Noninvasive evaluation of elastic properties for magnesium-calcium biodegradable alloys

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Abstract. Bone injuries can be fixed and stabilized using degradable implants from magnesium-calcium alloys. Mg and Ca being natural elements in human body, they are easiest to be absorbed without causing toxicity problems. The aim of the paper is to present the effect of Gd and Mn addition in 0.5wt.% in order to improve elastic properties of Mg-Ca₀.₅₋[E], (E = Mn or Gd) and possibility to be used as biodegradable materials. The addition of Mn / Gd in the binary MgCa alloy modify the structural properties of the alloy (analyzed as elastic properties, respectively crystallographic structure). The measurements and the results calculus were carried out using the ultrasound methods and the Resonant Ultrasound Spectroscopy.

1. Introduction

The human body can selfheal but in a limited measure, when the bones and surrounding tissues are damaged due to illness, breaks, injuries. Thus, the healing is supported by prostheses from biomaterials to increase the chance of good recovery.

The most used biomaterials are Mg based alloys, Mg being a natural element of the human body and it has an essential role in metabolism [1]. Mg alloys as biodegradable implant has as advantages lower density 1.738g/cm³, closed with cortical bone, protection against stress in orthopaedical implants, a good biocompatibility and non-toxicity [2], good degradation beneficial for temporary exposure to an implant. At the same time, disadvantages such as the low elasticity (sometimes beneficial in stress protection to avoid inducing deformities) should be mentioned; high rate of degradation (time of degradation must be correlated with the process of bone reconstruction) [3], the release of hydrogen may accumulate in the soft tissues around the implant [4].

The corrosion rate represents a constraint, being a major bottleneck in using Mg alloys due to the generated sub-products (hydrogen, OH-, hydroxide anion) [5,6].

The control of physical-chemical properties of Mg based alloy by doping with Ca, Y, Cu, Mn, Zr, Gd can lead to the improvement of mechanical properties by refining grains and intermetallic phases,
and, also, can control the degradation speed [7] (limited due to the solubility of elements in Mg). Studies over MgCa alloys with different Ca content show that the maximum solubility of Ca in Mg on the phase diagram is reduced [8,9] and increasing the Ca content make alloy to be brittle [10]. The influence of Ca content over the mechanical properties of MgCa binary alloys as well as over the electrochemical properties of alloys were well studied [11,12], trying to obtain microstructures with compromises between mechanical properties and degradability kinetics.

Addition of Mn to MgCa alloys helps to modify the morphology, form intermetallic phases which remove iron and other heavy metals in intermetallic compounds, leading to the increase of the corrosion, stress and creep strength [13] for a Ca concentration below 1wt.% [2]. Mn forms a protective layer during oxidation of Mg [14]. Mn is a micronutrient with a significant role in the metabolic cycle of amino acids but which can become neurotoxic when it is high in the alloy or overlaps with other elements in nutrition [15, 16]. Gd additions increase the strength of Mg alloys [17].

Variable content of E=Mn/Gd \( [x = 0.5; 1.0; 1.5; 2.0; 3.0 \text{ wt.} \%] \) is used to improve elastic properties (i.e. Young modulus \( E \); shear modulus \( G \) and Poisson ratio \( \nu \)) of MgCa alloy.

The paper analyzes the biodegradable MgCa\(_{0.5}\)(E) alloy where E is Mn or Gd and \( x=0.5 \text{ wt.} \% \), using non-invasive methods such as US and RUS and microstructural properties in order to promote this alloy in stabilizing bone fractures.

### 2. Materials and methods

The ingots of MgCa\(_{0.5}\)E\(_{0.5}\) alloys were obtained following the procedures developed by Faculty of Materials Science and Engineering, Gheorghe Asachi Technical University Iasi [18]. The MgCa\(_{0.5}\)Mn\(_{0.5}\) alloys were obtained from commercially pure Mg (99.7 wt.%) and Mg-15wt.% Ca (99%) and Mg-3wt.%Mn (98.9%) master alloys [19] and for MgCa\(_{0.5}\)Gd\(_{0.5}\) have been selected with high purity elements as raw materials Mg (99.7 wt.%) and Mg-15wt.% Ca (99%) and Mg-25wt.% Gd master alloys. The alloys were melted in an induction furnace under argon atmosphere in a graphite crucible as the method described in [19]. Samples with 10x10x10 mm were cut from mini-ingot without inducing flaws or thermal/mechanical stresses.

