Powder metallurgy preparation of Mg-Ca alloy for biodegradable implant application

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Abstract. Magnesium and its alloys are a promising candidate for implant application especially due to its biodegradability. In this study, Mg-7Ca alloys (in weight %) were processed by powder metallurgy from pure magnesium powder and calcium granule. Milling process was done in a shaker mill using stainless steel balls in various milling time (3, 5, and 8 hours) followed by compaction and sintering process. Different sintering temperatures were used (450°C and 550°C) to examine the effect of sintering temperature on mechanical properties and corrosion resistance. Microstructure evaluation was characterized by X-ray diffraction, scanning electron microscope and energy dispersive X-ray spectroscopy. Mechanical properties and corrosion behavior were examined through hardness testing and electrochemical testing in Hank’s solution (simulation body fluid). In this report, a prolonged milling time reduced particle size and later affected mechanical properties of Mg alloy. Meanwhile, the phase analysis showed that \(\alpha\) Mg, \(\text{Mg}_2\text{Ca}\), \(\text{MgO}\) phases were formed after the sintering process. Further, this study showed that Mg-Ca alloy with different powder metallurgy process would have different corrosion rate although there were no difference of Ca content in the alloy.

1. Introduction

Owing biodegradable properties, magnesium alloys have been intensively researched in these recent years [1-5]. Magnesium alloys can be used as a temporary implant which will be dissolved without the need for further surgery due to its biodegradation properties [6]. Moreover, magnesium alloys are beneficial due to its elastic modulus which is close enough to the human femur bone (15-20 GPa) [6]. Hence, it is assumed that magnesium alloys can minimize the risk of stress-shield phenomena which currently exist in other metallic implants such as stainless steel or titanium alloy [7, 8].

Though magnesium alloys has shown great potential to be used as bone implant material, more development is needed. The high corrosion rate of magnesium alloy is also unfavorable since magnesium alloy act as supporting device during bone recovery. Accordingly, it is important to ensure the alloying element of magnesium alloy can increase the degradation properties of magnesium alloy. Furthermore, alloying elements must show biocompatibility properties and also give no toxicity to the bone. Previous studies had been conducted for developing Mg-Ca based alloys [2, 9, 10], Calcium, as the main composition in human bone, showed a great performance in improving bone healing process, and having low density just like magnesium, is a desirable alloying element for biomedical application [2, 10].
Those previous studies had shown the possibility of processing Mg alloy into biomedical devices. Further, it should be noted that the chosen processing method will affect the applicability of magnesium alloy. Until now, limited efforts have been made to magnesium-based alloys through powder metallurgy method. Meanwhile, powder metallurgy is one of a solid-state method that can be chosen in processing magnesium alloy into a near net shape. Powder metallurgy also allows flexibility of alloy design with different elemental or master alloy powder in order to get better mechanical properties. Basically, powder metallurgy is competitive enough in comparison with conventional casting, forging, or machining route. However, processing magnesium through powder metallurgy was not as easy as it sounds.

Wolff et al. observed the difficulty process of sintering magnesium because sintering magnesium powder was strongly inhibited by a stable oxide layer [11] that would form immediately after exposure to air. It was concluded that calcium content would improve sinterability because it would protect the magnesium against additional oxide layer. This is based on the lower formation enthalpy of CaO (-635 kJ/mol) in comparison with MgO (-601 kJ/mol). It was also shown that the gas atomized master alloy Mg-7Ca turned out to be a promising candidate to sinter magnesium [11].

In the present work, mixing parameter and temperature sintering were varied in order to achieve the most optimum condition for preparing Mg-7Ca master alloy by means of powder metallurgy method. Moreover, structure, phase, and corrosion behavior of master Mg-7Ca master alloy were studied.

2. Materials and method
High purity magnesium powder (Merck, particle size: 0.06-0.3 mm) and calcium granules were used to prepare Mg-7Ca alloy. Calcium granules were previously crushed by mortar followed by mixing process with Mg powder in a shaker mill for 3, 5, and 8 hours. The final milled powder of Mg-7Ca alloy was then cold compacted under the pressure of 260 MPa. The resulted green compacts had a diameter of around 26.1 mm followed by sintering process. These green compacts were sintered in a different heat treatment profile which is 450°C and 550°C for an hour under Argon atmosphere. Heating rate used in this process was 5°C/minute. Each specimen was indexed based on its treatment, as shown in table 1.

