



Use of high energy milling and porosity insertion in the development of the MgZn system targeting biomedical applications

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Abstract: During the last decades, the study of biomaterials, which has been occupying a wide area, has been applied and complemented, with the objective of adapting to the advances in the standard of living of the population. With that in mind, the development of orthopedic implants with good long-term biocompatibility is increasingly necessary, as current materials intended for this purpose have many complications related to their mechanical properties and biocompatibility, characteristics necessary for materials with this purpose. Therefore, a relevant solution is the development of biodegradable metallic biomaterials, as they have excellent profiles for orthopedic implants, avoiding many problems found in currently used metals, such as toxicity and stress protection. Within this class of materials, magnesium is the fourth most abundant element in the human body and is important for bone regeneration. In this work, a new route for processing porous alloys of the MgZn system with 1.2 and 3% by weight of Zinc will be evaluated, using high-energy grinding, via powder metallurgy, where, in this research, we present promising characteristics since it presents the powder with suitable morphological characteristics for sample production without the need for a controlling agent that provides the porosity of the sintered material. Therefore, the development of metal alloys with porosity controlled by powder metallurgy is suitable for obtaining biomaterials with control of mechanical strength and modulus of elasticity, in addition to the possibility of controlling open porosity, essential for osseointegration.

Keywords: Biomaterials. Biodegradable alloys. High energy grinding. Porous magnesium alloys.

Introduction

Lately, studies have been carried out with metallic alloys based on Magnesium (Mg), in the search for the best composition for the manufacture of biocompatible and bioabsorbable orthopedic surgical implants, in addition to being the key to a series of biological functions in the human body, in the However, in recent years, the increased incidence of musculoskeletal injuries and defects caused by trauma, inflammation, sports and age, brings the need for greater demands for orthopedic implants, thus stimulating the development of the subclass of metallic biomaterials. Which are currently mainly represented by stainless steels and titanium alloys, since metallic biomaterials have great potential in load bearing applications, due to their mechanical properties in relation to other materials. However, they are still limited by the protective effects against stress caused by their high Young's modulus compared to natural bone and by replacement or removal surgeries that increase the cost and risk for patients ^[9,12]. Such characteristics may lead to the elimination of the step of removing the material implanted in the patient after complete bone consolidation of the fractured region, avoiding a second surgical procedure, which would have been impossible until the end of the 20th century. At this time, advances in alloys, surface treatments and coating technologies made it possible to control corrosive behavior, which would reduce contamination risks and

costs, reigniting the field of Mg-based biomaterials. Another important characteristic of Mg alloys is linked to their degradation, which generates products, mainly Mg ions, which do not present observable toxicity to human tissue, since Mg is the fourth predominant mineral in the human body, acting as an essential element in building bones and soft tissue. Likewise, when excess Mg ions do not cause complications, as they are transported by the circulatory system and excreted in the urine, without causing negative effects in the body ^[10].

However, there are still limitations related to the use of Mg alloys, because in fluoridated solutions, including body fluids, such alloys have a high rate of degradation, which leads to rapid corrosion, causing not only the premature loss of their mechanical integrity, but also resulting in accumulation of hydrogen in vivo, generating subcutaneous edema and alkaline elevation at the site. Thus, new alloys with addition of elements that increase their resistance to corrosion are in high demand. From a biocompatibility point of view, the most promising alloying elements are mainly concentrated in human nutrients, including Zn, Ca, Sn, Si and Sr ^[8,10,12].

Bearing this in mind, because from the point of view of mechanical properties, Zn is known as a good solid solution and precipitation intensifying agent in Mg alloys, being one of the main alloying elements used in Mg ^[1].

The use of metallic biomaterials began in the 1860s, when the metallurgical industry began to grow during

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the industrial revolution. Metallic materials occupy a prominent place in the engineering of biomedical implants because of their uniform properties (e.g., high strength and durability), ease of fabrication, and reasonable biocompatibility, all of which are desirable to achieve implant longevity^[3,6].

