Synthesis of Mg6Zn-xHAp Biocomposites Using Arc Plasma Sintering

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Abstract. Development of magnesium-based biomaterials as biodegradable bone implants has been done until now. One of the factors considered and developed is a method used in the synthesis process material. In this study, the synthesis process was done using Arc Plasma Sintering technology (APS). The APS was operated at a voltage of 12 Volts and a current of 1 ampere for 30 seconds. Biocomposites were characterized using XRD, SEM and Potensiostat. The XRD results showed that the crystal peaks in both biocomposites was shifted towards the right (larger theta). This identified that the biocomposite had a smaller distance between the crystal planes after the sintering process. The SEM/EDS results showed that on Biokomposit Mg6Zn-5% HAp green, there was only Mg element, while on Mg6Zn-7% HAp green besides element Mg, there was also element of Zn and HAp. The corrosion test results revealed that the Mg6Zn-xHAp corrosion rate was higher when the composition of HAp in the material was greater.

Keywords : Mg6ZnHAp, APS, Biocomposites

1. Introduction
The use of Mg as a bone implant is still being developed today. Various methods are carried out to synthesize Mg-based biomaterials [1,2] and various compositions are developed to improve the mechanical properties and corrosion resistance [3-6]. One research that is currently being developed is to make Mg composites with HAp [7-10]. HAp is calcium phosphate which contains hydroxide, a member of a group of minerals in bone. The results of previous studies indicate that artificial HAp can be well integrated with the environment around the bone, encouraging the formation of new bone, binding to newly formed bone and repairing damaged bone tissue [11]. In addition, HAp can also increase the corrosion resistance of implant materials [8].

The latest technology in the MgZn alloy system is the sintering process using the Plasma Sintering Arc (APS).APS technology is a sintering technology that utilizes plasma ionization of argon gas between the anode and cathode with the impulse current [12]. One of the advantages of APS is low energy consumption and fast sintering process. The use of Argon as a plasma producer makes the synthesized material protected from oxidation processes which may occur during sintering. This is a
major consideration in choosing APS for use in the manufacture of Mg-based biomaterials. The use of APS in the synthesis of MgZn alloys was first carried out by Marzuki et al [13]. Characterization of the resulting alloy was better than the alloy synthesized using Furnace. This underlies the use of APS in the manufacture of Mg6Zn-xHAp biocomposites in this study. The material to be synthesized in this study consists of two categories, namely materials with 5% HAp and materials with 7% HAp.

2. Experimental

2.1 Synthesis of Biocomposite

The materials needed to synthesize these biocomposites are magnesium powder, zinc powder, and hydroxyapatite powder. First, Zn powder was mixed with Mg powder using ball milling machine. Mass ratio of Mg to Zn was 94 : 6 and milling process was done for 4 hours with 300 rpm. After that, HAp powder was added to Mg6Zn mixture with two categories i.e 5% and 7% mass ratio. Then, each mixed category was milled again using ball milling for 30 minutes. Before sintering process is done, Mg6Zn-HAp powder was compressed first using uniaxial compaction machine at pressure 570 Mpa. Sintering process was done using Arc Plasma Sintering and was operated at the voltage of 12V, current of 1A, for 30 seconds.

2.2 Characterization of Biocomposite

Each Biocomposites was characterized using XRD, SEM and Potensiotat. Characterization using XRD was done in the range of 2θ from 25° to 80°. Phase of biocomposites was identified using High Score Expert software and their Full Width at Half Maximum (FWHM) calculation was performed using the software Match 2.2.1. The morphology of biocomposite was observed using Scanning Electron Microscopy (SEM) which was equipped with Energy-Dispersive X-Ray Spectroscopy (EDS). The corrosion rate was measured at a liquid NaCl, Ringer Lactate and distilled water using a potentiostat at room temperature.

3. Result and Discussion

3.1 Phase of Mg6Zn-xHAp Biocomposites

The material phase was identified through the results of X ray Diffraction using the High Score Expert software. The results are shown in Figures 1a and 1b. The crystal peaks detected by XRD for Mg6Zn5% HAp biocomposite consisted of 96.7% Mg peaks, 2% Zn peaks and 1.2% HAp peaks, whereas for Mg6Zn7% HAp, the detected crystal peaks consisted of 99.6% Mg peaks, 0.4% Zn peaks and 0% HAp peaks. Based on these results it was found that the Zn and HAp phases identified in the Mg6Zn7% HAp biocomposite were less compared to Mg6Zn5% HAp. This indicates that some of Zn atoms have been dissolve in magnesium, where their solubility in biocomposites Mg6Zn7% HAp is greater than in biocomposites HAp Mg6Zn5% HAp. The limit of Zn solubility in Mg alloy was 6.2% by mass at 340°C [14].

