Experimental, microstructural and tribological studies of the system Mg-2Ca-5Y

S Lupescu¹, C Munteanu¹*, B Istrate¹, D Luca², M Benchea¹ and G Mahu¹

¹ “Gheorghe Asachi” University of Iasi, Faculty of Mechanical Engineering Department, 43 “Dimitrie Mangeron” str., 700050, Iasi, Romania
² “Gheorghe Asachi” University of Iasi, Faculty of Material Science and Engineering Department, 41 “Dimitrie Mangeron” str., 700050, Iasi, Romania

E-mail: cornelmun@gmail.com

Abstract: Everyday, biomaterials are becoming more widespread in the medical field and also in the metallurgical, aerospace, and even automotive industries. Mg-based biodegradable biomaterials are increasingly being studied and improved for their use in the medical field, even if Mg has a low corrosion resistance and not only can be alloyed to increase its strength and biocompatibility. The most commonly used and known elements with which Mg can be: Ca, Zn, Zr, Gd, Y, Si, Mn, etc. The purpose of this paper is to investigate the properties of Mg-2Ca-5Y alloy in order if it is suitable for use for use in medical applications. Surface morphology was characterized by electronic scanning microscopy (SEM) with EDAX, optical microscopy and X-ray diffraction (XRD). Following the XRD analysis, it was observed that certain specific compounds were formed: Mg₂Ca, Mg₅Y, Mg₅₂Y₅ having the main structural hexagonal phase. Micro-indentation and scratch tests were also performed on the casted alloy. As a final conclusion it is shown that the Mg-2Ca-5Y is recommended for medical applications.

1. Introduction
Mg and their alloys have attracted many researchers for good damping capacity, low density, good stiffness and satisfactory mechanical resistance [1-5]. But the application of Mg-based alloys is quite low due to the casting process. Also, some researchers perform mathematical models on different casting and deposition processes to improve the technology flow [16]. Therefore, the wider application of these alloys is highly dependent on the development of new Mg-based materials with higher corrosion resistance. In general, there are three types of main ternary equilibrium phases in Mg-Ca-Y alloys [7]. There are Mg₂₄Y₅ with a cubic structure, Mg₂Ca with a hexagonal structure that can improve the biocompatibility, precipitation consolidation and grain boundary fixation, Y₂O₃ have high thermodynamics and have shown a reduced degradation rate of Mg-based alloys [9,13]. The RE elements refine the grain boundaries at solidification temperatures, especially for strength enhancing. This increases the operating temperature of Mg alloys used for the transport industry and improves flue and corrosion resistance [6]. The Mg-Ca-Y alloy has excellent properties especially for medical applications, but putting it into practice is limited due to the high cost of Y. In addition, the
mechanical properties of the Mg-Ca-Y alloy increase through specific processing technology [7]. The XRD patterns, microstructure and mechanical properties are investigated during this study [15].

2. Materials and methods

Input materials were purchased from HB Material, Changsha China, having the chemical composition shown in table 1. The samples used were prepared by mixing the appropriate proportions of Mg-based ingots (99.95%), Mg-15% Ca and Mg-30% Y [12]. From these ingots, an experimental composition of Mg-2Ca-5Y was prepared. This composition was prepared using an induction furnace at a temperature of 750 °C under the protection of an inert gas (Ar), and a graphite crucible covered with zirconia. After the ingots, which have 18 mm diameter and 30 mm height, were cooled to room temperature and removed from the furnace, the disks with 18 mm diameter and 4 mm height were cut from experimental ingots. These samples were polished with abrasive paper of different granulations from 150 to 1800 SiC in order to obtain a uniform surface [9]. The microstructures were investigated by electronic scanning microscopy (SEM Quanta 200 3D) equipped with an EDX detector. The surface of each sample was ground and polished to a final finish with an alumina suspension of 0.05 µm. The samples were etched using nitric acid 4% w/w in standard for 5-8 s, thoroughly washed with water and alcohol then dried with hot air. The Leica 5000 DMI optical microscope was used to highlight the microstructures. For diffraction and crystalline structure, an XRD Expert PRO MPD diffractometer with copper-\(\text{Xa}\) ray tube: \(\text{KA}: 1.54\ \text{A}\) was used in the \(2\text{Theta}\) range of \(20^\circ-100^\circ\). The apparent coefficient of friction, hardness and modulus of elasticity were measured using the CETR UTM-2 Tribomer. The micro-scaling analysis parameters are as follows: a constant load of 5 N at a distance of 4 mm for a single determination. And for the indentation test, we also performed determinations with a constant load of 5 N using a metal indenter.