The powder metallurgy technique is a form of processing that has been explored to obtain the appropriate composition, adding several methods adopted to control and evaluate both the corrosion and the biocompatibility of biomaterials in the intended metallic alloys. With this evolution, Mg and some of its alloys have stood out in research as a biodegradable metallic material suitable for biomedical filler applications with physical and mechanical properties similar to those of bones, making them excellent candidates for implant materials for the treatment of bones fractures. Mg alloys have shown encouraging results when used as tissue engineering scaffolds^[11].

Powder metallurgy, being a flexible manufacturing process capable of providing a wide range of new materials, microstructures and properties, creates several unique niche applications for powder metallurgy, such as wear resistant composites. The choice of a powder production process among several possibilities depends on: the understanding of the process, if it is economically viable, the final characteristics of the powder resulting from the process and if these characteristics are in accordance with the expected properties for the intended application^[5].

From there, several works and published scientific researches emerged involving the techniques that, lately, have been used for the production of metallic biomaterials. It was also verified that the mixture of different powders via milling can enable the induction of chemical reactions at temperatures much lower than those normally required, a process called mechanically activated synthesis^[7].

The present scientific and technological research work suggests the use of high energy milling and specific procedures of shaping and sintering at 580°C/2h in an argon atmosphere, for samples of the MgZn system, specifically Mg and Zn (with 1, 2 and 3 wt %) with variable porosity and density, for biomedical applications. Powder metallurgy techniques will be directly applicable and useful in defining sample geometries for microstructural, surface and mechanical characterizations. Thus, the studies of the present work will be concentrated on the process by metallurgy and high energy powder milling, which allow to improve the homogenization of the distribution of the elements of the MgZn systems.

Materials and methods

To obtain the samples, elemental powders of Mg and Zn were used in percentage by mass of the elements, the Mg powder supplied by the company Rima Industrial with a purity of 99.21% and the Zn obtained in alpha Aesar by thermo Fisher Scientific with a purity of 98.64% of the elements normalized to 100% by analysis performed

by X-ray fluorescence, in Axios MAX equipment, PANalytical brand, with semiquantitative analysis without standardization; at the Department of Materials Engineering, School of Engineering of Lorena, São Paulo State University – DEMAR–EEL–USP.

High energy milling of commercially pure powders was defined as a process to produce Mg samples with different Zn proportions. In each milling step, 3.5 g of powder were used to homogenize the mass elements used from the weight ratio of the mass of the balls to the mass of the powder of 5:1. Tungsten carbide (WC) balls and flasks were used for all grinding and a SPEX 8000D mill was used in the Department of Materials Engineering at Escola de Engenharia Lorena at Universidade Estadual Paulista – DEMAR–EEL–USP because this mill in its process delivers greater kinetic energy to the spheres and generates a grinding process that tends to be more severe, improving the homogenization of the powder mixture. The milling times used were 1, 2 and 4 hours, to verify the efficiency of the mixture through the appearance of phases/mixtures with the composition of interest, and thus the powders obtained in each milling time condition were named Mg2Zn–1h, Mg2Zn–2h and Mg2Zn–4h.

Characterizations are extremely important to quantify and qualify the microstructure and mechanical properties of powders and sintered materials obtained via powder metallurgy. The samples obtained by high-energy milling of the mixtures were characterized by X-ray fluorescence (XRF), X-ray diffraction (XRD) and scanning electron microscopy (SEM+EDS).

Results and discussion

After the high energy powder milling step, the results are presented for the Mg2Zn–1h, Mg2Zn–2h and Mg2Zn–4h samples. Table 1 presents the results of the X-ray fluorescence analysis of pure Magnesium and Zinc powders when mixed with the presence of impurities, used in the calculation of the concentrations of the elements detected in the starting material as shown in Table 2, where you can – to observe the presence of the elements Mg, Zn, Ca, Al, Na, P and Si, after grinding the presence of the element Sodium (Na) was verified. It was observed that the percentages of Zn decreased for times of 2h and 4h of milling. The presence of tungsten carbide was not detected in any of the samples. It can be seen that the concentrations of the elements in the powders are similar, and the composition of the powders is close to the Mg+1 wt% Zn composition. The concentrations of Mg and Zn were close to the composition of the Mg2Zn alloy. This is due to the presence of impurities, used in the calculation of the concentrations of the elements detected in the starting material, as shown in Table 1.

