Comparison of Hot-rolled Unalloyed Magnesium and Magnesium Alloys in terms of Biodegradability and Mechanical Properties

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Highlights
- Pure magnesium, ZXM100 and ZXM120 alloys were fabricated.
- Bio-corrosion and mechanical properties were investigated.
- ZXM100 can be applied as a biomaterial.

Abstract
In this study, hot rolling is properly performed on pure magnesium and two of Zn, Ca and Mn containing magnesium alloys. Biodegradability and mechanical properties are investigated comparatively in their rolled state. While the average grain sizes of the two alloys were close to each other, it was observed that the Mg-1.01Zn-1.63Ca-0.30Mn alloy had higher hardness (61.5 ± 0.2 HV) at hot rolled state. The lowest corrosion rate in electrochemical corrosion test on Mg-1.07Zn-0.21Ca-0.31Mn alloy is observed to be 1.772 mm/yr. As for the immersion corrosion test on the same alloy, the lowest corrosion rate is detected to be 0.054 mm/yr. Moreover, Mg-1.07Zn-0.21Ca-0.31Mn alloy has the highest tensile strength. Based on the results, it is ascertained that hot-rolled Mg-1.07Zn-0.21Ca-0.31Mn alloy possesses a better biodegradability and mechanical properties compared to hot rolled commercially unalloyed Mg and 1.01Zn-1.63Ca-0.30Mn alloy.

1. INTRODUCTION

There are many different types of materials such as metals and metal alloys, ceramics, and plastics to be used as biomaterials. Metals can be applied in much wider service conditions than plastics and ceramics due to their high strength and toughness [1]. One of important properties for implant biomaterials is biodegradability thanks to which further surgical procedures are avoided and long-term complications are reduced [2]. When considering biodegradability, magnesium (Mg) stands out with its easy degradation and non-toxic degradation products in environments containing Cl- ions [3,4]. However, due to the rapid and irregular degradation of unalloyed magnesium in body fluid environment, utilizing it as a biodegradable implant material in its pure form is hardly applicable. Because of that, it is inevitable to alloy pure Mg with harmless alloying elements and apply thermal and thermomechanical processes [5]. Therefore, many binary, ternary, and quaternary magnesium-based alloy systems have been designed and developed, and also continue to be developed to date. [6–8]. Mg-Zn-Ca-Mn as quaternary magnesium alloys have been evolved nowadays for biomedical applications thanks to their low production costs, improved mechanical properties, and moderate corrosion resistance [9–11].

The daily intake limit of Mg, Zn, and Ca are 700 mg, 15 mg and 800 mg for adults, respectively. Overdose of Zn results in Zinc deficiency. Zinc deficiency brings about growth and developmental delay, impaired parturition (dystocia), hypotension, bleeding tendencies, neuropathy, diarrhea, dermatitis, hair loss, poor appetite, and hypothermia. Excessive amount of Mg provokes nausea. Overdose of Ca hinders the absorption of other essential minerals by intestines [12].

In addition to alloying, surface treatment techniques such as coating can be utilized for the purpose of enhancing the corrosion resistance of magnesium alloys. Bordbar-Khiabani et. al [13] identify the impact

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of the acute inflammatory response on the electrochemical corrosion behavior of uncoated AZ91 Mg alloy, PEO, and PEO/BSP coatings. PEO/BSP coating is detected to supply more observable protection when it is compared to the simple PEO coating. In another study, Bordbar-Khiabani et al. [14] indicate that the duplex coating of ZPSL/PEO functions as a critical process in upgrading the anti-corrosional and in-vitro bioactivistic character of Mg. Whereas the study provides such successful results that the coating has a limited thickness on the substrate material constitutes the major disadvantage of it. Therefore, it is predicted that it will be much more efficient to make an implant material from a magnesium alloy that is uncoated, homogeneous and has a stable degradation rate.

In this study, exclusively designed two of Mg-Zn-Ca-Mn magnesium alloys were fabricated to function as biodegradable materials for fracture bone plate application without surface treatment application. Hot rolling after homogenization heat treatment was administered to the alloys following casting. By applying hot rolling to alloys after homogenization heat treatment, revealing their combined effects on their mechanical and biodegradability properties was targeted. In addition, unalloyed magnesium was produced as reference material by the same method, and it was subjected to the same heat treatment and thermomechanical processes.

