Effect of Electrolyte Constituent on Morphology and Composition of the Microarc Oxidation Coating on Magnesium Alloy

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Abstract. Microarc oxidation (MAO) coating was prepared on the surface of AZ91D magnesium alloy in Na$_2$SiO$_4$-NaOH-C$_3$H$_8$O$_3$ based electrolyte. The morphology and composition of the coating with different electrolyte constituent were analyzed by SEM and XRD. The result showed that the MAO coating was composed of loose layer and dense layer. The coating mainly comprised MgO, Mg$_2$SiO$_4$ and MgAl$_2$O$_4$. When the Na$_2$SiO$_3$ concentration was 20g/L, the pores of the coating were very uniform and the coating surface was smooth with homogeneous pore. The coating with addition of NaF to the electrolyte had the maximum thickness of 17~25μm.

1. Introduction
Magnesium is one of the most abundant light metals on earth. China has the biggest magnesium reserves in the world, accounting for more than 50% magnesium reserves of the world’s total. The density of magnesium and its alloy are less than 2g/cm$^2$. Moreover, they can be recycled and described as inexhaustible metal$^{[1,2]}$. With price reduction of the magnesium alloys, their advantages of light weight and high strength have come into being again, which makes them the first choice material for the light weight of automobile and motorcycle in industry. They are known as the green engineering material in the 21st century$^{[3]}$. Unfortunately, the equilibrium potential of magnesium is very low with -2.34V, indicating that magnesium and its alloys are easy to oxidize thermodynamically. In addition, the natural oxide film formed on the surface of the magnesium alloy has the poor stability and densification, so the corrosion is easy to occur. Because of these shortcomings, the corrosion resistance of magnesium and its alloys is very poor, which limits their further application$^{[4,5]}$.

One of the effective ways to improve the corrosion resistance of magnesium alloy is to provide a layer on the surface as a corrosion barrier to protect the substrate effectively$^{[6]}$. In recent years, surface modification technology for magnesium alloy has attracted much attention. Traditional techniques such as chemical conversion film, electroless plating and anodizing oxidation have been applied to magnesium alloy. Above methods are easy to operate and generate uniform film, which endows magnesium alloy with special functions. However, the density, corrosion resistance and adhesion to the substrate of the prepared films are unsatisfactory and only suitable for short term protection or as the base layer. Besides, some solutions containing fluoride or hexavalent chromium are easy to cause environmental pollution$^{[7,8]}$. Therefore, request for the surface treatment technology that can meet environmental protection and commercial value has become a top priority. Micro arc oxidation (MAO) is a new surface modification technology improved on the basis of anodic oxidation. It is one of the...
development directions of anodic oxidation for magnesium alloy, which has some advantages as homogeneous and hard coating, high good comprehensive performance and high treatment efficiency\[^9,10\]. In this paper, MAO was used to obtain the coating on the surface of AZ91D magnesium alloy. The influence of electrolyte constituent on morphology and composition of the magnesium alloy were studied.

2. Experimental

Experimental material was as cast AZ91D magnesium alloy. The cast ingot was cut into the samples with the size of 30mm×20mm×3mm by wire-electrode cutting device. After ground by 400 mesh, 800 mesh and 1000 mesh SiC sand paper, the samples were placed into an ultrasonic cleaner containing ethanol and dried at room temperature.

The alkaline electrolyte was prepared in distilled water with various Na\(_2\)SiO\(_3\) content with NaF as additive. The electrolyte constituent was shown in Table 1. Bipolar pulse MAO power supply was used. The AZ91D samples were connected to the anode of power supply and the stainless steel electrolytic cell was connected to the cathode. The samples were stabilized in alkaline electrolyte for 5 min. Turn on the power supply then adjust the frequency and duty cycle. Constant voltage mode was used to increase the voltage gradually, causing the arc igniting on the AZ91D surface. Afterwards, the voltage was adjusted to voltage of 450V and electric time of 15 min. The temperature of the electrolyte solution was controlled below 35°C by agitator. When the oxidation process was finished, the power supply was shut off. The samples were taken out and cleaned in the distilled water to remove the electrolyte and other contaminant remaining on the surface of the coating.

