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Contributed Paper

Effect of Heat-treatment on the Corrosion Resistance of AZ91 Coated with Aluminum Sputtering Film

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ABSTRACT

Magnesium alloys, which are lightest in the practical metals, have several superior characteristics such as dimensional stability and electromagnetic shielding. These characteristics would expect to be applied in many fields. While, magnesium alloys show low corrosion resistance. It is necessary to be improved it. In this study, we aim to improve the corrosion resistance of AZ91 with aluminum film by the sputtering deposition. Polarization curve measurement evaluated corrosion rate using the Tafel extrapolation method. SEM observation was carried out for surface observation of samples. Although corrosion resistance is not improved only by aluminum sputtering deposition due to defects in film, heat treatment for 3 hrs at 553K after sputtering deposition improved corrosion resistance of the AZ91 alloy. In the case of heat treatment at 623K and 673K for 3 hrs, magnesium atoms diffused through the aluminum film and reached to the surface of the film. Consequently, the heat treatments at these temperatures degraded corrosion resistance of the films. One the other hand by the heat treatment at 553K, corrosion resistance of AZ91 coated with the aluminum film increased with increasing heat treatment time. Thus, optimization of heat treatment after sputtering is important to obtain high corrosion resistance of the AZ91 magnesium alloy in this method.

Keywords: Magnesium alloy, corrosion, Aluminum, sputtering

1. INTRODUCTION

Magnesium alloy has lower specific gravity compared to other structural metals, the advantage of high specific strength, excellent dimensional stability, vibration absorption, cutting resistance and recyclability [1-3]. From an engineering view point, the application of magnesium alloys is expanding. For example, it is expected as a lower specific gravity material for efficiency of transportation equipment-related fields, particularly including automotive. However, magnesium alloy shows a lower potential than other metal materials on the ionization tendency. Therefore, improvement of corrosion resistance is important in order to utilize the superior features of magnesium [4]. Several coating methods to improve corrosion resistance have been reported in recent years [5,6]. In order to improve the corrosion resistance of the Mg alloy, we investigated the effect of aluminum film on the electrochemical properties of AZ91 alloy.

EXPERIMENTAL

1. Sample Preparation

Coating deposition was performed with a facing targets-type magnetron sputtering apparatus [Osaka vacuum, FTS-R2]. A1070 aluminum alloy was used as target in the form of 160mm × 100mm × 10mm. Borosilicate glass and AZ91 magnesium alloy plate of 25mm square were used as substrates. The AZ91 plated were wet-polished as a pretreatment, and then mirror-finished by buffing with 1 μm alumina. All substrates were cleaned ultrasonically with acetone, ethanol and propanol in the sequence for 10 min, respectively. The sputtering system was evacuated to a vacuum better than 5×10^{-4} Pa prior to deposition. Sputtering was carried out at 0.24 Pa of Ar atmosphere. During deposition, radio frequency power (13.56MHz) was fixed at 980W without substrate heating. After the deposition, each sample was heat treated in Ar atmosphere at 553K for 1, 3 and 9 hrs. Microstructure of these samples were observed by a SEM [JEOL, JSM-5900LV].

2. Polarization Curves Measurement

The AZ91 alloy with aluminum film was measured polarization curves to examine the basic electrochemical properties. Polarization curves measurement was used potentiostat [Bio logic, SP150]. Polarization curves measurement was carried out using a typical three-electrode method. Each electrode was used the Ag/AgCl (3.33 kmol·m-3KCl) electrode as a reference electrode, a Pt electrode as a counter electrode and the sample electrode reaction area of 1.0×10^{-4} m^2 in the working electrode, respectively. Polarization curves measurement was carried out in 3.5 mass% NaCl aqueous solution(pH = 5.35) as corrosion solution, and electrochemical cell that held 298K was degassed thoroughly using a high-purity nitrogen gas. Scanning of potential was carried out from 1.6 V to 0.0 V at a scan rate of 0.5×10^{-3} V·s-1, and recorded the logarithm of the current density and the potential. The corrosion rate of each sample was determined based on the result of the polarization curve measurement. Further, to obtain stable results, scanning for potential was started after pre-immersed for 30 minutes.

