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Trabalho apresentado durante o INTERCORR 2018, em São Paulo, no mês de maio de 2018.

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Effect of the anodizing potential on the corrosion behavior of the AZ31B magnesium alloy

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Abstract

Magnesium alloys have attracted much attention as biodegradable orthopedic and cardiac implants. They can be gradually dissolved, absorbed, consumed or excreted in human body environment. The fast degradation always leads to hydrogen evolution and alkalization of the solution. Anodization treatment is an electrolytic oxidation process in which the metallic surface is converted to an oxide film having desirable corrosion protective and functional properties. Investigations have been performed to study the effects of the electrolyte composition and electric parameters on the properties of the film. The aim of this work was to investigate the effect of the anodizing potential on the corrosion behavior of the AZ31B alloy. Samples were anodized using 20 V, 60 V and 120 V for 5 minutes in a solution consisted of 1 M NaOH and 0.5 M Na₂SiO₃. The corrosion protection ability of the anodized films was investigated by using potentiodynamic polarization (PDP). Film morphology was examined by scanning electron microscopy (SEM) and confocal laser scanning microscopy (CLSM). The results revealed that the film formed under 120 V provides the best morphology and anticorrosion behavior.

Keywords: anodizing, magnesium alloy, corrosion

Introduction

High corrosion rate is an intrinsic response of magnesium alloys to chloride containing solutions (1-5). Magnesium alloys as biodegradable implants had already been applied to the orthopedic surgery at the first half of last century (6,7). Although good biocompatibility was found during the clinical application, a large amount of hydrogen bubbles was accumulated next to the implant due its fast degradation, which would delay healing of the surgery region and lead to necrosis of tissues (1,2, 6). Further, OH⁻ anions, which is another aggressive by-product of the corrosion reaction in aqueous media have been found close to magnesium, promoting a pH alkalization near the biomaterial (8-10).

A strategy to solve these problems is to slow down the biodegradation (i. e. corrosion) of magnesium alloys, so Mg²⁺ ions, H₂ bubbles and OH⁻ ions will be release more slowly, which will allow the human body to gradually adjust or deal with the biodegradation products (1,6). Actually, one of major and popular technique for solving the problem is surface treatment is

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anodization (3,4,11). Anodization treatment is an electrolytic oxidation process in which the metal as anode is converted to an oxide film having desirable corrosion protective and functional properties (4,12). It can increase the film thickness, hardness, wear resistance, and provide a better adhesion and biocompatibility for primers than the bare metal.

Investigations have been performed to study the effects of the electrolyte composition, electric parameters (such voltage, current, waveform), post and pre-treatment on the properties of anodized film (3, 12-15). However, the effect of the anodization potential associated to constant time in silicate-hydroxide solutions was scarcely investigated. The anodizing conditions have a deep influence on the composition and microstructure of the anodic film as well. Therefore, the search for an appropriate set of these parameters, which interact with each other, is necessary to obtain a surface with the desired functionalities.

Thus, in the present work, films were grown on AZ31B magnesium alloy by anodization varying its potential formation in 0.5 M Na₂SiO₃ and 1 M NaOH solution. The protective characteristics of these films were investigated by using potentiodynamic polarization (PDP), scanning electron microscopy (SEM) and laser confocal scanning microscopy.

Experimental

Materials

Hot rolled AZ31B magnesium alloy sheet, composition: Al 2.33%, Zn 1.27%, Mn 0.68%, Fe 0.68% and Mg balance, provided by Xi'an Yuechen Metal Products CO. LTD., China. All the samples were connected with a copper wire in one side and then enveloped by epoxy resin adhesive mounted in a PVC holder, leaving an average area of 0.30 cm² as the working surface. The surfaces were sequentially grinded using SiC sand paper (from #220 to #2400 grit size), polished using diamond paste (0.6 μm) and cleaned using deionized water and ethanol, being subsequently dried in a warm air stream with conventional heat gun.

Anodizing treatment

Anodization experiments were performed by a DC Power supply, with the sample as the anode and the stainless steel plate as cathode. The electrolyte consists in 0.5 M Na₂SiO₃ and 1 M NaOH, prepared with deionized water (18.2 MΩ.cm). The duration of the tests was 5 minutes at room temperature. The samples were anodized under three different voltages: 20, 60 and 120 V. Finally, the oxide films were rinsed by ethanol.

Characterization

Scanning electron microscope (SEM – Model JSM-6010LA, Jeol) and confocal laser scanning microscope (CLSM – Model LEXT OLS4100, Olympus) were used for observing the surface morphology of the samples.