The microstructure of samples was analyzed using AxioCam MRc5-Zeiss. The final chemical composition MgCa\(_{0.5}\)E\(_{0.5}\) was analyzed by scanning electron microscopy (SEM FEI Quanta 200 3D, dual beam, equipped with energy dispersive X-Ray spectroscopy analysis unit—Xflash Bruker, Harvard, MA, USA) [20]. The phase composition, the types of crystal structure bulk samples, microstructural characteristics were obtained using a conventional X-ray diffractometer (Xpert Pro MPD PANalytical diffractometer (Phillips) with CuK\(\alpha\) radiation (figure 1).

![Figure 1](image1.png)

**Figure 1.** Observed, calculated and the difference between observed and calculated diffractograms for a) MgCa\(_{0.5}\)Gd\(_{0.5}\); b) MgCa\(_{0.5}\)Mn\(_{0.5}\).
The phase composition as well as type of crystal structure of crystallographic phase were determined by conventional X-ray diffractometers (Xpert Pro MPD PANalytical diffractometer (Phillips) with CoKα radiation and a BRUCKER AXS D8- Advance diffractometer) with Cu-Kα radiation. The tests of texture of the MgCa0.5Mn0.5 alloys were performed by using PowderCell program.

In order to determine the elastic properties of the samples, the ultrasound (US) method has been employed. The values of Poisson ratio, Young modulus, Shear modulus were calculated using two types of waves propagating in elastic medium, longitudinal c_l and transversal c_t.

The method uses pulse-echo technique with a delay line [21], required due to small dimensions of the samples. Send receiver US transducers were used for measurements, G5KB – GE for longitudinal waves, respectively MB4Y GE for transversal waves. The signals were generated using PR 5077 Pulser Receiver – Panametrics, using the method described in [22]. The results are presented in table 1 with references to binary alloy MgCa0.5.

| No. | Composition       | Density [Kg/m³] | Young modulus [GPa] | Shear modulus [GPa] | Poisson ratio | C_l [m/s] | C_t [m/s] |
|-----|------------------|----------------|--------------------|--------------------|---------------|-----------|-----------|
| #1  | MgCa0.5          | 1680           | 37.7               | 14.42              | 0.30          | 5555      | 2930      |
| #2  | MgCa0.5Mn0.5     | 1612           | 35.29              | 13.38              | 0.317         | 5584      | 2881      |
| #3  | MgCa0.5Gd0.5     | 1567           | 41.43              | 15.74              | 0.31          | 6105      | 3170      |

The RUS technique implies the scanning of resonance structure of a compact specimen, in order to determine the elastic properties. The information obtained from the spectra includes both the total matrix of density as well as information about geometry of the object and the homogeneity of the material. This procedure is used to distinct acceptable components from those with flaws as voids, density defects, modification of elastic properties that are reflected in the modification of resonance frequency [23]. The resonance frequencies of an object can be calculated by solving the equation for known geometry [24] or can be measured.

The Rayleigh-Ritz method is efficient and accurate to calculate natural vibration frequencies of the solids with parallelepipedal shapes. The efficiency is important for probabilistic formulation of inverse problem, which implies thousands of direct calculations of natural frequencies. Having the value of G, for a Poisson coefficient v between 0.28 and 0.31, the C_{11} and C_{12} can be determined [25].

For each value of Poisson coefficient determined by ultrasound, the frequencies of resonance spectrum were determined by numerical simulations, selecting the value of coefficient which minimize the function [26]

\[ F = \sum_{i=1}^{N} w_i (f_i - f_i^*)^2 \]  

(1)

The sample is placed between two identical piezoelectric transducers, P111.O.06P3.1 (figure 2), sustained by contact force, without coupling agents. The emission transducer is connected to a sinusoid voltage source with a sweep frequency between 60 si 320kHz in 100 kHz steps using a Network/ Spectrum/ Impedance Analyser (NSIA) type 4395A. The signal generated by NSIA is amplified and applied to the reception transducer that detects the vibration of sample recorded as pair of amplitude-frequency.
The excitation frequency is continuous varied, in the range of firsts two eigenmodes of vibration for the sample. When the excitation frequency is closer to resonance frequency of the sample, this will start resonate and generate vibrations that are translated by amplified deflection, the signals received by the transducers being filtered from noises and false signals.

The theoretical resonance frequencies are calculated for each sample upon a mathematical model of free vibration [27] using the initial estimation for elastic constants. The experimental set-up allows the tuning of parameters so that for each position of the sample (at corners contact) shall assure excitation of a maximum possible number of resonances. The calculation of resonance frequency is an eigenvalue problem [27,28].

3. Results and discussions

The resonance spectra were analyzed in the range of 120-230 kHz, for each sample were detected a considerable number of vibration modes, which were correlated with theoretical predictions for identifying.

