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Obtaining of light biocompatible magnesium alloys using levitation equipment under controlled argon atmosphere

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Abstract. The use of resorbable materials to make orthopedic implants is a new direction, with major benefits for both the patient and the surgeon. The purpose of a bioresorbable implant is to support the regeneration and healing of tissues, followed by completely dissolving after its purpose is achieved, being characterized by the biodegradability and biocompatibility capability. Magnesium is a natural element of the human body, the magnesium-based implant having the ability to be fully resorbed without inducing local or systemic toxic effects. Experimental alloys were obtained from 99.5% pure magnesium powders in which alloying elements (Ca) or micro-alloying (La, Ce) were added in the 0.5-5% range to identify the best bio-compatible alloy recipes. The metallurgical process was conducted in an induction melting equipment under a controlled atmosphere of argon, through levitation. The melting time for each alloy weighing 15 g was about 3 minutes, and the electrical parameters varied in the range: Voltage U_{mf} = 480 - 500 V; Current I_{mf} = 55 - 65 A; Frequency f_{mf} = 60 - 70 kHz; Power P_{mf} = 20 - 35 kW. Following the process, about 10% magnesium losses were obtained, due to the vaporization process. The samples obtained were characterized in terms of chemical composition, microstructure and micro-hardness. The micro-hardness values were ranging from 49 to 87.4 $HV_{0.2}$.

1. Introduction

At present, new generations of Mg-based metal materials appear to be particularly promising in the field of biocompatible implantable devices due to their ability to dissolve slowly in living tissues, without the need for further surgery to extract the implant. Furthermore, magnesium is a benign macro-element for living organisms, and the clinical trials show good resorbability and high biocompatibility of implants used for bone fixation [1]. The main application involving biodegradability is the execution of temporary implants which can be inserted into the human body in order to support problem areas (fractures, facial or maxillofacial reconstruction, artificial grafts, etc.) for a period of time before their slow dissolution [2-6].

The special mechanical properties (density and Young's modulus values similar to the bones' values, E = 10-30 GPa) and the controllable corrosion rate (resorbability in physiological environments) make magnesium alloys acceptable for use in cardiovascular interventions [7] and in

bone fracture repairs [8-11]. Since the properties of pure magnesium are not good enough to be used for prostheses, it is often alloyed with various other chemical elements [12-19]. The use of alloying elements such as Al, Ca, Li, Mn, Y, Zn, Zr and RE in Mg alloys can significantly improve the physical and mechanical properties of the alloy by: grain-size finishing, improving corrosion resistance, and increasing mechanical characteristics by forming intermetallic compounds [9, 17]. The metal ions released by biodegradable medical implants can affect the cells of the surrounding tissue, producing biological effects that occur over time, depending on the type and sensitivity of each organism. Typically, the estimator used for expressing toxicity is the toxic dose 50% (TD50) for associated bone cells (the MC3T3E1 and MG63 cell lines). In terms of toxicity to tissues in living organisms, the chemical elements are considered to feature mild, moderate and severe toxicity.

The elements with mild toxicity include Mg, Ca, Li, Al and Zr. However, some scientific reports have shown that certain elements featuring mild toxicity such as Al (500 nM), even at very low concentrations, induce the proliferation of associated bone cells [3].

Ca, Mn and Zn are oligo-elements essential to life and some rare earths with anti-carcinogenic properties should be the first choice for introducing in the chemical composition of magnesium alloys [2, 8, 14 and 15].

Calcium acts as a grain-size finishing agent in Mg alloys, stabilizing the grain size to concentrations up to 0.5% Ca, slightly decreasing in case of further additions. Binary Mg-Ca alloys were studied in particular by modifying the concentration from 0.5% Ca to 20% Ca [13]. The increase in the calcium concentration involves a higher Mg_2Ca secondary phase content, mainly distributed over the grain boundaries. The Mg_2Ca secondary phase is brittle and reduces the ductility of Mg-Ca alloys with increased Ca concentration. It also influences the corrosion resistance properties of Mg alloys. A high volumetric fraction of the Mg_2Ca secondary phase reduces the corrosion resistance of Mg-Ca alloys due to the formation of galvanic microcells. Therefore, it can be observed that an excessive concentration of Ca accelerates the corrosion rate of the Mg-Ca alloys, its optimal value being $\leq$ 1%wt Ca.

