Assessment of magnesium calcium alloys improved by rare earths addition for medical implants

A Savin1, F Novy2, ML Craus13, N Iftimie1, R Steigmann1, B Istrate4 and C Munteanu4
1National Institute of R&D for Technical Physics, Nondestructive Testing Department, 47 D. Mangeron Blvd, Iasi, 700050, Romania
2 University of Zilina, Faculty of Mechanical Engineering, Univerzitná 8215/1, 01026, Žilina, Slovak Republic
3Frank Laboratory for Neutron Physics, Joint Institute for Nuclear Research, 6 Joliot-Curie St., Dubna, Moscow Region, Russia
4Gh. Asachi Technical University, Faculty of Mechanical Engineering, 43 D. Mangeron Blvd, Iasi, 700050, Iasi, Romania
E-mail: asavin@phys-iasi.ro

Abstract. Biodegradable materials are used as alternative implants for orthopedic applications due to suitable strength, fatigue resistance, ductility and biocorrosion resistance which are features for biodegradable implants. Mechanical properties can be improved by adding alloying elements. The decrease of the corrosion rate of Mg can be induced by modifying the structure and phase distribution. Thus, Mg alloys have been designed to meet the requirements of bone repair implant materials by adding Calcium and Yttrium or Gadolinium. Mg based alloy with Ca and Y/Gd had been proved to be a biocompatible material, osteoconductive and biodegradable and can be used in bone repairs. The system is defined as Mg100-(n+x) Ca(n) RE(x), varying the RE concentration in order to slow the degradation process. Beside morphological combining characterization SEM, EDX, with non-invasive testing is required to be carried out the determination of mechanical characteristics. The interest in this study is to analyze the influence of RE over elastic properties of these alloys in order to choose the best values appropriate with human bones, using Resonant Ultrasound Spectroscopy and ultrasound method.

1. Introduction
The bone is a heterogeneous composite material, with a hard calcium-based matrix and mineral salts and is the most prone to fractures or tissue rupture [1]. Treating bone fractures involves all branches of engineering and medicine [2]. Using bone grafts in cases in which the bone damage is extensive – has proven to be unhelpful in a wide variety of cases. Bioimplants are the alternative to bone grafts. The first requirement of any biomaterial is biocompatibility with the host tissue [3]. The absence of biocompatibility leads to implant intolerance with secondary effects. Therefore, studying the properties of biocompatible materials which can be included in prostheses [4]. Mg based alloys (Mg as a resorbable and osteo-synthesis biomaterial) are good candidates for biocompatible materials and can be used for bone remodeling [5]. Selecting the alloy elements as well as surface modification techniques for biocompatible Mg-based materials are important steps to be taken in the obtaining structures which can be used in bone re-modelling [6]. In-situ medical studies are particularly
important as they emphasize the mechanical behavior of the prostheses on a long term as well as their resistance to biological corrosion.

Also, some researchers perform mathematical models on different casting and deposition processes to improve the technology flow [6]. Usually Ca is added to control corrosion rate of Mg alloys and thinning grain boundaries. Rare earths are often used as addition elements to improve alloys properties as biocompatibility and creep resistance. The system is defined as Mg100-(n+x) Ca(n) RE(x), (x = 0, 0.5, 1, 1.5 wt. %) varying the RE concentration in order to slow the degradation process. These range of tests are imperative in order to ensure the safety and reliability of these composite materials which are widely used as implants/coatings. The paper is aiming to study the properties of these alloys containing the smallest concentration of Gd (x=0.5 wt. %). This is justified, since an increased concentration of Gd in the alloy is also increasing the biotoxicity of these materials [7].

By combining morphological characterization with SEM, EDX, and non-invasive testing is required to be carried out to offer a better overview of the properties of this type of alloys. The interest in this study is to analyses the influence of RE over elastic properties of these alloys in order to choose the best values appropriate with human bones, using Resonant Ultrasound Spectroscopy (RUS) and ultrasound method (US). It is known that pure Mg has a poor mechanical performance, the mechanical requirements of the implant daily cannot be satisfied [8-10] and in addition Mg alloys have low corrosion resistance and therefore degrade rapidly in the human body.

