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Effect of Mg and Zn Composition Variations on Surface Characteristics and Flexural Strength of Biodegradable Mg-Zn-Ca Alloys by Powder Metallurgy Method

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Abstract

This study aims to determine the Mg-Zn-Ca alloy's surface characteristics and flexural strength using powder metallurgy methods. The Mg-Zn-Ca alloy was prepared by powder metallurgy method with three composition variations (89Mg-10Zn-1Ca, 93Mg-6Zn-1Ca and 97Mg-2Zn-1Ca). The Mg-Zn-Ca powder alloy was mixed with the dry milling process for 60 minutes. After mixing, the compaction process is carried out with a load of 200 MPa. Then, the sintering process was carried out at a temperature of 500 ℃ and held for 3 hours with a furnace fed with argon gas. The sintering results were characterized by the microstructure of the Mg-Zn-Ca alloy using SEM and XRD. After that, it was carried out to test the flexural strength of the Mg-Zn-Ca alloy. SEM results obtained that the 89Mg-10Zn-1Ca alloy sample has less porosity and a smaller pore diameter compared to the 93Mg-6Zn-1Ca alloy sample and the 97Mg-2Zn-1Ca alloy sample, which has more porosity and has a smaller diameter. Bigger pore. The results from XRD had the highest peak in the 89Mg-10Zn-1Ca alloy sample, seen from a crystalline spectrum of 82.4%. The results of the bending test, the most optimal flexural strength occurred in the 89Mg-10Zn-1Ca alloy sample, which was 0.579 Mpa.

Keywords: Powder metallurgy, Mg-Zn-Ca alloys, bone implant

1. Introduction

Biodegradable metals are considered the most superior materials for implant manufacturing. These materials degrade progressively after implementation, preventing the need for postoperative recovery [1]. Due to the acceleration of the human population, the need for orthopedic biomedical devices is also increasing. Among metals, magnesium offers biodegradable and biocompatible properties for use as implants [2].

Magnesium alloys can be selected as bone implants because Young's modulus of elasticity (40-45 GPa) is quite close to that of natural human bone (10-20 GPa) compared to other commonly used materials (stainless steel, titanium and cobalt-chromium-based alloys) [3]. As a result, magnesium can reduce the risk of stress-protective effects during the healing process after implementation caused by a mismatch between the implant and natural bone [4].

Magnesium being an implant means no further surgical procedures need to be performed to remove the implant from the body after the tissue has healed. This advantage can reduce health risks, including human pain and also the cost of surgery. In addition, magnesium plays an important role in the bone healing process, making it more useful for use as a bone implant material [2]. Although magnesium has many advantages as an implant, its use as an implant material has been limited due to its low corrosion resistance, reactivity in electrochemical solutions and rapid dissolution in body fluids [4]. In addition, the mechanical properties of magnesium are also lower than expected for load-bearing applications.

Therefore, alloying elements were selected to improve the basic properties of pure magnesium for further application as medical devices [5]. Zinc (Zn) is an important element for human nutrition after iron. Zn in the human body is found in the kidneys, liver, pancreas, tissues, muscles and bones. Zn element is also one of the best potential materials to improve the mechanical properties and corrosion resistance of Mg alloys [6]. Zn can also improve magnesium alloys' corrosion resistance and mechanical properties. Calcium (Ca) is a major element present in the body and is important in terms of chemical signalling to cells [7] and one of the elements that can control the corrosion rate of Mg. Ca is also a major component in bones that can enhance the healing process

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of bone tissue [8]. In addition, the addition of Zn can help reduce the damaging effect of metal impurities, namely Fe and Ni. Therefore, Mg alloys containing Zn are being further demonstrated and developed as promising materials for biomedical applications [9].

One of the magnesium alloys (Mg Alloy) tested is the Mg-Ca-Zn combination which was studied with three variations of Mg-Ca-Zn content. The test results showed that all alloys had no significant side effects on blood cell viability within 24 hours [10]. Magnesium and magnesium alloys also have a low density (1.74 – 2.0 g/cm^3) lower than titanium alloys (4.4 – 4.5 g/cm^3) [11]. For bone replacement applications, Ca is an element that can be used in Mg metal alloys; this is because Ca is the main composition in the human body which can shape the wound healing process [12].