The breaking resistance of the Mg-Ca alloys ranges between 90 and 280 MPa and the elongation at break ranges between 3 and 20%. The rapid reduction of resistance due to degradation does not represent a decisive factor for a degradable implant when used in tissue engineering applications; however, when used as a substitute for bone engineering, it is expected to provide temporary support for a sufficiently long period [2].

Generally, magnesium alloys can be machined by casting and plastic deformation (rolling or hot extrusion) [20]. The main disadvantage of using magnesium in medical engineering is the rapid corrosion rate and the release of hydrogen gas during corrosion. These can induce local and systemic toxic phenomena by modifying the pH or the gas accumulation [2]. In order to improve the corrosion behaviour, with positive effect on the biocompatibility of magnesium and its alloys, two main methods are envisaged, i.e. the adjustment of the microstructure by alloying and the mechanical machining and surface treatments by the use of coatings [19].

Mg-based alloys are extremely difficult to obtain due to the strong oxidation phenomenon in ordinary atmosphere, continued with the burning of magnesium and its alloys. Therefore, it is necessary to produce magnesium alloys in controlled environments, using special installations designed for this purpose, i.e. in an inert atmosphere of argon [2]. Thus, in the research, a number of magnesium alloys were obtained using an installation for melting in argon environment by electro-magnetic levitation. Because of the violent reactivity of the magnesium with the oxygen at 600 °C, calcium was added to the granular mixture, after which it was compacted by cold pressing. The results demonstrated the possibility of obtaining magnesium alloys with different Ca contents, highlighting problems related to calcium vaporisation, ignition of granular mixtures or lack of chemical homogeneity of the alloys.

2. Obtaining experimental Mg-Ca alloys

The Mg-Ca biodegradable alloys were obtained by means of melting installation in levitation equipped with a medium frequency converter under inert atmosphere (Figure 1). The following materials were used:

- Mg, purity 99.5%, grains with diameter of 2-5 mm, product code HP.Mg.2N5.100000;
- Ca, purity 98.5%, grains with diameter of 2-6 mm, product code HP.Ca.100000.

In order to obtain alloy recipes, technological calculations were carried out for a batch weight of 15 g, corresponding to the volume of the casting mould, taking into account the evaporation and oxidation losses specific to each element of approximately 10% wt.

Figure 1. Levitation melter with medium frequency converter and inert atmosphere.

For the compaction of granular mixtures and reduction of oxidation effects, cold pressing was performed using a 20 ft hydraulic press, obtaining 15 mm diameter and 10 mm height buttons (Figure 2).

Figure 2. Mg-Ca alloy buttons obtained by cold pressing.

The buttons obtained by cold pressing were subjected to induction melting under an inert atmosphere of argon, purity 5.3, 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, in argon atmosphere, into copper moulds, protected inside with refractory paint to avoid the adhesion of the liquid metal (Figure 3). 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 3. The Mg-Ca alloy button levitation melting inside the inductor.

Figure 4. The appearance of the alloy during solidification and after extraction from the copper mould.

3. Characterization of experimental magnesium alloys

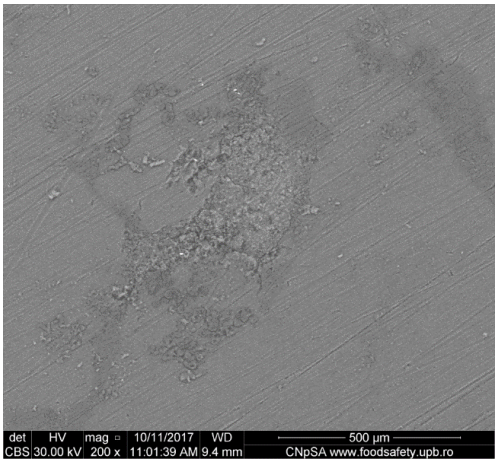
The magnesium alloys samples were used to determine the local chemical micro-composition in different areas, to establish the level of homogenization and to evaluate the tendency of segregation of the alloying and micro-alloying elements.

For the metallographic analyses, the samples were polished using metallographic abrasive paper of progressive grain sizes: 360, 400, 600, 800, 1000, followed by polishing on textile support impregnated with fine polishing solutions with alpha alumina particles (1, 0.7 and 0.25 μm grain sizes). No chemical attack solutions were used for electronic microscopy microstructural analysis in order to prevent any influence on the chemical composition values. The samples were examined using a QUANTA INSPECT F50 electronic scanning microscope, fitted with field emission gun (FEG) - 1.2 nm resolution, with energy dispersive X-ray Spectrometer (EDX) - MnKα 133 eV resolution, and an Olympus GX51 optical microscope. The values of the chemical compositions, determined by micro-zone analysis, for the set of 21 samples made of Mg-Ca experimental alloys are shown in Table 1.

