Plasma Electrolytic Oxidation of AZ91 Mg Alloy in the Sodium Stannate Electrolyte

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The effect of sodium stannate on Plasma electrolyte oxidation (PEO) process of AZ91 Mg alloy was systematically investigated. The oxide layer formed on an AZ91 Mg alloy created using an electrolyte containing sodium stannate formed a much thicker layer consisting of: MgO, SnO, Mg₂SiO₄, and MgF₂. The result of EDS analysis shows a tin enriched zone at the oxide layer/substrate interface. Corrosion resistance of the sample coated from the electrolyte containing sodium stannate was determined to be superior to that of the sample coated from the electrolyte without sodium stannate. As a result of salt spray test for 120 hrs, severe filiform corrosion is observed on the thin oxide layer of AZ91 Mg alloy without sodium stannate. However, the sample of the electrolyte containing sodium stannate shows localized pitting corrosion. Tin ions in the electrolyte influence on the growth rate of the oxide layer, especially resulting in a formation of dense barrier layer. The co-existence of dense MgO and SnO in the oxide layer could improve the corrosion resistance of the AZ91 Mg alloy. [doi:10.2320/matertrans.MC200797]

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1. Introduction

Magnesium alloys have a superior strength-to-weight ratio, high dimensional stability, lower density, better electromagnetic shielding than several other alloys but relatively poor corrosion resistance, especially in acidic environments and the saltwater conditions, because Mg is electrochemically the most active metal.¹,² One of the more promising ways to overcome corrosion is to apply a coating to the surface of the Mg alloy. Various surface treatments such as electrochemical plating, conversion coating and anodizing have been used to increase the corrosion resistance of magnesium alloys. Conversion coatings for Mg alloys have traditionally been based on hexavalent chromium (Cr⁶⁺) compounds, but have a lot of problems concerning health and environment issues.³,⁴ Recently, the toxicity of hexavalent chromium has imposed a strict limitation on the use of the chromate conversion coating. Several non-chromate solutions are thus developed, such as phosphate, stannate, rare earth salt and phosphate/permanganate solutions. These processes also have many disadvantages including only a marginal improvement of corrosion resistance, complicated manufacturing process, low productivity, and wastewater problems. Therefore, it is worth developing a new process of surface treatment to solve the above problems.

Plasma electrolytic oxidation (PEO) process is a relatively new surface treatment method to form oxide layer on magnesium alloys using an eco-friendly process.⁵⁻⁷ The constituents of surface oxides contribute to form the substrate and the anodic complexes form the electrolyte. In general, microstructures of oxide layers in the PEO process consist of an outer porous layer and an inner barrier layer.⁶,⁸ The composition and quality of the inner barrier layer have an influence on the corrosion behavior of coated Mg alloy surface. The structures created through the PEO process require strict control of various processing conditions, including: chemical composition, concentration of electrolyte, current density, and the alloy composition of substrate. Especially, the chemical composition of the electrolyte exerts a considerable influence on the properties and formation of an effective oxide layer for Mg alloy.⁹ Gonzalez-Nunez et al.⁹ reported that the conversion coating mainly consists of crystalline magnesium tin oxide nucleated on a corrosion film intimately contacted with the magnesium substrate. The thin layer formed by precipitation of MgSnO₃ at cathodic sites improves on the corrosion resistance of the magnesium alloy. The effects of solution composition and temperature on the microstructure and corrosion resistance of stannate conversion coatings on AZ61 magnesium alloys were investigated by Lin et al.¹⁰ The results showed that the corrosion resistance of the conversion coating was improved with finer particles, which were preferably formed at less alkaline solution with higher tin ion contents. Therefore, tin ions have a good influence on the corrosion resistance on the magnesium alloys during the conversion coating. However, a systematic study of the effects of tin ion in the electrolyte to improve on the corrosion resistance of magnesium alloys during the PEO process has not been well documented in the literature.

In this study, the effects of sodium stannate in the electrolyte on surface morphology, microstructure and chemical composition of the oxide layer of an AZ91 Mg alloy were investigated. Corrosion behavior of the coated AZ91 Mg alloy was also studied using potentiodynamic polarization test.