Mg-Zn-Ca alloy is a bio-inert implant material that has been developed recently. The human body has an inherent tolerance for Mg, Zn and Ca [8]. A smelting process is generally used to treat the Mg-Zn-Ca alloy, but in this study, a powder metallurgy process was used [5]. The Mg-Zn-Ca alloy exhibits better mechanical and corrosion properties than pure Mg. However, the Mg-Zn-Ca alloy requires further improvisation to make the implant material biodegradable [1]. Calcium dissolved in the magnesium matrix can soften Mg granules and increase strength without reducing the elasticity of Mg. Adding Ca over 1% by weight can cause a brittle intermetallic phase [13].

2. Materials and Methods

2.1. Material preparation

Pure Magnesium (Mg), Zinc (Zn) and Calcium (Ca) (purity > 98% of each powder) were prepared by powder metallurgy method, with the main material of the powder being magnesium (Mg). Powders of different types or different melting points must be mixed evenly. The Mg-Zn-Ca powder alloy was mixed with the dry milling process for 60 minutes. To get the desired sample, it is necessary to compact the powder in the mold as shown in Fig. 1.

The compaction pressure carried out by the compacting process in Fig. 2 with a load of 200 MPa. The solidification process at room temperature does not have adequate atomic bonding. The Fig. 3 show the sintering process that carried out at a temperature of 500°C and a holding time of 3 hours, and the furnace is supplied with argon gas in the sintering process to prevent oxidation. After sintering, as shown in Fig. 4 the desired sample in the furnace before discharge. The composition of the sample is in Table 1.

Table 1. Sample composition

Sample Code	Weight (%)		
	Mg	Zn	Ca
89Mg-10Zn-1Ca	89	10	1
93Mg-6Zn-1Ca	93	6	1
97Mg-2Zn-1Ca	97	2	1

Figure 1. Sample mold

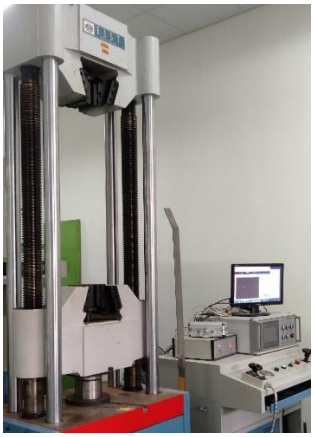


Figure 2. 200 Mpa compaction process using Universal Testing Machine

Figure 3. The sintering process takes 3 hours with a temperature of 500°C, and the furnace is supplied with argon gas

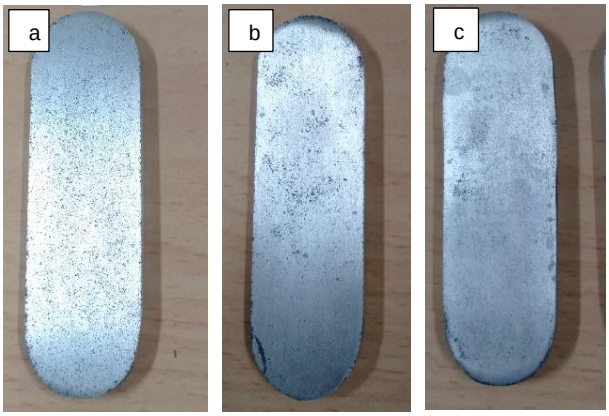


Figure 4. Mg-Zn-Ca alloy samples with sintering temperature 500°C: (a) 89Mg-10Zn-1Ca, (b) 93Mg-6Zn-1Ca and (c) 97Mg-2Zn-1Ca

2.2. Material preparation

The microstructure of the Mg-Zn-Ca alloy was observed using SEM (Scanning electron microscopy), which functions to view or analyze the surface of the Mg-Zn-Ca alloy sample by shooting high-energy electrons at the sample. The JEOL JCM 6000 plus test kit carried out the SEM test. The sample to be tested was previously mounted and sanded the surface until smooth using sandpaper size 3000.

2.3. XRD (X-Ray Diffraction)

XRD (X-Ray Diffraction) analysis was used to determine the phase and degree of crystallinity of the Mg-Zn-Ca alloy, which had been sintered for 3 hours. The XRD tool was used using the Shimadzu 700 XRD test tool.

2.4. Bending test

The bending test was carried out to determine the magnitude of the flexural strength of the Mg-Zn-Ca alloy sample. The bending test used was the three-point bending method, using two supports and one press. The flexure test was carried out using a Universal Testing Machine (UTM) test kit. The manufacture of flexural test samples refers to the JIS R 1601 standard.

