Mg-Zn-Y BIOCOMPATIBLE ALLOYS PRODUCED IN A LEVITATION FURNACE

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Abstract: *The Mg-Zn alloys have a controlled biodegradability in biological fluids. Alloys in the Mg-Zn system must be manufactured from high-purity raw materials, and the production process must be free of impurities from the crucibles. The mechanical properties of Mg-Zn alloys can reach values of tensile strength of 270 MPa and elongation at break of over 18%. The use of these alloys for bio-resorbable implantable devices does not allow the existence of a high level of impurities. For this reason, in the work has been used an installation for melting raw materials by levitation, which allows the metal alloy to be kept in an inert gas environment inside an induction coil, avoiding its contact with any other material. The induction currents generated in the levitational floating melt determine the mixing of the chemical elements and the homogenization of the alloy. In this paper, seven experimental Mg-Zn-Y alloys with different chemical compositions were produced and tested. To reduce the oxidation effect and to finish the grain, Y was added in the solid solution, as proportion from 0.5 to 5 wt. Microhardness tests and SEM microstructural analyzes were performed to evaluate the strengthening effects and the level of homogenization of the obtained solid solutions.*

Key words: Mg-Zn-Y alloys, biocompatible, levitation furnace, microhardness, microstructure

1. INTRODUCTION

The most important application that requires biodegradability is the use of temporary implants capable of supporting and repairing problem areas (fractures, facial or maxillofacial reconstruction, artificial grafts, etc.) for a limited period [1 - 3]. Using resorbable implants avoids surgical procedures to remove the implant, as it slowly dissolves in living tissues. The effect of progressive biodegradability is achievable with magnesium alloys. To obtain acceptable values for the mechanical, chemical or biocompatibility properties of implantable materials, high-purity magnesium-based alloys must be manufactured, to which biocompatible elements can be added, in different concentrations, with applications for restoring bone tissues or for the cardiovascular system.

It is a permanent concern of researchers to obtain a new class of Mg-based metal alloys with applications in the field of biocompatible materials, because they have properties of slow dissolution in biological fluids or living tissues. The mechanical tensile strength of magnesium is higher than that of biocompatible ceramic materials (hydroxyapatite), and the values modulus of elasticity and yield strength are closest to those of human bone. The longitudinal modulus of elasticity is about 50% of that of titanium alloys, which allows great flexibility, especially in the case of use for stents and orthopedic implants, only for small joints.

Magnesium is a macro-element with a benign action in the body, clinical studies proving that it has good resorbability and high biocompatibility in the case of implants used for bone fractures. At the same time, the density of Mg-base alloys is reduced, and Young's modulus of magnesium is close to that of bones (E = 10-30 GPa). Finally, magnesium alloys have controllable corrosion rates, which is why they can be considered resorbable in physiological environments. As a result, magnesium alloys have been considered acceptable candidates both for use in cardiovascular surgery and for the repair of bone problems [6, 7].

For biomedical applications, the composition of the material is considered a crucial factor, since many of the elements that make up the materials available for industrial applications are highly toxic to the human body. To improve the properties of magnesium, different alloying elements are used, especially those from the rare earth group. Magnesium alloys which are used as bio-resorbable alloys are part of the following metallurgical systems: Mg - Ca (Ca = 1-3%); Mg - Zn (Zn ≤ 5%); Mg - Y; Mg - Ce; Mg - Zr; Mg - Zr (0.5-1%) - Ca (1-2%); Mg - Si (0.6% O) - Ca (0.2-0.4%) etc. Among them, Y has a high solubility in Mg solid solution and is often introduced together with other rare earths to improve creep and corrosion resistance. Moreover, most REEs form intermetallic phases with Mg and Al, having a pronounced effect on corrosion resistance [9 - 11].

Based on research in the field of metal biomaterials and orthopedic implants, biodegradable magnesium alloys were the best solution for making implants used in small extremity surgery, such as ankle, tibia, hand, or fist fractures.

From a metallurgical point of view, the synthesis of Mg-based alloys is an extremely difficult process due to the strong oxidation phenomenon that occurs in the atmosphere, which continues with the almost complete combustion of the pure metal or its alloys. Therefore, the processes of obtaining magnesium alloys must be carried out in controlled environments, using special equipment specially designed for this purpose (i.e., vacuum and/or inert atmosphere). Therefore, the paper presents the results obtained using a proprietary facility, for melting by levitation of the metallic material, which allows the protection of the melt with inert gas and a minimal contact of the liquid metal with the crucible.

