MICROSTRUCTURAL ANALYSIS OF Mg-Ca AND Mg-Si-Ca BIODEGRADABLE ALLOYS

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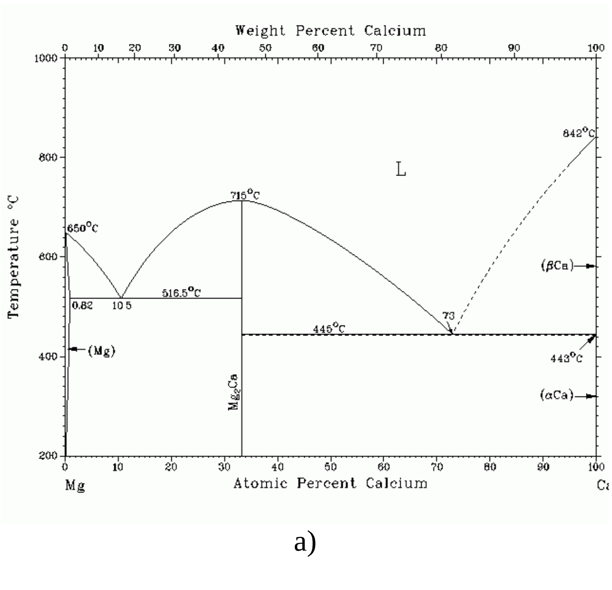
Abstract: Biodegradable materials begin to know ascension in the medical field as an alternative to biocompatible materials. Magnesium alloys show large attention as being a type of degradable biomaterials. Mg developed great interest as a potential biodegradable material in biomedical application, like orthopedic implants, with a large impact for medical field. Mg-Ca system known as biodegradable materials have established new research directions for orthopedic implants. Hydrogen release and low corrosion resistance are the main disadvantages of Mg alloys. Alloying with biocompatible elements is a solution to increase the corrosion resistance and microstructure refinement. In the past years many researchers used calcium as alloying element due its strong characteristics and its importance for the human bones and cells. The aim of this paper is to study two types of Mg-Ca alloys and a Mg-Si-Ca alloy, from SEM analyses point of view, X-Ray diffraction, and EDAX analysis.
Key words: Mg-Ca alloys, biodegradabile, SEM, XRD.

1. INTRODUCTION

Magnesium (Mg) alloys have been widely studied as biodegradable metallic material in recent years due to the relatively good biocompatibility and osteoconductivity [1–4]. Important aspects of magnesium alloys are low Young Modulus and similar values for yield and ultimate tensile strength, almost the same with the human body [5, 6]. Calcium fits best as alloying element in Mg-Ca and Mg-Ca-Si systems for orthopaedic applications [7]. Bones regeneration process can be significantly increased due the large spread of Calcium in the human body, respectively bone and the release ions of calcium and magnesium [7]. Similar densities of Ca (1.55 g/cm^3) and Mg (1.74 g/cm^3) will keep mechanical properties comparable with bones mechanical properties. The acceptable cost of calcium should also attract the use of Mg–Ca alloys in medical applications [5, 6]. Figure 1 presents Mg-Ca phase diagram and its specific transformation points[8]. The use of magnesium as a biodegradable metal has been considered as a promising biomedical material because of its unique propertie like: a larger fracture toughness than that of ceramics [9]. Therefore, Mg alloys can minimize or bypass the ''stress-shield'' phenomenon which exists in the current metallic implants made of stainless steel or titanium alloys [9]. Also, as the fourth most spread element, magnesium is essential to human metabolism, and is an essential nutrient in the human body. In particular, it has important influences on all vital functions like muscle, bone and heart function [3]. Like other metallic materials, magnesium is a degradable metal in the environment of the human body because its highly negative standard electrode potential induces much faster corrosion. It is not necessary an additional surgical operations for removal the implant. Li et al. [3] examined Mg–Ca alloys and showed that alloys with less than 1%Ca had good corrosion and mechanical properties with acceptable biocompatibility and highlighted according figure 2 (X-ray diffraction of Mg-Ca alloy) the hexagonal structure of α-Mg ang Mg_2Ca grains. XRD patterns [10, 11, 3] reveals two main phases: α-Mg and Mg_2Ca for these biodegradable alloys. α-Mg has a hexagonal crystallographic form and Mg_2Ca have also hexagonal crystallographic form In this paper, we study microstructure of three Mg-Ca and Mg-Si-Ca alloys with 0.63% Ca, 0.81% Ca respectively 0.29%Si and 0.33%Ca in order to see if there are any differences in the structure.



