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The Effects of Second Phase on Microstructure and Properties of Degradable as-cast Mg-Zn-Ca Alloy for Intrauterine Device (IUD) Applications

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The effects of second phase on microstructure, phase composition, properties of degradable Mg-xZn-1Ca alloys for Intrauterine Device (IUD) application were investigated. Mg-xZn-1Ca (named as ZXx1, x = 0, 1, 2, and 6, in wt.%) alloys were prepared by the gravity casting method. The second phase and microstructure of as-cast alloys were characterized by optical microscopy (OM), scanning electron microscope (SEM) and energy dispersed spectrometer (EDS), X-ray diffractometer (XRD). And degradation properties were investigated using immersion tests and electrochemical measurements. The results indicate that the Zn content is directly related to the proportion of second phases, such as Mg₂Ca, Ca₂Mg₆Zn₃, and Mg₇Zn₃. And these second phase gradually increases from short dots to a continuous coarse network; the grains are significantly refined with the increase of Zn content. And the corresponding tensile strength has changed. The best degradation rate of 0.3573 mm/y is found in ZX11 alloy because Mg₂Ca has a lower potential acting as the anode to be corroded preferentially, which ensures the integrity of the grain boundaries and prevents the magnesium matrix from being corroded.

Keywords: magnesium alloy, second phase, microstructure, property

1. INTRODUCTION

Magnesium-based alloys, being the lightest engineering materials, have attracted many scientific researchers' attention due to their high specific stiffness, high specific strength as well as the demands for energy conservation in the field of automotive and aerospace industries [1-3]. However, the corrosion resistance of most of the magnesium-based alloys cannot match the security requirements in

many applications because of the intrinsic characterization of the high electronegative potential of Mg (-2.37 vs. SHE).

Nevertheless, the application of magnesium alloys is greatly expanded in the field of medical science due to the degradability of Mg-based alloys.

As a matter of fact, with the release of the three-child Family Planning Policy, paramount progress has been made in the field of contraception, with landmarks such as the introduction of IUDs. Most of these being used in the stage of clinical application are the traditional non-degradable alloy IUDs such as stainless steel and copper, suitable for long-term contraception due to their corrosion resistance. And these materials for short-term contraception require a second surgery to remove them when it is no longer used; Removing IUDs repeatedly increases not only the medical costs but also causes great physical pain and mental stress to patients. Therefore, IUDs made of degradable alloys with a suitable corrosion rate is promising option to make contraception effective and pregnancy convenient.

Hence, degradable Mg alloys are up and coming candidates for IUD, which are due to their unique characteristics, including nontoxic degradation products to the human body. Besides, studies have demonstrated that the corrosion rate of most magnesium binary alloys is greater than 2mm/year, especially Mg-RE alloys that have good corrosion properties [4-6]. However, the rare earth elements are not cheap and have a disadvantage in production costs. Moreover, the commercial magnesium alloys containing aluminum are highly promising candidates because the corrosion resistance is more excellent than other Mg alloys can handle. But excessive intake of aluminum ions is harmful to the human body. Therefore, the selection of alloying elements is crucial to ensure biosafety.

Calcium (Ca), as the primary alloying element, is chosen due to its high nutrition for the human body as part of a wide variety of essential nutrients and, at the same time, the vital component of human bone to promote bone growth and biocompatibility. Moreover, zinc (Zn) is a human essential nutritional element required for the human body and plays a vital role in the growth and development of humans. In addition, Zn can also refine the grain and antibacterial effect that considerably improves the comprehensive properties of Mg-based alloy. Combining these two elements in magnesium alloy can improve strength and biocompatibility. Based on the above reasons, it is of great necessary going study degradable Mg-Zn-Ca alloy as promising IUD alloys. There is no doubt that the second phase is an essential factor dominating the evolution of the alloy microstructure and corrosion resistance properties. Related studies have found that the second phases, including the LPSO phase, isolate the matrix from the eutectic phase when distributed at the grain edges of the matrix, reducing the potential of the contiguous phases and inhibiting galvanic corrosion, thus achieving excellent corrosion resistance [7]. Song et al.[8] found that Zn and Y bearing magnesium alloys are more electrochemically stable than Mg matrix, which can lead localized corrosion occurred on the surface in given corrosive situation. Both the corrosion morphologies and electrochemical tests proved that the second phases greatly affect the corrosion process of Mg-Zn-Y-Zr alloy.

It has been widely confirmed the second phase is an influential factor in controlling microstructure and obtain excellent properties by optimizing content. Therefore, systematic works of Mg-xZn-1Ca alloy under different range of second phases have been conducted. In addition, the microstructure and tensile properties, and degradability will be studied in terms of the microstructure characterization and the content of the second phase.

