Synthesis and Characterization of MgZn-5%HAp Biocomposites

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ABSTRACT

In recent years, development of magnesium (Mg) as biodegradable implant has been very rapidly in orthopedic applications. This is due to its Young's modulus close to the young modulus of natural bone. However, Mg implants demonstrate higher biological activity which could cause high degradation rate in human bio-environment. Consequently, needed to develop Mg-based alloys with superior corrosion performance. In the present study, it has been attempted to develop biocomposite of Magnesium Zinc-5% Hydroxyapatite (MgZn-5%HAp) as a biodegradable bone implant. The biocomposites were prepared by adding 5wt.% powders to MgZn powder and then were sintered at temperature 350°C in a vacuum furnace for holding an hour. The characterization of MgZn-5wt%HAp biocomposite was examined by Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM/EDS) and X-ray diffraction (XRD) while corrosion tested by the potentiostat. The SEM/EDS and XRD results indicated that some of the Zn atoms have dissolved in Mg to form a MgZn solid solution. The SEM results also showed that the MgZn-5%HAp biocomposite has a microstructure with a matrix Mg and HAp at the grain boundary. The presence of HAp in the sample resulted in smaller crystallite size and corrosion rate compared to the one with MgZn alloy.

PACS numbers:
Keywords: MgZnHAp; HAp; biodegradable implant; biocomposite.
http://dx.doi.org/10.12962/j24604682.v15i1.3797

I. INTRODUCTION

Magnesium (Mg) is an alkaline earth element and it is in group II in the periodic table. It has a oxidation number +2 and is very reactive in a solution containing Cl^- [1]. Mg is one of the essential nutrients for the human body with the consumption needs of 240-420 mg/day [2] therefore it is classified to metal biomaterial. This metal has been extensively studied and developed over the last 16 years in the field of orthopedics [3–15]. The novel method in MgZn alloy synthesis was using arc plasma sintering [16]. Magnesium has preferred because it has a high biocompatibility properties in the human body, it is biodegradable in the body and also has a Young's modulus (41-45 GPa) which is closer to the Young's modulus of natural bone (3-20 GPa) [1, 7]. However the results of clinical trials indicate that pure Mg was too fragile, corrosion rate was very high in environments containing NaCl and it produce hydrogen gas after implantation [3, 16, 17]. These weaknesses must be addressed so that magnesium can be applied clinically as a biodegradable implant material. One strategythat can be done is by combining magnesium with other biomaterials, either metal or ceramic [18–25]. Zinc is a metal biomaterial has the same crystal system with Mg and its Young modulus is higher than magnesium so it has better mechanical properties than magnesium. From previous studies it was known that Zn a positive effect on corrosion resistance and strength of Mg [4, 26, 27]. MgZn alloys also produce hydrogen gas which was lower than the other Mg alloys [5, 28].

In this study, the MgZn will be composited with hydroxyapatite. Hydroxyapatite (HAp) is a calcium phosphate containing hydroxide, it is a member of a group of minerals in the bone that has a ratio of Ca/P of 1.67. Hydroxyapatite is the most stable crystalline calcium phosphate phases compared to the other at normal temperatures. The crystal structure of HAp most frequently encountered is hexagonal, having the P63/m space group symmetry with lattice parameters of a = b = 9432 Å, c = 6.881 Å, and $\gamma = 120°$ [29, 30]. The result of previous study showed that HAp syntesis can be well integrated with the environment around the bone, stimulated new bone formation, binding newly formed bones and repaired damaged

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TABLE I: Chemical Composition in the test solutions.

Chemical Composition	Ringer Lactate	NaCl 0,9%
Natrium Lactate ($C_3H_5NaO_3$)	1,55 g	-
Natrium Clhoride (NaCl)	3,0 g	4,5 g
Potassium Chloride (KCl)	0,15 g	-
Calcium Chloride ($CaCl_2.2H_2O$)	0,1 g	-
water Injection	500 ml	500 ml
Osmolarity	274 mOsm/l	308 mOsm/l

TABLE II: The content of ions in the test solution.

