Study into initial stages of plasma electrolytic oxidation of magnesium alloy

V R Mukaeva, O V Melnichuk, R A Vasilev, I M Lutfakhmanov and E V Parfenov
Ufa State Aviation Technical University, 450008, Ufa, Russia
E-mail: veta_mr@mail.ru

Abstract. In the present work, a coating growth during plasma electrolytic oxidation on magnesium alloy was investigated. We observed the initial stages: electrochemical anodizing accompanied by anodic dissolution; oxidation with low power spark discharges; oxidation with microarc discharges. The study discusses the evolution of morphology, porosity, elemental composition in comparison with the PEO electrical characteristics and optical emission of microdischarges. The kinetic model, which is consistent with the observed mechanism of coating growth, is constructed.

1. Introduction
Recently, significant attention has been paid to materials for temporary implants [1–3], such as cardiovascular stents, bone fixation devices, and scaffolds for bone regeneration [4–5]. Magnesium alloys are promising materials for the biodegradable implants. However, the dissolution rate of magnesium alloys in the human body is too high and should be decreased [6]. A formation of the coating on the magnesium implant by plasma electrolytic oxidation (PEO) is a promising way to increase the corrosion resistance. PEO is an environmentally friendly technology, which uses high voltages. PEO coatings have good adhesion properties, high wear and corrosion resistance [7, 8]. The porous structure of the PEO coatings is a favourable basis for the subsequent application of organic coatings [9].

This work is devoted to the study of the initial stages of the PEO coating growth on magnesium alloy AZ31 in pulsed voltage mode. Despite the fact that the voltage regulation implies maintaining the pulse amplitude at the same level, at the initial stage the voltage must be gradually increased from zero to the operating level to avoid the PEO soft start. This subject is insufficiently studied. As follows from the literature, for different materials and electrolytes, the effect of the initial stage of PEO on the properties of coatings can be different [10].

Therefore, the purpose of this work is to describe the mechanism of the PEO coating growth based on the analysis of current and voltage signals, coating morphology, elemental composition, and PEO optical emission intensity.

2. Materials and methods
The substrate material used for the present investigation was magnesium alloy AZ31B. Before the PEO, the samples were polished by P2000 SiC paper. The sample size was 15×10×2 mm.
We used PEO equipment (USATU, Russia) in the pulsed unipolar mode under voltage regulation. A silicate-alkaline electrolyte was used. The pulse amplitude was gradually increased from 0 to 460 V during first 50 s, then it was kept constant. The frequency of the voltage pulses was 3136 Hz, the duty cycle of the pulses was 50 %. We performed experiments with different treatment time as listed in table 1.

During the PEO, instantaneous current and voltage values were recorded with a sampling frequency of 1 MHz, the sampling time was 200 ms; recording were obtained every 1 s. Based on the data acquired, the average values of the current and voltage were calculated. AvaSpec-3648 (Avantes) optical emission spectrometer with a specialized remote fibre optic sensor was used to study the PEO discharge emission in the wavelength range of 180–1100 nm. The integration time of the measurements was 200 ms. To estimate the growth kinetics of the PEO coating, a chronoperametric method was used [11] according to the method described elsewhere [12, 13].

The elemental composition was determined using an EDX-800P energy dispersive X-ray fluorescence spectrometer. The coating thickness was measured by a DeFelsko Positector 6000 with an N-type sensor. Surface micrographs were obtained by JEM 6390 scanning electron microscope. We used ImageJ software for analysis of micrographs and porosity parameters estimation.

3. Results and discussion
In figure 1a, the voltage pulse amplitude ramps from zero to the operating level. Figure 1d shows that coating gains the most thickness $h$ during the voltage increase. The current density exhibits two peaks in time (figure 1b).

Let us consider the mechanism of the coating growth at the different stages of the PEO process. Figure 2 shows the surface micrographs of PEO coating. The coating thickness and porosity are indicated in table 1.

3.1. Substrate surface
There are visible stripes of the grit paper pretreatment and dot-like inclusions with a diameter of 1–3 μm on the micrograph of the sample surface before the PEO (figure 2a). The results of the EDX analysis of the clean region of the alloy surface (point 1) and inclusions (point 2) in table 2. The higher oxygen content at point 2 indicates that the inclusions are builds of native air-formed oxide MgO.

