Tribological aspects of some biodegradable magnesium alloys

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Abstract: *In recent years, biodegradable alloys have made their presence felt in a wide variety of fields, such as aeronautics, automotive and medical fields. Biodegradable alloys are considered to be the 3rd generation of biocompatible alloys, replacing classic alloys such as stainless steels and Co-Cr alloys. The paper aims to study the structural aspect and identify some mechanical characteristics of magnesium-calcium alloys used as biodegradable materials in the medical field. It has been observed the formation of a eutectic compound at the limit of magnesium grains and the relative constant value of the apparent coefficient of friction with increasing Ca concentration.*

Key Words: *magnesium alloys, tribological analysis, microstructure*

1. INTRODUCTION

Pure magnesium is considered relatively safe and is attractive for medical use. However, the presence of impurities in magnesium alloys such as iron, nickel and copper accelerates corrosion dramatically. The characteristic microstructure of pure magnesium consists of α-type grains having a hexagonal crystalline structure. The tolerance limit for these elements should be 0.005% for Fe and Ni and 0.05% for Cu. Unfortunately, Mg element has low mechanical strength, the cast magnesium having a yield strength of 21 MPa, the extruded alloy has 90-105 MPa and the laminated one has 115-140 MPa, [1].

Calcium is the most abundant mineral in the human body, representing about 2% of body weight. Most of it, 99%, is found in bones and teeth, where it has a structural role, while magnesium element is the fourth mineral in the human body, participating in more than 300 metabolic processes in the human body. Calcium as well as strontium belongs to group II of the periodic table, showing a relative solubility in Mg (1.34%) under equilibrium conditions, [2].

Wan et al. identified that magnesium alloying with 0.6% Ca improves bending and corrosion resistance, [3] and for low degradation, the calcium content must be between 0.6% and 1%, [4]. An alloy with a percentage between 1% and 3% Ca, leads to the decrease of the mechanical strength and elongation, [5,6], due to the consolidation of the fragile compound Mg_2Ca. The elastic modulus is a mechanical property, essential for orthopedic implants. The phenomenon of "stress-shielding", caused by the large gap between implant and bone stiffness, can lead to bone loss and eventually to failure of implantation, [7].

Hassel et al. and Drynda et al. studied the influence of calcium on the mechanical properties of Mg-Ca binary alloys. Magnesium alloying up to 4% Ca leads to increased tensile strength from approx. 200 MPa to 240 MPa. The fracture elongation decreases dramatically with the increase of the percentage of calcium, from values of about 14%, to about 5%,[6, 8].

2. MATERIALS AND METHODS

The present work contains data and results that are part of the PhD thesis "Research concerning the influence of some surface coatings on biodegradable metallic alloys used in the medical field".

Within the present scientific work, two chemical compositions of alloys from the Mg-Ca system were approached: Mg-0.7Ca, respectively Mg-1Ca. In order to develop these alloys, the Mg-Ca equilibrium diagram was taken into account and the knowledge of all the transformations that occur at different concentrations (figure 1), [9].

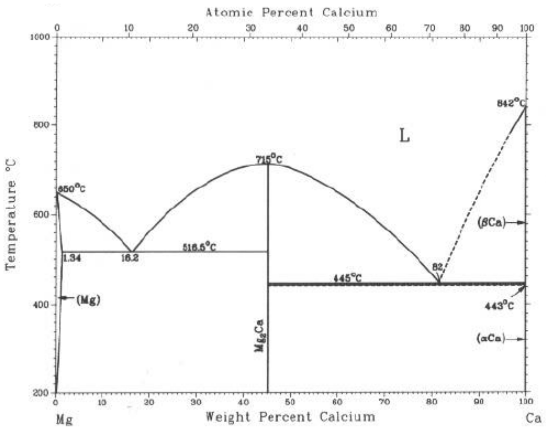


Figure 1. Binary diagram of the Mg-Ca alloy; [9]

The alloys from the Mg-Ca system was made from high purity components, Mg-98.5% and metallic Ca -99.9%. The manufacture of these alloys was carried out in a processing furnace with induction currents, a facility with compact converter and controlled atmosphere, type CTC50K15 [10] in zirconia crucibles. The control of the temperature of the metallic melt during the elaboration process was performed with an instant thermocouple.

