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DOCTORAL SCHOOL MATERIALS SCIENCE AND ENGINEERING

SUMMARY

PhD THESIS

Experimental research on surface treatments by oxidation in electrolytic plasma

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INTRODUCTION

Magnesium and its alloys are frequently used in engineering because they are lightweight and have very good properties: low density, high strength/weight ratio, very good dimensional durability and electromagnetic shielding, good machinability and high damping ability [1-3]. The main applications of magnesium and its alloys are found in the automotive, aerospace and communications fields [4]. Unfortunately, a Major disadvantage of these materials is low wear resistance in corrosive environments [5-8], which is why proper surface treatment is needed to improve the wear and corrosion resistance of magnesium and its alloys.

Electrolytic plasma oxidation (PEO) is a plasma-assisted electrochemical surface treatment that is used to convert light metal surfaces (e.g. Al, Mg and Ti) into hard and well-adhered oxide layers [9]. The process occurs at high anode potentials (typically several hundred volts) that trigger numerous micro-discharge events at the metal-electrolyte interface, instantly generating high pressure and temperature conditions that alternate with rapid cooling of the material by the surrounding electrolyte, thereby significantly affecting morphology, phase composition, and coating voltages [10] and leading to the formation of oxide phases at high temperatures, fused ceramic structures, pores and cracking networks.

In order to obtain optimal PEO coatings, repeated tests are performed varying key factors and analyzing/testing the quality of the coatings each time until the process is optimized.

The main goal of the research presented in this thesis was to develop an electrolytic plasma oxidation (PEO) plant for magnesium and its alloys and to obtain composite coatings with superior properties to the base material in terms of hardness, wear and corrosion resistance.

The targeted demonstration model started from the formulation of the concept and technological application which consisted in planning and designing the experimental installation of oxidation in electrolytic plasma for surface treatments and coatings; then it was approached to demonstrate the functionality of the concept through analytical and experimental studies that consisted in the actual construction and testing of the PEO experimental plant; and finally to validation under laboratory conditions of the system by (1) conducting PEO experiments on magnesium alloy AZ63 to obtain advanced composite coatings with superior properties compared to the base material, (2) advanced elemental, morphological and microstructural chemical characterization of PEO coatings and (3) testing PEO coatings to demonstrate hardness, wear resistance and corrosion properties.

The doctoral thesis is structured in 6 chapters, as follows:

- **Chapter 1. Current state of research on oxidation in electrolyte plasma**

The first chapter presents the principles of oxidation in electrolytic plasma (reaction kinetics), process parameters and their influence on the properties of PEO layers, coating characteristics and functional applications, layer characterization techniques obtained by PEO, together with bibliographic and scientometric study on publications related to the oxidation process in electrolytic plasma.

- **Chapter 2. Research methodology**

In the second chapter are presented the research directions and planning of the experimental activity, highlighting the objectives, stages and research methods.

- **Chapter 3. Design and construction of surface treatment plant**

The third chapter presents: computer-aided design (CAD) of a laboratory-level PEO installation, construction and commissioning of the plant as well as setting process parameters. Also in this chapter is presented the transposition of PEO technology and installation from laboratory to industrial level.

- **Chapter 4. Experimental research on the influence of PEO processing time on the alloy of Mg, AZ63**

Chapter 4 presents the experimental results concerning the investigation of PEO coatings obtained in aqueous sodium aluminate solution (10 g/l $NaAlO_2$) for processing times of 5, 10 and 20 minutes respectively.

- **Chapter 5. Experimental research on the influence of electrolyte in PEO of the alloy Mg, AZ63**

Chapter 5 presents the experimental results regarding the investigation of PEO coatings obtained in 3 electrolytes based on sodium phosphate (Na3PO4) and sodium aluminate ($NaAlO_2$), having different chemical compositions of sodium aluminate (15g/l, 20g/l and 25g/l $NaAlO_2$), for a constant processing time of 10 minutes.

- **Chapter 6. Conclusions and personal contributions**

Chapter 6 presents synthetically the results of experimental research on oxidation in electrolyte plasma on Mg alloys, highlighting original contributions.

After chapter 6 of conclusions and personal contributions, the structure of the thesis ends with the sections of Bibliography, List of published scientific works, List of abbreviations and symbols, and at the end are inserted the Annexes related to the research performed.

1. CURRENT STATE OF RESEARCH ON OXIDATION IN ELECTROLYTE PLASMA

1.1 PRINCIPLES OF OXIDATION IN ELECTROLYTIC PLASMA - REACTION KINETICS

Electrolytic plasma oxidation (PEO) is an electrochemical method used to obtain ceramic layers and ceramic oxides with very good properties regarding resistance to thermal wear and corrosion, dielectric properties, thermal insulation or adhesion to the interface. PEO is actually a conversion coating process for surface improvement that can be applied to many types of metallic materials, which tend to passivate into certain aqueous electrolyte solutions. In addition to the name electrolyte plasma oxidation (PEO), the terms micro-arc oxidation (MAO - *micro-arc oxidation*), anodic spark deposition (ASD - *anodic spark deposition*), chemical oxidation of plasma (PCO - *plasma chemical oxidation*) or anodic oxidation by spark discharge (ANOF - *anodic oxidation by spark discharge*) [11].

The principle of oxidation in electrolytic plasma is based on electrical discharges generated by a strong electric field in a system consisting of the substrate, the passivating oxide layer formed, a discharge zone in gas, plasma and electrolyte. These elements specifically determine the morphology, as well as the composition of the coatings produced. Electrical discharges generate plasma bubbles, in which, under anodic polarization, the surface material of the substrate is converted into a compound, consisting of the base material itself (including alloying elements), oxygen and electrolyte components.

Frank Simchen et al. [11] provides an overview of chemical reactions occurring during growth of the oxide or hydroxide layer, summarised in Table 1.1.

Tabel 1.1. Generalized chemical reactions that occur during the formation of the oxide or hydroxide layer.

Reaction			Description	Localization
H2O	↔	2H+ + O2−	Water dissociation	-
Me	→	Men^{+} + ne−		
$xMe^{n+} + yO2-$	→	MexOy	Metal oxidation / hydration	Anode
$xMen^{+} + y(OH)^{-}$	→	$Mex(OH)_{y}$		
$nH^{+} + ne-$	→	0.5nH2	Evolution of hydrogen	catod
xMe + *yH2O*	→	MexOy + *yH2*	general reaction	-

T.W. Clyne et al. [12] (Figure 1.1) summarizes very suggestively the cyclic evolution of reaction kinetics that generates the oxidation phenomenon in electrolytic plasma for a single pore in the following steps:

a) Initiation of discharge by dielectric piercing;
b) The current flow propagates through the expanding plasma and heat is released;
c) Oxide is formed in plasma, the vapor bubble increases, the current intensity decreases, the plasma cools;
d) The current stops, the plasma collapses and the bubble shrinks with condensation of the vapor, heating the electrolyte;
e) The pore is refilled with electrolyte, after which the cycle resumes.

