

Short Communication

Effect of Tungsten Carbide Particles on the Characteristics of PEO Coatings Formed on AZ31B Magnesium Alloy in Alkaline Electrolyte

Yang Zhang, Yaling Xu, Chengping Miao, Xiaohua Tu^{}, Jianxing Yu, Jiayou Li*

College of Biological and Chemical Engineering, Jiaxing University, Zhejiang, Jiaxing 314001, China;
Key Laboratory of Clean Chemical Process of Jiaxing, Zhejiang, Jiaxing 314001, China

*E-mail: tuxiaohua@mail.zjxu.edu.cn

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The oxide coatings were prepared on AZ31B magnesium alloy in the alkaline electrolyte with and without tungsten carbide (WC) particles by plasma electrolytic oxidation. The phase composition and surface morphology of the coatings were studied using X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. The anticorrosion performance of coatings was investigated by potentiodynamic polarization tests in 3.5 wt% NaCl solution. It was found that a more uniform and compact oxide coating with less micropores and cracks was formed in the alkaline electrolyte with WC particles. The XRD results showed that the coating formed in the electrolyte with WC particles mainly contains MgO, MgSiO₃, Mg₂SiO₄, and WC. The anticorrosion performance of the magnesium alloy was significantly improved by plasma electrolytic oxidation in the alkaline electrolyte with WC particles, as indicated in the results of potentiodynamic polarization tests.

Keywords: AZ31B magnesium alloy; plasma electrolytic oxidation; tungsten carbide; corrosion resistance

1. INTRODUCTION

Magnesium alloys have been extensively used in the electronics and automobile industries owing to the low density, high strength to weight ratio and excellent dimensional stability [1,2]. However, the further application of magnesium alloys has been impaired attributed to the poor corrosion resistance. So far, in order to improve the corrosion resistance of magnesium alloys, proper surface treatments such as anodization, electroless plating, electropolymerisation and chemical conversion coating were considered as the suitable methods to increase the corrosion resistance [3-6].

The plasma electrolytic oxidation (PEO), as a promising surface modification method developed from the traditional anodization, could generate a dense, thick and hard oxide coating on the magnesium alloy [7-14]. During PEO process, the performance of coatings is affected by potential, current density, temperature, chemical composition of electrolyte and so on. The chemical composition of electrolyte applied in the PEO process plays the most significant role in the formation of coating. The influence of electrolyte characteristics on the performance of the PEO coatings has previously been reported in many literatures [15-19]. In particular, addition of inorganic compounds such as Al_2O_3 , TiO_2 , SiO_2 , ZrO_2 , Si_3N_4 , etc., into the electrolytes has been found effective in further improving the corrosion resistance of PEO coatings [20-26].

Tungsten carbide (WC) has been widely used and investigated for its excellent properties such as good inert chemical behavior, high wear resistance and high hardness [27-30]. In this study, the WC particles have been found incorporated into the PEO coating from the alkaline electrolyte. The surface morphologies, compositions, hardness and anticorrosion performance of the PEO coatings formed in the alkaline electrolyte with and without WC particles were evaluated.

2. EXPERIMENTAL

Specimens of AZ31B magnesium alloy with a size of 20 mm × 20 mm × 2mm were cut from AZ31B plate. Prior to PEO treatment, the specimen surface was polished with successively finer grades of emery paper from 180 to 1000 grits. Then, the specimens were rinsed with distilled water and degreased with acetone.

Alkaline electrolyte used in the PEO process consisted of NaOH (10 g/L), Na_2SiO_3 (20 g/L) and $\text{Na}_2\text{B}_4\text{O}_7$ (15 g/L). The coatings were obtained in the electrolytes with and without 1.5 g/L WC. The treatment was performed by using a pulse electrical source. The electrical parameters were set as following: current density at 1 A/dm², duty cycle at 10%, frequency at 200 Hz. The PEO process time was 15 min and the temperature of the electrolyte was kept below 35 °C. In order to make the WC particles fully dispersed in alkaline electrolyte, the WC particles with an average size of 400 nm were pretreated by the anionic surfactant ($\text{C}_{12}\text{H}_{25}\text{C}_6\text{H}_4\text{SO}_3\text{Na}$) before being added into the electrolyte.

The scanning electron microscopy (SEM, HITACHI, S-4800) was used to observe the surface morphology of the coatings. The energy dispersive X-ray spectroscopy (EDX) was applied to detect elemental compositions of the PEO coatings on the magnesium alloy surface. The phase constituent of the coatings were analyzed by X-ray diffraction (XRD, DX-2600, China), using Cu K α radiation source. The microhardness of PEO coating was performed by HXS-1000 microhardness tester.