![Figure 1. Phase Identification of Biocomposites](image-url)
XRD pattern comparison of both composites to the XRD pattern of MgZn before and after being sintered using APS can be seen in Figure 2. In the figure we can see that the XRD biocomposites pattern is similar to the XRD Mg6Zn pattern, this shows that the presence of HAp does not preclude the formation of MgZn solid alloys after sintering processes. In the figure we find that the positions of the Mg peaks on both biocomposites are the same as the positions of the Mg peaks on MgZn after sintering using APS. But if we compare the pattern of the two composites to the XRD pattern of MgZn before being sintered, we can see that there is a slight shift in the Mg peak in the two biocomposites towards the larger theta (right direction). This indicates that the distance between the crystal planes of magnesium becomes smaller after the sintering process. This is because part of the Zn atom has replaced the position of the Mg atom after the sintering process. Zn has the same crystal system as Mg but the distance of the atom is slightly smaller than Mg \[5\]. Therefore, when Zn dissolves in Mg it will result in shorter distances between atoms.

![XRD Pattern](image)

**Figure 2.** XRD Pattern of material

### 3.2 Microstructure of Mg6Zn-xHAp Biocomposites

Microstructure of both biocomposites based on SEM results can be seen in the Figure 3. Figure 3a is a microstructure of Mg6Zn5%HAp with a magnification of 100 times. The figure shows microstructure with clear grain boundaries. The EDS results in Figure 4 (spot 1) shows that on green there is only Mg element and no Zn and HAp elements. While EDS results in grain boundaries (spot 2 and spot 3) shows the presence of Zn and HAp elements. Thus, we know that in the microstructures of Mg6Zn5%HAp, Zn and HAp occupy grain boundaries. Figure 3b is a microstructure of Mg6Zn7%HAp with a magnification of 100 times. Slightly different from previous material microstructure, Mg6Zn7%HAp microstructure shows microstructure with grain boundaries that are not so clear. The results of EDS in Figure 5 show that Zn and HAp occupy green and also grain boundaries. If it is considered in more detail, the intensity of Zn on the results of EDS MgZn7%HAp is lower than the intensity of Zn on the results of EDS MgZn5%HAp.
Figure 3. SEM image of Mg6Zn-xHAp biocomposite, (a) 5% HAp, (b) 7% HAp

Figure 4. EDS of Mg6Zn-5%Hap
Corrosion rate testing was carried out using 3 solutions namely NaCl, Aquabidest and Ringer Lactate. The three liquids represent human body fluids. The parameters obtained from measurements using potentiostat are shown in Table 1.

### Table 1. Parameters of potentiostat measurements

| Sample       | $\rho$ (g/cm$^3$) | EW  | $I_{corr}$ | Aquadest | NaCl | RL |
|--------------|-------------------|-----|------------|----------|------|----|
| Mg           | 1.738             | 12.16 | 0.71      | 2.87     | 1.13 |
| MgZn         | 1.8227            | 13.39 | 0.08      | 0.56     | 0.78 |
| MgZn-5HAp    | 1.8621            | 13.39 | 0.49      | 0.68     | 0.25 |
| MgZn-7HAp    | 1.8783            | 13.39 | 0.14      | 1.56     | 0.86 |

Furthermore, corrosion rate values were calculated using the Faraday equation.

$$CR = K \frac{I_{corr}}{\rho} EW$$

$CR$ is the corrosion rate in mils / year (mpy), $K = 0.129$ mils g / $\mu$A cm year, while $I_{corr}$ is the corrosion current density obtained from Tafel extrapolation in $\mu$A / cm$^2$, $EW$ is the equivalent weight of metal, lastly $\rho$ is the density of material tested in g / cm$^3$.[15].

Corrosion rate in comparisons of both biocomposites with MgZn and Mg are shown in Figure 6. When compared with the corrosion rate of MgZn both composites have a greater corrosion rate in all test solutions. The more HAp content in the material, the corrosion rate also tends to increase. However when compared with Mg, the corrosion rates of these two biocomposites are much lower,
meaning that the two biocomposites have Mg corrosion resistance. The highest corrosion rate value is in NaCl solution. This was influenced by the concentration of electrolytes contained in a higher NaCl solution (154 mEq / l) than in Ringer lactate (137 mEq / l). The higher electrolyte concentration will lead to greater corrosion rates, thus the corrosion rate produced will also be greater.

![Figure 6. Corrosion Rate of Material](image)

4. Conclusion

Mg6Zn-xHAp biocomposite has been successfully synthesized using APs technology. Mg6Zn-5% HAp Biocomposite has clear grain boundaries microstructure while Mg6Zn-7% HAp has microstructure with grain boundaries that are not clearly visible. The XRD pattern of the two biocomposites identified that some of the Zn atoms had dissolved in Mg and formed a solid solution which was marked by a shift in the peak of Mg towards a larger theta. From the results of the corrosion test it was found that the greater the content of HAp in the material the greater the corrosion rate where the greatest corrosion rate occurs in NaCl solution.

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