Ion	Ringer Lactate	NaCl 0,9%
Na^+	130 mEq/l	154 mEq/l
K^+	4 mEq/l	-
Lactate (HCO_3^-)	27,5 mEq/l	-
Cl-	109,5 mEq/l	154 mEq/l

bone tissue [31]. Furthermore, hydroxyapatite is a biodegradable ceramic that has a low corrosion rate. Some of these HAp properties underlie the idea of compositing HAp with MgZn to improve the corrosion resistance and bioactive properties of the implant.

II. EXPERIMENTAL

Synthesis and microstructure characterization of MgZn-5wt.%HAp biocomposites

A mixture of MgZn powder was obtained by mixing Mg and Zn powder with a composition of 94:6 using ball milling. Milling process used ceramic balls with average diameter 16.47 mm. Mixing was done for 4 hours to obtain a homogeneous mixture. MgZn-5wt.%HApbiocomposites were made by mixing MgZn powder with 5wt.% HAp powder used ball milling with a rotation speed of 300 rpm for 30 minutes. The ratio of ball-to-powder weight is 5:1. MgZn-5wt.%HAp powder was inserted into dyes and were compacted by uniaxially compaction machines under a pressure of 570 MPa at room temperature for 2 minutes. Then, the pellets were sintered at 350°C for holding 1 hour and were cooled to room temperature. MgZn-5wt.% HAp microstructure was characterized using X-ray Diffraction (XRD) in the range of 2θ from 25° to 80° and phase identification was done with *High Score Expert software*. MgZn-5wt.% HAp morphology was observed using *Scanning Electron Microscopy* (SEM) equipped with *Energy-dispersive X-Ray Spectroscopy* (EDS).

Corrosion rate test

The corrosion rate was measured at a liquid NaCl, Ringer Lactate and distilled water using a potentiostat at room temperature. Composition and ion content of each solution are given in Table I and Table II. MgZn Alloy and MgZn-5wt.%HAp biocomposites pellets were cleaned first with a polishing process. Then it was put in potentiostat equipment that has been filled test solution and then the corrosion rate was measured. Potentiostat using carbon rood as a counter electrode and a calomel electrode as the recommender. The corrosion rate was calculated from the corrosion current (I_{corr}) obtained from polarization curves using Tafel extrapolation.

The corrosion rate of materials is calculated with Faraday equation:

$$CR = K\frac{I_{coor}}{\rho}EW \quad (1)$$

CR is the corrosion rate in mils/year(mpy), K = 0.129 mils g/μA cm year, I_{corr} is the corrosion current density obtained from the Tafel extrapolation in μA/cm^2, EW is an equivalent weight of metal, ρ is the density of the material tested in g/cm^3 [32].

III. RESULTS AND DISCUSSIONS

Microstructure MgZn-5% wt.Hap Biocomposite

Figure 1 shows the SEM/EDS image of MgZn-5wt%HAp powder. It can be seen that hydroxyapatite particles are not visible and barely distinguishable in the mix, this is because the hydroxyapatite size is smaller than Mg and Zn. However, EDS results in each particle represented by 1, 2 and 3 indicate HAphas been evenly distributed in the mixture.

Figure 2 shows microstructure of MgZn-5wt.%HAp biocomposite. It can be seen that the MgZn-5wt.%HAp biocomposite has an Mg matrix. The EDS in position 1 showed that there were no Zn and HAp elements within the grain (dark colors), whereas EDS in position 2 showed Zn and HAp elements were at the grain boundaries (light colors). These results showed that some of the Zn atoms have dissolved in Mg and form a MgZn solid solution. This result is in accordance with what was reported by Silalahi in previous research [16]. Thus EDS results in Figure 2 indicated that the presence of 5% of HAp in the mixture does not hinder the formation of a solid solution MgZn in the sintering process.

