*Short Communication*

# Effect of Starch Addition in Alkaline Electrolyte on the Characteristics of Plasma Electrolytic Oxidation Coating on AZ31B Mg Alloy

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The oxide coatings were produced on AZ31B Mg alloy using plasma electrolytic oxidation (PEO) process in alkaline electrolyte with and without addition of starch. The properties and surface morphologies of the PEO coatings were studied by voltage—time curves, scanning electron microscopy (SEM), X-ray diffraction (XRD) and potentiodynamic polarization, respectively. It was found that the coating formed in the electrolyte with starch has more compact and uniform morphology than that formed in the electrolyte without starch. The XRD analysis showed that the compositions of coatings formed in the electrolytes with and without starch are almost the same, containing MgO, $MgSiO_3$, and $Mg_2SiO_4$. The results of potentiodynamic polarization tests showed that the coating formed in the electrolyte with starch enhanced the anti-corrosion characteristic.

## 1. INTRODUCTION

Magnesium alloys are used extensively in light weight engineering applications due to their excellent physical and mechanic properties such as low density and high specific strength. Despite the desirable properties mentioned above, the poor corrosion resistance of magnesium alloy restricts its widespread applications. Plasma electrolytic oxidation (PEO), which is an electrochemical surface treatment developed from the traditional anodic oxidation, has been reported to improve metal surface properties [1,2]. Many factors such as the electrical parameters, the composition of electrolyte and substrate were found affecting the coating properties formed by this technique; the composition of electrolyte particularly has significant effect on both morphology and compositions of PEO coatings

[3-6]. HAE and DOW are the most successful PEO technologies for Mg alloys; however, the electrolytes employed containing chromate, phosphate and fluoride which will inevitably bring tremendous harm to environment. Therefore, it is imperative to develop an environment-friendly electrolyte to improve the corrosion resistance of Mg alloy. The silicates and aluminates based electrolytes, as the substitutable electrolytes, are very attractive in reducing environment contamination as well as generating enhanced anti-corrosion performance [7-9]. The addition of additives in these electrolytes system is considered as a means to further improve the performance of the PEO coating. As the additives, the nanoparticles, sols, inorganics and organics have been selected to improve the anticorrosion abilities of Mg alloy [10-19].

So far, it is still a very active research field to find the additives in terms of environment-friendly requirement and coating performance improvement. In this paper, starch, as an organic additive, with no toxicity, was used in the alkaline electrolyte composed of NaOH, $Na_2SiO_3$, and $Na_2B_4O_7$. The surface morphologies, coating compositions and anti-corrosion performance of PEO coatings formed in the electrolyte with and without starch were investigated.

## 2. EXPERIMENTAL

AZ31B magnesium alloy was employed in this study, and its chemical composition was follows (in wt.%): Al 2.5~3.5, Zn 0.6~1.4, Mn 0.2, Si ≤0.1, Cu≤0.05, Ni 0.005, and Mg balance. The samples were cut to the size of 30 mm×20 mm×2 mm and polished with successively finer grades of emery paper from 180 to 1000 grits.

A DC pulsed electrical power supply was applied to the PEO process and the electrical parameters were set as following: frequency at 200 Hz, duty cycle at 10%, current density as 1 $A/dm^2$. The Mg alloy and the stainless steel were used as the anode and cathode separately. The electrolyte was composed of 45 g/L NaOH, 70 g/L $Na_2SiO_3$, and 90 g/L $Na_2B_4O_7$ with and without the addition of 10 g/L starch. All chemicals were of analytical grade and the solution was prepared with distilled water. The temperature of the electrolytes was kept below 30 °C by a water cooling system. The duration of PEO was 15 min. After PEO treatment, the coated samples with or without starch (marked as PEOst and PEOws respetively) were rinsed with water and dried in the air.

The surface morphology of the PEOst and PEOws was examined by a scanning electron microscopy (SEM, HITACHI, S-4800). The phase structure of the coatings were determined by X-ray diffraction (XRD, DX-2600, China), using Cu Kα radiation source. The coating thickness was measured using an eddy-current coating thickness measurement (DUALSCOPE MPO, Fisher). Each sample surface was measured for five times and the average value was given.