The amount of magnesium alloy and calcium particles was simultaneously introduced into the crucible under argon protection. Preheating of the crucibles was performed at 450° C and then the actual melting was performed at a temperature of 650 - 680° C, also in an argon controlled atmosphere.

The molding was done in a zirconia crucible, the mini-ingots taking the conical shape of the crucible. Microscopy samples were cut from ingots, mechanically grinding using abrasive papers and polished with 0.3 alumina solution, cleaned with distilled water, exposed in the open air and chemically attacked in order to highlight the microstructure.

The microstructures were obtained using a Leica 5000DMI optical microscope, and for performing higher magnification images a Quanta 3D scanning microscope (FEI, Hillsboro, OR, USA) - SEM equipped with a detector EDX was used for chemical composition analysis. The microhardness was done using a tribometer with indentation and scratch tests. The microscratch test was carried out, thus a constant load of 5N was applied at a distance of 4 mm with a speed movement of 3mm/s.

3. RESULTS AND DISSCUSIONS

Figure 2 (a-d) shows some optical microstructures of the Mg-0.7Ca (a, b) experimental alloys, respectively Mg-1Ca (c, d) at different magnification powers. Magnesium grains of polyhedral form and also the separation of the eutectic compound - Mg_2Ca with lamellar form, at the boundary of magnesium grains can be observed in the structure of the cast magnesium alloys.

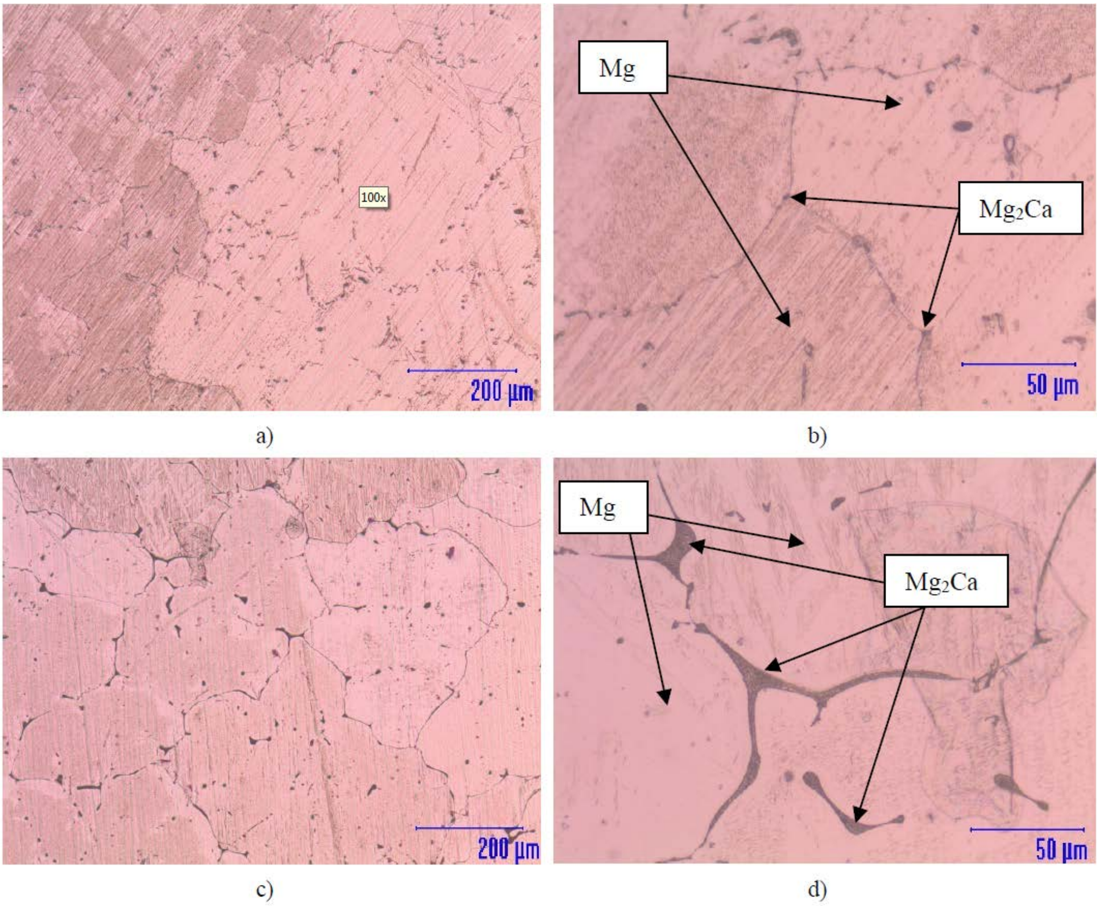


Figure 2. Optical microscopes for magnesium alloys: a), b) Mg-0.7Ca; c), d) Mg-1Ca

The values of chemical composition of the cast magnesium alloys are presented in Table 1.

