Immersed Corrosion Properties of the Microarc Oxidation Coating on as-cast AZ91D Magnesium Alloy

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Abstract. The microarc oxidation (MAO) technique was used to prepare the ceramic coating on the surface of as-cast AZ91D magnesium alloy. The corrosion resistance of the as-cast AZ91D alloy and the MAO coating was tested by immersion method. The microstructure of the AZ91D alloy was characterized by an inverted metallographic microscope. The corrosion morphology and composition of the MAO coating were characterized by SEM and XRD. The results showed that the prepared MAO coatings at 350V exhibited the porous morphology. After immersed in 3.5% NaCl solution for 48h, the corrosion resistance of the MAO coating was better than that of the substrate obviously.

1. Introduction
Among the nonferrous alloy structure material, magnesium alloys have lowest density from 1.7 to 2.0g/cm³ due to their hexagonal close-packed crystal structure. They have many excellent properties such as high specific strength and stiffness, good thermal conductivity, electromagnetic shielding, easy melting and casting and certain biocompatibility[1,2]. With the continuous development and demand of society, magnesium alloys have wide prospects in the lightweight components. However, their low electrode potential and loose surface film will accelerate corrosive rate when they stay in wet air or corrosive media for a long time[3,4].
In summary, proper surface protection must be carried out on magnesium alloy products before the use in order to improve their corrosion resistance. At present, with the application of magnesium alloys more and more widely, their surface treatment technology also develop rapidly, which can be divided into the following categories including chemical treatment, anodizing oxidation, metal coating and organic coating[5,6]. The microarc oxidation (MAO) developed in 1970s is a new type of magnesium alloy anticorrosion technology which overcomes the complex process disadvantage of other treatment methods. The MAO treatment is easy to operate, and the prepared coating is hard and uniform in thickness, which gives magnesium alloy better wear resistance and corrosion resistance. The MAO technique is especially suitable for the use of the friction components in severe environment[7-9]. In this paper, the ceramic coating on the surface of as-cast AZ91D magnesium alloy was obtained by MAO treatment. The effect of oxidation time on morphology of the MAO coating at 350V was studied. The corrosion resistance of the magnesium alloy substrate and the MAO coating during the immersion process was also discussed.

2. Experimental
The materials used in the experiment were as-cast AZ91D magnesium alloy. The cast ingot was cut into the samples with the size of 15mm×10mm×3mm by wire cutting equipment. After the samples...
were drilled the 1mm holes in the corner, 400mesh and 800mesh Al₂O₃ sand paper were used to grind the sample surface. Then the samples were immersed in the ultrasonic cleaner containing ethanol for 3min and dried to be used.

The alkaline electrolyte solutions with Na₂SiO₃, NaOH and C₃H₆O₃ were mixed together by distilled water. The equipment was a bipolar pulse MAO power supply, with AZ91D magnesium alloy sample as an anode and stainless steel electrolytic cell as a cathode. Placed the sample into the electrolyte, and turned on the power supply. The process parameters were set up with the frequency of 400Hz, duty ratio of 8% and voltage of 350V. The control time was 5min, 15min and 30min, respectively. The temperature of the electrolyte solution was controlled below 40℃. After the oxidation process was over, turned off the power supply and took out the samples. Finally, the samples were cleaned by distilled water and dried in the air. The MAO equipment was shown in Figure1.

The phase composition of the AZ91D magnesium alloy was analyzed by Bruker D-8 X-ray diffractometer. The surface morphology of the coatings was observed by JSM-6360LV scanning electron microscope (SEM). The AZ91D substrate and the MAO coatings were pressed at the bottom of the cylinder that filled with 3.5%NaCl solution to test their corrosion resistance.

3. Results and discussion

3.1. Microstructure of as-cast AZ91D alloy Style and spacing

According to X-ray fluorescence spectrometry analysis, the as-cast AZ91D magnesium alloy was mainly composed of 89.7% Mg, 9.5%Al and a small amount of Zn and Mn, as shown in Table 1. The metallographic microstructure of the AZ91D alloy was shown in Figure 2. It was found that the as-cast AZ91D alloy comprised solid solution of α-Mg, precipitated phase of β-Mg₁₇Al₂ and eutectic structure of (α+β). For the AZ91D magnesium alloy containing 89.7%Mg and 9.5%Al under the condition of equilibrium solidification, homogeneous crystal reaction occurred to generate α-Mg when the temperature cooled below liquidus temperature in the phase diagram. When the temperature decreased below the solidus temperature, β-Mg₁₇Al₂ precipitated from the supersaturated α-Mg solid solution, and this process would last until room temperature. However, during the actual solidification process, there existed component segregation for magnesium alloy castings, causing the left movement of eutectic point. Therefore, after the composition of solid solution reached the eutectic temperature, the eutectic phase of (α+β) was crystallized from remaining liquid phase.