Potentiodynamic polarization tests were carried out by using CHI 842B electrochemical equipment. All the electrochemical measurements were operated in the neutral 3.5% NaCl solution at 25 ℃. Measurements were conducted in a traditional three-electrode system with counter electrode using a large area platinum sheet and reference electrode using a saturated calomel electrode (SCE). The area of samples for the electrochemical tests exposed to the electrolyte was 1 $cm^2$. The scan rate was 0.1 mV/s.
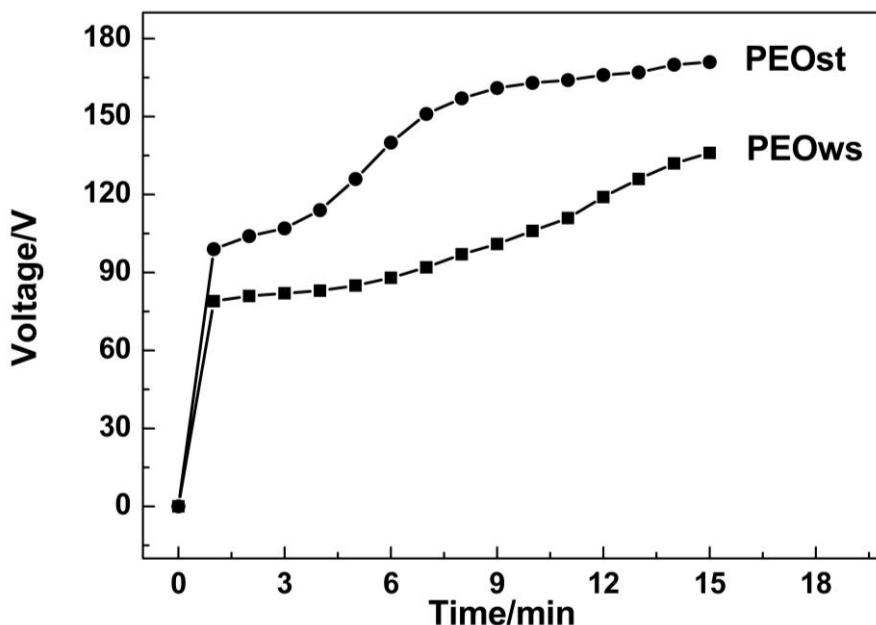
## 3. RESULTS AND DISCUSSION



**Figure 1.** The potential change with time during PEO process in the alkaline electrolytes.

Figure 1 shows the anodic potential changes with time under constant current. It is obviously that the curves could be divided to three stages, similar as reported by the literatures [13,20,21]. In the first stage, the cell voltage increases almost linearly with anodized time and the oxygen are released from the Mg alloy substrate. Accordingly a thin, compact coating has formed on the surface of Mg alloy. Then the PEO process enters into the second stage when one or two white and small sparks appears on the substrate at a voltage termed as the breakdown voltage. During this stage, the cell voltage remains almost unchanged with the continuous PEO process.
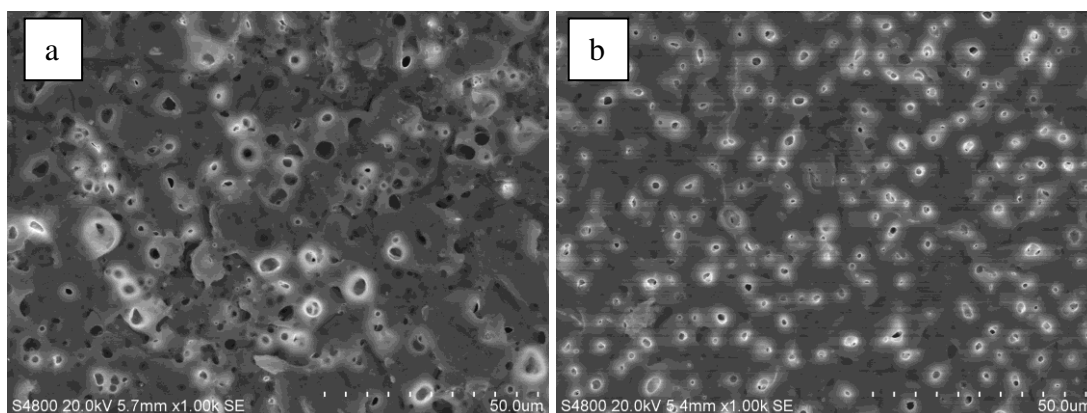


