Microstructures and Mechanical Study of Mg Alloy Foam Based on Mg-Zn-Ca-CaCO$_3$ System

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Abstract. Magnesium alloy, a material that has potential to use some applications such as aerospace components, computer parts, and mobile phones. Magnesium alloy can also be a popular candidate as an orthopedic implant material for biodegradability, non-toxicity, and mechanical and physical properties that are excellent. Magnesium, one of the main macro elements required for the proper functioning of the human organism, is used to test the materials for biodegradable implants. The main objective of this study was to find out the microstructure, and mechanical characteristics of the Mg-Ca-Zn-CaCO$_3$ alloy as porous implant materials are biodegradable. The presence of CaCO$_3$ on the alloy functions as a foaming agent expected to produce gas bubbles during manufacturing process taken place that will form pores in the alloy. Mg-Ca-Zn-CaCO$_3$ alloy was made by powder metallurgy method with three variations of composition (96Mg-Ca-3Zn-CaCO$_3$, 91Mg-Ca-3Zn-5CaCO$_3$, and 86Mg-Ca-3Zn-10CaCO$_3$ wt%). Milling process was by using a shaker mill for 2 hours to produce a powder size distribution which was more homogeneous. The mixed powder was uniaxially pressed at a pressure of 100 MPa for 2 minutes and 200 MPa for 3 minutes into green compacts with dimensions of 10 mm in diameter and 10 mm in length. The sintering process was carried out at 650°C with a variation of holding time of 10 and 15 hours, and then the specimens were cooled down at room temperature. Microstructural analysis was performed by using X-Ray diffraction technique and Scanning electron microscopy equipped with an energy disperse spectrometry (EDS). The mechanical characteristics were analyzed by using Universal Testing Machine. The density and porosity of specimen were further measured by using Archimedes method. The results show that the optimum microstructure and mechanical characteristics are the holding time of 10 hours. The value of compression was 208.398 N/mm$^2$, the density was 1.63 g/cc and a porosity was 18% on the composition of 86Mg-Ca-3Zn-10CaCO$_3$ wt%.

Keywords: Mg alloy, Microstructure, powder metallurgy method, mechanical characteristic, biodegradable

1. Introduction

For many years, people interact increasingly with metals. The pure or alloy metals have shown a significant role in many parts of daily life, especially in the medical field. The materials selection, as well as its composition and the correct process, are the key to be successful against many possible failures. One of metals that can be used for the biomedical application is magnesium, which has low density compared to other metals [1]. Magnesium and its alloys are widely used for structural
applications in the aerospace, biomedical and automotive industries as well as in electronics, and other household equipment which needs light-weight property [2-3].

Due to their excellent comprehensive performance compared with other materials, such as stainless steel, polymers, and ceramics, magnesium alloys become ideal implants [4]. The mechanical properties such as the fracture toughness are higher than hydroxyapatite, Young’s modulus and compressive yield strength are closer to those of cortical bone [5-6]. To improve its mechanical properties, people use alloying process. The choice of alloying elements and its composition are critical. Alloying elements determine the microstructure and therefore influence the properties of alloys [1,7].

The development of non-toxic and allergy-free biomaterials is one of the most important directions of material chemistry today[8]. Magnesium as one of the main macro elements required for the proper functioning of the human organism is used to test the materials for biomedical implants [2,9]. In fact, pure magnesium has low mechanical properties, which in turn disqualifies magnesium as a material for a medical implant. Proper selection of alloying elements is to improve the mechanical properties of magnesium [10] effectively.

Alloying with Zn and Ca not only enhances the hardness of magnesium alloys, thus to offer adequate support to the injured tissue or bone[10], but also they are non-toxic. Zinc is one of the most abundant nutritionally essential elements and is a co-factor for specific enzymes in bone [11]. On the other hand, calcium is a major component in human bone and is also beneficial to bone growth and or healing [12]. It means that Zn, and Ca have good biocompatibilities when incorporating with magnesium.

Cellular metals and metallic foams are metals with pores deliberately integrated into their structure. The terms of cellular metals or porous metals are general expressions referring to metals having a large volume of porosities, while the terms of foamed metal or metallic foams apply to porous metals produced with processes where foaming takes place [13]. Cellular metals are a relatively new class of engineering materials that can be fabricated with either a random or controlled cellular structure. A controlled cellular structure allows the precise control of the pore geometry and hence following material properties that can be important for some applications such as orthopedic implants [14,15].

Porous structure in the Mg-Ca-Zn alloy can be obtained by using a foaming agent. Foaming process is performed with the gas-releasing agent and other additives that produce a foamed alloy, which differs greatly from the matrix alloy [16,17]. Carbonate is one of the foaming agent used in the manufacture of metal cellular. Carbonate releases CO₂ or CO on heating which produces porous in alloy[18,19].