2. EXPERIMENTAL PROCEDURES

As-cast alloys were fabricated by putting pure Mg (99.9 wt. %) in an electric resistance furnace using a steel crucible, raising the temperature to 720°C, holding for 20 minutes, then mixing pure Zn (99.99wt%) and Mg-30%Ca alloy at 720°C holding for 30 minutes. The raw materials were melted under CO_2 and SF_6 protective atmosphere. The melted alloys were poured into mold, preheated at 200°Cand, then, cooled down to the ambient temperature. The main compositions of ZXx1 alloys are listed in Table 1

		contents (at.%)		
	Designed components	Mg	Zn	Ca
Alloy	(wt.%)	-		
ZX01	Mg-1Ca	99.39	0	0.61
ZX11	Mg-1Zn-1Ca	99.15	0.24	0.61
ZX21	Mg-2Zn-1Ca	98.64	0.75	0.61
ZX61	Mg-6Zn-1Ca	97.09	2.30	0.61

 Table 1. Chemical composition of ZXx1 alloy

The microstructure and elemental composition characterizations of ZXx1 samples were characterized by optical microscope (OM, Leica 2700M), scanning electron microscopy (SEM, MIRA3 TESCAN), Energy Dispersive Spectrometer (EDS) and X-ray Diffraction (XRD, TD-3500). The XRD scan range of 2θ was from 20° to 90° and scan rate was of 6° /min. The XRD patterns were analyzed with MDI Jade 6 software. The tensile properties were measured by the electronic universal testing machine (DNS100) with a tensile speed of 0.2 mm/min at room temperature.

The weight loss of ZXx1 alloys was measured by immersion test in simulated body fluid (SBF) at 25°C using a constant temperature water bath. The ratio of the surface area of the specimen (cm²) to immersion body fluid volume (ml) was set to 1:30. To ensure the concentration of the solution is stable, the solution is changed every 12 h, and the samples were immersed in chromic acid (200 g/l CrO₃) for 5-10 minutes to remove the corrosion products after the immersion test. The surface morphology of the corroded samples was characterized by SEM. Finally, the mass after removing corrosion products was weighed by an analytical balance, the corrosion rate was calculated by weight loss based on the following equation [9]:

$$C_R = \frac{8.64 \times 10^4 \times \Delta W}{A \cdot T \cdot D} \tag{1}$$

Where C_R (mm/year) is the average corrosion rate, ΔW (mg) is the weight loss, A (cm²) is the surface area exposed to the corroding solution, t (day) is the soak time, d (g/cm³) is the density.

The electrochemical behavior of ZXx1 alloys was tested by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP). The potentiodynamic polarization curves were measured via scanning the potential from -2.0 V to -1.0 V (vs. SCE) at a scan rate of 1 mVs⁻¹. A CH350H electrochemical workstation equipped with a three-electrode system was used for

electrochemical measurement. In the three-electrode system, the reference electrode is a saturated calomel electrode, and the platinum sheet as the auxiliary electrode. Every sample had an exposed area of $10 \text{ mm} \times 10 \text{ mm}$.

3. RESULTS AND DISCUSSION

3.1. Microstructure and phase identification

SEM, EDS images, and XRD patterns of the cast ZXx1 alloys are shown in Fig. 1. The ZX01 alloy is only Mg and Ca elements, so the alloy consists of the α -Mg matrix phase and Mg₂Ca second phases, where white-colored fine dots Mg₂Ca particles are distributed matrix grain interior (Fig. 1a). In the ZX11 alloy, as shown in Fig. 1b, a large number of second phases are gathered in the grain boundary and more dot-like second phases precipitate in the grain interior, part of the Mg₂Ca phase in the alloy changed into the Ca₂Mg₆Zn₃ phase with the addition of Zn. The number of diffusely distributed dotted second phases in the grain increases, and the elongated strips of second phases at grain boundaries are distributed in a network in Fig. 1c. Likewise, as shown in Fig. 1d, when the Zn content is 6wt%, the dot-like second phase inside the grain is densely diffused; second phases with a continuous network along the grain boundary are formed, where the Ca₂Mg₆Zn₃ phase reaches saturation, Mg₇Zn₃ phase appears. The presence of Ca₂Mg₆Zn₃ (Fig. 1b-d) and Mg₇Zn₃ phases (Fig. 1d) is confirmed by the XRD results shown in Fig. 1e.

