



POLITECNICO
MILANO 1863

**SCUOLA DI INGEGNERIA INDUSTRIALE
E DELL'INFORMAZIONE**



EXECUTIVE SUMMARY OF THE THESIS

Chemical optimization of Micro Arc Oxidation treatments on AZ31 magnesium alloy for degradation control

LAUREA MAGISTRALE IN BIOMEDICAL ENGINEERING - INGEGNERIA BIOMEDICA

Author: ELEONORA CONFALONIERI

Advisor: PROF. ROBERTO CHIESA

Co-advisor: DOCT. MONICA MOSCATELLI, ENG. MATTEO PAVARINI

Academic year: 2021-2022

1. Introduction

Magnesium is the lightest structural metal used in industry given its low weight and ability to form alloys with good mechanical properties. In the biomedical field, there is a growing need for the use of biodegradable metal implants in order to ensure proper healing of damaged tissue within the necessary time frame. In fact, these implants can support the tissue in the early stages of treatment, while then progressively decrease their support during the tissue regeneration or repair phase.

Magnesium has the characteristic of biodegradability in addition to good bioresorbability, biocompatibility and non-toxicity and it is part of many biological and metabolic reactions. In addition, this material has an elastic modulus comparable to that of bone tissue, high availability and it is easily machined on machine tools. Despite these advantages, magnesium has a corrosion rate that is difficult to control, causing the phenomena of localized corrosion, hydrogen accumulation, and an increase in alkaline pH near the corroded surface [1].

To cope with these disadvantages, different potential solutions have been explored, first of all, the fabrication of magnesium alloys and

then the coating of the material by a conversion technique such as Micro Arc Oxidation (MAO). This technique allows the generation of oxides that are compact, hard and adherent to the starting substrate without having significant costs. The resulting coatings are characterized by a dense inner layer and a more porous outer layer.

The first phase of the treatment is the same as in traditional anodizing while after reaching the breakdown potential it enters the proper MAO regime, where the so-called micro-arcs are generated and thicker oxide coatings are obtained, providing greater protection against wear and corrosion.

The MAO technique is characterized by specific process conditions (current density, treatment time and limiting voltage), electrical parameters (frequency, duty cycle) and the electrolyte solution. With regard to frequency the higher is the more it causes a decrease in porosity, pore diameter and the presence of cracks. Duty cycle, on the other hand, leads to coatings with higher thickness and larger pores.

Regarding the composition of the electrolyte solution, the anions most studied in the literature are silicates, aluminates and phosphates.

These can be incorporated in the coating and increase its growth rate; they also modulate the potential of breakdown thus allowing to save time and/or energy in reaching it.

Among these compounds, sodium silicate is one of the most studied and most widely used components of MAO electrolytic solutions as it allows to obtain more stable and thicker coatings leading to a better corrosion resistance compared to that given by phosphates [2]. The optimal concentration according to the literature appears to be 10 g/L.

Other compounds widely used in this technique are hydroxides, particularly potassium and sodium ones, which prevent consistent dissolution of the metal at the anode.

However, there are conflicting opinions regarding the optimal concentration of potassium hydroxide for the MAO treatment of magnesium alloys and there are few studies investigating the effect of sodium hydroxide. In addition, there is no clear comparison between the two hydroxides, their choice being arbitrary in the different works.

In addition to these electrolytes, additives (e.g., sodium tetraborate, potassium fluoride, glycerol) can be included in the solution, either to improve the properties of the produced coatings or to provide them with additional functionality.

Potassium fluoride is a component often included in MAO technique solutions because of its effects on improving the corrosion resistance of the made coating, but its amount must be dosed appropriately since it causes an increase in pore diameter at the same time. According to the literature, the concentration of 8 g/L seems to achieve the right compromise.

The aim of this thesis is to exploit Micro Arc Oxidation treatments in order to provide magnesium alloys with greater corrosion resistance and durability from a physiological point of view. Thus, the objective concerns the generation of a resistive coating on AZ31 alloy that is thick, compact and uniform, with a small pore diameter and low porosity percentage, well adhered and free of elements that could affect corrosion resistance such as the presence of cracks.

In particular, this paper will focus on the composition of the electrolyte solution in order to

explore the effect of one of the main components on the quality of the coating.

2. Materials and Methods

Rectangular AZ31B magnesium alloy specimens (20*10 mm with a thickness of 0.5 mm) were used for the coating process. All specimens were subjected to a cleaning pretreatment. MAO treatment was performed with both an AST 1501 voltage-controlled alternating current generator (Ametek, USA) and an N5772A direct current generator (Agilent, USA).

The experimental apparatus consisted of a solution placed in a 500-mL beaker that was stirred on a thermo-agitating plate at room temperature. Samples were grasped by a titanium clothespin coated with insulating sheath. The grasp was connected directly to the anode. The cathode, on the other hand, was connected to an AISI 304 steel mesh placed in the beaker and used as a counter electrode.

The electrolytes used for the MAO process are summarized in Table 1.

