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# Preparation and Basic Characterization of Novel Zinc-based Alloys for Intracorporeal Implants

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Abstract: Zinc is considered to be a suitable element for the preparation of bioresorbable materials that can gradually degrade in the human body without the production of toxic compounds and undesirable hydrogen gas. Zn is characterized by a much lower corrosion rate in saline compared to magnesium-zinc and its alloys. Therefore, in this work we investigate Zn-0.4Mg-0.4Ca-xMn alloys with 0, 0.2, 0.4, 0.6 0.8 and 1.1 wt. % Mn. The elements Mg, Ca and Mn were selected to improve the mechanical properties and biocompatibility of pure Zn. The microstructure of the alloys was studied by optical light microscope and SEM equipped with EDX analyzer. The mechanical properties were studied by measuring the microhardness using Vickers method. The results of the experimental part of this work show a trend of improvement in the mechanical properties of the alloys with increasing Mn content. The immersion tests were carried out in Hank's solution and after 6 months the material retained its shape integrity.

Keywords: biodegradable zinc-based alloys, microstructure, microhardness

## 1. Introduction

In bone and vascular regenerative medicine, bioresorbable metals could serve as the next generation of temporary medical implants. Their implementation could greatly reduce the need for costly and risky additional surgeries to replace or remove permanent implants. For load bearing, hard tissue reconstruction, and scaffolds, metal implants are still the best choice. Stainless steels, cobalt-chromium alloys, and titanium alloys are the three most popular biomedical metallic materials right now [1]. These alloys show highest mechanical strength and corrosion resistance because they are chemically inert [2]. As a result of their much higher Elastic modulus than bone tissue, the "stress shielding" effect is occurred and can lead to bone atrophy and poor bone remodeling. Long-term corrosion and wear can also result in the release of toxic ions and particles, which can cause allergies and inflammation [3,4]. As a result of their development, biodegradable metals are expected to degrade and get absorbed in vivo as tissues heal and grow, and corrosion products released by them are expected to be metabolized and eventually excreted. The three classes of biodegradable metals that have been proposed for temporary implants are magnesium (Mg), iron (Fe), and zinc (Zn). Although magnesium (Mg) iron (Fe) based alloys have been extensively researched over the last two decades, Mg alloys haven not shown satisfactory mechanical properties, biocompatibility, and controlled degradation rate in physiological environments. On the other hand, Fe alloys show suitable mechanical properties, but their corrosion rate is slow and excess of iron in physiological environment are connected with inflammatory reaction and infection [5]. While biodegradable materials like polymers and magnesium alloys have improved greatly in terms of their mechanical strength (UTS < 350 MPa), there is still a huge gap between them and metallic materials like

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cobalt chromium alloys, stainless steel and titanium-based alloys (UTS > 500 MPa) [6]. There is therefore an urgent need to develop novel metallic materials for use in biomedical applications that provide similar mechanical strength as titanium-based implants, but which degrade in a controlled manner in the body after implantation. Zn alloys offer a promising alternative to current implant materials because of their unique physical properties that make them an ideal candidate for load-bearing implants and soft tissue repairs [7].

### 1.2. Zinc-based biomaterials

As a promising alternative to magnesium and iron, zinc and zinc-based alloys have only recently been added to the list of bioresorbable metallic materials. Below are some of the benefits of zinc and its alloys in medical applications.

It is an essential trace element in the human body, just like magnesium and iron. It is in over 300 enzymes and proteins, so it is essential to our health. For proper nucleic acid metabolism, protein synthesis, cell division, and cell function, zinc must be present [8]. An adult's daily allowance of zinc is 15-40 mg, much lower than it is for magnesium. Because Zn has a lower corrosion rate, it is likely to release at a much lower rate than the daily allowance is set [9]. It is possible that zinc ions released during the degradation of the implant could integrate into the host's normal metabolic process without causing systemic toxic effects [10].

The electrode potential of zinc, -0.762 V, falls between that of magnesium (-2.372 V) and iron (-0.444 V) [10]. Hence, pure zinc has an intermediate degradation rate (faster than Fe and its alloys, but slower than rapidly degrading magnesium and its alloys) due to passive layers formed by corrosion products [11]. The low melting point, low chemical reactivity, and good machinability of zinc alloys make them easier to cast and process. Unlike magnesium-based alloys, zinc alloys can be melted in air [12].

