Int. J. Electrochem. Sci., 7 **(2012)** 9573 - 9579

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Effects of Sucrose on Anodized Film Formed on AZ31B Magnesium Alloy in Environmental-Friendly Electrolyte

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Received: 21 August 2012 / *Accepted:* 7 September 2012 / *Published:* 1 October 2012

An environmental-friendly electrolyte, which contained an addition of sucrose, was used to prepare an anodized film on AZ31B magnesium alloy under the constant current density of 1 A/dm^2 at room temperature. Effects of sucrose on the properties of anodized film were characterized by scanning electron microscopy (SEM), energy dispersion spectrometry (EDS), X-ray diffraction (XRD), potentiodynamic polarization and electrochemical impedance spectroscopy (EIS), respectively. The results show that the anodized film formed in the electrolyte with addition of 10g/L sucrose has superior uniform surface and higher corrosion resistance than that obtained in other conditions.

Keywords: AZ31B magnesium alloy; anodizing; sucrose; corrosion resistance

1. INTRODUCTION

Magnesium alloys are have been used extensively in light weight engineering applications because of their excellent physical and mechanic property such as low density and high specific strength [1]. However, the poor corrosion resistance of magnesium alloys restricts their further application [2].

Anodizing treatment which is one of the popular surface protective technologies for Mg alloy can produce a thick, hard, adherent and abrasion-resistance film [3-5]. Unfortunately, environmental harmful inorganic (such as toxic chromate [6], harmful phosphate [7] and fluoride [8]) or toxic organic electrolytes (such as 1H-benzotriazole [9] and borate-benzoate [10]) were still employed in the anodizing electrolytes. Therefore, an environmental-friendly anodizing treatment is needed for the corrosion protection of Mg alloy.

In this paper, an environmental-friendly alkaline electrolyte of 45 g/L NaOH, 70 g/L Na_2SiO_3, 90 g/L $Na_2B_4O_7$ containing sucrose as additive was investigated for the AZ31B Mg alloy. The effect of sucrose on morphology, composition and phase structure of the anodized film were investigated by SEM, EDS and XRD. The corrosion resistances of the anodized film were evaluated by potentiodynamic polarization and EIS.

2. EXPERIMENTAL

2.1 Materials

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 $\leq$0.1, Cu$\leq$0.05, Ni 0.005, and Mg balance. Samples of 30mm×20mm×2mm were mechanically cut from large foils and polished with successively finer grades of emery paper from 180 to 1000 grits. The area of samples for the electrochemical tests exposed to the electrolyte was 1 cm^2.

2.2 Preparation of anodized film

The direct current mode was applied to the anodizing for 15 min at room temperature with current density of 1 A/dm^2. The AZ31B Mg alloy and the stainless steel were used as the anode and cathode. The anodized electrolyte was composed of 45 g/L NaOH, 70 g/L Na_2SiO_3, and 90 g/L $Na_2B_4O_7$ with the addition of 0, 5, 10, 15g/L sucrose.

2.3 Characterization

The surface morphology of the anodized films was examined by a scanning electron microscopy (SEM, HITACHI, S-4800). Energy dispersive spectrometry (EDS) attached to SEM was used to detect elemental composition of the anodized film on the magnesium substrate. The phase structure of the films was determined by X-ray diffraction (XRD, DX-2600, China), using Cu Kα radiation source.

Potentiodynamic polarization was carried out using CHI 842B and electrochemical impedance spectroscopy (EIS) was employed using AUT 84466. All the electrochemical measurements were operated in the neutral 3.5% NaCl solution at 25 ºC. Measurements were conducted in a traditional three-electrode system, counter electrode is a large area platinum sheet and reference electrode is a saturated calomel electrode (SCE).

3. RESULTS AND DISCUSSION

3.1 Surface morphology

Figure 1 presents the morphologies of anodized films which were produced in the electrolyte with and without the sucrose. It is clearly seen from Figure 1(a) that the film formed in the electrolyte without sucrose demonstrated a rough surface appearance. Many micropores with 5~10 μm in diameter can be found on the surface of the magnesium alloy, indicating that the film can be easily eroded. Figure 1(b) is the morphology of anodized film with addition of 5 g/L sucrose in electrolyte. It can be seen that the surface of the anodized film is uniform and the pores became smaller. Obviously, with increasing the sucrose concentration, the film became more uniform and less micropores, which formed in the electrolyte with addition of 10 g/L sucrose, as shown in Figure 1(c). However, when the added concentration of sucrose was 15 g/L, the surface morphology of the film no longer changed. It was indicated that the optimum concentration of the sucrose was 10 g/L.

