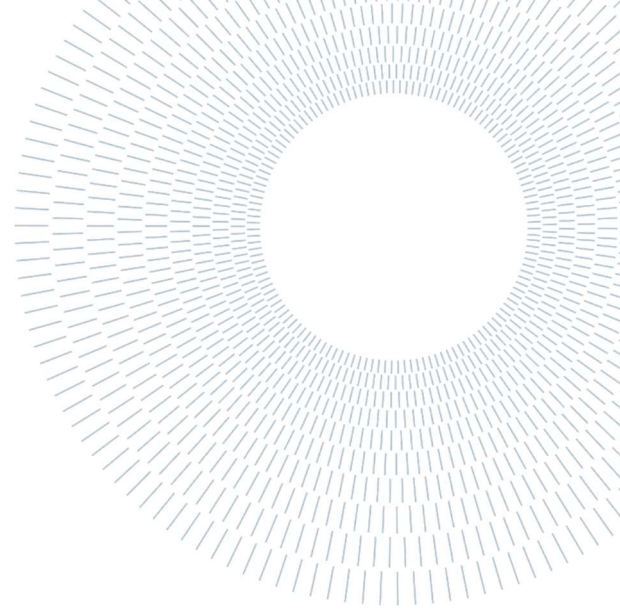




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EXECUTIVE SUMMARY OF THE THESIS

Optimization of a protective coating on magnesium alloy using Plasma Electrolytic Oxidation technique

TESI MAGISTRALE IN BIOMEDICAL ENGINEERING – INGEGNERIA BIOMEDICA

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1. Introduction

In a global scenario in which life expectancy at birth for healthy people in developed countries is continuously growing and in which the number of people over 65 years old is estimated to double within 25 years, orthopedics is becoming more and more crucial for an increasing number of people to preserve an adequate quality of life.

Magnesium [1] is attracting particular interest as a material to be used in short-term orthopedic prostheses (such as clips, screws, suture threads, etc.), due to its mechanical properties similar to those of natural bone and of its biodegradability [2]. In particular, magnesium features an elastic modulus which makes it possible to avoid the phenomenon of stress shielding [3], which involves the under-stressing of the newly formed bone callus and the consequent impairment of fracture healing. Furthermore, the biodegradability of magnesium allows avoiding a second surgery to remove the device, thus reducing costs for the healthcare system and, above all, avoiding further risks and pain for the patient. However, magnesium and its alloys are subject to a corrosion rate [4] that is too high to

allow the complete healing of fractures in a physiological environment.

To cope with excessively rapid corrosion dynamics, the application of coatings is a key solution. Among the most relevant coatings applicable to magnesium, the Plasma Electrolytic Oxidation (PEO) technology is recently gaining particular attention [5].

The PEO technique is a plasma anodic oxidation process that involves high voltage anodic oxidation to produce a conversion oxide which is well adherent to the underlying substrate. The high chemical stability of the ceramic oxide produced via the PEO technique can give the Mg greater resistance to corrosion, acting as a physical barrier to hinder the penetration of the external electrolyte into the substrate. This technique can delay the loss of mechanical integrity and avoid an excessive release of hydrogen gas, which is harmful to body tissues. Moreover, PEO treatments represent a particularly interesting solution among the developed coating techniques, as they are versatile and relatively quick and simple to apply.

In particular, the soft sparking technique, a variant of the PEO treatment in which the traditional positive polarization of the sample is alternated

with a negative polarization, is gaining some interest due to the possible implications of its exploitation on magnesium.

The aim of this technique is indeed to obtain a more compact coating, with better surface resistance to corrosion, through a less aggressive oxidation regime than standard PEO. The objective of this work was thus to optimize the electrical parameters of the PEO treatment on an AZ31 magnesium alloy substrate, to improve the coating compaction and the corrosion resistance of the substrate.

In particular, the influence of the electrical process parameters was studied, focusing on the total duration of the treatment, the waveform model used and the duration of the anodic phase in the duty cycle to obtain deep, compact and homogeneous coatings.

2. Plasma Electrolytic Oxidation treatment

2.1. Samples

Strips of AZ31 magnesium alloy (*RL3 srl*), with a width of 1.5 cm, were used as substrate for the PEO treatment.

