Ultrasound methods for determining the influence of yttrium in Mg-0.5Ca-xY

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Abstract. Biodegradable materials are used as alternative implants for orthopedic applications due suitable strength, fatigue resistance, ductility and biocorrosion resistance which are features for biodegradable implants. Mechanical properties can be improved by adding alloying elements. Mg alloys have been designed to meet the requirements of bone repair implant materials by adding Calcium and Yttrium. Usually Ca is added to control corrosion rate of Mg alloys and thinning grain boundaries. The system is defined as Mg-0.5Ca-xY (x=0.5, 1, 1.5), varying the Y concentration in order to slow the degradation process. Beside morphological characterization with SEM, EDX, noninvasive testing is required to be carried out the determination of mechanical characteristics. The paper presents the influence of Yttrium 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

Biomaterials are materials used to make medical devices for the purpose of repairing or replacing tissues or organs whose functioning is defective or below an acceptable level [1]. Biocompatibility is a unique property of biomaterials, being defined as the property of biomaterials not producing side effects with surrounding tissues in the body in which they were implanted [1].

The importance of biomaterials has increased once with the innovations in medicine, especially those in surgical techniques that have made possible to use biomaterials for replacing body parts that have lost their function due to illness, aiming at improving the function and correcting the abnormality. As biodegradable material [2], the implant has the properties of degrading in the same time with the surrounding tissues or after the accomplishment of the role for which it has been used.

Bones are the organs most exposed to trauma, as dynamic tissues that perform a variety of functions. They have the capacity of reshape in function of the internal or external stimuli. Losing bones tissue become a natural phenomenon once with aging, the replacing being made by bones surgery. The bone itself, is a composite made from extracellular organic matrix, containing collagen, approximate 30-35% from dried bone assures the flexibility and elasticity and calcium phosphate, especially hydroxyapatite, 65-70% contributing to stiffness and hardeness of the bone [3].

Magnesium as degradable material [4] has been used first time for the ligaments of blood vessels, later being used as material for osteosynthesis [5]. Alloysed with Al, Zn, the mechanical features were improved, Mn being used as a secondary alloying element to remove impurities (Fe, Ni, Cu as the main impurities encountered in Mg alloys) by incorporating them into intermetallic phases [6].
Calcium (Ca) and zirconium (Zr) have a positive effect on mechanical properties at low concentrations of 2wt% and respectively 0.42wt%, while rare earth (RE) can form intermetallic phases with Mg, improving the mechanical strength of the alloy. 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. Once released into the body by the alloy degradation process, the alloying elements must be completely reabsorbed without producing local or systemic toxic effects. From all of these, Al is not compatible with use in medical applications due to toxic effects. Zn, Mn, Li and RE can induce toxic effects at certain concentrations. Ca it shows the best biocompatibility, no toxic effects, being, as Mg, an element present naturally in the human body. It is known that pure Mg has a poor mechanical performance, the mechanical requirements of the implant daily cannot be satisfied [4, 7-8], and in addition Mg alloys have low corrosion resistance and therefore degrade rapidly in the human body. Thus, the development of new types of Mg alloys using new alloying elements has emerged as a natural necessity.

The Mg Ca Y alloy has been studied and tested for biodegradable materials. The impact of Y on mechanical properties followed by biological analysis is an important step in the study, with major concerns over the use of Mg alloys for carrier implant materials.

This paper proposes to analyses the influence of yttrium concentration over elastic properties using Resonant Ultrasound Spectroscopy (RUS) and ultrasound method (as noninvasive methods) to examine mechanical properties (i.e. Poisson ratio, Young modulus, Shear modulus) of biomaterials based on magnesium alloy Mg 0.5Ca xY with different ratios composition of Y(x= 0.5; 1.0; 1.5; wt%), RUS assuring an evaluation on the entire material mass, and by EDX and SEM, the chemical structure of the studied alloys has been established.