RESULTS AND DISCUSSION

Figure 1 shows results of the polarization curve measurements. Aluminum film on glass substrate is shown in Figure 1(a), AZ91 magnesium alloy substrate Figure 1(b), AZ91 alloy with aluminum film Figure 1 (c), AZ91 alloy with aluminum film annealed at 553K for 3 hrs in Ar atmosphere Figure 1 (d), AZ91 alloy with aluminum film annealed at 623K for 3 hrs in Ar atmosphere Figure 1 (e), and a AZ91 alloy annealed at 673K for 3 hrs in Ar atmosphere Figure 1 (f), respectively. From the results of the polarization curve measurement, corrosion potential (E_{corr}) of each sample was -1.20, -1.50, -1.42 and -1.32V, respectively. The corrosion current (I_{corr}) of each sample was determined using the Tafel extrapolation method. It was as follows 3.59×10^{-4}, 0.94, 99.4, 2.70×10^{-2}, 46.4, and 3.78 A/m^2, respectively.

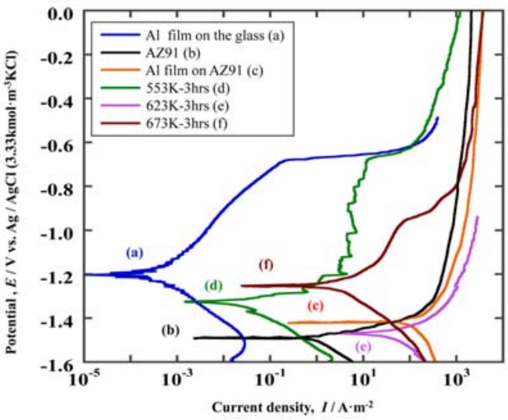

Figure 1. Polarization curve of samples measured in 3.5 mass % NaCl solution at 298K; Al film on grass substrate (a), AZ91 magnesium alloy substrate (b), AZ91 alloy with aluminum film (c), AZ91 alloy with aluminum film annealed at 553K for 3 hrs (d), AZ91 alloy with aluminum film annealed at 623K for 3 hrs (e) and AZ91 alloy with aluminum film annealed at 673K for 3 hrs (f) [7]. All samples were annealed in argon atmosphere.

E_{corr} or I_{corr} in Al film on glass substrate is the target value of our study. In comparison with Figure 1 (b), E_{corr} and I_{corr} of Figure 1 (c) are high. It can be considered that Al film promoted the cathode reaction. In comparison Figure 1 (c) with Figure 1 (d), the corrosion potential is further increased, by annealing at 553K for 3 hrs after deposition. The corrosion rate is significantly reduced. Thus, the corrosion resistance is improved. It can be thought that the corrosion rate is reduced by suppression of the anode reaction by Al rich layer that produced at Al film/substrate interface due to thermal diffusion. In this case of heat treated at 623K and 673K for 3 hrs, magnesium atoms diffuses through the aluminum film and reached the surface of the film. Therefore the heat treatments at these temperatures degrade corrosion resistance of the films. Figure 2 shows results of surface observation by SEM before heat treatment and heat treated at 553K for 1, 3 and 9 hrs. Figure 3 shows the results of cross section observed by SEM. Defects are found on the surface of the samples before heat treatment and heat treated for 1 hr. However, defects are not found on the surface of heat treated for 3 and 9 hrs, because of recovery of the defects on surfaces by heat treatments. According to the results of cross section observation by SEM, gaps were seen at the interface between Al film and substrate. It is thought that the gaps formed by peeling of the film during cutting. While, adhesion of the film and the substrate was recognized in partial regions in heat treatment for 1 hr. In the cases of heat treated for 3 and 9 hrs, peeling of the films was not observed. Therefor the long heat treatment shows improvement of adhesion between Al film and substrate by thermal diffusion. Figure 4 shows results of the polarization curve measurements in the influence of the heat treatment time. AZ91 alloy with aluminum film annealed at 553 K for 1 hr in Ar atmosphere Figure 4 (g), AZ91 alloy with aluminum film annealed at 553 K for 3 hrs in Ar atmosphere Figure 4 (d), and AZ91 alloy with aluminum film annealed at 553 K for 9 hrs in Ar atmosphere Figure 4 (h). From the results of the polarization curve measurement, corrosion potential (E_{corr}) of each sample was -1.13, -1.33, and -1.43V, respectively. The corrosion current (I_{corr}) of each sample was determined using the Tafel extrapolation method. It was as follows 2.37×10^{-2}, 1.26×10^{-2} and 7.50×10^{-3} A/m^2, respectively. The corrosion rate tends to be reduced with heat treatment time, and the corrosion resistance is improved in longer heat treatment time. Figure 5 shows Evans diagram for polarization of samples were annealed in Ar atmosphere after deposition.

Anodic reaction and Cathodic reaction is inhibited by annealing at 553K after deposition. Anodic reaction is more inhibited with the heat treatment time, because of improvement of adhesion between Al film and substrate by thermal diffusion. Cathodic reaction is inhibited by heat treatment, because solution doesn't reach to the pore due to surface diffusion of aluminum film.