3.2. Anodizing stage (I)
At this stage, the pulse amplitude reached 170 V after $t_1 = 24$ s, and the average current density was 0.26 A/cm². The average coating thickness $h$ was 3.5 μm. Micrographs (figure 2b) and elemental composition analysis of the surface shows the uneven growth of the coating with the homogeneous areas (point 3) and chaotic silicon containing builds of various diameters (point 3). Forsterite formation explains the presence of the silicon following reaction (3).

The following reactions are assumed to proceed at the anode:

$$\text{Mg}^0 - 2e^- \rightarrow \text{Mg}^{2+}$$

$$\text{MgO} + 2\text{H}^+ \rightarrow \text{Mg}^{2+} + \text{H}_2\text{O}$$

$$\text{Mg}_2\text{SiO}_3 + 2\text{H}^+ \rightarrow \text{Mg}^{2+} + \text{SiO}_4^{2-} + \text{H}_2\text{O}$$

$$\text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^-$$

$$2\text{H}_2\text{O} - 4e^- \rightarrow \text{O}_2 + 4\text{H}^+$$

$$\text{Na}_2\text{SiO}_3 \rightarrow 2\text{Na}^+ + \text{SiO}_4^{2-}$$

$$\text{Mg}^{2+} + 2\text{OH}^- \rightarrow \text{Mg(OH)}_2$$

$$\text{Mg(OH)}_2 \rightarrow \text{MgO} + \text{H}_2\text{O}$$

$$2\text{Mg}^{2+} + \text{SiO}_4^{2-} + 2\text{OH}^- \rightarrow \text{Mg}_2\text{SiO}_4 + \text{H}_2\text{O}$$

$$2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO}$$

Also, small pittings with a diameter of several micrometers appeared (figure 2b, point 5) as a result of local anodic dissolution [14]. This dissolution leads to a peak in the current density when the pulse amplitude $U_m$ reaches 80–90 V. The elemental composition of (point 5) shows a small proportion of silicon relative to oxygen, which indicates the predominant precipitation of
magnesium oxide and hydroxide compounds. By the amount of silicon, the forsterite content at (point 4) is higher than at (point 5).

3.3. Spark discharge stage (II)
The coating on the next studied interval $t_2 = 33$ s differs from that at $t_1$ by the presence of small pores on the coating surface. The voltage increase led to the appearance of many small short-live luminescent spark microdischarges on the sample surface. The power of these discharges was insufficient for significant growth of the coating; therefore, the coating thickness did not change within the range of measurement error. The optical emission of the spark microdischarges is not as intense as the emission of the microarc discharges, so the OES spectrum at the $t_2$ is shown in the zoomed graph (figure 3).

3.4. Stage (III) of microarc discharges
The intervals $t_3 = 51$ s, $t_4 = 1$ min, $t_5 = 5$ min correspond to the voltage at which more powerful and long-life microarc discharges contribute to the intensive growth of the coating. Figure 2 (d,e,f) shows large pores, and it can be noted that the porosity and the average pore size increase with the processing.

| Sample No. | Time $t$ | Amplitude of pulses $U_m$ (V) | Coating thickness $h$ (μm) | Porosity $P$ (%) | Average pore size $d$ (μm) |
|------------|----------|-------------------------------|-----------------------------|-----------------|-----------------------------|
| 1          | 24 s     | 170                           | 3.5±0.45                    | –               | –                           |
| 2          | 33 s     | 290                           | 2.7±0.67                    | 12.22±1.2       | 0.4±0.2                     |
| 3          | 51 s     | 456                           | 7.2±0.33                    | 13.13±1.5       | 1.8±0.7                     |
| 4          | 1 min    | 460                           | 10.19±0.54                  | 14.42±1.9       | 2.1±1.0                     |
| 5          | 5 min    | 460                           | 12.28±0.79                  | 15.4±0.8        | 2.7±1.7                     |
time (table 1). Time $t_3$ corresponds to a rapid current decrease (figure 1b), because of the high growth rate of the coating and increase in its electrical resistance.

