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Synthesis of Biodegradable Mg-Zn Alloy by Mechanical Alloying: Effect of Milling Time

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Abstract

Magnesium (Mg) is one such promising light weight metal, which is currently utilized for bio-engineering applications. Mg possesses a number of attractive characteristics that make Mg-based materials potential candidates to serve as implants for load-bearing applications in the medical industry due to its good biocompatibility and biodegradability. However, Mg and its alloys are susceptible to suffer attack in chloride containing solutions, e.g. the human body fluid or blood plasma. Thus, alloying with other metal elements is the most effective tool to improve mechanical properties and corrosion resistance of Mg. In this current work, binary Mg-Zn alloy was produced using mechanical alloying (MA) followed by compaction and sintering. The aim of this work was to study the effect of milling time on binary magnesium-zinc (Mg-Zn) alloy synthesized by mechanical alloying. A powder mixture of Mg and Zn with the composition of Mg-10wt%Zn was milled in a planetary mill under argon atmosphere using a stainless steel container and balls. Milling process was carried out at 250 rpm for various milling times i.e. 1, 2, 5, 10 and 15 hours. 3% n-heptane solution was added prior to milling process to avoid excessive cold welding of the powder. Then, as-milled powder was compacted under 400 MPa and sintered in a tube furnace at 350 °C in argon flow. The refinement analysis of the x-ray diffraction patterns shows the presence of Mg-Zn solid solution and formation of $MgZn_2$ when Mg-Zn powder was mechanically milled for 2 hours and further. A prolonged milling time has increased the density and microhardness of the sintered Mg-Zn alloy.

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Keywords: Mg-Zn alloy ; mechanical alloying; microhardness

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1. Introduction

Magnesium (Mg) stands out as a potential candidate for temporary implants in biomedical applications due to its light weight, as well as its elastic modulus and compressive yield strength that are compatible with those of natural bone[1, 2]. The density of Mg is 1.738 g/cm3, which is only slightly less than that of natural bone (1.8–2.1 g/cm3), while the elastic modulus of pure Mg is 45 GPa, as compared to human bone (40–57 GPa)[3]. Accordingly it can reduce the chance of stress shielding effects observed in the case of higher modulus materials such as titanium[4]. Mg is biocompatible and biodegradable in human body fluid, thus eliminating the need for a second operation to remove a temporary implant. However the use of Mg alloys is generally not advisable because most alloying elements can be toxic to the human body (except for Ca alloys, for example)[5]. For example, excessive copper amounts have been linked to neurodegenerative diseases like Alzheimerr's and in high doses of aluminium has been shown to increase estrogen-related gene expression in human breast cancer cell when cultured in a laboratory setting[6]. Compared to several other metal ions with similar chemical properties, zinc (Zn) is relatively harmless. It is vital for many biological functions and plays a crucial role in more than 300 metabolic activities of the body's enzymes and is considered essential for cell division and the synthesis of DNA and protein[7]. Whereas intoxication by excessive exposure is rare, Zn shortage is widespread and has a detrimental impact on growth, neuronal development, and immunity, and in severe cases its consequences are lethal. Thus, in this study, Mg-Zn was produced by mechanical alloying (MA) since it is an effective route to produce metallic alloys with fine microstructure[8,9]. MA i.e. high-energy ball milling enables high energy impact on the charged powder by collision between the grinding media and powder particles, which causes severe plastic deformation, repeated fracturing and cold welding of the particles leading to nanocrystalline materials formation[10, 11,12]. Generally, however, little information is available regarding the production and bulk properties of Mg alloy prepared by MA technique. Hence, further investigation need to be performed in order to produce Mg-Zn alloys with the desired properties. In this present study, density and microhardness were investigated in order to ensure the alloys produced have ranges close to that of human bones.

