Diagnostics of the thickness of a plasma electrolytic oxidation coating on a nanostructured Mg-Sr alloy

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Abstract. This study is focused on the development of a method for controlling the thickness of a plasma electrolytic oxidation (PEO) coating on a new nanostructured Mg-2wt%Sr alloy. The process of high pressure torsion of a solution-treated Mg-2wt%Sr magnesium alloy was investigated. A significant reduction in the grain size to 500 nm was attained. The PEO coating process on the new nanostructured Mg-2wt%Sr alloy was studied. The produced coating was compared with a PEO coating with a coarse-grained structure. The waveforms of unipolar voltage pulses of a power source were studied, and electrical transients that can be described by an exponential of the second order were revealed. The relationship between the time constant of the electrical transient exponent and the thickness of the PEO coating was justified. A method for estimating the thickness of the PEO coating on the surface of the Mg-2wt%Sr alloy in terms of the parameters of the electric transient was proposed.

1. Introduction

Magnesium and magnesium alloys are of a great interest for biomedical applications, since they have a number of advantages compared to other materials [1, 2]. In particular, magnesium is a biodegradable material, and it has a Young's modulus close to that of a human bone [3]. A biodegradable magnesium implant enables avoiding a second surgery on a patient after a fracture unites [4]. Also, magnesium, as a chemical element, is vital for the human body, and it can be considered as a medical material that encourages bone tissue restoration.

The general disadvantage of all magnesium alloys is low strength and considerable corrosion rate; therefore, studies on the enhancement of the mechanical and corrosion properties of magnesium implants are actively carried out globally at the cutting edge of chemical and material science. Several technological treatments for a magnesium alloy and its surface can be applied in order to solve this problem: (i) alloying using a biocompatible Sr element; (ii) refinement of a grain structure via methods of severe plastic deformation, such as high pressure torsion (HPT) and equal channel angular pressing [5, 6]; (iii) applying a biocompatible coating by plasma electrolytic oxidation (PEO) [7, 8].

Properties of coatings on biodegradable implant surface have a significant influence on the dissolution rate. The PEO process helps to achieve the required surface properties better than other methods, and it has advantages in terms of environmental safety and effectiveness [9]. Coating thickness is its most important property. In-situ diagnostics and accurate achievement of the coating thickness will help to control the dissolution rate of the coated implant.

One of the in-situ ways to obtain information about the coating thickness is to study the electrical characteristics of the electrolyzer in response to the input pulses generated by the power supply. Therefore, the aim of this study is to develop a method for controlling the thickness of the PEO coating on a new nanostructured Mg-2wt%Sr alloy during the treatment.

2. Experimental

2.1. Material and surface characterization
A Mg-2wt%Sr magnesium alloy was chosen as the initial material. The samples were subjected to solution treatment at a temperature of 450 °C for 20 hours, followed by quenching. The thermal treatment of the Mg-2wt%Sr samples was carried out in an electric furnace Nabertherm (in air atmosphere).

The microstructure of the Mg-2wt%Sr sample after the solution treatment is shown in figure 1. The microstructure of the alloy is a solid solution (α-Mg) with a separated eutectic (α-Mg + Mg$_{17}$Sr$_2$) at the grain boundaries. The average grain size of α-Mg was 85 μm. The volume fraction of the eutectic phase was 20.9%.
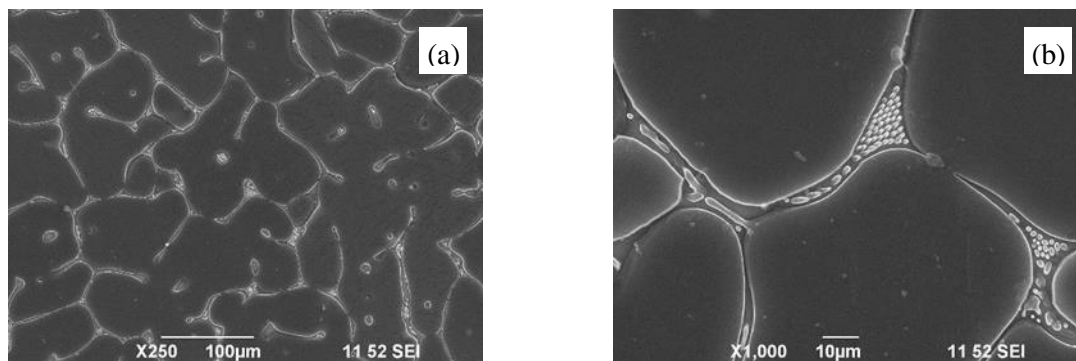

Figure 1. Microstructure of Mg-2%Sr alloy in the solution-treated state.

