ANNALS of Faculty Engineering Hunedoara – International Journal of Engineering
ISSN 1584 - 2665 (printed version); ISSN 2601 - 2332 (online); ISSN-L 1584 - 2665

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EXPERIMENTAL RESEARCH OF THE MECHANICAL PROPERTIES OF BIO–DEGRADABLE MAGNESIUM ALLOYS FOR AN ORTHOPEDIC APPLICATION

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Abstract: Magnesium and its alloys have long been used in orthopaedic implants due to their biocompatibility properties. In the last decades, due to the development of materials science and technology, interest in magnesium and magnesium alloys increased. Choosing the essential elements as alloying elements to optimize composition design for new biodegradable Mg alloys with good biocompatibility seems to be the most effective method of eliminating some fundamental problems. The selection of alloying elements in biodegradable Mg alloys should be based not only on the improvement of mechanical properties, but also on the consideration of biocompatibility. The addition of alloying elements can improve the strength of Mg by means of a grain–refining mechanism and solid solution strengthening. This paper presents the results of the actual experimental research on the mechanical properties of some biocompatible magnesium–based alloys.
Keywords: magnesium alloys, biomaterials, implant production, mechanical testing, and plastic deformation

1. INTRODUCTION

Usage of biomaterials in the replacement of parts of the body affected by illness, trauma and infections throughout life is very common [1].

Driven by the increasing economic burden associated with bone injury and disease, biomaterial development for bone repair represents the most active research area in the field of tissue engineering [2].

Metallic materials are the most common choice when talking about their use in orthopaedic applications, such as repairing or replacing damaged bone tissue [3].

The mechanical properties of some biodegradable metal biomaterials studied so far are presented in Table 1.

To improve the mechanical properties of implants made of magnesium alloys, the main impurities encountered in these alloys were considered, such as: Iron (Fe), Nickel (Ni), Copper (Cu).

Manganese as an alloying element has the property to clean these impurities in the alloy. Frequently used in the metallurgical industry to produce Magnesium alloys are Aluminium (Al), Zinc (Zn), Manganese (Mn), Calcium (Ca), Lithium (Li), Zirconium (Zr) and rare earths (RE). Zinc improves the qualities of most mechanical alloys, and Calcium and Zirconium have a positive effect on mechanical properties, at low concentrations, 2 wt% and 0.42 wt%.

Critical defects in bone have in many cases presented insurmountable challenges to the current standard treatment for bone repair. In this context, one of the intensively researched classes of metals in the last centuries is the 'biodegradable metals'.

Over the time, many tests have been done on biodegradable metals.

Implants made of metallic materials (metals or alloys) have shown their functionality in implantology; however, they are subjected during use to the action of external forces (mechanical tests).

The effect of these external mechanical attempts is that when they create internal forces, the metallic materials can deform.

Table 1. The mechanical properties of some biodegradable metal biomaterials [4]

Metallic biomaterial (name, metallurgical state, chemical composition [wt%])	Density [g/cm3]	Drip limmit [MPa]	Rupture tension [MPa]	Young's module [GPa]	Elongation [%]
316L type austenitic stainless steel, deformed state and heat treated Fe, 16–18.5%Cr, 10–14%Ni, 2–3% Mo, <2%Mn, <1%Si, <0.03%C	8.00	190	490	190	40
Iron, deformed condition and heat treated 99.8%Fe	7.87	150	210	200	40
Fe35Mn, Fe, 35.5% Mn, 0.04 C	–	235	550	–	32
FeMnPd, obtained by powder metallurgy and thermomechanical treatment Fe, 10.2%Mn, 0.92%Pd, 0.12%C	–	850	1450	–	11
Magnesium, Heat treated state 99.98% Mg	1,74	90	160	45	3
WE43, Heat treated condition Mg,3.7–4.3%Y,2.4–4.4%Nd,0.4–1%Zr	1,84	170	220	44	2
MgZnMnCa alloy, Molded state Mg, 0.5%Ca, 2.0%Zn, 1.2%Mn	–	70	190	–	9
MgCa alloy, Extruded state Mg, 1%Ca	1,74	140	240	45	11

