Effect of Pulse Frequency on Corrosion Behavior of AZ91 Mg Alloy Treated by Microarc Discharge Oxidation Coating

In Jun Hwang¹, Young Gun Ko²*, Kang Min Lee¹ and Dong Hyuk Shin¹,*

¹Department of Metallurgy and Materials Engineering, Hanyang University, Ansan 425-791, Korea
²School of Materials Science and Engineering, Yeungnam University, Gyeongsan 712-749, Korea

The paper demonstrated the anti-corrosion properties of an AZ91 Mg alloy fabricated via microarc discharge oxidation under an AC condition with various pulse frequencies ranging from 60 Hz to 2000 Hz. The structural features and phase compositions of the coating layers were characterized by utilizing scanning electron microscope and X-ray photoelectron spectroscopy. The optimum frequency for the coating layers with thick, uniform thicknesses was found to be 500 Hz for the conditions used in this study. This fact was explained by the change in the mode of spark discharge during coating, resulting in the occurrence of surface cracks as well as the transformation of Mg(OH)₂ to MgO. Potentio dynamic polarization tests in 3.5 mass% NaCl solution revealed that the sample coated at a frequency of 500 Hz exhibited a corrosion potential of −1.42 V (vs. Ag/AgCl), suggesting a better corrosion resistance as compared to the other conditions.  [doi:10.2320/matertrans.M2010395]

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1. Introduction

Recently, growing interest has focused on the development of surface treatment methods for Mg alloys since they were most inclined to be active against corrosive environments among light metallic materials, which impeded the commercialization in various engineering applications.¹⁻⁴) To this end, active research attempts have been made recently and successful results have been reported for valve metals by a utilizing microarc discharge oxidation (MDO) technique where dielectric breakdown were readily promoted on the anode by plasma-assisted high energy.⁵⁻⁷) Depending on the substrates, metal oxide films with thin thicknesses were generated during the MDO coating so as to enhance corrosion and wear resistances. However, surface structure and resulting corrosion characteristics of the MDO-coated Mg alloys were comparatively less documented than those of Al alloys because the coating layer formed on the Mg alloys sometimes contained the surface cracks as well as many micro-pores. According to the earlier work by Yerokhin et al.,⁸) such imperfections could be controlled by knowing how to handle the coating parameters such as frequency, current density, etc., if the electrolyte used was the same. For instance, Srinivasan et al.⁹) reported using a pulsed direct current source with a lowest frequency of 10 Hz yielded relatively thick and compact coating layers, causing superior anti-corrosion properties. In their results, however, coating thickness varied with respect to frequencies ranging from 10 to 1000 Hz. Thus, it is still unclear how the frequency changes the surface morphology and corrosion response under the same coating thickness condition. This indicated that more research is necessary to gain an insight into the role of frequency during the coating. Therefore, it is pertinent to determine the frequency suitable for improving the coating characteristics of Mg alloys. In this study, MDO coatings are performed on AZ91 Mg alloys in an alternating current mode. The structure and composition of Mg alloys treated by MDO coating at various frequencies ranging from 60 to 2000 Hz are compared. The influences of frequency on corrosion resistance are also discussed based on potentio dynamic polarization behavior.

2. Experimental

An AZ91 Mg alloy plate whose chemical compositions were Mg-8.29Al-0.38Zn-0.31Mn (in mass%) was cut into 30 x 50 x 2 mm samples. Prior to MDO coating, the samples were grit-blasted mechanically with #1000 abrasive papers, rinsed with distilled water, and cleaned in pure ethanol. As illustrated in Fig. 1, a machine equipped with stirring and cooling systems was used to perform MDO coating with an applied current density of ~100 mA/cm². An electrolyte was prepared with a composition of 0.13M KOH + 0.05M KF + 0.02M Na₂SiO₃ and the temperature of the electrolyte remained constant below 30°C. Details of the MDO coating were found elsewhere.¹⁰,¹¹) To study the influence of electrical frequency on the structural change and corrosion behavior of the coating layers, four distinct conditions of 60, 500, 1000, and 2000 Hz were used. The surface and cross section images of the coating layers formed were observed utilizing a scanning electron microscope (SEM). Before using SEM, all samples were sputtered with a thin gold layer in order to avoid surface electron charging. The phase compositions of the coating layers were assessed using a Bruker X-ray diffractometer with Cu Kα radiation. For surface chemical analysis, X-ray photoelectron spectroscopy (XPS) was used. A potentio dynamic polarization testing machine, which comprised three different electrodes (substrate as a working electrode, platinum plate as a counter electrode, and Ag/AgCl as reference electrode), was utilized to evaluate the corrosion characteristics of the MDO-treated AZ91 Mg alloy. The corrosion potential ($E_{corr}$), corrosion current density ($i_{corr}$), and anodic and cathodic Tafel slopes