2. Materials and methods
The Mg 0.5Ca xY having selected with high purity elements as raw materials (Mg-99.7%, Mg-15Ca and Mg-30Y master alloys) were melted in an induction furnace under argon atmosphere in a graphite crucible [9-10]. The final chemical composition 0.5Ca and xY (determined as an average of at least four values for same sample was performed by repeated casting operations and was analyzed by EDX using SEM Quanta 200 3D DUAL BEAM coupled with an EDS-EDAX detector.
A further EDX analysis of chemical composition of Mg0.5Ca sample (Figure 1b) confirm that no other elements except Mg, Ca and Y are present in the alloy. SEM images (Figure 1a) emphasize that the microstructure of the Mg0.5xY alloys are semi-compacted, may be yttrium grains remain still remain unfused. The cube samples, with 10 mm side, has been cropped using MAXIEM 1530 have been studied and probes was embedded in resin prepared using EpoFix Resin Struers product. The samples surfaces have been prepared for metallography analysis using DiaPro 3\(\mu\)m diamond suspensions and Tegramin 30 equipment for grinding and polishing. Hardness was measured with NOVA 360 instrument for indentation time 10seconds and 5x10\(^3\) gf. Microscopic analysis was obtained used AxioCam MRc5-Zeiss.

For calculated mechanical parameter was used ultrasound method by echo pulse method, described in \([11]\) in order to determined Young modulus \(E\), shear modulus \(G\) and Poisson ratio of sample using longitudinal velocity wave \(C_l\) and transversal velocity wave \(C_t\) presented in table 1. The average values of hardness were obtained from five different areas of faces of sample remain approximatively constant. The small differences are due to the influence of alloying elements that influence compactness.

### Table 1. Sample characteristics.

| Sample | Y Comp. (%wt) | length [mm] | Density [g/mm\(^3\)] | Young modulus [GPa] | Shear modulus [Gpa] | Poisson ratio | \(C_l\) [m/s] | \(C_t\) [m/s] | HV5 |
|--------|----------------|-------------|------------------------|----------------------|---------------------|---------------|-------------|-------------|-----|
| #1     | 0.5            | 9.94        | 1649.84                | 112.96               | 37.79               | 0.28          | 5282        | 2948        | 52.8|
| #2     | 1.0            | 10.04       | 1693.77                | 118.44               | 36.50               | 0.31          | 5442        | 2868        | 38.9|
| #3     | 1.5            | 10.19       | 1696.78                | 118.44               | 36.16               | 0.31          | 5610        | 2931        | 37.5|

*the sample present a crack at surface*

Resonant ultrasound spectroscopy (RUS) as method has the ability to emphasize the modification of resonance frequencies for a given material. The natural frequency depends on the elasticity, size and shape of the object - RUS exploits this solid property to determine the elastic tensor of the
material. These frequencies depend on the size, shape, density and elastic properties of the sample. Each frequency corresponds to a particular fascicle of propagating waves and the exchange of modes [12]. These maxims should be repeated at $1/f$ intervals, where $f$ is the resonance frequency. A sufficient set of experimental data on the measured resonance frequencies can provide information about the sample properties that have been tested.

Determining the material properties from the resonant frequencies is an extremely difficult mathematical problem but, in principle, it can be solved. Obviously, for this purpose, it is absolutely necessary to use appropriate algorithms and calculation programs. The FEM or Rayleigh-Ritz method must be used to estimate the eigenfrequencies of normal modes.

3. Experimental set-up, results and discussions
Methods based on the time of flight measurement evaluate the elastic wave velocities that occur in the material as well as their attenuation. Making these determinations involves using waves with a wavelength much smaller than sample sizes. For these samples, a signal delay block was used. The longitudinal velocity wave $C_l$ and the transverse velocity wave $C_t$ presented in Table 1 were determined by the experimental assembly, Figure 3.

![Figure 3. Ultrasound determination of propagation velocities.](image)

RUS involves exploring the resonant structure of a compact sample such as cube, parallelepiped, or short cylinder. In the RUS method, ultrasounds were generated and received using two compressing waves transducers P111.O.06P3.1 US type with 60kHz central frequency. A transducer produces vibration and the other converts the resonance motion into an electrical signal. The sample is supported by the contact force; it does not require gluing or coupling agents.