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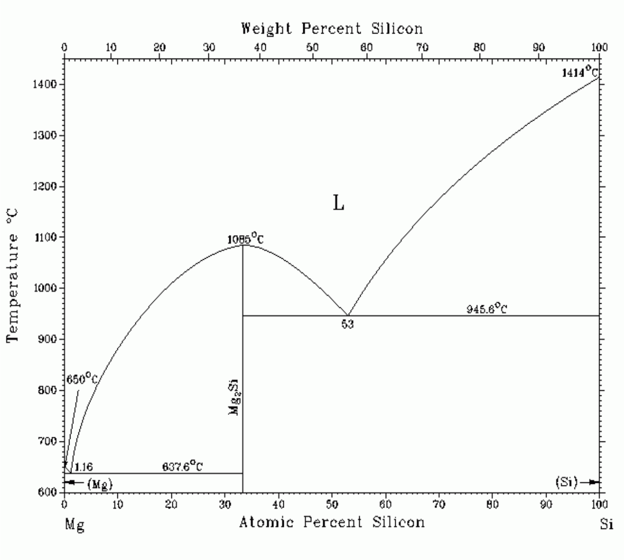


Fig. 1. a) Mg-Ca phase diagram [8]; b) Mg-Si phase diagram, [14]

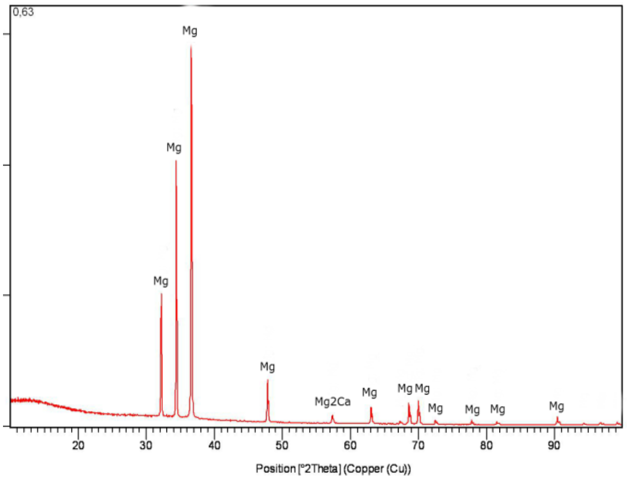


Fig.2. X-ray diffraction of 0.63%Ca sample, [10,11,3]

Table 1. Element influence for biomedical magnesium alloy [12, 13]

Element	Technological aspect(s)	Biological aspect(s)
Aluminium	Improves strength and ductility(solid-solution hardening, precipitation, grain refinement), corrosion resistance and castability	Risk factor in generation of Alzheimer's disease; can cause muscle fi bre damage; decreases osteoclast activity
Calcium	Improves strength (solidsolution hardening, precipitation, grain refinement) and creep resistance; reduces castability	Most abundant mineral in human body; tightly regulated by homeostasis
Lithium	Reduces strength yet improves ductility/formability (change to bcc lattice structure); reduces corrosion resistance and density	Possible teratogenic effects
Manganese	Improves strength and ductility (grain refinement); improves creep resistance; improves corrosion resistance in combination with aluminium (precipitation that picks up iron)	Essential trace element; important role in metabolic cycle and for the immune system; neurotoxic in higher concentrations
Silicon	Reduces ductility; improves creep resistance and high-temperature strength (precipitation); reduces corrosion resistance and castability	
Strontium	Improves strength and ductility (grain refi nement); improves creep resistance and high-temperature strength	
Zinc	Improves strength, yet reduces ductility in high concentrations (solid-solution hardening, precipitation); improves castability	Essential trace element (immune system, co-factor); neurotoxic at higher concentrations
Zirconium	Improves strength, ductility and high-temperature strength (strong grain refinement) in absence of aluminium	