Table 1 summarizes the physical and mechanical properties of some existing non-degradable and degradable metallic biomaterials, along with the properties of bone tissues. It can be seen that pure Zn exhibits the lowest $\sigma_{UTS}$, $\sigma_{TYS}$, and $\varepsilon$ among all metallic biomaterials. Therefore, the development of Zn alloys with higher $\sigma_{UTS}$, $\sigma_{TYS}$ and $\varepsilon$, is one of the major challenges in terms of biomedical applications. The mechanical properties of Zn alloys can be improved by varying their microstructure through alloying, fabrication techniques, and subsequent thermoforming treatments [13].

## 2. Experimental procedure

Completely new metal alloys with the composition consisting of four elements have been prepared and characterized, consisting exclusively of bioresorbable elements Zn, Ca, Mg, that are present in the human body and to which the body has a natural biocompatibility. In order to improve the mechanical and chemical properties, these alloys have been microalloyed with Mn. The following compositions were prepared: Zn-0.4Mg-0.4Ca-xMn (x=0, 0.2, 0.4, 0.6, 0.8, 1.1 wt.%). Elements with high purity Zn (Heneken 99.995%), Mg (Alfa Aesar 99.98%), Ca (Alfa Aesar 99.5%), Mn (Alfa Aesar 99.3%) were used in the synthesis of the material. The preparation of the pre-alloys was carried out by gravity casting using a Schmelzofen Goldbrunn 1000 crucible melting furnace. The melting was carried out in graphite crucibles at a temperature of 650˚C. The melt was kept at this temperature to ensure that all elements have dissolved and then stirred for 10 minutes, in an inert atmosphere of protective argon gas (Ar purity= 99.999%). The alloy was cast

Table 1: Comparison of mechanical and physical properties of bone tissue and biomaterials [14,15].

| Tissue/Material | ρ(g/cm$^3$) | $\sigma_{UTS}$ (MPa) | $\sigma_{TYS}$ (MPa) | E (GPa) | ε (%) |
|---|---|---|---|---|---|
| *Cortical bone* | 1.8-2.0 | 35-283 | 105-114 | 5-23 | 1.07-2.1 |
| *Trabecular bone* | 1.0-1.4 | 1,5-38 | 1-12 | 0.01-1.6 | 2.20-8.5 |
| *316L stainless steel* | 8.0 | 450-650 | 200-300 | 190 | 30-40 |
| *Co-Cr alloys (ASTM F90)* | 9.2 | 860 | 310 | 210 | 20 |
| *Ti-6Al-4V (annealed)* | 4.4 | 895-1025 | 825-869 | 110-114 | 6-10 |
| *Pure Mg* | 1.7-2.0 | 90-190 | 65-100 | 41-45 | 2-10 |
| *Pure Fe* | 7.8 | 180-210 | 120-150 | 211.4 | 40 |
| *Pure Zn (As cast and hot rolled)* | 7.14 | 18-140 | 10-110 | 1.2-2.1 | 0.3-36 |

into graphite molds, the castings being cylindrical in shape. For the additional thermomechanical processing of pre-alloys by rapid cooling method, the Melt spinner SC from Edmund Buhler was used, which offers low-pressure casting of melt into a cooled Cu mold (Fig. 1). The melting was carried out in an inert atmosphere of protective Ar gas (Ar purity = 99.999%). The samples were melted using high frequency induction heating. The melt was cast at 650°C. In this process, the pressure difference of the device was set to ΔP=20kPa to ensure uniform ejection of the melt into the cooled mold. By this process, ingot-shaped castings with a diameter of 3 mm and a length of 130 mm were prepared from each alloy.

Metallographic samples were prepared using standard procedures for XRD and SEM analyses. A Tescan Vega 3 LMU electron microscope equipped with an EDX (energy dispersive spectrometer) was used to assess the real chemical composition of the alloys. Analytical balances, supplemented with the ABT-A01 adapter, were used to determine the density of all samples by the Archimedes method. Light microscopy was used to observe the microstructure of the prepared pre-alloys samples as well as the samples after rapid cooling. In this analysis, grain sizes and shapes were examined. Prior to this observation, the surfaces of the metallographic sections were etched with Nital (Ethanol 96% and $HNO_3$ 4%) to highlight the microstructures. Microhardness measurements were performed on a Wilson - Wolper Tukon 1102 microhardness tester with a Vickers indenter. The load used was 0.1 kg with a dwell time of 10 s. Phase analysis of all prepared samples was carried out by X-ray diffraction on a Philips Xpert Pro diffractometer. The degradation of the castings after rapid cooling was determined by weight loss measurements. The samples were air dried before each measurement.

Figure 1: Melt spinner SC, version with the possibility of low-pressure melt casting into a cooled Cu mold.