Nomenclature

MA	Mechanical alloying
Mg	Magnesium
XRD	X-ray diffraction
Zn	Zinc

2. Experimental Procedure

A mixture of elemental Mg powder (99.00 % pure, < 227.41 µm) and Zn powder (99.00 % pure, < 121.65 µm) corresponding to Mg-10wt%Zn was mechanically milled for various milling times of 1, 2, 5, 10 and 15 hours. Mechanical alloying was carried out using a high-energy Fritsch Pulveristte P-5 planetary mill under argon atmosphere. The powder to ball weight ratio of 1:10 was kept constant during the milling process using 20 mm-diameter stainless steel balls. 3% n-heptane solution was added onto the powder mixture prior to the milling process to prevent excessive cold welding of the elemental alloy powders. The as-milled powders were cold pressed under 400 MPa and subsequently were sintered at 350 ºC for an hour in argon flow. Qualitative X-ray diffraction (XRD) analysis was done to identify the presence of element and phases. Density of the green and sintered alloy was measured using pycnometer density equipment according to Archimedes' principle. Vickers microhardness test was carried out by applying an indentation load of 500 gf for 10 seconds.

3. Results and discussion

3.1 Phase Analysis

As shown in Fig. 1, XRD pattern for most of all mechanically alloyed samples produced at different milling times showed the presence of α-Mg phase after sintering process. However, at 1 hour of milling peak of Zn still can be identified. This phenomenon explained that solid solution of Zn into Mg was not completely occurred within an hour. Prolong to 2 hours, no more Zn peak was detected which suggested that the time was sufficient for Zn to solid solved into Mg matrix. In addition to α-Mg, secondary phase of γ-$MgZn_2$ phase peaks can be clearly identified in the samples which were milled at 2 hours and further. In Mg-Zn composition, solubility limit of Zn in Mg phase is 6.2 wt% at eutectic temperature (340 ºC) but it is very little at room temperature. The produced samples were alloyed with 10 wt% of Zn. Since the added Zn was exceeded its solubility limit in Mg, the formation of complete α-Mg phase was restricted and resulted in the formation of secondary phase of γ-$MgZn_2$. Therefore, the formed crystal phase in the milled alloy was not only solid-solution α-Mg but contained γ-$MgZn_2$ as well. In addition, the peaks of Mg in the sintered alloys were shifted to the left-hand side due to solid solution formation. During formation of solid solution, smaller radius of Zn (134 pm) atoms took place as impurities in the larger Mg (157 pm) lattice. The replacement of Zn in the host site caused a reduction of the lattice. In addition, the shifted angles were also caused by a reduction of crystallite size and/or the accumulation of lattice strain during mechanical alloying[8]. This indicated that the formation of fine crystallite which is due to the increasing number of collisions per unit time during milling process.

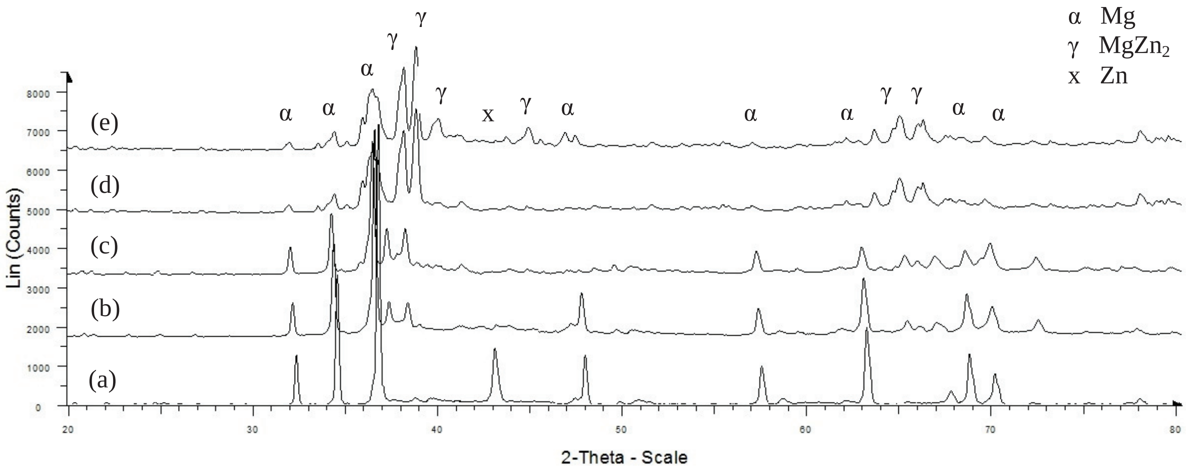

Fig. 1. XRD patterns for sintered Mg-10wt%Zn alloys those were mechanically milled (a) 1 hour (b) 2 hours, (c) 5 hours, (d) 10 hours and (e) 15 hours