Phase of MgZn-5% wt.Hap Biocomposite

XRD patterns MgZn-5wt.%HAp biocomposite before and after the sintering process are shown in Figure 3. HAp crystal peaks were not apparent in the XRD pattern MgZn-5wt.% HAp biocomposites. It is caused by two things in the first, HAp presentation in the mix is relatively smaller than MgZn. The second, position of the highest peak of HAp (31.773°) almost coincides with one of the high peak positions of Mg (32.194°). But when it was selected in the narrower range of 2θ (25°-40°) and a range of smaller intensity (300-1100), it was seen that HAp peak appears on 31.7° that behind lattice plane 211 (Figure 3).

If the diffraction pattern of sintered and unsintered MgZn-5wt.%HAp biocomposites were compared. We can be seen that the Mg peaks shift to the right (larger 2θ) as shown by Figure 4(a). In the Bragg law, it is known that 2θ inversely proportional to the crystal plane spacing. An increasing of

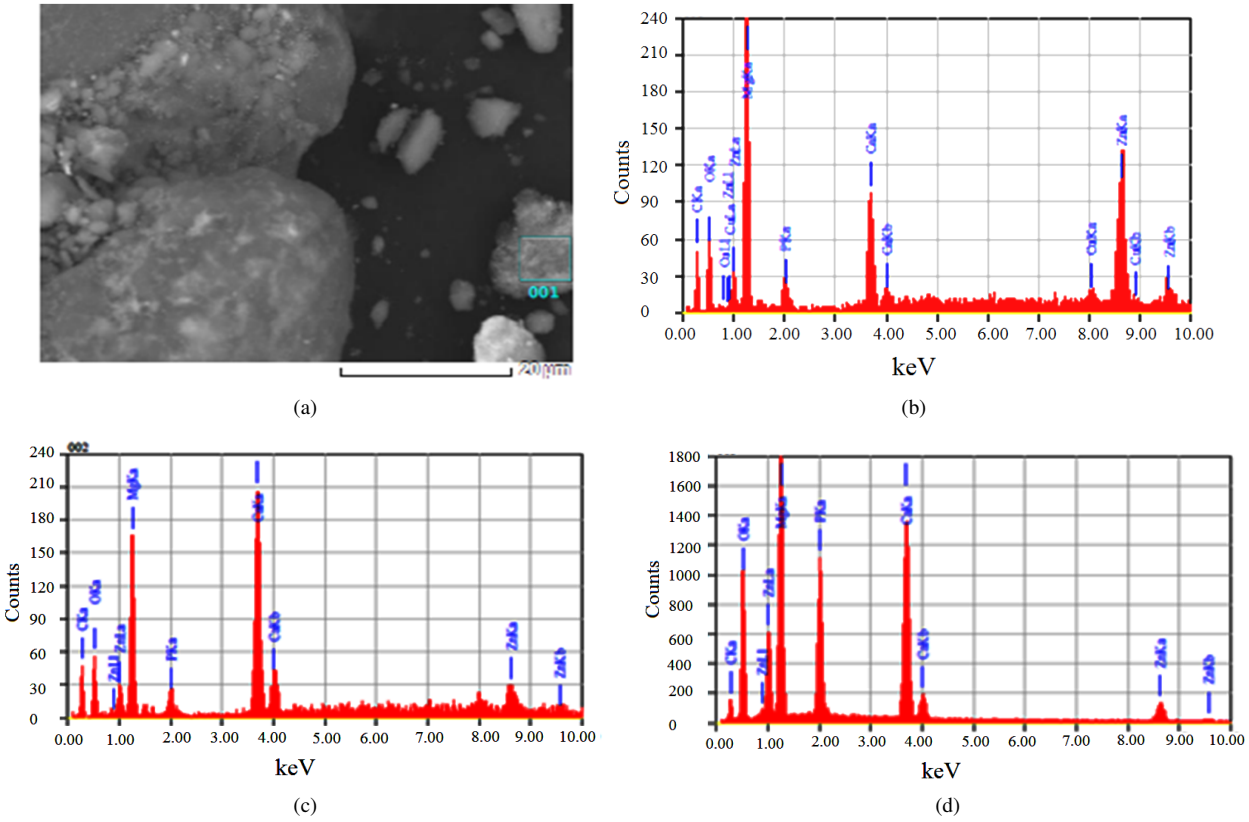


FIG. 1: EDS of MgZn-5wt.%Hap powder.

2θ show crystal plane spacing become smaller. Therefore, Mg peaks shift in the XRD patterns of MgZn-5wt.%HAP biocomposite indicates that the crystal plane spacing of Mg in the crystal system is getting shorter. Diminution of the crystal plane spacing was caused by partially Zn atoms dissolved into Mg form a solid solution MgZn. The solubility of zinc was also confirmed by decreased of the Zn peaks intensity as shown by Figure 4(b). The formation of MgZn solid solution shows that the MgZn-5wt.% HAp biocomposite has been successfully synthesized by a sintering process at a temperature of 350°C withholding for 1 hour.

Crystalite size