Potentiodynamic polarization tests were carried out to evaluate the corrosion performance of the coatings by using CHI 842B electrochemical equipment in 3.5 wt% NaCl solution at 25 °C. Electrochemical measurements were conducted using a traditional three-electrode cell with AZ31B magnesium alloy or coated alloy as the working electrode, a large area platinum sheet as the counter electrode and a saturated calomel electrode (SCE) as reference electrode. Prior to the electrochemical measurements, the electrodes have been immersed 600 s in the NaCl solution. The potentiodynamic

polarization curves were operated at a scan rate of 1 mV/s. The area of working electrodes for potentiodynamic polarization tests was 1 cm².

3. RESULTS AND DISCUSSION

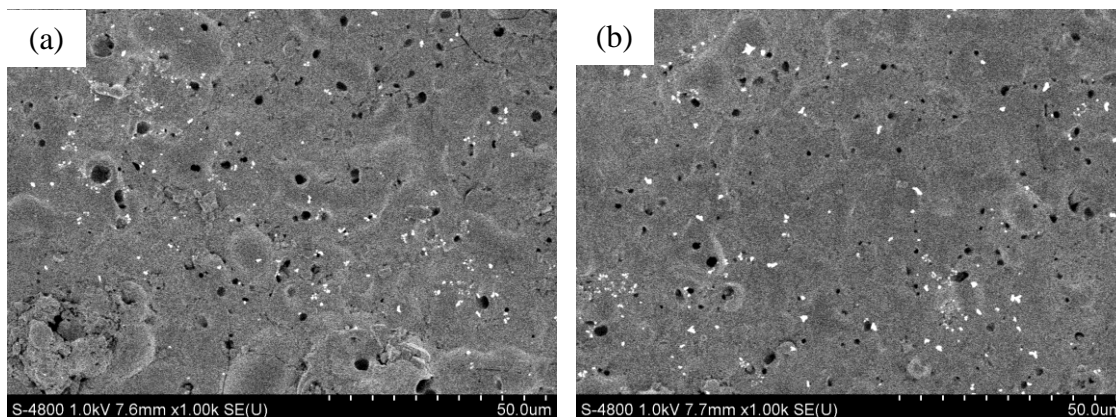


Figure 1. SEM micrographs of PEO coatings formed in the electrolyte without (a) and with (b) WC particles

The morphologies performance of PEO coatings formed in the alkaline electrolyte with and without WC particles are presented in Figure 1. It can be seen from Figure 1(a) that the PEO coating formed in the alkaline electrolyte without WC displays a porous surface appearance. A few microcracks and many micropores with a diameter range from 2 to 8 μm can be found on the surface. Micropores were formed on the surface of the coatings duo to the oxygen and molten oxide thrown out of the discharge channels, whereas microcracks were formed by thermal stress ascribed to the rapid solidification of molten oxide in the relative cool electrolyte [31]. This porous coating has an open structure that allows corrosive ions to penetrate into the magnesium alloy matrix easily and cause corrosion. With addition of WC particles into the alkaline electrolyte, the magnesium alloy surface was covered with the PEO coating (Figure 1(b)), is much more uniform as compared with that of Figure 1(a). Less and smaller micropores are observed and the cracks of coating also reduce. Thus, adding WC particles to the alkaline electrolyte has a significant effect on the surface morphology of the PEO coating.

Table 1. The content (wt %) of elements in PEO coatings formed in the electrolyte with and without WC

PEO coating	O	Na	Mg	Si	Al	C	W	S
Without WC	53.85	3.34	32.51	9.65	0.64			
With WC	56.96	7.83	20.99	8.76	0.49	3.29	0.63	0.14

The quantitative analysis of the PEO coatings is clearly demonstrated in Table 1. The elements O, Na, Mg, Si and Al were found in the surface of the PEO coatings both formed in the electrolyte

with and without WC. The elements O and Si mainly ascribed to the incorporation species into the PEO coatings from the electrolyte, Mg and Al came from the substrate. The elements W, C and S were detected in the PEO coating formed in the electrolyte with WC. The characteristic element W is believed to be from the WC particles, S is from the anionic surfactant, while C may be from both the WC particles and anionic surfactant. It is concluded that the WC particles and the electrolyte species penetrated into the coating during the PEO process.