**Table 2.** The results of EDS analysis of the surface.

| Point No. | Mg     | O      | Al     | Si     | Na     | Zn     |
|-----------|--------|--------|--------|--------|--------|--------|
| 1         | 96.2±0.2 | 0.4±0.2 | 2.5±0.05 | –     | –     | 0.9±0.04 |
| 2         | 86.9±1.7 | 8.8±4.7 | 3.4±1.9 | –     | –     | 1.0±0.05 |
| 3         | 73.5±5.2 | 20.3±3.2 | 1.7±0.12 | 2.7±1.1 | 1.0±0.3 | 0.7±0.13 |
| 4         | 25.7±13.0 | 55.1±7.5 | 1.2±0.7 | 11.7±1.7 | 6.0±3.3 | 0.4±0.16 |
| 5         | 49.8±13.2 | 40.9±12.4 | 1.7±0.2 | 4.5±2.9 | 2.4±1.5 | 0.7±0.13 |

**Figure 2.** Micrographs of the sample surface without coating (a), with a coating after PEO duration $t_1 = 24$ s (b), $t_2 = 33$ s (c), $t_3 = 51$ s (d), $t_4 = 1$ min (e), $t_5 = 5$ min (f).

It can be noted that the microdischarges are bright during this stage (figure 1c), and the optical emission spectrum shows distinguishable lines of the Mg substrate and the components of the aqueous electrolyte. After reaching the peak of the brightness, the optical emission intensity decreases following the current density (figure 1c). By the moment $t_4$, the coating thickness is
Further increase in the processing time does not lead to a significant increase in the coating thickness. After \( t_5 \), the coating thickness reaches a value of 12.28 \( \mu m \). The optical emission becomes weak, the number of micro-discharges decreases.

**Figure 3.** Optical emission spectra of the anode during the PEO of the AZ31B alloy at times \( t_{1.5} \).

### 4. Kinetic model of the PEO process

The current density transients were approximated using Curve Fitting Toolbox. The kinetic model contains three terms: the first for Mg dissolution (equation (1)), the second for 3D crystallisation of precipitate products (equation (3, 4)), and the third for the oxygen evolution (equation (2)). The derivation of the formulae for the first two terms is described elsewhere [12, 13], the third term is presented as a constant \( j_C \):

\[
j = j_0 \exp\left(\frac{-t}{\tau}\right) + zFC \sqrt{\frac{D}{D}} (1 - \exp\left(\frac{-t}{\tau}\right)) + j_C,
\]

where \( j_0 \) – initial (maximum) current density; \( m \) – the type of crystallisation; \( z \) – nuclear charge; \( F \) – Faraday’s constant; \( c \) – concentration of Mg in the film; \( D \) – diffusion coefficient; \( \tau \) – time constant of nucleation.

We assumed \( m = 1 \) so that the crystallization is instantaneous to simplify the calculations. The Mg concentration was calculated for the forsterite \( Mg_2SiO_4 \), as the predominant oxide in the coating. We approximated the current density curve at the stage of spark and microarc discharges, because the most intense surface transformation occurs at this stage.

Figure 4 shows the experimental (1) and modeled current density curves. The parameters of the kinetic model (5) are presented in table 3.

As follows from figure 4, the dissolution processes make the greatest contribution into the initial stage of the process: a rapid current increase reflects this fact.

**Figure 4.** Experimental (1) and mode modelled current density for PEO of the AZ31B alloy in a silicate-alkaline electrolyte. Model current density: (2) – total; (3) – partial dissoluton; (4) – 3D crystallization; (5) – oxygen evolution.
3D crystallization prevails in the time region after the intersection point of curves 3 and 4. It can be noted that the coating actively grows this time. As shown in figure 1, the PEO process longer than $t_{d}$ does not lead to a significant increase in the coating thickness; however, the current density remains at a constant level of 0.22-0.26 A/cm$^2$. Therefore we introduced the term $j_c$ to describe the constant component which supposedly stands for the electrochemical processes of gas liberation on the anode surface and gas electrical breakdown in the coating pores.

Therefore, the kinetic model confirms the observed mechanism of coating growth. The model quality was assessed by determination coefficient $R^2$, which is 0.94; therefore, the model can be considered as adequate.

