The Role Of Annealing On Biodegradation Behavior Of Mg-Zn-Ca Alloy Prepared From Commercial Mg Sacrificial Anode

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Abstract. Magnesium and its alloys offers great potential application for biodegradable implant due to its low corrosion resistance, high biocompatibility, favorable mechanical properties, and young modulus similar to bone. However, there are still many challenges to be solved. In this work, Mg-Zn-Ca alloy were prepared from commercial Mg sacrificial anode, Mg-Ca master alloy, and pure Zn (99%) through casting process. Melting and alloying operations were conducted in a graphite crucible, using a home made melting facility. The influence of annealing treatment on the alloys performance were studied. Microstructure observations of the alloys were conducted using optical and scanning electron microscope equipped with energy-dispersive X-ray spectroscopy. The microhardness of the alloys were evaluated using Brinell hardness indentation. In vitro biodegradation behaviors of Mg-Zn-Ca alloy were evaluated through immersion test in Ringer Laktat solution. The results show that Mg-Zn-Ca alloy fabricated in our work exhibit minimum corrosion rates. Annealing treatment at 300 °C (8 hour, air cooling) alter the microstructure of Mg-Zn-Ca alloy. The microhardness of Mg-Zn-Ca alloys slightly increased from 43 (as cast) to 53 BHN (as annealed). The corrosion rate of the alloys was increased from 8 mm/year (as cast) to 17 mm/year (as annealed). This is suspected due to grain refinement and extensive formation of needle structures causing anodic couples with the matrix.

Keywords: Biodegradable, Casting, Corrosion, Implant, Magnesium, Mg-Zn-Ca alloy.

1. Introduction

Indonesia is the world’s fourth most populated country with 250 million populations [1]. By 2025, the elderly population is expected to grow by more than 40%, making Indonesia one of Asia’s fastest aging countries (Fletcher, 2011). This will have a huge impact on an economical and societal level, especially in the healthcare sector. The concentrated population in main Indonesian cities has created chronic crowd traffics dominated by motorcycles that in turn contributes to high traffic accidents causing a high incidence of traumatic bone fractures [3]. As a results, the amount of patients requiring bone surgery in Indonesia is growing, and the need of implanted orthopedic devices for surgeries is huge. According to BMI Research 2017[4], the Indonesian medical device market is projected to rise by a compound annual
growth rate (CAGR) of 9.6%, which should bring it from USD 850 million in 2016 to USD 1,350 million in 2021. Around 1-2% of Indonesian medical devices market are shared by orthopedic/prosthetic implants. Based on those fact, research on orthopedic implant are very challenging in the future.

In bone grafting and healing of broken bones, permanent implant material are widely used, for examples stainless steels, titanium and its alloy [5]. If the bone is declared to have recovered, second removal surgery must be conducted again to remove the residual implant. This additional surgery can itself damage the bone and is an obvious inconvenience to the patient. Therefore it would be desirable to make an implanting a material that would degrade or be resorbed in the body.

The concept of non permanent implant materials departs from the phenomenon of bone grafting as follows: (i) In the early stages, bone connections should be reinforced by implantable material. (ii) Along with the healing time, the bone connection will be stronger so that the strengthening of the implant material can be reduced. (iii) In the final stages, bone connections are no more require reinforcement from the implants. This is only possible, when the implant material dissolve or be absorbed in the body, a characteristic which is called biodegradable [6].

Thus, the rate of bone strengthening and absorption rate of the implant material by the body is a parameter that must be determined precisely, research on the topic is widely open and challenging in the future [7].

Magnesium are excellent candidates for biodegradable implant materials. Magnesium is required in human body for metabolism and biological mechanism. The human body can absorb magnesium in relatively high amounts, 400 mg daily for men and 310 mg per day for women [8]. Magnesium based alloy, has been proposed as better biodegradable materials for load-bearing applications due to their superior combination of strength and ductility over polymers. However, concern about their rapid corrosion, corresponding hydrogen evolution, and subsequent loss of mechanical strength impedes the development of Mg alloys in clinical applications [9]. Therefore, maintaining the appropriate corrosion rate is very critical for biodegradable implants made from magnesium.