2. THE OBTAINING OF METALLIC MATERIAL FROM THE Mg-Zn-Y SYSTEM

The Mg-Zn-Y biodegradable alloys were obtained using levitation melting equipment equipped with a medium frequency converter under inert atmosphere, from ERAMET laboratory – University Politehnica of Bucharest (Figure 1) [4].

Figure 1. Melting equipment in inert atmosphere by levitation equipped with medium frequency converter.

In the experiment, the following raw materials were used:

- Mg with purity of 99.5%, as grains with diameter of 2-5 mm, product code HP.Mg.2N5.100000.
- Zn with purity of 98.5%, as grains with diameter of 2-6 mm.
- Y with purity of 99%, as grains with diameter of 2-5 mm.

To obtain alloy recipes, technological calculations were carried out for a batch weight of 15 g, corresponding to the volume of the casting mold, considering the evaporation and oxidation losses specific to each element of approximately 10% wt. The chemical compositions of the metal alloys designed for the obtaining process are presented in Table 1.

Table 1: Experimental Mg-Zn-Y alloys

P1	P2	P3	P4	P5	P6	P7
Mg0.5Zn0.5Y	Mg1Zn1Y	Mg1.5Zn1.5Y	Mg2Zn2Y	Mg3Zn3Y	MgZn4Y	Mg5Zn5Y

To compact the granular mixtures and reduce the oxidation effects, the alloy mixtures were cold pressed in the mold, using a 20 ft hydraulic press, resulting in compacted products with a diameter of 15 mm and a height of 10 mm (Figure 2) [5].

Figure 2. Compacted buttons made from metal powders.

The buttons obtained by cold pressing were subjected to induction melting under an inert atmosphere (5.3 quality Argon), at a pressure of 2.4 atm. The metallurgical melting process of a batch lasted between 2 and 3 minutes, depending on the working parameter values adopted: medium frequency voltage U_{mf} = 480 - 500 V; medium frequency current I_{mf} = 55 - 65 A; working frequency f_{mf} = 60 - 70 kHz; power P_{mf} = 20 - 35 kW. The molten alloy was cast freely, also in argon atmosphere, into copper molds protected inside with refractory paint, to avoid the adhesion of the liquid metal (Figure 3).

Figure 3. Image during the levitation melting process of the Mg-Zn-Y alloy button inside the inductor coil.

After solidification, the end zones of the mini-ingots were removed and the cylindrical surfaces were mechanically machined by turning, to remove the zones of contact with the casting mould (Figure 4). Disc shape samples of 1.2 mm in thickness and 11 mm in diameter were taken from each alloy type for cell proliferation tests and metallographic analysis (Figure 4).