Table 1. Composition of the as-cast AZ91D alloy.

| Elements | Mg     | Al     | Zn    | Mn    |
|----------|--------|--------|-------|-------|
| Content (wt%) | 89.6722 | 9.5231 | 0.617 | 0.1876 |
3.2. Morphology of the MAO coating

Figure 3–Figure 5 showed the surface morphology of the MAO coating prepared at different oxidation time. The surface morphology of the MAO coating was similar to the volcanic cone where many micropores were surrounded by molten oxides. These micropores were both the reaction channel to connect the solution with the substrate, and the passage from where the molten oxides produced and ejected. When the oxidation time was 5min, the surface was uneven and distributed the micropores with the diameter of 5–20μm in Figure 3. When the oxidation time was 15min, the surface was smooth and the diameter of micropores decreased to 5~15μm. When the oxidation time prolonged to 30min, the micropores distributed evenly with the diameter of 2~10μm. Due to the increase of the coating thickness, the breakdown arc became finer and the surface quality was improved.

3.3. Corrosion morphology of the MAO coating

Corrosion morphology of the AZ91D substrate and the MAO coating immersed in 3.5%NaCl solution for 48h was shown in Figure 6–Figure 9. As for AZ91D alloy, the overall corrosion occurred, resulting in a large number of corrosion products and cracks. After the MAO coating formed on the surface of AZ91D alloy, this ceramic coating hindered corrosive medium from diffusing into the substrate, which offered the protection for AZ91D. When the oxidation time was 5min, the coating was so thin that the barrier from the corrosion medium was weak. Consequently, the micropores were filled with the corrosion products, resulting in the decrease of the pore size, as shown in Figure 7. With the increase of oxidation time, the thickness of the coating increased, which could significantly prevent from the corrosion medium. Therefore, the pore size of the coatings changed little, as shown in Figure 8 and Figure 9.

3.4. Corrosion products composition of the MAO coating

Figure 10 and Figure 11 presented the corrosion products composition of the AZ91D alloy and the MAO coating immersed in NaCl solution for 48h. The corrosion products of AZ91D alloy were
mainly composed of Mg (OH)₂, Al (OH)₃ and Mg₂(OH)₂Cl·3H₂O. The corrosion products of MAO coating mainly consisted of Mg(OH)₂ and Al(OH)₃. In addition, Mg and Mg₁₇Al₁₂ were from AZ91D magnesium alloy, and MgO, Mg₂SiO₄ and MgAl₂O₄ were the composition of the MAO coating.

Figure 6. Corrosion morphology of the AZ91D substrate.

Figure 7. Corrosion morphology of the MAO coating with oxidation time of 5min.

Figure 8. Corrosion morphology of the MAO coating with oxidation time of 30min.

Figure 9. Corrosion morphology of the MAO coating with oxidation time of 30min.

Figure 10. Corrosion products composition of the AZ91D alloy.

Figure 11. Corrosion products composition of the MAO coating.

3.5. Analysis of corrosion mechanism

Table 2 illustrated the mass changes of the AZ91D substrate and the MAO coatings before and after immersion corrosion. According to above results, it was concluded that the pitting corrosion was the main corrosion form of the AZ91D magnesium alloy in NaCl solution. The main reactions from (1) to (3) were as follows.

Anodic reaction  
\[ \text{Mg} = \text{Mg}^{2+} + 2e^{-} \]  
(1)

Cathodic reaction  
\[ 2\text{H}_2\text{O} + 2e^{-} = \text{H}_2 + 2\text{OH}^- \]  
(2)

Overall reaction  
\[ \text{Mg}^{2+} + 2\text{OH}^- = \text{Mg(OH)}_2 \]  
(3)

The Mg(OH)₂ formed on the surface of Mg was a passivation film which offers protection for Mg. However, the diffusion and adsorption of active anion Cl⁻ destroyed this passivation film, exposing the AZ91D substrate in NaCl solution. The β-Mg₁₇Al₁₂ and the adjacent α-Mg in the magnesium alloy preferentially developed a galvanic-type corrosion cell, resulting in the corrosion of α-Mg. As corrosion rate of α-Mg accelerated, β-Mg₁₇Al₁₂ began to fall off and serious pitting pits formed on the Mg alloy surface. Therefore, the corrosion of Mg alloy was aggravated and the weight lost.
When the MAO coatings were immersed in NaCl solution, the hydrolysis occurred between the phase composition of the coatings and NaCl solution. The reaction products of MgCl₂ dissolved in water, while Mg(OH)₂ and Al(OH)₃ deposited on the surface of the coatings, which blocked some micropores. Consequently, the weight of the MAO samples increased.

| Category          | Before corrosion | After corrosion | Mass change |
|-------------------|------------------|----------------|-------------|
| Substrate         | 0.954            | 0.940          | -0.014      |
| Coating with 5min | 1.084            | 1.090          | 0.006       |
| Coating with 15min| 0.915            | 0.917          | 0.002       |
| Coating with 30min| 1.084            | 1.090          | 0.006       |

4. Conclusions
The MAO coating prepared on the surface of AZ91D magnesium alloy presented porous structure. With the prolongation of oxidation time, the size of the micropores on the coating surface decreased. The coatings fabricated at 350V for 30 min obtained small and uniform micropores with 2~10μm in diameter. The result of immersed corrosion showed that the corrosion resistance of the MAO coating was higher than that of AZ91D substrate. The MAO coating prepared at 350V for 30 min had the best corrosion resistance.

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