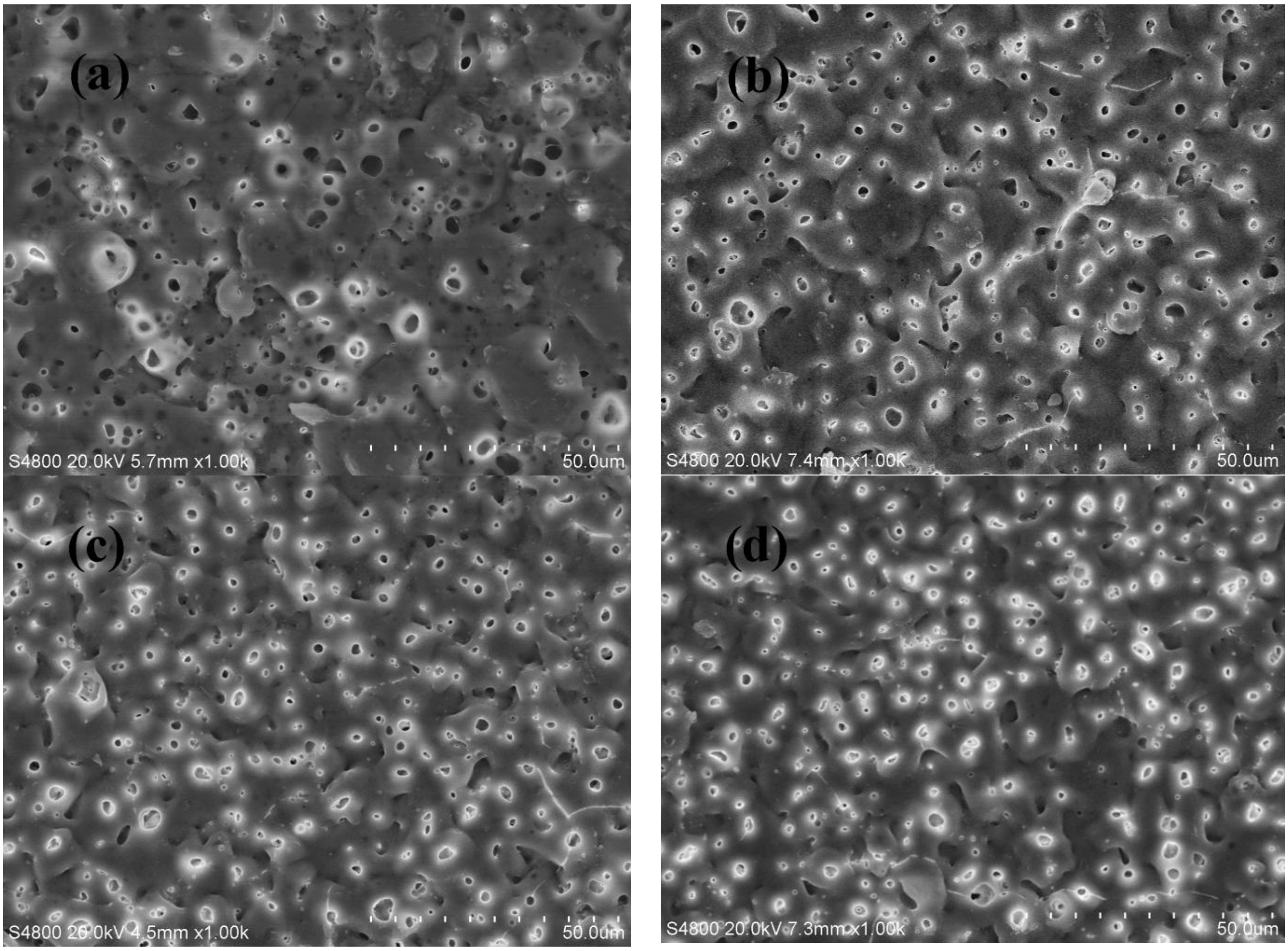

Figure 1. SEM images of anodized film in alkaline sodium silicate and sodium borate with addition of sucrose: (a) 0 g/L, (b) 5 g/L, (c) 10 g/L, (d) 15 g/L

3.2 EDS and XRD analysis

The composition and the structure of anodized film processed in the electrolyte with and without sucrose have been identified by EDS and XRD, respectively. As shown in Table 1, it is clearly demonstrated that the anodized film mainly composed of O, Si and Mg as well as the trace of Na and Al. The elements O and Si mainly ascribed to the incorporation species into the anodized film from the electrolyte, Mg and Al came from the substrate. It was worthy to point out that the characteristic element C of sucrose was detected with addition of 10g/L sucrose. These results indicated that the addition of sucrose participated in the anodic oxidation process and affected the element composition of the anodized film.

The XRD patterns of the anodized film formed in the electrolyte with and without the addition of sucrose was presented in Figure 2. It was shown that the two XRD patterns displayed almost the same conditions. This could be ascribed to the porous surface of anodized film which can not be avoided whether the electrolyte contained or excluded the addition of sucrose, as shown in Figure 1. On this frame, the X-ray can easily penetrate the porous anodized film [9,11]. Moreover, we have not found any peaks associated with the C element, so we considered that the C element may be amorphous in the anodized film.