5. Conclusions
The study shows that in the pulsed unipolar PEO mode, 70...80 % of the coating thickness is formed during the first 45...50 s of the PEO. During this time, the voltage is increased from 0 to the operating level of 460 V. The growth of the coating proceeds through the following stages: electrochemical anodizing accompanied by anodic dissolution; oxidation with low power spark discharges; plasma electrolytic oxidation with microarc discharges. During the anodizing stage, the coating has growth centers visible in micrographs. Micro sparks lead to the formation of the small pores less than a micrometer. The transition from the spark to the microarc discharges characterizes the time interval of the rapid growth of the coating to the limiting maximum thickness. The PEO process kinetic model, which is consistent with the observed mechanism of coating growth, is proposed and justified.

Each identified stage of the PEO process makes an important contribution to the PEO coating structure. Therefore, to ensure the specified characteristics of the coating in the uni- and bi-polar mode under voltage regulation, it is important to program the duration and trajectory of the voltage increase from the moment the source is switched on.

Acknowledgments
The study was carried out under the scholarship or Russian Federation President № СПИ-1962.2019.4

References
[1] Agarwal S, Curtin J, Duffy B and Jaiswa S 2016 *Materials Science and Engineering: C* **68** 948–63
[2] Zhao D, Witte F, Lu F, Wang J, Li J and Qin L 2017 *Biomaterials* **112** 287–302
[3] Hussein R O, Zhang P, Nie X, Xia Y and Northwood D O 2011 *Surface and Coatings Technology* **206** 1990–7
[4] Witte F 2010 *Acta Biomaterialia* **6** 1680–92
[5] Zeng R, Dietzel W, Witte F, Hort N and Blawert C 2008 *Advanced Engineering Materials* **10** B3 B14
[6] Hariprasad S, Gowtham S, Arun S, Ashok M and Rameshbabu N 2017 *Journal of Alloys and Compounds* **722** 698–715
[7] Gnedenkov S V, Khrisanfova O A, Zavidnaya A G, Sinebryukhov S L, Egorkin V S and Nistratova M V 2010 *Surface and Coatings Technology* **204** 2316–22
[8] Arrabal R, Matykina E, Hashimoto T, Skeldon P and Thompson G E 2009 *Surface and Coatings Technology* **203** 2207–20
[9] Parfenov E V, Parfenova L V, Dyakonov G S, Danilko K V, Mukaeva V R, Farrakhov R G, Lukina E S and Valiev R Z 2019 *Surface and Coatings Technology* **357** 669–83
[10] Zhang X, Cai G, Lv Y, Wu Y and Dong Z 2020 *Surface and Coatings Technology* **400** 126202
[11] Damaskin B B, Petrii O A and Tsirlina G A 2006 *Russian Journal of Electrochemistry* **43** 981–2

| $j_0$ (A·cm$^{-2}$) | $D$·10$^{-6}$ (s·cm$^{-2}$) | $\tau$ (s) | $j_c$ (A/cm$^2$) |
|-----------------|----------------|--------|---------------|
| 0.92±0.03       | 11.01±0.63  | 15.10±2.13 | 0.07±0.01    |

Table 3. Parameters of the current density approximation equation $j(t)$.  

| $j_0$ (A·cm$^{-2}$) | $D$·10$^{-6}$ (s·cm$^{-2}$) | $\tau$ (s) | $j_c$ (A/cm$^2$) |
|-----------------|----------------|--------|---------------|
| 0.92±0.03       | 11.01±0.63  | 15.10±2.13 | 0.07±0.01    |
[12] Snizhko L O, Yerokhin A L, Gurevina N L, Misnyankin D O, Ciba A V and Matthews A 2010 *Surface and Coatings Technology* **205** 1527–31

[13] Lazarev D M, Farrakhov R G, Mukaeva V R, Kulyasova O B, Parfenov E V, Yerokhin A L 2020 *Surface Engineering and Applied Electrochemistry* **56** 83–92

[14] Aliasghari S, Rogov A, Skeldon P, Zhou X, Yerokhin A, Aliabadi A and Ghorbani M 2020 *Surface and Coatings Technology* **393** 125838