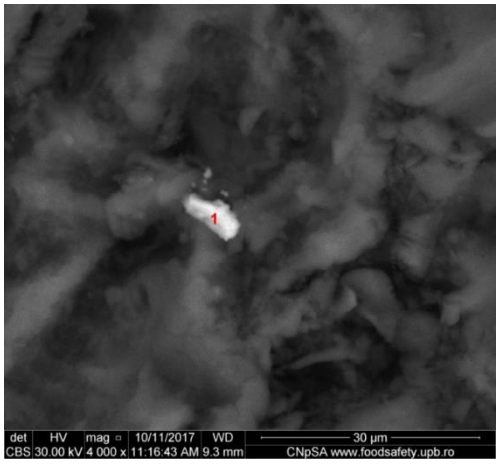
Table 1. Chemical composition of Mg-Ca alloy samples

Sample code	Chemical composition					
	Mg		**Ca**		**O / Si / La / Ce**	
	Atomic percentage, at%	Weight percentage, wt%	Atomic percentage, at%	Weight percentage, wt%	Atomic percentage, at%	Weight percentage, wt%
0	100	100	-	-	-	-
1	86.13	87.49	3.22	5.39	10.65	7.12
2	95.83	96.88	0.35	0.58	3.82	2.54
4	97.97	98.4	0.26	0.42	1.78	1.17
5	95.19	96.49	0.31	0.51	4.5	3
6	95.85	96.93	0.31	0.52	3.84	2.55
7	97.08	97.63	0.45	0.74	2.47	1.64
8	93.23	95.02	0.43	0.72	6.34	4.25
9	91.34	93.75	0.39	0.66	8.26	5.58
10	84.99	87.22	2.6	4.4	12.41	8.38
11	91.84	94.05	0.44	0.75	7.71	5.2
12	96.94	97.45	0.53	0.88	2.53	1.67
13	95.24	96.21	0.62	1.04	4.13	2.75
14	94.14	95.7	0.37	0.62	5.49	3.67
15	85.83	89.09	1.2	2.05	12.98	8.86
16	92.63	94.37	0.68	1.14	6.69	4.48
17	95.16	95.5	1.31	2.17	3.53	2.33
18	89.9	92.26	0.9	1.52	9.2	6.21
18 inclusion	69.22	58.06	29.25	40.45	**Si** = 1.53	**Si** = 1.48
18 central zone	49.35	45.27	0.38	0.57	**La** = 1.48 **Ce** = 3.62 **O** = 45.17	**La** = 7.70 **Ce** = 19.12 **O** = 27.27
19	94.16	94.78	1.36	2.25	4.48	2.97
20	93.9	95.1	0.83	1.39	5.27	3.51
21	98.68	97.84	1.32	2.16	-	-

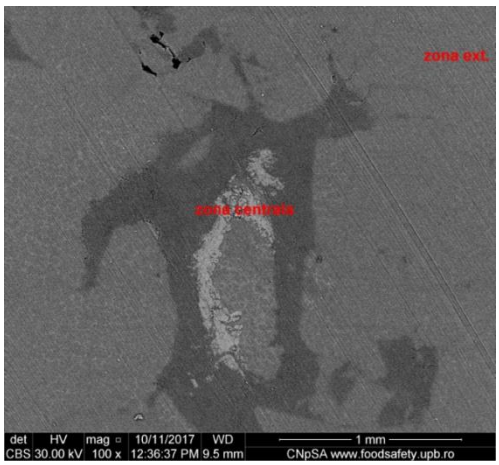
The microstructural analysis revealed that the metal matrix of the Mg-Ca alloys generally has a dendritic appearance, and the easily fusible Mg_2Ca eutectic is located in the inter-dendritic zone (Figure 5).



a) Central zone of sample 18



b) Inclusion in central zone of sample 18



c) Segregation in central zone of sample 20

Figure 5. The micro-structural aspect of Mg-Ca alloys in the analyzed range.