In order to establish the effect of Ca and Si and other elements, Witte et.al and Sillekens et al. mentioned that calcium helps to solid solution formation and strengthening.It also acts as a grain refining agent and additionally contributes to grain boundary strengthening.In binary Mg-Ca alloys phase Mg2Ca is formed. Silicon reduces ductility, improves the corrosion resistance and castability.

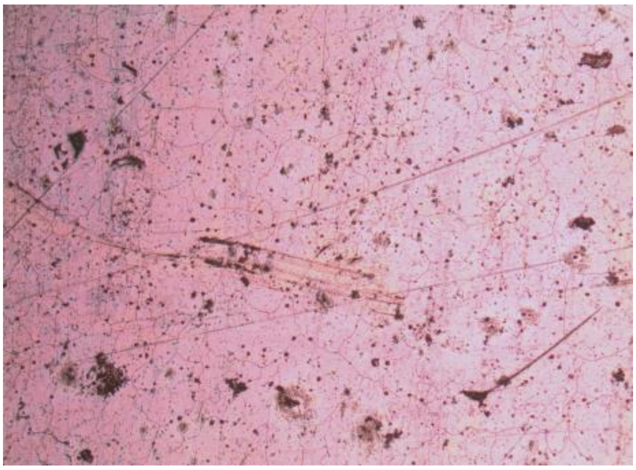
2. EXPERIMENTAL PROCEDURE

Samples of Mg-0.63%Ca and Mg-0.81%Ca and Mg-Ca-Si were obtained in a high frequency induction oven with 20KHz with an inert atmosphere, equipped with vacuum under pressure evacuation system. As cast specimens were homogenized (573K/24h/water) and hot laminated (60% thickness reduction at 673-723K) [10]. The final chemical composition and SEM images were made by EDAX – Fei Quanta 200 3D dual beam. The specimens were investigated with electronic microscopy (SEM), optical microscopy using a Leica DMI 5000 ,X-ray diffraction (XRD) with an E'Xpert PRO MPD diffractometer from Panalytycal. Samples were grinded with SiC paper up to 2000 grit and polished with an alumina suspension of 3µm. Etching was performed using a solution of 0.6 ml H_2SO_4 and 100ml alcohol.

3. RESULTS AND DISCUSIONS

3.1. Evolution of microstructure

Figure 3 presents the optical metallographic structures for the samples with 0.63%Ca at 100X and 500X. These microstructures show solid solution of polyhedral shape grains with uniform granulation in whole metallic base.



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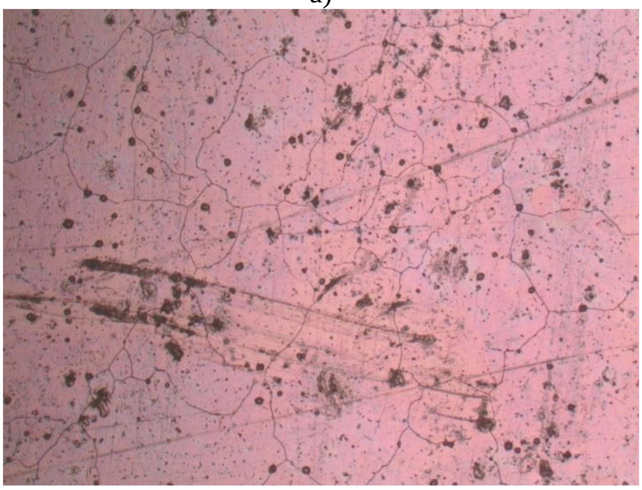