Using the mechanical parameters presented in table 1, the eigenfrequencies were determined using Comsol Multiphysics 5.4. The mesh statistics are minimum element quality 0.2127, average element quality 0.6867, tetrahedron 16316, triangle 1536, edge element 120, vertex element 8.

The emphasized results show that the RUS method, complementary to the US, SEM methods, allows the characterization of the material as a whole. It can be observed that a prediction over modification of internal structure from the changes of modes, result expected because dislocations or crystallographic modifications affect the elastic parameters.

The frequencies obtained by calculation, for the optimization of elastic parameters for the sample supposed as perfect homogeneous and isotropic with regular shape (in this case cube), are found in the frequencies interval of the spectrum experimentally determined. The calculated frequencies have not all correspondent in the frequency spectrum, the number of calculated values being larger than those associated to the spectrum.

The RUS spectrum has been processed using the inverse numerical procedure described in [26]. For these materials, the elastic constants were determined.

The paper offers a method for identification of adequate modes for cubic samples, useful for interpretation of RUS results. The modal shapes obtained by simulation were associated to the phase composition for the addition elements in the composition of MgCa_{0.5} (E) (where E=Mn/Gd - 0.5 wt. %).

Figure 3 presents the results of simulation for sample #1 and #2 used for identifying of resonance frequency.
The colors from cubes represent the magnitude of displacement during vibration.

Figure 3. A selected interval of the RUS spectrum of a magnesium alloy with Gd addition.

For representative modes resonant peaks, the modal shape obtained by the RUS the corresponding modal shapes determined within the inversion are normalized to the fundamental torsional frequency. Identification of modes was done as follow torsion doublet d1, shear s1 and flexural a1.

The answer has been recorded in a large number of points to cover the full frequency spectrum range. The frequency sweep has included a large number of excitation frequencies. According to [29] the modes observed on samples must falls into the following three categories: torsional axisymmetric; extensional and flexural modes (these modes occur in pairs named doublets, with the same resonance frequency).

Despite these, a number of resonant frequencies that not emphasize the influence of elements from the witness sample can be observed (i.e. the interval 140-150kHz, respectively 170-185kHz). The representative modes obtained by simulation for the cubic samples are for $v=0.31$, in agreement with literature. The missing of vibrations as well as the minimal displacements appears in high blue, the maxima in red and the intermediated ones in yellow or green.

The torsional modes are those having maxima on corners and lack of vibration displacements along the rotation axis and on the middle of the surface between two edges. The modes were identified by the difference as response to the applied excitation, slight deviations from the cubic shape are possible and they bring a variation of less than 5% in the resonant frequency of the first ten modes. Small deviations do not interfere with interpretation.

From the graph it can be seen that the simulation of information is very important in determining the resonances in the investigated spectrum. The modes were visually identified by analyzing the shape of the mode predicted by nodal eigenvectors [30]. Initially, the frequency change analysis has included over 18 modes. For several reasons, it has been established that in the frequency range, 9 modes provide the best information on the samples.

First of all, on the homogeneity, there were 5 relatively large changes of frequencies in the spectrum; keeping a small error percentage (approx. 2% for most samples) compared to the frequency determined by simulation and RUS. Many higher order modes have similar mode shapes and tend to change in appearance as the frequency increases, making it inadequate to identify the mode in the frequency spectrum.

Figure 4 presents the results of simulation for sample #1 and #3 used for identifying of resonance frequency.
Figure 4. A selected interval of the RUS spectrum of a magnesium alloy with manganese addition.

For these materials, the elastic constants were determined. Several oscillation modes have been identified (i.e. extensional, flexural and torsional - the frequencies of these modes depending by the shear velocity of the sample).

In both resonance spectra, the superior modes present a similarly variation but with changing of the phase. The modal shapes obtained by simulation were associated to the phase composition for the addition elements in the composition of Mg0.5Ca(E) (where E = Mn or Gd in 0.5 wt. %).

However, for each sample it should be noted that in some ways, the measured data followed the same trend as those obtained by simulation, compensated by a few percent.

4. Conclusions
Resonance Ultrasound Spectroscopy is an effective tool for identifying the elastic modules of a material. The method is based on estimating resonant frequencies, based on an eigenvalue and eigenfunction method. The analysis of the resonance spectra can be used to determine the acceptance criteria of the samples without flaws (pores, inclusions, casting defects, etc.).

The method was applied to MgCa0.5E0.5 alloys where E = Gd or Mn knowing that the introduction of Gd / Mn as alloying elements in the binary alloy MgCa alloy determines the modification of the crystallographic structure of the basic matrix. Inhomogeneities can be identified by resonant frequency shift, peak splitting, amplitude change and changes in quality factor. RUS spectrum changes both in amplitude and in phase in the presence of discontinuities.

5. References
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