Chemical and structural analyze of experimental biodegradable ZnMgY alloy

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Abstract. Beside biocompatible classic metallic materials, biodegradable metals (BMs) like alloys of zinc (Zn-based) present a high potential as an alternative solution for permanent implants elements generally being applied for fractures restorations or other similar medical conditions. An experimental alloy, ZnMgY, was obtained using an induction furnace from high purity materials (Zn: 99,995 and master alloy MgY: 65-35 wt%), in Argon atmosphere. Microstructure of the alloy (after mechanical grinding and polish plus chemical etching) and chemical insights (before chemical etching) were taken using optical microscope (Zeiss+Motic digital camera for image acquisition) scanning electron microscope (SEM VegaTescan LMH II, SE, 30 kV, 16 mm WD) and dispersive energy spectroscopy (EDS Bruker, PB ZAF, Automatic mode of analyze, Point and Mapping features). The experimental alloy was five times re-melted in the induction furnace using a ceramic crucible. The experimental alloys present a good chemical homogenization without porosity, metallic inclusions or segregation.

1. Introduction

Metals have a long history in using them as a material for implants used in the medical field [1–4]. The desire to use metals is due to their unique combination of properties, including good mechanical strength, ductility, hardness, wear resistance and formability. In terms of biocompatibility, the first generation of metal materials used for applications as an implant had the first requirement to be inert in the physiological environment [5–7]. Recently, biodegradable metals such as magnesium (Mg), iron (Fe) and zinc (Zn) have been increasingly accepted as implant material [8–15,16,17]. Of the three candidate metals, zinc is the most recently introduced [9].

Biodegradable metals are best suited for implants with temporary functions in the body. Two promising medical applications of bio-resorbable metals are the manufacture of orthopaedic stents and fasteners. A biodegradable material requires specific properties before becoming viable. Research suggests that some of the problems related to magnesium and iron can be addressed using zinc [18,19]; hence the considerable increase in scientific interest in this metal.

For biodegradable Zn metals, the mechanical properties of the alloy may be influenced by (i) type, (ii) number and (iii) the quantity or concentration of alloying elements. A wide range of compositions...
has already been studied; i.e. (i) pure, (i) binary, (iii) ternary, and (iv) quaternary combinations of Zn with other elements [20]. More than ten types of zinc alloy systems have been developed for biomedical applications including the Zn-Mg system; Zn-Fe; Zn-Ca; Zn-Li; Zn-Zr; Zn-Sr; Zn-Mn; Zn-Ge.

Zinc-based biodegradable alloys exhibit a corrosion rate between Mg- and Fe- based alloys being proper for many medical applications. These alloys possess different processing and economic advantages, a very good ability to be poured, fluency, and other metallurgical and mechanical properties which are very competitive with other ferrous and non-ferrous materials. Zinc material represents an essential trace element in biological environment and human body. In case of an adult biological system which has approx. 2–3g of Zn, is many biological functions from enzymatic catalysis to cellular neuronal processes. In the same time zinc element have contributions in blood pressure regulation in the arteries.

In this article the authors present some preliminary results, microstructural and compositional insights, about the obtaining of a new alloy based on zinc with addition of magnesium and yttrium for medical applications as biodegradable alloy.

2. Experimental details
A new alloy was obtained from high purity zinc (99.995%) and MgY (65-35 wt%) master alloy using an induction furnace under Ar atmosphere. A 100 grams’ ingot was realized and, after wire cutting of a 10/5 mm disk, was mechanically prepared for chemical and structural analyses. The chemical composition proposed was Zn3Mg1Y (wt%) based on metallic charge calculation. For bigger weight percentages of Y extremely fragile alloys were obtained.

Microstructure of the alloy (after mechanical grinding and polish chemical etching with FeCl3 was used) and chemical insights (before chemical etching) were taken using optical microscope (Zeiss+Motic digital camera for image acquisition) scanning electron microscope (SEM VegaTescan LMH II, SE, 30 kV, 16 mm WD) and dispersive energy spectroscopy (EDS Bruker, PB-ZAF, Automatic/Element list mode of analyse, Point (90 µm diameter), Line and Mapping features).

3. Experimental results
Optical micrographs, figure 1, present a good homogeneity of the material with two different components, a matrix and few compounds of white colour with two different geometrical shapes: rectangular and round.

![Figure 1. Optical micrographs (a) 200x and (b) 600x.](image)

With a magnesium content around 3 wt. %, zinc grains are not recognized in optical micrographs. It is a eutectic structure containing Zn and intermetallic compounds according to Zn–Mg, Zn-Y and Mg-Y phase diagrams [21, 22].
Figure 2 shows SEM micrographs of experimental alloy after grinding and chemical etching for two different scales: (a) 500x and (b) 2500x. As a general aspect, figure 2 (a), present a homogeneous microstructure without pores, cracks or fissures. Also an evenly distribution of compounds is observed at macro-scale that usually is considered a proper fact in material degradation. The induction melting process through his turbulent currents mix the alloy components increasing the chemical and structural homogeneity of the alloy. At higher amplification powers of the structure, figure 2 (b), three different phases can be observed noted with 1 (rectangular compounds), 2 (round compounds) and 3 (matrix).

Chemical composition determination was realized before and after chemical etching of the surface. Energy dispersive spectroscopy (EDS) was used to identify the main elements of the experimental alloy. The energies characteristic for Zn, Y and Mg (keV) elements are presented in figure 3 (a) spectrum. Chemical composition was determined in three different areas of the sample and the quantified results are given in table 1 first 3 position and average values. The signal was taken from a one millimeter square area and given as weight and atomic percentages.