2. Materials and methods
Mg alloys used in medical applications have the selection of alloying elements not only based on their ability to improve mechanical properties and corrosion rate, but also on their biocompatibility degree [8]. Alloying Mg-based materials with other elements increases their mechanical properties. Depending on the alloying metal, different structural characteristics of the alloy can be obtained, including a small dispersion in grain sizes as well as more homogeneous structures [11]. By introducing dopant elements (Mn, Gd, Yn or Zr) in the Mg0.5Ca, an improvement of the metal ductility and resistance can be obtained, and the formation of eutectic phases can be favourable (e.g. α-Mg + Mg2Ca). The Mg0.5Ca(Y/Gd)x for (x=0, 0.5, 1, 1.5 wt. %) having selected with high purity elements as raw materials (Mg-99.7%, Mg-15Ca and Mg-25Gd master alloys) were melted in an induction furnace under argon atmosphere in a graphite crucible. The final chemical composition 0.5Ca and (x wt. %)Y/Gd was performed after repeated casting operations and was analysed by EDX using SEM Quanta 200 3D DUAL BEAM coupled with an EDS-EDAX detector. The chemical composition of the alloy was analysed with a Scanning Electron Microscope SEM VEGA II LSH manufactured by the TESCAN Co., the Czech Republic, coupled with an EDX QUANTAX QX2 detector manufactured by the BRUKER/ROENTEC Co., Germany. A microstructure with interconnected pores within the alloying matrix can lead to a low density implant whose mechanical properties can be modified given that the pore size and shape have major effects on the elastic properties of the metals [12]. The Mg-0.5Ca-xY (x=0, 0.5, 1, 1.5 wt. %) alloy with a varied Y concentration has been presented in [13]. A new strategy is however necessary for the study of Mg-based alloys doped with rare elements as these display superior mechanical properties, creep resistance and bio-corrosion and do not trigger a toxicity response once implanted in the body [14]. EDS analysis of chemical composition of Mg0.5Ca xGd samples are present in table 1.

| No | Samples         | Mg wt.% | Ca wt.% | Gd wt.% |
|----|-----------------|----------|---------|---------|
| #1 | Mg-0.5Ca        | 99.48    | 0.47    |         |
| #2 | Mg-0.5Ca-0.5Gd  | 98.72    | 0.67    | 0.61    |
| #3 | Mg-0.5Ca-1.0Gd  | 98.36    | 0.67    | 0.96    |
| #4 | Mg-0.5Ca-1.5Gd  | 97.62    | 0.59    | 1.79    |
For the SEM analysis, samples with cubic geometries (10 mm size) have been synthesized. This sample shape has been necessary to facilitate an analysis using RUS. The samples have been cut and embedded into an EpoFix Struers resin for a metallographic analysis using DiaPro 3 μm diamond suspensions and Tegramin 30 equipment for grinding and polishing. During the sample preparation, a slightly deformed surface layer is usually created. To eliminate this layer, we applied a chemical treatment (for 10s was applied 55 vol % ethanol with 30 vol % distilled water, 10 vol% acetic acid, and 5 vol % of nitric acid). Figure 1 emphasizes the typical grains of α Mg, with formation of eutectic Mg2Ca compounds, having lamellar aspect at the grains boundary. The morphology of the surfaces have been examined for all the Mg0.5Ca1xGd, knowing that grain refinement can lead to an increased mechanical resistance [15] and that the presence of grain boundaries possible could stop the formation of dislocations. Including Gd in the base alloy also increases the corrosion resistance [16]. It is well known that structural factors such as grain sizes, shapes, distributions as well as deformation twins as well as dislocations have a high contribution to corrosion existence [17].

![Figure 1. SEM of sample#2; magnification: 250X.](image1)

![Figure 2. Representative microstructure of grains for sample #2.](image2)

The SEM surface micrographs have shown that these are semi-compact. Figure 2 emphasizes the microstructure of sample #2 using an AxioCam MRc5-Zeiss. Twining inside the twinning zone is high for this sample. According to Ref. [18], local stress fields associated with twinning play an important role in material behaviour during deformation and fractures, but are difficult to characterize experimentally. Non-destructive testing using ultrasound-based methods have been done to determine the longitudinal and transversal propagation speeds in these samples as well as for the determination of the homogeneity degree in these samples, the Young’s modulus, shear modulus and Poisson ratios. This characterization method offers volumetric details.

3. Experimental set-up, results and discussions
The experimental setup used for the determination of propagation speed is shown in figure 3. Methods based on the time of flight measurement evaluate the elastic wave velocities that occur in the material as well as their attenuation [19].

![Figure 3. Ultrasound determination of propagation velocities.](image3)
Longitudinal velocity wave $C_l$ was measured using a sensor G5KB GE with central frequency of 5 MHz, the coupling being assured by coupling gel; transversal velocity wave $C_t$ was determined with a sensor MB4Y GE with central frequency of 4 MHz. The PR 5073 Pulser Receiver Panametrics NDT USA is used for the emission impulses and the reception of the signals.

The equations for calculating these velocities are discussed in [20] and the results are shown in table 2.

**Table 2.** Some mechanical characteristics of Mg-0.5Ca-xGd.

| Sample | Gd Comp. (%wt.) | length [mm] | Density [g/mm$^3$] | Young’s Modulus [GPa] | Shear modulus [GPa] | Poisson’s ratio | $C_l$ [m/s] | $C_t$ [m/s] |
|--------|----------------|-------------|--------------------|-----------------------|---------------------|----------------|-------------|-------------|
| #1     | 0              | 10.32       | 1680.49            | 37.7                  | 14.42               | 0.307          | 5555        | 2930        |
| #2     | 0.5            | 9.98        | 1567.30            | 41.43                 | 15.74               | 0.315          | 6105        | 3170        |
| #3     | 1.0            | 9.78        | 1524.31            | 42.43                 | 16.24               | 0.305          | 6171        | 3265        |
| #4     | 1.5            | 10.47       | 1650.97            | 44.86                 | 17.03               | 0.316          | 6204        | 3212        |

Hardness was measured with NOVA 360 instrument for microindentation time 10s having value 43.8HV5. Microscopic analysis was obtained used AxioCam MRc5-Zeiss (figure 4).

