

Characterization and corrosion behavior of biodegradable Mg-Ca and Mg-Ca-Zn implant alloys

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Abstract. In the present study binary Mg-xCa (x=0.5 and 1.25wt.%) and ternary Mg-1Ca-xZn (x=0.5 and 1.5wt.%) alloys are produced by casting the molten metal in a metal die at a temperature of 740°C. The microstructure analysis of the Mg-Ca and Mg-Ca-Zn alloys were studied by OM, SEM and EDX. The corrosion behavior of alloys was evaluated via potentiodynamic polarization test in Kokubo solution. The result exhibited that the grain size decrease with rising Ca content in Mg-Ca alloys and degree of grain size reduction further decreased by adding Zn to Mg-1Ca-Zn alloys. The microstructure of Mg-Ca alloys were constituted of primary Mg and lamellar eutectic (α -Mg+Mg₂Ca) phase, Whilst Mg-1Ca-Zn alloys were composed of primary Mg and eutectic (α -Mg+Mg₂Ca+Ca₂Mg₆Zn₃) phases. In addition with increasing Ca and Zn the amount of Mg₂Ca and Ca₂Mg₆Zn₃ increased respectively in grain boundaries. Electrochemical test shows that the addition of Zn leads to improve corrosion resistance of the Mg-1Ca-Zn alloys as a result of the formation of Ca₂Mg₆Zn₃ phase, whilst the addition of more than 0.5 wt% Ca to Mg-Ca alloys result in decrease corrosion resistance due to the formation Mg₂Ca.

1. Introduction

There are various metallic and polymeric materials that are compatible for use as implants in human body [1-3]. Though biodegradable polymers are widely used, attention has now been given to biodegradable metals which can provide the strength required during the healing process and eventually absorbed by the body [4,5]. Hence there is no need for implant removal or secondary surgery which carries a certain risk factor and cause psychological stress for patients [5]. Magnesium alloys have recently received attention due to their excellent biological and degradable properties. These alloys can be used among other things as vascular stents [6-8]. Mg is a fundamental element in human body which exists in metabolism and bone tissues where normal adult consume about 300–400mg per day. In addition bulk Mg has an elastic modulus and specific density close to that of human bones [4,9]. However poor corrosion resistance and high degradation rate of magnesium alloys is the essential dilemma of its use as biodegradable implants [9,10]. Alloying has been widely known to increase corrosion resistance and improve mechanical properties of magnesium alloy. It was reported that adding alloying elements such as Aluminum (Al) increases the yield strength and ultimate tensile strength at ambient temperature and grain refinement, but Al is harmful to neurons where it can mix with inorganic phosphates causing its decline in the human body [4,11]. Zirconium, another alloying element, act as a grain refiner but it cause health problem such as lung and liver cancer [4]. Some rare earth (RE) elements such as Ce and Pr lead to a decrease degradation rate in vivo, but result in hepatotoxicity to the human body [12]. Therefore Al, Zr and RE are not appropriate elements especially with high concentration in magnesium alloys for biomedical application [13-14]. The aim of this study was to analyse Ca, Mn and Zn as alloying elements for biomedical applications [13]. Pervious study showed that Mg-Ca [15], Mg-Zn [13], Mg-Ca-Zn [16] and Mg-Mn-Zn [11,17] were used as most promising biodegradable materials [13]. Calcium and zinc, which are fundamental elements in the human

body, were known to improve corrosion resistance and mechanical properties [4,13,14]. Despite many researchers evaluated the properties of Mg–Ca and Mg–Ca–Zn alloys the microstructure analysis and corrosion mechanism had received little attention. Therefore comprehensive studies on this are required to improve the usage of these alloys for medical applications. The main objective of this study is therefore to conduct microstructural analysis and evaluation of the corrosion behaviour of Mg–Ca and Mg–Ca–Zn alloy.

2. Materials and methods

Pure magnesium ingot (99.99% Mg), Mg-40Ca master alloy and high purity Zn (99.99 wt.%) were used as starting materials. The materials were melted under argon gas in a mild steel crucible at 740 °C with around 45 min holding time. Following melting and alloying processes the molten metal with different content of calcium (0.5 and 1.25wt %) and zinc (0.5 and 1.5wt %) accompanied by 30 s string were poured into a pre-heated mild steel mould to attain an ingots. The chemical compositions of the as-cast Mg-xCa and Mg-1Ca-xZn alloys are listed in Table 1. Several specimens with dimensions of 20 mm×80 mm were cut from the ingot then it was mechanically wet ground with 320 to 4000 SiC grit paper until all visible scratches were removed for further microstructural and microhardness experiments.