3.2 Microstructure Observation

Fig. 2 shows the microstructure of Mg-10wt%Zn alloys that were milled at different milling time. Alloys that were synthesized at shorter time (1 hour) resulted in larger size and higher amount of pores which represented as black spots. As the time was increased, compacted microstructure reduced with respect to size and distribution of pores. The reduction of pore size and its distribution at longer time increased the contact area between grains leading to enhance densification effect, sinterability and its properties afterward. The increased elimination of pores at 10 hours compared to that at 1 hour of milling suggested that better densification of the binary Mg-10wt%Zn alloy was achieved by mechanical alloying of the Mg-10wt%Zn mixture at a prolonged milling time, coupled with appropriate compaction and sintering processes.

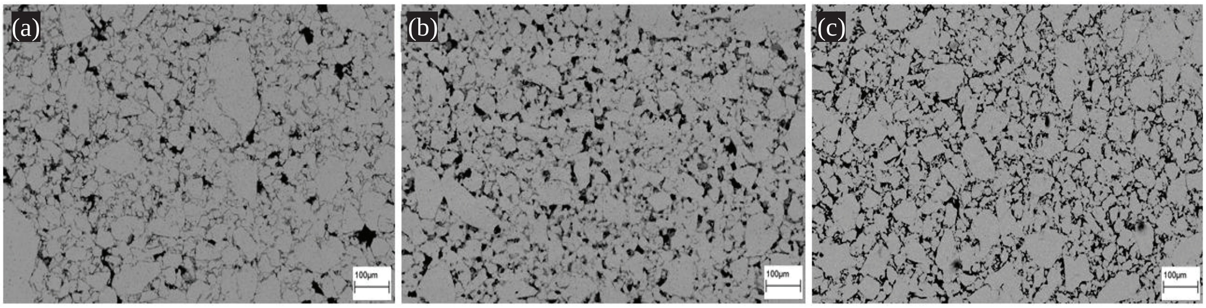

Fig. 2. SEM micrographs for (a) 1hour, (b) 5 hours, and (c) 10 hours

3.3 DensityMeasurement

As the milling time increased, the green and sintered densities of the compacted Mg-10wt%Zn alloy increased (Fig. 3). The sintered compact exhibited a higher density than that of the green body. This may be due to the presence of pores inside the green body since the pores were not fully eliminated due to plastic deformation in the powder upon consolidation. During sintering, atom diffusion occurred and reduced the presence of pores. Hence, higher density was attained by the sintered compact. This result can be explained by powder refinement of particles which was caused by higher kneading during mechanical alloying, lowering the distance between particles[10]. As a result, densification during sintering was improved. According to Fig. 3, sintered density of Mg-Zn alloy was increased with increasing in milling time and reached highest value of 1.813 g/cm^3 for 10 hours of milling. A further increase in milling time up to 15 hours led to a decrease in the density of the alloy. Reduction of density was mainly affected by the excessive heat generation at higher milling time and caused the occurrence of cold welding during mechanical alloying[11]. Then, the compressibility of the as milled alloy reduced which resulted in the lowering of its densification effect and its properties afterward.