The EDS elemental analysis of the second phase at the grain boundary revealed that the Zn and Ca atomic ratio is approximately 3:2, where Zn-enriched second phases consisting of Mg, Ca, and Zn elements. Larionova et al.[10] reported that composition of the precipitated phase in the Mg-Zn-Ca alloy depends on the Zn/Ca atomic ratio.





Figure 1. SEM, EDS images, and XRD patterns of the ZXx1 alloys (a) ZX01 (b) ZX11 (c) ZX21 (d) ZX61 (e) XRD patterns

Hence, the presence of Ca2Mg6Zn3 only in the Mg-matrix is the ZX21 alloy. While the EDS analysis in the second phase of ZX61 showed that the atomic ratio of Mg and Zn was approximately 7:3, indicating the existence of the Mg_7Zn_3 phase in addition to the Ca₂Mg6Zn₃ phase in the second phase.

OM images and the corresponding grain size (counted by Nano measure analysis software) of the ZXx1 alloys are shown in Fig. 2. It is noted that the average grain size of the alloys was 226 μ m, 201 μ m, 164 μ m, and 32 μ m in decreasing order with increasing content of Zn, which shows that Zn plays a role in refining the grain size. The grain shape of alloys changes from dendrite to equiaxial crystal with the gradual increase of secondary phase grains. It may more likely occurs in the solidification process when the solubility of Zn in the Mg matrix drops rapidly, and a large amount of Zn elements are enriched at the front edge of the solid-liquid interface, resulting in constitutional undercooling.



Figure 2. OM images of ZXx1 alloy (a) ZX01 (b) ZX11 (c) ZX21 (d) ZX61

3.2. Mechanical properties

Tensile strain-stress curves and corresponding mechanical properties of ZXx1 alloys are illustrated in Fig. 3. It is noted that the tensile strength of the cast alloy gradually increases, and the ultimate tensile strength of the ZX61 alloy reaches 206 MPa, which is 87% higher than that of the ZX01 alloy in Fig. 3b. It is because the ZX61 alloy has the smallest grain size and a large amount of network second phases; when the grains are subjected to external plastic deformation; some dislocations inside

the grains slip to the grain boundaries to form dislocation plugging. More force is needed to produce plastic deformation due to refined grains and more dislocation plugging so that the alloy has the highest tensile strength. While the yield strength and elongation tend to increase and then decrease in Fig. 3b, the yield strength and elongation of the ZX21 alloy reach a peak of 70MPa and 14%, respectively, which is significantly higher than that of ZX01 alloy. According to the Hall-Page formula [11], the alloy yield strength increases with the reduction of grain size, grain refinement makes plastic deformation more uniform, less stress concentration, and larger grain boundary area, resulting in the winding grain boundary effectively blocking the crack expansion. However, the elongation decreases to 10.88% in ZX61 alloy, which is attributed that the continuous coarse network second phases at the grain boundary have a cutting effect on the matrix [12], which quickly becomes a potential source of cracks during the tensile process, making damages preferentially arise and expand in the second phase together.



Figure 3. mechanical property of ZXx1 alloys: (a)Tensile strain-stress curves of ZXx1 alloy (b) corresponding mechanical properties

3.3. Corrosion resistance performance

SEM microstructures provided in Fig. 4 show the corrosion surfaces of the alloy with the removal of corrosion products. As shown in Fig. 4a, it is clear that intensive Mg₂Ca phase pitting occurred on the alloy surface, accompanied by a large corrosion crater formed by the detachment of the substrate. In ZX01 alloy, the Mg₂Ca phase as the anode corrodes preferentially because the Mg₂Ca phase potential is lower than the α -Mg matrix phase, leaving a dense pitting crater on the alloy surface, while eroding the grain boundary will make the matrix phase lose its skeleton and fall off, thus forming a corrosion crater on the alloy surface, intensifying the corrosion to occur along with the corruption to the interior of the alloy. The pitting also happened on the surface of alloy ZX11 in Fig. 4b, the distribution of second phases of Mg-1Zn-1Ca in grain boundary is schematically shown in Fig. 4f. The Mg₂Ca phase distributed inside the grain and on the grain boundary is preferentially corroded, while the network Ca₂Mg₆Zn₃ phase distributed at the grain boundary has a higher potential than the α -Mg phase and Mg₂Ca phase which is protected in the event of galvanic corrosion and is more wholly retained at the grain boundary as a skeleton. So pitting occurs only at the grain boundaries, still the grain boundary was not completely

eroded, which leads the ZX11 alloy to have the most significant resistance corrosion performance with a minimum value of 0.3573mm/y in Fig. 4e.