Table 1. Element percent of the anodized film on the surface of Mg alloy substrate from EDS

Anodized film	Weight (%)					
	O	Na	Mg	Si	Al	C
Without sucrose	55.7	6.2	28.3	9.1	0.7	--
With sucrose	53.9	3.1	34.1	8.8	1.1	5.8

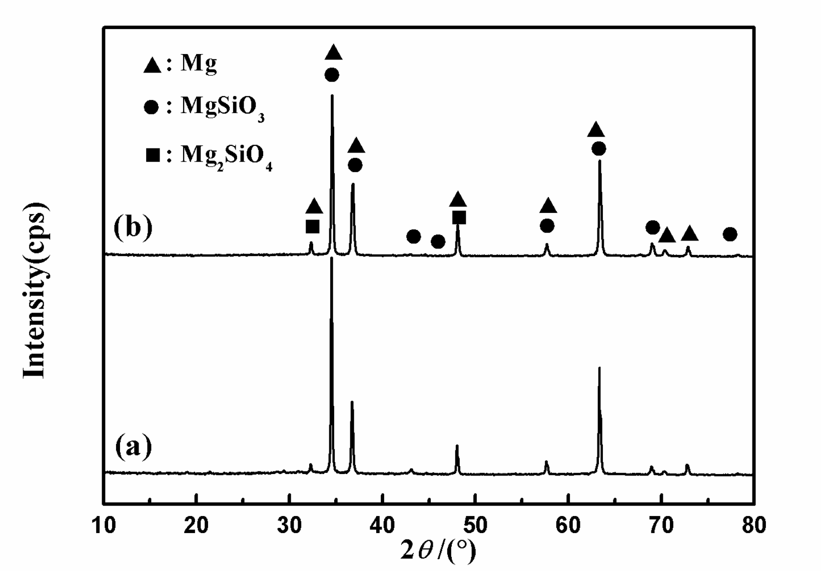

Figure 2. XRD patterns of anodized films formed in the electrolyte without (a) and with (b) the addition of sucrose

3.3 Polarization curve

The potentiodynamic polarization curves and electrochemical parameters of the anodized film are shown in Figure 3 and Table 2, respectively. The corrosion potential (E_{corr}), corrosion current density (j_{corr}), and anodic/cathodic Tafel slopes (β_a and β_b) were obtained from potentiodynamic polarization curves in Figure 3. These results are summarized in Table 2. Based on the approximately linear polarization behavior near OCP (open circuit potential), the polarization resistance (R_p) values were determined using the equation [10].

$$R_p = \frac{\beta_a \beta_b}{2.303 j_{corr} \left(\beta_a + \beta_b\right)} \qquad (1)$$

For the anodized film formed in the absence of sucrose, E_{corr}, j_{corr} and R_p are -1.448V, 2.334×10^{-7} A/cm^2, 2.330×10^{6} Ωcm^2, respectively. For the anodized film formed in the electrolyte with sucrose, E_{corr} is shifted to the positive direction (Figure 3), j_{corr} is reduced, and R_p is increased (Table 2). When there is 10 g/L of sucrose in the electrolyte, E_{corr}, j_{corr} and R_p are -1.317 V, 1.605×10^{-8} A/cm^2, 2.627×10^{7} Ωcm^2, respectively (Table 2). With the further increasing of sucrose concentration (15 g/L), E_{corr} is shifted to the negative direction (Figure 3), j_{corr} is increased, and R_p is decreased (Table 2). These results suggested a big enhance in the corrosion protection performance of the anodized films [9,10], and the anodized film with excellent anticorrosion performance could be produced in the electrolyte with the addition of 10g/L sucrose.

