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The Effect of Zn Addition on Bioabsorbable Mg Alloys

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Magnesium has drawn a lot of interest as a possible material for biodegradable implants throughout the past 10 years. Biodegradable implants are preferred over non-biodegradable metallic alloys including titanium (Ti), cobalt-chromium (Co-Cr), and stainless steel because of concerns about secondary infections, metal ion release, and stress shielding. Furthermore, further procedures are frequently necessary for the removal or replacement of conventional metallic implants following patient recovery due to their lengthy healing period and non-biodegradable nature [1].

However, the corrosion behavior of magnesium alloys remains a critical challenge for their use in bioimplants, as excessive degradation can lead to premature mechanical failure and adverse biological effects [2].

In this study, we evaluate the corrosion resistance, microstructural characteristics, and mechanical properties of two magnesium alloys: $MgCa_2Zn_1$ and $MgCa_2Zn_2$. These alloys were synthesized through a controlled casting process and subjected to heat treatments to enhance their mechanical stability.

To assess their suitability for biomedical applications, we conducted electrochemical and immersion corrosion tests in simulated body fluid (SBF), analyzed their microstructure using optical and scanning electron microscopy (SEM, and measured their hardness using Vickers microhardness tests. The results provide insights into the influence of zinc content on the overall performance of these alloys and their potential for use in biodegradable implants.

Alloys were produced in the levitation induction melting furnace inside a controlled environment. The magnetic field generated in metallic components facilitated the manipulation, heating, and melting of solid materials within a specifically designed inductor powered by a medium frequency converter (Fig. 1). Two types of alloys were obtained: Sample 1 (Mg-Ca_2-Zn_1) and Sample 2 (Mg-Ca_2-Zn_2). A series of preliminary operations was conducted on the samples, entailing their embedding in epoxy resin or a catalyst mixture at a 4:1 ratio, followed by demolding after 24 hours. The specimens were then polished at 150 rpm with a force of 15 N utilizing the Struers TegraPol-11 polishing system. The sophisticated carbide grinding method was employed. Carbide abrasive sheets of increasing grit were utilized, first with P400 grit and concluding with P2500 grit. Ultimately, mirror polishing cloths were utilized with a 0.06 μm colloidal silica polishing slurry (see Fig.1).

The Vickers microhardness test is conducted with the Affri durometer, model DM8. Three different weights of 1 g, 5 g, and 10 are applied using a durometer with an x50 increase. After that, the load is chosen, and the test begins in the microdurometer [3].

In addition, the samples were submerged in an ultrasonic unit for five minutes to eliminate any remaining contamination. The sample preparation methods for metallographic analysis were performed according to ASTM E3-11:2017 [4]. Three electrodes are utilized in the electrochemical assessments: a reference electrode (saturated calomel), a counter electrode (platinum electrode), and a working electrode (the sample being analyzed), in compliance with ISO 10271:2020. The specimen is immersed in an electrolyte inside an electrochemical cell. The following elements were measured in mmol/L in the Ringer Grifols solution: Na+ 129.90; K+ 5.40; Ca2+ 1.80; Cl– 111.70; and C3H5O3 27.20. Utilizing a BioLogic Essential SP-150 potentiostat-galvanostat, three techniques were progressively employed to examine the corrosion behavior of the alloys: corrosion potential, corrosion rate, and electrochemical impedance spectroscopy. Impedance measurements were conducted using "Potentio Electrochemical Impedance Spectroscopy" in compliance with ISO 16773-1-4:2016 [5,6].

The image from Fig.2a exhibits a distinct contrast between phases, likely indicating different intermetallic compounds or precipitates within the magnesium matrix. The bright regions suggest the presence of secondary phases, possibly Mg_2Ca or Zn-rich phases. The structure appears more interconnected, with fine networks of secondary phases distributed throughout the matrix. The increased presence of bright phases indicates a higher degree of solidification segregation or intermetallic compound formation.