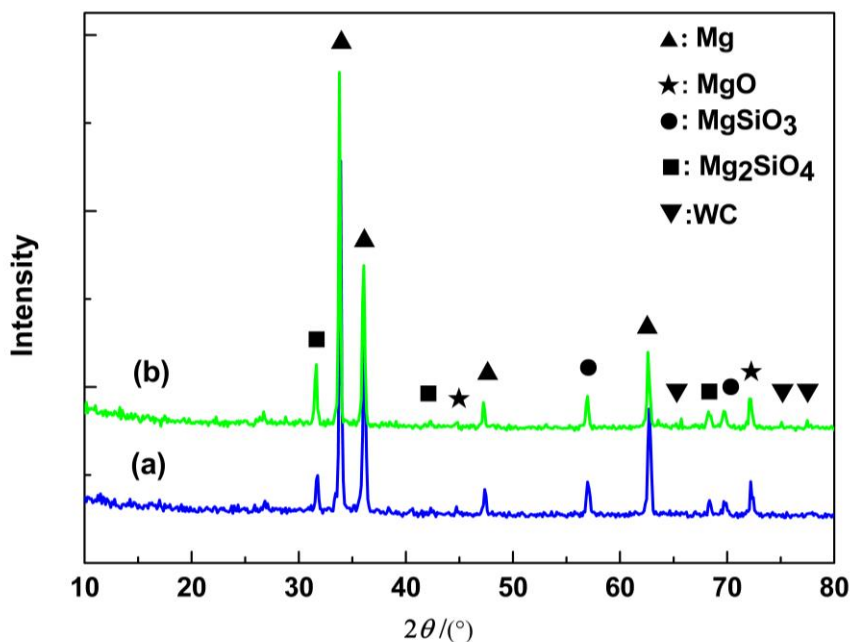


Figure 2. XRD patterns of the PEO coating formed in the electrolyte without (a) and with (b) WC particles

The composition of the PEO coatings formed in the electrolyte with and without the WC particles was further investigated by XRD. The XRD patterns, as shown in Figure 2(a), indicating that the PEO coating formed in the electrolyte without WC particles is mainly composed of MgO, MgSiO₃, and Mg₂SiO₄. However, with the addition of WC particles in the alkaline electrolyte, the XRD pattern of corresponding PEO coating changes significantly. It can be seen from Figure 2(b) that the distinguished peaks of WC (65.7°, 75.1° and 77.6°) are apparently detected. It is indicated that WC particles participated the formation of coating during the PEO process. It is noticeable in both cases that the peaks corresponding to the magnesium alloy substrate are stronger than those of the others. This is due to a very thin layer of coatings obtained during PEO process. The average thickness of the PEO coatings obtained in the electrolyte with and without WC particles measured in this study were 16.6 μm and 13.4 μm, respectively. Hence, the X-ray can easily penetrate the thin PEO coatings [32].

The corrosion resistance of the magnesium alloy substrate and PEO coatings formed in the electrolyte with and without WC particles were evaluated by potentialdynamic polarization in 3.5 wt% NaCl solution. Figure 3 depicts the potentialdynamic polarization curves of all three samples. The corrosion potential (E_{corr}) and corrosion current density (j_{corr}), which were obtained from potentialdynamic polarization curves in Figure 3 are summarized in Table 2. The magnesium alloy

substrate exhibits a corrosion potential of -1.548 V, and the associate corrosion current density is 4.169×10^{-5} A/cm². As for the magnesium alloy coated in the electrolyte without WC particles, the corrosion potential (-1.447 V) of PEO coating shifts about 101 mV to the positive direction and its current density (4.237×10^{-7} A/cm²) reduced approximately by two orders of magnitude with respect to that of magnesium alloy substrate. For the PEO coating produced in the electrolyte with WC particles, the corrosion potential (-1.201 V) shifts significantly (347 mV) to the positive direction and its current density (1.225×10^{-8} A/cm²) reduced approximately by three orders of magnitude. It is shown that the superior anticorrosion performance of the magnesium alloy coated in the electrolyte containing WC particles can be attributed an increase of coating thickness and a decrease of micropores and microcracks, as well as the WC particles incorporation into the oxide coating [22].