The surface and interface morphology of the coating were observed by JSM-6360LV scanning electron microscope equipped with EDAX FALCON60S spectrometer. The composition of the coatings was analyzed by BRUKER D-8 X ray diffractometer.

Table 1. The electrolyte constituent.

| Serial number | Na\(_2\)SiO\(_3\) | NaOH | C\(_3\)H\(_8\)O\(_3\) | Distilled | NaF |
|---------------|-----------------|------|---------------------|-----------|-----|
| 1              | 10g             | 5g   | 10ml                | 1L        |     |
| 2              | 20g             | 5g   | 10ml                | 1L        |     |
| 3              | 30g             | 5g   | 10ml                | 1L        |     |
| 4              | 20g             | 5g   | 10ml                | 1L        | 1g  |

3. Results and discussion

3.1. Effect of electrolyte constituent on morphology of the MAO coating

In this paper, Na\(_2\)SiO\(_3\)-NaOH-C\(_3\)H\(_8\)O\(_3\) electrolyte is selected as the basic solution for MAO. Na\(_2\)SiO\(_3\) can help magnesium alloy to passivate rapidly in the electrolyte and increase the interface resistance between magnesium alloy and electrolyte, which has quickly raised the initial voltage of MAO process to prevent the excessive dissolution of AZ91D anodization. Therefore, Na\(_2\)SiO\(_3\) is the main film forming agent in the electrolyte. The electrolyte doped with NaOH can beautify the appearance of the coating. In a certain concentration range, the higher the content of NaOH, the smoother appearance of the coating, so NaOH is used as a performance improvement agent. In addition, NaOH can not only provide conductive Na\(^+\) and OH\(^-\) in the electrolyte, but also keep the solution strong alkaline and control the pH value. The addition of C\(_3\)H\(_8\)O\(_3\) to the electrolyte can avoid the tip discharge to a certain extent, and also make the film more uniform, which can effectively improve the appearance quality of the MAO coating.
Figure 1–Figure 3 show the surface morphology of the MAO coatings prepared with various Na$_2$SiO$_3$ concentration. The coatings presented porous surface. When an electric current was applied, an ordinary anodic oxide film produced on the AZ91D alloy. The breakdown of the oxide film resulted in the microarc discharge then the oxidation was further penetrated into the deep layer. Finally, porous oxidation coating formed by the fusion and solidification of the oxide. When the Na$_2$SiO$_3$ concentration was 10g/L, the surface pores of the coating was not uniform, as shown in Figure 1. When the Na$_2$SiO$_3$ concentration was 20g/L, the pores of the MAO coating are very uniform and the coating surface was smooth with homogeneous pores as shown in Figure 2. When the Na$_2$SiO$_3$ concentration was 30g/L, the arc was unstable and the coating contained less pores as shown in Figure 3. Therefore, the best Na$_2$SiO$_3$ concentration in the basic solution was 20g/L.

Figure 4–Figure 6 present the interface morphology of the MAO coating with different Na$_2$SiO$_3$ concentration. The thickness of the coating was 11–13μm with 10g/L Na$_2$SiO$_3$, 12–16μm with 20g/L Na$_2$SiO$_3$, and 14–20μm with 30g/L Na$_2$SiO$_3$. With the increase of Na$_2$SiO$_3$ concentration, electrical conductivity of the solution and the amount of the SiO$_3^{2-}$ involved in the coating formation increased, resulting in the increase of the thickness coatings. When Na$_2$SiO$_3$ concentration continued to rise, the stability of the electrolyte decreased and the formation of the coating was hindered. Thus, the film thickness decreased. As can be seen from above figure, the MAO was composed of loose layer and dense layer. The loose layer ceramic film had porous structure with large thickness. While the dense layer was compact and thin, it was closely connected with the substrate.