Analyzing the X-ray diffractograms, Figure 1, it is possible to verify that the most intense peaks present in the samples under analysis are those of the element Mg

with compact hexagonal crystalline structure (Mg–HCP), which appears for the three milling times of the system. In this analysis, the MgZn 2 and magnesium oxide (MgO) phases, along with the presence of tungsten carbide, were verified for the three grinding times. After identifying all the phases present in the samples with the help of Malvern's HighScore Panalytical, this multifunctional software package with the Plus option, it was possible to obtain a semi-quantitative analysis of the milled powders and after identifying the peaks with the reference database, from the Crystallography Open Database (COD) by agglomerative analysis, based on its likeness. This results in a much better overview, similar or nearly identical are found,

diffraction patterns and phase positions. identified they were plotted with the support of the program OriginPro 8.5^[2,4].

Powder samples were subjected to SEM+EDS analysis to assess morphologies. In Figure 2, which shows micrographs taken at 1500X magnification, the flake-shaped particles highlighted in light gray were determined by EDS to be composed of zinc. These particles are larger at milling times of 1 and 2 hours (Figures 2A and 2B, respectively). In the grinding time of 4 hours (Figure 2C) small zinc and tungsten particles can be found, also in the form of flakes, distributed on the surface of the magnesium particles.

Table 1 – Analysis of pure Mg and Zn powders, obtained by X-ray fluorescence, expressed in percentage by mass of the elements, normalized to 100%.

Mg		Zn	
Element	Concentration	Element	Concentration
Mg	99,21 %	Zn	98,64 %
Ca	0,51 %	Mg	0,91 %
Al	0,24 %	Ca	0,41 %
P	0,03 %	P	0,02 %
Si	0,01 %	Al	0,02 %
		Si	0,01 %

Table 2 – Analysis of powder samples after grinding at 1, 2 and 4 hours of Mg₂Zn, obtained by X-ray fluorescence, expressed in percentage by mass of the elements, normalized to 100%.

Mg ₂ Zn-1h		Mg ₂ Zn-2h		Mg ₂ Zn-4h	
Element	concentration	Element	concentration	Element	concentration
Mg	97,77 %	Mg	98,26 %	Mg	97,92 %
Zn	1,46 %	Zn	0,81 %	Zn	0,86 %
Ca	0,37 %	Ca	0,54 %	Ca	0,78 %
Al	0,21 %	Al	0,32 %	Al	0,37 %
Na	0,16 %	Na	0,03 %	Na	0,04 %
p	0,02 %	p	0,03 %	p	0,02 %
Si	0,01 %	Si	0,01 %	Si	0,01 %

Figure 1 – X-ray diffractograms of powder samples: (A) Mg 2Zn 1h, (B) Mg 2Zn 2h and (C) Mg 2Zn –4h.