As Zn content increases (see Fig.2c), the microstructure appears somewhat more refined or less interconnected than in Fig.2a. There is still evidence of secondary phases, but they appear more dispersed rather than forming an extensive network. The difference in dwell time (30 μs vs. 100 μs) may slightly affect contrast and clarity, but the overall trend suggests that increasing Zn content alters the microstructural formation. The refined structure in the Fig.2c indicates a possible grain refinement effect due to the additional Zn content.

In EDS spectra (see Fig.2b and Fig.2d) the highest intensity peak corresponds to Mg, confirming that magnesium is the primary element in the alloy.

A distinct peak, suggesting the presence of calcium-rich phases (likely Mg_2Ca intermetallic compounds), is similar in both spectra due to the same concentration of Ca in the alloys.

A smaller peak, indicating the presence of zinc, which may be in solid solution or form Mg-Zn-based intermetallic compounds, has double intensity in the alloy $MgCa_2Zn_2$.

It was assessed by analyzing the microhardness values of the samples. Sample 1 showed a mean microhardness of 59.0 HV and a median of 60.0 HV, with a standard deviation of 9.0 HV, indicating a symmetric distribution and moderate variability. The values ranged from 41.3 HV to 74.0 HV (see Fig.3).

Sample 2, had a mean microhardness of 63.8 HV and a median of 63.6 HV, also showing a symmetric distribution. However, it exhibited a higher standard deviation of 10.3 HV and a broader range, from 37.4 HV to 87.0 HV, reflecting greater variability (see Fig.3).

The results indicate that Sample 2 has a higher average microhardness, suggesting greater resistance to deformation, but with increased variability, possibly due to microstructural heterogeneity or processing conditions. The symmetry in the data distribution is confirmed by the proximity of the mean and median in both samples (see Fig.3).

A higher corrosion potential indicates that the alloy is less electrochemically active, i.e. it has a lower tendency to corrode (see Fig.4a). Zn is a nobler element than Mg, so as its content in the alloy increases (from 1% to 2%), the corrosion potential shifts to more positive values, suggesting higher corrosion resistance.

An alloy with higher Zn content (sample 2) may form a more homogeneous microstructure or lead to the formation of more stable and protective passivating films on the Mg surface, reducing the dissolution of the metal in the corrosive medium (a lower corrosion rate, see Fig.4b). It is also possible that Zn reduces the activity of the anodic sites in the alloy, slowing down the corrosion reaction rate [7].

One major benefit of magnesium alloyed with small levels of biogenic elements, like zinc, is that it has long-term biocompatibility. Biogenic elements are found in large quantities in the body. Because children are the main beneficiaries of resorbable orthopedic implants, it is essential to carefully assess the biocompatibility and long-term toxicity of various alloying elements.

Increasing Zn from 1% to 2% influences the phase distribution and morphology.

Higher Zn content leads to the formation of finer intermetallic structures, improving corrosion resistance of the alloy.

The microhardness analysis highlights significant differences between the two samples, with Sample 2 showing higher hardness but greater variability. These results emphasize the need to consider both central tendency and variability when assessing material properties. Further research into microstructural and processing factors is recommended to optimize the materials mechanical performance (see Fig.4).

The presence of Mg_2Ca, MgZn, or other intermetallic phases impact the alloy's corrosion resistance and overall performance.