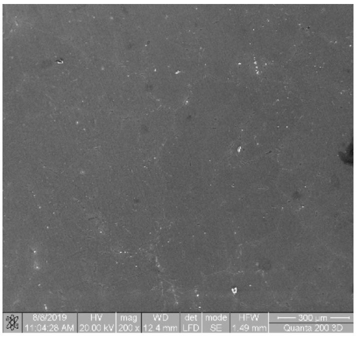
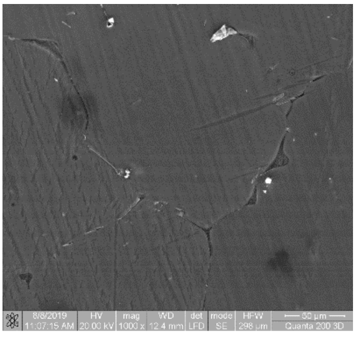
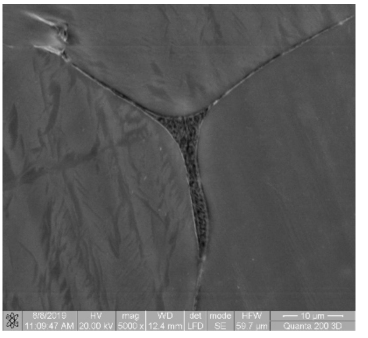
Table 1. Chemical composition of the experimental alloys

Chemical composition	%Mg (wt.)	%Ca (wt.)
Mg-0.7Ca	99.38	00.62
Mg-1Ca	99.06	00.94

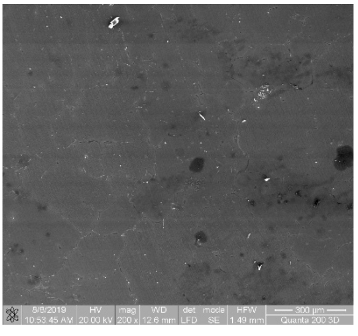
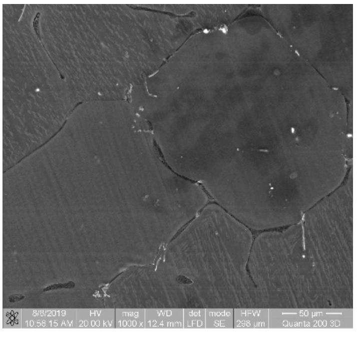
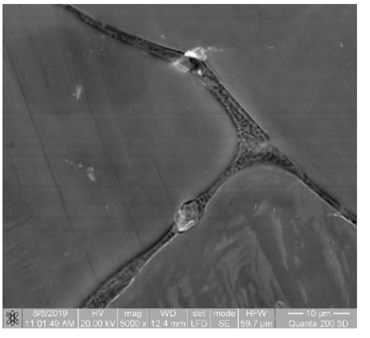
Figure 3 shows images by scanning electron microscopy, using the LFD (large field detector) detector on Mg-0.7Ca (a, b, c) alloys and Mg-1Ca (d, e, f), respectively.

The results are in agreement with the optical microscopes, showing the α-Mg grains and the eutectic compound Mg_2Ca. These results are consistent with the structures shown by [11],

[12] and [13], certified as biodegradable materials.

