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EXECUTIVE SUMMARY OF THE THESIS

Rivestimenti sol-gel di $Mg(OH)_2$ su lega di magnesio AZ31: sintesi, caratterizzazione e studio della cinetica di degradazione.

TESI MAGISTRALE IN BIOMEDICAL ENGINEERING – INGEGNERIA BIOMEDICA

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1. Introduction

Metallic materials have long been fundamental in the biomedical field, especially in the orthopedic sector where they are used in the production of prostheses, internal and external fixators and in any system that requires the mechanical properties of metals in load situations. In fact, these materials show excellent mechanical resistance and fracture toughness, which makes them preferable to ceramic and polymeric materials. The most traditionally used materials are stainless steels, titanium and its alloys and chromium-cobalt alloys: however, all of them are easily subject to corrosion and wear [1,2,9]. This triggers an inflammatory response in the body, inducing a phenomenon (stress shielding) that causes a decrease in bone density and possible aseptic mobilization of the prosthesis [3,15]. These metals also have the disadvantage of not degrading within the body over time, resulting in the need to carry out a further invasive intervention when they need to be removed, with the possibility of infections [3,8,10].

For this reason, additional materials with the ability to degrade over time were sought and in recent years magnesium has proved to be among the best candidates thanks to its multiple characteristics. In fact, in addition to being a biocompatible material, it is not cytotoxic, it is easily workable and has density and mechanical properties very close to those of bone [1,3,5,6,7,12]. Unfortunately, it presents problems, too, related to its high corrosion rate. In fact, by corroding too quickly (there is an important loss of mechanical properties between 12 and 18 days), it generates a considerable accumulation of gaseous hydrogen around the system in a very short time, which causes an increase in pH and possible necrosis of the fabrics [7].

To overcome this problem, two strategies have been proposed, with the aim of increasing the corrosion resistance of magnesium. The first involves the use of magnesium alloys (the most common are made of aluminum: AZ31, AM60 and AZ91), the second consists in coating the magnesium on the surface. These techniques can also be used together.
The coatings can be conversion or deposition. The coatings obtained by conversion consist in the formation of coatings through reactions between the sample and the surrounding environment. Those obtained by deposition involve the creation of metal, ceramic or polymeric coatings. Among the most used conversion techniques, Micro Arc Oxidation (MAO), also known as Plasma Electrolytic Oxidation (PEO) and hydrothermal treatment are distinguished, while Dip Coating stands out among the deposition techniques.
Dip Coating is a deposition technique that allows to obtain a coating with multiple and variable characteristics depending on the solution in which the sample is immersed. It is a widely used treatment as it is inexpensive and very easy to perform, which allows the generation of a film on the entire sample, regardless of the shape, size and morphology of the specimen itself. It consists in the immersion and extraction of a sample inside a solution through a mobile guide that moves at a controlled speed and allows to generate a coating on the substrate of micrometric dimensions. By acting on the speed of the mobile guide, on the concentration of the solution and on the number of immersions of the sample, it is possible to modify the thickness of the coating [10].

2. Aims and purposes

The purpose of this thesis project is to create a coating that slows down the degradation of magnesium within the human body. The coating must consist of a film based on magnesium hydroxide nanoparticles, obtained starting from a sol-gel solution in which the AZ31 magnesium alloy samples are immersed using Dip Coating. This solution must have a good adhesion capacity, to ensure that the coating remains adhered to the magnesium substrate during its degradation process within the SBF solution in vitro. The samples will be evaluated in terms of morphology and adhesion capacity of the various coatings and those showing the best results will be subjected to degradation tests to evaluate their degradation kinetics.