Crystallite of MgZn alloys and MgZn-5wt%HAp biocomposites were calculated based on X-ray diffraction pattern using Scherrer equation:

$$D = \frac{K\lambda}{\beta cos\ \theta} \tag{2}$$

where D is the size of crystallite, K is a constant related to the crystalline form, the value used is 0.9 λ is the X-Ray wavelength used, which is 1.5418 Åin Cu, and β is the FWHM value in each crystal plane. FWHM values on alloys and biocomposites are calculated using *Match 2.2.1* software. The results of the calculation of MgZn alloy crystallite and MgZn-5wt%HAp biocomposites are shown in Table III.

TABLE III: The crystallite size of MgZn alloy and MgZn-5wt%HAp biocomposites.

Sample	D (nm)
MgZn unsintered	41.68
MgZn alloy	49.01
MgZn-5wt%Hap biocomposites	41.75

The results of the crystallite measurements in Table III show that MgZn alloy crystallite size greater than MgZn unsintered. This showed the recrystallization of alloys due to heat treatment in the sintering process [33]. MgZn-5wt% HAp biocomposite also undergo the same heat treatment as MgZn alloy but the crystallite size is smaller than MgZn. The result suggests that the presence of HAp in the sample may limit the recrystallization process due to heat treatment resulting in smaller crystallite size. Previous studies have also reported similar results when compiling Mg with HAp [34, 35]. The size of the crystallite was not enlarged due to the presence of Ca in the HAp [4]. Thus it can be said that HAp is a good refiner for Mg alloys.

Corrosion test

Corrosion testing carried out on intravenous fluids NaCl 0.9%, Ringer lactate, and distilled water. These liquid represent the human body fluids. The SS 316L was used as biodegrad-