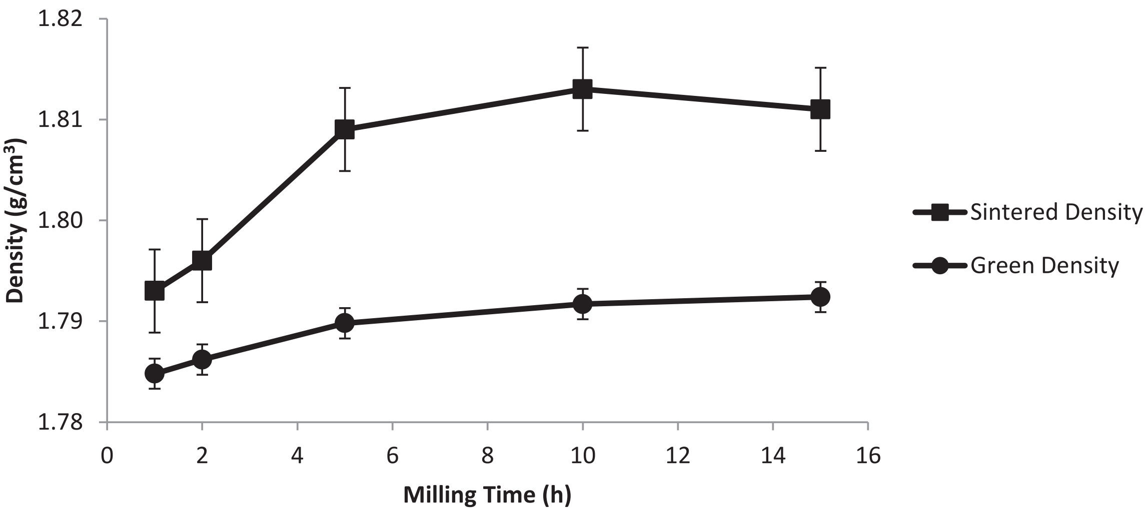

Fig. 3. Green density and sintered density of Mg-10wt%Zn compact at different milling times

3.4 *Microhardness of Sintered Alloy*

As shown in Fig. 4, microhardness of Mg-10wt%Zn alloy increased from 66.73 HV to 88.72 HV when milling time was increased from 1 hour to 10 hours. The increase in microhardness value of the alloy was mainly attributed to the work hardening mechanism which took place due to severe plastic deformation during uniaxial consolidation[12]. In addition, as milling time increased, the dispersion of Zn particles in the Mg matrix were also increased during sintering and resulted in stronger bonding between alloying and matrix particles. Consequently, densification effect was improved which then enhanced microhardness of the sintered alloys. However, up to 15 hours of milling time, microhardness was dropped to 87.66 HV. This situation can be explained by the reduction of densification effect due to the low compressibility of as-milled alloy during compaction.

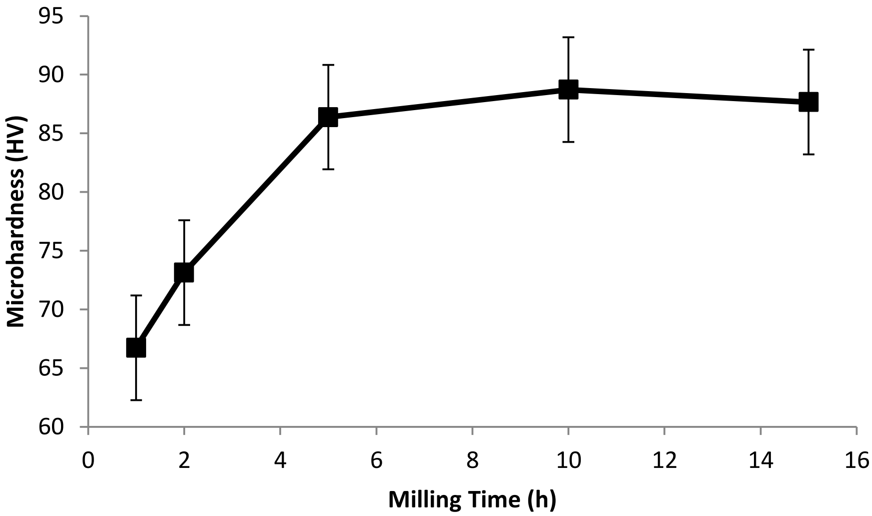

Fig. 4. Microhardness of compact sintered Mg-10wt%Zn alloy at different milling times.

4. Conclusion

In this paper, Mg-10wt%Zn was prepared in solid state route using mechanical alloying of Mg-Zn powder mixture with a variation of milling times. XRD diffraction pattern showed the phase of α-Mg solid solution and secondary phase of γ-$MgZn_2$ were formed in the alloys that were mechanically milled at 2 hours and further. Alloy prepared at prolong milling time up to 10 hours showed higher green density, sintered density and microhardness due to refinement of mixture particle size but then reduced at longer milling time owing to excessive heat generation and lowering in its densification effect. The alloy milled at 10 hours of milling time provided the highest properties in both density and microhardness which were 1.813 g/cm^3 and 88.72 HV, respectively.

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