	Na_2SiO_3 (M)	KOH (M)	NaOH (M)
Si005	0.05	0	0
K005	0.05	0.05	0
K01	0.05	0.10	0
K1	0.05	1.00	0
Na005	0.05	0	0.05
Na01	0.05	0	0.10
Na1	0.05	0	1.00

Table 1: List of electrolyte solutions made

Once the solution that could provide the best results in terms of coating's quality was selected, potassium fluoride was included to evaluate its contribution. Two other solutions (K01F007 and K01F014) were made in which the fluoride concentration was 4 g/L and 8 g/L, respectively. Conductivity and pH were measured for all the solutions made.

Regarding the process parameters for MAO treatments under direct current, current densities, treatment time and voltage were set.

Current densities of 120 mA/cm² were set for

Si005 and K005 solutions, while a density of 20 mA/cm² was set for Na005 solution. Instead, the treatment time was set at 600 s. The following current densities were set for the other solutions:

- 20 mA/cm² for solutions K01 and Na01;
- 5 mA/cm² for solutions K1 and Na1;
- 20 mA/cm² for solutions K01F007 and K01F014.

The treatment time was set at 900 s.

DC treatments were only carried out in order to construct the voltage curve to be applied in pulsed current.

In pulsed current MAO treatments, the parameters of interest are the voltage of breakdown, the final voltage, the frequency and the duty cycle. Square waves with a frequency of 800 Hz and duty cycle of 40 % and 50 % were set.

For all solutions, where possible, the breakdown voltage, the final voltage, two consecutive transients (ramps) and finally the steady state were set. To make direct comparisons between the solutions of interest, the trends were equalized to the condition with slower voltage growth at the same concentration of the hydroxide type. For solutions K01F007 and K01F014, the voltage and transient values of solution K01 were applied in order to examine the contribution of potassium fluoride alone. For the solutions that allowed proper treatments to be performed three replicates were made per sample.

The samples were then visually examined to make a preliminary assessment of the coatings' quality in terms of compactness, irregularity or uniformity. Solutions that did not yield adequate results in terms of DC treatment steps, or current and macroscopic appearance of the coatings generated in pulsed current were discarded. Next, thickness measurements were performed on three replicates per sample using a Fischer Dualscope FMP100. In order to analyze the surface morphology of the coating, a scanning electron microscopy analysis was performed with a ZEISS model EVO50 with EDS Bruker Quantax 200 microanalysis. Images were acquired by both secondary and back scattering electrons with magnifications between 1000x and 10000x. The images were then analyzed both qualitatively, in terms of homogeneity and presence of defects and/or

cracks, and quantitatively. For quantitative analysis, pore diameter and porosity were calculated on back scattered images using ImageJ software. Finally, corrosion tests were carried out for samples K01, K01F007 and K01F014 by potentiodynamic polarization in SBF realized by Kokubo [3] method. The potentiostat Metrohm Autolab PGSTAT30 was employed; data extrapolation was then carried out by Tafel [4] method.

3. Results and discussions

The results of the conductivity measurements showed an increase in conductivity with concentrations due to the increase in the amount of dissolved ions in solution. The solutions with potassium hydroxide were found to be more conductive than the sodium containing ones, confirming the findings in the literature.

During the direct current treatment of Si005, K005 and Na005 solutions, the typical treatment steps observed in MAO processes were not achieved. In addition, for these conditions pulsed current treatment also failed to achieve sufficiently low and constant current values.

Considering the K01, Na01, K1 and Na1 solutions, differences in terms of the maximum potential reached in the DC tests could be derived. Particularly, in the more concentrated solutions, the voltages reached were significantly lower than in solutions K01 and Na01. With respect to the pulsed current treatment, on the other hand, it could be seen that solutions K01 and Na01 were characterized by lower and more constant current values than the corresponding more concentrated solutions, which toward the final part of the treatment reached very high currents.

Sodium and potassium hydroxide solutions with 0.05 M molarity did not lead to the generation of sufficiently uniform and adherent coatings in both DC and pulsed current tests so they were not considered for the following characterizations.

Among the K01, Na01, K1 and Na1 samples, those that showed the most adherent and uniform coatings were K01. Regarding the samples made with the most concentrated solutions, thin coatings were obtained with a clearly metallic appearance. This result is

confirmed by the thickness measurement. The more dilute solutions are instead characterized by greater thicknesses and smaller standard deviations, particularly the K01 samples (Table 2).

	Average value (μm)
K01	6.040 ± 0.676
K1	1.060 ± 0.448
Na01	4.330 ± 1.179
Na1	1.060 ± 0.519

Table 2: Measured thickness of samples K01, K1, Na01 and Na1

The surface morphology of samples K01 and Na01 showed fairly uniformly distributed porosities (Figure 1a and Figure 1b). Samples K1 and Na1 were found to be characterized by grains (Figure 1c and Figure 1d), a negative aspect from the point of view of surface roughness of the coating.