*Corresponding author, E-mail: younggun@ynu.ac.kr, dhshin@hanyang.ac.kr
(ba and bc) were evaluated to determine the electrochemical response. These were derived from the potentiodynamic polarization curves after Tafel extrapolation.12) First, both ba and bc can be obtained from the anodic and cathodic Tafel slopes in the polarization curves. In addition, the corrosion current density (i_{corr}) and corrosion potential (E_{corr}) can be determined at the point where the anodic and cathodic Tafel slopes meet together.

3. Results and Discussion

Figure 2 presents SEM micrographs revealing the surface coating layers formed in the silicate electrolytes at various frequencies ranging from 60 to 2000 Hz. Irrespective of the applied frequency conditions used here, all samples coated by the MDO process contained a number of micro pores which were uniformly distributed in the coating layers. As discussed earlier, these micro pores resulted from the microarc discharge when the responding voltage exceeded the breakdown voltage.13) It is obvious that, as the frequency value increased, the average size of the micro pores was observed to decrease whereas their populations increased. The change in frequency influenced the number of transitions between the anode and cathode pulses.14) The electrical flow reversed within a short duration of time as the frequency increased, implying that the anode pulse was interrupted by the cathode pulse so that the discharging microarc became reluctantly more dispersed and even smaller.15) Thus, this would change in pore structure shown in Fig. 2. In addition, some micro cracks were seen forming on the surface of the Mg alloy sample coated via the MDO process at frequencies beyond 1000 Hz.

The thicknesses of the coating layers are shown in Table 1. Since the corrosion properties highly depended on the thicknesses of the coating layers, the thicknesses should be reasonably similar in order to consider the sole effect arising from the working frequency. The thickness of the coating layer was estimated to be \( \sim 10 \mu m \).

As shown in Fig. 3, X-ray diffraction (XRD) analyses were used to inspect the chemical composition of the MDO coatings prepared under the four different frequency conditions. As can be seen from the XRD patterns, the peaks corresponding to MgO, Mg_2SiO_4, and MgF_2 compounds were detected in their coating layers. The formation of the coating layers on the Mg alloy could be attributed to the outward migration of \( \text{Mg}^{2+} \) from the substrate and the inward migration of \( \text{SiO}_4^{4-}, \text{F}^- \), and \( \text{OH}^- \) from the silicate electrolyte under the effect of high potential. When the
concentrations of Mg$^{2+}$, SiO$_3^{2-}$, F$^-$, and OH$^-$ reached a critical value at the interface between the anode and electrolyte, film formation started to take place by the following reactions:\(^1\text{6,17})\)

\[
\begin{align*}
\text{Mg}^{2+} + 2\text{OH}^- \rightarrow \text{Mg(OH)}_2 \rightarrow \text{MgO} + \text{H}_2\text{O} & \quad (1) \\
2\text{Mg}^{2+} + \text{SiO}_3^{2-} + 2\text{OH}^- \rightarrow \text{Mg}_2\text{SiO}_4 + \text{H}_2\text{O} & \quad (2) \\
\text{Mg}^{2+} + 2\text{F}^- \rightarrow \text{MgF}_2. & \quad (3)
\end{align*}
\]

The XPS spectra (Mg 2p 3/2) of the Mg alloy sample coated via MDO coating at four different frequencies are shown in Fig. 4. It was established that the binding energies at 49.4 and 50.3 eV were related to the existence of Mg(OH)$_2$ and MgO, respectively.\(^1\text{8–20})\) Each peak obtained was divided into two small peaks by deconvolution work. Although the direct comparison of peak height (or intensity) was qualitative, it is apparent that the relative ratio of MgO/Mg(OH)$_2$ in the coating layers was likely to increase gradually as the working frequency increased. This suggested that the coating layer contained a large amount of Mg(OH)$_2$ for the coating at 60 Hz whilst the MgO content in the coating layer was maximized at 2000 Hz. An increase in the working frequency led to a change in the microarc discharge behavior together with a rapid transition between the anode and cathode pulses during the coating.\(^2\text{1,22})\) Accordingly, it is thought that the dehydration reaction of Mg(OH)$_2$ to induce MgO in the coating layer was promoted by increasing the applied frequency. Hence, such a transformation accompanying the volume expansion would lead to the formation of some appreciable cracks in the coating layer. This was in good agreement with the previous observation displayed in Fig. 2.

