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CORROSION PROPERTIES OF Mg-Ca-Gd ALLOY APPLIED TO BIODEGRADABLE IMPLANTS

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Abstract. *Magnesium (Mg) alloys have the characteristic of bioabsorption, non-toxicity, physical and mechanical properties similar to bone. The purpose of this work is to investigate the corrosion properties of magnesium-calcium-gadolinium (Mg-Ca-Gd) alloy with a new composition. Samples from the Mg-Ca-Gd and Mg-Ca alloys were underwent potentiodynamic polarization tests and were analyzed by optical microscopy and surface roughness measurements. The results of the both alloys were compared in order to evaluate the effect of addition of Gadolinium. Comparing the results of both alloys, at all rates the Mg-Ca-Gd alloy had a more positive corrosion potential and a drop in the corrosion rate. The Magnesium-calcium-gadolinium alloy presented best corrosion resistance with corrosion rate until 1/10 smaller than Magnesium-calcium alloy, depending on the tests conditions.*

Keywords: *Biocorrosion, Magnesium-rare earth alloys, biodegradable implants, Tafel extrapolation.*

1. INTRODUCTION

One of the main advantages of biodegradable implants is that the second surgery is unnecessary, reducing or excluding long-term problems caused by permanent implants. Within this context, studies of magnesium (Mg) alloys have been done, due to the characteristic of bioabsorption, non-toxicity and excellent physical and mechanical properties similar to bone. (Staiger, *et al.,* 2006) However, the applications of these alloys are still very modest due to the high rates of degradation and consequent loss of mechanical properties in environments with pH levels between 7.4 and 7.6, which corresponds to the pH of physiological environment. (Kannan and Raman, 2008) Another disadvantage of the Mg alloys is that when reacting with aqueous solutions hydrogen gas is produced and can result in the formation of gas pockets in the implanted area. (Persaud-Sharma and McGoron, 2012) The selection of the elements that will make up the alloy is the most important method of modifying the corrosion resistance of the material and controlling the reactions involved in the process. Magnesium-rare earth (Mg-TR) biodegradable alloys exhibit precipitation hardening due to high solubility of the secondary elements in the solvent matrix. (Chen, *et al.*, 2014) It is known that this characteristic improves creep properties, corrosion and increases mechanical strength. (He, *et al.,* 2013) The purpose of this work is to compare the corrosion properties of magnesium-calcium-gadolinium (Mg-Ca-Gd) alloy with Mg-Ca alloys.

2. EXPERIMENTAL

Samples from the Mg-Ca-Gd and Mg-Ca alloys were cutted and polished with SiC abrasive papers of #320, #600, #800 and #1200. Then, they were cleaned ultrasonically in acetone, alcohol and rinsed in deionized water. The potentiodynamic polarisation (PDP) was performed in a three-electrode configuration with Mg alloy as working electrode, platinum foil as the counter electrode and calomel electrode as reference. The corrosion test was conducted using 0.9% NaCl solution as the electrolyte at 37°C and controlled rates of 0.1 and 1 V/s. The surfaces of the samples were analyzed by optical microscopy and the surface roughness measurements were did using a profilometer. All the analysis were done before and after corrosion tests.

3. RESULTS AND DISCUSSION

The curves raised during the PDP test are shown in Fig. 1, for each alloy and each sweep rate. For the case of the Mg-Ca alloy, the higher the sweep rate used more negative was the corrosion potential (Ecorr). It was verified that for the two alloys, the behavior of the cathodic and anodic curves were very similar in all test. The corrosion rate (i_{corr}) varied inversely with the corrosion potential. The more negative the potential, the higher the rate. For the case of the Mg-Ca-Gd alloy, it was found that the cathodic curves had similar behavior at all rates. However the addition of the rare earth element is evidenced in the anodic region of polarization.

Comparing the results of both alloys, at all rates the Mg-Ca-Gd alloy had a more positive corrosion potential and a drop in the corrosion rate. This indicates greater resistance to corrosion of this alloy. It is noteworthy that in both tests, the curve of the Mg-Ca-Gd alloy polarized near the same region, apparently having no influence by the sweep rate.