2. Experimental Method
Magnesium powder (purity 98.5%, particle size 0.06-0.3 mm), Zinc powder (purity 99%, particle size < 45 μm), Calcium granule (purity 98%) and CaCO₃ (purity 98.96%, particle size < 30 μm) were purchased from Merck. Magnesium powder, Zinc powder, and Calcium (Ca) granule were reduced by using a shaker mill. Mg, Zn and Ca as a base alloy were mixed with CaCO₃ as the foaming agent with a ratio: 96Mg-Ca-3Zn-CaCO₃, 91Mg-Ca-3Zn-5CaCO₃, and 86Mg-Ca-3Zn-10CaCO₃ wt%.

Milling process was by using a shaker mill for 2 hours to produce a powder size distribution which was more homogeneous. The mixed powder was uniaxially pressed at pressure of 1 00 MPa for 2 minutes and 200 MPa for 3 minutes into green compacts with dimensions of 10 mm in diameter and 10 mm in length.

The green compact was heat treated in a tube furnace under an argon atmosphere. The sintering process was carried out at 650°C with a variation of holding time of 10 and 15 hours and the specimens were cooled down at room temperature. Microstructural analysis was performed by using X-Ray diffractometer (Shimadzu XRD-7000), and Scanning electron microscopy (JEOL, JSM-6390A Japan) equipped with an energy disperse spectrometry (EDS). The mechanical characteristics were analyzed by using compression testing by using Universal Testing Machine (Shimadzu AGS-10 KN) with dimensions of Ø10 mm x 10 mm at room temperature and rate of 1.33 mm/min. The density was
measured by using Archimedes method. Along with the mechanical analysis, we also measured the porosity of the specimens.

3. Results and Discussion

3.1. Microstructure Analysis

3.1.1. X-ray Diffraction Analysis. The microstructural analysis was performed by using X-Ray diffraction technique used to investigate the existing phase in the Mg-Ca-Zn-CaCO$_3$ alloys. X-Ray Diffraction pattern of sample sintered with different Holding Time of 10 and 15 hours is shown in Figure 1 and 2.

![XRD Pattern of Mg-Ca-Zn-CaCO$_3$ sintering at 650ºC Holding Time of 10 Hours.](image)

In Figure 1, Mg peaks are detected in all of the samples. During the sintering process, the formed intermetallic phases were MgZn, Mg$_2$Ca, and Ca$_2$Mg$_5$Zn$_{13}$. MgZn and Mg$_2$Ca have been formed in the alloy of 1% CaCO$_3$, while Ca$_2$Mg$_5$Zn$_{13}$ phase appeared in the alloy of 10% CaCO$_3$. MgZn phase can increase the mechanical properties of the alloy. However, Mg$_2$Ca phase will make the alloy becomes brittle and rigid [5]. In alloys with a long holding time of 10 hours, the phase of Mg$_2$Ca formed was less than MgZn phase. MgZn phase is the most phase formed on the alloy with 10% CaCO$_3$ that has the best mechanical properties of all alloys.
Different from the holding time of 10 hours, sintering alloy at 650°C Holding time of 15 hours produced a phase of Mg₂Ca quite a lot compared to the phase of MgZn (Figure 2). The amount of phase formed Mg₂Ca resulting alloy becomes very brittle and rigid thereby lowering mechanical properties.

3.1.2. SEM Analysis. Microstructure analysis using SEM was to observe pore structure in the alloy and second phase which formed during sintering process. Figure 3 reveals the morphology magnesium alloy (Mg-Ca-Zn-CaCO₃) with three different compositions, sintering at 650°C, holding time of 10 and 15 hours.

The addition of foaming agent with 1, 5, and 10% CaCO₃ also shows pores formed have a greater size and tends to be shaped spherical. Pore size in the alloy composition 1, 5, and 10% CaCO₃ that is less than 100, 50-200, and 100-300 µm. Alloys with 1 and 5% CaCO₃ showed many pores with small size and enclosed generated from volume shrinkage during the sintering process takeing place, while the pore formed in the alloy composition with 10% CaCO₃ has a larger size and allow the formation of interconnected pores.
3.2. Mechanical Properties
Mechanical testing for the alloy is density, porosity and compression test. Actual density was obtained through Archimedes' method through the medium of water, and a theoretical density was obtained by calculating the density of each of the elements of the alloy composition. Base on the density of the sample, actual porosity was obtained based on the calculation of the ratio between actual density and the theoretical density of the specimen with the testing standard used was ASTM 378-88. The actual density is shown in Table 1.