The corrosion behavior was assessed in a potentiostatic/galvanostatic (Model MULTIAUTOLAB 101, Autolab) using a typical three-electrode configuration. The cell consisted of a Ag/AgCl (KCl 3 M saturated) as the reference, a platinum wire as the counter electrode and the sample as the working electrode. The tests were conducted in a phosphate buffer solution (PBS), which contains: 0.2 g/L KCl, 0.2 g/L, KH₂PO₄, 8 g/L NaCl, 1.150 g/L Na₂HPO₄ (anhydrous). The solution was prepared with deionized water and analytical grade reagents. The tests were performed at room temperature. First, the open circuit potential

(OCP) were monitored for 1 hour. Next, the samples were subjected to potentiodynamic polarization in a potential region of -500 mV (vs. OCP) to 0 V at a scanning rate of 1 mV/s.

Results and discussion

SEM images of the AZ31B magnesium alloy in the as-polished and anodized conditions are shown in Fig. 1. The bare substrate (Fig. 1a) showed some cracks on its surface. The film formed under 20 V (Fig.1b) produced a non-uniform and defective distribution of the film along the substrate. The same features can be observed for the 60 V condition, in which the film did not spread over the whole surface, although its particle size and coverage were higher than those of the 20 V-film. The film formed at 120 V covered the whole substrate and is denser and thicker than the others. However, this condition promoted some holes of different sizes caused by sintering (12,13). Furthermore, although high anodizing voltages are capable of increasing the film thickness, they also creates pores and micro-cracks as well (14-16).

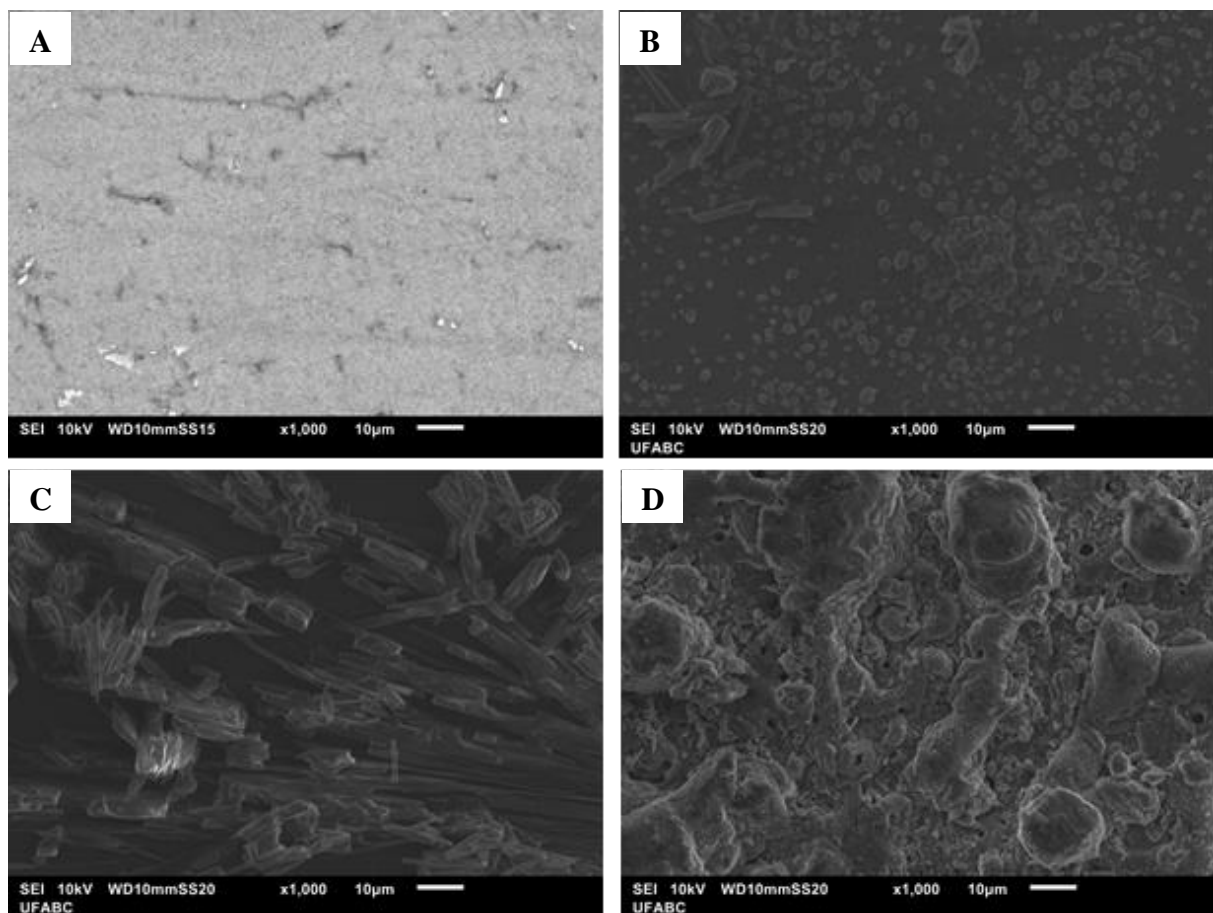


Figure 1 – SEM micrographs of the AZ31B alloy in the as-polished and anodized conditions: A) As-polished; B) 20 V; C) 60 V and D) 120 V.

