The Effect of Zn in as-Cast Mg-Zn Alloys for Biodegradable Materials

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Abstract. This research presents the analysis of microstructure, mechanical, and corrosion behavior of three Mg-Zn binary alloys, Mg-1Zn, Mg-3Zn, and Mg-5Zn. The result of metallography for as-Cast Mg-Zn alloys with different Zn content shows that the presence of Zn will cause grain refinement effect to the microstructure of Mg-Zn alloys and allows the formation of γ phase of Mg-Zn precipitation along the grain boundaries. The addition of Zn also significantly increases the mechanical properties of magnesium alloys corresponding to fine grain strengthening and second phase strengthening effect. Immersion test in Ringer’s solution show that the addition of Zn in magnesium alloys reduce its corrosion rate by improving magnesium alloys corrosion potential.

Keywords: corrosion properties, grain refinement, magnesium alloy, mechanical properties

1. Introduction
The application of Magnesium alloys as implant material is the most developed alternative due to its close mechanical properties to human’s bone so it will not cause stress shielding effect during bone healing process [1]. In addition, the usage of magnesium alloy as implant materials does not require second surgical method to carry out the implant plate as it is dissolved inside human body. The problem found in magnesium alloy is that the degradation rate is too fast, so it will be dissolved faster than the human’s bone recovery time. Refining the alloy composition is one of the keys to overcome that problem.

Previous research found that Mg, Ca, and Zn did not have cytotoxicity [2], it is also found that Zn is important nutrition with one of the most abundant amounts in human body [3], so it is naturally safety for biodegradable implant applications. Finding the optimum Zn content in Mg alloys paid a lot of attention in developing biomedical implant materials. Several researchers were also discussed the mechanical properties of Mg-Zn alloys and shown that the presence of Zn may increase the mechanical properties of Mg alloys while also increase the corrosion resistance of Mg [4]. This work tries to systematically study the effect of Zn towards microstructure, mechanical properties, and corrosion behavior of Mg-Zn alloys fabricated from Mg sacrificial anode and pure Zinc in as-cast condition.
2. Experimental Methods
Magnesium alloys were prepared from Magnesium ingots (99.3%) and Zinc ingots (99.975%) through casting process. Magnesium and Zinc were prepared to get final zinc content 1 wt%, 3 wt%, and 5 wt% alloys. All the raw materials surface was grinded to remove the oxide layer. Casting operations were conducted in a graphite crucible, using induction furnace protected by CO$_2$ + HFC-134a mixed gas to eliminate the presence of oxygen inside the furnace and thus suppress loss of magnesium. The casting temperature is between 700$^\circ$C and 730$^\circ$C with 20-30 minutes holding time. The molten magnesium alloys then poured to a mold and formed the ingots when it solidifies.

**Table 1.** Chemical composition of Mg-Zn alloys.

| Mg Alloy with Zn | Detected elements (wt.%) |
|-----------------|--------------------------|
|                 | Al  | Mn  | Si  | Cu  | Ni  | Fe  | Cd  | Pb  | Zn  | Mg  |
| 1%wt            | 0.1 | 0.495 | 0.0495 | 0.01985 | 0.00099 | 0.02975 | 0.00025 | 0.0000 | 0.999 | 98,307 |
| 3%wt            | 0.1 | 0.485 | 0.0485 | 0.01955 | 0.00097 | 0.02925 | 0.00075 | 0.00018 | 2.99277 | 96,321 |
| 5%wt            | 0.1 | 0.475 | 0.0475 | 0.01925 | 0.00095 | 0.02875 | 0.00125 | 0.0003 | 4.98795 | 94,335 |

2.1 Microstructure
The Microstructure were examined by standard metallography process. Samples for microstructure observation are cut from ingots and grinded on sandpapers up to 5000 grit then polished with alumina paste and etched in a solution of chromic acid. Microstructure observations of the alloys were conducted using optical microscope.