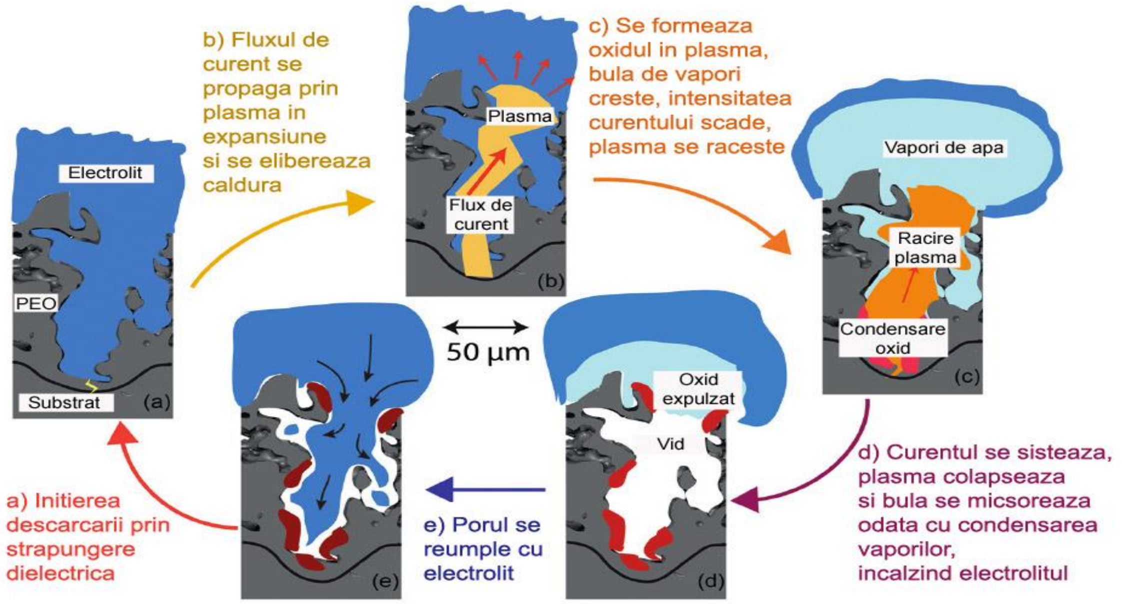


Figura 1.1. Evolution of reaction kinetics leading to PEO explained for a single pore. (figure adapted from [12])

Frank Simchen et al. [11] best illustrates the evolution of discharges on a sample of magnesium alloy AZ31 during the PEO process in an alkaline silicate solution (figure 1.2). The bright spots represent the discharge areas and their brightness is a measure of the intensity of the discharge phenomenon. As can be seen from Figure 1.2, throughout the PEO process, although the number of discharges decreases, they increase in intensity.

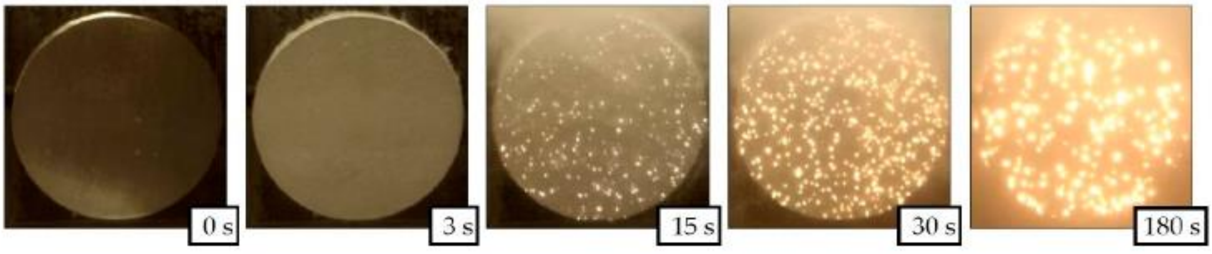


Figura 1.2. Evolution of discharge distribution and intensity relative to PEO process time for a magnesium alloy AZ31 in an alkaline silicate electrolyte [11].

In the following, the different dependencies of the PEO process are discussed, primarily depending on the composition of the substrate, the electrolyte used, the electrical regime applied, as well as their mode of interaction, with direct implications on properties designed to meet concrete applications.

The flowchart of the PEO process is best represented by Frank Simchen et al. [11] (figure 1.3) and schematically presents the stages of the oxidation process in electrolytic plasma and the dependencies of the characteristics of the coatings of the finished product on the PEO process parameters.

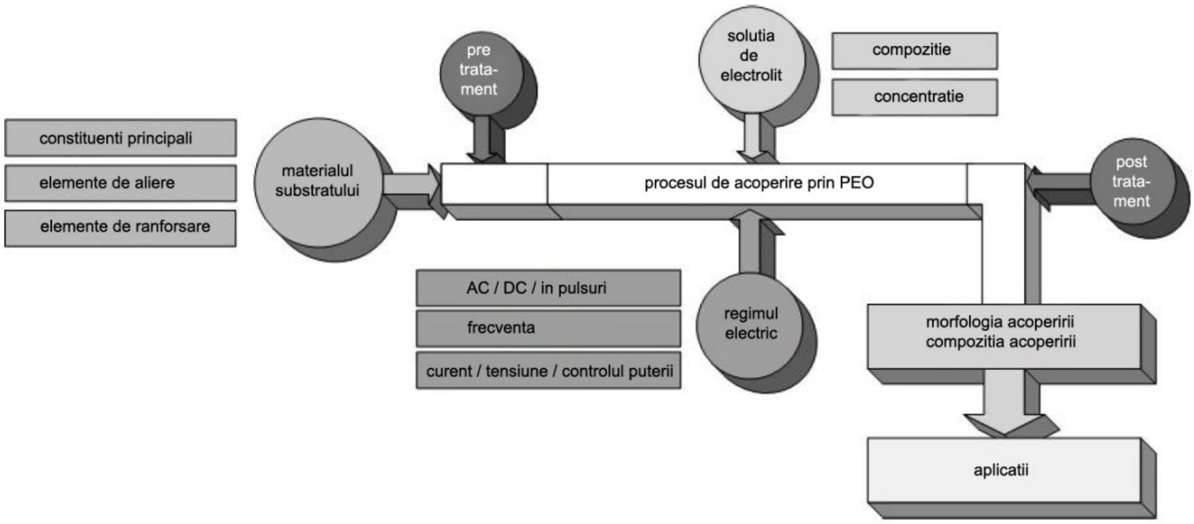


Figura 1.3. Schematic representation of the PEO process and its dependence on substrate material, process parameters and targeted applications. (Figure adapted from [11])

1.2 PROCESS PARAMETERS AND THEIR INFLUENCE ON LAYER PROPERTIES

SUBSTRATE

Oxidation in electrolyte plasma into low-concentration aqueous electrolytes is actually a coating process by conversion. Therefore, the nature of the oxide strongly depends on the composition of the substrate. The metal ions participating in electrochemical reactions during the PEO process (Table 1.1) are determined, in principle, by the base material. In general, the metal oxides of the substrate are the main constituents of coatings. The substrate conversion naturally includes alloying elements and metal precipitates as well as reinforcement phases in the case of metal matrix composites.

ELECTROLYTE

Electrolyte solutions are classified according to their passivation or dissolution behavior relative to the substrate.

As for the incorporation of foreign compounds into the oxide layer, electrolytes are classified as follows [9]:

(1) electrolytes leading only to the incorporation of oxygen,
(2) electrolytes leading to incorporation of foreign compounds by anions,
(3) electrolytes leading to incorporation of foreign compounds by cations; and
(4) electrolytes containing macroscopic particles, which are incorporated into the oxide layer by cataphoretic processes.

Common salts used for oxidation in electrolytic plasma in alkaline media for aluminium, magnesium, titanium and their alloys are, inter alia, silicates, phosphates, aluminates, fluorides, borates and stanates (salts of stanic acid).

According to Gh. Barati Darband et al. [13], alkaline electrolytes are particularly indicated for the oxidation of magnesium and its alloys in electrolytic plasma, since acidic media lead to the dissolution of the anode.

WORKING PARAMETERS

Frank Simchen et al. [11] specifies that the electrical regime during PEO can be determined by the control parameters (current density or cell voltage), the type of current/voltage parameter (continuous, alternating or pulse) and the definition of the regime (frequency, pauses, limits, fill factor, etc.). To these can be added as working parameter the duration of the process or the oxidation time in electrolytic plasma.