Corrosion behavior of magnesium in general depends upon its composition. Alloying magnesium with others element such as zinc, calcium, aluminium, manganese, lithium, silver, etc., enhances the corrosion resistance [10]. Zinc and Calcium have been alloyed with magnesium to increase the corrosion resistance, and have given good results [11]. However, further information is essential to optimize the biocompatibility of Mg-Zn-Ca alloy in body. Heat treatment process have been widely reported able to improve the corrosion resistance of various Mg alloys [12-13]. Heat treatment may homogenize and refine the microstructure typically present in magnesium alloys. Despite many studies have been done on mechanical and corrosion properties of Mg-Zn-Ca alloys, there are still problems regarding the optimal composition, alloy source/purity and processing method to achieve optimum mechanical and corrosion properties. In this works, for the first time, the fabrication of Mg-Zn-Ca alloys from commercial Mg sacrificial anode are demonstrated. The influence of heat treatment on corrosion resistance of Mg-Zn-Ca alloys in Ringer solution are reported.

2. Materials and Methods

Pure Mg and Mg-Zn-Ca alloy were prepared from commercial Mg anode, Mg-Ca master alloy, and pure Zn (99%). Melting and alloying operations were conducted in a graphite crucible,
using a home made melting facility, as shown in Figure 1. A mixture of HFC 134a (5% volume ratio) and CO\textsubscript{2} gas (balance) was used as a protection gas to prevent Mg from oxidation/burning. The melt were kept for 10 minutes to ensure that all the requiring alloying elements were dissolved in the melt alloy, and then poured into a steels mould to make Mg or Mg-4\%Zn-0.2 \%Ca ingots. Chemical composition of Mg and Mg-4Zn-0.2Ca were analyzed using atomic absorption spectroscopy (AAS). Annealing heat treatment at 300 °C for 8 hour was carried out followed by air cooling.

![Figure 1. Inhouse Magnesium Melting Facilities developed in ITB](image)

For microstructure observation, the alloys were ground with SiC abrasive papers with successive grades from 200 to 2000 and polished up to mirror finish with 0.5 micron diamond suspension. Polished Mg-Zn-Ca alloy were etched by picric solution (5 mL acetic acid, 10 mL water, 6 gr picric acid and 100 mL ethanol). As polished Mg alloy were etched by oxalic acid solution (2 gr oxalic acid, 100 mL water). After etching, the alloys were cleaned with distillated water and alcohol, and then dried by hot air. Microstructure observations of the alloys were conducted using Nikon optical microscope. Scanning electron microscope (SEM, Hitachi) equipped with energy-dispersive X-ray spectroscopy (EDX) were used to reveal the microstructure at higher magnification. EDX point analysis were conducted to determine the phase available within the microstructure. Phase identification also was carried out by X-ray diffractometry (XRD). The microhardness of the alloy were evaluated using Brinell hardness indentation. In vitro biodegradation behaviors of Mg and Mg-Zn-Ca alloy were evaluated through immersion test in Ringer Laktat solution. The immersion test procedure was carried out according to the ASTM: G1-03 [14].

### 3. Results and Discussion

#### Microstructural analysis

The chemical composition of as-cast Mg alloys obtained from the atomic absorption spectroscopy (AAS) were listed in Table 1. The amount of impurities element in Mg and Mg-Zn-Ca alloys were relatively low.

| Table 1. Chemical composition of as cast Mg and Mg-Zn-Ca alloys |
|-------------------|---|---|---|---|---|---|---|---|---|---|
| Alloy             | Zn | Ca | Al  | Mn | Fe  | Ni  | Cu  | Si  | Mg  |
| Pure Mg           | 0.006 | 0.005 | 0.58 | 0.007 | 0.028 | 0.0001 | 0.002 | 0.04 | Balance |
| Mg-Zn-Ca          | 2.65 | 0.05 | 0.02 | 0.008 | 0.007 | 0.000 | 0.001 | 0.02 | Balance |
For Mg-Zn-Ca alloys, the concentration of Zn and Ca element are relatively low compared to the initial targeted design. This might be due to evaporation during melting operation.

The optical microstructure of as-cast Mg and Mg-Zn-Ca alloys with different heat treatment are summarized in Figure 2. The as-cast Mg alloy consisted of primary α-Mg. On the other hands, the as-cast Mg-4Zn-0.2Ca alloy consisted of primary α-Mg and secondary phases with needle-like appearance. After annealing heat treatment, the microstructures of Mg-4Zn-0.2Ca alloys were slightly changes. The grain size was smaller compared to that as-cast specimen. Moreover, extensive formation of needle like secondary phase were found to increases at the annealed Mg-Zn-Ca alloys microstructure. Figure 3 shows SEM micrographs of as-cast Mg, as-cast Mg-Zn-Ca and as-annealed Mg-Zn-Ca alloy. The corresponding EDS analysis suggested that the Mg alloys consist only of α-Mg solid solution phase.