| Alloys       | Mg/Y | Fe  | Ni  | Cu  | Si  | Al  |
|--------------|------|-----|-----|-----|-----|-----|
| Pure Mg     | Mg(99%) | 0.07% | 0.002% | 0.05% | 0.08% | 0.09% |
| Mg15Ca      | Ca(15.29%) | 0.004% | 0.001% | 0.003% | 0.013% | 0.011% |
| Mg30Y       | Y(28.05%) | 0.010% | 0.001% | 0.001% | 0.006% | 0.011% |

3. Results and discussions

3.1. Structural analysis

3.1.1. Optical images.

The optical images of the Mg-2Ca-5Y alloy are shown in figure 1. However, the addition of Y led to the refining of the microstructure. It is presented that the addition of Y can significantly improve the alloy’s properties. As it was presented before, Y has an active element surface and it can easily segregate at the liquid–solid interface or be absorbed onto the growth front.[10] The effect of Y content on grain refinement of the as-cast alloys is possibly related to the strong growth restriction effect of Y atoms. However, this needs to be further confirmed. Firstly, according to lattice matching principle, Y has the similar lattice structure with Mg and can be the core in magnesium alloys. Therefore, a large amount of Y will significantly improve the rate of degradation, Y grains are being also separated but not in totality.

![Figure 1. Optical images of Mg-2Ca-5Y alloy surface](image-url)
3.1.2. **Scanning electron microscopy.**

The aspects of morphology and microstructure in more detail are presented in figure 2 (a, b, c, d). The images are made at different sizes up to 5000X and they highlight some of the phases of Mg alloy after casting and show the compactness and homogeneity of morphology and surface. The grains of alloys have taken different forms after casting the material depending on each master alloy. In figure 2, SEM images show that the Mg-Ca microstructure is in the Mg$_2$Ca lamellar phase, this phase being formed at the grains boundary. Ca atoms are easy to segregate to the grain boundaries. Thus, the segregated Ca atoms may impose a strong drag force on the recrystallized grain boundaries, which also suppresses the growth of the recrystallized grains [11].

![SEM images](image)

**Figure 2.** SEM images of Mg-2Ca-5Y surface

3.1.3. **EDX analysis**

After scanning with the electronic microscope, the approximate chemical composition with an EDX system was checked and the results obtained are shown in figure 3. It is noted that the Y grains or fused with Ca but not entirely.

![EDX analysis](image)

**Figure 3.** Chemical composition of Mg-2Ca-5Y sample

3.2. **XRD analysis.**

The XRD analysis was performed on a Panalytical XPERT Pro MPD diffractometer, X-ray Cu and Cathode tube.

The XRD patterns are shown in figure 4, where pure magnesium is highlighted at 90.46º (2 Theta - as the highest peak). Parameters of all compounds are shown in table 2. The Mg$_2$Ca, Mg, Mg$_2$Y, and MgY compounds were highlighted. The diffraction showed a cubic crystallographic structure. It was shown that Mg$_2$Ca has the same hexagonal crystallographic structure as pure Mg.

![XRD analysis](image)

**Table 2.** Lattice parameters of Mg-2Ca-5Y

| Compound  | Space Group | Crystal system | a (Å) | b (Å) | c (Å) | α (°) | β (°) | γ (°) | Cell volume (10$^6$ pm$^3$) |
|-----------|-------------|----------------|-------|-------|-------|-------|-------|-------|---------------------------|
| Mg$_2$Ca  | P63/mmc     | Hexagonal      | 6,2700| 6,2700| 10,1400| 90    | 90    | 120  | 343,13                    |
Table 3 - Values for Young modulus, hardness, scratch, coefficient of friction and stiffness for all three tests