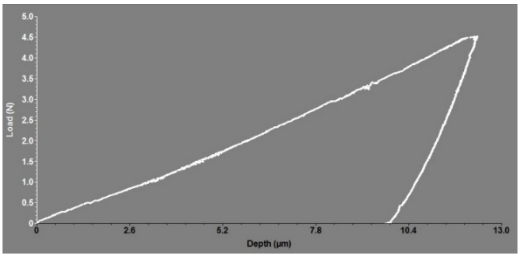
a) b) c)

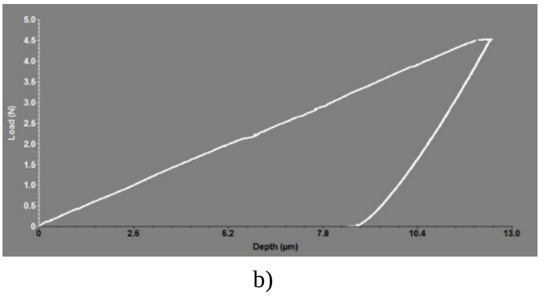




d) e) f)

Figure 3. SEM images of the magnesium alloys microstructure:
a), b), c) Mg-0.7Ca; d), e), f) Mg-1Ca

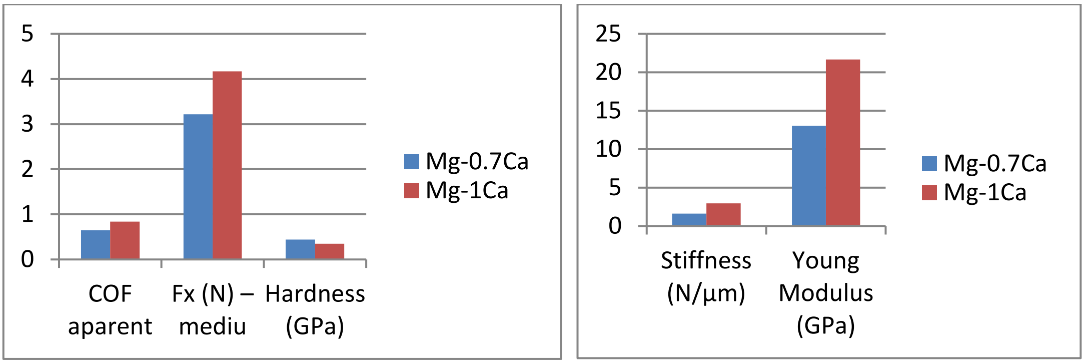
Figure 4 shows the force-depth curves after the micro-indentation test. For better accuracy of the measurements, three determinations were made in different areas. Thus, an average of the values was obtained indicating the Young modulus, stiffness and hardness of the two experimental alloys. By alloying magnesium with calcium, it was desired to obtain some metallic materials with the Young modulus and hardness values similar to the biological bone. Figure 5 shows the graphs with values for these parameters, observing similar values for hardness around 360 MPa for Mg-1Ca and 430 MPa for Mg-0.7Ca, respectively (Figure 5a).In contrast to Young's modulus and stiffness, an increase of 1% Ca concentration is observed. The elasticity modulus values are similar to Mg-Ca alloys, tests carried out by [14].





a) b)

Figure 4. Force-depth curves for the micro-indentation test



a) b)

Figure 5. Comparative graphs of micro-indentation and micro-scratch tests

The micro-scratch tests revealed the depth scratches in correlation with the surface and have the following values: 19 µm for the Mg-0.7Ca alloy and 40 µm for the Mg-1Ca alloy, respectively. Figures 6 and 7 show the aspects of the scratch produced by indenter using scanning electron microscopy and the 3D profile of the surfaces. The plastic deformation at the surface of the test result is 1 µm (Mg-0.7Ca) and 3 µm (Mg-1Ca), respectively.