The Resonant Ultrasound Spectroscopy (RUS) implies the investigation of resonant structure of a compact sample as cube, parallelepiped or short cylinder [21]. The method is based on the estimation of resonant eigenfrequencies [22], based on an eigenvalue and eigenfunction method. The experimental set-up is presented in figure 5(a) and in figure 5(b) is presented the sample layout between the sensors.

**Figure 4.** Example of a formed Vickers indentation (100X).

**Figure 5.** RUS Experimental setup: (a) schematic block diagram; (b) sample measurement.

The RUS method, is based by ultrasounds generated and received using two compressing wave transducers without contact force and without contact solutions [22].
The diagonal contact ensures the polarization orientation for a minimum torsion response but maximum flexural or symmetric axial modes [23]. The method is based on the principle that the resonant mechanical response of solids is strongly related to the elasticity modulus, shape and density and allows to identify the sample inhomogeneities. The technique is applicable only to samples with well defined, but small dimensions. Resonant (or natural) frequencies of a system can be either measured or calculated by solving equations of motion for the known shape [24]. The reverse is also true; if resonant frequencies of an object are known, its elastic properties can be determined [24-26]. Inhomogeneity in an object may be identified from a resonant frequency spectrum by resonant frequency shifts, peak splitting, increases in peak width and changes in amplitude. The resonant frequencies are influenced by the material geometry as well as the elastic constants of the material which define the relationship between the applied stress $\sigma$ and strain $\varepsilon$. For the sample testing, we applied a frequency sweep between 120 and 210 kHz in 100 Hz steps. The signal detected by the Network/Spectrum/Impedance Analyzer 4395A Agilent has been then amplified and applied to the ultrasounds sensor. The resonance spectrum is shown in figure 6.

The first peak of the RUS spectrum for sample #2 appears at a frequency of 131 KHz. To evaluate what resonances will be observed for the sample, it is necessary to simulate the resonant frequencies and compare these with those experimental obtained to four specimens with different concentration of Gd. Numerical simulations (in a wide variation range of $G$ and $\nu$) it resulted that always the first peak corresponds to a torsional mode which, in addition, is the fundamental torsional mode. Using procedure indicated in [27] and taking $G$ at the determined value, the value of the Poisson coefficient $\nu$ was swept within a reasonable limit in accordance with the values determined between 0.3 and 0.32, which implies the modification of the $C_{11}$ and $C_{12}$ elements in the elastic matrix C [28]. In [29] it is show that each mod a samples must fall into the following three categories [30]: torsional axisymmetric pure share motion; extensional axisymmetric mixtures of compression and shear modulus; flexural modes (these modes occur in pairs named doublets, with the same resonance frequency). Most of the natural frequencies of an oscillating cube do not respond to analytical solutions. Figure 7 describes the typical response of the two tested samples, #1, and #2 in a frequency range comprised between 120-210 kHz chosen based on our preliminary analysis performed on similar alloys.

The oscillation eigenfrequencies were calculated based on the parameters set presented in Table 2 using SolidWorks 2018, Simulations Toolbox. Note that the figures in SolidWorks are ¾ view, with the axes associated with them. The theoretical predictions are used to identify the frequencies in the resonance spectrum. A better correspondence can be obtained between the FEA and RUS results, which can be expected given the near perfect geometry of the samples. The frequency sweep has included a large number of excitation frequencies. We estimate that the four modes with the smallest orders delivered the best frequency data, two extensional modes (#1(a); #2(a)) and two flexural modes (#1(b); #2(b)) for samples.
Figure 7. Representative modes for 120-210 kHz frequencies range samples: 
#1 (a) extensional 124 kHz; (b) flexural 219 kHz; and #2 (a) extensional 205 kHz; 
(b) flexural 131 kHz.

In most cases, approximation methods as finite element method (FEM) or Rayleigh-Ritz method [31] must be used for estimating the eigenfrequencies of normal modes. Red colour represents maximal displacements and the minimal ones are presented in blue. The simulated information is very important to determine which of the resonances are observable for an investigated spectrum. The modes were identified by visual analysis of the mode shape predicted by nodal eigenvectors.

4. Conclusions
New alloy elements such as Y, Nd and Gd are can open a wide variety of perspectives for Mg based materials used in biomedical applications as they have the potential to improve the strength and fracture resistance. Mg alloys, with the chemical structure Mg0.5CaGd, have a variety of properties which depend on the chemical composition. Morphological analysis using EDS as well as RUS was required to correlate the data obtained with those proposed by the research, i.e. the proximity of mechanical parameters of the alloy to the human bone. Deformation twins and the presence of many sample areas with a lack of clear grain orientation as well as a high local dislocation density can be emphasized through the analysis of RUS spectra, based on various peak shifts occurring at specific resonance frequencies.

5. References
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