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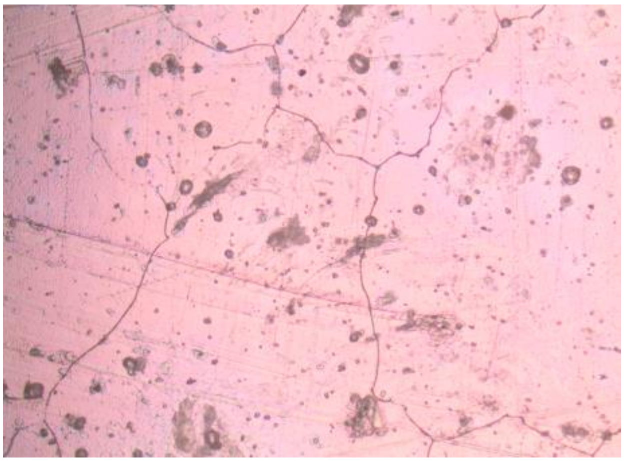

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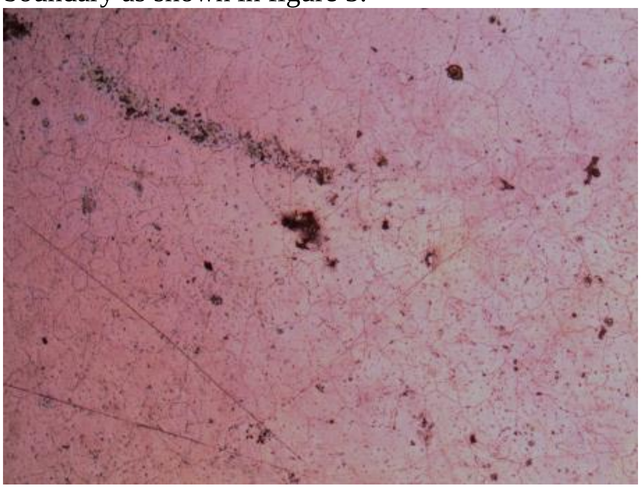
Fig.3. Optical images of 0.63%Ca sample:
a) 100x; b)200x; c) 500X

Figure 4 expose optical metallographic microstructures for the sample with 0.81%Ca at 100X and 500X. Figure 4b presents the structure of the solid solution grains with a dimensional variety of form.

With the addition of Si in alloy's chemical composition, Mg_2Si phase is formed beside the typically α-Mg form. Needle-like Mg2Si phases formed and tended to distribute along the grain boundary as shown in figure 5.



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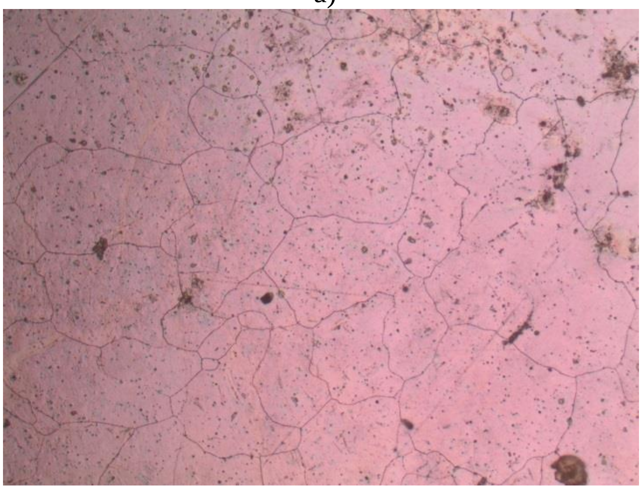