The solution-treated samples of the alloy under investigation in the form of disks with a diameter of 20 mm and a thickness of 2 mm were subjected to high pressure torsion for structure refinement [5]. The alloy disks under investigation were deformed at room temperature, at a speed of 1 rpm, with an applied pressure of 6 GPa; the number of revolutions was 10. During HPT the sample temperature reached 50-80 °C.

Analysis of the microstructure was carried out with a JEM6390 scanning electron microscope (SEM) with an accelerating voltage of 10 kV. To reveal the alloy microstructure, the cross-sections were etched with the following solution: 2.5 mg picric acid; 2.5 ml. acetic acid; 5 ml. distilled water; 50 ml. ethyl alcohol. The average grain size was calculated using the linear intercept method from the SEM images.

Study of the nanostructure was performed on a JEOL JEM-2100 transmission electron microscope (TEM) at an accelerating voltage of 200 kV. The foils for the TEM investigation were prepared using a Tenupol-5 double-jet electro-polishing machine with the following electrolyte: 30% HNO$_3$, 70% methanol. The average grain size was estimated by averaging the maximum and minimum grain sizes, according to the dark-field images. The number of the analyzed grains was 300.

2.2. Plasma electrolytic oxidation

The following Mg-2wt%Sr samples were used for the plasma electrolytic oxidation: solution-treated samples, with the initial coarse-grained structure (CG); samples with a nanostructure after HPT processing (nano).

The PEO treatment was performed using a unipolar voltage-controlled power supply. Square waveform voltage was applied to the sample connected as an anode; and the electrolyzer connected as a cathode. The processing parameters are given in table 1. The electrolyte composition which enables producing biocompatible Ca- and P- compounds in the PEO coating was chosen as elsewhere [10]. The coating thickness was measured by a Defelsko Positector 6000 eddy current gauge.

Table 1. Parameters of the PEO treatments and coating thickness.

Sample No.	Mg-2%Sr structure	Coating thickness (μm)	Electrolyte (g/L)	Temperature ($^\circ$C)	Voltage pulse amplitude (V)	Frequency (Hz)	Duty cycle (%)	Time (min)
1	CG	11.5	12 g/L $Na_7PO_4 \cdot 12H_2O$	20	470	500	10	10
2	nano	14.3	2 g/L $Ca(OH)_2$					

During the PEO treatment, the instantaneous values and DC components of current and voltage were recorded at a sampling frequency of 1 MHz, and at a rate of 1 s^{-1} by an automated data acquisition system L502 (L-Card, Russia) running under the LabVIEW control software.

3. Results and discussion

3.1. Microstructure of CG and nanostructured Mg-2wt%Sr alloy and PEO coating

As a result of the HPT processing, a new structure was produced in the Mg-2wt%Sr alloy, as shown in figure 2. During the HPT processing, the eutectic was destroyed and partially dissolved; its volume fraction became 17.5% (figure 2a). TEM studies revealed a strong refinement of the average grain size down to 500±37 nm (figure 2b).

Figure 3 shows the surface images of the PEO coating on CG and nanostructured Mg-2wt%Sr alloy. The coating thickness h on the nanostructured sample is 14.3 ±1.5 μm, and on the CG sample −
11.5 ±1.4 μm. The thicker coating on the nanostructured samples can be explained by the fact that this structure of this alloy has much higher total length of the grain boundaries which provide favorable conditions for the appearance of microdischarges [11].

Study of the SEM images using ImageJ software revealed the porosity of the coatings. It was found that the porosity of the coatings on CG and nanostructured samples is the same: 22.0 ±0.1%. Therefore, the electrical properties of the coatings that are discussed below do not depend on porosity.
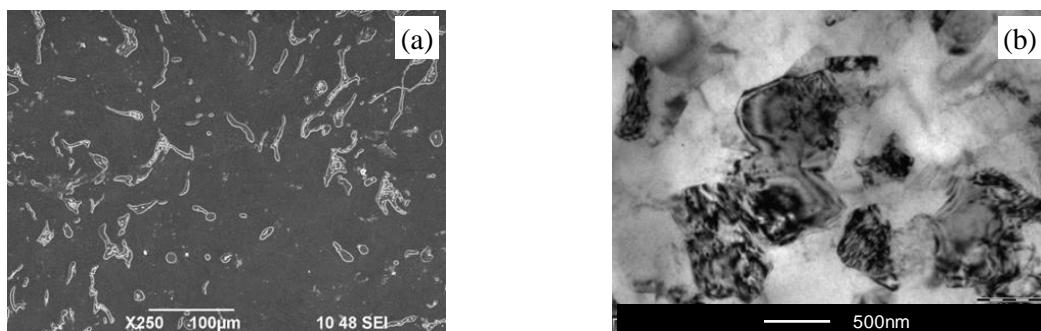

