Microstructural analysis of biodegradable Mg-0.9Ca-1.2Zr alloy

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Abstract. Magnesium alloys have applications in aerospace and medical applications as biodegradable orthopedic implants. Alloying with biocompatible elements, such as calcium or zirconium contribute to refining the the microstructure and improves corrosion resistance with the formation of an eutectic compound - Mg₃Ca at boundary alpha-Mg grains. The purpose of this paper is to present the microstructure throw optical and scanning electron methods and phase and constituents identification with X-ray analysis. The results showed the presence of alpha-Mg grains with formation of a mechanical compound - Mg₃Ca and appearance of alpha-Zr phase relatively uniformly distributed in nests.

1. Introduction
Magnesium alloys are considered by some researchers to be the 3rd generation of biomaterials [1]. First biodegradable alloys dates back from 1878, when researchers used magnesium alloys in a human body as implants [2]. Pure magnesium has as melting point the value of 650 °C, the boiling point in the range of 1090 °C and the specific weight is 1738 kg/m³. Magnesium and its alloys show a modulus of elasticity and a yield strength much closer in value to the values of human bone compared to some biomaterials [3, 4].

Zirconium and calcium have a relatively low solubility in magnesium alloys and exhibits mechanical mixture with forming some precipitates [5], but significantly improves the mechanical strength and corrosion resistance [6].

Mg alloys Zr shows a high damping capacity (about 80%) which help to reduce vibrations generated by movement and the implant / bone effort [7]. Some researchers have identified that alloying magnesium with a concentration of 1%-3% calcium, leads to lower mechanical strength and the specific elongation [8,9], due to the consolidation of Mg₃Ca compound. Zhou et al [10] have identified that Mg-1Ca-0.5Zr or Mg-1Ca-1Zr possesses superior mechanical properties, corrosion resistance and good biocompatibility.
2. Materials and methods

Casting of Mg-alloys 0.9Ca-1.2Zr was carried out using an induction-current equipment having a controlled atmosphere of argon 5.0 from the Faculty of Materials Science and Engineering, University “Politehnica” of Bucharest, Laboratory of casting and refining metal alloys [11]. The selected elements were of high purity, using a magnesium alloy with a purity of 99.7%, metallic calcium particles (99.9%) and a master-alloy Mg-25Zr. They were used zirconia ceramic crucibles. In order to obtain alloys concentrations there were considered the following cast mass calculation: Mg: 28 g; Ca: 0.1 g; Mg-25Zr: 0.7 g. The melting of the alloy was carried out in the temperature range of 680°C, mini-ingots of 29g resulted. Figure 1 presents the EDS spectrum and the chemical composition of the biodegradable Mg-0.9Ca-1.2Zr alloy. In order to determine of the optical microscopy it was used a Leica 5000 DMI optical microscope, scanning electron microscopy was carried out using microscope SEM QUANTA 200 3D, and for obtaining diffraction peaks it was used X-ray diffractometer with Cu anode X’Pert Pro MPD.

3. Results and discussions

3.1. Optical microstructure

Figure 2 reveals the microstructure of magnesium alloys at 50X, 100X, respectively 500X magnitude with alpha type grains, zirconium constituents distributed in clusters and an intermetallic compound (Mg2Ca) identified at magnesium grains boundary.

![Figure 1. EDS spectrum and chemical composition of Mg-0.9Ca-1.3Zr.](image1)

![Figure 2. Optical images of Mg-0.9Ca-1.2Zr alloy: (a) 50X; (b) 100X; (c) 500X [13].](image2)
3.2. SEM microstructure
Microstructure analyzed before with optical images is confirmed by electron microscopy analysis at different magnifications (figure 3). These aspects were also confirmed by other researchers [9, 10]. In figure 3 (a-c) is presented groups of zirconium constituents distributed in clusters, while in figure 3d at a magnification of 10000X is shown a mechanical mixture called Mg₂Ca.

![Figure 3. SEM images of Mg-0.9Ca-1.2Zr alloy: (a) 500X; (b) 1000X; (c) 5000X; (d) 10000X [13]](image)

3.3. XRD analysis
Diffractogram of Mg-0.9Ca-1.2Zr alloy is presented in figure 4. α-Mg is the predominant phase and it is identified at 20 angle: 36.51°, having a hexagonal crystalline structure. Secondary phases identified are: α-Zr at 20: 91.44° having also a hexagonal type crystalline structure and an eutectic compound Mg₂Ca having a monoclinic structure. Using the Scherrer calculation method [12] and the crystallite size was calculated for the three phases: α- Mg: 28.89508 nm; α- Zr: 21.62416 nm; Mg₂Ca: 25.57983 nm.
4. Conclusions
The purpose of this paper was to obtain a biodegradable Mg-0.9Ca-1.2Zr alloy with possible medical applications. Repeated casting were carried out for obtain the alloy, using a predetermined burden in a controlled atmosphere of argon melting facility. Optical and SEM microscopy have revealed the typically polyhedral alpha magnesium grains microstructure, a mechanical mixture Mg2Ca founded at grains boundary and segregation of alpha zirconium constituents, which are relatively uniform distributed. XRD analysis presents phases and constituents of the alloy, magnesium and zirconium have been identified with hexagonal crystalline structure and the mechanical mixture - Mg2Ca with monoclinic crystalline structure. The research will be continued with mechanical analysis, for identifying the Young modulus and with in vitro / in-vivo analysis in specific cellular culture medium so that the Mg-0.9Ca-1.2Zr can be used as biodegradable implants for medical field.

5. References
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