3. Results and Discussion

3.1. SEM (Scanning Electron Microscopy) analysis

The SEM results show that, in general, the microstructure of the Mg-Zn-Ca alloy after sintering at 500°C and holding for 3 hours, there is an indication that the porosity of the resulting powder will differ with variations in composition and sintering temperature. Alloy sample 89Mg-10Zn-1Ca (Fig.5a) has less porosity compared to alloy sample 93Mg-6Zn-1Ca (Fig. 5b) and alloy sample 97Mg-2Zn-1Ca (Fig. 5c). The 89Mg-10Zn-1Ca alloy sample has a smaller pore diameter than the 93Mg-6Zn-1Ca and 97Mg-2Zn-1Ca alloy samples with a larger pore diameter.

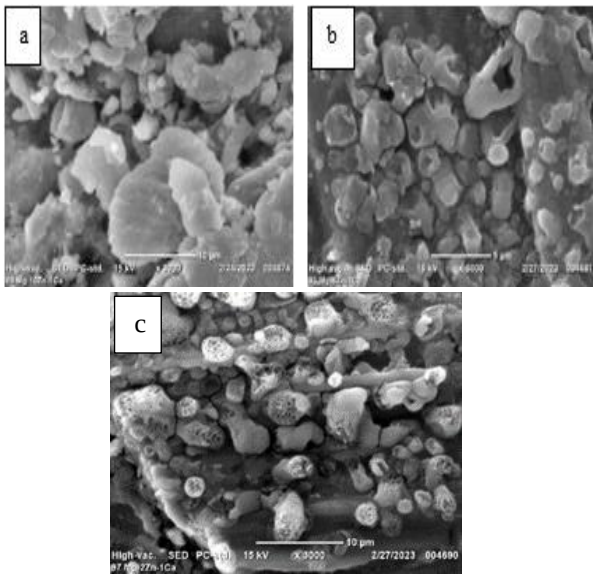


Figure 5. SEM photo magnification of 3000x Mg-Zn-Ca alloy sample sintered at 500°C holding time of sintering 3 hours with the alloy; (a) 89Mg-10Zn-1Ca, (b) 93Mg-6Zn-1Ca and (c) 97Mg-2Zn-1Ca

Adding Ca and Zn elements to Mg alloys can affect the corrosion rate. Adding Zn to Mg alloys can increase the potential for corrosion because Zn has a fairly high electronegativity. Conversely, the presence of Zn can reduce corrosion resistance [8]. It can be seen from the SEM results for each variation of the alloy sample that there is little difference in which the sample has a lumpy or irregular morphological shape. This is caused by grain bonding and particle growth in the hydrothermal and sintering processes [14]. Alloy samples have pores or cavities due to the emergence of pores in the powder metallurgy method, so they cannot be avoided even after the sintering process. These pores or cavities trigger oxidation [15].

Figure 6 shows the cross-sectional results of the Mg-Zn-Ca alloy microstructure with 100x magnification. From Fig. 6, it can be seen that the addition of Zinc (Zn) will give a different microstructure from the alloy. Figure 6 shows that the sintering process of alloy samples can produce porosity due to differences in alloy sizes and melting points. Where magnesium (Mg) has a higher melting point compared to Zinc (Zn): (Magnesium 650°C and Zinc 419°C), so the phenomenon of diffusion and change will be faster if more Zinc (Zn) is added to the alloy. t a sintering temperature of 500°C, the pores formed in alloy sample (a) 89Mg-10Zn-1Ca are fewer than in alloy samples 93Mg-6Zn-1Ca and 97Mg-2Zn-1Ca.

The formation of micropores is also caused by the evaporation of Zinc (Zn) due to the influence of temperature. At the sintering temperature of 600 and 650°C, the temperature is too high for Zinc (Zn), thus forming micropores in the Mg-Zn-Ca alloy.

