrasonically washed by acetone, then in the next step polished again in the glove box, to remove any oxide layer just before the electroplating. The electroplating experiments were carried out in the glove box under Ar by current pulse electrolysis with the conditions: frequency 4 Hz, duty ratio 80%, current density 1.7 mA cm⁻², and charge volume 15 C cm⁻². The ionic liquid was maintained at 283 K by water cooling.

The adhesive strength of the Al film to the Mg alloy substrates was measured by a pull-off adhesion tester.
3. Results and Discussion

Silver white surfaces were formed on all substrates at the electroplating. In the AZ series alloys, there are no obvious differences from the Al electroplated surface. Figure 1 shows photographs of the Al electroplated on (a) pure Mg and (b) AZ121. The photos show small blisters on the pure Mg substrate (a), and there are no blisters on AZ121 substrate. This result suggests that the Al electroplated film on pure Mg is not perfectly adhesive in all areas.

Table 1 shows the results of the adhesion strength tests of the Al electroplated films on pure Mg, AZ31, AZ61, AZ91, and AZ121; with increases in the Al content of the specimens, the adhesion strength increases.

Then, to better understand the effect of the Al content in the Mg alloy substrates on the adhesion of the Al electroplated films, the surface morphology and cross-sections of the electroplated films were observed by SEM and EDS.

Figure 2 shows surface SEM images of the electrodeposits formed on (a) pure Mg and (b) AZ121. In (b) AZ121, the substrate is covered with dense Al electrodeposits without defects and with crystal sizes of 2–5 μm, and this surface appearance was similarly observed in the other AZ series alloys. However with (a) pure Mg there were pinholes observed on the surface, and this could be ascribed to a more intense exchange reaction on the pure Mg substrate compared with the other substrates. This would be a reason why the adhesion strength of the Al electroplated film on the pure Mg was weaker than on the other substrates.

Figure 3 shows cross-sectional SEM images of electrodeposits formed on (a) AZ31 and (b) AZ121. Relatively flat Al electroplated films are formed on both substrates. In (a) AZ31, the electroplated films displayed crevices between the Al electroplated film and the substrates. However, there were no crevices in the AZ121 cross-section. This may suggest that the adhesion of Al electrodeposits improved with increases in the Al concentration in the Mg alloy substrate.

The Mg alloys consist of a Mg solid solution phase (Mg-rich α-phase) and an intermetallic phase (γ-phase, Mg7Al3 and a β-phase, Mg2Al3). When the compositions of the substrates are different, the adhesion strength of Al electroplated films changed as shown in the results in Table 1. In the alloy substrate, small particles from 0.2 to 1.0 μm were observed in the SEM images. The EDS analysis was performed on the small particles, and the particles composition were close to Mg 3 to Al 2 (atomic ratio), from this the following discussion assumes that the intermetallic phase on the substrate is only γ-phase. To compare the adhesive strength of the Al electroplated films on the α-phase and that on the γ-phase, the EDS mapping profile of the interface between the Al electroplated film and the AZ121 substrate was measured for Al, Mg, and O, and Fig. 4 shows the SEM images and EDS element mapping images of Al, Mg, and O. From the distribution of Al, the strong signal of the top part is the electroplated film, parts with medium strength Al signals were detected in the AZ121 substrate representing γ-phase (Mg7Al3) (the parts surrounded by circles). From the distribution of O, there are small amounts of oxygen at the interface between the Al electroplated film and AZ121 substrate. This may be due to a small amount of dissolved oxygen or water in the ionic liquid. The presence of oxygen in the Mg profile may be due to Mg oxide formed at or after the dry polishing. However it is shown that the oxygen content on the γ-phase is lower (the parts surrounded by circle) than that on the α-phase. Therefore the adhesive strength of...
the Al electroplated film on the γ-phase strongly depends on the amount of γ-phase because the amounts of oxide on the γ-phase is lower than in other parts. It is considered that the oxide formation rate on the γ-phase is slower than on the α-phase because the reactivity of Al with oxygen is lower than that of Mg, and as a result the exchange reaction between the Al ions in the electrolyte and the Mg in the substrate are inhibited on the γ-phase.

The ratio of γ-phase on each of the Mg alloy surfaces was calculated from the areas of the γ-phase and other areas (α-phase) on the surface SEM images. Figure 5 plots the relationship between the ratio of the γ-phase on the Mg alloys and the adhesive strength of the Al electroplated film on the Mg alloys. The adhesive strength increased linearly with increases in γ-phase on the Mg alloy surface, and the adhesive strength of pure Mg is about 0.1 MPa smaller than that suggested by the estimated line. The solid line in Fig. 5 shows the adhesion strength of Al electroplated film on α-phase dispersed containing γ-phase, the γ-phase does not exist in α-phase at contents close to pure Mg. The α-phase probably consists of Mg, 1 mass% Zn, and a little Al. It is considered that oxides tend to form in the order of Mg, Al, and Zn, and so that there is less oxide on the α-phase than on pure Mg. The differences in the amounts of the oxides can possibly be ascribed to their difference in adhesive strength on pure Mg and α-phase. Overall, it is concluded that the adhesion of Al electrodeposits is affected by the amount of oxides on the substrates. That is, in this study, it is considered that the increase in the ratio of the γ-phase with less oxide formation on the Mg alloy is strongly related to the increase in the adhesive strength.

4. Conclusions

In the Al electroplated films formed on different Mg-Al alloys in AlCl3-EMIC ionic liquid, it was found that the adhesive strength of the Al electroplated film and Mg alloy substrate showed the following relationship.

- The adhesive strength was affected by the ratio of γ-phase in the Mg alloys and it increased with increasing ratios of γ-phase on the Mg alloy surface.
- On the γ-phase, the adhesive strength of the electrodeposits is stronger than that of the α-phase, because there is little oxide formation on the γ-phase.

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