Before carrying out the treatment, each sample was pickled by immersion in a solution of 4 M acetic acid CH_3COOH (23%) and 1 M nitric acid HNO_3 (4.2%) for 10 seconds, to remove eventual surface impurities or spontaneously formed oxide. Following pickling, each sample was rinsed in Milli-Q water for another 10 seconds and subsequently dried using compressed air.

2.2. Electrolytic solution

To carry out the treatment, a solution composed of 1 g/L of sodium hydroxide (NaOH) and 10 g/L of sodium metasilicate pentahydrate ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$) was used. The conductivity of the solution is equal to 8.00 mS and the pH is equal to 12.43.

During the PEO treatment, the electrolyte solution was kept in agitation using a magnetic stirrer coupled with a stir bar.

2.3. Electrical process parameters

The PEO treatments were carried out in pulsed current (in voltage control) with an *Asterion AST 1501* generator. The treatment involves an initial

transient of 1 minute, until the maximum set voltage of 300 V is reached, and the voltage is then maintained until the end of the test.

The bipolar waveform used involves the succession of an anodic phase and a cathodic phase, interspersed with a rest period, which is repeated at the end of the cathodic phase. The ratio R between the amplitudes of the anodic and cathodic phases is equal to 0.5.

3. Analysis and characterizations

A characterization of the obtained coatings was then performed through morphological and chemical-physical analyses, to study their topography and elementary chemical composition.

3.1. Scanning Electron Microscopy

In this thesis work, Scanning Electron Microscopy (SEM) images obtained through a *Zeiss Evo 50* microscope are reported, to evaluate the topography of the selected samples. The surface of the films and their cross section, obtained through metallographic sections, were evaluated by means of backscattered electron images.

3.2. Energy Dispersive X-ray Microscopy

Using an *IncaX-sight X-EDS 7060* probe, equipped to the SEM, an Energy Dispersive Spectrometry (EDS) analysis of the cross sections of the coatings was carried out. The collected EDS maps were aimed at evaluating the distribution of the elements along the thickness of the coating.

3.3. Evaluation of the coating thickness

Starting from the images of the sections obtained via SEM, with the use of the ImageJ software, the thickness of the coatings was measured. For each coating, the average and standard deviation of 30 measurements is reported.

3.4. Electrochemical corrosion tests

To evaluate the corrosion behavior of the optimized samples in physiological environment, potentiostatic polarization tests were performed in

The internal profile of the coating shows an almost constant depth along the entire interface with the substrate. The internal layer is compact, adherent to the metal substrate and constitutes almost the entire thickness of the coating. Moreover, it presents a granular morphology in the areas close to the substrate, while it is smoother in the areas close to the external layer.

The outer layer, however, remains slightly porous. From the EDS image shown (Figure 4), it is possible to notice that the Si is concentrated in a thin surface layer; the oxygen, on the other side seems to have gone deeper, forming a very homogeneous and constant layer.

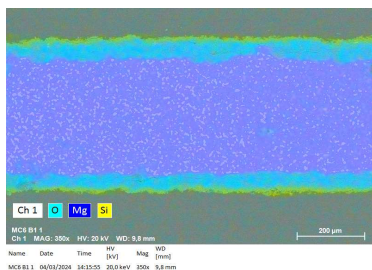


Figure 4: Image obtained via EDS on the optimized sample.

The total thickness of the coating is equal to $\sim 65 \mu\text{m}$ and the ratio between compact and porous layer varies from 1.5 to 5.6 depending on the sample region.

As regards the corrosion tests, the free corrosion potential of the treated samples ($-1.35 \pm 0.03 \text{ V}$) is significantly more positive than that of the untreated reference sample (-1.56 V). For all replicates, the corrosion current, normalized on the area, is approximately three orders of magnitude lower than that of the untreated sample ($2.18 \cdot 10^{-3} \text{ A/cm}^2$), averaging at a value of $3.52 \cdot 10^{-6} \text{ A/cm}^2$. Moreover, the polarization resistance of the coated samples ($6129.63 \pm 3224.07 \Omega$) is undoubtedly higher than the untreated sample one (38.45Ω).

Looking at the scratch tests, from Figure 5, the presence of evident cracks cannot be noticed either inside the groove or outside the edge of the scratch.