In general, the interactions of the substrate/electrolyte combination with the electrical regime are complex and still the subject of much research. Since, unlike other electrolytic surface treatment methods, PEO results in the formation of ohmic layers with high resistance, they affect (especially in the case of controlled current regimes) the extent to which the predefined electrical pulse is correctly mapped/projected in the experimental setting.

1.3 CHARACTERISTICS OF PEO COATINGS AND FUNCTIONAL APPLICATIONS

Oxidation in electrolytic plasma allows to obtain functional surfaces/coatings that are superior to the substrate in terms of their mechanical characteristics (hardness, wear resistance, adhesion to metal substrates), thermal protection and corrosion resistance.

Studying the morphology and properties of PEO layers on aluminum alloys (AlMgSi1), produced in an alkaline silicate electrolyte using a rectangular pulsed bipolar-current, M. Sieber et al. [14] identifies a general structure of the coatings (Figure 1.4) consisting of the amorphous barrier layer, the working layer which is characterized by numerous microcracks and small defects, as well as the rough and less compact technological layer at the top of the coatings which has numerous pores (open and closed).

With the successive increase in the depth of penetration in the section, the number of defects is substantially reduced, which is why, in order to optimize PEO layers for tribological applications, the technological layer is sometimes removed by an additional surface polishing step.

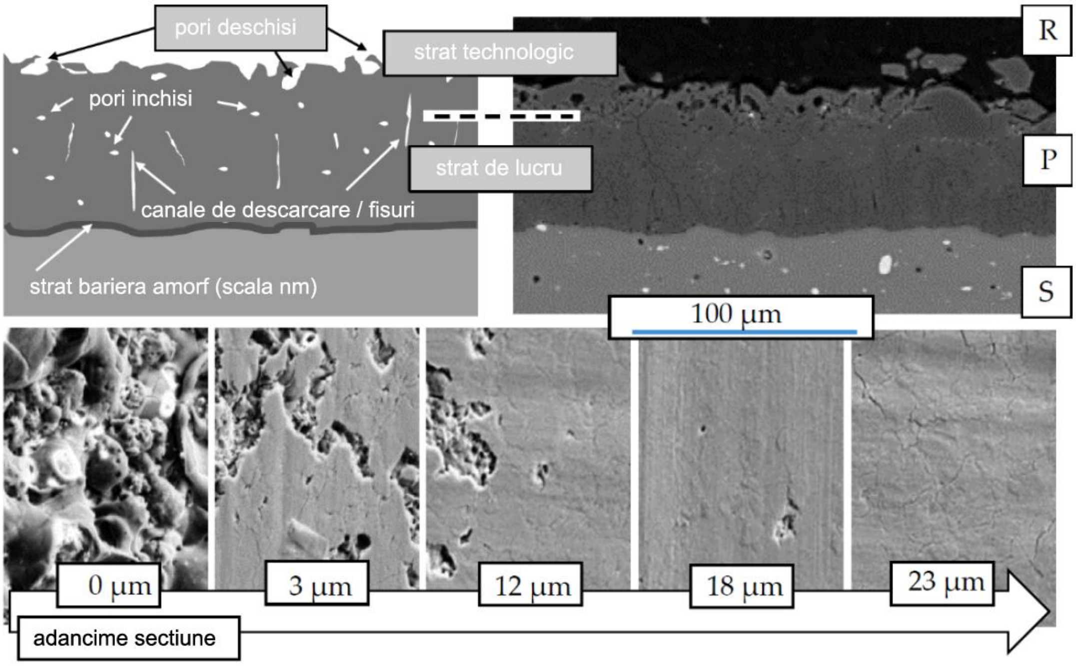


Figura 1.4. The morphology of a PEO layer produced on the AlMgSi1 alloy, the schematic representation and micrographs of a cross-section (R - Embedding resin, P - PEO coating, S - Substrate), surface view of the film, as well as several sectional views at different depths of penetration, showing an increase compactness of layer structure. (Figure adapted from [14])

PEO coatings on magnesium and titanium materials show less mechanical stability than those produced on aluminum alloys because oxide phases obtained by substrate conversion such as cubic MgO or rutile TiO_2 and anatas (tetragonal modifications of TiO_2) have a lower hardness than aluminum oxide. For this reason, for PEO treatment of these materials, highly concentrated process media are often used, to change the phase composition of the produced layers in favor of more resistant compounds by incorporating concentrated electrolytic components. Moreover, subprocesses during layer formation lead to PEO coatings on Mg and Ti alloys with a much less compact structure than that obtained for Al materials.

Frank Simchen et al. [11] summarizes in the 2020 review the main contributions in the field of PEO, classifying them according to application and substrate material (Table 1.2).

Tabel 1.2. Applications and examples of PEO treatments applied to different materials [11].

Projected application/property	Base material/substrate
Protection against corrosion and wear	Al, Mg, Ti, Zn, Brass, Fe / Steel, Nb, Be, Ta, materiale tip c-grafit
Adjustment of radiation behavior, improved thermal emission, reduced absorbance	Ti, Mg
Decorative purpose (by coloring)	Al, Mg
Improving thermal insulation	Of
Medical field, hydroxyapatite (HA) formation to improve bioactivity	Zr, Ta, Ti
Contributions to the phenomenon of photoluminescence	Hf
Contributions to the phenomenon of catalytic activity	Fe

1.4 PEO LAYER CHARACTERIZATION TECHNIQUES

The most commonly used characterization techniques for evaluating the quality and properties of PEO layers are:

1. Scanning or scanning electron microscopy (SEM) is used to examine surface morphology and topography. SEM analysis is often combined with elemental analysis by energy dispersive spectrometry (EDS) to determine the chemical composition of layers using various scanning modes (point-scan, line-scan, or mapping).

2. X-ray diffraction (XRD) is used to identify and quantify crystal phases shown in the oxide layer.

3. X-ray photoelectron spectroscopy (XPS) allows analysis of the chemical state and elementary composition of the layer surface.

4. Atomic force microscopy (AFM) provides three-dimensional images of the surface, allowing direct measurement of surface roughness and topographic features at the nanometer level.

5. Hardness and adhesion tests measure the mechanical strength of the oxide layer.

6. Corrosion tests.

7. Electrochemical impedance spectroscopy (EIS) is a technique used to measure the corrosion resistance of oxide layers, providing information about the electrochemical behavior of the metal-layer-liquid system.

These characterization techniques are essential for the development and optimization of oxidation processes in electrolytic plasma, allowing researchers and engineers to adjust layer properties according to specific application requirements.

1.5 PEO SCIENTOMETRY STUDY

Conform bazei de date Web of Science - Core Collection [15], the evolution of publications and citations on the topic of oxidation in electrolytic plasma has increased rapidly in the last 2 years, the number of publications exceeding 400 articles, proceedings and reviews per year, which shows a growing interest in this topic.

The Scientometric Study shows a significant increase in the number of publications per year since the 2000s, with a notable peak in the last 5 years indicating that oxidation in electrolytic plasma remains a vibrant and expanding research topic. As technology matures, research is expected to focus on optimizing processes and exploring new applications.

The approach to electrolytic plasma oxidation of magnesium or magnesium alloys began much later, in 2002, but it has also grown and continues to grow to this day.

The top countries that are interested in the oxidation process in electrolyte plasma according to the number of publications on PEO include: People's Republic of China (754 publications representing 42,455% of the total), South Korea (181 publications representing 10,191% of the total) and Iran (176 publications representing 9,910% of the total).