The behaviour of a piece under mechanical stresses produced by external forces depends on certain attributes specific to the metallic material from which the piece is made, called mechanical properties.
Typically, mechanical tests are the one who proves the mechanical properties of metallic materials, consisting in the requesting specimens under conditions appropriate to highlight the properties sought.
Mechanical tests provide qualitative data on the behaviour of materials under the appropriate stress conditions of these tests, and the values of physical or conventional quantities, called mechanical characteristics, which can be used as quantitative parameters for the expression of mechanical properties [4].
Although initial shortcomings such as corrosion and insufficient strength have been overcome, more recent designs of bone replacing biomaterials have not solved all problems. Moreover, clinical studies of newer biomaterials types have failed to show a superior outcome.
Much attention has been given lately to the surface processing and surface coating of metals with the purpose to achieve fast and intensified biosynthesis of connective tissue between the supporting implant placed in contact with the traumatized bone.
Despite that, scientific evidence to date strongly suggests that bone loss after implantation of prostheses is caused by stress shielding which plays a greater role than the size of the area of bone–plate contact [5].
Moreover, it has been proven long time ago that mechanical aspects and mainly the rigidity of synthetic bone are the most crucial factors influencing the post–surgical healing process [6].
On the other hand, elastic fixation allowing the motion for bending, torsion, and shear as well as compression/distraction is not desirable as it leads to delayed union or non–union.
The ideally designed synthetic bone shall be mechanically resistant, assure stability without causing rigidity, and shall stimulate bone cells to promote osteointegration. Such a complex task requires several newly developed material combinations, advanced manufacturing techniques and careful validation. With respect to mechanical performance, the Young's modulus of Mg alloy is 45 GPa, being significantly lower than that of the steel alloys and aluminium alloys.
Metallic biomaterials have been investigated in non–conventional reconstructive surgery of hard tissues / organs [7] and perspectives have been established for the development of new magnesium–based alloys for bone tissue engineering and regeneration [8].

2. EXPERIMENTAL

— Materials and methods

Based on the above observation, the present investigation aimed to the manufacturing and characterization of magnesium alloys with different concentrations, as indicated in table 2.

Table 2. The chemical composition of the investigated magnesium alloys

Product	Zn	Zr	Y	Ca	Ag	Fe	Si	Ni	Cu	Others each	Mg
	%	%	%	%	%	%	%	%	%	%	%
ZQ63	7.2	1.3	0.20	–	1.5	0.005	0.01	0.001	0.001	0.01	balance
ZQ71	6.4	1.0	0.16	–	2.5	0.004	0.01	0.001	0.001	0.01	balance
MgCa	–	–	0.02	0.99	–	0.002	0.01	0.001	0.001	0.01	balance

— The role of alloying elements

≡ Calcium

Calcium is the fifth most widespread element in the earth's crust. A certain amount of added Ca can improve the metallurgical quality of the Mg alloys, attenuating the oxidation both in the melt and in the casting during the heat treatment. The addition of Ca can improve grains and thus increase resistance and creep resistance. The reason why Ca is a good alloying element in the biodegradation of magnesium alloys is its benign biological effects.

It is an essential element of the human body and, almost 99% of its content can be found in bones and teeth. Oral Ca administration may help develop strong bones and treat bone related diseases, such as osteoporosis [9]. It has been reported that inadequate exposure to sunlight and Ca intake during rapid growth at puberty can lead to hypocalcemia, hypovitaminosis D and possibly rickets [10].

≡ Zinc

Zinc has a solid solubility of 6.2 wt%, which can provide the possibility of forming solid curing solutions and related to the curing age. The high zinc content of the Mg alloys will increase the temperature of the recrystallization interval, reducing the fluidity of the alloy and thus damaging the cast ingot.

Zinc is an essential element for the human body, involved in bone metabolism, maintaining physiological functions in the body and improving the activity of osteoblast phosphatase in bones [11]. However, neurotoxicity is reported in Zn at high concentrations [12]. Zn^{2+} is also considered to have antibacterial properties.

≡ Silver

Silver is a precious metal element, quite ductile and malleable. The solubility of Ag in Mg is 15.14 wt% (3.83at%), which is much higher compared to Ca, Sr, Zn and many other common alloying elements in Mg alloys.