The corrosion properties of the AZ91 Mg alloys treated via MDO coating at four different frequencies were assessed by potentiodynamic polarization tests under a seawater condition in comparison to the uncoated counterpart and the results are shown in Fig. 5. The corrosion potential ($E_{\text{corr}}$), the current density ($i_{\text{corr}}$), and the anodic and cathodic Tafel slopes ($b_a$ and $b_c$, respectively) were determined from the polarization curves. The polarization resistance ($R_p$) values were calculated based on the electrochemical equation proposed by Stern and Geary.\(^2\text{3,24})\)

\[
R_p = \frac{b_a \times b_c}{2.303i_{\text{corr}}(b_a + b_c)}
\]

The results of the polarization tests are summarized in Table 2. Since the polarization resistance was inversely proportional to the current density, the sample that possessed a low corrosion density exhibited a better corrosion resistance. The sample coated at 500 Hz exhibited the lowest current density of $\sim 4.55 \times 10^{-8}$ A/cm$^2$ among the conditions in this study, implying that 500 Hz offered a better corrosion resistance as compared to the other frequencies. Also, the sample treated at 500 Hz exhibited the highest polarization resistance of $7.80 \times 10^5$ $\Omega$-cm$^2$, which was approximately one-order higher than the sample treated at 60 Hz and was also two-orders of magnitude higher than the samples treated at frequencies higher than 1000 Hz. Since, in
terms of electrochemical stability, MgO was reported to be stronger than Mg(OH)$_2$, increasing the amount of the MgO content in the coating layer was beneficial for improving the corrosion properties, so the polarization resistance increased as the working frequency increased up to 500 Hz where no cracks were detected. On the other hand above 500 Hz, micro cracks appeared. Chloride ions penetrated with ease through the micro cracks presumably working as a short circuit path, causing localized pitting corrosion. This was noxious to the anti-corrosion properties of the MDO-coated sample. Thus, we believed that a frequency of 500 Hz will be the suitable condition for MDO coating satisfying good corrosion properties.

4. Summary

The influence of the working frequency on the surface morphologies and corrosion properties of the MDO-coated AZ91 Mg alloy was studied. As the working frequency increased, several important things were noticed: the micro pores caused by the discharging microarcs decreased in size and increased in number, and surface cracks appeared due to the transformation of Mg(OH)$_2$ to MgO due to the accompanying volume expansion was accompanied. In terms of the corrosion resistance, the samples treated at 500 Hz exhibited a corrosion potential of $-1.42$ V (vs. Ag/AgCl), suggesting a better corrosion resistance than the other frequencies since the micro cracks on the coating layers allowed the penetration of the corrosion medium containing chlorine ions into the substrate. As a result, the coating with superior corrosion resistance was obtained at the frequency of 500 Hz.

Acknowledgements

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REFERENCES


Table 2 Results of the potentiodynamic polarization tests of the MDO-coated samples in 3.5 mass% NaCl solution.

<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
<th>$E_{corr}$, V</th>
<th>$i_{corr}$, A/cm$^2$</th>
<th>$b_1$, V</th>
<th>$b_2$, V</th>
<th>$R_p$, $\Omega$-cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>60 Hz</td>
<td>-1.44</td>
<td>$1.23 \times 10^{-7}$</td>
<td>0.145</td>
<td>0.208</td>
<td>$2.33 \times 10^2$</td>
</tr>
<tr>
<td>500 Hz</td>
<td>-1.42</td>
<td>$4.55 \times 10^{-4}$</td>
<td>0.167</td>
<td>0.160</td>
<td>$7.80 \times 10^2$</td>
</tr>
<tr>
<td>1000 Hz</td>
<td>-1.46</td>
<td>$1.03 \times 10^{-6}$</td>
<td>0.211</td>
<td>0.224</td>
<td>$4.58 \times 10^4$</td>
</tr>
<tr>
<td>2000 Hz</td>
<td>-1.50</td>
<td>$4.51 \times 10^{-6}$</td>
<td>0.099</td>
<td>0.102</td>
<td>$5.28 \times 10^3$</td>
</tr>
</tbody>
</table>