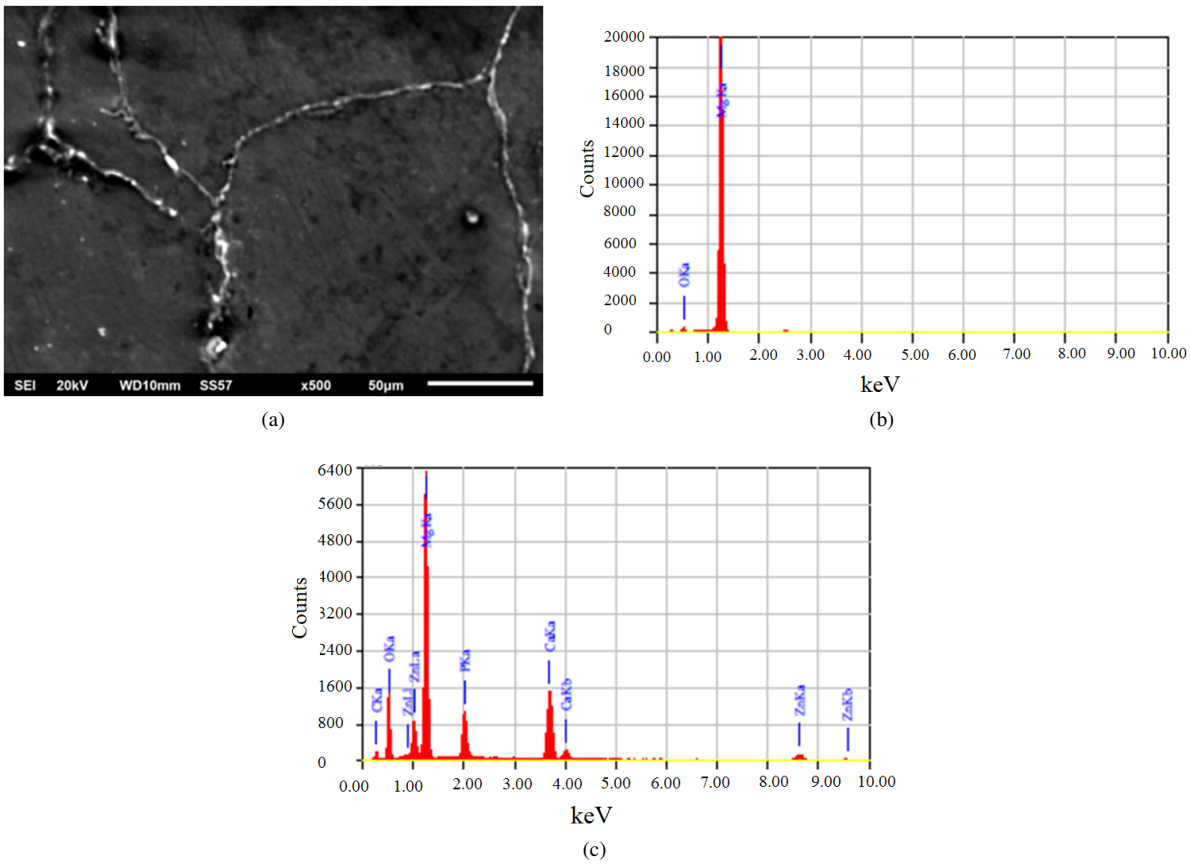


FIG. 2: SEM/EDS of MgZn-5wt.%HAp biocomposite.

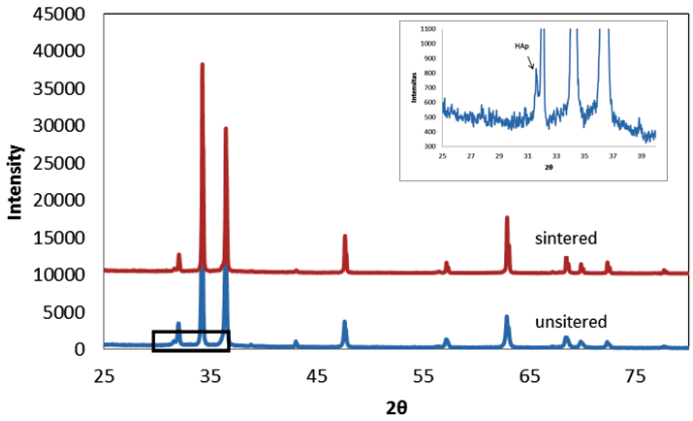
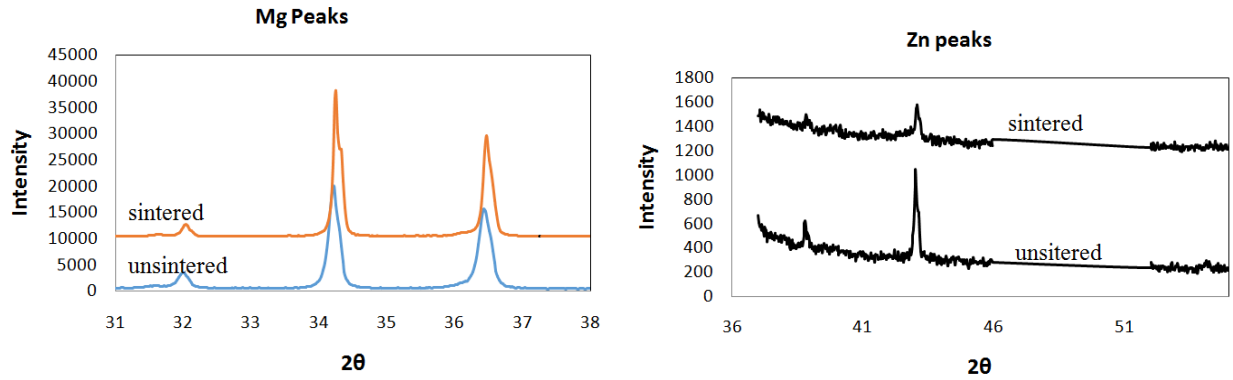