As shown in Fig 4c, the grain boundary of ZX21 alloy appears to have deep corrosion grooves. At the same time, the corrosion degree of the magnesium matrix surface is aggravated. The Ca₂Mg₆Zn₃ phase as the cathode at the grain boundary forms a micro-electric couple with the magnesium matrix phase as the anode preferentially corroded, which indicates the the corrosion of the ZX21 alloy initiates from α -Mg adjacent to the grain boundary. So the Ca₂Mg₆Zn₃ phase is dislodged as the corrosion proceeds and cannot be maintained at the grain boundary. In the case of ZX61 alloy, the amount of secondary phase alters the cathode/anode area ratio (Fig. 4d). The network Ca₂Mg₆Zn₃ and Mg₇Zn₃ phase as the cathode, whose potentials are higher than α -Mg phase, intensifies the galvanic corrosion effect, and the surface suffers from severe local corrosion accompanied by apparent grain shedding phenomenon. And as the electrode reaction proceeds, the localized corrosion areas will extend, and the entire alloy surface is corroded without residual second phase and the corrosion rate reaches a maximum of 0.8482mm/y.





Figure 4. SEM images of ZXx1 alloy (a) ZX01 (b) ZX11 (c) ZX21 (d) ZX61 and (e) The corrosion rate of ZXx1 alloy (f) Sketch map of second phases distribution of ZX11

3.4. Electrochemical test

Furthermore, the electrochemical polarization curves of ZXx1 alloys in simulated body fluid (SBF) were recorded further to investigate the degradation properties (Fig. 5), and the corresponding corrosion current density (I_{corr}) and polarization resistance (R_P) parameters variation are obtained (Table 3). It can be seen that the catholic curves of ZX11 and ZX21 alloys shift forward relative to ZX01 and ZX61 alloys. This shift represents the change of cathodic kinetics [13]. The corrosion potential of these alloys is basically in the range of -1.55V to -1.45V, the corrosion rate is not necessarily related to corrosion potential, corrosion potential is a thermodynamic parameter which only plays a predictive role, and cannot directly explain the corrosion rate. While the corrosion rate is a kinetic parameter which characterizes the rapidity of corrosion directly. Compared with the anode curve of alloy ZX01 with the largest corrosion current densities, the other three groups of anode curves have occurred with more obvious defluxion. At the same cathodic potential (marked by the broken line in Fig. 5), the corrosion current density of ZX61 alloy was obviously higher than ZX11 alloy, indicating the fast cathodic hydrogen evolution rate on ZX61 alloy and the low cathodic hydrogen evolution rate on ZX11 alloy. This is due to that more micro-galvanic-couples were established (more high-potential second phases in ZX61 alloy shown in Fig. 1). The ZX11 alloy has the smallest corrosion current density with value of 3.27μ A·cm², which reflects the best corrosion resistance performance. Due to increased high-potential second phases within the ZX21 and ZX61 alloys, which intensified the galvanic coupling corrosion effect. So the corrosion current densities of the ZX21 alloy and ZX61 alloy have increased. Likewise, the R_p of ZX11 alloy is higher than three other alloys. The higher R_p value is the better corrosion resistance of the alloy. The R_P was calculated according to following equation [14]:

$$R_p = \frac{\mathbf{B}_a \cdot \mathbf{B}_c}{2.3(\mathbf{B}_a + \mathbf{B}_c) \cdot I_{corr}}$$
(2)

Where, βc stands for cathodic slopes, βa stands for anodic slopes, and I_{corro} is corrosion current density. The corrosion rate of the alloy is directly proportional to R_p value, with ZX11 alloy having the largest R_p value. It means that the ZX11 alloy has the most fantastic corrosion resistance performance.



Figure 5. Polarization curves of ZXx1 alloys in SBF solution

Table 2. Fitting results of polarization curves of ZXx1 alloys

Alloy	$E_{corr}(V)$	$I_{corr}(\mu A/cm^2)$	$R_p(\Omega.cm^2)$
ZX01	-1.475	26.60	207.3
ZX11	-1.524	3.27	7476.5
ZX21	-1.507	6.39	3.801.9
ZX61	-1.455	10.57	2.314.2