The addition of Ag is envisaged for improving the strength of the alloys for a durable solid solution effect. To date, the most important characteristic of Ag for clinical use has been its antibacterial property. The most important utility of silver is currently a biocide to prevent infection of places with long–term problems, including burns, traumatic wounds and diabetic ulcers [13]. The extremely high bioactivity of Ag + can rapidly penetrate bacterial membranes, causing cell distortion and loss of viability through interaction with enzymes and other proteins in bacteria. Although Ag is considered hazardous to human beings at risk of argyrias, Hardes et al. (2007) and Bosetti et al. (2002) found that the presence of Ag has negative effects on the biocompatibility of the materials [14,15].

≡ Zirconium

Zirconium has an effect that changes the structure of the alloy so that its content does not exceed 0.002%. Addition of Zr can result in higher purity and therefore a more corrosion resistant Mg alloy. The distribution of Zr is concentrated in the central area of a particle. Thus, the alloy is less resistant to corrosion along the cell boundary [16].

— Mechanical testing

The behaviour of a material can be predicted depending on the tensile properties, other than uniaxial tensions. The strength of a material is the main concern, which is measured by the stress necessary to determine plastic deformation, being the maximum effort that the material can withstand. In technical design, the measures of strength to be used are considered.

Also, ductility is the ability of the material to deform plastic before fracturing, rather being in the material specifications to ensure quality and toughness. Low ductility in a tensile test often is accompanied by low resistance to fracture under other forms of loading.

Elastic properties also may be of interest, but special techniques must be used to measure these properties during tensile testing, and more accurate measurements can be made by ultrasonic techniques.

The alloys were as–cast into moulds, and subsequently, for the improvement of the mechanical properties, they were subjected to thermal treatments such as hot extrusion and hot laminar casting. As a result of thermal treatment, the grains of alloys have diminished, which leads to better corrosion resistance.

Improving the quality of mechanical properties can be done by adding very low concentrations of calcium, zirconium, silver and zinc.

Magnesium alloy samples to be subjected to mechanical tests have been properly prepared in order to avoid unsatisfactory and incorrect test results. It is important to track the exercise and preparation of specimens, to ensure the accuracy and influence of test results. The cross–sectional area of the specimen should be smallest at the center of the reduced section to ensure fracture within the gage length (figure 1a). For this reason, a small taper is permitted in the reduced section of each of the specimens. Rectangular specimens shall be 6 mm wide in accordance with Figure 1b [17].

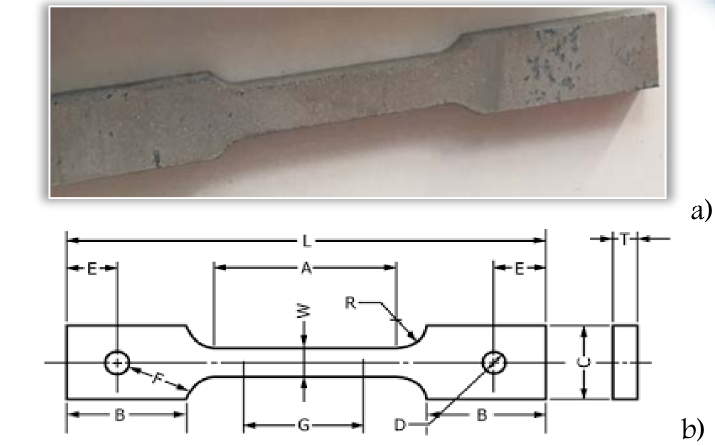

Figure 1. Rectangular Tension Test Specimens
a) experimental test sample; b) schematic representation [17]

Legend	Dimension, mm Subsize specimen 6mm Wide
G-Gage length	25.00±0.10
W-Width	6.01±0.05
T-Thickness	Thickness of material
R-Radius of fillet, min	6
L-Overall length, min	100
A-Length of reduced section, min	32
B-Length of grip section, min	30
C-Width of grip section, approximate	10

Tensile tests are performed for several reasons, their results being used for the selection of materials in engineering applications. The tensile properties are included in material specifications to ensure quality and in developing new materials and processes. The cross–sectional area of the gage section is reduced relative to that of the remainder of the specimen so that deformation and failure will be localized in this region. The gage length is the region over which measurements are made and is centred within the reduced section. The distances between the ends of the gage section and the shoulders should be great enough so that the larger ends do not constrain deformation within the gage section, and the gage length should be great relative to its diameter. Otherwise, the stress state will be more complex than simple tension [18–20].

3. RESULTS AND DISCUSSIONS

Five experiments were performed for each type of magnesium alloy and based on the experimental results were drawn stress–strain curve. After performing the test, at the appearance of the breaking effect the sample shows as in Figures 2–4.