At national level, according to the Web of Science database - Core Collection [15], from 2011 until now (09.04.2024), we have a total number of 26 publications on PEO with authors affiliated to institutions in Romania. Also at national level, but on the topic of oxidation in electrolytic plasma of magnesium or magnesium alloys, according to the Web of Science database - Core Collection [15], starting with 2018, when there is the first evidence in the database, until now (09.04.2024), we have a total number of only 3 publications with authors affiliated to institutions in Romania and one article out of the 3 is part of the research of this thesis, which shows initiative and originality of the topic addressed, at least at national level.

2. RESEARCH METHODOLOGY

2.1 RESEARCH DIRECTIONS

The main research directions consist in the construction of an electrolytic plasma oxidation plant (PEO) for magnesium and its alloys and obtaining composite coatings on magnesium alloy AZ63 (6%Al, 3%Zn), with superior properties to the base material in terms of hardness, wear resistance and corrosion resistance.

The choice of magnesium alloy AZ63 was made due to the fact that this alloy is of interest in industrial applications, it is easy to purchase and, as evidenced by the previous chapter, there is no experimental research at national level on improving surface properties by oxidation in electrolytic plasma on AZ63.

The justification for choosing the research topic lies in the fact that oxidation in electrolytic plasma is an efficient and environmentally friendly method of obtaining protective coatings with properties superior to the base material or even compared to those obtained by other techniques. PEO is a versatile technique and can be easily customized to suit real applications in demand on the market today. PEO is a constantly developing technique, far from reaching its saturation threshold.

The degree of novelty is that, through PEO, new protective coatings can be obtained on light alloys based on Mg, with properties superior to films obtained by other techniques, in terms of compactness of the PEO layer, degree of coating of the substrate surface, hardness and adhesion of the PEO layer, corrosion and wear resistance, etc. The applicability of the PEO technique is extensive and includes parts and assemblies from areas such as: automotive and aerospace engineering (cylinders/pistons, valves, rotors or turbines), manufacturing (tools for cutting, turning, milling or sharpening), sports (bicycle parts or frames), medicine (buffers for implants – e.g. HA on Ti), etc.

2.2 PLANNING EXPERIMENTAL WORK

The experimental plan shall include the following activities:

A1. Design of a pilot PEO plant for surface treatment of Mg alloys;

A2. Construction and commissioning of PEO plant;

A3. Performing PEO tests on representative samples;

A4. Morpho-structural characterization of the obtained coatings (OM, SEM-EDS, XRD); This step also includes the study of corrosion behaviour, tribological and hardness tests of PEO samples;

A5. Optimization of process parameters;

A6. Validation of experimental research;

A7. Dissemination of results; The obtained results are disseminated during experimental research activities by publishing scientific articles in prestigious journals.

The Gantt diagram of the projected experimental activities is shown in figure 2.1.

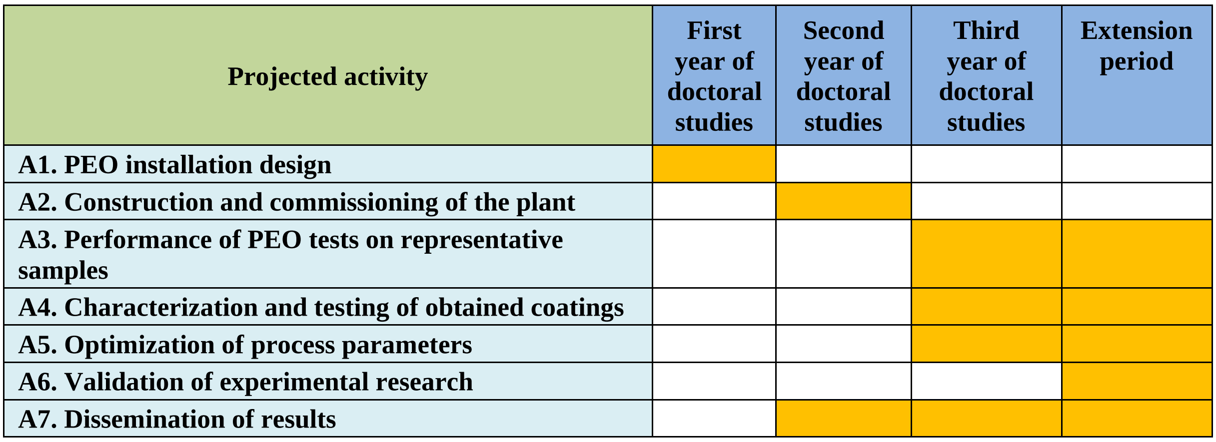


Figura 2.1. Gantt diagram of experimental activities

The experimental procedure for characterization and testing of the obtained coatings included:

1. Preparation of samples

2. Metalography

3. Electron microscopy

5. Microstructural analysis by X-ray diffraction

6. Tribological and hardness tests

7. Study of corrosion behavior

For the study of chemical, physico-structural and mechanical characteristics of PEO coatings were used a number of modern and complementary techniques, grouped on the following types of analyzes:

1. Film size analysis, morphology, porosity and roughness of surfaces;

2. Elemental chemical composition and microstructural analysis;

3. Tribological and hardness tests;

4. Study of corrosion behavior.

3. DESIGN AND CONSTRUCTION OF SURFACE TREATMENT PLANT

3.1 CAD DESIGN OF PEO INSTALLATION

The CAD design of the PEO installation was carried out using Surface-EDGE software. According to the design, the installation shown in Figure 3.1 has the following general composition:

(1) - movable metal frame;
(2) - electrolyte tank (D=300 mm; H=350 mm);
(3) - electrolyte cooling unit (*chiller)* to keep it at constant temperature;
(4) - electrolyte recirculation system to homogenize the electrolyte and keep it at constant temperature;
(5) - sample handling system to insert and remove sample from electrolyte;
(6) - power supply MARIS GX 150/1000;
(7) - generator bipolar de curent RD400;
(8) - control panel;
(9) - temperature sensor for monitoring the temperature of the electrolyte in the vat.