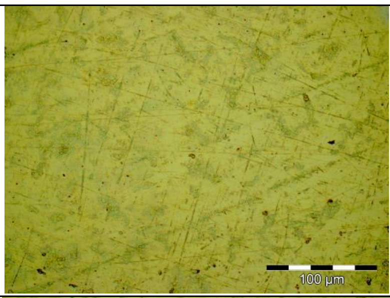
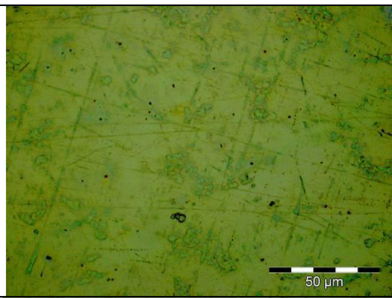
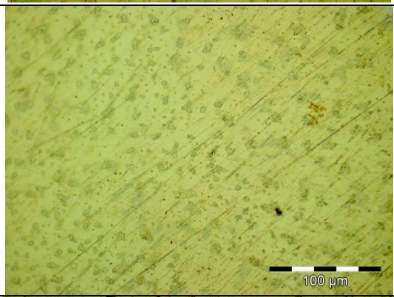
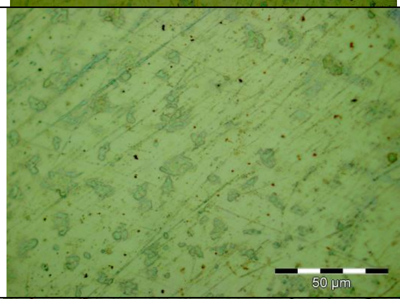
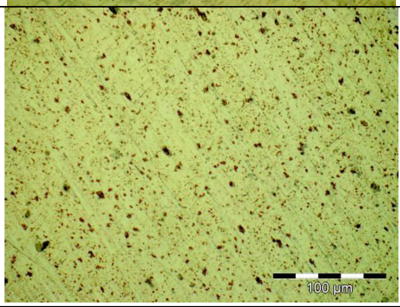
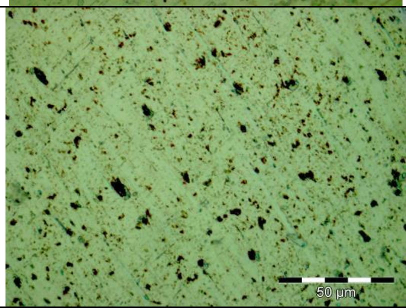
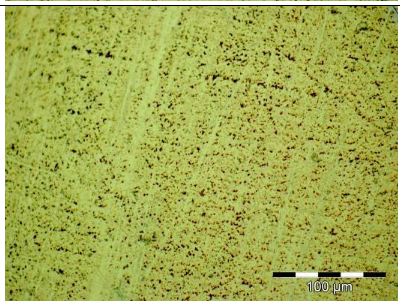
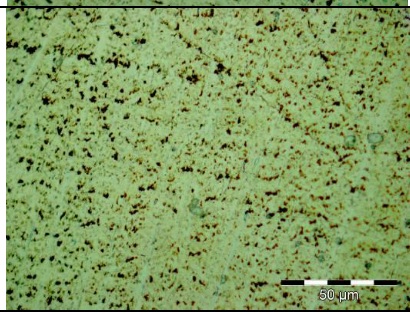
Figure 4. Mini-ingots casts and prepared for examination.

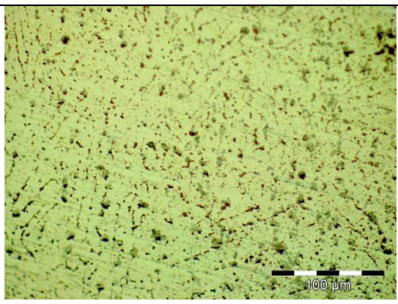
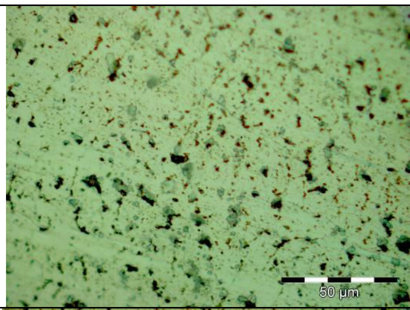
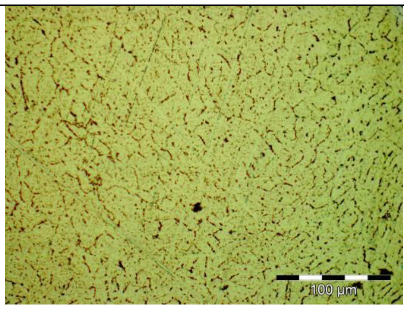
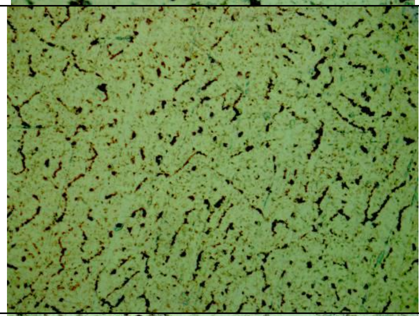
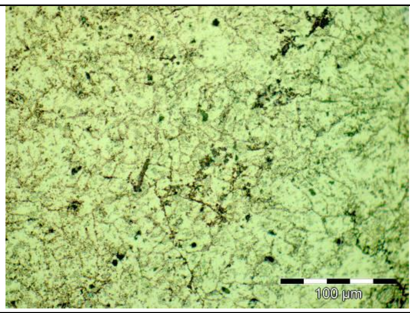
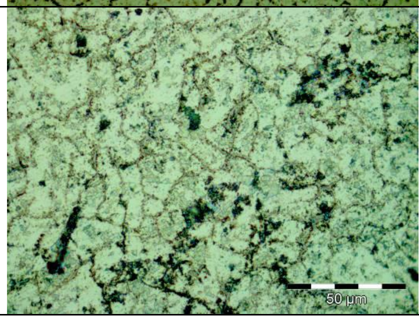
3. RESULTS AND DISCUSSION