2. Experimental Procedures

Chemical composition of AZ91 alloy used in this study was analyzed to be 8.29 mass% of Al, 0.83 mass% of Zn, and 0.31 mass% of Mn. AZ91 Mg alloy plate with 2 mm thick cut into samples with 30 mm × 50 mm. Prior to the experiments, the samples were polished with 1000 grit silicon carbide paper, rinsed with de-ionized water, and ultrasonically cleaned in ethanol. The samples were dried in warm air.
after cleaning. PEO process was conducted with 20-kW equipment which has a glass-vessel container with a sample holder as the electrolyte cell, a stainless steel used as the cathode, stirring and cooling system. The PEO process was performed in KOH(5 g/L) + KF(5 g/L) + Na$_2$SiO$_3$(3 g/L) electrolyte with and without addition of Na$_2$SnO$_3$(3 g/L). Temperature of electrolyte was maintained at 20 to 30°C during PEO process. Applied current density was 2 A/dm$^2$. Surface morphology and cross-sectional image of the ceramic layer were observed using a scanning electron microscope (HITACHI, S-4800), coupled to energy dispersive X-ray spectroscopy (EDS). Phase analysis of the oxide layer was analyzed using X-ray diffraction with Cu-K$\alpha$ radiation and excitation source at a grazing angle 2°. Potentiodynamic polarization to evaluate corrosion resistance of the coated AZ91 Mg alloy was carried out in 3.5 mass% NaCl solution using Reference 600 Potentiostat (Gamry Instruments). After the electrochemical testing system became stable, scans was conducted at a rate of 1 mV/s from −0.25 V versus open circuit potential to 0.25 V versus the reference electrode in a more noble direction. Salt spray test was conducted under conditions described in ASTM-B117 for 120 hrs at 35°C. Salt spray test consists of exposing the coating surface to 5 mass% NaCl solution. For surface chemical analysis, X-ray photoelectron spectroscopy (XPS) was performed with a ESCA(PHI 5800) system.

3. Results and Discussion

Figure 1 shows surface morphology of oxide layer in an AZ91 Mg alloy coated from two different electrolytes for 5 min. It is seen that the surface morphology coated from the two electrolytic solutions has porous microstructures and some round-shaped shrinkage pores observed in the crater centers. The surface of the sample coated from electrolyte without sodium stannate consists of small spherical and longish pores. In general, the oxide layer formed on the AZ91 Mg alloy applied in the PEO process composed of two different layers; an outer porous layer and an inner barrier layer, which is very thin layer with the thickness of 100~300 nanometers.$^{5,8,11}$ The pores exist only in the outer porous layer and interconnect with each other, but do not cross-over through the inner barrier layer to the AZ91 Mg alloy substrate. Thickness of oxide layer is measured to be ~2.3 μm (Fig. 1(c)). In contrast, the sample coated from the electrolyte with sodium stannate exhibits relatively coarse pores and pores of ≤1 μm are well separated and evenly distributed over the surface and the thickness of the oxide layer is ~6 μm (Fig. 1(d)). The thickness of barrier layer the sample coated from the electrolyte with and without sodium stannate is around 250, 200 nm, respectively. The coating application parameters during the PEO process such as breakdown voltage, critical voltage, and final voltage strongly depend on the types of electrolyte. The type of electrolyte is one of the important factors influencing the growth rate of the coated oxide layer. The growth rate in the electrolyte with sodium stannate is much higher than that in the electrolyte without sodium stannate. Therefore, it is believed that tin in the electrolyte influences the growth rate of the oxide layer.

The cross-section images of the oxide layer in the AZ91 Mg alloy coated from the electrolyte with sodium stannate with a variation of the coating time are shown in Fig. 2. The thickness of the oxide layer coated for 2 min is about
1.5 µm. The oxide layer on the AZ91 Mg alloy exhibits compact and dense pores. The coating thickness increases with an increase in the coating time (Fig. 2(d)). As the oxide layer grows with increased coating times, it is seen that the porous layer grows rather than the barrier layer. The pores are randomly distributed in the porous layer. Especially, in the case of the oxide layer coated for 10 min, relatively sparse big pores are seen on the porous layer as shown in Fig. 2(c). Guo et al.\textsuperscript{12) reported that instantaneous temperature in the micro-arc zone could reach several thousand degrees, so the surrounding electrolyte was relatively cool compared with the molten oxide. These pores served as micro-arc discharge channels through which the molten oxide was thrown out of the surface.

The result of the EDS analysis of surface for the oxide layer is shown in Fig. 3. The component of the oxide layer in the electrolyte containing sodium stannate consists of oxygen, tin, silicon, magnesium, and aluminum. The two later elements come directly from the oxidation of substrate. Presence of tin and oxygen indicates that components of electrolyte have intensively incorporated into the micro-arc oxidation reactions to form oxide layer on AZ91 Mg alloy. The presence of elements derived from the electrolyte also indicates that the composition of oxide layer can be changed by adjusting the components and concentration of the electrolyte.

Figure 4 shows the elemental distribution through the cross-section of the oxide layer in the electrolyte containing sodium stannate coated for 5 min. EDS depth profile clearly showed the strong peak of Tin at the interface of oxide layer and substrate. Also, the content of Mg within the oxide layer is lower than that in the alloy substrate and it gradually increases to the direction of substrate. In reverse, content of oxygen gradually decreases.

XRD patterns for the oxide layer of AZ91 Mg alloy coated from electrolyte with sodium stannate are shown in Fig. 5. Oxide layers of the AZ91 Mg alloy consists of MgO, SnO, Mg\textsubscript{2}SiO\textsubscript{4}, and MgF\textsubscript{2}. The XRD patterns show that MgO is the main oxide residing on the coated AZ91 Mg alloy. The existence of SnO peaks indicates that tin ions in the electrolyte are participants in the oxide formation reaction and have been incorporated into the oxide layer.