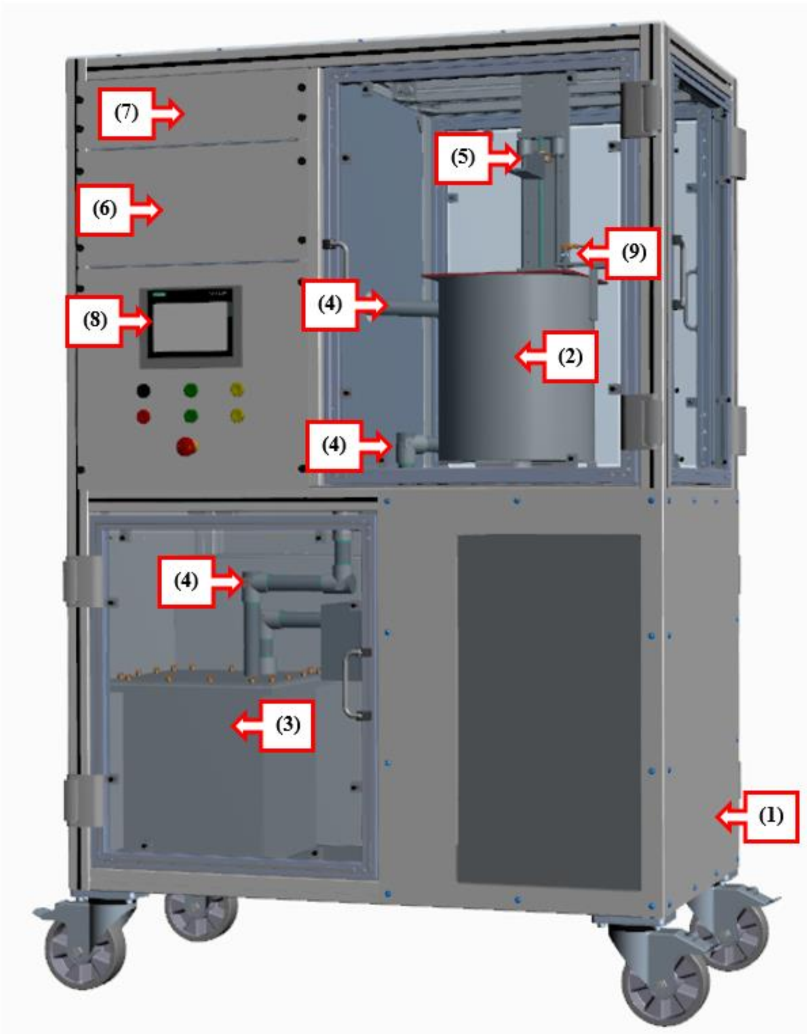


Figura 3.1. CAD design for PEO installation – side view

3.2 CONSTRUCTION AND COMMISSIONING OF THE PLANT

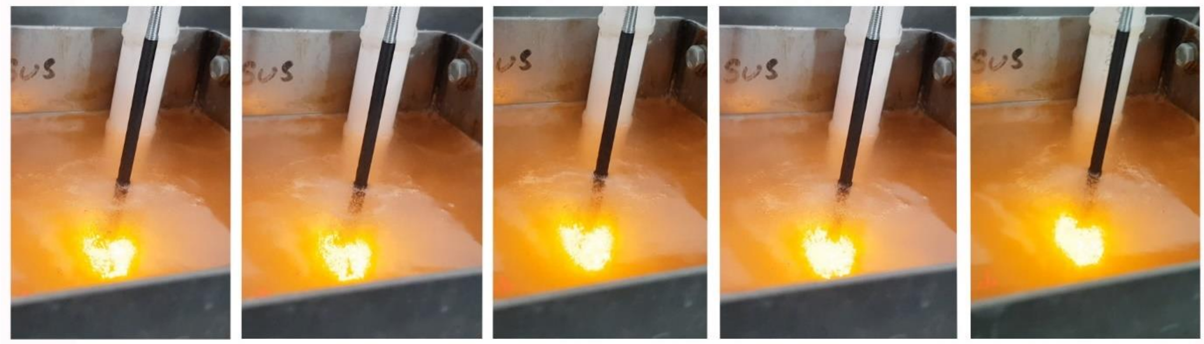
The constructed plasma oxidation plant (figure 3.2) has the following characteristics:

- Overall dimensions: 1202x745x1845 mm;
- Power supply MARIS GX 150/1000 (P:15kW, U:1000V, I:30A)
- RD400 bipolar current generator that can generate voltage 0 - 1000V DC or pulsed, current 0 - 37.5 A, DC or 0 - 200 A per pulse, with a power 0 - 30 kW DC and a frequency in the range of 0.5Hz - 75kHz;
- Supply voltage: 380V;
- Bowl dimensions: D = 300 mm; H=350 mm,
- Total volume ~ 25 liters; usage volume ~ 20 liters;
- Maximum part dimensions: D=100 mm; height 100 mm.

Figura 3.2. Overview - Built electrolytic plasma oxidation plant

Commissioning and testing of the plant shall be carried out using samples of magnesium alloy AZ63 in sodium aluminate electrolyte ($NaAlO_2$) at a constant current of 2A.

3 PEO tests were performed at different processing times of 5, 10 and 20 min. The oxidation process in electrolyte plasma proceeded normally, and white porous ceramic coatings were obtained on the surface of the magnesium alloy (figure 3.3).



a.

b.

c.

Figura 3.3. Preliminary tests: a) PEO process in a NaAlO2 electrolyte at a constant current of 2A and a PEO processing time of 10 min., b) raw magnesium alloy AZ63, c) ceramic coating obtained by PEO on magnesium alloy AZ63

X-ray diffraction analyses performed on the raw sample of Mg alloy, AZ63, and on the 3 samples obtained by PEO at different PEO processing times, confirmed the deposition of ceramic layers consisting mainly of MgAl phases$_{2O4}$ and MgO. The detailed results are presented in Chapter 4 of this sentence and are disseminated in the ISI article entitled "*The Influence of Processing Time on Morphology, Structure and Functional Properties of PEO Coatings on AZ63 Magnesium Alloy*"[16].

3.3 INDUSTRIAL TRANSPOSITION OF THE PEO EXPERIMENTAL PLANT

Given the fact that the successful construction and testing of the PEO plant at laboratory level was successful, it was decided to move to the next technological level by transposing the technology and the PEO installation at industrial level. For this, a power supply was purchased from Plasma Technology (figure 3.4).

The analysed plant comprises a processing tank, a cooling vat, a cooling coil and a current and pulse source. The processing tank has a total capacity of 25 litres, of which 20 litres are actually usable. Permanent recirculation of electrolyte fluid is provided by a transfer pump, which maintains resistance in the electrolyte environment. This continuous recirculation process has two essential objectives: firstly, cooling the electrolyte liquid, and secondly, its constant homogenization. The material used to manufacture the bowl is stainless steel type 316L, having a thickness of 3 mm. This choice was made to guarantee the achievement of a strong and durable structure that ensures a long service life.

Figura 3.4. Overview images - Plasma Technology power supply for industrial PEO plant

In order to cope with the new industrial configuration, the re-design and construction of the electrolytic tank and the electrolyte cooling and recirculation system were carried out (figure 3.5).

Figura 3.5. CAD design and construction - bowl with electrolyte cooling and recirculation system

Commissioning and testing of the plant is performed using samples of magnesium alloy ZE41 (3.5–5% Zn, 0.4–1% Zr, 0.8–1.7% rare earth elements), in a mixed electrolyte of 10 g/l Na2SiO3 (supplier – *Sigma Aldrich*), 6 g/l Na3PO4 (supplier – *Thermo Scientific*) and 2 g/l NaOH (supplier – *Emsure*), in unipolar mode at a frequency of 600 Hz and a constant current of 3 A for a process duration of 5 minutes (Figure 3.6).

a. b. c.

Figura 3.6. Representation a) crude ZE41 alloy, b) PEO process on Mg ZE41 alloy and c) PEO coating on Mg ZE41 alloy

X-ray diffraction analyses have shown coatings with compounds based on Mg silicates (Mg2SiO4) as the majority phases.

4. EXPERIMENTAL RESEARCH ON THE INFLUENCE OF PEO PROCESSING TIME ON MG AZ63 ALLOY

The experimental research consisted in investigating the influence of PEO processing time on the composition, structure and protective properties of PEO coatings on the alloy AZ63 Mg formed in aluminate electrolyte.

Samples of the alloy Mg, AZ63, were cut into a disc with a diameter of 20 mm and a thickness of 4 mm. Each disc thus obtained was fitted with a threaded hole with a diameter of 2 mm to ensure electrical contact through a 316L steel rod. The samples were polished with different grains (up to 2000) and then ultrasound-cleaned in acetone. The total sample area subjected to the PEO process was approximately 8.76 cm2 [16].

The PEO process consisted of using a direct current of 2A, in positive pulsed mode, in galvanostatic mode (constant current intensity). Thus, the current density applied to magnesium alloy samples was 2A/8.76 cm$^{2=0.23\ A/cm2}$.

Experimental conditions for obtaining samples:

- Electrolyte: 10 g/l NaAlO2 (supplier - Sigma-Aldrich, Merck Group, Germany) without other additives;
- curent 2A-ct;
- pH electrolit 12,3;
- electrical conductivity k=11.5 mS/cm;
- PEO processing time: 5 min for S1, 10 min for S2 and 20 min for S3.