CLSM images of the AZ31B magnesium alloy in the as-polished and anodized conditions are shown in Fig. 2. In Tab. 1, roughness average values (Ra) of each condition are presented. As can be perceived from the images, all the coating conditions exhibited a heterogeneous surface. The anodized layers obtained at 20 and 60 V are porous and it did not cover the whole surface. In turn, the 120 V-film is more homogeneously distributed. From the results

shown in Tab. 1, the Ra values increases with the anodizing potential in agreement with the literature (17, 18).

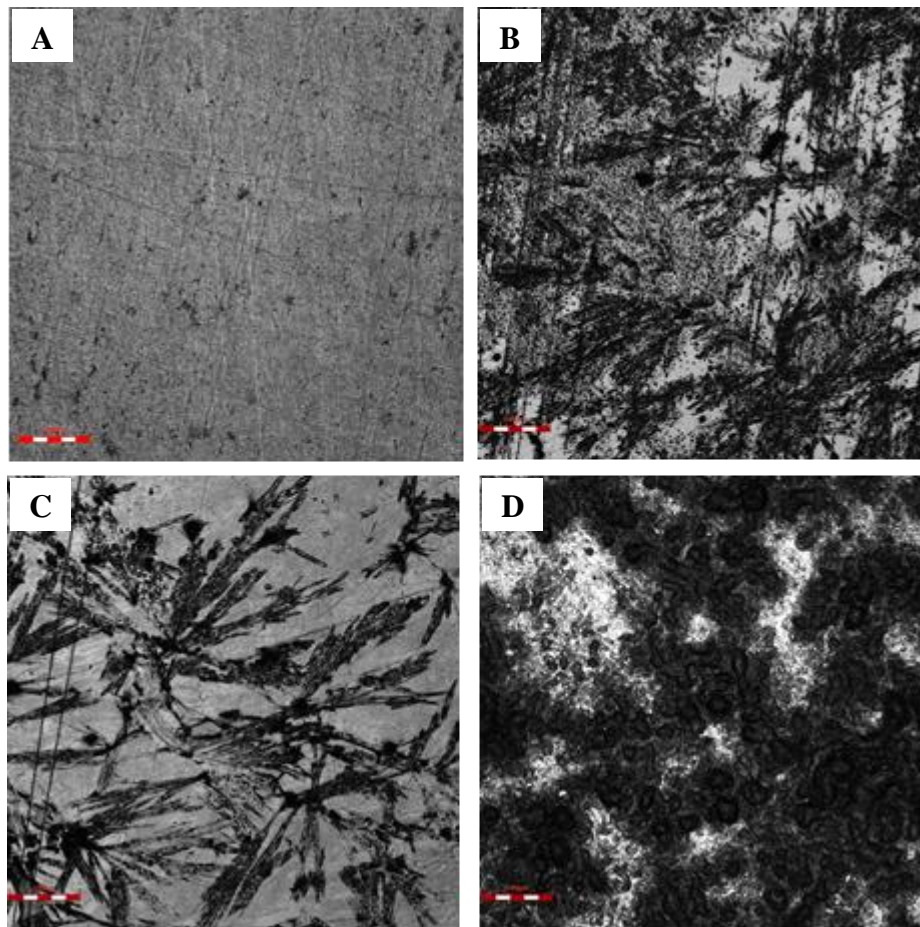


Figure 2 – CSLM images of the AZ31B alloy with and without anodized films A) As polished; B) 20 V; C) 60 V and D) 120 V.

Table 1 – Roughness average parameter of the AZ31B alloy samples determined from the CLSM micrographs shown in Fig. 2.