Nyquist diagrams and bode diagrams were obtained from the EIS test of ZXx1 alloy, have been available in Fig. 6, the Nyquist diagrams of these four alloys have a high-frequency capacitive loop and medium-frequency capacitive loop, the former corresponds to the degradation product layer on the surface, and the latter indicates the attack on the Mg substrate. The radius of the capacitive loop is related to the charge transfer resistance of the active corrosion electrode. The higher charge transfer resistance indicates a higher barrier to the alloy dissolution and, in turn, a lower corrosion rate. The Nyquist curve of ZX11 alloy has the maximum radius for both of high-frequency capacitive loop and medium-frequency capacitive loop, corresponding to the best corrosion resistance, and with the highest impedance modulus in Fig. 6b, which represents superior corrosion resistance performance [15]. Fig 6c shows the fitted equivalent circuit, the EIS results after fitting, as shown in Table 4. The R_s is the solution resistance, the R_{ct} is charge transfer resistance and the R_f is firm resistance. Combined with the above

analysis, ZX11 alloy has the best corrosion resistance performance due to corroded Mg_2Ca phases preferentially, and the highest R_{ct} and R_f values are consistent with the results of the immersion test. Hence, both immersion test and electrochemical characterization revealed a similar corrosion behavior.



Figure 6. The EIS results of ZXx1 alloys (a) Nyquist plots (b) Bode plots (c) Equivalent circuit

Alloy	Rs	CPE _{dl}	l	R _{ct}	CPE _f		R _f
	$(\Omega \cdot cm^2)$	$(Y/\mu\Omega^{-})$	n _{dl}	$(\Omega \cdot cm^2)$	(Y/μΩ ⁻	n _{dl}	$(\Omega \cdot cm^2)$
		$^{1} \cdot cm^{2} \cdot s^{n}$)			$^{1} \cdot cm^{2} \cdot s^{n}$)		
ZX01	125.7	10.85	0.86	7981	485.44	0.83	1784
ZX11	119.2	12.96	0.86	8904	263.19	0.91	4424
ZX21	120.7	15.38	0.83	8782	256.02	0.66	2768
ZX61	68.6	15.04	0.91	6890	49.16	0.62	1657

 Table 3. The EIS fitting results

The corresponding properties of Intrauterine Device (IUD) materials were listed in Table 4. It can be seen that traditional Intrauterine Device materials such as iron-based, copper-based, and titanium-based alloys have a higher corrosion potential (E_{corr}) compared with magnesium-based alloy and varied in the range of -0.3 to -0.1 V. The corrosion rates are 0.0017mm/y, 0.0276mm/y, 0.0149mm/y respectively and Ti-6Al-7Nb alloy has the the lowest corrosion rate[16]. However, the corrosion rate of traditional IUD materials are too low to meet current contraceptive requirements and not easily degradable for short-term contraceptive purposes. aluminum ions released during corrosion of Ti-6Al-7Nb alloy are harmful to humans. In Cu-0.4Mg alloy, over released Cu²⁺ could induce irregular vaginal bleeding, cramping, pelvic inflammatory disease[17]. The corrosion rate of ZX11 alloy is moderate and

meets the short-term contraceptive requirements, it has the advantages of good biocompatibility, degradability and safety. So the ZX11 alloy has a great potential for Intrauterine Device (IUD) Applications.

IUD materials	E _{corr} (V)	$I_{corr}(\mu A/cm^2)$	Corrosion
			Rate(mm/y)
Medical grade stainless	-0.114	0.15	0.0017
steel			
Cu-0.4Mg	-0.215	2.31	0.0276
Ti-6Al-7Nb	-0.273	0.05	0.0149
ZX11	-1.524	3.27	0.3573

Table 4. corresponding properties of Intrauterine Device (IUD) materia	als
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4. CONCLUSIONS

(1) The addition of Zn significantly refines the grains. The average grain size was refined from 226 μ m to 32 μ m, and the second phase was significantly increased, transforming from a punctiform Mg₂Ca phase to a semi-continuous short rod-like Ca₂Mg₆Zn₃ phase and then to a continuous distribution of network Mg₇Zn₃ phase and Ca₂Mg₆Zn₃ phase at the grain boundaries.

(2) With the increase of Zn content, the strength of the alloy increased significantly. The mechanical properties of ZX21 alloy YS, UTS and EL were 70MPa, 178MPa and 14%, respectively, where the yield strength and elongation went the highest, while the tensile strength of ZX61 alloy reached the highest 206MPa. However, the coarse reticulated second phase at the grain boundary cuts the matrix, reducing yield strength and elongation.

(3) ZX11 alloy has the best corrosion resistance with an average corrosion rate of 0.3573mm/y, which is due to the low potential of the Mg₂Ca phase, the Mg₂Ca phase acts as the anode to be corroded preferentially, protecting the integrity of the grain boundaries, thus improving the corrosion resistance of the alloy.

CONFLICTS OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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