The oxidation in electrolytic plasma of Mg and its alloys to sodium aluminate-based electrolyte is governed by the following electrochemical reactions at metal/oxide and oxide/electrolyte interfaces[17]:

Interfaţa metal oxid

- Anodic dissolution of magnesium

$$Mg \rightarrow Mg^{2+} + 2\bar{e} \quad (1)$$

- Oxygen evolution reaction

$$4OH^- \rightarrow 2H_2O + O_2 \uparrow + 4\bar{e} \quad (2)$$

Oxide/electrolyte interface

The free cation of Mg (ec. 1) is combined with the anions in the electrolyte according to the equations:

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2 \quad (3)$$

$$Mg(OH)_2 \rightarrow MgO \downarrow + H_2O \quad (4)$$

And

$$Mg^{2+} + 2AlO_2^- \rightarrow MgAl_2O_4 \downarrow \quad (5)$$

The time dependence of morpho-structural features investigated by analysis of SEM-EDS and XRD showed that:

- PEO coatings formed on magnesium alloy AZ63, in additive-free NaAlO2 electrolyte, were composed mainly of Mg, Al and O (figure 4.1);

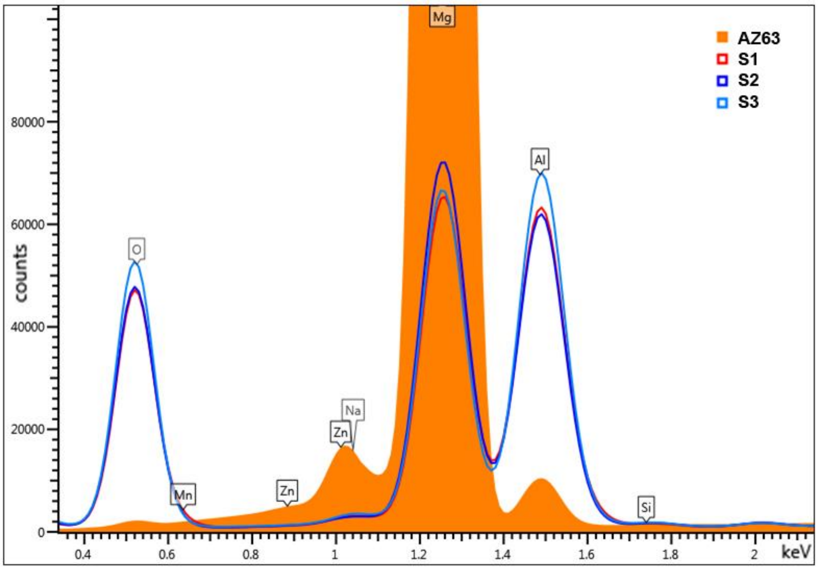
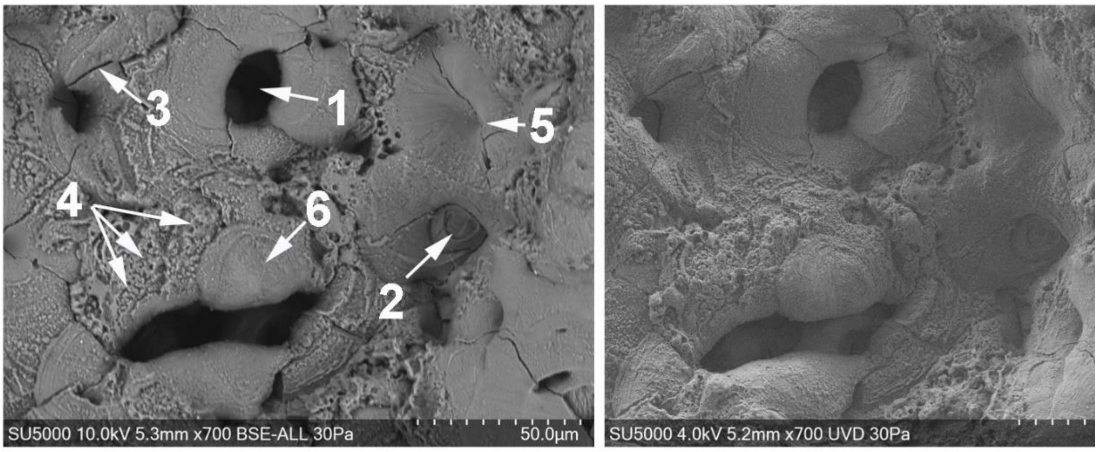


Figure 4.1 Overlapping EDS spectra for crude magnesium alloy AZ63 and 3 PEO samples

- Although PEO coatings have similar characteristic surface structures (Figure 4.2), a decrease in relative apparent porosity and an increase in surface roughness have been observed with increasing processing time (Table 4.1);



a. b.

Figure 4.2. SEM micrographs showing the morpho-structure of a sample surface S2 at an magnification of ×700 obtained in (a) backscattered electrons and (b) secondary electrons.

The following characteristic structures are distinguished: (1) deep pores, (2) superficial pores, (3) radial microcracks, (4) sintered particles, (5) completely closed pore collapse zone, and (6) molten material resolidified on the pore edge.

Tabel 4.1. Results of porosity and roughness analysis

Sample code	S1	S2	S3
Mean porosity ± SD (%)	19.17 ± 1.96	14.59 ± 1.40	11.30 ± 1.36
Sa - average surface roughness ± SD (μm)	4.28 ± 2.04	4.17 ± 0.29	5.23 ± 1.03

- PEO coatings contain mainly from the crystalline phase $MgAl_{2}O_{4}$, its relative ratio increasing with processing time (figure 4.3);

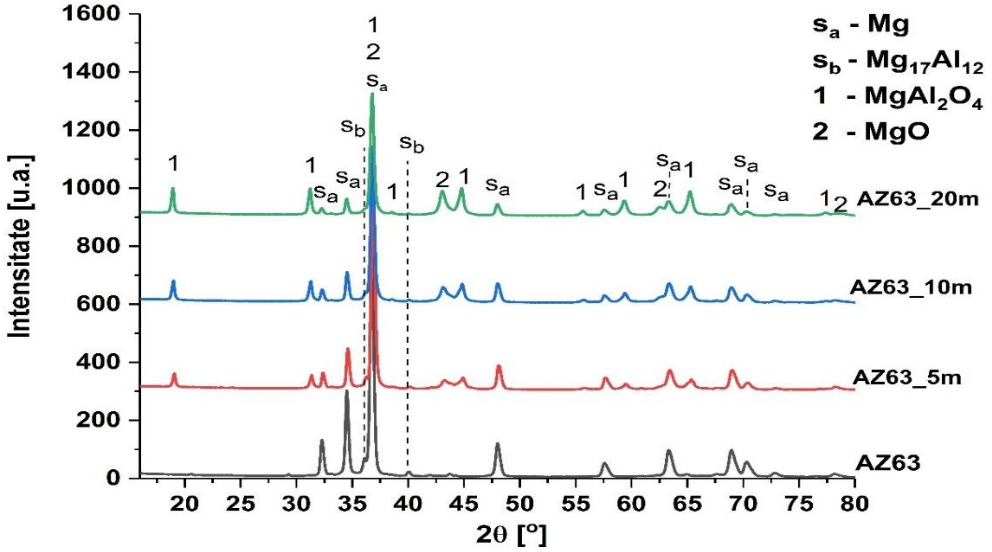


*Figura 4.3. **Sa** – Mg (substrate) (DB card number 04-006-2605); **Sb** – Mg17Al12 (DB card number 04-010-7477); **1** – MgAl2O4 (DB card number 04-007-4175); **2** – MgO (DB card number 01-076-2583)*

- The thickness and compactness of the coatings (and barrier layer) increased with processing time (Table 4.2).