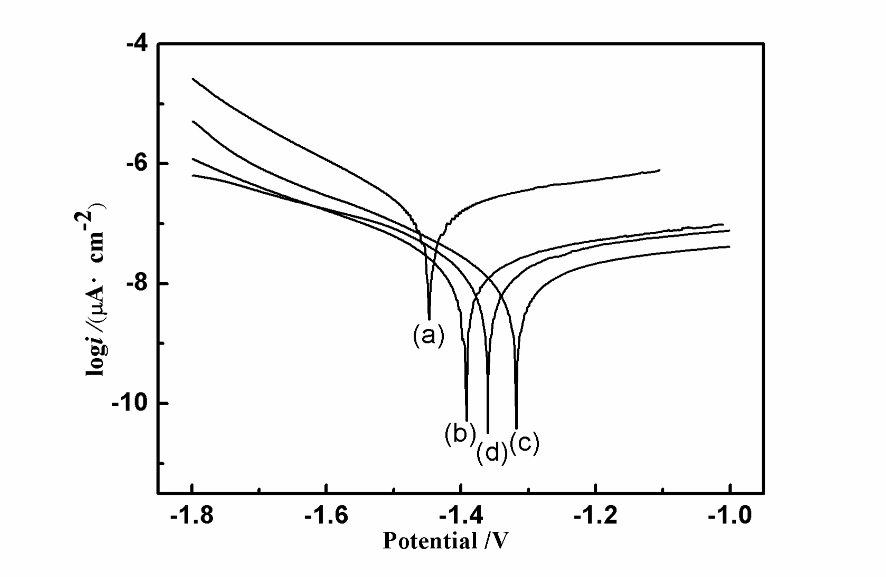

Figure 3. potentiodynamic polarization curves for AZ31B Mg alloy treated with addition of sucrose: (a) 0 g/L, (b) 5 g/L, (c) 10 g/L, (d) 15 g/L

Table 2. Electrochemical parameters related to potentiodynamic polarization curves

	E_{corr}(V)	β_a (mV)	β_b (mV)	R_p(Ωcm^2)	j_{corr}(A/cm^2)
(a)	-1.448	-6.184	1.570	2.330×10^{6}	2.334×10^{-7}
(b)	-1.392	-4.180	1.462	1.667×10^{7}	2.822×10^{-8}
(c)	-1.317	-4.292	1.255	2.627×10^{7}	1.605×10^{-8}
(d)	-1.361	-4.304	1.436	1.724×10^{7}	2.712×10^{-8}

3.4 EIS test

The corrosion resistance of the anodized AZ31B Mg alloy in 3.5% NaCl solution was evaluated by EIS at the open circuit potential. Figure 4 shows the Nyquist plot of anodized films produced in the electrolyte with and without the sucrose. As shown in Figure 4, there is one capacitive loop for the anodized films. The diameter of capacitive loop in the Nyquist plane represents the polarization resistance of the working electrode, the higher of the polarization resistance, the stronger anticorrosion property [9,10,12].

The results showed that the polarization resistance of anodized films processed in the electrolyte without sucrose was 11600 kΩ·cm^2. It also can be obtained from Figure 4 that the addition of the sucrose influenced the anticorrosion property of the anodized films. With increasing sucrose concentration, the semicircles in the Nyquist plot expanded, indicating a better anticorrosion performance. When the concentration of sucrose is 10g/L, the increase of polarization resistance up to 27700 kΩ·cm^2, as depicted in Figure 4. However, when the concentration of sucrose was 15 g/L, the polarization resistance decreased, the value of which is 20000 kΩ·cm^2. The result indicated that the corrosion resistance of anodized film has been improved obviously due to the addition of sucrose, which was in accordance with the results obtained from the potentiodynamic polarization technique.

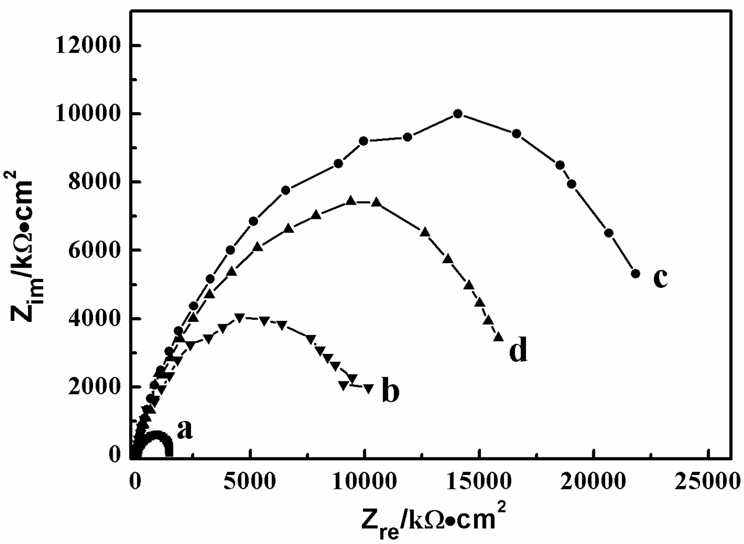

Figure 4. Nyquist plot for the anodized films formed in the electrolyte with the addition of sucrose: (a) 0 g/L, (b) 5 g/L, (c) 10 g/L, (d) 15 g/L

4. CONCLUSIONS

The microstructure and corrosion resistance of anodized film on AZ31B magnesium alloy processed in the electrolyte without and with sucrose was investigated. With the addition of sucrose in the electrolyte, the quality of the anodized film was greatly improved. And the anodized film with excellent anticorrosion performance could be produced in the electrolyte with the addition of 10g/L sucrose.

ACKNOWLEDGEMENT
This work was supported by the Research Projects of Zhejiang Educational Committee (Y201122429).

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