![Microstructure images](image1.png)  
(a) Mg, as cast  (b) Mg-Zn-Ca, as cast  (c) Mg-Zn-Ca, as annealed

Figure 2. Optical microstructure image of (a) Mg as-cast, (b) Mg-4Zn-0.2Ca, as-cast (c) Mg-4Zn-0.2Ca, as annealed.
The XRD pattern of the as-cast Mg alloy, as-cast Mg-Zn-Ca alloy and as annealed Mg-Zn-Ca alloys is shown in Figure 4. The XRD patterns indicates that only peak corresponding to α-Mg matrix have been observed in Mg and Mg-Zn-Ca alloys. The formation of second phase particles in Mg-Zn-Ca alloys were not observed both for as cast and as annealed condition. Compared to that of pure Mg alloys, the intensity of (101) peak increases, while the intensity of (002) peak decreases in Mg-Zn-Ca alloys, both for as cast and annealed condition. This indicates that the addition of Zn and Ca element into Mg matrix might influence the preferred crystal growth orientation. Annealing treatment conducted on Mg-Zn-Ca alloys do not change the phase constituent in the alloys.

Figure 3. SEM image of (a) Mg as-cast, (b) Mg-4Zn-0.2Ca, as-cast (c) Mg-4Zn-0.2Ca, as annealed

Figure 4. X-ray diffraction patterns of Mg and Mg-Zn-Ca alloy at different heat treatment condition.
Hardness test results

Figure 5 shows the average hardness of Mg alloys after casting and annealing. There is not a large difference in final hardness between different alloys. The hardness of Mg in as cast condition is 38 BHN. The hardness of Mg-Zn-Ca alloy in as cast condition is 43 BHN, while that for annealed condition is 53 BHN. The addition of Zn and Ca in Mg-Zn-Ca alloys does not change the hardness of Mg alloys, as both element was diluted in α-Mg solid solution. Annealing treatment conducted on Mg-Zn-Ca alloys slightly modify the final hardness. This is related to the extensive formation of needle like structures in the alloys and grain size refinement. This indicates that the effect of Zn and Ca addition is more significant on the recrystallization behavior and final grain size after annealing.

Immersion test results

Figure 6 shows the corrosion rate obtained from weight loss of Mg, Mg-Zn-Ca as cast and annealed Mg-Zn-Ca alloys, after immersion in ringer solution for 168 hour. The average corrosion rate for Mg, Mg-Zn-Ca and annealed Mg-Zn-Ca alloys were 65.9, 8.33 and 17.59 mm/year, respectively. For comparison, the average corrosion rate of biodegradable Mg-4Zn-0.2Ca alloys (as-cast) in Hank’s solution are 2.05 mm/years [11]. The addition of Zn and Ca element into Mg matrix improves the corrosion resistance of the alloys significantly. After annealing, the corrosion rates of Mg-Zn-Ca alloys slightly increases compared to that as cast condition. This was related to the extensive formation of needle like structures after annealing and grain size reduction. Needle like structures in Mg matrix may act as a micro-cathode, resulted in the formation of galvanic couples with the Mg matrix. The increases of needle like structures in Mg-Zn-Ca alloys may increases the formation of micro-cathode, which finally increase the galvanic corrosion rates in the alloys. Furthermore, the reduction in grain size after heat treatment on Mg-Zn-Ca alloys increases the corrosion rate of the alloys. The finer the grains, the larger the effective grain boundaries which lead to the higher risk of corrosion. Grain boundaries act as a weak or critical section for various type of corrosions, mainly intergranular type.
Figure 6. Corrosion rate of Mg alloys obtained from weight loss of Mg, Mg-Zn-Ca as cast and annealed Mg-Zn-Ca alloys, after immersion in ringer solution for 168 hour.

4. Conclusions

This study shows that the performance of Mg-Zn-Ca alloys prepared from the commercial Mg anode is promising for implant application in the future. Our result shows that Mg-Zn-Ca alloy fabricated in our work exhibit minimum corrosion rates in ringer solution. Annealing treatment at 300 °C (8 hour, air cooling) alter the microstructure of Mg-Zn-Ca alloy, by introducing grain size reduction and high density of needle like structures. The microhardness of Mg-Zn-Ca alloys slightly increased from 43 (as cast) to 53 BHN (as annealed). The corrosion rate of the Mg-Zn-Ca alloys was increased from 8 mm/year (as cast) to 17 mm/year (as annealed). This is suspected due to grain refinement and extensive formation of needle structures causing anodic couples with the matrix.

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