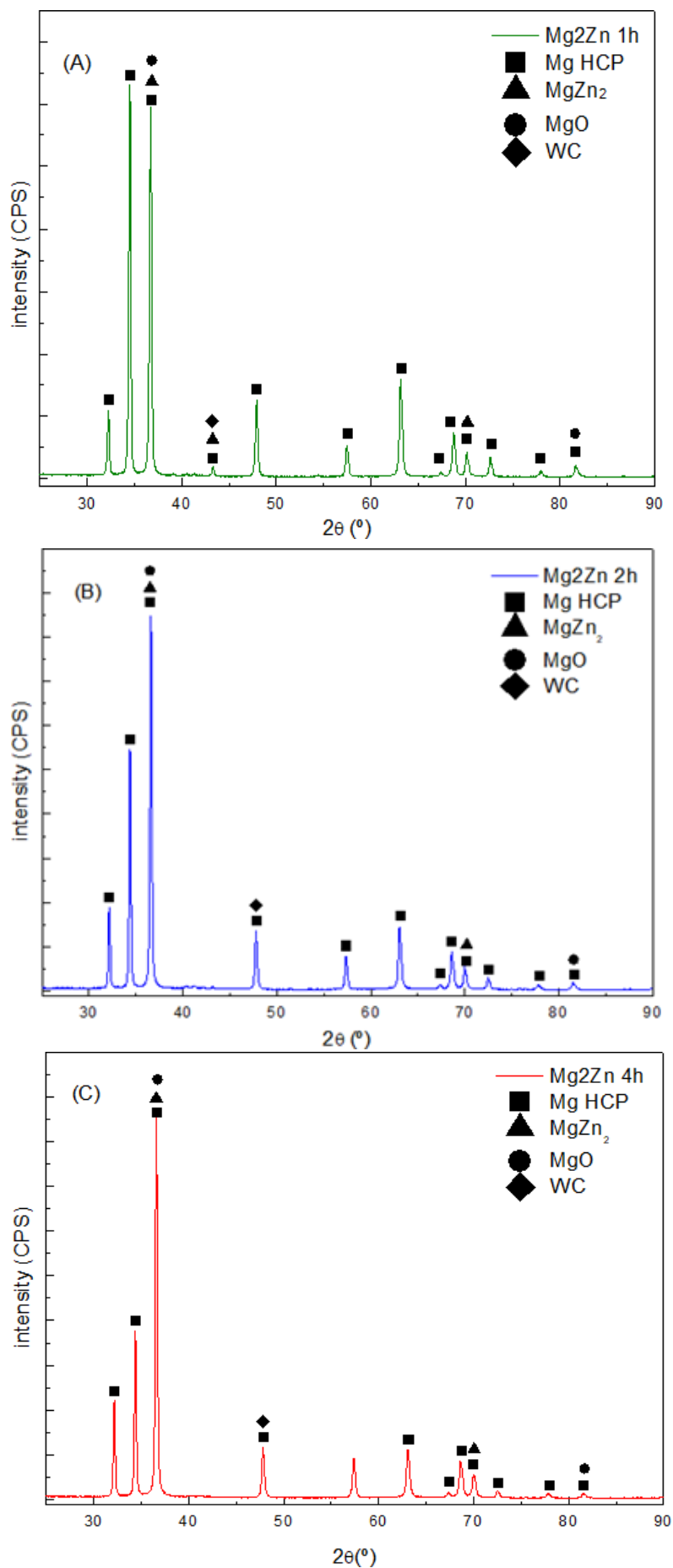
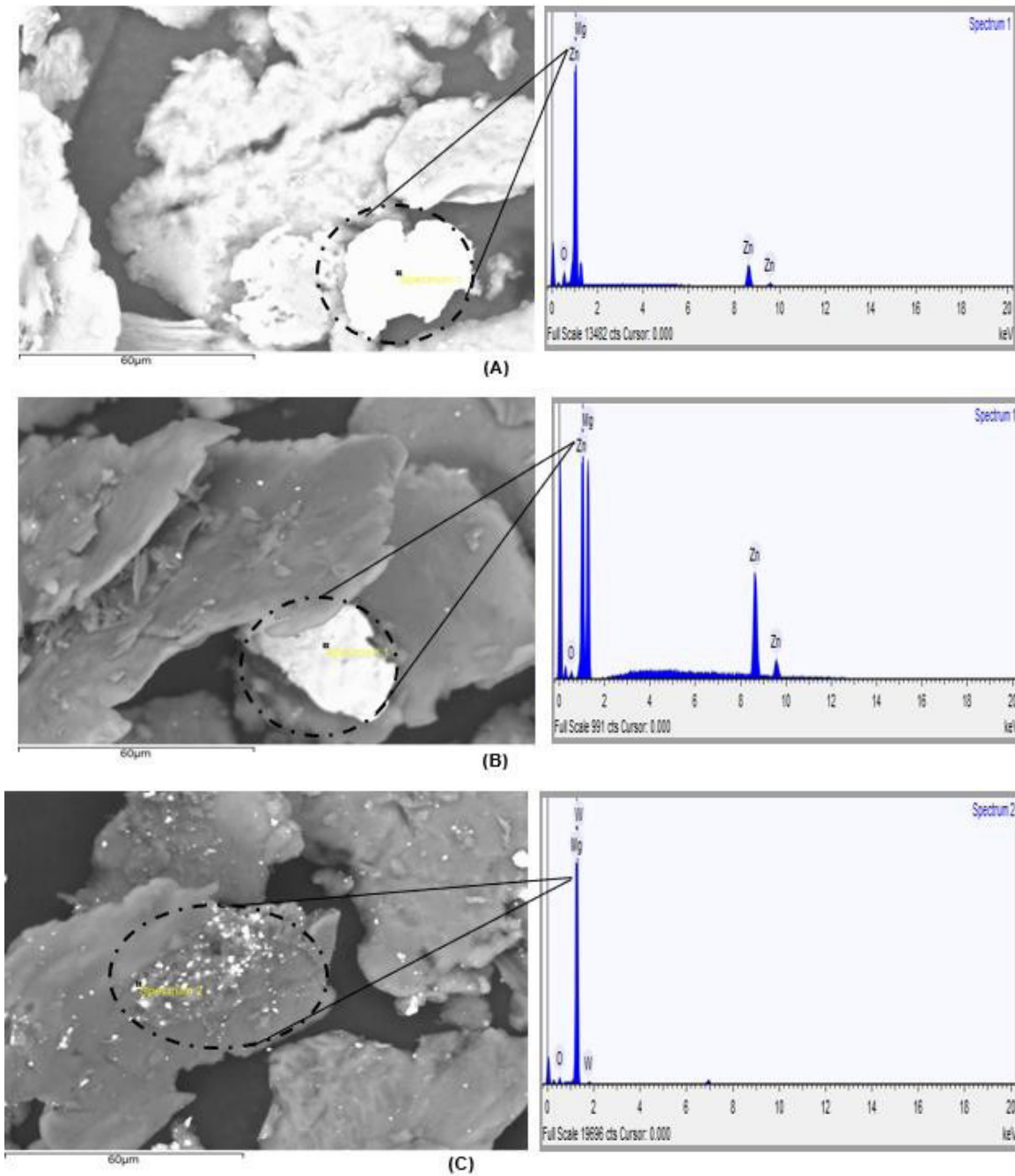