The morphology of specimens was studied using Optical (Olympus BX60F5) and scanning electron microscopy (Jeol Jsm-6380LA) equipped with EDS analyses. Microhardness value of the samples was measured by Vickers hardness tester (Shimadzu) using 5 Kg force.

Electrochemical tests were conducted using potentiodynamic polarization in Kokubo solution at pH 7.66 at a temperature of 37°C in an open air. A three-electrode cell was used for electrochemical measurements where the reference electrode was saturated calomel electrode (SCE), the counter electrode was made of graphite rod, and the specimen was the working electrode. For all specimens potential scanning rate was fixed at a constant scan rate of 0.5 m V/s initiated at -250mV below the open circuit potential. The surface area exposed to the Kokubo solution was 1.6 cm².

3. Results and discussion

3.1. Microstructure characterization

Fig. 1 shows the optical microscopy of Mg-xCa alloys (x=0.5 and 1.25wt%) and Mg-1Ca-xZn (x=0.5 and 1.5wt%). The microstructure of Mg-Ca alloys consist of α (Mg) matrix and Mg₂Ca intermetallic phase. Fig. 1a shows Mg-0.5Ca alloy composed of almost equiaxed large grain structure, containing a small content of Mg₂Ca phase along the grain boundaries. Fig. 1b shows that the grain size of Mg-1.25Ca alloy decrease significantly compared to Mg-0.5Ca alloy, as result of increasing Ca content. Figs. 1c and d show microstructure of Mg-1Ca-Zn alloys consists of α -Mg solid solution, Mg₂Ca and Ca₂Mg₆Zn₃ intermetallic compound which located along the grain boundaries and junction. It also can be seen that the addition of Zn to Mg-1Ca-Zn alloys result in further decreased in grain size. Fig. 2 shows SEM micrographs of the Mg-xCa and Mg-1Ca-xZn alloys with different percentages of Ca and Zn respectively. Microstructure of Mg-Ca alloys were mainly composed of primary Mg and eutectic phase (α -Mg+Mg₂Ca) which denoted with arrow. Fig. 2 b shows that the Mg₂Ca phase located both on the grain boundaries and within grains of α -Mg matrix. Also it was obvious that the amount of Mg₂Ca phase in the grain boundary of Mg-0.5Ca alloy lower than Mg-1.25Ca alloy. However microstructure of Mg-1Ca-Zn alloys was composed of primary Mg and eutectic (α -Mg+Mg₂Ca+Ca₂Mg₆Zn₃) phases [11,16]. Figs. 2 c and d show that the Mg₂Ca and Ca₂Mg₆Zn₃ phase were located within grain boundary and interdendrities inner grain which denoted with arrow. Fig. 3a shows the EDS analyses of eutectic structure along the grain boundary of Mg-Ca alloy. The analyses shows that a composition of second phase consist of 93.75at.% Mg and 6.25at.% Ca. The analyses also show the grain boundaries of alloy rich of Ca while α -matrix is deprived of it. However the analyses of second phase within grain boundaries of Mg-Ca-Zn alloy shows that it composed of 76.24at.% Mg, 10.74at.% Ca and 13.02at.% Zn (Fig. 3b).

Table 1. Analyzed compositions of Mg-Ca and Mg-1Ca-Zn alloys

Alloy designation	Mg	Ca	Zn
Mg-0.5Ca	99.43	0.57	—
Mg-1.25Ca	98.73	1.27	—
Mg-1Ca-0.5Zn	98.36	1.08	0.56
Mg-1Ca-1.5Zn	97.36	1.08	1.56

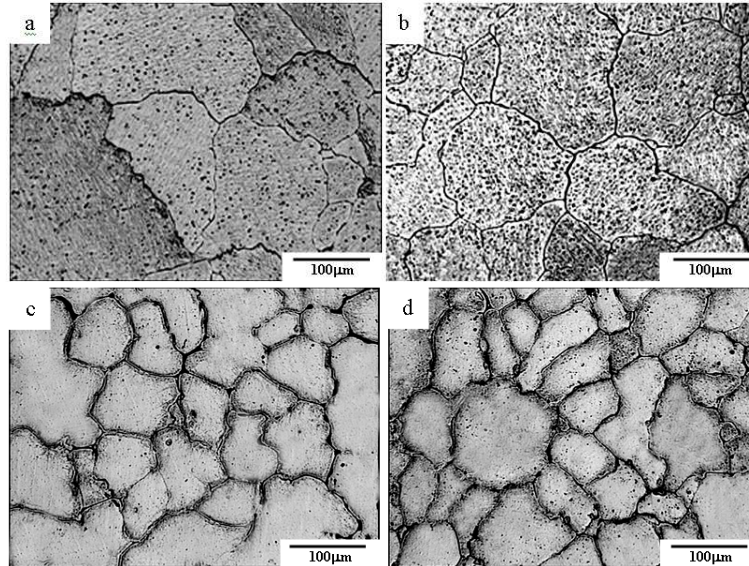


Fig. 1. Optical microscopic image of specimens: (a) Mg-0.5Ca, (b) Mg-1.25Ca, (c) Mg-1Ca-0.5Zn and (d) Mg-1Ca-1.5Zn