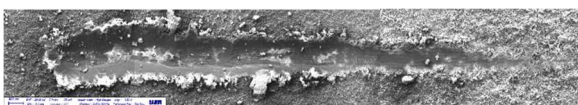


Figure 5: SEM image of one of the scratches performed (with a load range of 0.03-30 N) on a replicate of the sample made with optimized parameters.

However, it is possible to notice whiter areas within the groove, relating to the exposed substrate, at a distance of approximately 4.3 mm from the start of the scratch. The curves obtained for the different scratches are similar: indeed, a critical value can be identified around 12 N, at which the acoustic emission of these samples begins to grow and oscillate until the end of the test. The residual depth shows a gradual increase as the normal force increases. Near the critical load, its value is equal to $26.84 \pm 11.84 \mu\text{m}$.

5. Discussion

5.1. Cause-effect hypothesis of optimal parameters

It can be deduced that a smaller area at the interface allows for less dispersion of the currents and, therefore, enhances the concentration of the discharge phenomena on the effective surface of the samples.

Furthermore, the increase in temperature during the process and the convective motions close to the sample could be closely related to the diffusion of oxygen in the internal layer of the coating. It was so decided to find a compromise in terms of agitation of the electrolyte solution, to improve the diffusion of the electrolytes, while avoiding excessive overheating of the solution itself.

From the obtained results it can be observed that a less aggressive anodic component allows for a more consistent evolution of the sparking process. Moreover, it is possible to assume that a longer treatment time favors the process of oxygen diffusion deep into the substrate.

5.2. Relationship between morphology, corrosion resistance and coating cohesion

From the corrosion tests carried out, the behavior of the treated samples was significantly better than that obtained on the untreated magnesium sample, in terms of corrosion resistance. This behavior is in line with the morphology of the optimized coatings, which present homogeneous and deep thicknesses, useful for insulating the magnesium substrate from the aggressive external environment. By comparing the residual depth values obtained with the average thickness of coatings, it is possible to conclude that the critical load observed is not

related to adhesion but more likely to cohesion; for this load, in fact, the interface with the substrate is not reached.

5.3. Hypotheses on the mechanism of coating formation

In almost all the coatings obtained, the formation of two layers was observed: a thin superficial one, where Si is concentrated, and a thicker internal one where almost only magnesium and oxygen are present. If the external layer of Si is adequately adherent, thin and porous, oxygen appears to reach deeper regions inside the original substrate. Indeed, the shape evolution of the section of the internal layer, observed in the coatings produced, suggests an initially punctual penetration mechanism with radial diffusion of oxygen under the surface. Subsequently, an increase in the density of these penetration points occurs. When two or more points are sufficiently close to each other, the oxidized areas join together forming a partially continuous internal layer; subsequently, the phenomenon proceeds until it creates continuity throughout the sample.

In detail, a spot formation behavior of the internal coating can be found, with the formation of multiple inlets along the sample, with a "potato-like" shape. The oxygen, therefore, seems to diffuse starting from points that extend vertically and which could be assimilated to the discharge channels that develop during the PEO process, from which the diffusion of oxygen could then start, also thanks to the high presence of oxygen ions in the plasma region. Subsequently, as the duration of the treatment increases, the oxygen which has penetrated deeply has the opportunity to also spread longitudinally to form a continuous and homogeneous layer along the entire sample.

6. Conclusions

During the tests, the soft sparking phenomenon was obtained. However, a clear link between the actual occurrence of the soft sparking phenomenon and the positive results obtained on the samples could not be determined.

The most promising coatings were obtained by minimizing the sample-solution-air interface, in addition to reduced agitation and the application of a quadratic waveform with an anodic duty cycle of 25% for a treatment duration of 20 minutes.

In terms of corrosion resistance, the mechanical characteristics obtained on the selected sample represent a positive starting point for the development of effective protective PEO coatings on magnesium. The optimization of the treatments could be carried forward in future research, to try to obtain coatings that go into depth in a more consistent and, above all, homogeneous way.

In particular, given the reduced thickness of the porous layers, compared to the compact one, and given that the former probably favor localized corrosion due to the presence of pores, a subsequent mechanical removal of the outermost portion of the coatings could be evaluated.

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