| Material  | Structure | Phase  | a (nm) | c (nm)  | β (°) | V (m/s) | E (GPa) | H (GPa) | F (GPa) | stiffness  |
|-----------|-----------|--------|--------|---------|-------|---------|---------|---------|---------|------------|
| Mg        | P63/mmc   | Hexagonal | 3.2089 | 3.2089  | 5.2101| 90      | 90      | 120     | 46.46   |
| Mg$_{24}$Y$_5$ | I-43m    | Cubic  | 11.130 | 11.130  | 11.130| 90      | 90      | 90      | 1429.81 |
| MgY       | Pm-3m    | Cubic  | 3.8000 | 3.8000  | 3.8000| 90      | 90      | 90      | 54.87   |

3.3. Scratch and micro-indentation analysis.

Figure 5 shows the scratch and indentation test of the Mg-2Ca-5Y sample. Three attempts were made in 3 different areas, resulting in small differences between them, which show the influence of alloying elements in different areas. Table 3 shows the values for young modulus, hardness, scratch, coefficient of friction and stiffness for all three tests. The coefficient of friction has an average value about 0.74. The results of the micro-indentation test showed a depth between 7.947 μm and 11.256 μm without fracture. Since the young modulus of the human bone is between 8 and 40 GPa, from the state of art documentation, and after the indentation test, the young modulus of the Mg-2Ca-5Y alloy is about 10 GPa. The indentation test was performed at 5 N applied force, resulting an average depth of 10 micros. Other methods, like tensile test, will result a young modulus similar to the human bone.
c) N3

d) Chart of the friction coefficient variation according to the unit of time for Mg-2Ca-5Y

Figure 5. Results of the indentation test for Mg-2Ca-5Y

The penetration trace of the scratch test is not uniform and have different widths as it is observed in figure 6a and b. This test demonstrates that the material obtained after casting does not have a uniform structured and fairly compact composition.

Figure 6b shows that during scratching test, the material breaks at the boundary of Mg grains, where Mg-Ca compound like Mg2Ca has the lowest breaking resistance.

Table 3. Some mechanical properties of Mg-2Ca-5Y

| Mg-2Ca-5Y | N1  | N2  | N3  |
|-----------|-----|-----|-----|
| Depth [μm]| 9.934 | 7.947 | 11.256 |
| Stiffness [N/μm]| 1.454 | 1.009 | 1.254 |
| Young modulus [GPa]| 11.176 | 8.630 | 9.005 |
| COF | 0.718 | 0.756 | 0.747 |
| Hardness [GPa]| 0.369 | 0.463 | 0.327 |

Figure 6. Scratch marks.

After the scratch test, the trace is not uniform over the entire surface of the test, the width trace varies between 183.59-285.64 μm. Also, after the 3 indentations in different areas of the alloy, the traces diameter has very small differences, which shows that the alloy does not have a homogeneous surface.

4. Conclusions

The aim of this work was to obtain a new Mg-based biodegradable alloy, which is composed of two-elements (Ca, Y) for better corrosion resistance, high biocompatibility, elasticity as close to that of the human bone and degradation in time as much as possible. A possible application could be the use of these materials in medicine and especially orthopaedics. Influence of Yttrium contributes to a greater corrosion and mechanical resistance. Morphology research, x-ray diffraction, micro-indentation and
micro-scratch, as well as the EDX test are necessary in order to improve the material through future studies for better osteointegration with the human body. After the XRD test was found that the following crystalline compounds are: Mg$_2$Y$_5$, MgY, Mg$_2$Ca. Mg-Ca has a hexagonal crystallographic structure and Mg$_2$Y$_5$, respectively MgY have the crystalline cubic structure. The addition of Y and Ca in the Mg alloy helps in terms of mechanical and morphological properties. Young modulus is similar to human bone, which makes the alloy to be a proper solution as Mg biodegradable implants. Researches of this material will continue with other tests and experiments in order to obtain biodegradable prostheses that successfully replace classical Co-Cr, Ti and stainless steel alloys.

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Acknowledgment
„This work was supported by a grant of the Romanian Ministry of Research and Innovation, CCCDI – UEFISCDI, project number PN-III-P1-1.2-PCCDI-2017-0239 / 60PCCDI 2018 , within PNCDI III”