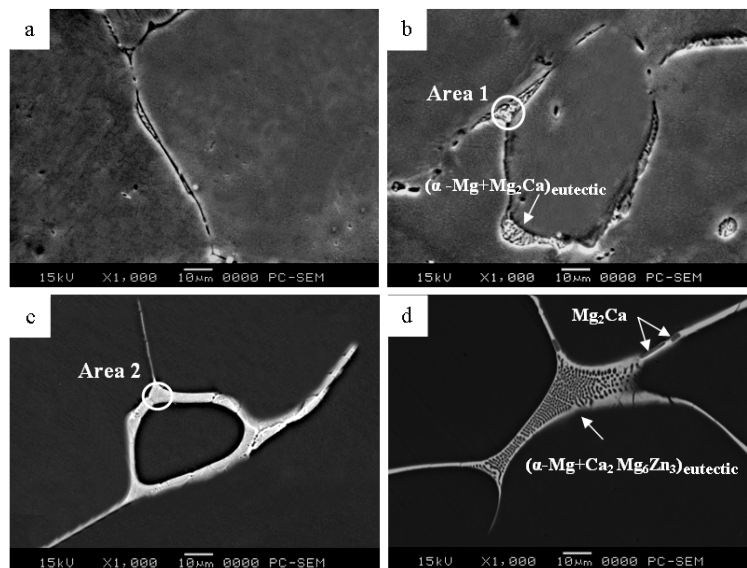


Fig 2. SEM micrographs of specimens: (a) Mg-0.5Ca, (b) Eutectic structure of Mg-1.25Ca, (c) Mg-1Ca-0.5Zn and (d) Eutectic structure of Mg-1Ca-1.5Zn

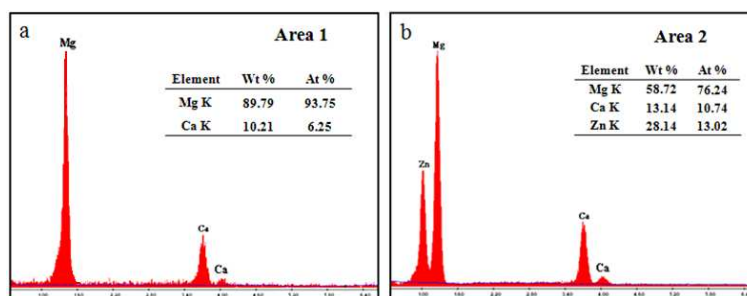


Fig 3. EDS analyses of eutectic structure: (a) area 1 and (b) area 2

3.2 Hardness behavior

The Vickers hardness value of Mg-xCa and Mg-1Ca-xZn are shown in Fig. 4. In Mg-Ca alloys can be seen that with increasing the Ca content the hardness value increase noticeably. The hardness value of Mg-0.5Ca is 36.8 Hv and this value escalates sharply to 46.1 Hv for Mg-1.25Ca. Improvements in hardness value are attributing to solid solution effect, reduction in grain size of α -Mg and precipitation of Mg_2Ca [14]. However further increase in hardness value occurs with rising Zn content in Mg-1Ca-Zn alloy specimens. As can be observed, hardness value of the specimens increased from 48.5 to 52.7 HV with increasing Zn content from 0.5 to 1.25 wt%. Zn. This phenomenon as result of precipitation of $Ca_2Mg_6Zn_3$ particles within α -Mg grains and reduction of grain size [14].

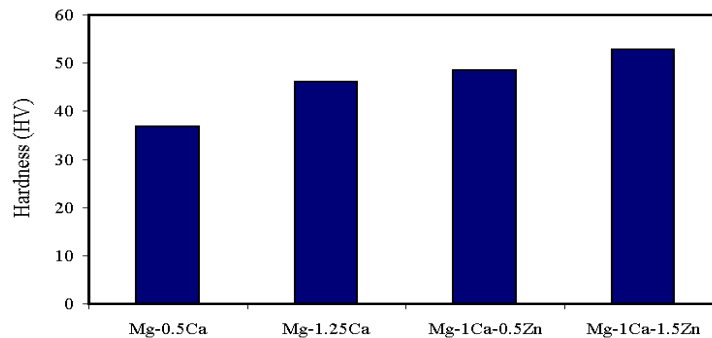


Fig 4. Effect of calcium and zinc content on the hardness value of Mg-Ca and Mg-1Ca-Zn alloys, respectively