3. Materials and methods

For the experimental work, specimens in magnesium alloy AZ31 were used (96 wt.% Mg, 3 wt.% Al, 1 wt.% Zn, Goodfellow, England) with a rectangular shape of size 0.5x1.5 cm and thickness of 0.5 cm. Each sample was subjected to a process of cleaning with abrasive paper, washing in acetone, further cleaning process in nitric acid, ultrasonic bath for 5 minutes. The samples were then coated with a sol-gel coating containing magnesium hydroxide nanoparticles using the Dip Coating technique. The Dip Coater parameters were chosen based on the literature. The parameters evaluated were the following: sol-gel solution (based on 1. $Mg(NO_3)_2$ and NaOH; 2. $MgCl_2$ and NaOH; 3. $MgCl_2$ and NH_4OH), "silane / solution containing $Mg(OH)_2$" ratio, residence time of the sample in solution during the dive and, finally, number of dives (1 or 3).
To observe the corrosion rate of the treated samples, an in vitro degradation test was performed in SBF [11]. The end of each sample (0.5 cm) was wrapped with Teflon to preserve the coatings and to prevent the entire sample from degrading if the coating did not work as hoped. The samples were then immersed in falcon containing 50 ml of SBF and evaluated in 3-time intervals: 7, 14 and 21 days. For each of them, three samples treated by type and three untreated samples, as control group, were examined. Every day 50% of the SBF solution contained in each falcon was changed to simulate the exchange of body fluids [14]. For each sample, extracted after a certain time interval from the SBF, a cleaning process was carried out with a solution of 180 g / L of chromium trioxide for 20 minutes at room temperature and under the hood, to remove any residual degradation [13].
To examine the level of degradation of the treated and untreated samples, and therefore to evaluate the effectiveness of the coatings, the mass variation of the samples was measured by weighing.
Optical microscope and SEM analyzes were carried out to study the morphology of the specimens, while XRD and EDS analyzes were carried out to investigate the crystalline phases of the surface coating and to conduct an elementary analysis on the latter.

4. Results and discussion

Choice of sol-gel solution

To obtain sol-gel coatings, three types of solutions were prepared based on:

- Mg $(NO_3)_2$ and NaOH;
- $MgCl_2$ and NaOH;
- $MgCl_2$ and NH_4OH.

and for each of them TEM analyzes were carried out, the results of which showed nanoparticles of magnesium hydroxide in a solution of spherical or oval shape for the first two solutions and "rod" for the third, in accordance with the literature [4].

For the XRD analyzes, the three solutions were placed in an oven at 400 °C and calcined, with the aim of obtaining MgO nanoparticles. Their presence, in fact, would not only have guaranteed the existence of $Mg(OH)_2$ nanoparticles in solution before the heat treatment, but would also have given the certainty of being able to perform a deposition coating with these solutions on a substrate other than magnesium, with a higher melting point, such that it can be subjected to heat treatment with the coating at 400 °C, obtaining a coating of MgO and therefore significantly less soluble in water.

The results confirmed the presence of Periclase (MgO).

Coating on slides

The coatings on slides, obtained by immersing them in the solutions under examination and subsequent heat treatment in an oven at 120 °C for 1.30 h, did not show good adhesion to the substrate, therefore silane was added (GPTMS) to the starting sol-gel solutions with a proportion of 1.5 : 1. It gave the coating an adhesion function.

Oven temperature and residence time

The slides kept in an oven at 120 °C for 1.30 h and 2.30 h did not bring good results: after 24 hours of stability tests in distilled water, the coatings underwent "swelling", remaining adhered to the substrate only in localized points. On the other hand, the coatings kept in the oven at a temperature of 160 °C for 4h, showed better results: only after 3 weeks in distilled water, they begin to show less adhesion to the substrate.

"Silane / Mg $(OH)_2$" quantity ratio

Three different solutions were prepared for each of the three starting sol-gel solutions based on the proportion "Solution with silane: Solution containing $Mg(OH)_2$": 1.5: 1; 1.5: 2; 2: 1.

For each of them XRD analyzes were performed to verify the presence of $Mg(OH)_2$ nanoparticles. The XRD analyzes of the powders of the NI_SI and NI_S solutions (see table 1) did not show the presence of Mg (OH) 2 unlike the other powders in which Brucite was identified in different quantities depending on the solution under examination.