In figure 3 (b) are presented five points (each 90 µm diameter) for chemical analyze of the main components identified from the microstructure (figure 2 (b)) that appear under different aspects (matrix,
rectangular or round shape). The chemical composition results are presented in table 3 as compared to the average composition of the entire sample.

The selected points for analyse comprises the main formations of the alloy. In the first point of analyse (rectangular formation) (chemical composition given in table 1, point 1, figure 3 (b)) the results show the presence of a ZnY (Zn8Y) compound with approximately 11 wt% of Y which is bigger than average percentage of Y in the alloy. In case of this compound no Mg was identified so the new phase ZnY was formed during the melting and solidification of the alloy from high purity Zn and MgY master alloy. The second analysed point is on an elongated formation, figure 3 (b), that present a high content of zinc with less Mg and Y content as average and a different structural shape than rectangular formations or matrix (point 3 of analyse). This compound contains 1.4 at% Mg and 0.2 at% Y (Zn1.4Mg0.2Y).

| Elements | Analysed area | Zn wt% | Zn at% | Mg wt% | Mg at% | Y wt% | Y at% |
|----------|---------------|--------|--------|--------|--------|-------|-------|
|          | Area 1        | 95.76  | 90.9   | 3.3    | 8.4    | 0.93  | 0.65  |
|          | Area 2        | 96.02  | 91.34  | 3.16   | 8.08   | 0.82  | 0.58  |
|          | Area 3        | 95.9   | 91.18  | 3.2    | 8.19   | 0.89  | 0.63  |
|          | **Average**   | **95.89** | **91.14** | **3.22** | **8.22** | **0.88** | **0.62** |
|          | Point 1 (figure 3 (b)) | 89.12  | 91.76  | -      | -      | 10.88 | 8.24  |
|          | Point 2 (figure 3 (b)) | 99.2   | 98.4   | 0.52   | 1.4    | 0.28  | 0.2   |
|          | Point 3 (figure 3 (b)) | 96.28  | 92.16  | 2.79   | 7.19   | 0.93  | 0.65  |
|          | Point 4 (figure 3 (b)) | 99.12  | 99.2   | 0.8    | 0.59   | 0.08  | 0.22  |
|          | Point 5 (figure 3 (b)) | 99.43  | 98.48  | 0.57   | 1.5    | -     | -     |
| EDAX error % |          | 2.25   | -      | 0.4    |        | 0.4   |        |

The third point, figure 3 (b) (chemical composition shown in table 1) is selected on the alloy matrix (more than 50% of the structure). Chemical composition of the matrix is near the average composition determined on the alloy. Point 4 (figure 3 (b)) shows an area mainly formed by zinc with reduced percentages of dissolved Mg and Y. The fifth area analyzed, point 5, figure 3 (b), shows areas with no Y dissolved in zinc and the formation of ZnMg phase. XRD analyze will explain the formation of different compounds between Zb, Mg and Y in this experimental alloy. A high percentage of magnesium is presented dissolved in the matrix and less in other compounds. The alloy shows phases with a high percentage of yttrium (in a reduced contribution at general scale) and as dissolved element in zinc matrix and complex three elements compounds.

In figure 4 elements Zn, Mg and Y chemical composition variation on a line selected are presented. The elemental variations confirm the chemical compositions presented in table 1 and the formation of compounds with more or less yttrium.

All element variations during the selected line are homogeneous and the presence of compounds with a higher Y percentage at similar distances, figure 4 (b), can help at generalization of corrosion and degradation rate. In figure 5 elements distribution is present on a selected area, figure 5 (a), with the highlight of compounds with more yttrium, figure 5 (e), and a homogeneous distribution of zinc and magnesium.
Figure 4. Elements Zn, Mg and Y chemical composition variation on a line selected on the experimental alloy (a) Zn, Mg and Y variations and (b) detail of Mg and Y signal variation.

Figure 5. Elements distribution (a) selected area of distribution, (b) all elements distribution and (c) Zn, (d) Mg, (e) Y distributions.

Distributions of both Mg and Y elements confirm the results from chemical composition analyze highlighting the areas with more Mg or Y also those without these elements. No clear interfaces are observed between the matrix and the other components (phases, compounds etc.). In order to evaluate the mechanical properties, the material will be the subject of tensile/compression test, micro-hardness and scratch test and also dynamic mechanical analyze with results proposed for a further paper.

4. Conclusions

A new chemically and structurally homogenous alloy based on zinc was obtained using induction melting under Ar atmosphere. In order to avoid the fragility of the alloy we maintain the alloying
percentages of Mg and Y under 3.5 wt% respectively 1.5 wt% based on previous studies of the same authors. The presence of different constituents was observed through optical and electronic microscopy (OM, SEM). The chemical composition of the matrix and other compounds was determined with respect for the main elements: Zn, Mg and Y. Compounds like ZnY, ZnMgY and ZnMg were identified.

A further investigation of the experimental alloy must be realized using XRD, XPS and EBSD equipment in order to establish all the components, chemical and structural properties. For medical applications of this alloy as biodegradable material the corrosion behaviour of all the chemical and structural components will be analysed as different materials and also as a complex alloy. Different behaviour at corrosion resistance between the matrix and the other compounds is expected.

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