The mechanical characteristics of the new experimental Mg-Ca alloys obtained in levitation were determined by microhardness measurements in different zones (centre, edge) using the Shimadzu HMV 2T microhardness Vickers tester. The $HV_{0.2}$ microhardness measurements were performed on cross-sectioned samples of the Mg-Ca experimental alloys after grinding with metallographic paper. The measurements were made in line, from the edge to the centre of the samples, maintaining a minimum distance between indentations of 300 μm. The pushing force of the penetrator was 200g, and the penetration time was 10 seconds. A set of 5 successive measurements was performed for each sample and the point values, the mean value and the coefficients of variation were recorded; the data obtained is presented in Table 2.

Table 2. Hardness values measured on Mg-Ca experimental alloys samples

Sample code	Values	Mean value	Variation coefficient	Standard error
0	47,1; 48; 51; 57; 63,9	53.4	13.15	7.02
1	51,3; 48,8; 48,8; 47,5; 48,6	49.0	1.39	2.85
2	59; 41; 46,8; 48,4; 52,8	49.6	6.74	13.59
4	58,4; 58,8; 61,1; 52,6; 51,4	56.5	4.22	7.48
5	56,2; 50,8; 69,4; 66,1; 72	62.9	9.04	14.37
6	72,4; 63,8; 66,5; 63,5; 72,4	67.7	4.43	6.54
7	73,1; 87,4; 8,6; 9,5; 94,2	87.4	8.51	9.74
8	70,3; 72; 66,7; 60,3; 64,1	66.7	4.71	7.06
9	71,6; 71,4; 65,6; 72,8; 76,9	71.7	4.05	5.65
10	76,2; 64,7; 69,1; 78,8; 61,7	70.1	7.31	10.42
11	65,4; 67,3; 60,3; 59,7; 59,1	62.4	2.98	5.06
12	85; 58,3; 76,8; 75,8; 59,5	71.1	11.69	16.44
13	60,9; 62,5; 66,8; 68,2; 66,8	65.0	3.15	4.85
14	68,9; 66,3; 66,8; 56,9; 63	64.4	4.94	7.28
15	67,6; 61,7; 62,4; 72,7; 67	66.3	4.46	6.73
16	60; 56,4; 60,3; 70,8; 59,9	61.5	5.45	8.86
17	69,3; 69,8; 70,4; 65; 61,3	67.2	3.91	5.82
18	57,4; 65,5; 68,5; 68; 61,3	64.1	4.72	7.36
19	69,6; 76; 68,4; 76,3; 71,3	72.3	3.65	5.04
20	73,8; 68,3; 67,1; 66,6; 60,8	67.3	4.64	6.89
21	65,5; 65,2; 71,1; 66,4; 71,6	68.0	3.11	4.58

Samples were collected from each set of Mg-Ca alloys for testing the cell proliferation behaviour of some live bone cells collected by surgery (Figure 6). The time interval between bone tissue collection and use on metal matrices submerged in compatible solutions was less than 2 hours. After this time interval, the results can no longer be considered conclusive as the process of irreversible cell degradation is installed. The results of the cell proliferation tests showed a tendency for the formation and proliferation of live cells on the surface of the Mg-Ca system experimental alloys only if the Ca percentage is less than 2.5% Ca.

Figure 6. Set of samples prepared for the cell proliferation test.

4. Conclusions

- Mg-Ca alloys can be obtained by melting in the levitation installation under an inert environment, consisting of argon, for protection against rapid oxidation.
- The purity level of the alloys depends on the quality of the metal materials used and on the working conditions (inert gas protection for the melt, the use of perfectly clean solidification moulds, constant heating parameters).
- The degree of homogeneity of the Mg-Ca alloys depends on their Ca concentration. At concentrations up to 2wt%Ca, the homogeneity is acceptable, as no clusters of Mg_2Ca compounds are noted in the central zones of the ingot. The tendency to separate in the form of compounds (Mg_2Ca or oxides) occurs at higher Ca concentrations.
- The hardness of the Mg-Ca alloy metal matrix increases with the Ca content increase, the values ranging from 49 to 87.4 $HV_{0.2}$. For some samples, the increase in hardness was also determined by the presence of inclusions (Si, La, Ce) coming either from paint contamination on the surface of the solidification mold or from the metallic materials used.
- Low homogeneity zones occur as a result of the formation of compounds (Mg_2Ca or oxides), leading to relatively large hardness oscillations (10-20% HV), depending on the measuring zone.

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