Microstructural analysis and mechanical properties of biodegradable Mg-1.3Ca-5.5Zr alloy

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Abstract. Magnesium based alloys begin to be known as biodegradable materials used in medical field. Zirconium and Calcium as alloying elements, improve mechanical strength, creep resistance and refine microstructure. Also, Ca is the most spread mineral in the human body, which contributes to the osteosynthesis phenomenon. The aim of this paper is developing two original Mg-Zr-Ca biodegradable alloys, characterizing from the point of view of the microstructure, X-ray diffraction, Young modulus and scratch test. Results show evenly distributed clusters of zirconium and Mg₂Ca arranged at Mg grains boundary. Also, values of Young modulus are between 25-27 GPa similar to bones Young modulus, thus avoiding the formation of “stress shield effect”.

1. Introduction
Magnesium is a biodegradable metallic material with young modulus nearest of all biomaterials that of human bone, avoiding the occurrence of the effect of “stress shield” phenomenon that occurs mainly in the implants of steel, Co-Cr alloys and titanium alloys [1-3].

Also, Ca is the most spread mineral in the human body, which contributes to the osteosynthesis phenomenon. The aim of this paper is developing two original Mg-Zr-Ca biodegradable alloys, characterizing from the point of view of the microstructure, X-ray diffraction, Young modulus and scratch test. Results show evenly distributed clusters of zirconium and Mg₂Ca arranged at Mg grains boundary. Also, values of Young modulus are between 25-27 GPa similar to bones Young modulus.

The history of biodegradable magnesium based alloys started after Sir Humphrey Davy discovered in 1808 the Mg element. The first laboratory MgCl₂ electrolisis cell was created in 1852 by Robert Bunsen, [4]. First orthopedically usage of a Mg-Mn implant was made by Mc Bride in 1938, by using Mg-Mn plates for improving the osteosynthesis phenomena [5].

Pure Magnesium is considered relatively safe and attractive for medical use. However, the presence of impurities such as iron, nickel and copper dramatically accelerates the corrosion. Microstructure of pure magnesium consists of α-type grains having a hexagonal crystalline structure type [6]. Zirconium is known as a strong refiner for magnesium alloys. This element is usually used in alloys with zinc, rare earth, Y, Th and is not expected to be alloyed with elements such as Al and Mn. Mg-Zr
alloys show a high damping capacity (about 80%), which help to reduce vibrations generated by movement and effort at the interface implant / bone [7].

Gu et al indicate that addition of 1% Zr leads mechanical strength improvement and specific elongation of the alloy, an ultimate tensile strength of 171.87 MPa and an elongation of 27% [8].

Calcium and strontium are belonging to second group of the periodic table showing a relative solubility under equilibrium conditions in Mg (1.34%). Supersaturated calcium magnesium alloys give Mg2Ca compound at the boundary between grains [9].

Wan et al have identified that alloying magnesium with 0.6% Ca improves bending strength and corrosion resistance, [10] and for a slow biodegradation, the percentage of calcium should be between 0.6% and 1%, [11]. Alloying with a percentage between 1% and 3% Ca, leads to lower mechanical strength [12,13].

2. Materials and methods

Processing Mg-Ca-Zr alloy was done in a induction current with controlled atmosphere facility, CTC50K15 type, using zirconia crucibles. Tracking metallic melt temperature during the process is done using a thermocouple. This facility is the property of Faculty of Materials Science and Engineering, University “Politehnica” of Bucharest, Laboratory of casting and refining metal alloys [14].

For the elaboration Mg-Ca-Zr alloy were used as raw materials pure magnesium (99.7%), pure calcium particles and a master Mg-25Zr alloy. The amount of pure magnesium alloy, pure metallic calcium particles and Mg-25Zr master alloy were added at the same time in the crucible under argon protection. Pre-heating was performed at 450ºC and the melting itself was conducted at a temperature of (650-680)ºC, also in a controlled atmosphere of argon. Casting was conducted in a crucible of zirconia, mini-ingots (specimens) taking the conical shape of the crucible.

SEM images and EDS chemical composition was obtained with a SEM Quanta 200 3D Dual Beam microscope. XRD analysis was carried out using a X’Pert Pro MPD diffractometer and mechanical properties were measured using CETR UMT-2 Tribometer. For micro-scratch analysis it was used a constant load method with a load of 5N on a distance of 4 mm, for a single determination. In figure 1 is shown the EDS analysis and the chemical composition of the biodegradable Mg-1,3Ca-5,5Zr alloy after casting.