Conditions	Roughness average (Ra)
As-polished	0.07 ± 0.01
20 V	0.28 ± 0.05
60 V	1.35 ± 0.24
120 V	1.39 ± 0.18

Potentiodynamic polarization curves of the AZ31B magnesium alloy in the as-polished and anodized conditions are shown in Fig. 3. The values of corrosion potential (E_{corr}) and corrosion current density (I_{corr}) were determined from the curves using the Tafel extrapolation method, considering only the cathodic branches. The results are displayed in Tab. 2. As can be observed in Fig. 3, the E_{corr} values were not substantially affected by the presence of the anodized films; it indicates that the electrochemical stability of the system was not modified. However, the corrosion current density, in turn, was strongly affected by the anodized layers, especially for the 120 V condition for which i_{corr} is reduced by almost one order of magnitude

with respect to the as-polished material. This parameter denotes the capability of the substrate to withstand anodic dissolution. According to Chai et al. (2008), the electric parameters of the anodizing process such as voltage and current density have marked effect on the film thickness and morphology. At higher potentials is expected to obtain thicker anodized layers, meanwhile it promotes an increase in the roughness and porosity of the film, which is in agreement with the literature (18,19). An incipient passive region is perceived in the anodic branch of the polarization curves for the anodized samples, while the bare substrate presents an active dissolution. This behavior suggests that the anodizing treatment produces a protective coating in the AZ31B magnesium alloy.

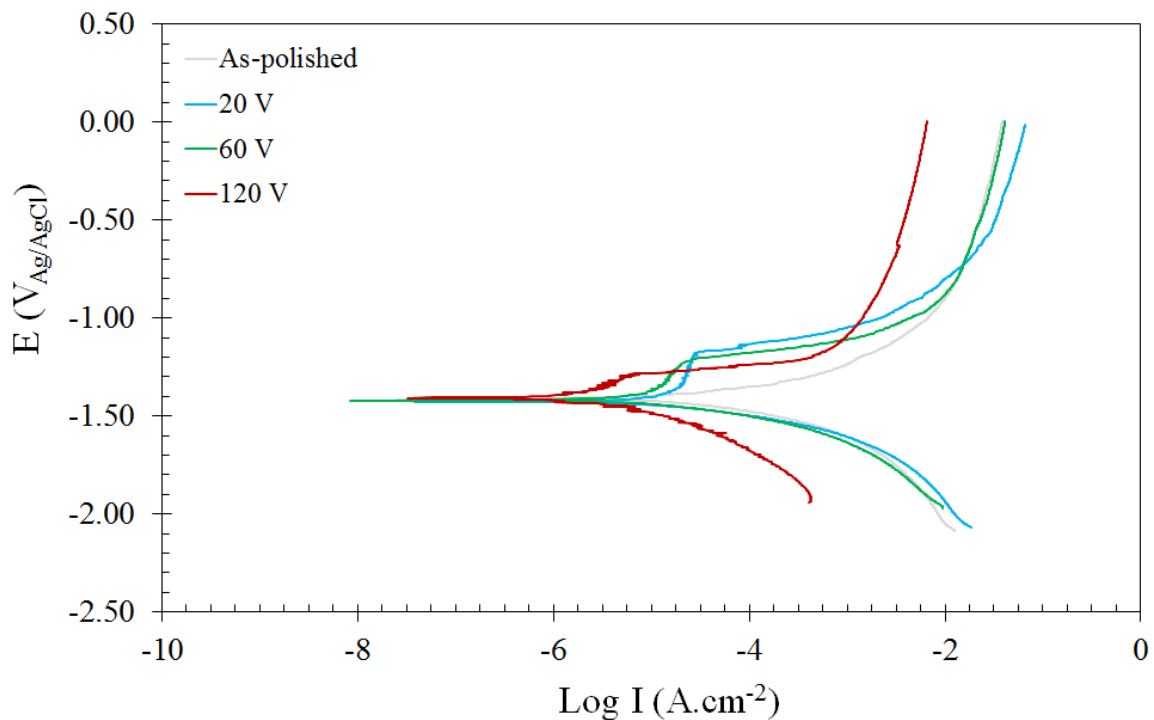


Figure 3 – Potentiodynamic polarization curves of the AZ31B alloy in the as-polished and anodized conditions in PBS electrolyte at room temperature.

Table 1 – Electrochemical parameters of the AZ31B alloy samples determined from the potentiodynamic polarization curves shown in Fig. 3

Conditions	E_{corr} ($V_{\text{Ag/AgCl}}$)	I_{corr} ($\mu\text{A}\cdot\text{cm}^{-2}$)
As-polished	-1.410	34.1
20 V	-1.428	25.4
60 V	-1.420	13.1
120 V	-1.409	3.5

Conclusions

Oxide films were produced on AZ31B magnesium alloy by anodization treatment in 1M NaOH and 0.5 M Na_2SiO_3 solution during 5 minutes varying the formation potential. The anodized layers morphology were investigated by SEM and CLSM, it indicated that the anodizing potential mainly affect the roughness and compactness of the films. The results

obtained by the polarization curves are in a good agreement with the morphology analyses. The film formed under 120 V is thicker and covered the whole surface providing the best dissolution resistance.

Acknowledgements

The authors are grateful to the Brazilian agency CAPES for the financial support and to the Multiuser Central Facilities (UFABC) for the experimental support.

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