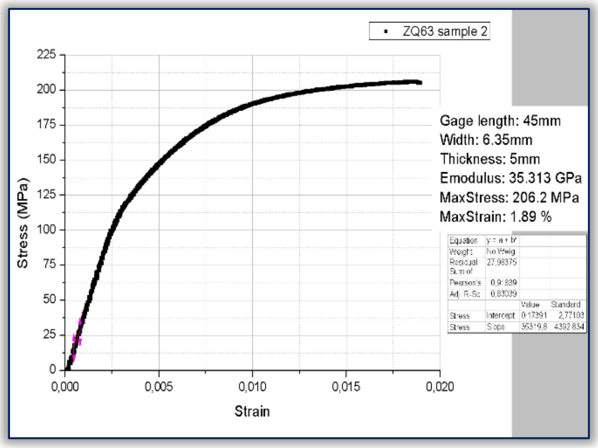

Figure 2. Stress–strain curve for ZQ63 alloys

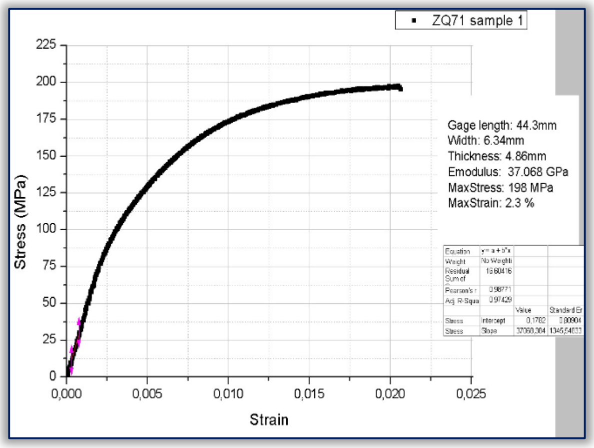

Figure 3. Stress–strain curve for ZQ71alloys

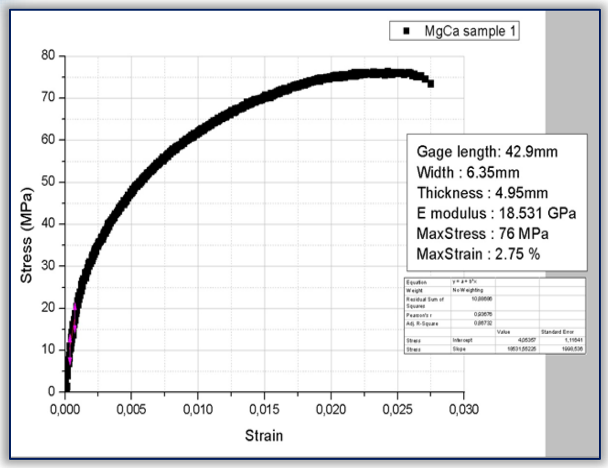

Figure 4. Stress-strain curve for MgCa alloys

By analysing the results obtained in the mechanical testing of the three types of magnesium alloys studied, shown in the figures 5–19, the following conclusions can be drawn:

- Average values of Elastic Modules was registered for the test alloy ZQ71– 35,827 GPa, and the minimum for the test alloy MgCa–17,446 GPa, while for the test alloy ZQ 63 the average value was 35,381 GPa. The justification of these results can be made by the presence of the elements Zn, Zr and Ag in the alloys ZQ71 and ZQ 63, the percentage concentration of Ag in the ZQ71 alloy gives it the highest value for Elastic Modules. The comparative graphical representation of the values for the three types of alloys is shown in the figure 6.
- Average values of Maximum Stress was registered for the test alloy ZQ63–177,28 MPa, and the minimum for the test alloy MgCa–68,452 MPa, while for the test alloy ZQ 71 the average value was 148,82MPa. The justification of these results can be made by the presence of the elements Zn, Zr, Y and Ag in the alloys ZQ71 and ZQ 63, the percentage concentration of Ytriu in the ZQ63 alloy gives it the highest value for the Maximum Stress. The comparative graphical representation of the values for the three types of alloys is shown in the figure 7
- Average values of Maximum Strain was registered for the test alloy MgCa– 1,7274%, and the minimum for the test alloy ZQ71– 1,514%, while for the test alloy ZQ 63 the average value was 1,458%. The justification of these results can be given by the fact that in the MgCa alloy there are no elements Zn and Zr, which negatively influence of Maximum Strain. The comparative graphical representation of the values for the three types of alloys is shown in the figure 8.