![Figure 1. EDS spectrum and chemical composition of Mg-1,3Ca-5,5Zr.](image-url)
3. Results and discussions

3.1. Structural analysis

3.1.1. Optical microstructure
In Figure 2 (a-c) is presented the optical microstructure of Mg-1.3Ca-5.5Zr at different magnifications. Microstructure of the alloy consists in α-Mg grains with an eutectic compound Mg₂Ca at the grains boundary and a relatively evenly distributed α-Zr phase.

![microstructure images](image)

*Figure 2. Optical images of Mg-1.3Ca-5.5Zr alloy: a) 50X; b) 100X; c) 500X.*

3.1.2. SEM microstructure
Secondary electron images are used for analyzing the microstructure of Mg-1.3Ca-5.5Zr alloy. In figure 3 (a-c), at different magnifications is seen the typical microstructure of α-Mg with α-Zr agglomerations, and the Mg₂Ca identified at grain boundaries. The microstructure is confirmed by research done by [9,15,17].

![microstructure images](image)

*Figure 3. SEM images of Mg-1.3Ca-5.5Zr alloy: a) 500X; b) 1000X; c) 5000X.*

3.2. XRD analysis
XRD diffraction analysis is revealed in Figure 4. The diffraction pattern reveals the α-Mg predominant phase around 2θ angle: 36.58 ° having a hexagonal crystal system. Mg₂Ca eutectic type compound is found at 2θ angles: 69.94 ° and 99.12 ° with a crystal structure of monoclinic type. Lattice parameters of all identified compounds are shown in table 1.
Table 1. Lattice parameters of Mg-1.3Ca-5.5Zr compounds

| Compound       | Space Group | Crystal system | a (Å)  | b (Å)  | c (Å)  | α (º) | β (º) | γ (º) | Cell volume (10⁶ pm³) |
|----------------|-------------|----------------|--------|--------|--------|-------|-------|-------|----------------------|
| Mg             | Mg          | P63/mmc        | 3.2093 | 3.2093 | 5.2103 | 90    | 90    | 120   | 46.47                |
| 1.3Ca-5.5Zr    | Mg2Ca       | A2/a Monoclinic | 10.1352| 10.8408| 6.2341 | 90    | 90    | 90    | 684.96               |
| alloy          | Ca          | Im-3m Cubic    | 3.5590 | 3.5590 | 3.5590 | 90    | 90    | 90    | 45.08                |
| Zr             | Mg2Ca       | P63/mmc        | 3.2300 | 3.2300 | 5.1400 | 90    | 90    | 120   | 46.44                |

Figure 4. XRD patterns of Mg-1.3Ca-5.5Zr alloy.

The crystallite size was calculated according to the Scherrer equation[16], and the values for each compound are shown in Table 2.

Table 2. Crystalite size of compounds (nm)

| Compound                  | α - Mg | α - Zr | Mg2Ca   |
|---------------------------|--------|--------|---------|
| Mg-1.3Ca-5.5Zr alloy      | 37.4275| 30.68117| 22.6364 |

3.3. Scratch and micro-indentation analysis

Micro-scratch results were performed using scanning electron microscope, by obtaining images of scratch profile at different magnifications, 2D and 3D profile surface.

Figure 5 presents SEM images (a-c), 2-D (e) and 3-D (d) profile surface of the "scratch" test. Figure 5 a), b) is presented the head-ends of scratch marks, then a SEM image at 500X magnification, highlighting the fracturing of the material appearance. After doing the test, it was measured an apparent friction coefficient whose value is 0.598.
The variation-curve of the micro-indentation test is presented in Figure 6 and it represents the response of the material during a load –displacement curve. Three determinations were performed and the average was calculated. A Rockwell diamond indenter having an applied load of $F_{Z} = 5N$ on the surface of the sample was used for measurements.