2.2 Mechanical Properties
Mechanical properties were tested by tension test based on ASTM B557M-02A l. The tension test was carried out with Tarno Grocki testing machine. Testing specimen are cut from the cast ingots and machined to form the tension test specimen. Specimen with a gauge length of 45 mm and diameter 9 mm with screwed grip was selected for tensile test.

2.3 Immersion Test and Hydrogen Evolution Measurement
Immersion tests were carried out in simulated body fluid (SBF) using Ringer’s solution (compositions are listed in Table 2) in accordance with ASTM G31-72. The temperature of the solution was adjusted at 37 ± 1$^\circ$C to simulate the average temperature of human body. The immersion was held for 4 days. After immersion process done, the samples were taken out from the solution and cleaned with chromic acid (200 g/l CrO$_3$) to remove surface corrosion products without removing any amount of metallic Mg. Then the samples were rinsed with distilled water, dried in air, then measure the mass loss of sample to calculate the corrosion rate.

The hydrogen evolution volume was measured along with immersion test in SBF. The evolved hydrogen was collected by installing a funnel and a burette above the specimen (shown in Figure 1). The hydrogen formed by the reaction between Mg alloys with SBF will be caught by the burette and push the SBF solution down so the volume can be measured. The hydrogen evolution rate, $V_H$ (ml/cm$^2$ day) was calculated from the total hydrogen released for the whole immersion test duration. The hydrogen evolution rate, $V_H$ (ml/cm$^2$ day) have relation to corrosion rate, $R_H$ (mm/year), and can be calculated using following equation;

$$R_H = 2.279V_H$$ (1)
2.4 Electrochemical Measurement

Electrochemical tests were carried out at 37 ± 1°C in a chamber with Ringer’s solution on a VersaStat® automatic laboratory corrosion measurement system using a standard three-electrode configuration, with a saturated calomel as a reference, a graphite electrode as the counter and the sample as the working electrode. The working surface is ground on sandpapers up to 1000 grit, and then is cleaned by the alcohol and dried in air with only one side of 0.05 cm² exposed to the Ringer’s solution for the test. All the measurements are measured at a scanning rate of 1 mV s⁻¹.

Table 2. Chemical composition of simulated body fluid used in the study.

| Compound       | Amount (mg/l) |
|----------------|---------------|
| NaCl           | 6000          |
| KCl            | 400           |
| CaCl₂·2H₂O     | 270           |
| C₃H₅NaO₃       | 3120          |

3. Results and discussion

3.1 Microstructure and Chemical Composition

Figure 2 illustrates the microstructure of Mg-1Zn, Mg-3Zn, and Mg-5Zn. It can be seen from the microstructure shown in Figure 2b and 2c that the grain size of Mg-5Zn is finer than Mg-3Zn. The pure Mg have average grain size of 350 μm [5], while the grain size measured in the microstructure of Mg-3Zn and Mg-5Zn are 86.7μm and 56.94μm. It shows that the presence of Zn cause grain refining effect in casting of Mg alloys. It was widely accepted that the presence of Zn limits the grain growth and drive the nucleation of α- Mg and thus the grain size will be refined [6]. The refinement efficiency of a solution element can be determined by the calculation of a growth restriction factor (Q). It has been documented [7] that Zn had a higher Q value than Al (4.32) and Y (1.70). Zn has 5.31 growth restriction factor value, meaning that Zn has more effective grain refinement effect.

Figure 2a shown different typical microstructure than the others. This is because the presence of Cu that contaminate the molten in casting process. The contamination of Cu indicated when undissolved Zn ingots discovered after casting so electron probe micro-analyzer (EPMA) characterization was conducted (Table 3) to detect the content of Zn. The result shows that there was Cu content inside the alloys was relatively high. As can be seen in the Figure 2d, there are 16 wt% of Cu but that is not the
exact fraction of Cu since EPMA is semi-quantitative characterization. As the casting process carried out at 700-750°C, a eutectic reaction between Cu stirrer and molten magnesium probably occurs because the stirrer is the only possible source of Cu. Based on a previous research [8], the microstructure shown in Figure 2a have same characteristics as Mg-Zn-xCu alloys which is show thick grain boundary. The eutectic intermetallic (MgZnCu) are solidified along the branches of the dendritic structure. Therefore, it is also stated that with increasing Cu content cause the degree of forming of dendritic structures will increase.