Table 2: Summary table of selected properties of prepared pre-alloys

| *Sample*<br>*Pre-alloys* | *EDX*<br>*[wt.%]* | *Density*<br>*[g/cm³]* | *Microhardness*<br>*$HV_{0,1}$* |
|---|---|---|---|
| Zn | Zn | 7.14±0.02 | 39.6±4.0 |
| Zn-0.4Mg-0.4Ca | Zn-0.24Mg-0.37Ca | 6.96±0.02 | 83.3±5.7 |
| Zn-0.4Mg-0.4Ca-0.2Mn | Zn-0.53Mg-0.37Ca-0.2Mn | 7.00±0.02 | 86.8±5.2 |
| Zn-0.4Mg-0.4Ca-0.4Mn | Zn-0.45Mg-0.42Ca-0.38Mn | 7.00±0.02 | 87.3±4.9 |
| Zn-0.4Mg-0.4Ca-0.6Mn | Zn-0.6Mg-0.48Ca-0.56Mn | 6.99±0.02 | 88.6±10.1 |
| Zn-0.4Mg-0.4Ca-0.8Mn | Zn-0.55Mg-0.43Ca-0.85Mn | 7.01±0.02 | 99.8±10.9 |
| Zn-0.4Mg-0.4Ca-1.1Mn | Zn-0.44Mg-0.38Ca-1.15Mn | 7.01±0.02 | 108.5±9.4 |

Table 3: Summary table of selected properties of rapid cooling processed alloys

| *Sample*<br>*After rapid cooling* | *EDX*<br>*[wt.%]* | *Density*<br>*[g/cm³]* | *Microhardness*<br>*$HV_{0,1}$* |
|---|---|---|---|
| Zn | Zn | 7.15±0.02 | 39.4±4.1 |
| Zn-0.4Mg-0.4Ca | Zn-0.37Mg-0.4Ca | 7.01±0.02 | 90.2±4.2 |
| Zn-0.4Mg-0.4Ca-0.2Mn | Zn-0.32Mg-0.29Ca-0.24Mn | 7.04±0.02 | 99.9±4.8 |
| Zn-0.4Mg-0.4Ca-0.4Mn | Zn-0.35Mg-0.41Ca0.4Mn | 7.00±0.02 | 108.4±4.3 |
| Zn-0.4Mg-0.4Ca-0.6Mn | Zn-0.42Mg-0.44Ca-0.6Mn | 7.01±0.02 | 116.6±3.2 |
| Zn-0.4Mg-0.4Ca-0.8Mn | Zn-0.36Mg-0.43Ca-0.8Mn | 7.07±0.02 | 130.6±6.0 |
| Zn-0.4Mg-0.4Ca-1.1Mn | Zn-0.30Mg-0.36Ca-1.1Mn | 7.07±0.02 | 127.6±7.2 |

## 3. Results and Discussion

The second column of Tab. 2 and Tab. 3 contains information of the real chemical composition of the produced alloys. The real chemical composition differs from the desired one by up to 2 wt. % for pre-alloys and by 0,1 wt.% for alloys after rapid cooling. In the process of remelting and rapid solidification of the alloys, the chemical composition of the alloys was thus better homogenized. The third column shows that density is higher in the samples after rapid cooling. The reason may be internal porosity in gravity cast samples. The elements Mg and Ca do lighten the Zn matrix, but the addition of Mn increases the density slightly. The fourth column of Tab. 2 and Tab. 3 contain information on the microhardness of the pre-alloys and casts after rapid cooling. As will be shown, rapid cooling of the melt resulted in significant grain refinement, which is accompanied by hardening of the alloys. With increasing Mn content hardening of the alloys occurs. The highest microhardness value of 130.6±6.0 was measured for Zn-0.4Mg-0.4Ca-0.8Mn alloy after rapid cooling. The addition of Mn increased the microhardness by an average of 30% for the pre-alloys and 40% for the rapidly cooled castings. Rapid cooling versus casting increased the hardness of the alloys by approximately 25%. Microhardness was higher than similar alloy Zn-1Mg-0.1Mn after hot rolling, which showed microhardness 107.82 Hv [16].

Using the Rietveld refinement method of XRD data, the sizes of the lattice parameters a and c as well as the volumes of the basic unit cells of all samples were determined. From Table 3 it is clear that the effect of alloying, is to decrease the lattice parameter c, while increasing the parameter a. The result is the substitutional hardening of the Zn matrix. These alloys crystallize in a hexagonal lattice with space group P63/mmc.

