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To cite this article: S Dobrița et al 2018 IOP Conf. Ser.: Mater. Sci. Eng. 374 012027

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# **Preliminary Results on the Corrosion Behaviour of a New Biodegradable Metallic Material Based on Zinc**

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Abstract. The class of biomaterials (metallic, polymer or ceramics) has applications as implants with a temporary function. Among magnezium (high corrosion rate) and iron (slow corrosion rate) based biodegradable alloys a new class based on zinc try to fullfill the gap between the first two alloy systems concerning the degradation rate. The role of these alloys is to provide some specific characteristics for a limited period of time. In this article preliminary results based on microstructural and chemical characteristics of a Zn-Mg alloy are presented. The results were obtained using optical and electronic microscopy (MO and SEM) and dispersive energy spectroscpy (EDS) and X-ray diffraction (XRD).

#### 1. Introduction

Ideally, biodegradable coronary stents should provide a compromise between mechanical integrity and degradation [1, 2]. Degradation should begin at a very low speed to maintain the optimal mechanical integrity of the stent until the process of complete remodeling takes place completely, a process lasting from 6 to 12 months, and then with the progression of degradation, the mechanical properties [3, 4]. Once the recovery process has been completed, the degradation rate must be sufficiently high so that no intolerable accumulations or degradation material occur around the deployment area or the main organs. An example for the temporary use of an implant that was introduced to open a narrowed artery. These temporary implants are based on the initial concept of stents, but introduced into different physiological environments to have different specific functions. Temporary cardiovascular implants should open the thickened artery and keep it open until the blood vessel reshapes and then degenerate gradually, being replaced by new blood vessel tissues [5, 6].

In the case of temporary orthopedic implants, such as fixing a bone with bolts or rivets, the material must support the bone fractured sufficiently until it reoccurs and then degrade and be replaced by the new bone tissues. A reasonable degradation period for these stents may be between 12 and 24 months after implantation [2, 7]. These periods are also supported by sufficient data or evidence for all clinical cases and may vary from case to case.

In this sense, the concept of biodegradable material is: "temporarily creating support for the healing process of diseased tissue and progressive degradation after this process." From this definition appear two major directions: 1) temporary support; 2) degradation. Biodegradable metallic materials must also be bioactive, to interact positively during the healing process. Both the metals and the degradation process and their products must not cause adverse effects in the healing process [8].

The mechanical properties of metals include the use of alloying elements, thermomechanical treatments and new processing methods. The use of alloying elements that can form an anticorrosive

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coating on the surface of metals, for example Cr for stainless steels, should be avoided in order to make the alloys degradable or less resistant to corrosion [9].

Biodegradable metals must provide adequate mechanical support to support the healing process during implantation. However, it is difficult to define a support period as close as possible to medical reality depending on the various interventions that take place.

Mechanical integrity of biodegradable metals can theoretically be predicted by performing "in vitro" degradation tests. Kannan et al. performed low-tension tension tests on Mg-Al alloys by correlating mechanical properties and material degradation [3, 10]. The results showed that the elongation at alloy AZ 91% Ca in SBF (simulated human fluid) decreases by approximately 15-20% compared to initial air properties. Biodegradable metals have to decompose into a complex physiological environment that belongs to the human body by combining the kinetics of degradation with the healing period. Degradation products should be transported and removed from the body in order not to cause local or systematic accumulation.

In this paper we analyzed through linear and cyclic potentiometry the corrosion behavior in a SBF solution of two zinc-based alloys with applicative potential in the medical field.

## 2. Materials and methods

An experimental alloy Zn-Mg was obtained through classical melting in induction furnace. The behavior of two experimental samples: zinc and zinc-magnesium at electrocorosion in a simulated body fluid [11-14] with the chemical composition shown in Table 1 was analyzed.

The chemical composition (ions)[mmol/dm <sup>3</sup> ]	Na <sup>+</sup>	$\mathbf{K}^+$	$Mg^{2+}$	Ca <sup>2+</sup>	Cl	HCO <sub>3</sub>	HPO <sub>4</sub> <sup>2</sup>	$SO_4^2$
SBF	142	5	1.5	2.5	147.8	4.2	1	0.5
Human blood plasma	142	5	1.5	2.5	103	27	1	0.5

**Table 1.** The chemical composition of the electrolyte solution.

The samples were analyzed for electro-corrosion resistance using a potentiostat with a threeelectrode cell. Teflon embedded samples were investigated at linear and cyclic potentiometry. After potentiometry sample surfaces were analyzed by electronic microscopy and EDS chemical analysis.

### 3. Results and discussions

For the experiments, a laboratory potentiostat with a 3-cell electrode was used: calomel, platinum and the third electrod was the experimental alloy mounted in a teflon support. The results of linear (Tafel) and cyclic potentiometry are shown in Figure 1 (a) and (b) respectively.



Figure 1. Electro-chemical resistance analysis (a) Tafel diagram; (b) cyclic diagram.