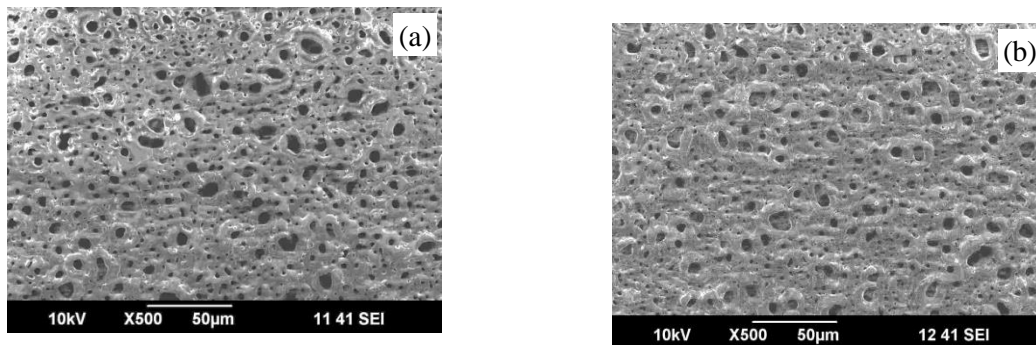**Figure 2.** Microstructure of Mg-2%Sr alloy after HPT: (a) SEM, (b) TEM.

Figure 3. SEM images of the resulting surface after the PEO of CG (a) and nano (b) Mg-2wt%Sr.

3.2. Electrical characteristics of the PEO process of CG and nanostructured Mg-2wt%Sr alloy

For analysis of the PEO electrical characteristics, the instantaneous values of voltage were represented as waveforms. The voltage waveforms at the beginning of the treatment and after 10 minutes are shown in figure 4. The evolution of the DC components of the current and voltage during the PEO are presented in figure 5. As it can be seen from the waveforms, the shape of the electrical signal changes in long time scale (curves 1 and 2 in figure 4). It is known that in the equivalent circuit of the PEO electrolyzer, the coating can be represented as two series branches containing a resistor and a capacitor in parallel [12]. Therefore, electrical transients seen in figure 4 appear as a reaction to switching off the power supply current pulses. Within the PEO process, the duration of electrical transients increases, which is associated with an increase in the coating thickness as shown elsewhere for CG Mg and CG Al [10, 12]. This study extends this method to a nanostructured substrate.

The curve fitting for the electrical transients was obtained using the following equation:

$$u(t) = A_1 e^{-\frac{t-t_0}{\tau_1}} + A_2 e^{-\frac{t-t_0}{\tau_2}} + C, \qquad (1)$$

where A_1, A_2, C are integration constants; τ_1 and τ_2 are time constants; t_0 is the starting time of the voltage fall, t is time.

Evolution of time constants τ_1 and τ_2 during the PEO treatment is shown in figure 6. According to figure 6, the value of the time constant τ_1 is comparable with the value of the voltage pulse cycle. The value of τ_1 increases exponentially and tends to approach a constant value. The values of the time constant τ_2 are an order of magnitude smaller than that of τ_1; this time constant grows linearly. The difference in τ_2 between CG and nanostructured substrate is negligible.
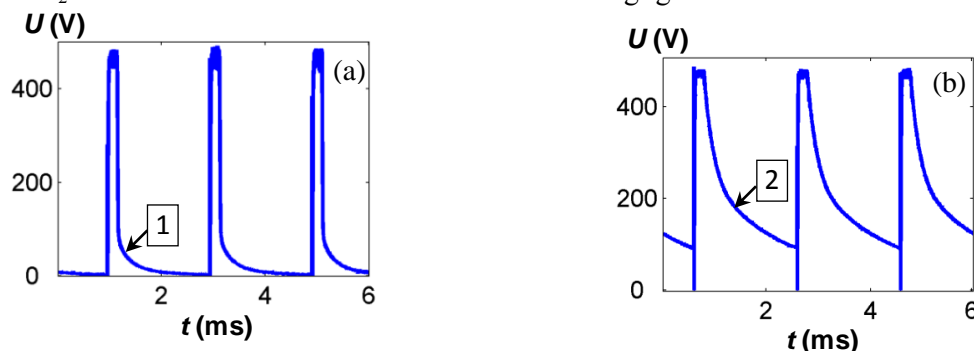