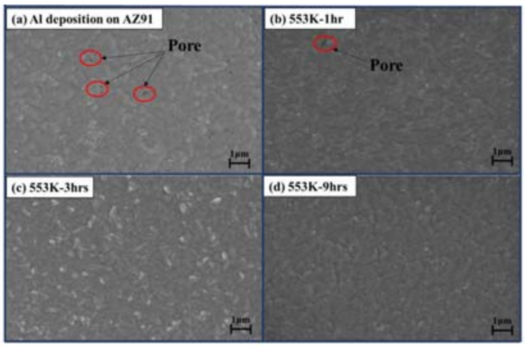

Figure 2. Secondary electron image of surface of samples; AZ91 alloy (a), AZ91 alloy with aluminum film annealed at 553K for 1 hr (b), AZ91 alloy with aluminum film annealed at 553K for 3 hrs (c) and AZ91 alloy with aluminum film annealed at 553K for 9 hrs (d).

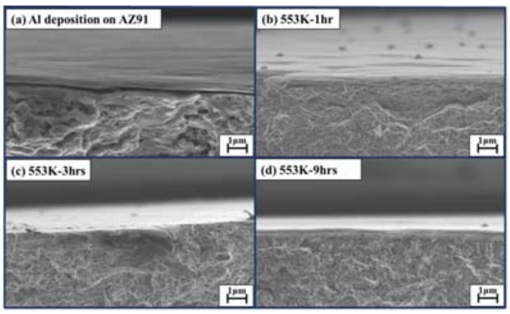

Figure 3. Secondary electron image of cross section of samples; AZ91 alloy with aluminum film (a), AZ91 alloy with aluminum film annealed at 553K for 1 hr (b), AZ91 alloy with aluminum film annealed at 553K for 3 hrs (c) and AZ91 alloy with aluminum film annealed at 553K for 9 hrs (d).

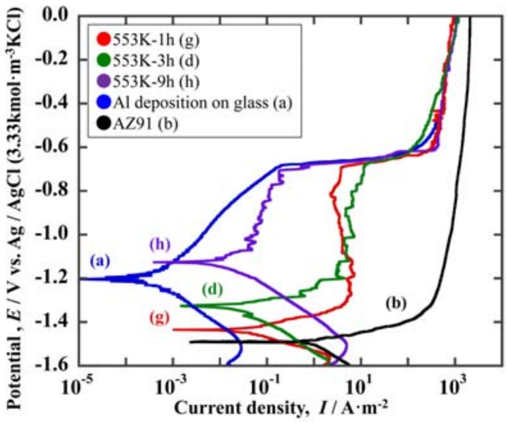

Figure 4. Polarization curve of samples measured in 3.5 mass % NaCl solution at 298K; AZ91 alloy with aluminum film annealed at 553K for 3 hrs (d), AZ91 alloy with aluminum film annealed at 553K for 1 hr (g) and AZ91 alloy with aluminum film annealed at 553K for 9 hrs (h) compared with aluminum film on the glass (a) and no coating AZ91 (b).

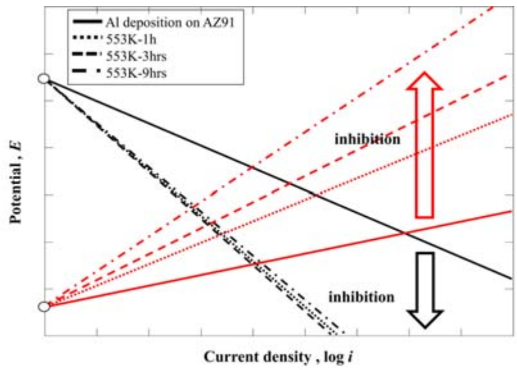

Figure 5. Evans diagram for polarization of Al deposition on AZ91. Samples were annealed in argon atmosphere after deposition.

CONCLUSIONS

The corrosion resistance was not improved only by the aluminium sputtering deposition, but also by performing heat treatment after deposition at 553K. The heat treatment at higher temperatures deteriorated the corrosion resistance due to diffusion of magnesium atoms to the surface. The corrosion rate tends to be reduced, and the corrosion resistance is improved with heat treatment at 553K. Recovery of the pore read inhibition of cathodic reaction in aluminum film, because no contact between aluminum film and diffusion layer. The samples heat treated for 9 hrs showed the best corrosion resistance in this study. It was about 1/120, in comparison with AZ91 substrate. Thus, utility of aluminum spattering film was shown for improving corrosion resistance of AZ91D magnesium alloy.

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