Table 1. Density of Mg-Ca-Zn-CaCO₃ alloys.

| Composition       | Temperature and Holding Time | Average Density (g/cc) |
|-------------------|------------------------------|------------------------|
| 96Mg-3Zn-1Ca-1CaCO₃ | 650°C 10H                    | 1.74052                |
|                   | 650°C 15H                    | 1.62929                |
| 91Mg-3Zn-1Ca-5CaCO₃ | 650°C 10H                    | 1.66324                |
|                   | 650°C 15H                    | 1.73733                |
| 86Mg-3Zn-1Ca-10CaCO₃ | 650°C 10H                    | 1.63743                |
|                   | 650°C 15H                    | 1.65307                |

Table 1 shows that the alloy with 10% CaCO₃ which was sintered at 650°C with holding time of 10 h has the lowest density of 1.63743. Meanwhile, the alloy with the highest density is shown by the specimen with 1% CaCO₃ of 1.74052. Before sintering process, the density of Mg alloy (Mg-Ca-Zn-CaCO₃) was about 1.73 gr/cc. Increase in density on the sample as in alloys with 1% CaCO₃ sintered at 650°C with holding time of 10H most likely occurred due to the formation of the oxide layer during the sintering process. The presence of oxide will increase the mass of the sample so that the effect is on density. The decrease in density was caused by the formation of pores in the alloy. Pore was
formed by the decomposition reaction of CaCO$_3$ as a foaming agent. The oxide layer is almost always the case in every sintering process. However, it was minimized by flowing inert gas which was argon during the heating process. The increase in density in the range of 1% CaCO$_3$ was due to the small pores formed so as not comparable with the existing oxide layer. The density reduction on the alloy was to signify the formation of pores. Changes in density values are presented in the following graphical.

![Graph](image)

**Figure 4.** Chart Density of Mg-Ca-Zn-CaCO$_3$ alloys.

It can be seen from Figure 4, that the density of Mg alloy with holding time of 10 h decreased with increasing the amount of CaCO$_3$ on the alloy served as a foaming agent. A large number of pores formed resulting density decreases. However, this phenomenon did not apply to holding time of 15 h. The density obtained irregularly caused by sintering was too long so that the alloy became brittle and much apart.

| Composition   | Temperature and Holding Time | Average Porosity (%) |
|---------------|-----------------------------|----------------------|
| 96Mg-3Zn-1Ca-1CaCO$_3$ | 650°C 10H 650°C 15H | 8.56273 14.35947 |
| 91Mg-3Zn-1Ca-5CaCO$_3$ | 650°C 10H 650°C 15H | 14.63004 10.95897 |
| 86Mg-3Zn-1Ca-10CaCO$_3$ | 650°C 10H 650°C 15H | 18.52912 17.76913 |

Table 2 shows that the highest porosity was 18.52912%, which belonged to the alloy with 10% CaCO$_3$ holding time of 10 H. as well as the density, porosity increases with increasing amount of CaCO$_3$ in the alloy. Obtaining porosity of 18.52912%, this means an increase of 5% compared to previous research that only earned a maximum of 13% that the Mg alloy composition at 10% CaCO$_3$ with sintering temperature 650 °C Holding time of 5 H [20]. However, porosity in the Holding Time of 15H became irregular due to the sintering process was too long resulting samples becoming brittle and making it difficult to analyze. 650 °C is the melting temperature of Magnesium so that the temperature limits allowed for sintering the powder metallurgy method. To obtain the pore in large quantities, we performed variations of the holding time. However, Holding time for 15 H resulted in Mg alloy became brittle and partly destroyed. With these conditions, the density and the number of pores could not be analyzed and did not produce accurate data.
Compression test was performed to determine the mechanical strength of the alloy. Based on Table 3, the mechanical strength of Mg was still weak, with the addition of Zn it can increase the mechanical strength. Proportional to the percentage of porosity which is owned by a sample, the result of compression strength test showed the higher the percentage of porosity, then the value of compression strength will be smaller. Therefore, the presence of Zn which improves the mechanical properties can be offset shaft formed by the foaming agent.

Table 3. Compression test of Mg-Ca-Zn-CaCO$_3$ alloys.

| Composition          | Temperature and Holding Time | Compression Test (N/mm$^2$) |
|----------------------|------------------------------|-----------------------------|
| 96Mg-3Zn-1Ca-1CaCO$_3$ | 650°C 10H                    | 233.389                     |
|                      | 650°C 15H                    | 201.644                     |
| 91Mg-3Zn-1Ca-5CaCO$_3$ | 650°C 10H                    | 211.301                     |
|                      | 650°C 15H                    | 213.788                     |
| 86Mg-3Zn-1Ca-10CaCO$_3$ | 650°C 10H                   | 208.398                     |
|                      | 650°C 15H                    | 210.792                     |

4. Conclusion
Magnesium alloy foam has been successfully prepared through powder metallurgy method. From microstructure analysis, sintering process of Mg-Ca-Zn-CaCO$_3$ alloys produces intermetallic phase of MgZn, Mg$_2$Ca, and Ca$_3$Mg$_2$Zn$_3$. The existence of Zn which produces MgZn phase improves the mechanical properties of the alloy. In the present study, optimum microstructure and mechanical characteristics are the Mg-Ca-Zn-CaCO$_3$ alloys sintered at 650 °C with holding time of 10 hours. The value of compression of 208.398 N/mm$^2$, the density of 1.63 g/cc and the porosity of 18% on the composition of 86Mg-Ca-3Zn-10CaCO$_3$ wt%.

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