Figure 7 and Figure 8 show the surface and interface morphology of the coating with addition of NaF to the electrolyte. The coating was smooth with the thickness of 17–25μm, indicating that NaF as additive could significantly improve the thickness of MAO coating. Because NaF is a strong electrolyte, a small amount of addition will obviously increase the ionic concentration then enhance the conductivity of the electrolyte. In the constant voltage mode, the greater was the conductivity of the solution, and the smaller was the resistance, so the increase of the electrolyte current raised the driving force in the reaction process of the MAO and accelerated the ion migration in the solution to the coating. The increase of F$^{-}$ concentration enhanced the migration speed of Mg$^{2+}$ in the discharge.
channel to certain extent, so that more Mg\(^{2+}\) and O\(^{2-}\) could be combined to accelerate the growth rate of the coating, which was beneficial to the formation of thick coating.

\[ \text{Figure 7. Surface morphology of the coating with addition of NaF} \]

\[ \text{Figure 8. Interface morphology of the coating with addition of NaF} \]

### 3.2. Composition of the MAO coating

Figure 9 and Figure 10 are the element distribution of the surface and interface of the MAO coating with NaF as additive. According to above figure, the main elements of the coating were Mg, O, Si, Al and Na. XRD patterns of the MAO coating are shown in Figure 11 and Figure 12. It was known that the MAO coatings formed in the electrolyte of sodium silicate were mainly composed of MgO, MgAl\(_2\)O\(_4\) and Mg\(_2\)SiO\(_4\). The coating without NaF contained a small amount of SiO\(_2\), and the coating with NaF contained small amount of NaF, AlF and Na\(_3\)Al. The cubic structure of MgO was fundamentally different from the amorphous phase formed by the anodized oxidation and the chemical conversion coating on magnesium alloy. In the oxidation process, the microarc discharge released great energy. Under the instantaneous high temperature and high pressure, Mg atoms melted in the micro region and spread through the discharge channel. Due to liquid quenching of the electrolyte, Mg atoms were rapidly combined with the oxygen atoms adsorbed on the surface of the alloy to produce MgO and precipitated from the electrolyte.

\[ \text{Figure 9. Surface energy spectrum of the coating with NaF.} \]

\[ \text{Figure 10. Interface line scanning of the coating with NaF.} \]
Figure 11. XRD pattern of the coating without NaF.

Figure 12. XRD pattern of the coating with NaF.

SiO$_2$ came from the combination of Si element in the AZ91D substrate with oxygen atoms adsorbed on the alloy surface. The appearance of high melting point of MgO and SiO$_2$ not only proved that the instantaneous temperature of the microarc region was very high, but also indicated that the ions in the solution were directly involved in the chemical reaction near the microarc region. The formation of Mg$_2$SiO$_4$ and MgAl$_2$O$_4$ was due to the electrochemical deposition between electrolyte composition and the AZ91D surface, which contributed to the improvement of corrosion resistance of the AZ91D alloy. The high temperature and pressure environment provided the energy required for the formation of the MgAl$_2$O$_4$ spinel. The distribution of the AlO$_2^-$ in the electrolyte and the distribution of Mg in the alloy helped the formation of the complex stable spinel molecules. Owing to small molecular lattice parameters and a large number of ionic charges, MgAl$_2$O$_4$ had high density and high melting point. It not only improved the densification of the MAO coating, but also inhibited the exfoliation of the oxide coating under the action of thermal stress because the thermal expansion coefficient of MgAl$_2$O$_4$ was similar to that of the AZ91D substrate.

4. Conclusions
The MAO coating on AZ91D magnesium alloy was obtained from Na$_2$SiO$_4$-NaOH-C$_3$H$_8$O$_3$ based electrolyte. The coating was composed of loose layer and dense layer. The loose layer ceramic has porous structure with large thickness, and the dense layer was compact and thin. The coating mainly comprised MgO, Mg$_2$SiO$_4$ and MgAl$_2$O$_4$. When the Na$_2$SiO$_3$ concentration was 20g/L, the pores of the MAO coating were very uniform and the coating surface was smooth with homogeneous pore. The coating with addition of NaF to the electrolyte had the maximum thickness of 17~25μm.

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