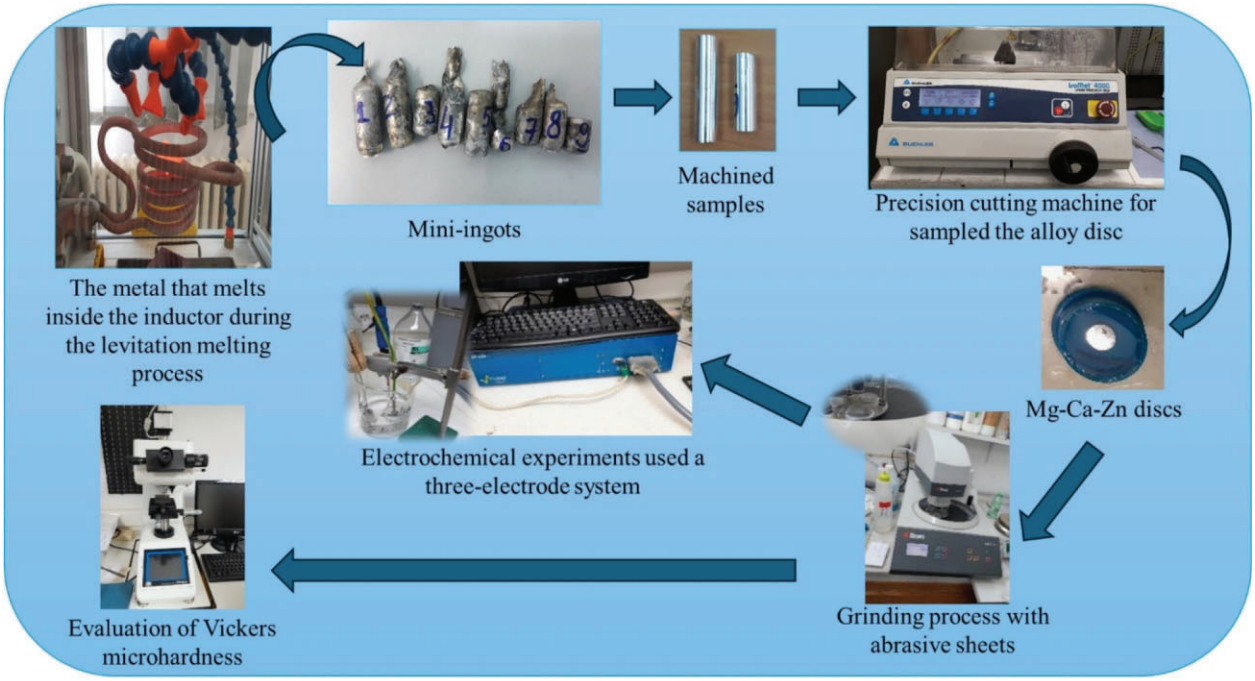

Fig. 1. Obtaining Mg-base alloys in levitation, samples' preparation and testing.

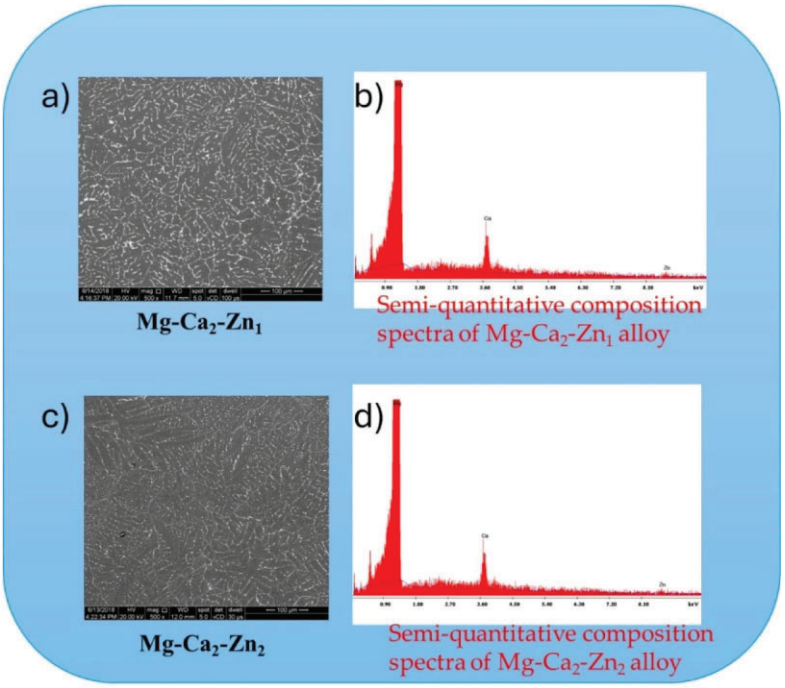

Fig. 2. SEM microstructure of Mg-Ca-Zn alloys.