| Specimen Code | Milling Time (hour) | Sintering Temperature (°C) |
|---------------|---------------------|---------------------------|
| 3M-450C       | 3                   | 450°C                     |
| 5M-450C       | 5                   | 450°C                     |
| 8M-450C       | 8                   | 450°C                     |
| 3M-550C       | 3                   | 550°C                     |
| 5M-550C       | 5                   | 550°C                     |
| 8M-550C       | 8                   | 550°C                     |

The microstructure of as sintered alloys were observed by scanning electron microscope (SEM) and phase formation were analyzed by X-ray diffraction (XRD). Mechanical properties of these alloys were examined through hardness testing of each specimen. To investigate corrosion behavior in vitro, electrochemical testing had been done in Hank’s solution [12] at pH 7.4 and 37°C under air atmosphere. The counter electrode material was graphite, the specimen was working electrode, and the reference electrode was saturated calomel electrode (SCE). The potential scanning rate was fixed at 1.5V/s. Potential corrosion (E_{corr}) and corrosion rates (Corr rate) were observed.

3. Results and discussion
Figure 1 shows the powder condition before and after milling process. It could be seen from figure 1, milling process would reduce particle size after 3 hours, but in a prolonged duration, milling process would not reduce the particle size (for 5 hours and 8 hours). Time of milling during powder metallurgy process should be optimized due to its importance to create a homogeneous green compact. But it
should be noted that the level of contamination might be increased and unfavorable phases might be form if the duration of milling were prolonged [13]. Further, in a prolonged duration of milling agglomeration can occurred. Therefore, the longest time of milling might not always be the best milling time. The reduction process is related to the collision between ball mill and the particles. As for mechanical alloying, it is defined by a high energy ball milling process which deformation, fracture, and welding are repeatedly occurred in between constituent powders and grinding media to form a homogeneous alloy microstructure [13]. During milling process, the particles break up into smaller particles making it easier to be dispersed in the alloy.

![SEM images of Mg-7Ca alloy. (a) Before milling and after milling for (b) 3 hrs, (c) 5 hrs and (d) 8 hrs.](image)

**Figure 1.** SEM images of Mg-7Ca alloy. (a) Before milling and after milling for (b) 3 hrs, (c) 5 hrs and (d) 8 hrs.

![XRD spectra for as-milled powder before sintering and after sintering process.](image)

**Figure 2.** XRD spectra for as-milled powder before sintering and after sintering process.

Further analyses were done through XRD examination. Figure 2 shows XRD spectra of Mg-Ca alloy which revealed qualitative analysis of phase formation. Based on figure 2, some Mg characteristic peaks are shown. It was presumed that Mg$_2$Ca phase characteristic peaks would be shown after milling process before sintering process due to mechanical alloying between Mg and Ca, yet no clear evidence is shown for Mg$_2$Ca phase. Although different milling times were used in processing Mg-7Ca alloy, the XRD pattern of each parameter is not showing any broader or sharper peak difference. But there is a peak shifting slightly to the left by increasing milling duration which is related to the tendency of Mg$_2$Ca formation when milling process would be prolonged. Moreover the resulted XRD spectra shows MgO phase formation at 63.3° during milling process. From figure 2 it can also be seen a peak shifting from 36.03° (Mg phase) before sintering to 34.36° (Mg$_2$Ca phase) after sintering process. This phenomenon is more likely caused by the existence of Mg$_2$Ca phase after
sintering process. It had shown that sintering temperature affected phase formation in Mg-Ca alloy and also increasing of MgO phase characteristic peak. It means sintering process tends to create MgO phase which is unfavorable in Mg-7Ca alloys. It was presumed that MgO phases could be avoided by the addition of calcium. Unfortunately, calcium addition can no longer inhibit MgO phase formation especially after sintering process at 450°C and 550°C although the reaction occurred under argon atmosphere. Moreover, figure 2 shows that higher sintering temperature will increase the tendency of MgO phase formation. Indeed, it is generally accepted that chemical reactions occur more rapidly at higher temperatures. However, MgO is accepted as a biologically non toxic oxide for biomedical devices [1].

Figure 3 depicts SEM images of Mg-7Ca alloy after sintering process, while table 2 gives an EDS quantitative analysis from figure 3. From figure 3, it can be seen that some of micro pores do exist in the Mg-7Ca alloy. Some bubbling spot were shown in figure 3a and 3b, on the other hand figure 3c shows a better microstructure with smaller pores. Bubbling spot and porosity will affect properties of Mg-Ca alloy. Increasing milling duration tends to reduce surface roughness of Mg-Ca alloy. When sintering temperature is higher, given by figure 3d-f, it will also reduce surface roughness of Mg-Ca alloy. Specimen with 550°C sintering temperature has smoother surface, smaller pores, shows densification process occurred better than 450°C. Furthermore, based on EDS result, value of oxygen content from each Mg-7Ca alloy was high (around 19-33 wt.%). EDS result can not exactly measure the oxygen content from each specimen, but it can give an illustration of each specimen tendency on MgO phase formation. Hereby, the SEM images confirms that increasing milling time would increase MgO formation as shown by the XRD result.