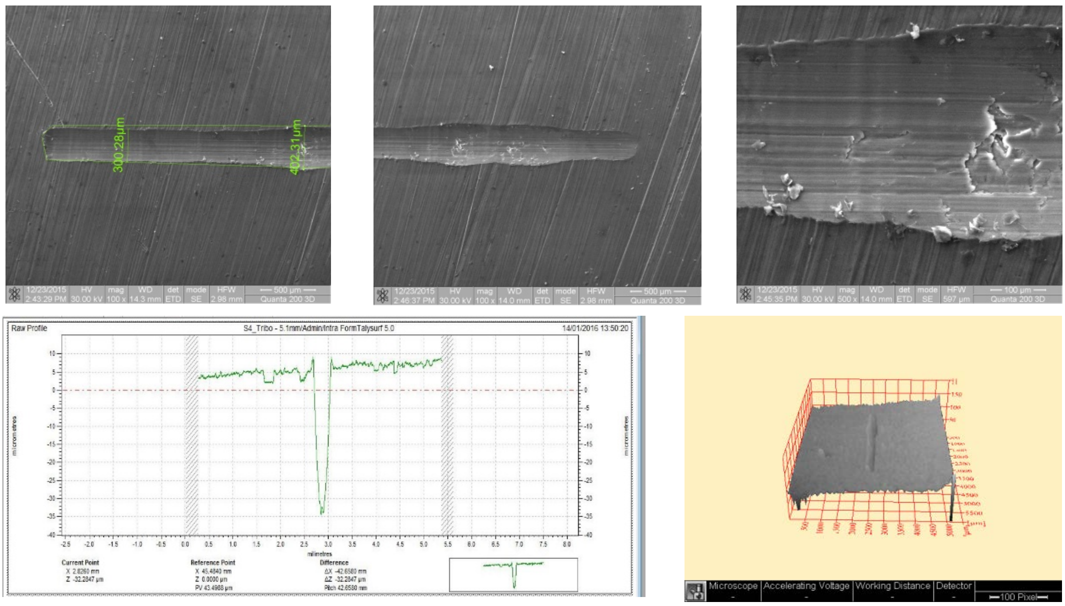
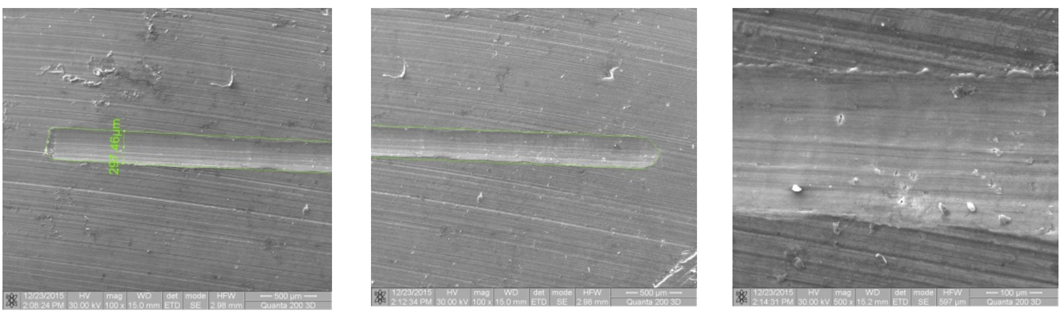


Figure 6. SEM images and 3D profile of the scratch test - Mg-0.7Ca



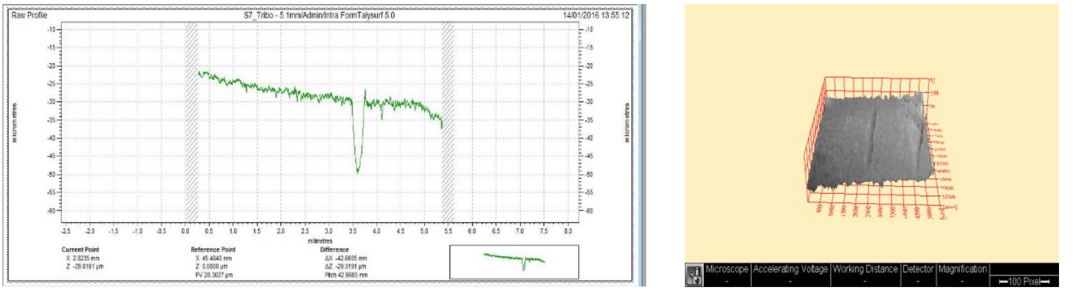


Figure 7. SEM images and 3D profile of the scratch test - Mg-1Ca

The apparent friction coefficient and the modulus of elasticity undergoes an increase of the values at the concentration of 1% Ca. The Young modulus for the Mg-0.7Ca alloy is 13.02 GPa and 21.66 GPa for Mg-1Ca, respectively (Figure 5).

4. CONCLUSIONS

The purpose of this work is to highlight the morphological, microstructural and tribological aspects of biodegradable alloys in the Mg-Ca system: Mg-0.7Ca and Mg-1Ca, respectively. The Mg-Ca alloys that have been studied have a polyhedral magnesium grain structure, and the presence of calcium leads to the formation of a eutectic lamellar structure at the grain boundary. From a tribological point of view, the micro-indentation and micro-scratch tests have shown a similar character of the hardness of the two alloys, but for the rest of the characteristics, an increase of the values for the Mg-1Ca alloy (apparent friction coefficient, Young modulus, stiffness) has been observed.

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