![Figure 6. The variation curve of the micro-indentation test of Mg-1,3Ca-5,5Zr alloy.](image)

Mg-1,3Ca-5,5Zr sample shows a strain load of approximately 9.5 $\mu$m and a strain release of approximately 7.17 $\mu$m resulting an elastic deformation of 2.33 $\mu$m. Micro-indentation tests results are presented in table 3, showing that the alloy’s Young modulus is around of 27 GPa similar to Young modulus human bone value.

| Table 3. Some mechanical properties of Mg-1,3Ca-5,5Zr alloy |
|---------------|----------------|----------------|----------------|
| COF | Hardness (HV) | Young Modulus (GPa) | Stiffness(N/$\mu$m) |
| Mg-1,3Ca-5,5Zr | 0.598 | 44.08 | 26,853 | 3.285 |
4. Conclusions
The Mg-1.3Ca-5.5Zr alloy investigated in this paper was produced by a controlled atmosphere facility using zirconia crucibles. The alloy is classified as a Mg-Ca-Zr biodegradable material presenting α – Mg grains with Mg₂Ca compound positioned at grain boundary. Also Zr-phase is relatively uniform distributed in the microstructure. XRD analysis showed the presence of a hexagonal crystal form for Mg and Zr phases, respectively monoclinic system for Mg₂Ca. Scratch tests and microindentation tests present an average value for apparent COF in range of 0.6 at the maximum load of 5N. These alloy present lower values of young modulus and hardness compared with the classic orthopedic biomaterials, which represent an important point of view in eliminating the “stress shielding effect”.

References
[1] Staiger M P, Pietak A, Huadmai J and Dias G 2006 Magnesium and its alloys as orthopedic biomaterials: A review Biomaterials 27 (9) pp 1728-1734
[2] Minciună M G, Vizureanu P, Achitei D C, Sandu AV, Berbecaru A and Sandu I G 2016 Structural characterization and properties analysis of CoCrMoSi alloys Journal of Optoelectronics and Advanced Materials 18 (1-2) pp 174-178
[3] Bălătău M S, Vizureanu P, Țierean M H, Minciună M G and Achitei D C 2015 Ti-Mo Alloys used in medical applications Advanced Materials Research 1128 pp 105-111
[4] Kammer K 2000 Magnesium Taschenbuch Alu Media
[5] McBride E D 1938 Magnesium screw and nail transfixion in fractures South Med J 31(5) pp 508-515
[6] Friedrich H E and Mordike B L 2005 Magnesium Technology—Metallurgy, Design Date, Applications Springer Berlin/Heidelberg/New York
[7] Tsai M H, Chen M S, Lin L H, Lin M H, Wu C Y, Ou K L and Yu C H 2011 Effect of heat treatment on the microstructures and damping properties of biomedical Mg-Zr alloy Journal of Alloys and Compounds 509 pp 813–819
[8] Gu X N, Zheng Y F, Cheng Y, Zhong S P and Xi T F 2009 In vitro corrosion and biocompatibility of binary magnesium alloys Biomaterials 30(4) pp 484–498
[9] Salahshoor M and Guo Y 2012 Biodegradable Orthopedic Magnesium-Calcium (MgCa) Alloys, Processing, and Corrosion Performance Materials 5 pp 135-155
[10] Wan Y, Xiong G, Luo H, He F, Huang Y and Zhou X 2008 Preparation and characterization of a new biomedical magnesium–calcium alloy Materials & Design 29(10) pp 2034–2037
[11] Kirkland N T, Birbilis N, Walker J, Woodfield T, Dias G J and Staiger M P 2010 In-vitro dissolution of magnesium-calcium binary alloys: Clarifying the unique role of calcium additions in bioresorbable magnesium implant alloys Journal of Biomedical Materials Research Part B: Applied Biomaterials 95B pp 91–100
[12] Li Z, Gu X, Lou S and Zheng Y 2008 The development of binary Mg-Ca alloys for use as biodegradable materials within bone Biomaterials 29(10) pp 1329–1344
[13] Hassel T and Bach F W 2007 Production and properties of small tubes made from Mg-Ca0.8 for application as stent in biomedical science In Proceedings of the 7th International Conference on Magnesium Alloys and Their Applications pp 432–437
[14] *** www.eramet.ro
[15] Crimiu C I, Istrate B, Munteanu C, Antoniac I, Matei M N, Earar K 2015 XRD and Microstructural Analyses on Biodegradable Mg Alloys Key Engineering Materials 638 pp 79-84
[16] Patterson A 1939 The Scherrer formula for X-ray particle size determination Phys. Rev. 56 pp 978-982
[17] Plavanescu (Mazurchevici) S., 2014 Biodegradable composite materials – Arboform: A review, International Journal of Modern Manufacturing Technologies, Vol. VI(2), 63-84.