3.1. Microstructural analyses of the alloys from the Mg-Zn-Y system

The microstructural analyzes were performed on the disc-type samples with a thickness of about 3 mm, taken with the IsoMet 4000 precision cutting machine from the LAMET laboratory. The samples were polished with metallographic abrasive papers in the sequence: Grit 500, 600, 800 then they were polished with abrasive powders (MicroPolish BH1103) with a grain size of 0.3 microns and MetaDi fluid polishing liquid impregnated on a textile support. The analysis of the polished surfaces was performed with the Olympus GX 51 microscope equipped with Analysis image processing software. The microstructural images of the samples are presented in Table 2.

Table 2: Microstructural analyses of the alloys from the Mg-Zn-Y system

Sample	Microstructure, x500	Microstructure, x1000
Mg0.5Zn0.5Y		
Mg1Zn1Y		
Mg1.5Zn1.5Y		
Mg2Zn2Y		

Mg3Zn3Y		
Mg4Zn4Y		
Mg5Zn5Y		

All the samples analyzed show a dendritic microstructure, with small precipitates of compounds (Mg7Zn3, Mg24Y5) having different morphologies, depending on the concentrations of Zn and Y alloying elements. From the binary diagrams Mg-Zn and Mg-Y for concentrations below 10%Y in the Mg-Y binary alloy, a compact hexagonal solid solution of the MgY type is formed, with separation of chemical compounds like Mg24Y5 type, and for the Mg-Zn binary alloy, a eutectic reaction occurs at the concentration of 29%Zn, with the formation of the Mg7Zn3 eutectic [8].

3.2. Microhardness analyses of the alloys from the experimental samples

To assess the degree of hardening of the advanced purity magnesium by adding biocompatible alloy elements such as Zn and Y, there were conducted microhardness tests on the surfaces of the samples, after grinding them with metallographic abrasive paper. The microhardness values were measured on the metallographically prepared surfaces, using the Shimadzu HMV 2T apparatus.

The measurement conditions were as follows: 25°C ambient temperature, 52% humidity, 0.1N pressing force, and 15 second indentation time. To highlight the mechanical homogeneity of the alloys, 5 measurements were made in different areas of the samples (edge and center), the values being presented in Table 3.

Table 3: Microhardness values for alloys in the Mg-Zn-Y system

Sample	Individual values, HV 0,1	Average value
Mg0.5Zn0.5Y	55.4; 57.4; 56,8; 58.4; 65.7	58,8
Mg1Zn1Y	62.1; 64.9; 67.4; 60.0; 65.3	63,9
Mg1.5Zn1.5Y	86.7; 80.7; 80.0; 87.9; 78.0	82,7
Mg2Zn2Y	76.7; 76.6; 82.0; 84.7; 85.5	83,5
Mg3Zn3Y	89.0; 98.2; 88.4; 81.8; 95,8	90.6
MgZn4Y	90.0; 90.4; 95.9; 88.7; 93.7	91,7
Mg5Zn5Y	94.0; 91.4; 94.9; 89.7; 96.7	93,3

4. CONCLUSIONS

The Mg-Zn-Y alloys can be successfully obtained in the levitation induction melting equipment under argon inert protection environment that allows the reduction of oxidation effects.
The purity of the alloys depends on the quality of the raw materials used and on the working conditions (inert gas protection for the melt, perfectly clean solidification molds, constant heating parameters, gas and smoke elimination during melting).
The homogeneity of the metal matrix of the Mg-Zn-Y alloys depends on the method of production. If granular materials of advanced purity are used, it is possible to better homogenize and distribute the alloying elements in the metal matrix, and the compression allows maintaining the shape of the sample during melting.
The combined analyses of the chemical composition, microhardness and metallographic examination reveal an increased compositional non-homogeneity of the Mg-Zn-Y alloys samples due to the very short melting time (about 2-3 minutes per batch) and the special conditions for obtaining in induction field and levitation effect. However, the materials obtained are mechanically and microstructurally stable.
The hardness of the Mg-Zn-Y alloy metal matrix increases with the Y content increase, the values ranging from 58.8 to 93.3 HV0.1.

5. ACKNOWLEDGEMENTS

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