NOME SOLUZIONE FINALE	COMPONENTI SOLUZIONE SOL-GEL	PROPORZIONE SILANO : IDROSSIDO DI MAGNESIO
NI_SI	$Mg(NO_3)_2$, NaOH	1.5 : 1
NI_S	$Mg(NO_3)_2$, NaOH	2 : 1
NI_I	$Mg(NO_3)_2$, NaOH	1.5 : 2
CI_SI	$MgCl_2$, NaOH	1.5 : 1
CI_S	$MgCl_2$, NaOH	2 : 1
CI_I	$MgCl_2$, NaOH	1.5 : 2
CA_SI	$MgCl_2$, NH_3	1.5 : 1
CA_S	$MgCl_2$, NH_3	2 : 1
CA_I	$MgCl_2$, NH_3	1.5 : 2

*Table 1: Summary of the various types of solutions obtained to carry out the coatings.**

Stability of coatings

Each of the prepared solutions was used to perform Dip Coating on slides with 1 and 3 dives. After being kept in the oven for 4 hours at 160 °C, the slides were placed inside falcon containing distilled water at 37 °C inside the oven and subjected to the stability test. The slide dipped once in CA_S solution (see table 1) was the only one to show the first signs of degradation only after 42 days from when it was placed inside the falcon with distilled water, the other coatings began to peel off or melt from the slide much earlier. The XRD analyzes carried out on the slides showed the presence of Brucite on the slides immersed in CA_S, CA_I and CA_SI solutions (see table 1), unlike those performed on all the other slides, which did not show any crystalline phase.

Furthermore, in order to highlight possible differences in wettability between the different

* Legend of the first column. FIRST LETTER: initial of the name of the precursor; SECOND LETTER: initial of the reagent (sodium hydroxide or ammonia); LETTERS AFTER "_": SI = silane/$Mg(OH)_2$ ratio in accordance with the literature; S = greater quantity of silane (compared to literature); I = greater quantity of $Mg(OH)_2$ (compared to the literature).

coatings and underline those between the coated slides and the control slide, "contact angle" measurements were carried out on three slides for each type of coating, depending on the solution. sol-gel used. Through variance graphs (one-way ANOVA test), it was found that regardless of the type of solution used for the coating and the number of immersions, the presence of a coating around the substrate provides the sample with a greater degree of hydrophobicity.

Coating of AZ31 magnesium alloy samples

Observing the results of the XRD analyzes carried out on slides and powders, of the stability tests in water of the slides and taking into account the statistical tests, the CA_S coatings at 1 and 3 dips were found to be the best coatings (table 1). Therefore, it was decided to continue the experiments on samples of magnesium alloy AZ31, choosing as the sol-gel coating the one related to the CA_S solution. The XRD analyzes related to the CA_S samples with 1 and 3 layer coating show not only the presence of Brucite, but also of Periclase (MgO), unlike the untreated sample which has only Mg.

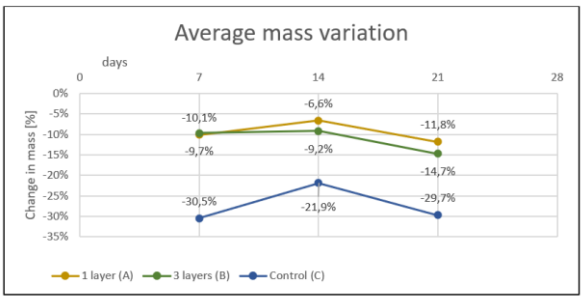

Figure 1: Graph of the mass variation of the three samples during the 21 days of immersion in SBF

Degradation test

The trend of the mass variation measured during the degradation test is shown in a graph that clearly describes the results obtained (Figure 1). It is noted that over 21 days, the untreated sample underwent a strong degradation process, with a total mass loss of almost 28% of the original weight. The curves relating to the treated samples, on the other hand, show how the degradation after 7 and 14 days is only superficial and how it begins to occur more in the bulk only after 21 days of testing in SBF. These results were largely confirmed by SEM-EDS and microscopic analyzes.