The behavior at electro-corrosion in SBF of the two metallic materials is similar to the generalized corrosion type, resulting from the form of cyclic potentiometry curves. Both alloys fall within a corrosion potential range of 1.425 to 1.475 V with an increased corrosion (the potential is of the order of volts).

From the characteristic Tafel diagrams of the two alloys, a higher corrosion rate of the Zn element and a decrease (as a conclusion of the degradation rate) with the addition of Mg element is observed. Although magnesium has a higher corrosion rate than pure zinc, the alloy exhibits a moderate decrease in corrosion rate over the pure zinc element. Parameters obtained from the electrocorosion resistance tests of the experimental samples are shown in Table 2.

Sample/	E(i=0)	Current	Polarization	Beta a	Beta c	Corrosion rate
Parameters		intensity	resistance			
	[mV]	[µA/cm <sup>2</sup> ]	[ohm*cm <sup>2</sup> ]	[mV]	[mV]	[cm/Y]
Zn	1469	107.6	377.98	25.4	160.1	1.352
ZnMg	1450	98.8038	394.34	41.7	159.7	1.241

Parameters obtained from the corrosion resistance test are close to the two SBF samples with corrosion rates ranging from 1.352 cm/year for Zn and 1.241 cm/year for ZnMg respectively. These speeds are actually a corrosion of 1.12 to 0.75 mm per month, parameters that cover many metallic requirements for medical applications.



**Figure 2**. State of the surface of the experimental alloys after the electro-corrosion resistance tests (a) Zn 100x; (b) Zn 500x; (c) Zn 2000x; (d) ZnMg 100x; (e) ZnMg 500x; (f) ZnMg 2000x.

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The values of the parameters obtained for the two materials are very close and the order of the corrosion rates can be easily influenced by the experimental conditions such as the surface condition of the 2 materials, favoring the formation of gas bubbles during the experiment, etc. For these reasons, the experiments on the two alloys must be repeated and at this time the corrosion rates obtained or their order can not be confirmed using a magnetic stirrer to eliminate gas during the experiment.

After the corrosion resistance tests, the surface state of the three experimental materials by SEM (VegaTescan LMH II) electron microscopy was analyzed at different amplification powers (100x, 500x, and 2000x).

Figure 2 shows the state of the surface of the experimental alloys after electro-corrosion resistance tests a) Zn 100x, b) Zn 500x, c) Zn 2000x, d) ZnMg 100x, e) ZnMg 500x, f) ZnMg 2000x.

Both samples corroded all over the surface confirming the generalized corrosion character of the corrosion cyclic curves. The electro-corrosion test carried out in the case of pure zinc underlines its multigranular structure, Figure 2 (a) and (b). At the micrometric level it is observed the formation of some compounds on the surface of the material above the zinc sheets, Figure 2 (c). The compounds resulted from the interaction of the material with the electrolyte solution and showed no mechanical stability on the surface in appearance. Also, both samples also show stronger pitting areas, areas that have favored the corrosion process and where impurities, diffused material phases or microstructural defects have been found.

The surfaces of the metallic samples were investigated by X-ray energy spectroscopy using a Bruker EDS detector (EDAX). The analyzes were performed on a surface area of  $4 \text{ mm}^2$  per sample. Qualitatively identified elements are passed, depending on the energies they participate in the compounds on the surface, in the spectra of Figure 3 for (a) Zn and (b) ZnMg.



Figure 3. X-ray energy specter (a) Zn; (b) ZnMg.

Table 3 shows the chemical composition of the experimental alloys after electrocorosion tests in mass and atomic percentages. The error of EDAX equipment for each element is also given. The presence of oxygen and carbon on the surface is due to the passage of these elements from the electrolyte solution to the surface of the metallic material.

Alloy/element	Zn		0		Mg		С	
	wt%	at%	wt%	at%	wt%	at%	wt%	at%
Zn	74.77	40.19	19.21	42.22	-	-	6.01	17.59
ZnMg	68.12	34.55	19.04	39.46	6.78	9.24	6.06	16.74
Error EDAX %	2		1.26		0.56		1.39	

**Table 3.** Chemical composition of experimental alloys after electro-corrosion tests.

All the samples show the oxidation of the surface of the alloys and formation of oxides on the surface of the metallic material to be passed into the electrolyte solution. It is noted that chemical analyzes will be resumed after cleaning the samples with technical alcohol and ultrasonography. At this time, it was desired to capture the surface of the experimental materials immediately after the electrocorosion tests to analyze the behavior of the materials during the corrosion process.

## 4. Conclusions

Zinc alloys can be a suitable solution for medical or industrial applications of degradable materials that provide degradation periods ranging from those given by magnesium alloys and those derived from iron-based alloys.

Zinc alloying with different chemical elements, also degradable and in various mass or atomic percentages, leads to the modification of its behavior in electrolyte solutions.

According to the experimental results obtained from the electrocorosity tests, zinc alloying with Mg leads to a decrease of the corrosion rate of pure zinc in SBF solution (human fluid similar to that of human). Aligning with various degradable chemical elements can be considered a method of controlling the rate of degradation of these alloys in various biological or electrolyte media.

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