![Figure 2](image1)

**Figure 2.** Microstructure of magnesium alloy with a) 1 wt% Zn, b) 3 wt% Zn, and c) 5 wt% Zn.

**Table 3.** EPMA Analysis results of Mg with 1 wt% Zn.

| No | Element | Crystal | Peak WL (nm) | K-ratio | Mass% |
|----|---------|---------|--------------|---------|-------|
| 1  | Mg      | RAO/CHI | 0.99006      | 0.76696 | 77.75 |
| 2  | Mn      | LiF/CH4 | 0.21026      | 0.00714 | 0.64  |
| 3  | Cu      | LiF/CH4 | 0.15363      | 0.16777 | 16.03 |
| 4  | Zn      | LiF/CH4 | 0.14309      | 0.05813 | 5.59  |

3.2 Mechanical Properties

Table 4 shown the mechanical properties of Mg-xZn alloys as the result of tension test. The presence of Zn increases the tensile strength and yield strength of Mg-Zn alloys. The increase of strength can be explained by Hall-Petch relationship, about grain boundary and strength relation. On the other hand, based on the Mg-Zn binary phase diagram, the maximum solubility of Zn in Mg at room temperature is 1.6 wt%. The excess of Zn content may generate the solid solution strengthening. In addition, when Zn content is 5 wt%, several MgZn phase will precipitate along grain boundaries which improving the strength of Mg-Zn by dispersion strengthening [8]. So, these grain refinement, solid solution strengthening, and second phase strengthening contribute to improve the mechanical properties of Mg-Zn alloys. In the other hand, the presence of second phase can decrease the elongation of the alloys because it is dispersed along grain boundary could be new crack source. As shown in table 2, Mg-3Zn have higher elongation than Mg-5Zn. While Mg-1Zn failed at much lower elongation because the contaminant of Cu that makes this alloy become too brittle as MgZnCu particles may become the nucleation sites of microcracks [9].

**Table 4.** Mechanical properties of Mg-Zn

| Material | Yield Strength (MPa) | UTS (MPa) | Maximum Elongation (%) |
|----------|----------------------|-----------|------------------------|
| Mg-1%Zn  | 56                   | 111.6     | 1.2                    |
| Mg-3%Zn  | 76.5                 | 166.62    | 9.3                    |
| Mg-5%Zn  | 77.6                 | 188.6     | 7.77                   |
3.3 Immersion Test and Hydrogen Evolution Measurement

Figure 3 show the hydrogen evolution rate of Mg-Zn alloys as function of immersion time. According to hydrogen evolution measurement, the corrosion rate of Mg-1Zn, Mg-3Zn, and Mg-5Zn respectively are 487.17 mmpy, 1.488 mmpy, and 5.081 mmpy. For Mg-1Zn, the result only listed until 4 hours of testing because the hydrogen evolution occurs too fast as the hydrogen formed excess the burette volume capacity in 4 hour and 20 minutes. Based on an earlier research [10], it is proven that the presence of Cu in Mg based alloys, allow the formation of Mg2Cu precipitation in grain boundary which is an electrochemically noble phase. The phase formed exhibits hydrogen generation around 300 times more than pure magnesium and cause the test results for Mg-1Zn relatively much higher than Mg-3Zn and Mg-5Zn. Whereas for immersion test, the result for the samples respectively are 162.55 mmpy, 2.03 mmpy. And 8.041 mmpy. Based on immersion and hydrogen evolution test, it is shown that alloying with Zn reduce the corrosion rate of magnesium [11] except for Mg-1Zn which is caused by the contaminant of copper in the alloy. It also can be seen that Mg-3Zn has higher corrosion resistance than Mg-5Zn. This happen because with higher content of Zn exhibits more presence of secondary phase in the alloy. The potential difference between the phases causes a micro-galvanic effect in the alloy which finally increase the corrosion rate as the volume fraction of the second phase increase [11].