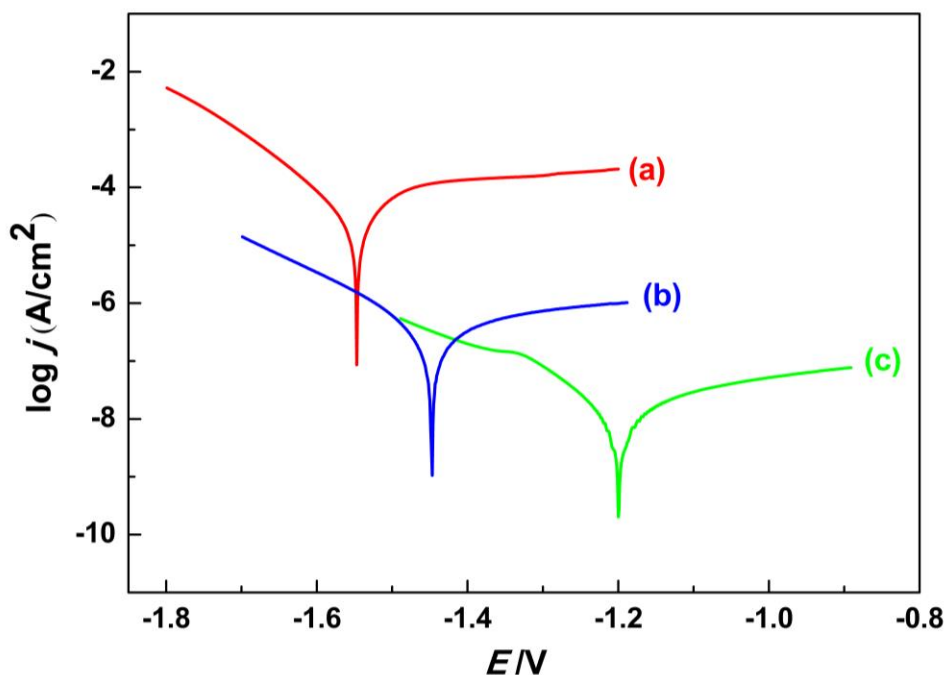


Figure 3. Potentiodynamic polarization curves of magnesium alloy substrate (a) and PEO coatings formed in the electrolyte without (b) and with (c) WC particles

Table 2. Electrochemical parameters related to potentiodynamic polarization curves

Sample	E_{corr} (V)	j_{corr} (A/cm ²)
Magnesium alloy substrate	-1.548	4.169×10^{-5}
Coating formed in electrolyte without WC particles	-1.447	4.237×10^{-7}
Coating formed in electrolyte with WC particles	-1.201	1.225×10^{-8}

The microhardness of AZ31B magnesium alloy substrate and PEO coating with and without WC particles is shown in Figure 4. Apparently, the microhardness of the magnesium alloy substrate could be enhanced significantly after PEO process and a doubled microhardness is found in case of PEO coating formed in alkaline electrolyte without WC particles. And the microhardness of PEO

coating is further improved after PEO process in alkaline electrolyte with WC particles, which is about five folds compare to the substrate. The value is up to 365 HV. This can be attributed to the introduction of WC particles into the ceramic coating during the PEO process, which is confirmed by XRD results.

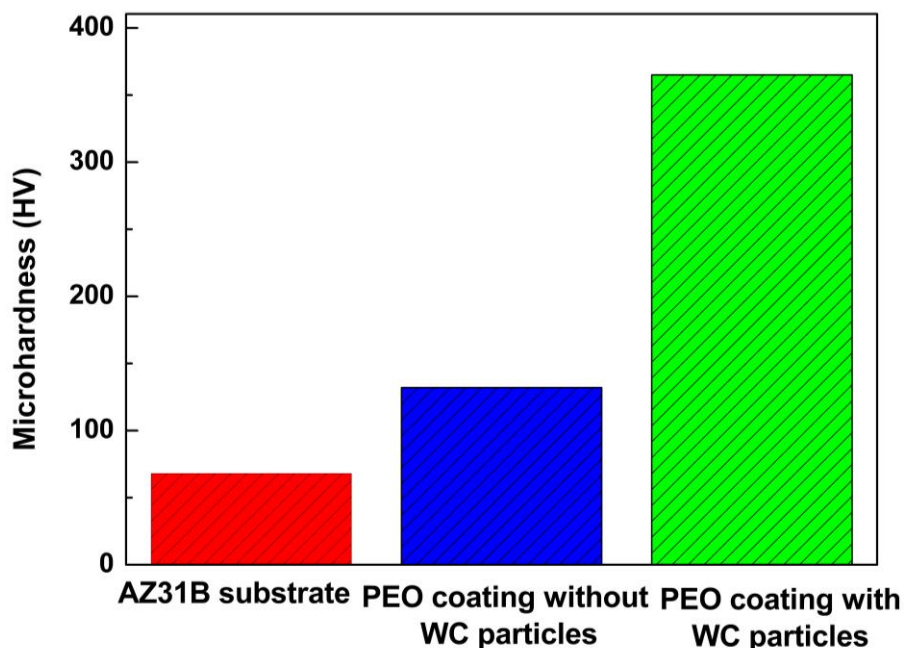


Figure 4. Microhardness of AZ31B substrate and PEO coating formed in the alkaline electrolyte with and without WC particles

4. CONCLUSIONS

Oxide coatings were prepared on AZ31B magnesium alloy using plasma electrolytic oxidation in alkaline electrolyte with and without WC particles. The surface of PEO coating produced in the alkaline electrolyte with WC particles was more uniform with less structural imperfections than that of coating produced in the electrolyte without WC particles. XRD analysis proved that the composition of sample treated in the alkaline electrolyte with WC particles contained MgO, MgSiO₃, Mg₂SiO₄, and WC. It is shown from the corrosion tests that the corrosion resistance of PEO coating produced in the alkaline electrolyte with WC particles was improved. The microhardness of PEO coating with WC particles is improved with the value of 365 HV.

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