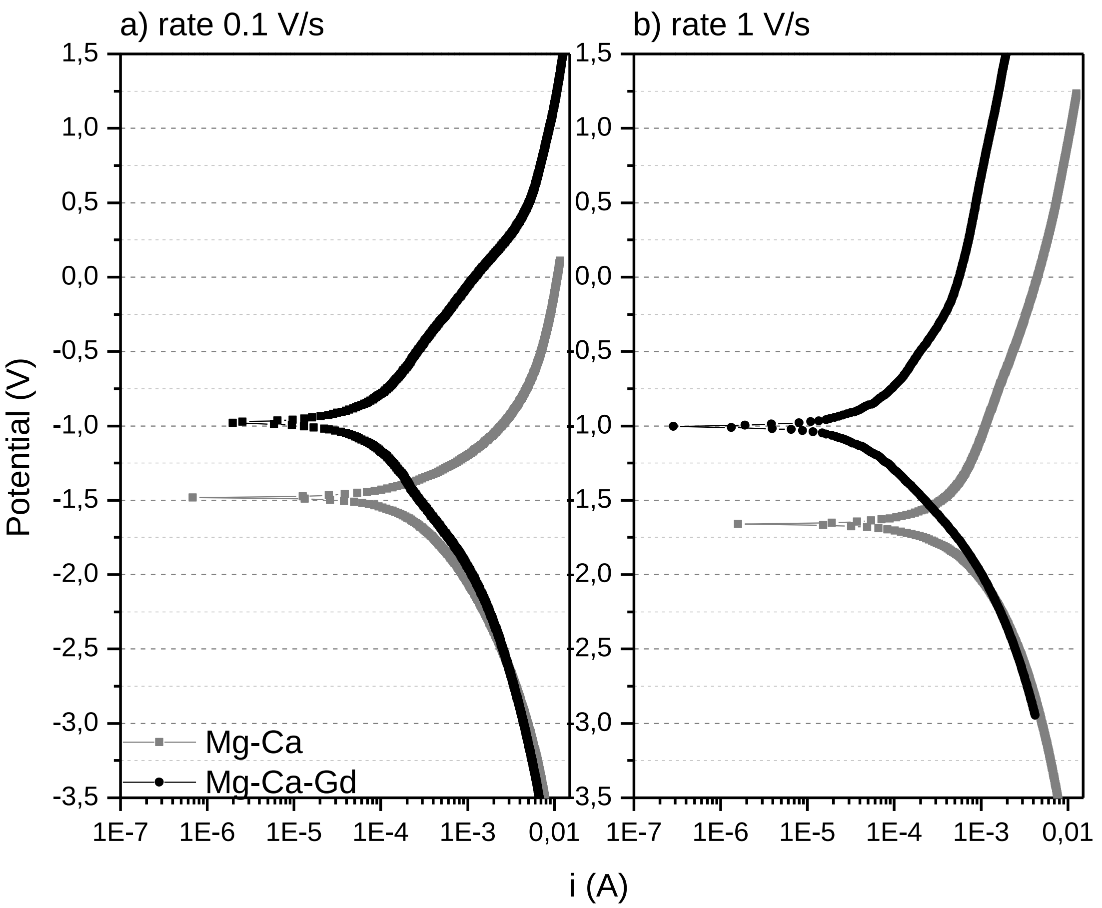

Figure 1. Polarization curves of Mg-Ca alloy and Mg-Ca-Gd applying differents rates of 0.1 V/s (a) and 1 V/s (b) using 0.9% NaCl at 37°C.

The open circuit potential (OCP) were collected directly from the potentiostat, during the stabilization of the samples. With the curves of Fig. 1, corrosion potentials (E_{corr}) and corrosion currents (i_{corr}) were found and thus calculated the corrosion rates in mm/year. These data are shown in Table 1.

Table 1. The OCP values were obtained after 15 minutes of stabilization. Corrosion potentials (E_{corr}) were found directly by curves and corrosion currents (i_{corr}) via Tafel extrapolation. The column CR is relative to the calculated values for corrosion rates in mm/year.

		Rate: 0.1 V/s			Rate: 1 V/s		
Alloy	**OCP (V)**	**E_{corr} (V)**	**i_{corr} (A/cm²)**	**CR (mm/year)**	**E_{corr} (V)**	**i_{corr} (A/cm²)**	**CR (mm/year)**
Mg-Ca	-1.791	-1.485	2.679E-3	61.175	-1.677	5.363E-3	122.46
Mg-Ca-Gd	-1.569	-0.983	6.782E-4	15.487	-1.011	5.023E-4	11.470

Observing the samples on the optical microscope, the initial surface finish was found to be similar for the two compositions (Fig. 2a and b). This fact can be verified with the profile data found in Tab. 2. Images were taken of the border region between the exposed area during the test and the isolated area (Fig. 2c and d). You can clearly see the circular mark that the O-ring left on the surface. Fig. 2e and f were made from the centers of the corroded areas and it is noticed that in the Mg-Ca alloy there are more particles on the surface. In this case the Mg underwent corrosion and the regions with Ca are degraded more slowly. The Mg-Ca-Gd sample, although severely corrosive, also coarsen more evenly. The fact that this alloy has a higher content of magnesium and its compositions of calcium and gadolinium are almost balanced, contributed to this fact.