Table 4: Lattice parameters of castings after rapid cooling

| *Sample after rapid cooling* | *Lattice parameters* | | |
|---|---|---|---|
| | *a [μm]* | *c [μm]* | *V [μm³]* |
| Zn | 0.2665 | 0.4947 | 30.421 |
| Zn-0.4Mg-0.4Ca | 0.2666 | 0.4946 | 30.437 |
| Zn-0.4Mg-0.4Ca-0.2Mn | 0.2670 | 0.4928 | 30.417 |
| Zn-0.4Mg-0.4Ca-0.4Mn | 0.2671 | 0.4921 | 30.417 |
| Zn-0.4Mg-0.4Ca-0.6Mn | 0.2672 | 0.4920 | 30.413 |
| Zn-0.4Mg-0.4Ca-0.8Mn | 0.2672 | 0.4917 | 30.400 |
| Zn-0.4Mg-0.4Ca-1.1Mn | 2.673 | 4.912 | 30.397 |

After observing the microstructure, it can be concluded that there was a significant refinement of the grains due to rapid cooling, with the formation of a homogeneous supersaturated solid solution (Fig. 2).

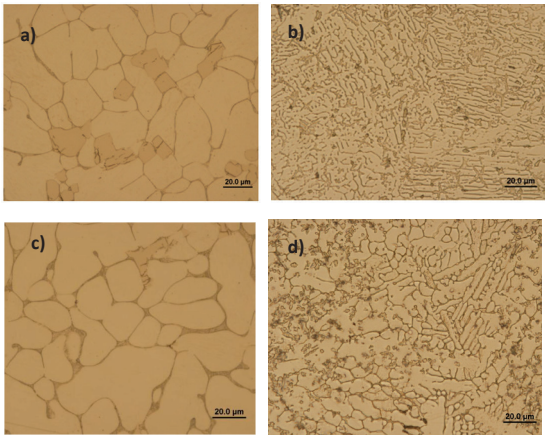


Figure 2: Comparison of the typical microstructure of pre-alloys and castings after rapid cooling in light microscope images a) Zn-0.4Mg-0.4Ca pre-alloy, b) Zn-0.4Mg-0.4Ca after rapid cooling, c) Zn-0.4Mg-0.4Ca-0.6Mn pre-alloy, d) Zn-0.4Mg-0.4Ca-0.6Mn after rapid cooling.

Results of immersions tests for 6 months (4320 hours) in the Hank's solution, during which the mass loss of ingots was recorded at regular intervals, is shown in Fig. 3. The highest weight loss was recorded for the Zn-0.4Mg-0.4Ca-1.1Mn sample, namely 3.6%. Samples with Mn contents of 0.2, 0.4, 0.6 wt.% have much smaller mass loss of about 0.25% and dissolve more slowly and thus from the functional point of view their use could be directed to long-term implants. A layer of corrosion products has formed on the surface of some samples, which is accompanied by a measured increase in mass. After the test, the ingots still retained their shape integrity.

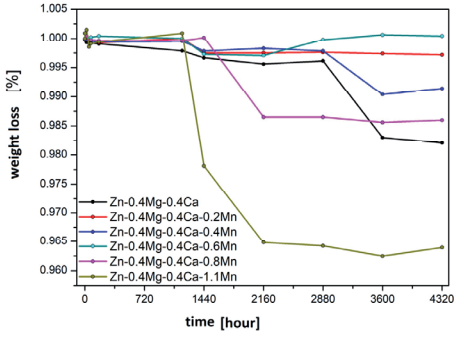


Figure 3: Weight loss of the processed castings.

## 4. Conclusions

Zinc alloys Zn-0.4Mg-0.4Ca-xMn (x = 0, 0.2, 0.4, 0.6, 0.8, 1.1 wt. %) consisting exclusively of elements to which the body has natural biocompatibility were prepared and characterized. The alloys were prepared, by gravity casting in a protective Ar gas atmosphere and were processed by a rapid cooling method. Rapid cooling process produced a supersaturated solid solution with a significantly refined microstructure. Elemental EDX analysis confirmed the desired elemental composition. From the measured X-ray diffraction data, the lattice parameters and the volume of the ground cell of all the investigated samples were determined. With the gradual addition of Mn, the c parameter decreases while the parameter of the basal plane increases. Microhardness measurements showed that the process of rapid cooling of the melt resulted in grain refinement resulting in an increase in hardness. The highest microhardness value of 130.6±6.0 was measured for Zn-0.4Mg-0.4Ca-0.8Mn alloy after rapid cooling.

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