Tabel 4.2. Summary table with average PEO layer thicknesses

DETERMINATION	SAMPLE CODE		
	S1	S2	S3
Average PEO layer thickness ± SD (μm)	15.14 ± 4.21	23.78 ± 11.64	36.60 ± 9.22
Average thickness of the barrier layer ± SD (μm)	0.36 ± 0.06	0.66 ± 0.08	0.67 ± 0.05

The functional properties of the surface determined by means of Vickers measurements of microhardness and potentiodynamic polarization were correlated with time-dependent morpho-structural characteristics, as follows:

- An improvement of 2 orders of magnitude in corrosion protection properties (Table 4.3) was correlated with an increase in MgAl2O4 content, coating thickness and a decrease in apparent porosity;

Tabel 4.3. Calculated values of corrosion potential, corrosion current density and corrosion rate for analysed samples

Cod proba	**Ecorr (V vs. SCE)**	**icorr (μA/cm^2)**	**Vcorr (mmpy)**
AZ63	-1.49	510	11.1
S1	-1.48	155.9	4.0
S2	-1.35	29.14	2.4
S3	-1.39	8.33	0.8

- A 5-fold increase in Vickers microhardness (Table 4.4) was correlated with an increase in coating roughness, layer thickness, and an increased crystalline phase ratio ($MgAl_{2}O_{4}$).

Tabel 4.4. Vickers micro-hardness values for PEO gauges and coatings

Cod proba	AZ63	**S1**	**S2**	**S3**
HV/0.3 (GPA) ± SD	0.88 ± 0.09	2.04 ± 0.09	3.42 ± 0.17	4.44 ± 0.12

5. EXPERIMENTAL RESEARCH ON THE INFLUENCE OF ELECTROLYTE IN PEO OF THE ALLOY MG AZ63

The experimental research consisted in investigating the influence of electrolyte composition on mechanical and anticorrosive properties of PEO layers obtained on alloys of Mg AZ63.

The alloy of Mg AZ63 was cut into discs with a diameter of 20 mm and a thickness of 4 mm. They were polished with different grain sizes of up to 1400, cleaned in ultrasonic bath in acetone and then subjected to oxidation in electrolytic plasma.

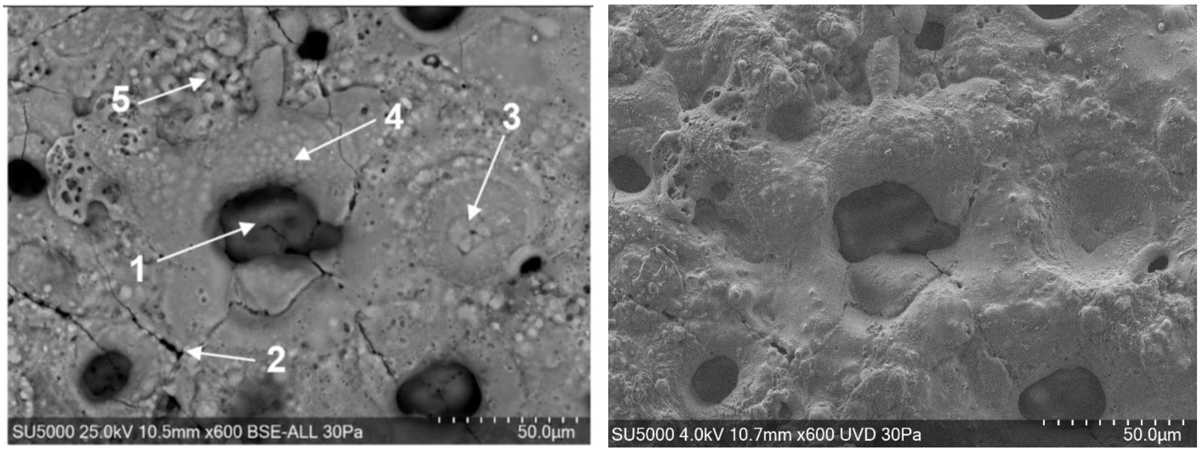
The oxidation conditions in electrolytic plasma were as follows: frequency 150 Hz, galvanostatic pulsed unipolar regime, current density 0.13 A/cm^2, average fill factor of 25% and processing time of 10 minutes. The maximum amplitude of the working voltage was about 450 V [18]. 3 electrolyte-based combinations were used: Na3PO4 (provider– *Thermo Scientific*) şi $NaAlO_2$ (provider- *Sigma-Aldrich, Merck Group*Germany). The composition and properties of the aqueous electrolytes used in the process are shown in Table 5.1.

Tabel 5.1. Features of the electrolyte

Sample code	**Electrolit**		
	Composition	**pH**	**Electrical conductivity (mS/cm)**
S1	10g/l Na3PO4 + 15g/l NaAlO2	12.7	24.5
S2	10g/l Na3PO4 + 20g/l NaAlO2	12.8	27.4
S3	10g/l Na3PO4 + 25g/l NaAlO2	12.9	30.1

The dependence on electrolyte composition (*10g/l Na3PO4 + 15g/l NaAlO2; 10g/l Na3PO4 + 20g/l NaAlO2; 10g/l Na3PO4 + 25g/l NaAlO2*) of morpho-structural characteristics investigated by analysis of SEM-EDS and XRD showed that:

- Surface morphology is relatively similar and typical to PEO samples (figure 5.1).



a. b.

Figura 5.1. (a) SEM micrographs in backscattered electrons for sample S1(×600) and (b) SEM micrographs in secondary electrons for the same surface.

The main morphological structures of the surface are: 1 – major and minor pores, 2 – radial micro-cracks, 3 – collapsed closed pores, 4 – resolidified melt zones and 5 – sintered particles.

- There were no significant differences between PEO surface porosity and roughness samples (Table 5.2).

Tabel 5.2. Average values of porosity and surface roughness obtained by PEO.

Sample code	**Average surface porosity ± SD (%)**	**Average surface roughness ± SD (µm)**
S1	3.99 ± 0.14	5.8973 ± 0.5897
S2	3.75 ± 0.04	5.9813 ± 0.5981
S3	2.98 ± 0.07	6.0903 ± 0.6090

- Data on average coating thickness show an increase in PEO coating thickness from sample S1 to S3 (Table 5.3).

Tabel 5.3. Average values of thickness of PEO coatings

Sample code	Average layer thickness ± SD (μm)
S1	34.48 ± 9.57
S2	39.34 ± 8.44
S3	46.25 ± 11.91

- X-ray diffraction analyses showed that the three coatings have similar compositions, showing a structure consisting of spinel, magnesium oxide and magnesium phosphate (figure 5.2). Increased contraction of sodium aluminate resulted in increased by mass of the spinel phase $MgAl_{2O4}$ (Table 5.4).