2. MATERIALS & METHOD

Unalloyed Mg as reference material and two distinctive Mg-Zn-Ca-Mn magnesium alloys were fabricated by gravity casting into a mold produced by hot work tool steel. Chemical compositions of them were given in Table 1. Homogenization heat-treated alloys were examined and their results were published in a previous study [15].

Table 1. Results of XRF analysis for unalloyed Mg and the alloys (wt. %) [15]

| Designation | Zn   | Ca   | Mn   | Mg    |
|-------------|------|------|------|-------|
| F-Mg        | -    | -    | -    | 99.99 |
| ZXM100      | 1.07 | 0.21 | 0.31 | Balanced |
| ZXM120      | 1.01 | 1.63 | 0.30 | Balanced |

The details of the casting system, mold design and heat treatment are extensively explained in the previous study [15].

Rolling was carried out at a speed of 20 rpm in a twin roll rolling mill with a roller diameter of 200 mm. A total of 30% deformation was executed in 3 passes, with 10% deformation at each pass to all samples that had 4.5 mm initial thicknesses. Before the first pass, each sample was heated to 400 °C and held at this temperature for 30 minutes. Then, samples were kept at 400 °C temperature for 15 minutes between passes and the next pass was applied.

Microstructure analysis before and after immersion corrosion test was carried out with a Carl Zeiss ULTRA PLUS FESEM (Field Emission Scanning Electron Microscopy). Tensile tests with Zwick/Roell Z600 Universal Test Machine and hardness tests with Q10 A+ QNESS Micro Hardness Test Machine were applied to characterize the mechanical properties of the alloys. The tensile test speed was 2 mm/min. at 37±1 °C.

Immersion corrosion tests and electrochemical corrosion tests were applied to bring out the biodegradability performance of the materials. Equipment, test condition and details of potentiodynamic polarization test and also immersion corrosion test were given in previous study [15]. LONZA Hanks’ BSS was used as simulated body fluid corrosive media.

3. RESEARCH FINDINGS AND DISCUSSION

SEM micrographs of the unalloyed magnesium and alloys were given in Figure 1. ZXM100 and ZXM120 alloys have finer grains when they are compared to F-Mg. Average grain sizes were given in Table 2. Depending on the alloying elements added in ZXM100 and ZXM120 alloys, a fine grain structure,
approximately 5 times finer than unalloyed magnesium, was observed from the SEM micrographs of the alloys. Therefore, it can be said that alloying elements refined the average grain size of unalloyed magnesium. Du et al. [16] figured out that the amount of grain refinement amplified as Ca amount amplified in their study with Mg-3Al-xCa alloys. When microstructures of ZXM100 and ZXM120 alloys are compared, it is observed that a hollow structure is formed in ZXM120 alloy. The reason for this is that the ZXM120 alloy consists of a divorced eutectic (α-Mg + Ca₂Mg₆Zn₃ + Mg₂Ca) phase since the Zn/Ca ratio is less than 1.2 at.% [17]. Since electrochemical potentials of the phases are as Ca₂Mg₆Zn₃ > α-Mg > Mg₂Ca [18], the Mg₂Ca phase together with the grain boundaries reacted with the etchant during the etching and caused such a hollow like structure.

Table 2 shows the hardness test results of unalloyed magnesium and alloys. The hardness of unalloyed magnesium increased by about 60% by alloying. When the ZXM100 and ZXM120 alloys are compared, it was determined that the hardness of the ZXM120 alloy is higher than the ZXM100 (~1 wt.%) alloy, since the total amount of alloying elements in the ZXM120 (~3 wt.%) alloy is higher.

Table 2. Vickers hardness and average grain sizes of unalloyed magnesium and alloys

| Designation | Hardness [HV] | Average Grain Size [µm] |
|-------------|--------------|-------------------------|
| F-Mg        | 35.7 ± 0.6   | 102                     |
| ZXM100      | 56.9 ± 1.2   | 21                      |
| ZXM120      | 61.5 ± 0.2   | 18                      |

Figure 1. Scanning Electron Microscope images of a) F-Mg b) ZXM100 c) ZXM120 after hot rolling
Tensile test results of the unalloyed magnesium and alloys were given in Table 3 and stress vs. strain curves were given in Figure 2. The yield strength of unalloyed magnesium was improved by alloying about 64%. The yield strength of ZXM120 alloy could not be measured because it was fractured before the yield point. This can be attributed to the hollow-like microstructure observed in ZXM120 alloy (Figure 1c) because it reduces the strength of the material by creating stress concentration points [19]. The fact that the tensile strength of the ZXM120 alloy is even below the tensile strength of the unalloyed magnesium supports this argument. In the case of ZXM100 alloy, it was determined that yield and tensile strengths of ZXM100 alloy compared to unalloyed magnesium were improved but its elongation was decreased.