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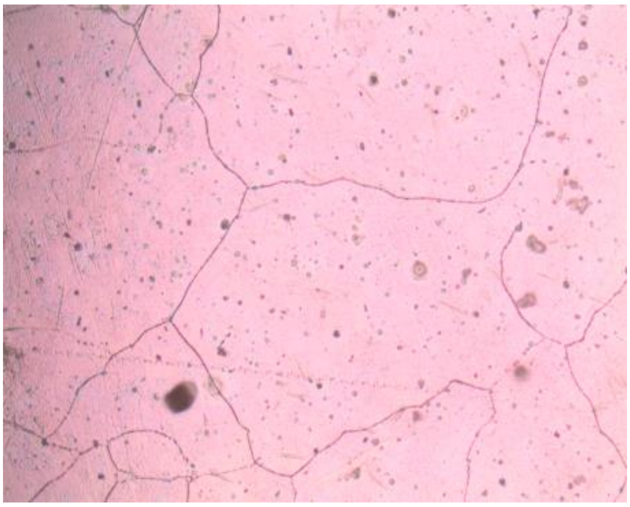

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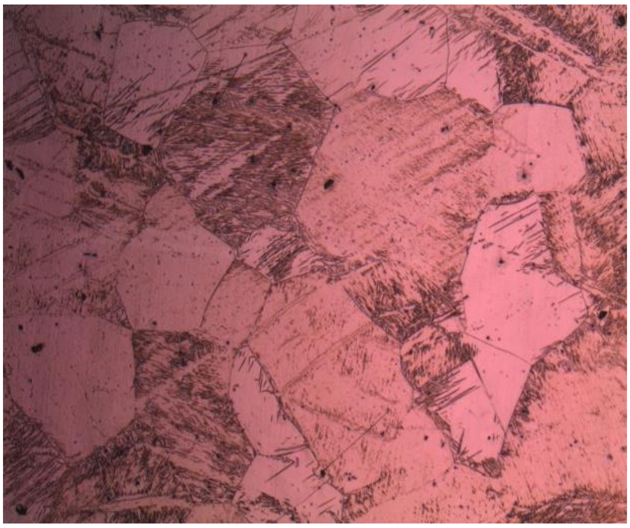
Fig.4. Optical images of 0.81%Ca sample:
a) 100x; b) 200x; c) 500x



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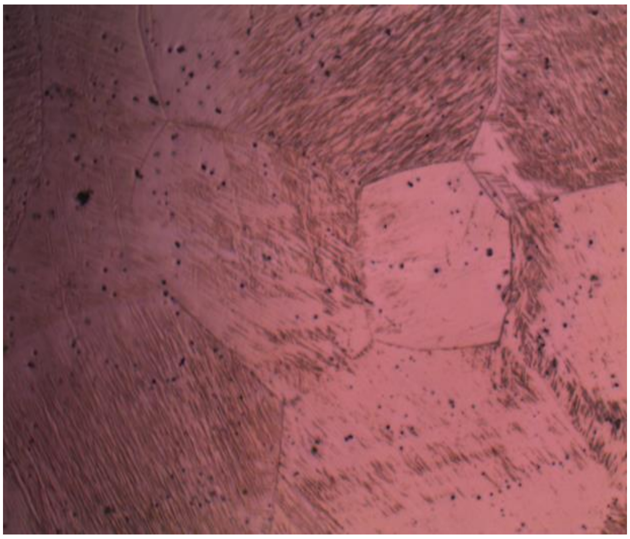

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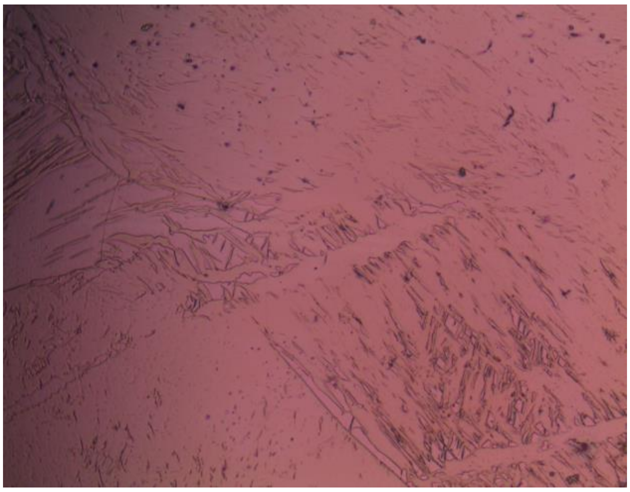