Figure 2 – Powder micrographs of Mg2Zn–1h (A), Mg2Zn–2h (B) and Mg2Zn–4h (C) samples, obtained by SEM+EDS with 1500X magnification.



Conclusion

With the XRF analysis of the elementary powders, it was possible to verify the loss of zinc mass with the increase of the milling time. High energy grinding allows introducing many defects in the powder particle structure. In addition to zinc being a light element, due to the high energy grinding being very severe, the friction between the particles generates irregularities on their surfaces, which leads to deformations and fractures in the particles of the elements used in this research, reducing their sizes, mainly to Zinc, due to its greater hardness. In addition, because they are in the form of flakes, the particles have greater roughness, lower packing density and greater angle of repose, which may allow the presence of pores for the sintered system.

Through the study of high energy grinding in a SPEX mill, it was possible to verify that the magnesium powder ground with 2% by weight of Zinc, for the grinding times of 1, 2 and 4 hours, presented particles of different sizes in the form of flakes. The presence of tungsten carbide was verified through SEM+EDS and XRD analysis, from the flask and grinding balls, which became a contamination in the powder obtained by the procedure.

It was possible to verify that the grinding times were not enough for the homogenization of the powders, since the analyzes show pure Mg with HCP structure, but it was possible to verify the presence of phases with $MgZn_2$ in the grinding of the elementary powders, which shows how much grinding heats the powder and predicts phase formation in the grinding process.

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