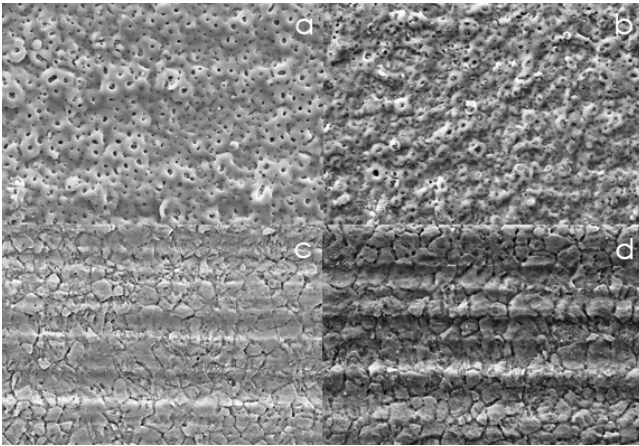


Figure 1: Surface morphologies observed for samples (a) K01, (b) Na01, (c) K1 and (d) Na1

From a quantitative point of view, samples Na01 showed the highest percentage of porosity with the highest average pore diameter value. In contrast, K1 samples showed the lowest values of these two parameters (Table 3).

Samples	Porosity (%)	Feret's diameter (μm)
K01	6.889 ± 2.318	0.650 ± 0.295
K1	4.816 ± 1.069	0.493 ± 0.099
Na01	9.841 ± 1.121	0.681 ± 0.059
Na1	5.555 ± 0.965	0.532 ± 0.087

Table 3: Calculated surface porosity and pore size of samples K01, K1, Na01 and Na1

Therefore, the best overall results could be obtained with potassium hydroxide than with sodium hydroxide and with the concentration of 0.1 M.

Basing on coating thickness and morphology, solution K01 was selected and compared with solutions K01F007 and K01F014 in order to evaluate the contribution of the potassium fluoride additive.

In pulsed current, low and constant current values were obtained for solution K01F007, while for solution K01F014, strong current discharges were observed in the final section of the test.

Macroscopically, coatings well adhered to the substrate were obtained with both solutions but a lower uniformity was observed for the K01F014 samples. The thickness was greater for both solutions.

By analyzing the surface morphology, it can be seen that well-defined pores were obtained for the three types of samples (Figure 2).

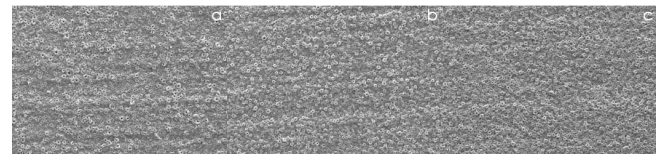


Figure 2: Surface morphologies observed for samples (a) K01, (b) K01F007 and (c) K01F014

The percentage and diameter of pores increased with increasing potassium fluoride concentration. Despite this, however, in corrosion tests by potentiodynamic polarization, the obtained results (Table 4 and Table 5) showed an increase in corrosion resistance as the potassium fluoride concentration increased in the defined range, together with a decrease in corrosion density and corrosion rate, indicative of a more protective coating.

Samples	J_{corr} (mA/cm ²)	CR (mm/year)
AZ31	0.330	7.430
AZ31 DECAP	0.140	3.140
K01	0.136±0.024	3.090±0.560
K01F007	0.022±0.012	0.514±0.285
K01F014	0.025±0.005	0.560±0.110

Table 4: Results obtained by Tafel extrapolation for untreated and MAO-treated samples

Samples	Polarization resistance (Ω)
AZ31	123.400
AZ31 DECAP	239.070
K01	166.226±86.090
K01F007	1151.930±735.910
K01F014	2437.600±230.090

Table 5: Mean values of polarization resistances calculated by Tafel extrapolation for untreated and MAO-treated samples

4. Conclusions

The results obtained showed that:

- potassium hydroxide enables the generation of a better quality coating than sodium hydroxide;
- the 0.1 M hydroxide concentration leads to a thicker, more uniform, and more compact coatings than both higher and lower concentrations; conversely, coatings with a higher percentage of porosity and pore diameter are obtained;
- the addition of potassium fluoride in the 0.07-0.14 M range results in a marked improvement in corrosion resistance and greater coating thickness for samples treated in the most concentrated solution; however, increasing the amount of dissolved fluoride, the porosity and the pore size of the coatings' surfaces also grow significantly.

Based on the results, solution K01F014 was selected because it provided a significant improve-

ment in corrosion resistance compared to the other solutions analyzed.

As a future development of this thesis work, a coupling between the MAO technique and another conversion technique, specifically hydrothermal treatment, could be carried out. Indeed, it is shown in the literature that hydrothermal treatments following MAO can promote the reduction of pore depth and pore size, which could allow to further improve the corrosion resistance of the treated substrates [5].

References

- [1] Hornberger H. et al. *Acta Biomaterialia*, **8**: 2442–2455, (2012).
- [2] Ghasemi A. et al. *Surface and Coatings Technology*, **204**:1469–1478, (2010).
- [3] Kokubo T. et al. *Biomaterials*, **27**:2907–2915, (2006).
- [4] Atrens A. et al. *Encyclopedia of Interfacial Chemistry*, pages 515–534, (2018).
- [5] Chang L. et al. *Corrosion Science*, **72**:118–124, (2013).