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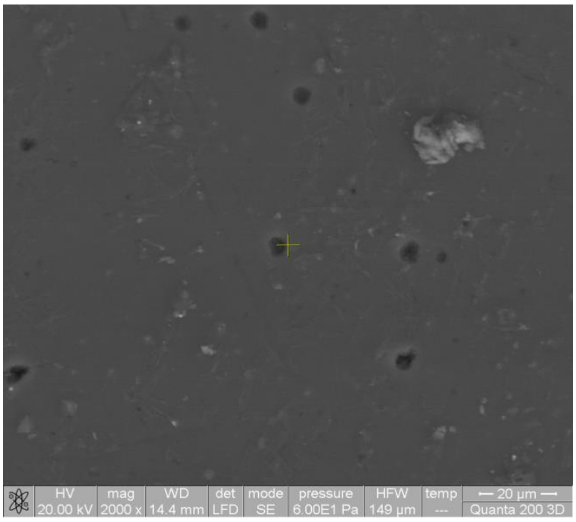
Fig.5. Optical images of Mg-Ca-Si biodegradable alloys: a) 100X; b)200X; c) 500X

Polyhedral shape grains of Mg-Ca are also present in figure 6 within SEM images of samples 0.63% Ca and 0.85% Ca.



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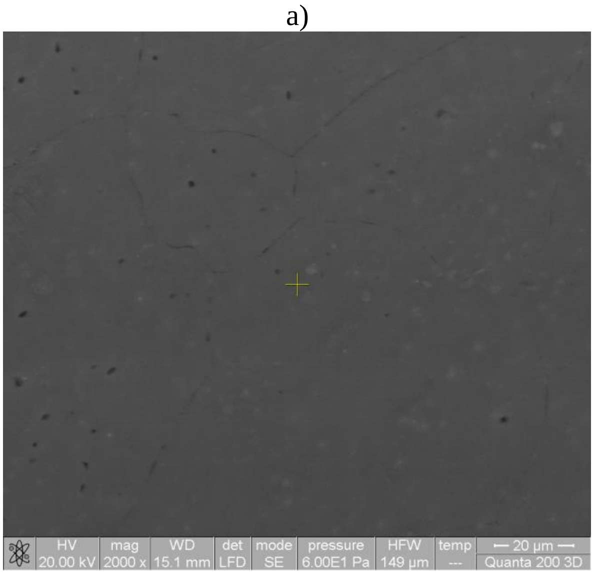

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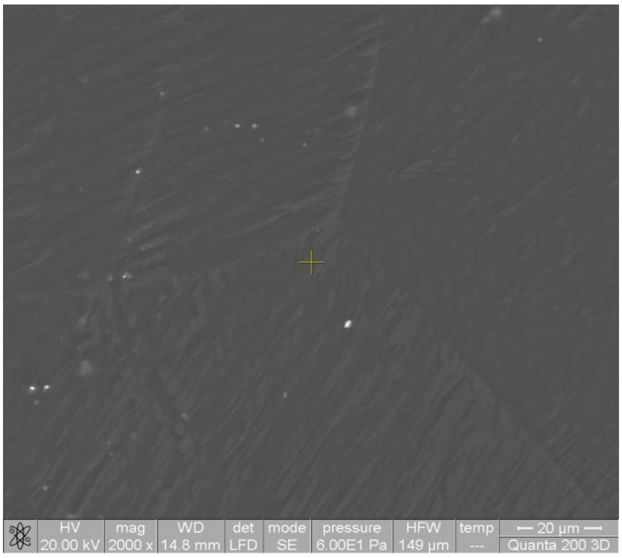