![Figure 3. SEM images of as-sintered Mg-Ca alloy in different heat treatment profile. (a). 3M-450°C, (b) 5M-450°C, (c) 8M-450°C, (d) 3M-550°C, (e) 5M-550°C, (f) 8M-550°C.](image)
Table 2. Composition analysis obtained by EDS.

| Element | Specimen codes | 3M-450°C | 5M-450°C | 8M-450°C | 3M-550°C | 5M-550°C | 8M-550°C |
|---------|----------------|----------|----------|----------|----------|----------|----------|
| O       |                | 20.85    | 19.23    | 33.53    | 32.62    | 27.11    | 28.73    |
| Mg      |                | 79.00    | 80.31    | 66.02    | 67.50    | 72.58    | 70.54    |
| Ca      |                | 0.14     | 0.26     | 0.42     | 0.08     | 0.31     | 0.73     |

To see mechanical properties trend on Mg-Ca alloys with different powder metallurgy parameters, hardness testing was done. Table 3 shows hardness number of each specimen according to its milling time. It can be seen that hardness property will increase by increasing milling time. Not only milling time, sintering temperature will also increase the hardness number of Mg-Ca alloy. Increasing mechanical properties is in line with the formation of Mg$_2$Ca phase which has higher mechanical properties. Further, mechanical properties are also related to total porosity. Along with SEM images where smaller pores were created in higher sintering temperature (550°C), mechanical properties also increase. Depends on the application of the end product, phase formation in Mg-Ca alloy must be controlled to avoid excessive brittleness which may lead to crack due to the precipitation of Mg$_2$Ca. Although mechanical properties will increase by milling time addition and sintering temperature, the corrosion potential might not give a similar trend.

Table 4 shows corrosion properties of the resulted Mg-Ca alloy which represent nobler potential corrosion in comparison with Mg in some reference. Zhang et al. [14] reported electrochemical testing of Mg and Mg-Zn alloy in SBF solution, in which Mg had -1.62 V, while Gu et al. [15] mentioned potential corrosion of Mg was -1.7 V. Here it can be concluded that better potential corrosion is achieved with the addition of Ca. From the electrochemical testing, it can be seen that corrosion rate will increase by milling time increasing. It may also relate to the formation of Mg$_2$Ca phase. Mg$_2$Ca has higher electrochemical activity than Mg phase so that galvanic corrosion may occur more [16]. Since corrosion rate is an important consideration for biodegradable implant, lower corrosion rate is preferable.

Table 3. Milling time vs average hardness property (HVN).

| Specimen Codes | 3M-450°C | 5M-450°C | 8M-450°C | 3M-550°C | 5M-550°C | 8M-550°C |
|----------------|----------|----------|----------|----------|----------|----------|
| Hardness Number (HVN) | 42.18    | 45.85    | 49.03    | 44.86    | 47.09    | 51.33    |

Table 4. Corrosion properties of Mg-Ca alloys in Hank’s solution obtained from the polarization test.

| Specimen Codes | E Corr | Corr Rate (MPY) |
|----------------|--------|-----------------|
| 3M-450°C       | -1.54  | 0.138           |
| 5M-450°C       | -1.58  | 1.962           |
| 8M-450°C       | -1.55  | 1.418           |
| 3M-550°C       | -1.58  | 0.311           |
| 5M-550°C       | -1.57  | 0.424           |
| 8M-550°C       | -1.59  | 1.640           |

4. Conclusion
In this study, milling time and temperature sintering were varied. It was shown that milling process for 3, 5 and 8 hours could be used to form intermetallic phase Mg$_2$Ca. Not only Mg$_2$Ca phase, after
sintering process MgO phase was also existed. Increasing milling time tends to form Mg$_2$Ca phase which can increase the mechanical properties of Mg-Ca alloy. Based on this study, variation on sintering process affects densification process. Sintering temperature also affects mechanical properties whereas higher sintering temperature would give higher mechanical properties. Moreover, from corrosion testing, it can be seen that the longer duration of milling can also reduce corrosion resistance. This study showed that Mg-Ca alloy with different powder metallurgy process would have different corrosion rate although there were no difference of Ca content in the alloy. To be used as biodegradable implant, specimen with lower corrosion rate may be chosen. This study shows that optimization process should be continue with 550° C sintering temperature.

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