Figure 4. Voltage waveforms: on the 1st minute of the PEO (a); on the 10th minute of the PEO (b).
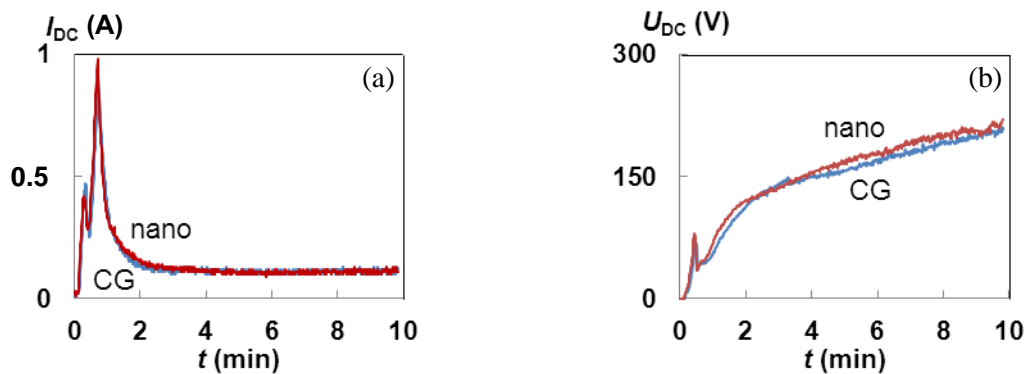
Figure 5. Evolution of DC current (a) and voltage (b) components during PEO of CG and nanostructured Mg-2wt%Sr alloy.
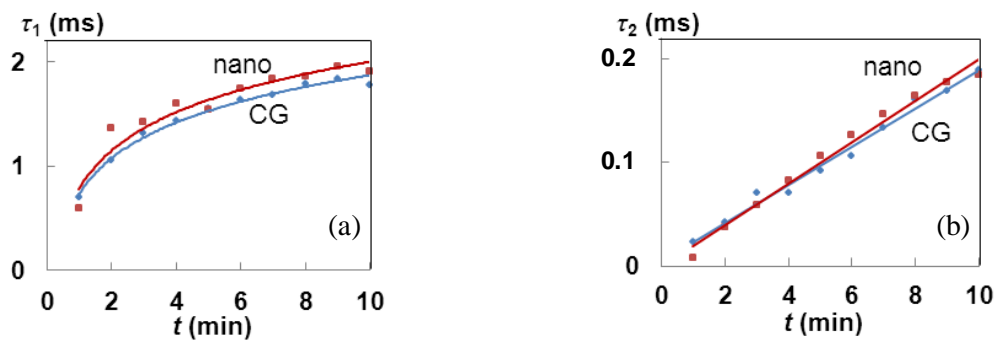

Figure 6. Evolution of the time constants τ_1 (a) and τ_2 (b) during PEO of CG and nanostructured Mg-2wt%Sr alloy.

Usually, a PEO coating on Mg alloy has a porous outer and a very thin compact inner layer [13]. This is reflected in two distinct time constants standing for the two layers of the coating structure both in the electrochemical impedance spectroscopy of PEO coatings on Mg [14] and in this study. These time constants characterize dielectric relaxation processes within those layers [10] as

$$\tau_1 = R_1 C_1, \tau_2 = R_2 C_2. \tag{2}$$

where R_1, R_2 – coating layer resistance, C_1, C_2 – coating layer capacitance.

Therefore, considering similar porosity of the outer layer for both CG and nanostructured samples, the outer layer capacitances should be the same; consequently, the resistances and time constants reflect the coating thickness.

As a result, taking into account the influence of the coating growth on electrical transients during the PEO, the coating thickness h can be evaluated as:

$$h = k_1 \cdot \tau_1 \tag{3}$$

where k_1 is a calibration constant. The coefficient k_1 is calculated from experimental data; for this study it is 7.0±0.3 [μm/ms].

Moreover, since there is a functional relationship between the duration of the electrical transients defined by the time constants, and the area under the waveform graph of the voltage pulses, the coating thickness can also be determined from the DC voltage component U_{DC} (figure 5) as

$$h = k_2 \cdot U_{DC} \tag{4}$$

The benefits of this method include simpler hardware and software implementation. The disadvantage is that the result of calculation of the coating thickness will be affected by the amplitude

of the voltage pulses, which can vary according to the processing program or because of unstable operation of the power supply; therefore, this approach needs further investigation.

4. Conclusion

Studies have shown that the application of HPT processing to a solution-treated Mg-2wt%Sr alloy with an average grain size of 85 μm leads to a significant refinement of the average grain size down to 500 nm.

Studies of the PEO coating on a new Mg-2wt%Sr alloy have been conducted. Investigation of the coating properties has shown that within the same treatment time, a thicker coating is formed on samples with smaller grain size. The porosity of the coating does not depend on the grain size of the alloy. The physical properties of the coating, such as electrical resistance, capacitance and thickness, have a significant effect on the transient processes caused by the power supply pulses.

A diagnostic method for determining the coating thickness during the PEO process for both coarse grained and nanostructured Mg-2wt%Sr alloy has been developed; this helps to carry out measurements without interrupting the technological process.

Accurate attainment of the specified thickness of a biocompatible coating on the surface of implants will help to control the dissolution rate of the future temporary implant in a human body for successful bone repair.

Acknowledgments

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