After performing the test, at the appearance of the breaking effect the sample shows as in figure 5.

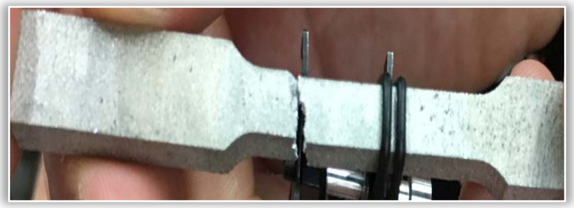

Figure 5. Specimens after testing

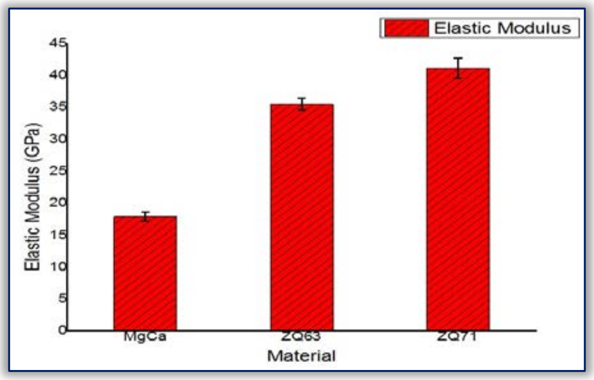

Figure 6. Elastic modulus compared to the three types of magnesium alloys studied

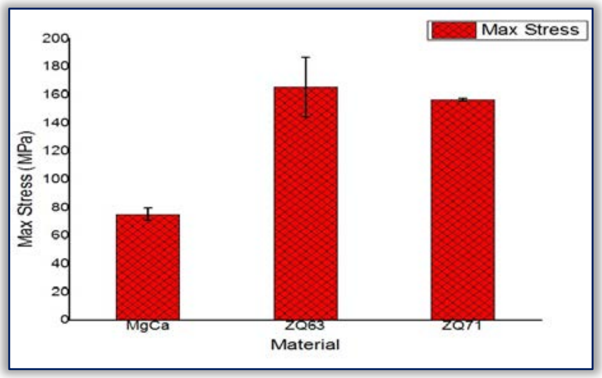

Figure 7. Maximum stress compared to the three types of magnesium alloys studied

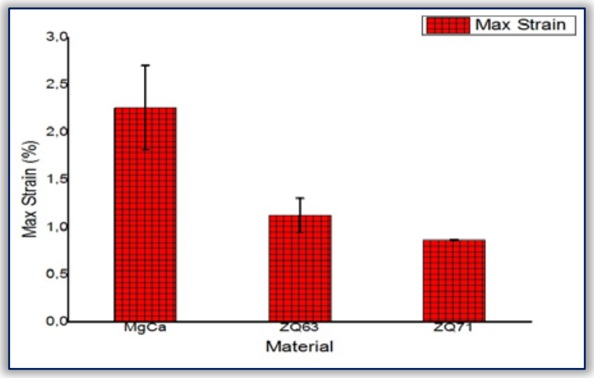

Figure 8. Maximum strain compared to the three types of magnesium alloys studied

4. CONCLUSIONS

Most magnesium alloys that have been investigated so far as potential implant materials are quite complex and contain alloying elements with toxic potential.

The alloying elements influence the mechanical and physical properties of magnesium alloys in industrial applications. However, alloying is limited when designing magnesium alloys for biomedical applications when the toxicity of alloying elements is considered.

Biodegradable magnesium alloys have several advantages over the biodegradable materials used today, such as polymeric, bio ceramic and composite materials, due to their superior mechanical properties. The mechanical properties are less than the one for stainless steel 316L or Ti, and more superior than polymers.

Acknowledgment: All the authors contributed equally to the development of the experimental research and were done as a result of participating of Elisa–Florina PLOPEANU in a training program at the University of Patras Greece (01/03/2018–31/05/2018).

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ANNALS of Faculty Engineering Hunedoara – International Journal of Engineering
ISSN 1584 – 2665 (printed version); ISSN 2601 – 2332 (online); ISSN–L 1584 – 2665

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