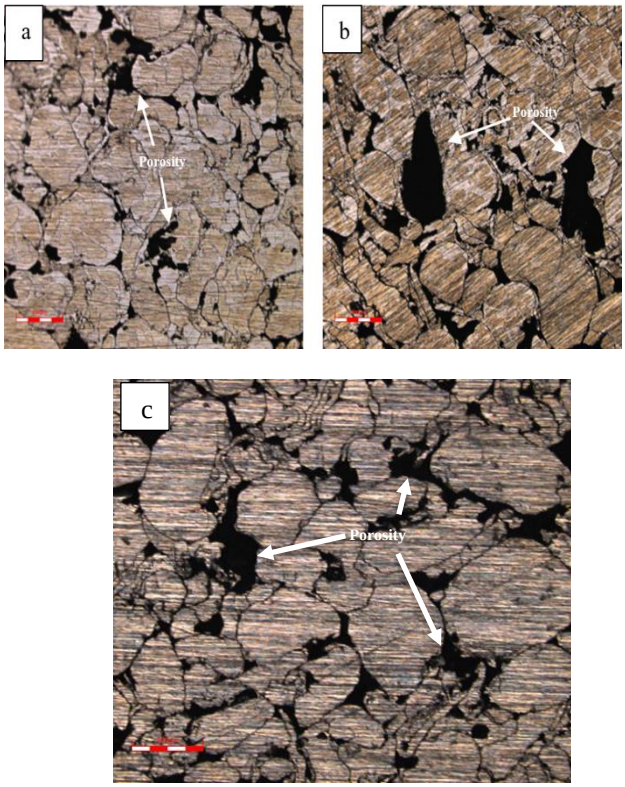
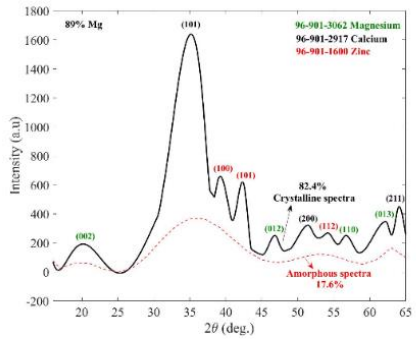


Figure 6. Microstructure photo magnification of 100x Mg-Zn-Ca alloy samples sintered at 500°C holding time of sintering for 3 hours with alloys: (a) 89Mg-10Zn-1Ca, (b) 93Mg-6Zn-1Ca and (c) 97Mg-2Zn-1Ca

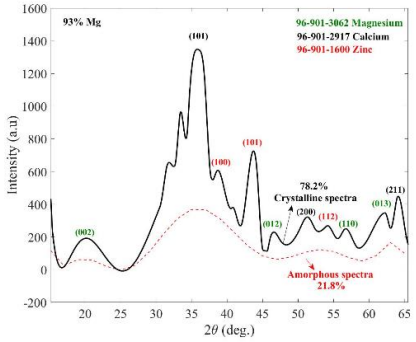
For each different composition, the more Mg and Zn reinforcing mixture, the more the spread of the reinforcing powder is seen in the microstructure so that the porosity value is getting smaller [16].

3.2. XRD Analysis

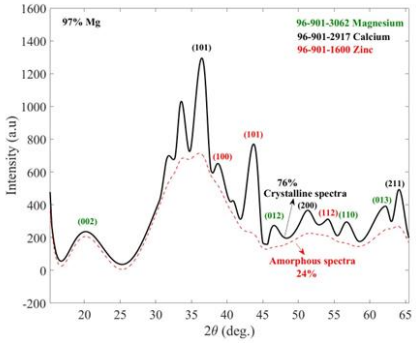
The XRD test in this study was carried out to determine the phases present in the Mg-Zn-Ca alloy, which was sintered at 500°C and held for 3 hours by the powder metallurgy method. Figure 7 shows the diffraction results in the sintering of the Mg-Zn-Ca alloy, where the phases formed have visible differences; the highest peak occurred in the 89Mg-10Zn-1Ca alloy sample seen from a crystalline spectrum of 82.4%. The difference that appears is the peak height of the fraction where the peaks of the Mg phase decrease in each alloy; this indicates more and more bound Zn. The 93Mg-6Zn-1Ca alloy sample has a crystalline spectrum of 78.2%, while the 97Mg-2Zn-1Ca alloy has a crystalline spectrum of 76%.



(a)



(b)



(c)

Figure 7. XRD test results for Mg-Zn-Ca alloy sintering temperature 500°C with alloys: (a) 89Mg-10Zn-1Ca, (b) 93Mg-10Zn-1Ca and (c) 97Mg-2Zn-1Ca

This is possible because the more Zn, the porosity decreases due to the densification process, causing the grain surface area to decrease and the reactivity to oxygen to decrease. One of the disadvantages of powder metallurgy is that it has a high surface area, making it reactive to oxidation.