![Figure 4. RUS measurement a) the scheme of connection; b) Photo of experimental test.](image)
The frequency sweep performed was between 80kHz and 320kHz in 100Hz steps using a Network/Spectrum/Impedance Analyzer (NSIA) type 4395A Agilent USA. The signal generated by NSIA is amplified using a broadband Amplifier A1012AG TC Power Conversion Inc. and is applied to an ultrasound transducer. The signal provided is received by an identical transducer and applied to the analyzer port B according to the scheme shown in Figure 4a, to be further processed by the PC.

Most of the natural frequencies of an oscillating cube do not respond to analytical solutions. By performing numerical simulations (for samples of similar dimensions to those taken in the study, in a wide variation range of G and v) it resulted that always the first peak corresponds to a torsional mode which, in addition, is the fundamental torsional mode. For such a mode, the fundamental frequency of the mode is given by \( f = \frac{m}{2d} \cdot \sqrt{\frac{G}{\rho}} \) where \( f \) is the measured frequency, \( d \) is the height of the sample, \( G \) is the shear modulus, \( \rho \) is the density and \( m \) is an integer. For fundamental mode, \( m=1 \).

Under these conditions, \( G = 36.16 \text{GPa} \) for sample #3. Using procedure indicated in [12] and taking \( G \) at the determined value, the value of the Poisson coefficient \( v \) was swept within a reasonable limit in accordance with the values determined between 0.28 and 0.31, which implies the modification of the \( C_{11} \) and \( C_{12} \) elements in the elastic matrix C. For each the value of \( v \), the frequencies of the ultrasonic resonance spectrum modes have been determined by numerical simulations, selecting that value of the Poisson coefficient that minimizes the function

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

where \( N \) is the number of peaks in the spectrum, \( f_i^c \) is the \( i^{th} \) calculated frequency, \( f_i^m \) is the measured and \( w_i \) is the weighting factor. The oscillation eigenfrequencies were calculated based on the parameters set presented in Table 1 using SolidWorks 2014, Simulations Toolbox.

![Figure 5](image-url)  
Figure 5. Representative modes for 120-210 kHz frequencies range: a) flexural mode; b) extensional mode.

These simulations are required to determine the frequency range sweep. The RUS spectra for samples #1-#3 in the frequency range 120kHz-220kHz were plotted (Figure 6). The samples are
fixed between transmitter and receiver transducers in corners so that the condition of the surface is stress-free. At the same time, the grip on the corners ensures the condition of obtaining a large number of resonant frequencies.

![Figure 6](image)

Figure 6. Resonance ultrasound spectra for the sample.

The inhomogeneities from sample can be identified from the resonance spectrum, due to the resonance frequencies swift, peaks splitting, increasing of height and magnitude modification. The method is based on the estimation of resonant eigenfrequencies [13], based on an eigenvalue and eigenfunction method [14-18].

It can be noticed that by the presence of anomalies within the samples (pores or pores clusters) the RUS spectrum changes in both amplitude and phase [19-22]. In this case, it is not the question of determining the elastic size by the proposed method but only by a data inversion, considering that the matrix of the model is not well conditioned.

4. Conclusions
Magnesium alloy used as biodegradable materials display a variety of properties and depends on the chemical composition and biocompatible elements that are included. Addition of calcium and yttrium at magnesium alloys improve the mechanical properties, yttrium contributed to obtained special corrosion resistance.

The Mg-based alloys were obtained in an induction arc melting furnace in argon atmosphere, and were characterized (microstructural and chemical analysis) with SEM Quanta 200 3D with EDX. Morphological analysis using EDX as well as microindentation 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.

The ultrasonic resonance allowed the determination of the Young modulus, the shear modulus and Poisson ratio of the sample, starting from data characterizing the material in the entire volume, not only at the surface, using longitudinal velocity wave and transverse velocity waves.

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