Table 3. Tensile test results of unalloyed Mg and alloys

| Designation | Rp0.2 [MPa] | Rm [MPa] | A [%]  |
|-------------|-------------|----------|--------|
| F-Mg        | 83 ± 1.3    | 156 ± 2.4| 8.9 ± 0.4 |
| ZXM100      | 129 ± 2.2   | 194 ± 3.2| 1.3 ± 0.1 |
| ZXM120      | -           | 96 ± 1.6 | 0.2 ± 0.01 |

Figure 2. Stress vs Strain curves of unalloyed magnesium and alloys

Electrochemical and immersion corrosion tests were executed to ascertain the biodegradability of samples and results are given in Table 4. Electrochemical and immersion corrosion test results were given in Table 4 and SEM images of corroded surfaces of samples after 48 hrs. immersion were given in Figure 3. The corrosion rates figured out once the electrochemical corrosion test and the immersion corrosion test were consistent with each other.

Table 4. Corrosion rates of the samples

| Designation | Corrosion Rate (mm/yr.) |
|-------------|-------------------------|
|             | Potentiodynamic polarization test | Immersion test for 48 hrs. |
| F-Mg        | 2.279                    | 0.405                      |
| ZXM100      | 1.772                    | 0.054                      |
| ZXM120      | 2.223                    | 0.331                      |

ZXM100 alloy has the lowest corrosion rate while unalloyed magnesium has the highest corrosion rate in both electrochemical corrosion and 48 hrs. immersion corrosion. Despite the increase in the amount of added alloying elements in the ZXM120 alloy, the reason for the increase in the corrosion rate compared to the ZXM100 alloy can be the existence of the Mg2Ca intermetallic phase in the structure.
Due to the low electrochemical potential of this phase (Mg$_2$Ca), $\alpha$-Mg is preferably degraded in the alloy. This results in the corrosion progressing rapidly into the alloy (Figure 3c). This is seen in the post-corrosion microstructure images given in Figure 3. While the corrosion rate of ZXM100 alloy progressed more regularly, the ZXM120 alloy progressed more irregularly towards the inside of the alloy in the hollow regions due to the Mg$_2$Ca phase. Also, during the immersion corrosion test, the surface activity contains a set of reactions which involve ion exchange, precipitation and dissolution [20]. As a result of these activities, cracking and pitting form on the surfaces of the Mg alloys following immersion in SBF solution as demonstrated in Figure 3b and Figure 3c.

Figure 3. Scanning Electron Microscope images of a) F-Mg b) ZXM100 c) ZXM120 after 48 hrs. immersion corrosion

Figure 4 shows the immersion time vs. corrosion rate graph of F-Mg, ZXM100, ZXM120 alloys. It can be observed that especially F-Mg and ZXM120 alloys show quite aggressive degradation up to about 12 hrs. immersion time. This form of degradation can also be seen from the SEM images in Figure 3.
Figure 4. Immersion time vs. corrosion rate graph of F-Mg, ZXM100, ZXM120

In the ZXM100 alloy, a regular degradation pattern (Figure 3b) and a very low rate of decomposition are observed during the entire immersion period (from 4 hours to 48 hours).

As a result, hot rolled ZXM100 alloy containing low proportions of alloying elements without MgCa phase in the structure meets the requirements in terms of both mechanical properties and biodegradability properties for fracture bone plate material.

4. CONCLUSION

In this study, unalloyed magnesium, ZXM100 and ZXM120 alloys were fabricated by gravity casting. Hot rolling after homogenization heat treatment was applied to all produced materials. Properties of the materials were analyzed comparatively in the hot-rolled state, and the following results were obtained.

- Due to the MgCa intermetallic phase in the structure of Mg-1.01Zn-1.63Ca-0.30Mn alloy, it is lower in both strength properties and biocorrosion properties compared to Mg-1.07Zn-0.21Ca-0.31Mn alloy.
- The Vickers hardness of the Mg-1.01Zn-1.63Ca-0.30Mn alloy was the highest due to the hardening effect of increased alloying elements.
- Mg-1.07Zn-0.21Ca-0.31Mn alloy can be considered as biodegradable implant material with its improved strength and biodegradability properties.

CONFLICTS OF INTEREST

No conflict of interest was declared by the authors.

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