![Figure 3. Hydrogen evolution measurement results.](image)

Previous research [12] mentioned that there exist a very fine particles, Mg$_x$Zn$_y$ secondary phase, locate on the grain boundary of Mg-Zn alloys. The phase called by Mg$_x$Zn$_y$ because the size of this particles is several hundred nanometers. Thus, it is so difficult to precisely determine the chemical composition of that phase. Although this white particle exist in Mg-xZn alloys has a relatively low volume fraction, it will contribute to the corrosion resistance of Mg alloys since it is nobler than Mg matrix. The volume fraction of the white particles increases as the content of Zn increase. This result fits the corrosion rate obtained in this research where Mg-3Zn have better corrosion resistance than Mg-5Zn.

3.4 Electrochemical Measurement

The electrochemical polarization curves are shown in Figure 4 and the electrochemical data based on the curves shown in Table 5. The variation of data obtained caused by the difference of chemical
content of each alloy and the phase formed in casting process. This result confirms the corrosion rate obtained in immersion and hydrogen evolution measurement which is also indicate that Mg-3Zn and Mg-5Zn have the significantly lower corrosion rate than Mg-1Zn. The polarization curves for both Mg-3Zn and Mg-5Zn show similar characteristics, the anodic sides are visible with passivation tendency below the breakdown potential point, the point where the polarization curve’s slope become more linear. The existence of passivation tendency at the anodic side indicate the presence of oxide films formed on the surface of the Mg alloys [13,14]. However, the fact that the anodic current densities slowly rise with increasing anodic potential below the breakdown potential means the oxide film formed has porous structure [15].

![Figure 4. Electrochemical behavior measurement results.](image)

Table 5. Corrosion rate calculated from immersion, hydrogen evolution, and electrochemical measurement of Mg-Zn alloys in Ringer’s solution.

| Materials | Corrosion potential, $E_{corr}$ (mV vs SCE) | Current density, $I_{corr}$ (µA) | Corrosion rate, $R_i$ (mmpy) | Hydrogen evolution rate, $V_H$ (ml/cm²/day) | Corrosion rate for Hydrogen evolution $R_H$ (mmpy) | Corrosion rate for immersion test, $C_R$ (mmpy) |
|-----------|--------------------------------------------|---------------------------------|----------------------------|---------------------------------|---------------------|---------------------|
| Mg-1Zn    | -1.432                                     | 300.181                         | 54.305                     | 213.745                         | 487.17              | 162.55              |
| Mg-3Zn    | -1.621                                     | 3.135                           | 0.5744                     | 0.6504                          | 1.4882              | 2.03                |
| Mg-5Zn    | -1.591                                     | 3.035                           | 0.5492                     | 2.2032                          | 5.021               | 8.041               |

The corrosion rate obtained by electrochemical measurement are contrast with immersion and hydrogen evolutions result where Mg-3Zn were better than Mg-5Zn. This could be happened because current density/I$_{corr}$ calculated from electrochemical curve is a function of surface area. While the passive layer of Mg alloys formed and exposed to SBF, the porous structure attacked and forming a pitting corrosion. As pitting corrosion happen, only several areas will be attacked extremely by
corrosion so the result of corrosion rate calculated by Tafel curve and immersion test might have different results.

4. Conclusion
The influence of Zn in as-cast Mg-xZn alloys were studied in this paper. The presence of Cu contaminant in Mg-xZn alloys improve strength, reduce ductility, refine the grain size, and increase the corrosion rate. Thus, increase the hydrogen gas generation significantly. The average grain size of Mg-xZn alloys reduce as the Zn content increase which also cause the strength increase meanwhile the ductility of alloys decreases. The corrosion rate measured by immersion test shows that Mg-3Zn have better corrosion resistance. While for electrochemical test, Mg-5Zn has higher corrosion resistance.

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