**Figure 2.** SEM Micrographs of (a) PEOws and (b) PEOst

In the final stage, the sparks start to grow in size and decrease in number; in addition, their colors changing from white to orange. It is noteworthy that the breakdown voltage in presence of

starch is higher than that without the addictive. This may duo to the hydroxyl groups in the starch molecular structure absorption on the surface of Mg alloy [22].

Surface morphologies of the coatings formed in the alkaline electrolyte with and without starch are illustrated in Figure 2. It is clearly seen from figure 2(a) that the surface of PEOws demonstrates a rough surface appearance. Many micropores with 5~10 μm in diameter and some microcracks can be found on the surface, indicating that the film can be easily eroded. Micropores were formed by the molten oxide and the oxygen thrown out of the discharge channels, whereas microcracks result in thermal stress duo to the rapid solidification of molten oxide in the relative cool electrolyte [3]. With the addition of starch, as shown in Figure 2 (b), the surface of the PEOst is uniform and the micropores became smaller. Therefore, the addition of starch in the electrolyte can make a significant reduction of porosity in the surface morphology.
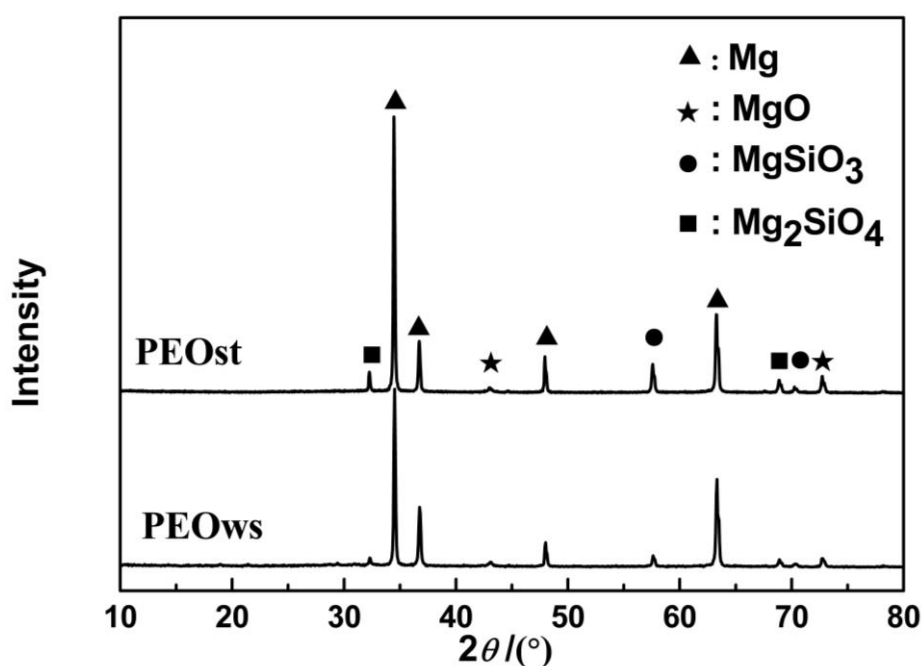