The peaks that appear in the Mg-Zn-Ca alloy samples are areas with Miller indices (002), (102), (100), (101), (012), (200), (112), (110), (013) and (211). Adding Zn powder causes changes in the XRD peaks to become sharper. This is because the more atoms in the order, the better the structure. This indicates the growth of the amorphous phase into a crystalline phase. As a result, the amorphous phase decreased, and the crystalline phase increased, as shown in Figure 7, that the amorphous phase in the 89Mg-10Zn-1Ca alloy sample (Fig.7a) is 17.6%. While the alloy sample 93Mg-6Zn-1Ca (Fig. 7b) has an amorphous phase of 21.8%, and the alloy sample 97Mg-2Zn-1Ca (Fig. 7c) has an amorphous 24%.

The Zn alloy in the Mg-Zn intermetallic phase is a thermally unstable phase with increasing strength and creep resistance properties. The Mg-Zn phase will form intermetallic and will affect the mechanical properties of the Mg alloy, which is known to increase the hardness of the Mg-Zn-Ca alloy [16]. However, this intermetallic phase can also cause galvanic corrosion and brittleness so that, in certain amounts, it can reduce the corrosion rate of Mg alloys.

3.3. Bending test

From the results of the bending test in Fig. 8, the most optimal flexural strength occurred in the 89Mg-10Zn-1Ca alloy sample, which was 0.579 MPa, while the lowest was in the 97Mg-2Zn-1Ca alloy sample, which was 0.506 MPa. From the bending tests that have been carried out, it can be seen in the 89Mg-10Zn-1Ca alloy that the more Zn powder added to the alloy, the more flexural strength properties of the alloy will increase. This means that more Zn powder added to the Mg-Zn-Ca alloy sample can increase the flexural strength of the alloy.

Adding Zn as much as 1-4% by weight to magnesium (Mg) can improve the Mg-Zn-Ca alloy's mechanical properties and corrosion resistance [8]. Figure 8 shows a decrease in the porosity value caused by an increase in the porosity formed in the alloy sample.

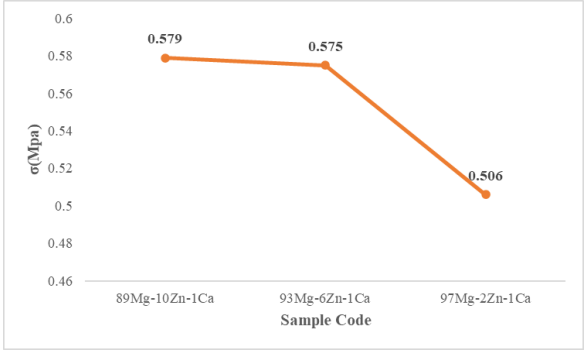


Figure 8. Graph of Mg-Zn-Ca alloy bending test results with the sintering temperature of 500°C

The 89Mg-10Zn-1Ca alloy sample has high flexural strength compared to other alloy samples. The decrease in The decrease in the flexural strength value was caused by the formation of the oxide, in this case, the MgO phase. The MgO, ZnO or CaO phases due to the oxide process formed during sintering can reduce the value of the mechanical strength of the resulting alloy sample [6].

4. Conclusion

a. The SEM results show that the 89Mg-10Zn-1Ca alloy sample has less porosity compared to the 93Mg-6Zn-1Ca alloy sample and the 97Mg-2Zn-1Ca alloy sample. The 89Mg-10Zn-1Ca alloy sample has a smaller pore diameter than the 93Mg-6Zn-1Ca and 97Mg-2Zn-1Ca alloy samples with a larger pore diameter.

b. From the results of diffraction in the sintering of the Mg-Zn-Ca alloy where the phases formed, there are visible differences; the highest peak occurred in the 89Mg-10Zn-1Ca alloy sample seen from a crystalline spectrum of 82.4%. The difference in the peak height of the 93Mg-6Zn-1Ca alloy has a crystalline spectrum of 78.2%, while the 97Mg-2Zn-1Ca alloy has a crystalline spectrum of 76%.

c. From the flexural test results, the most optimal flexural strength occurred in the 89Mg-10Zn-1Ca alloy sample, which was 0.579 MPa, while the lowest was in the 97Mg-2Zn-1Ca alloy sample, which was 0.506 MPa.

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