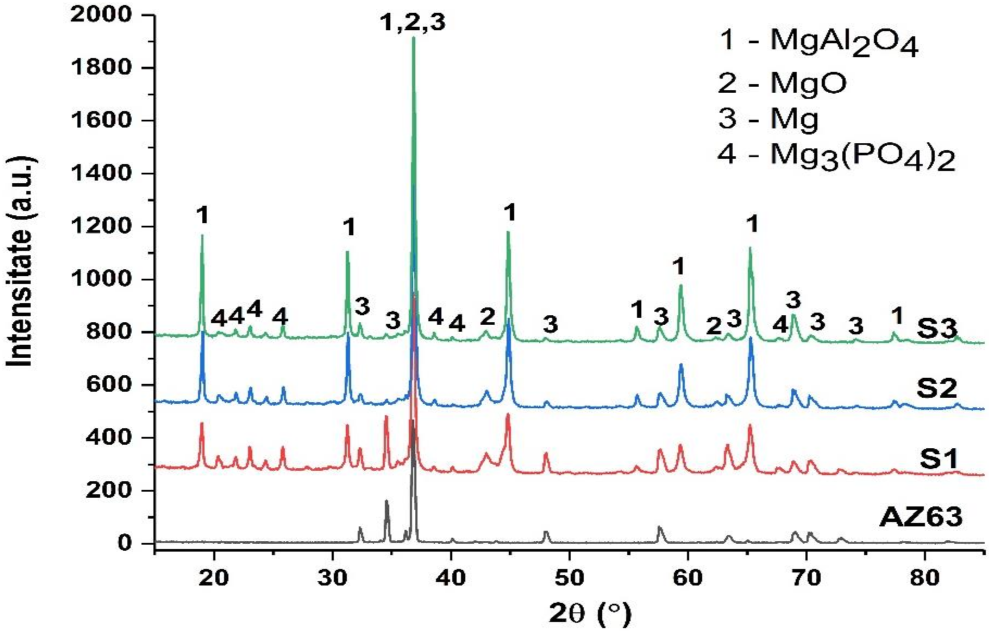


Figura 5.2. XRD spectra and qualitative phase analysis for AZ63 base alloy and PEO-treated samples

Tabel 5.4. Quantitative phase analysis of PEO processed samples

Sample	Quantitative phase composition (wt ± SD, %)			
	MgAl2O4	***MgO***	***Mg***	***Mg3(PO4)₂***
S1	34.75±0.57	41.67±3.86	11.45±0.41	12.13±1.13
S2	62.16±0.56	23.69±0.56	5.08±0.27	9.09±0.87
S3	74.69±0.62	15.19±3.69	4.69±0.3	5.43±0.64

Tribological analysis shows that all samples subjected to processing have tribological characteristics superior to the substrate, the sample obtained in the electrolyte with the least amount of *NaAlO2*, ***S1***, having the highest hardness, the best adhesion and the lowest degree of wear. In contrast, sample ***S3*** has the lowest coefficient of friction.

In terms of corrosion protection, impedance studies suggest that oxide layer formation is a multi-step reaction process involving intermediates adsorbed on the surface, which are produced by the charge transfer reaction during the corrosion process.

In the Nyquist representation and in the Bode representation, better resistance of the S2 sample is observed, both by higher capacitive loop values at high frequencies and by the high impedance value. The reduced value of the inductive loop, in the Nyquist representation, of this sample indicates that the absorption process is lower.

6. CONCLUSIONS AND PERSONAL CONTRIBUTIONS

6.1 CONCLUSIONS

The main scientific motivation behind the research lies in the fact that magnesium alloys are considered some of the most promising structural materials of the future. However, due to their poor corrosion resistance, their future applications are limited. Therefore, the study and development of the oxidation process in electrolytic plasma to improve corrosion resistance and mechanical properties of magnesium alloys is a current and interesting concern.

The main goal of these researches was the **design and construction** of an electrolytic plasma oxidation plant at laboratory level to **obtain ceramic coatings** on Mg alloys, AZ63, with superior properties to the base material in terms of hardness, wear resistance and corrosion resistance. Subsequently, we moved to the next technological level by transposing the technology and the PEO installation at industrial level.

The targeted demonstration model consisted of performing PEO tests on Mg AZ63 alloys and validating under laboratory conditions coatings with superior properties obtained by:

- ✓ conducting PEO experiments on Mg AZ63 alloys to obtain advanced ceramic coatings with superior properties compared to the base material;
- ✓ advanced elemental, morphological and microstructural chemical characterization of PEO coatings;
- ✓ and testing PEO coatings to demonstrate hardness, wear resistance and corrosion properties.

The experimental research conducted focused on two main studies:

I. Influence of processing time on morpho-structural characteristics and corrosion resistance of alloys of Mg, AZ63, in sodium aluminate electrolyte

II. Influence of electrolyte composition (*10 g/l Na3PO4 + 15 / 20 / 25 g/l NaAlO2*) on mechanical and anticorrosive properties of PEO layers obtained on alloys of Mg, AZ63.

Personal contributions to these researches consisted of designing and building the electrolytic plasma oxidation plant at laboratory level, preparing samples of Mg, AZ63 alloy, designing the PEO processing model and investigation methods, preparing samples, electrolyte solutions and performing PEO tests. In order to perform the characterization and testing of the obtained PEO coatings, we collaborated with the following collectives:

- SEM-EDS and XRD: Advanced Materials Laboratories within the Regional Research and Development Center for Innovative Materials, Processes and Products for the Automotive Industry (CRC&D-Auto), National University of Science and Technology Politehnica of Bucharest – University Center Pitesti

- Tribology: Group for elementary processes in plasma and applications, National Institute of Laser, Plasma and Radiation Physics (INFLPR), Magurele, Ilfov County.
- Corrosion: Faculty of Materials Sciences and Engineering, "Gheorghe Asachi" Technical University of Iasi and ELSSA Laboratory SRL of Piteşti.

The innovative contribution consists in the construction of the plant at industrial level (according to subchapter 3.3), commissioning and obtaining ceramic coatings through PEO on magnesium alloy, ZE41. The experimental research was validated by the results of phase analysis by X-ray diffraction.

6.2 TARGETED APPLICATIONS AND DEVELOPMENT PROSPECTS

AZ63 alloy (6% Al, 3% Zn) is one of the widely used magnesium alloys being a versatile material with a wide range of potential applications due to its beneficial properties such as low weight, good tensile strength and favorable strength-to-weight ratio. The choice of AZ63 for a particular application depends on a number of factors, such as performance requirements, weight, cost, machinability and corrosion resistance – where the magnesium alloy itself, without surface treatments, is deficient.

The experimental research carried out and presented in this thesis has shown that composite coatings with superior properties to the base material in terms of hardness, wear and corrosion resistance can be obtained through the oxidation process in electrolytic plasma, which increases the range of possible applications for alloy AZ63.

Taking into account the above, as well as the technical solutions that were obtained (and presented in this sentence) for the functionalization of the surfaces of the magnesium alloy, AZ63, by oxidation in electrolytic plasma, it is desired, as a development perspective, to move the process from laboratory to industrial level for targeting the following types of applications:

- ✓ **Sports and recreational equipment**
- ✓ **Parts and components of the automotive industry**
- ✓ **Portable electronics**
- ✓ **Aeronautics and space industry**

Research will also focus on obtaining ceramic coatings with superior properties on magnesium alloy, ZE41, which has a higher ductility, making it suitable for applications requiring a combination of mechanical strength and ductility, such as die-castings, vehicle components and sports equipment.

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List of published scientific papers

1. **I Patrascu**, M C Ducu, A D Negrea, S G Moga, A G Plaiasu, "Overview on plasma electrolytic oxidation of magnesium alloys for medical and engineering applications", IOP Conf. Series: Materials Science and Engineering 1251 (2022) 012001, doi:10.1088/1757-899X/1251/1/012001 (Anexa 1)

2. Moga S., Negrea D., Ducu C., Malinovschi V., Schiopu G., Coaca E., **Patrascu I (autor correspondent)**, "The Influence of Processing Time on Morphology, Structure and Functional Properties of PEO Coatings on AZ63 Magnesium Alloy", Appl. Sci. 2022, 12, 12848. https://doi.org/10.3390/app122412848 (Anexa 2)

3. **Ion Patrascu**, Aurelian Denis Negrea, Viorel Malinovschi, Cristian Petrica Lungu, Ramona Cimpoesu, Marian Catalin Ducu, Adriana-Gabriela Schiopu, Sorin Georgian Moga, „Magnesium AZ63 Alloy Protective Coatings by Plasma Electrolytic Oxidation in Mixed Aqueous Electrolytes", Engineering, Technology & Applied Science Research, Vol. 14, No. 3, 2024, 14248-14256, DOI: https://doi.org/10.48084/etasr.7303 (Anexa 3)