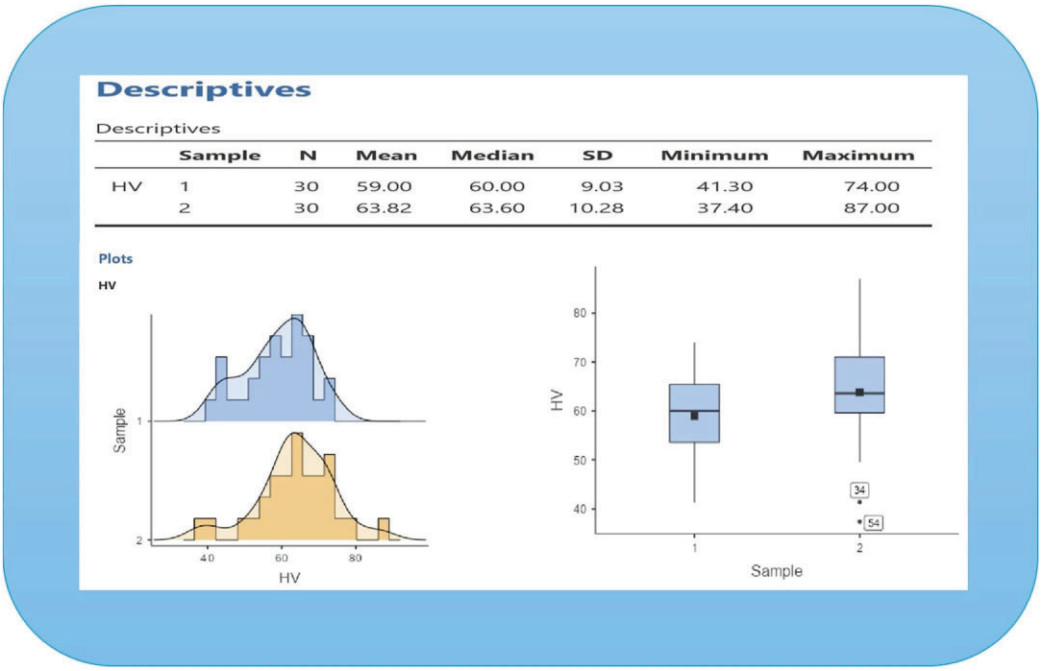

Fig. 3. Microhardness statistics.

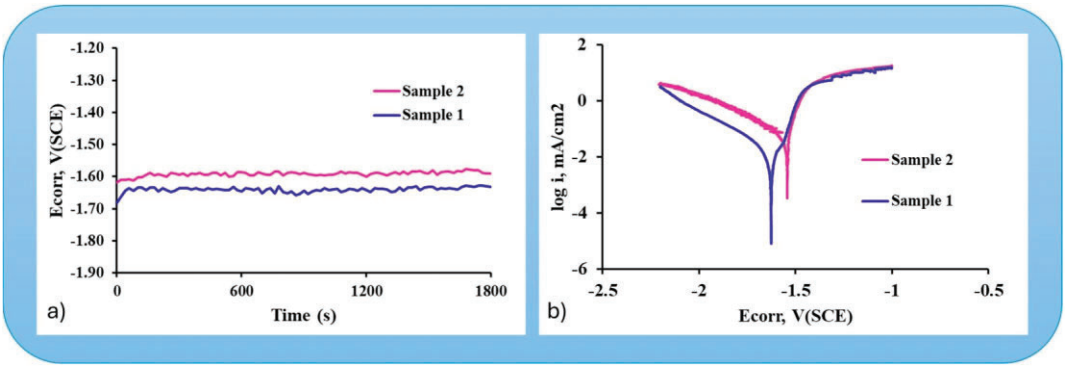

Fig. 4. Electrochemical testing of the samples.

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