5. Conclusions

Overall, the produced samples proved to be a valid solution to the problem of the excessive degradation rate of magnesium, since the results obtained show an increase in the degradation times. The two types of coatings ultimately showed very similar corrosion resistance properties. This circumstance may be due to the high speed of extraction of the sample from the solution, which may have led the coating to thin and drag the excess to the bottom of the sample due to an effect of gravity. Under these conditions the two types of coatings tend to closely resemble each other, and the properties delivered to the sample tend to be similar. Furthermore, it has been possible to verify that this mechanism involves an inhomogeneity in the formation of the coating and an increase in pores and cracks on it [5].

For these reasons, in the future, attention could be paid to the optimization of the immersion parameters of the sample in solution, particularly to the immersion / extraction speed and the viscosity of the solution itself.

Furthermore, we could think of carry out a substrate conversion technique before the Dip Coating technique. An example could be the hydrothermal treatment, which would give the sample an additional protective layer of $Mg(OH)_2$.

Bibliography

[1] Jian S.-Y., Ho M.-L., Shih B.-C., Wang Y.-J., Weng L.-W., Wang M.-W., et al. Evaluation of the Corrosion Resistance and Cytocompatibility of a Bioactive Micro-Arc Oxidation Coating on AZ31 Mg Alloy. *Coatings*. 2019;9:396.

[2] Ratner, B.D.; Hoffman, A.S.; Schoen, F.J.; Lemons, J.E. *Biomaterials Science: An Introduction to Materials in Medicine*, 3rd ed.; Elsevier: Amsterdam, The Netherlands, 2012.

[3] Erne P, Schier M, Resink TJ. The road to bioabsorbable stents: reaching clinical reality? *Cardiovasc Intervent Radiol* 2006; 29:11-6.

[4] Muzi E. Il Processo Sol-Gel per la Sintesi del Vetro: Dalle Nanoparticelle al Bulk, Tesi di Laurea, Politecnico di Torino

[5] Witte F. The history of biodegradable magnesium implants: A review. *Acta Biomaterialia*. 2010;6:1680-92.

[6] Jacobsen, N.; Hensten-Pettersen, A. Occupational health problems and adverse patient reactions in orthodontics. *Eur. J. Orthod*. 1989, 11, 254–264.

[7] Sun Z.L., Wataha J.C., Hanks C.T. Effects of metal ions on osteoblast-like cell metabolism and differentiation. *J. Biomed. Mater. Res*. 1997, 34, 29–37.

[8] Vahey J.W., Simonian P.T. Carcinogenicity and metallic implants. *Am. J.Orthop*. 1995,24,319–324.

[9] Huiskes R, Weinans H., Van Rietbergen B. The relationship between stress shielding and bone resorption around total hip stems and the effects of flexible materials. *Clin. Orthop. Relat. Res*. 1992, 274, 124–134.

[10] Rizzardi F. *Sistema Multitrattamento di Modifica Superficiale della Lega di Magnesio AZ31 per Rallentarne la Corrosione*, Tesi di Laurea, Politecnico di Milano

[11] Fang H.-W., Li K.-Y., Su T.-L., Yang T.C.-K., Chang J.-S., Lin P.-L., et al. Dip coating assisted polylactic acid deposition on steel surface: Film thickness affected by drag force and gravity. *Materials Letters*. 2008;62:3739-41.

[12] Henrist C., Mathieu J.P., Vogels C., Rulmont A., Cloots R. Morphological study of magnesium hydroxide nanoparticles precipitated in dilute aqueous solution. *Journal of Crystal Growth*. 2003;249:321-30.

[13] Setola R., Nacci A., Semeraro G.R., Frallonardo L. Bagnabilità di una Superficie: L'Angolo di Contatto, https://farelaboratorio.accademiadellescienze.it/esperimenti/fisica/52

[14] Kokubo T., Takadama H. How useful is SBF in predicting in vivo bone bioactivity? *Biomaterials*. 2006;27:2907-15.

[15] Krishna L.R., Sundararajan G., Aqueous corrosion behavior of micro arc oxidation (MAO)-Coated magnesium alloys: A critical review, *Jom*, vol. 66, no. 6, pp. 1045–1060, 2014.