FIG. 3: Diffraction patterns of sintered and unsintered MgZn-5wt.% HAp biocomposites.

able control because it was widely used as a bone implant innert. The effect of the HAp in the sample was observed by comparing it with MgZn alloys. Figure 5 shows the MgZn-5wt.%HAp biocomposites corrosion rate in the test solution. Based on the figure, we can see that MgZn-5wt.%HAp biocomposites has better corrosion resistance than the MgZn alloys for each test solution. These results indicate that HAp can improve the corrosion resistance of the MgZn alloy with composites process. Increasing of corrosion resistance was caused by HAp occupy grain boundaries in the microstructure MgZn-5wt% HAp biocomposites (Figure 2) where grain boundaries are the most rapid corrosion of materials [36, 37]. HAp is a bioceramic and has good corrosion resistance, therefore when HAp occupies the grain boundaries, it will automatically protect grain boundaries from the corrosion processes. The corrosion rate of MgZn-5wt.%Hap biocomposite is 0.5631 mpy equivalent to 0.0143 mm/year, this value was far below the maximum limit allowed corrosion rate in the biodegradable material is 0.5 mm/years [4].

IV. CONCLUSION

MgZn-5wt% HAp biocomposite have been synthesized by a sintering process at 350°C and 1-hour detention. HAp is a good refiner for Mg and its alloys in which the addition of 5% HAp can result in smaller crystallite size. Addition of 5% HAp can also improve the corrosion resistance of materials to a solution containing Cl^-. This is a new discovery in the synthesis of Mg-based bone implant material that has never been done before.



(a) (b)

FIG. 4: (a) Mg peaks shift, (b) reduction of Zn peaks intensity on XRD pattern of MgZn-5wt.% HAp biocomposites .

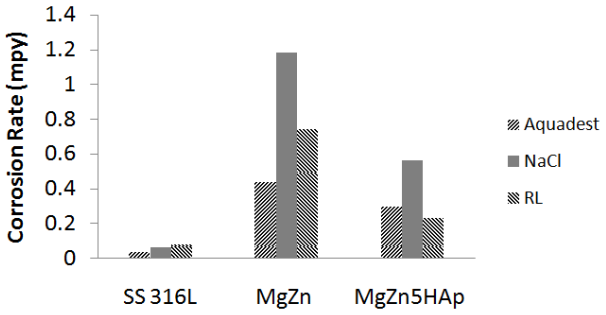


FIG. 5: Corrosion rate in test solution.

Acknowledgments

Acknowledgments are submitted to PSTBM-BATAN SERPONG which has facilitated the process of synthesis and material testing in this research.

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