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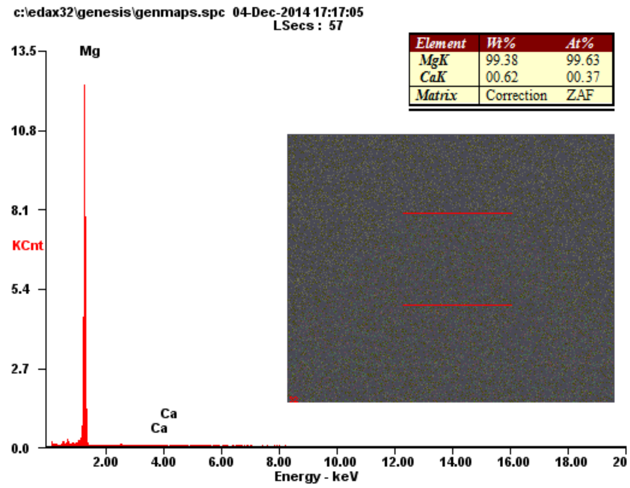
Fig.6. SEM images of Mg-Ca alloys:
a) Mg-0.63%Ca-2000X; b) Mg-0.81%Ca-2000X
c) Mg-Si-Ca-2000X

In figure 7 are presented the values of EDAX analysis for samples of 0.63%Ca and 0.81%Ca, respectively 0.29%Si and 0.33%Ca. Despite being a semi-quantitative and semi-qualitative analysis, values gained from this determination show similar values as it was obtained from casting.



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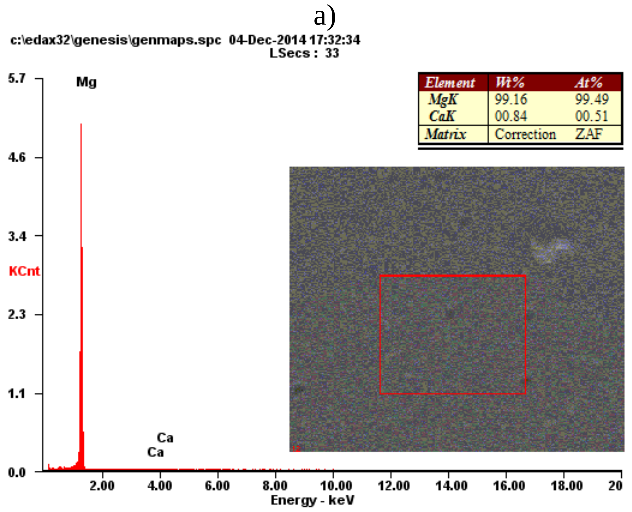

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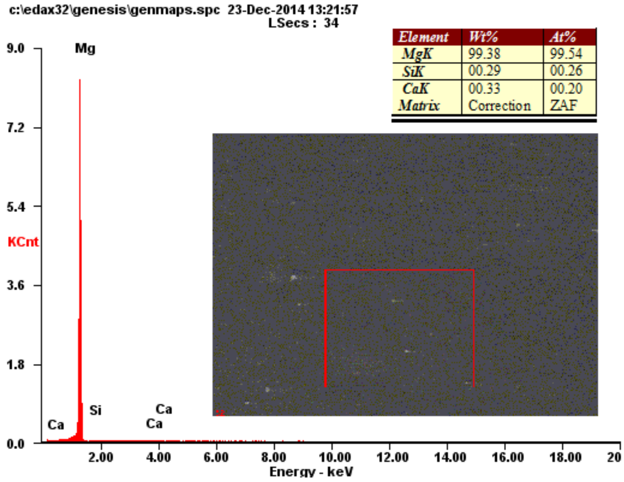

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Fig.7. EDS analysis of Mg-Ca alloys: a) Mg-0.63%Ca; b) Mg-0.81%Ca; c) Mg-Si-Ca

4. CONCLUSIONS

The analysis of the microstructures by optical microscopy, and electronic microscopy on Mg-0.63%Ca, respectively Mg-0.81%Ca, show an increase of the α-type solid phase as known microstructure, highlighting large surfaces of the grain boundaries which will determine the alloy to a fast biodegradation. Mg-Ca alloys reveal a single α-Mg phase with large grain size accompanied by some holes inside the grains.With addition of Si, needle-like Mg_2Si phases formed and tended to distribute along the α-Mg grain boundary. EDAX analysis showed the chemical composition of the selected alloys.

5. REFERENCES

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