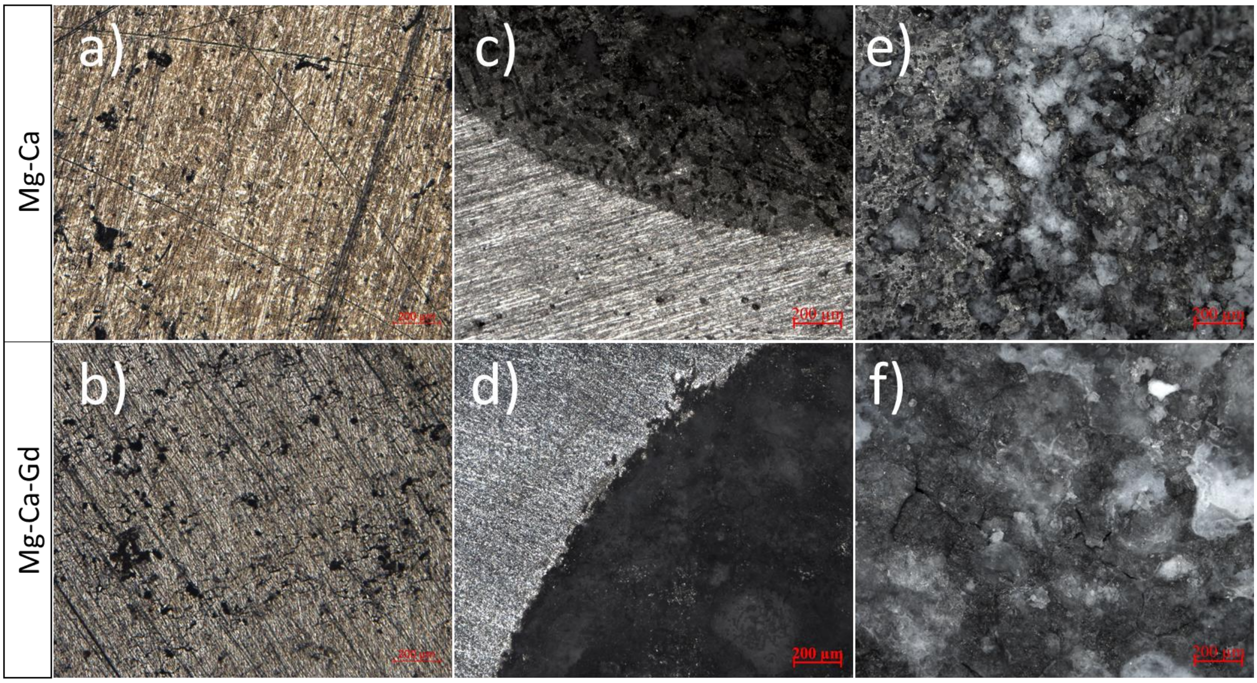

Figure 2. Images of optical microscopy, all with 50x magnification. Surface of the Mg-Ca (a) and Mg-Ca-Gd (b) alloys before the potentiodynamic polarization tests. Limit regions between the areas exposed to the tests and the sealed areas, for the sample Mg-Ca (c) and Mg-Ca-Gd (d). Center of samples after corrosion test, Mg-Ca (e) and Mg-Ca-Gd (f).

After the PDP test, the samples again had the Ra values of their measured surfaces. It was found that the mean values were close, for the two alloys. However, the standard deviation of the Mg-Ca alloy was higher indicating that there was considerable variation in the measured points.

Table 2. Values obtained from Ra before and after the potentiodynamic polarization (PDP) tests, with their respective averages and standard deviations (SD). The measurements were made in triplicate for each case.

	Ra (µm) before PDP		**Ra (µm) after PDP**	
Alloy	**Mean**	**SD**	**Mean**	**SD**
Mg-Ca	0.275	0.008	2.740	2.618
Mg-Ca-Gd	0.236	0.008	2.550	0.207

4. CONCLUSIONS

The Magnesium-calcium-gadolinium alloy presented best corrosion resistance with corrosion rate until 1/10 smaller than magnesium-calcium alloy, depending on the test conditions.

5. ACKNOWLEDGEMENTS

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