Figure 6 shows an XPS survey spectrum of the oxide layer in an AZ91 Mg alloy coated with the electrolyte containing sodium stannate for 5 min. Specimens are subjected to etching by argon ion beams. Compositions of the oxide layer are composed of tin, magnesium, oxygen, aluminum, silicone. Other impurities such as N, Ca are

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also detected. To observe the chemical condition (binding condition) of elements composing the surface layer, an individual spectrum is measured for Sn4d to clarify the reacting products in the oxide layer formed in the electrolyte with sodium stannate. The binding energy of 26.5 eV analyzed by XPS spectra (Fig. 7) indicates the formation of SnO,\textsuperscript{13}) consistent with the XRD analysis.

Corrosion resistances for an oxide layer on AZ91 Mg alloys coated with the electrolyte, with and without sodium stannate are evaluated through an electrochemical potentiodynamic polarization test, conducted in a 3.5 mass% NaCl solution. Figure 8 exhibits the potentiodynamic polarization curve of the coated AZ91 Mg alloys formed from different solutions. It is well known that corrosion potential and current density are often used to characterize the corrosion protective properties of the oxide layer.\textsuperscript{14}) In general, it was reported that the high corrosion potential and low corrosion current density, results in a low corrosion rate and good corrosion resistance of the oxide coatings.\textsuperscript{15}) As shown in
Fig. 8 Potentiodynamic polarization curves of oxide layer on AZ91 Mg alloy coated from the electrolyte with/without sodium stannate.

Fig. 9 Potentiodynamic polarization curves of oxide layer on AZ91 Mg alloy with coating time.

Table 1 Results of potentiodynamic corrosion tests of AZ91 Mg alloy in 3.5 mass% NaCl solution.

<table>
<thead>
<tr>
<th>Coating time</th>
<th>$E_{corr}$ (V)</th>
<th>$i_{corr}$ (A/cm²)</th>
<th>$R_p$ (Ω/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 min</td>
<td>−1.55</td>
<td>$3.07 \times 10^{-7}$</td>
<td>$1.02 \times 10^6$</td>
</tr>
<tr>
<td>5 min</td>
<td>−1.52</td>
<td>$1.26 \times 10^{-7}$</td>
<td>$3.09 \times 10^5$</td>
</tr>
<tr>
<td>10 min</td>
<td>−1.39</td>
<td>$1.93 \times 10^{-10}$</td>
<td>$1.73 \times 10^8$</td>
</tr>
</tbody>
</table>

$$R_p = \frac{b_a^+b_c}{2.303i_{corr}(b_a + b_c)}$$

The results of the potentiodynamic polarization test are summarized in Table 1. The corrosion potential is approximately $−1.39$ V (vs. SCE) in the oxide layer on an AZ91 Mg alloy coated for 10 min. It is much higher than that of the two different conditions. The polarization resistance increases with increased coating times. Especially, the polarization resistance of the oxide layer on AZ91 Mg alloy exhibits $1.73 \times 10^8$.

The results of salt spray testing for 120 hrs in this study are shown in Fig. 10. Shi et al. reported that the corrosion of the coatings in Mg alloys initiated from tiny pits, progressed into pitting corrosion, and finally became localized or filiform corrosion. The main corrosion type was pitting corrosion in Mg alloy with an electrolyte containing Cl⁻ ion. It was observed that the corrosion of the coated sample initiated from localized pitting. Then it developed into filiform corrosion or general corrosion. The results of salt spray testing are in agreement with the corrosion resistance of potentiodynamic polarization tests. Severe filiform corrosion is observed on the thin oxide layer of AZ91 Mg alloy without sodium stannate. However, the sample of the electrolyte containing sodium stannate shows localized pitting corrosion. It is clear that tin ions have a good influence on the corrosion resistance. Also, the thickness of the coatings plays an important role in the corrosion resistance of the coatings in the AZ91 Mg alloy as previous shown in Fig. 1(c), (d).
4. Conclusions

The PEO process with and without sodium stannate, when applied to an AZ91Mg alloy was investigated. The oxide layer formed on an AZ91 Mg alloy created using an electrolyte containing sodium stannate formed a much thicker layer consisting of: MgO, SnO, Mg$_2$SiO$_4$, and MgF$_2$. Corrosion resistance of the sample coated from an electrolyte containing sodium stannate was determined to be superior to that of the sample coated from the electrolyte without sodium stannate. Tin ions in the electrolyte were also found to participate in the oxide formation reaction and are incorporated in the formed oxide layer, especially resulting in a formation of barrier layer which has a positive influence on corrosion resistance. The existence of SnO in the barrier layer with the thickness of 250 nm could improve the corrosion resistance of the AZ91 Mg alloy.

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REFERENCES