3.3 Electrochemical measurements

Table. 2 and Fig.5 show the electrochemical polarization parameters and curves of the Mg-xCa and Mg-1Ca-xZn alloys, respectively. In Mg-Ca alloys obviously can be seen that corrosion potential shift to nobler direction with increasing Ca content. While corrosion current density increased from 0.186 to 0.227 $mAcm^{-2}$ with rising Ca content from 0.5 to 1.25 wt%. This is as consequence of the a high electrochemical activity of Mg_2Ca than α -Mg and it is a more anodic than α -Mg [16]. It was reported [19,20]that the galvanic corrosion occurs between the Mg matrix and Mg_2Ca phase. This means higher Ca content lead to increase in corrosion rate of Mg-Ca alloys. It also can be seen that the corrosion potential and the pitting potential shift to positive direction by adding Zn element in Mg-1Ca-Zn alloys. Table 2 also shows that the corrosion current density i_{corr} and corrosion potential E_{corr} , and pitting potential of specimens extracted from the curves. It was reported that [16] the standard electrode potentials increased with the following sequence: $Mg_2Ca < Mg < Ca_2Mg_6Zn_3$ as consequence of, Mg had higher standard electrode potential compared to Ca. Therefore Mg_2Ca phase corroded faster than Mg matrix due to, Mg matrix act as cathode and Mg_2Ca phase act as anode. However at the interface between Mg matrix and $Ca_2Mg_6Zn_3$, the Mg matrix act as anode and $Ca_2Mg_6Zn_3$ phase act as cathode[16,19]. By comparing Mg-Ca and Mg-1Ca-Zn alloys, the corrosion resistance of the alloys which contain Zn was improved due to formation of condense passive film. On the polarization curve of the Mg-1Ca-xZn alloy, there is sudden drop in electrochemical parameter which represents the pitting potential E_{pt} . As seen in Fig. 5 the pitting potential shift to the nobler value with adding Zn content, which indicatives more stability of the passivation film and the corrosion resistance. Furthermore the addition of Zn element can decrease the influence of Ni and Fe on corrosion properties and enhance the corrosion resistance of Mg [9].

Table 2. Electrochemical parameters of specimens in Kokubo solution attained from the polarization test

Specimen	Corrosion potential E_{corr} (mV)	Corrosion current density, i_{corr} (mA/cm^2)	Pitting potential E_p (mV)
Mg-0.5Ca	-1876	0.186	-
Mg-1.25Ca	-1986	0.227	-
Mg-1Ca-0.5Zn	-1767	0.167	-1589
Mg-1Ca-1.5Zn	-1648	0.132	-1490

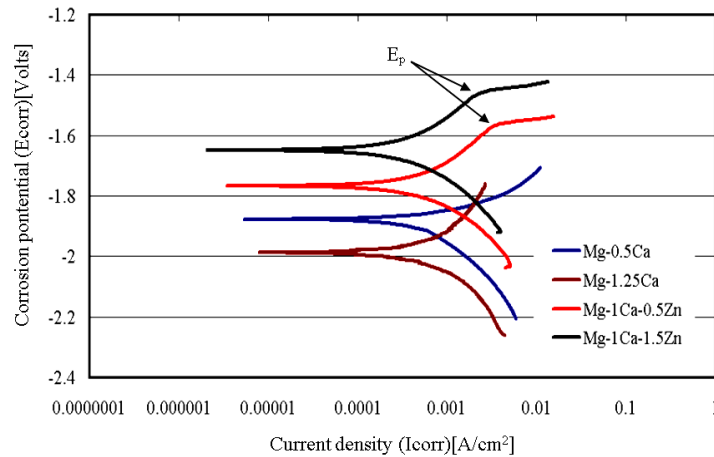


Fig 5. Potentiodynamic polarization curves of Mg-Ca alloy and Mg-1Ca-Zn specimens in Kokubo solution.

4. Conclusions

1. The microstructure of Mg-Ca alloys are constituted of primary Mg and lamellar eutectic (α -Mg+Mg₂Ca) phase, Whilst Mg-1Ca-Zn are composed of primary Mg and eutectic (α -Mg+Mg₂Ca+Ca₂Mg₆Zn₃) phases.
2. The grain size of Mg-Ca alloy decreased with increasing Ca content and degree of grain size reduction decreased by adding Zn to Mg-1Ca-Zn alloys which is the main reason of improvements in hardness value.
3. Electrochemical test shows that the addition of Zn leads to improve corrosion resistance of the Mg-1Ca-Zn due to formation of Ca₂Mg₆Zn₃ phase, While addition of more than 0.5 wt% Ca to Mg-Ca result in decrease corrosion resistance as result of formation Mg₂Ca.

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