**Figure 3.** XRD patterns of PEOws and PEOst

Figure 3 shows the XRD results of PEO coatings formed in the electrolyte with and without starch. The compositions of the PEO coatings formed in the electrolytes with and without starch are almost the same including MgO, $MgSiO_3$, and $Mg_2SiO_4$. It is noticeable in both cases that the peaks corresponds to the Mg alloy substrate are stronger than the others. This is due to a very thin layer of coatings obtained during PEO process. The average thickness of the PEOst and PEOws is 15.8 μm and 14.7 μm, respectively. Moreover, as shown in Figure 2, the porous surface with micropores and microcracks cannot be avoided completely; whether the electrolyte contains or excludes starch. Hence, the X-ray can easily penetrate the porous PEO coating [21,23].
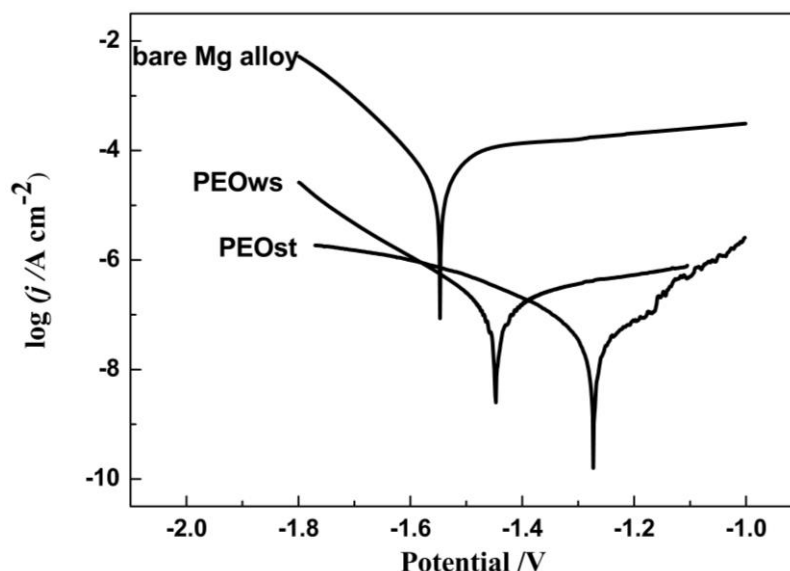
**Figure 4.** Potentiodynamic polarization curves of bare Mg alloy, PEOws and PEOst in 3.5 wt% NaCl solution.

The anti-corrosion properties of bare Mg alloy, PEO coating formed in the alkaline electrolyte without and with starch were studied by the potentiodynamic polarization technique in 3.5wt% NaCl solution, as presented in Figure 4. And the corrosion potential ($E_{corr}$), corrosion current density ($j_{corr}$), anodic ($\beta_a$) and cathodic tafel slopes ($\beta_c$) were shown in Table 1.In a typical polarization curve, positive corrosion potential corresponds to better corrosion resistance. Compared to the bare Mg alloy (-1.548 V/SCE), the corrosion potential of PEOws shifts about 100 mV to the positive direction. The corrosion potential of PEOst further shifts 174 mV in a positive direction compared with PEOws. As shown in Table 1, the $j_{corr}$ of PEOst reduced by an order of magnitude, compared to the $j_{corr}$ of PEOws. The different anti-corrosion properties of PEO coatings can be attributed to the increase of coating thickness, reduction of roughness, together with the enhancement of coating compactness, which jointly lead to the better anti-corrosion characteristics.

**Table 1.** Electrochemical parameters related to potentiodynamic polarization curves

|  | $E_{corr}$(V) | $\beta_a$ (V/decade) | $\beta_c$ (V/decade) | $j_{corr}$(A/cm$^2$) |
|---|---|---|---|---|
| Bare Mg alloy | -1.548 | 0.114 | 0.193 | $4.169\times10^{-5}$ |
| PEOws | -1.448 | 0.162 | 0.637 | $2.334\times10^{-7}$ |
| PEOst | -1.274 | 0.135 | 0.122 | $1.897\times10^{-8}$ |

## 4. CONCLUSIONS

PEO coatings were prepared on AZ31B Mg alloy in alkaline electrolyte with and without addition of starch. The PEO coating formed in the electrolyte with starch had more uniform

morphology, smaller micropores and less mircocracks when compared with the coating formed in the electrolyte without starch. The XRD analysis indicated PEO coatings formed in the electrolytes with and without starch containing MgO, $MgSiO_3$, and $Mg_2SiO_4$. The results obtained from the potentiodynamic polarization tests showed that PEO coating formed in the electrolyte with starch enhanced the anti-corrosion performance with a higher positive shift on value compared with coating formed in the electrolyte without starch.

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